



INVESTIGATION INTO THE PHOTOCHEMICAL BLEACHING OF PULP UTILIZING VARIOUS LIGHT SOURCES

by

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ABSTRACT

Since pulp and paper as products are commodities, the pulp and paper industry are constantly looking for any advantage that will keep production costs down and improve profitability. One of the main sources of cost in any pulp and paper mill is the vast quantity of energy used. Thus, any alternative or disruptive technology that reduces energy usage or costs would provide a strong incentive for research. Photochemical bleaching is one such potentially disruptive technology. In this research, three potential light sources for the photochemical bleaching of pulps were investigated, namely, solar radiation, microwave discharge electrodeless lamps (MDELs), and ultraviolet light emitting diode arrays (UV LED arrays). Of the three, only the UV LED array was shown to be both viable and practical.

The photochemical bleaching of a post-oxygen stage Cloquet Aspen kraft pulp was successfully undertaken with solar radiation as a light source for both pure caustic soda and alkaline peroxide as bleaching reagents. The addition of metal oxide additives or the semiconductor photocatalyst titanium dioxide gave poorer photobleaching performance due to the increased opacity of the pulp suspension and the low intensity of the radiant light source. Given that a full five days were required to achieve a small photobleaching effect, the use of solar radiation, although viable, is not practical as a technology.

The ignition and sustained “burning” of a Primarc MDEL were shown to be random and erratic due to the lack of calibration and tuning of the Roto SYNTH microwave oven’s irradiation chamber for the Primarc MDEL. Of the various reactor designs investigated, the suspended MDEL “bucket” reactor was shown to be the best performer and most viable alternative. However, investigation of the photochemical bleaching of Cloquet unbleached kraft paper-grade pulp with the suspended MDEL “bucket” reactor design and the Roto SYNTH microwave reactor oven for microwave irradiation, gave no statistically significant differences between the controls without a MDEL and the MDEL irradiated experiments.

The photochemical bleaching of Cloquet unbleached kraft paper grade pulp with the UV LED array was successful when using only pure caustic soda, alkali peroxide and alkali oxygen as bleaching reagents. As regards to the overall bleaching performance, the alkali peroxide and

alkali oxygen options performed similarly while the pure caustic soda option performed slightly more poorly. Based on the literature reviewed, the hydroxyl radicals generated in the photobleaching process were the active bleaching species in all three cases. In an extension of the alkali peroxide evaluation, the impact of pulp suspension pH, temperature and consistency, as well as the UV radiant intensity level (i.e. UV LED array power levels) were further evaluated. In addition, various photocatalysts were investigated for the alkali peroxide option, as well as various photosensitizers for the alkali oxygen option. Successful photochemical bleaching occurred across the entire pH range tested (i.e. pH 2.5 to 11.0) with better performance at the alkaline pH range with a maximum performance at pH 10.5. Photochemical bleaching increased with temperature from 25 to 43 °C, whereafter it plateaued up to 75 °C. Increased pulp suspension consistency from 0.5 to 1.5% gave a reduction in photochemical bleaching performance, whereafter it plateaued up to a consistency of 3.0%. Photochemical bleaching increased linearly with illuminant intensity as the UV LED array power levels were increased from 10 to 100%. Of the photocatalysts tested, only titanium dioxide and cerium dioxide were successful in improving the alkali peroxide photobleaching of pulp at the charge levels used (5.0 and 20.0 kg t⁻¹ respectively). None of the photosensitizers tested (i.e. methylene blue and rose bengal) operated successfully for the alkali oxygen photobleaching of pulp in the experimental work undertaken.

The photochemical bleaching of various starting pulps (Cloquet kraft unbleached, Ngodwana PHK unbleached, Stanger unbleached, Saiccor acid sulfite unbleached, Gratkorn magnesite unbleached, and Somerset continuous kraft unbleached) was successful for all starting pulps. However, bleaching performance varied from pulp to pulp.

A comparison of the thermal elemental chlorine free (ECF) and total chlorine free (TCF) sequences with the thermophotochemical TCF sequence for bleaching paper grade pulps, showed that the thermal ECF and thermophotochemical TCF sequences were both successful in achieving the target brightness (i.e. 89%) while the thermal TCF sequence underperformed slightly (i.e. 85%). The thermophotochemical TCF sequence gave acceptable pulp properties for viscosity, hand sheet pulp strength, and fibre morphology as compared to the thermal ECF sequence as a control sequence, while the thermal TCF gave significantly weaker pulps. For bleaching dissolving grade pulp, both the thermal ECF (as a control sequence) and the thermophotochemical TCF sequences were successful in achieving target brightness and above (i.e. 91%). Both sequences gave final viscosities within the target range (500 to 560 ml g⁻¹). In addition, both sequences gave acceptable carbohydrate sugar contents, alkaline solubilities, and

Sappi quick reactivity indexes. Lastly, both pulps also had similar fibre morphologies showing a reduction to shorter fibre lengths due to chemical refining during both bleaching processes.

“Pseudo” second order reaction kinetics were established for the oxidants: alkaline peroxide, pure caustic soda, and alkaline oxygen for photochemical bleaching utilizing the UV LED array reactor, with strong kinetic relationships demonstrated for pulp extent/rate of delignification and brightness development, but, a weak relationship for pulp viscosity. Results demonstrated that the three oxidants utilized different chemical mechanisms for generating the hydroxyl radical species employed for bleaching, with the best results obtained for the hydrogen peroxide and the poorest for the pure caustic soda. An observed discrepancy between the “pseudo” first order reaction kinetics in Marcoccia’s investigation and the “pseudo” second order reaction kinetics in this study were due to differences in the conditions, apparatus and charges employed in both.

The final conclusion drawn from this study is that photochemical bleaching of pulp, using an ultraviolet light emitting diode array at 365 nm, can serve as a viable alternative to thermally-driven bleaching provided certain technical issues can be resolved (i.e. operational consistency and comparative energy efficiency of thermal- versus photo-bleaching).

PREFACE

The experimental work described in this thesis was carried out in the Sappi Technology Centre (Pretoria), from April 2012 to July 2021, under the supervision of Professor Bice S. Martincigh.

These studies represent original work by the author and have not otherwise been submitted in any form for any degree or diploma to any tertiary institution. Where use has been made of the work of others it is duly acknowledged in the text.

DECLARATION - PLAGIARISM

I, Craig David Pearcey, declare that

1. The research reported in this thesis, except where otherwise indicated, is my original research.
2. This thesis has not been submitted for any degree or examination at any other university.
3. This thesis does not contain other persons' data, pictures, graphs or other information, unless specifically acknowledged as being sourced from other persons.
4. This thesis does not contain other persons' writing, unless specifically acknowledged as being sourced from other researchers. Where other written sources have been quoted, then:
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LIST OF ABBREVIATIONS

Abbreviation	Full term
DEL	Discharge electrodeless lamp
ECF	Elemental chloride free
MDEL	Microwave discharge electrodeless lamp
PHK	Pre hydrolysis kraft
TCF	Total chlorine free
UV	Ultraviolet
Vis, VIS	Visible

INTRODUCTION

This thesis discusses an investigation into using light as an energy source to drive the chemical bleaching of pulp as an alternative to thermal energy, which is typically supplied as steam in the pulp and paper industry. Three distinct light sources were evaluated: solar radiation, visible and ultraviolet light from a microwave discharge electrodeless lamp, and narrow band ultraviolet light from a ultraviolet light emitting diode array. The advantage of light is that it is more selective in its chemistry than thermal processes. As regards studies reported in the literature, microwave discharge electrodeless lamps have never been evaluated for bleaching pulp as yet and such a study would advance knowledge in this area significantly. In regards to light emitting diode arrays, the increasing availability of commercial ultraviolet light emitting diode arrays also makes them a natural choice for such a study.

1.1 The pulp and paper industry

Pulp and paper is categorized as a commodity, a soft commodity as it is produced from a fibre source (e.g. timber) that is typically grown rather than mined. In general terms, a commodity can be classified as an item or product (whether raw material, manufactured item/product or certain services) that is produced in economically significant quantities while being considered fungibility (i.e. commodities of the same grade are generally considered roughly equivalent regardless of who produces it) which are typically sold on the spot market. As with any commodity, certain general aspects or economic principles apply. These include: (i) volume of product sold, (ii) cost per unit or ton sold, (iii) sell/factory-gate price per unit or ton sold, and (iv) profit margin per unit or ton sold. A more detailed discussion of these aspects follows.

- Volume of product sold

Commodities are usually produced in significant quantities, the exact volume being dependent on the type of commodity and the market demands. This tends to make commodities easily available in notable quantities within most countries and communities. The tendency of being easily available and available in large quantities tends to strongly and negatively impact the sales price driving the sales price down and reducing profit margins. One approach employed to negate this is the economics of scale of production in which the more a commodity is produced, the more of it is sold, and the higher the profits from selling more. However, at the same time, the more there is of a commodity, the greater the downward pressure there is on its sales price, which works against the value set for the spot sales price. If the commodity becomes too readily available, the market may be swamped, forcing large sale price reductions and potentially collapsing the market by flooding it. In such over supplied markets, certain

manufacturers typically are forced out of business after becoming unprofitable or incurring large financial losses.

- Costs per unit or ton

The cost of harvesting, mining or producing a commodity is strongly dependent on the cost prices of the raw materials, labour, energy and equipment involved. Often, many raw materials and equipment are brought in from outside sources which are strongly influenced by the existing oil price and the existing currency exchange rate. In addition, many of these raw materials are subject to the impact of inflationary increases. All these can impact the size of the profit margin, regardless of the downward pressure on the sales price. In addition, sudden and unexpected shortages of bought in raw materials, labour, energy and equipment can temporarily paralyse a commodity producer, necessitating sourcing these from alternative suppliers/sources which are usually considerably more expensive or can greatly curtail production volumes. This can cause a commodity producer to become unprofitable. However, operational cost for a commodity producer can also be significantly reduced by the economies of scale, as producers with larger facilities and equipment tend to be more economically efficient, costing less to produce more. Thus, larger producers spend less for making a given commodity improving profit margins.

- Sell/factory gate price per unit or ton

The sell/factory gate price of a commodity is the full and final cost involved in the production and shipping of a commodity to its destination. This includes the sum of the costs for raw materials, labour, energy, equipment and shipping. Overall, the sell/factory gate price does not include any profit margin. The costs involved are also subject to the aforementioned influences stated prior. In addition, the economies of scale also significantly influence the sell/factory gate price. Lastly, when the sell/factory gate price becomes unsustainable, the commodity producer will attempt to pass these prices (or part thereof) onto the customer as an increase in the sell/factory gate prices. Depending on the market conditions, this is not always possible, which may result in even more dramatic action to be taken.

- Profit margin per unit or ton

The profit/profit margin is a set value added on top of the sell/factory gate price of the commodity to ensure the profitability of the commodity producer and the producer's financial health. Commodity producers that produce large quantities of their commodities tend to have the smallest profit margins. This is due to the economies of scale allowing for acceptable profit levels from larger quantities produced, making the producer more cost-effective. When business becomes unsustainable and profit margins become challenging or collapse, the more dramatic actions taken may include: (i) remediation of existing facilities (often involves shutdown or sale of unprofitable production facilities – temporarily or permanent), (ii) a change to new commodity grades that are more profitable, (iii) upgrade or increase of production capacity to make better use of the economies of scale, (iv) a complete change of the type

of commodity produced, and (v), lastly, a shut of the business. Disruptive technology can also have an impact here.

Looking at the four general commodity aspects above in regards the pulp and paper industry, the volume of pulp and paper grades produced globally is large at about 198 million tons in 2022, having grown steadily from 62 million tons in 1961 (Figure 1.1) [1]. The trends also shows the typical frequent “boom and bust” cycles that the pulp and paper industry is well known for. Thus, the issue of the economies of scale is extremely important to the pulp and paper industry, with the size of mills generally having increased over time to take advantage of the higher efficiency associated with ever larger mills (i.e. larger scales of production). By rough rule of thumb, in about the 1990s and 2000s a pulp mill producing about 1 million tons per annum was considered to be a large pulp mill, whereas in the 1980s to 1990s this value was only about 500,000 tons per annum. Presently (i.e. 2010s to 2020s), a large mill typically produces about 2.5 million to 3.5 million tons per annum, with the possibility of even larger mills proposed for the future.

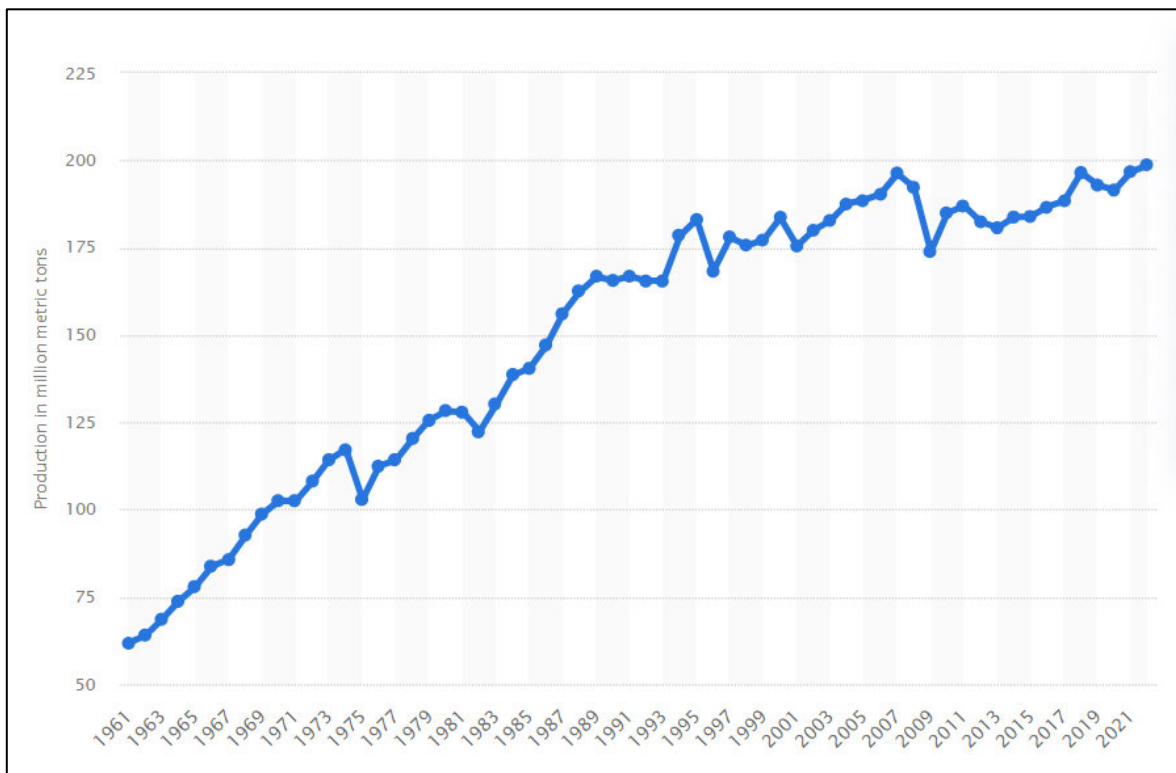


Figure 1.1: Annual global pulp production from years 1961 to 2022 [adapted from 1].

As regards the aspect of production costs, the main raw materials for the pulp and paper industry are timber, caustic soda, sulfuric acid, sulfur, pulping “cake salt” (sodium sulfite), sodium chlorite or sodium chlorate, oxygen, and hydrogen peroxide. It should be noted that this list is not exhaustive and a review of the costs of some of these raw materials would give an adequate overview of the cost

pressures that the pulp and paper industry is experiencing. Firstly, crude oil impacts the prices of all raw materials as it is central to the logistics chain and the transport of these raw materials. When the crude oil price increases, the cost of all raw materials also increases by an equivalent amount (although the increase is typically delayed by a short period). Looking at oil prices over the period of 2000 to 2004, a general upwards trend in crude oil prices as benchmarked by the Brent crude oil price is observed, resulting in a general increase in all raw material costs, both inherent and logistic (Figure 1.2) [2]. Secondly, the most important raw material for the pulp and paper industry is timber (i.e. lumber) which is the feedstock for producing pulp and paper grades. Timber prices showed periodic increases as illustrated for the period 2000 to 2020, although the market appears to show periods of lengthy price stability (Figure 1.3) [3]. Thirdly, the cost for caustic soda (mostly employed in kraft and soda pulping) showed increases over a period of 2002 to 2023 with periods of sudden short-term peak demand (Figures 1.4 to 1.5) [4, 5]. Fourth, sulfuric acid also showed a general rise in costs with periods of prolonged stability for the period 1973 to 2024 (Figures 1.6 to 1.7) [6, 7]. Fifthly, hydrogen peroxide (which is used for bleaching) showed a small increase in costs over the period 2015 to 2024 with periods of sudden short-term peak demand (Figure 1.8) [8]. Lastly, for sodium chlorite or similar chlorine bleaching reagents (as illustrated by the supply from China), there was a small increase in costs from 2012 to 2022 (Figure 1.9) [9]. Interestingly, Figure 1.9 also showed a general increase in caustic soda costs which is consistent with prior shown increases. Overall, the cost data (Figures 1.2

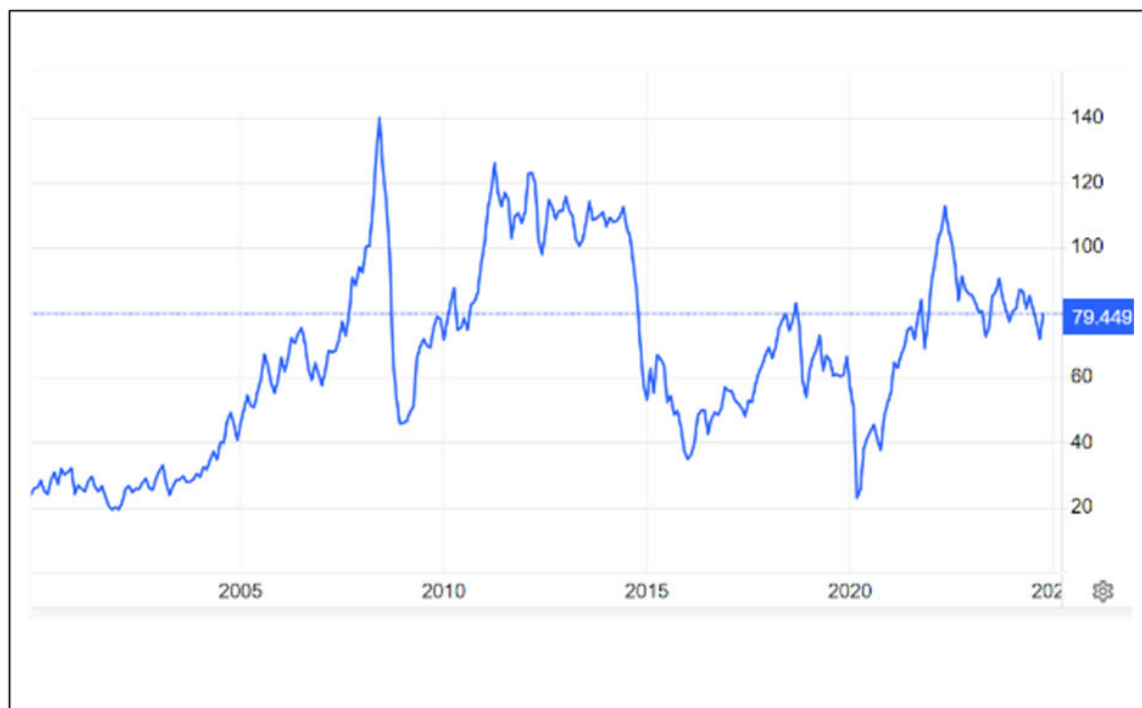


Figure 1.2: Cost of Brent crude oil from years 2000 to 2024 [2].

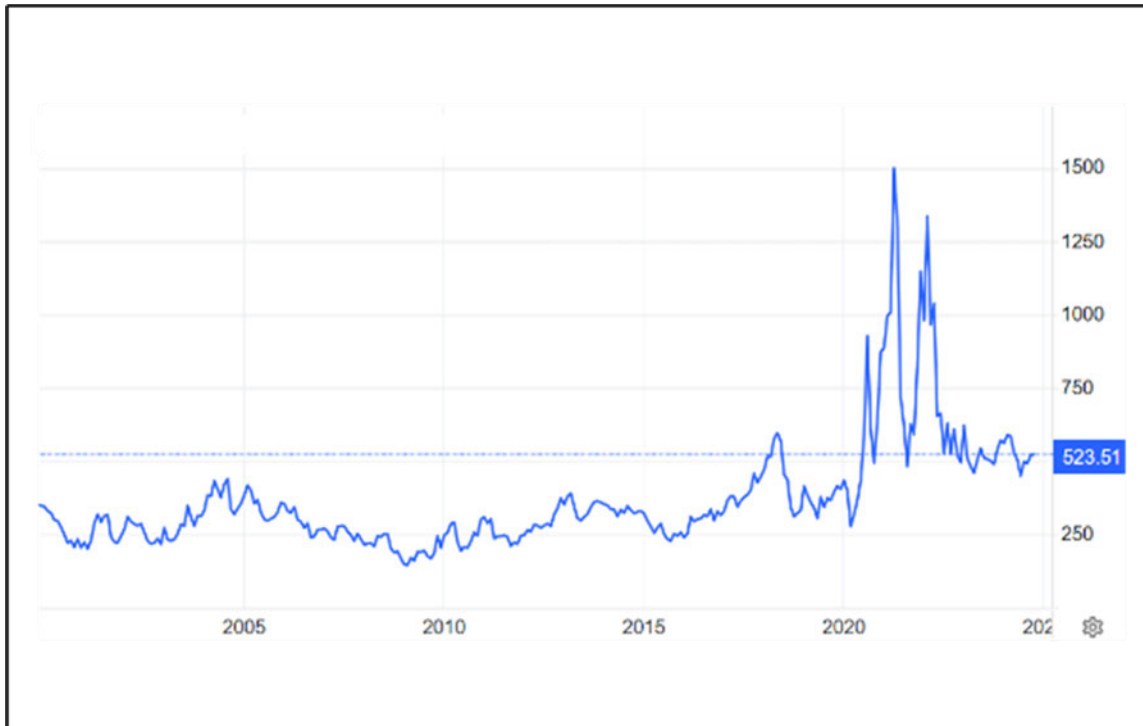


Figure 1.3: Cost of timber/lumber from years 2000 to 2020 [3].

to 1.9) show the general trend of increased costs for all raw materials reviewed over time. This places cost pressure on pulp and paper mills that employ various strategies to rationalize these costs to improve profit margins, but, the overall outcome is that ultimately these increased costs are eventually passed onto their customers (often belatedly).

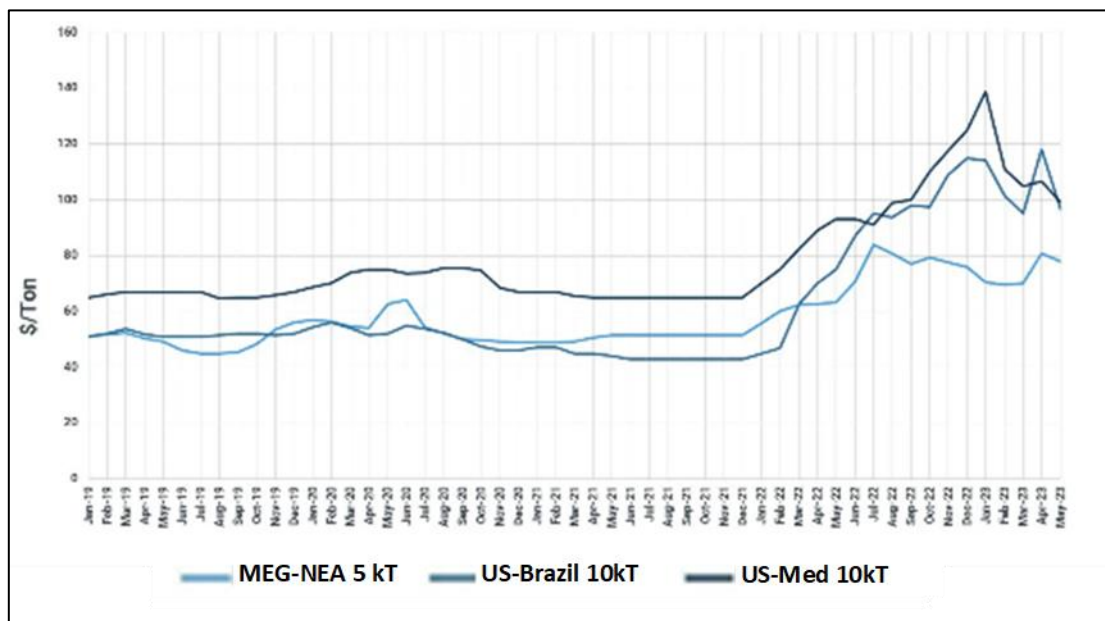


Figure 1.4: Costs of caustic soda from three regions for years 2019 to 2023 [4].

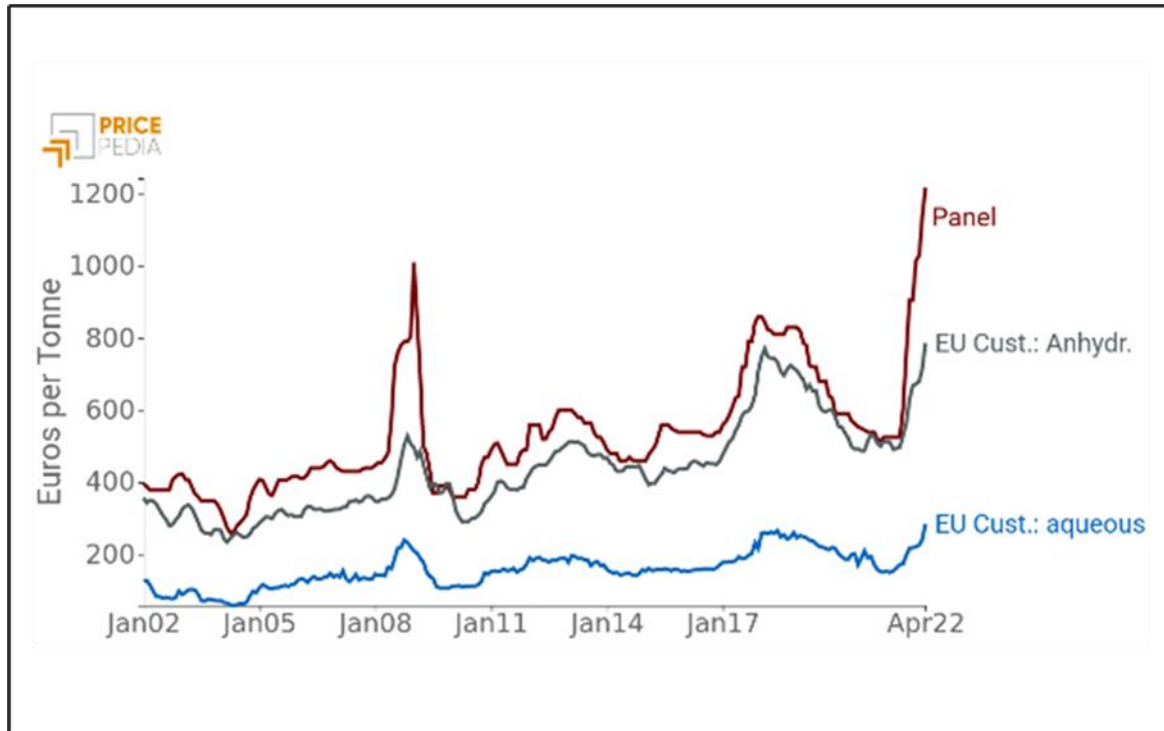


Figure 1.5: Costs of caustic soda for EU for years 2002 to 2022 [5].

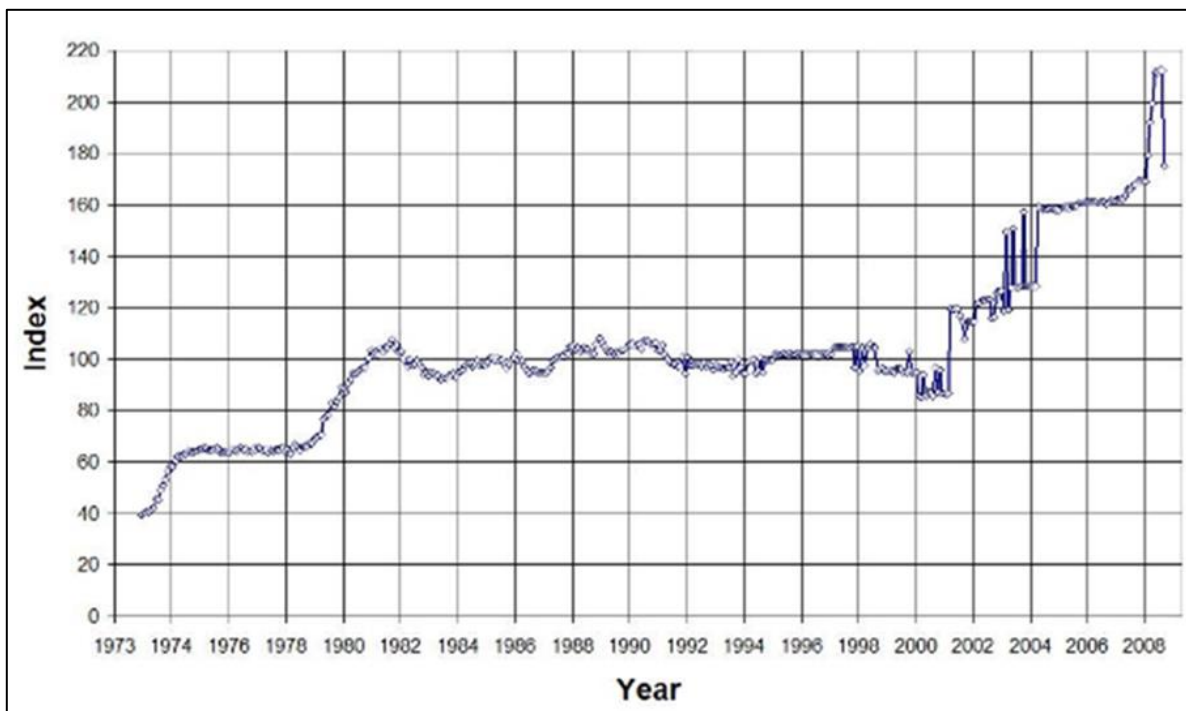


Figure 1.6: Costs of sulfuric acid for years 1973 to 2008 [6].

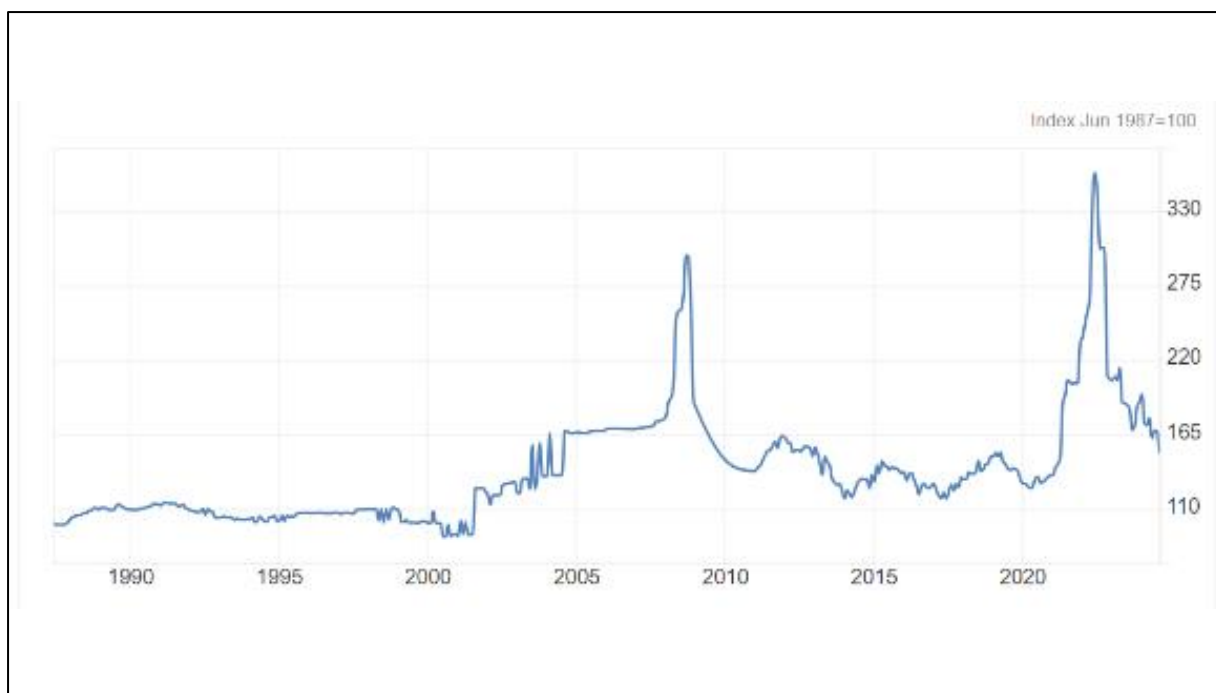


Figure 1.7: Costs of sulfuric acid as indexed for 1987 = 100, for years 1990 to 2024 [7].

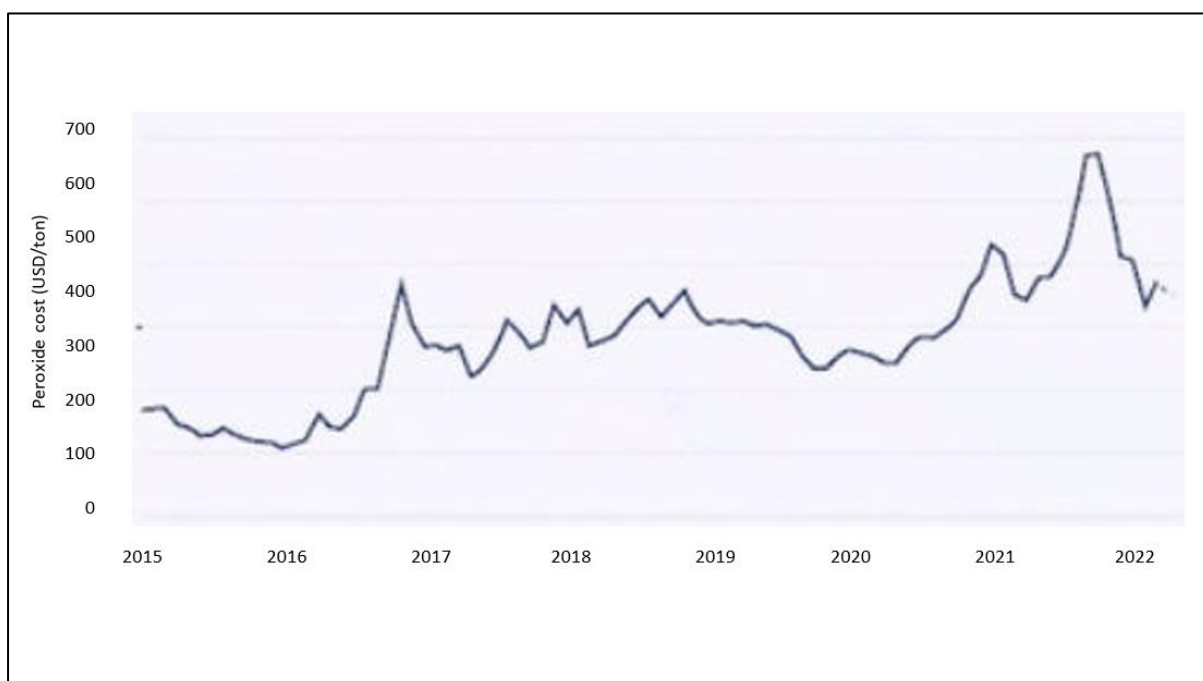


Figure 1.8: Costs for hydrogen peroxide for years 2015 to 2022 [8].

As regards the aspect of sell/factory gate price and profit margins, the sales prices for unbleached softwood kraft, fully bleached softwood kraft, and fully bleached hardwood kraft all showed a general

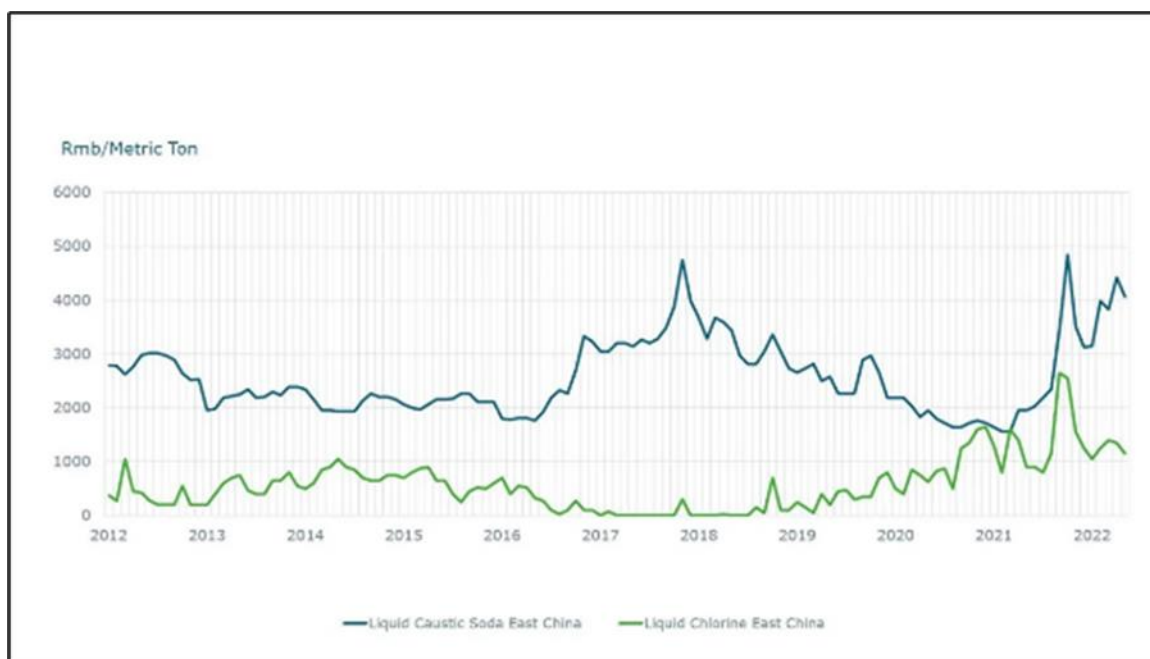


Figure 1.9: Costs of sodium chlorite and similar (given as liquid chlorine) for years 2012 to 2022 [9].

upward trend over time (Figures 1.10 - 1.12) [10, 11, 12]. Thus, the sales prices of the pulp and paper grades (UBK, NBSK, NBHK, etc.) increased as the production costs (raw materials, energy, labour, etc.) increased, although both do not always correlate with each other over time and amount. In addition, the profit margin varied depending on the location of the pulp and paper mill, the logistics of its raw material and the production technology employed at the mill. This combination varies from mill to mill, and is never the same. On some occasions, the mill is not always able to pass the full cost increases onto the customer. This often results in lower profit margins making the mill less financially viable. In an effort to address these and obtain the best combinations of volume, production costs, sell/factory gate costs, and profit margins, many pulp and paper producers look to: (i) further optimization of their industry processes, looking to reduce chemical expenditure (use less and use cheaper alternatives) and improve chemical recovery, washing and machine processes, (ii) change to more profitable pulp and paper grades (whether rebranding or completely different products), (iii) increase production volumes by increased production capacity which typically involves significant capital expenditure (this may result in a complete rebuild of a pulp and paper mill's entire pulping and bleaching production line – together with the associated accessories), and (iv) remediation/shut-down of existing production capacity that is not profitable while focusing on capacity that is profitable. Disruptive technologies can have a significant impact on these options, particularly around the aspect of process optimization with a specific focus on energy.

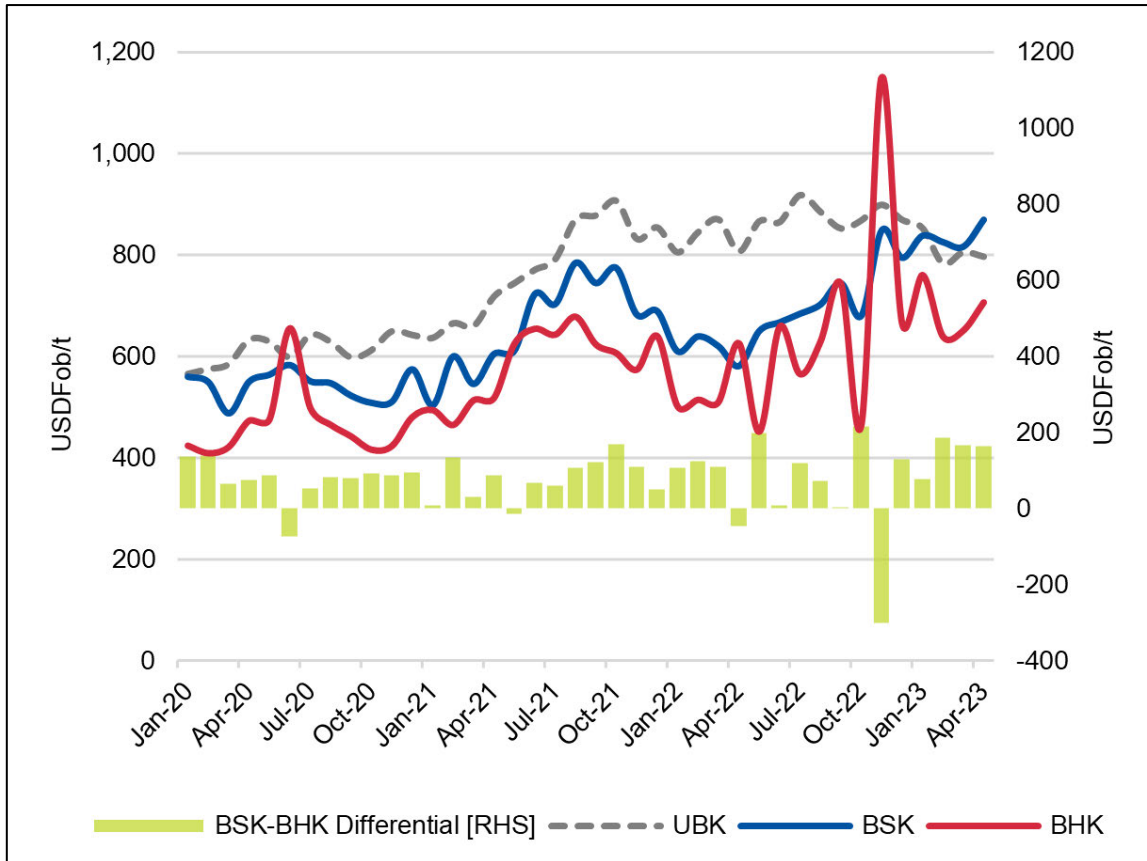


Figure 1.10: Price of unbleached kraft (UBK), bleached softwood kraft (BSK) and bleached hardwood kraft (BHK) from years 2020 to 2023 [10].

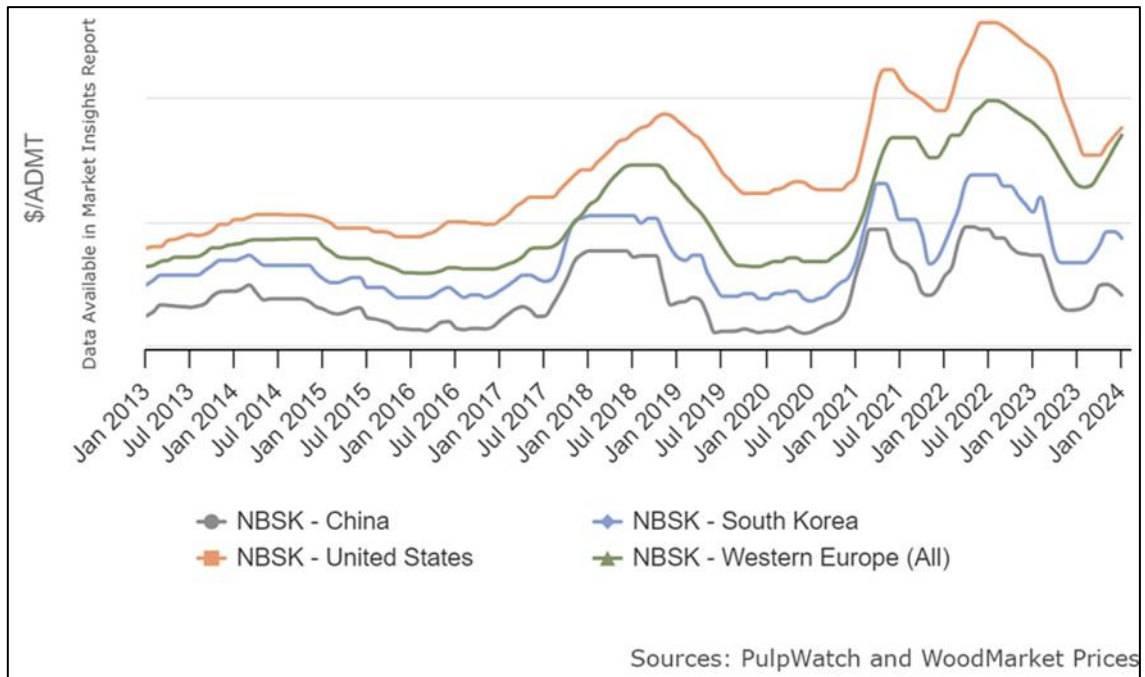


Figure 1.11: Price of northern bleached softwood kraft pulp (NBSK) from China, South Korea, USA and Western Europe for years 2013 to 2024 [11].

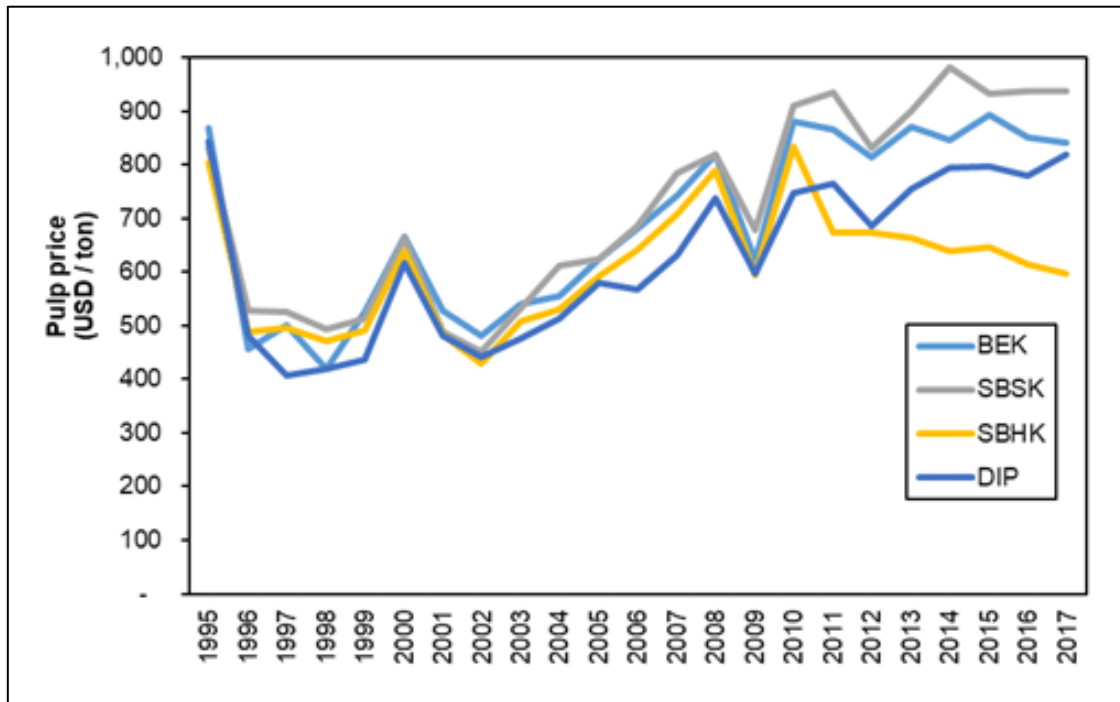


Figure 1.12: Price of bleached Eucalyptus kraft (BEK), southern bleached softwood kraft (SBSK), southern bleached hardwood kraft (SBHK), deinked (DIP) from years 1995 to 2017 [12].

Pulp and paper mills consume a great amount of energy, some of which is usually obtained from the national electrical grid or from coal, oil and bark boilers. However, most pulp and paper mills also have chemical recovery boilers which provide a large portion of their energy needs and recover most of the pulping chemicals, by burning the concentrated spent pulping liquor (i.e. black liquor) as a fuel and chemical reductant source (Figure 1.13) [13]. Their exact efficiency and what portion of their energy needs are met is dependent on the equipment present and varies for each individual mill. Efficiencies can be such that some mills are almost totally energy self-sufficient. Thus, the subsequent issue as regards energy is as much to do with the efficiency of its use as opposed to the total quantity the mill uses. Most of the processes in a pulp and paper mill are driven by high and medium pressure steam as an energy source, but at a high conversion efficiency. However, as regards the bleaching process, that efficiency is not as good and involves simply injecting steam into the pulp suspension with the bleaching reagents to drive the bleaching process via prolonged retention in bleaching towers (Figure 1.14) [14]. Thus, the energy for bleaching is applied completely indiscriminately and the bleaching processes would benefit from a more targeted/selective energy application. Such an approach would be considered a disruptive type technology as it would change the cost versus energy dynamics for a pulp and paper mill. Photochemical bleaching would be such a disruptive and highly selective approach.

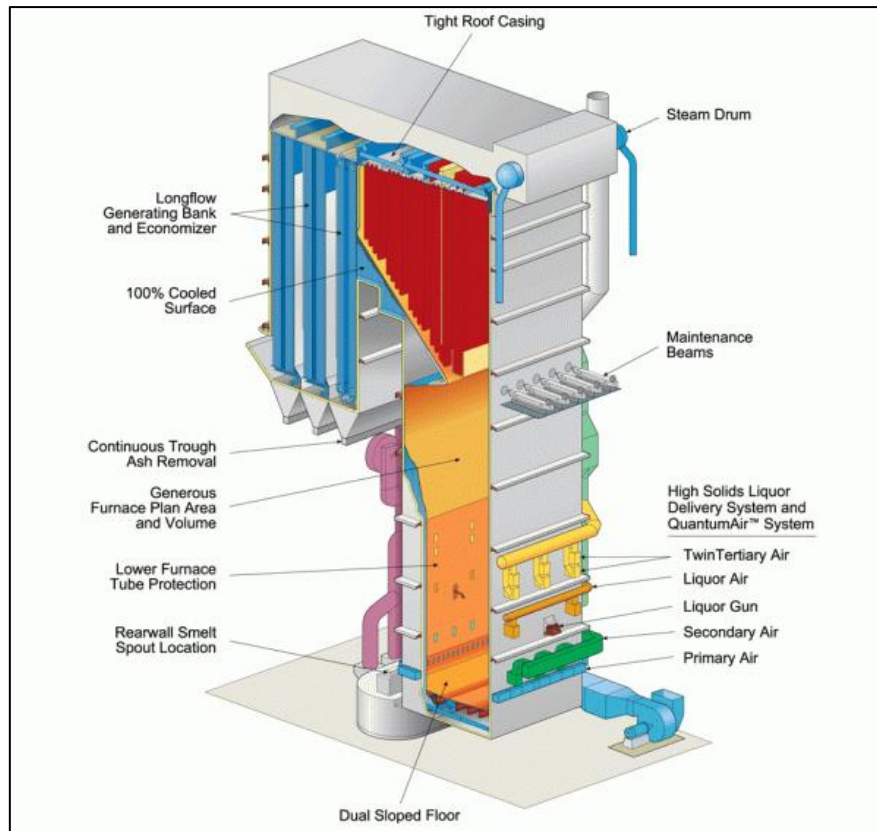


Figure 1.13: Babcock and Wilson chemical recovery boiler typical to the pulp and paper industry [13].

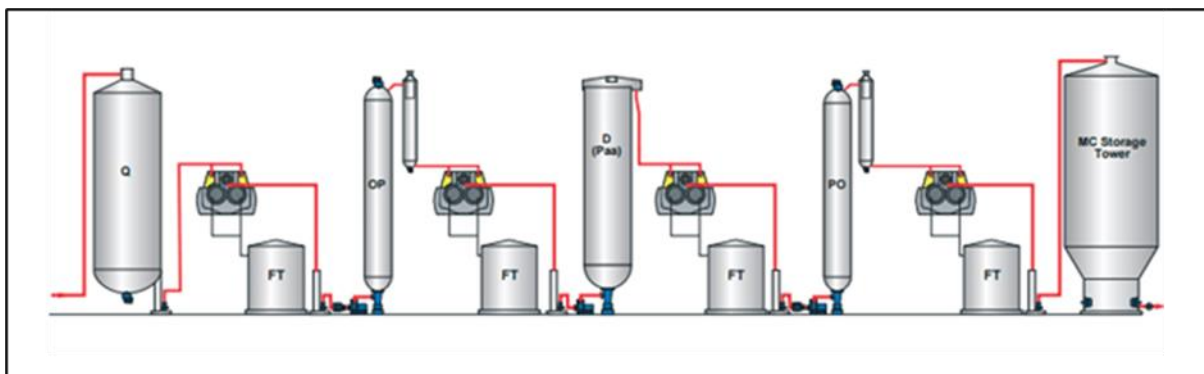


Figure 1.14: Schematic of a typical pulp and paper mill bleaching sequence showing the associated bleaching towers [14].

1.2 Bleaching of pulp

Bleaching is the process of whitening or brightening a discoloured pulp out of a pulping digester or related processes via oxidative degradation and then solvation of the pulp chromophoric material (i.e. colour-generating material) which consists primarily of lignin. Bleaching is undertaken with the aim of retaining or engineering in certain desired properties (not only brightness) in the pulp produced, e.g. adequate pulp physical strength for good paper making. Bleaching is typically performed in large

industrial sealed tall vessels utilizing various oxidative or alkaline reagents for the bleaching process (i.e. oxidative degradation and solvation respectively). Bleaching of pulp is not undertaken in a single step or stage as this is not cost-effective and is, also, highly damaging to the pulp. Thus, bleaching is undertaken in multiple steps involving various oxidative or solvation/extraction stages with wash stages between each step. The wash water used in the bleaching process is applied to the process washers in a counter-current manner, with the cleanest water used to wash the final bleaching stage's pulp and the most fouled wash water used for the first bleaching stage's washings. Bleaching reagents typically used in the pulp and paper industry include oxygen, ozone, elemental chlorine (i.e. Cl_2), chlorine dioxide (i.e. ClO_2), hypochlorite, hydrogen peroxide, and, occasionally, various peroxy organics or peracids. Sodium hydroxide (caustic soda) is, as a strong alkaline source, used for the solvation/extraction stages or to adjust the pH of pulp suspensions, containing various added bleaching reagents, when the bleaching stage requires alkaline pH values. Conversely, sulfuric acid is often employed in the industry to adjust pulp suspensions to acidic pH values. Sulfuric acid is employed due to it being a strong acid and also in that it is not a halogen-based acid. Pulp is typically pumped from one stage to the next using centrifugal pumps with the bleaching reagents added to the pulp in these pumps which ensure good mixing of all components during the pumping process. However, certain bleaching reagents require specialized equipment during their application, e.g. high shear mixers and ozone reactors for ozone bleaching. In the pulp and paper industry, heat (i.e. thermal energy) is used to drive these chemical reactions and processes. This heat is typically provided as steam which is abundantly available in pulp and paper mills. Although most mills are almost totally energy (steam) self-sufficient, and energy conversion is particularly high in mills, the application of steam to the bleaching process tends to lack this high energy transfer efficiency – particularly when viewed in conjunction with the “cool” counter-current pulp washing process. This poorer heat efficiency is made worse by the fact that most bleaching wash water streams contain halogenated organics generated in the bleaching process and are, thus, typically sewered after use, together with any residual heat energy, rather than being recycled back to the mill. This “inefficiency” allows for the possibility of alternative energy sources to drive the bleaching process.

1.3 Problem statement

As the pulp and paper industry is an extremely competitive market with very small profit, any improvement in the bleaching process can have a marked effect on the profit margins of the mill. The possible areas of improvement would include the cost of raw materials and reagents, the optimal application of these raw materials and reagents, and the cost and type of energy used to drive the bleaching process. As most mills are close to being at optimal reagent charges and operational conditions for their bleaching processes, further optimization here would yield very small benefits. However, given the poorer efficiency of steam as an energy source, the possibility of improvement here

is far more promising. Thus, the question arises: are alternative sources of energy viable alternatives to drive the bleaching processes of pulp?

1.4 *Central hypothesis of the thesis*

The central hypothesis, based on the above problem statement, would be: that light (particularly ultraviolet light) could be successfully employed as an alternative energy source, to heat or thermal energy (i.e. steam), to drive pulp bleaching processes. Three possible light sources that should be tested include solar irradiance (i.e. the sun), microwave discharge electrodeless lamps, and ultraviolet light emitting diode arrays.

1.5 *Aims and objectives*

The aim of this thesis was to evaluate various unique photochemical bleaching illumination sources to address the lack of research into microwave discharge electrodeless lamps (MDELs) and ultraviolet light emitting diode arrays (UV LED arrays), while also expanding on the use of solar radiation, in the photochemical bleaching of pulp. The overall objectives of this study were to:

- Design and test a laboratory-scale bleaching reactor which employs either sunlight, a commercial MDEL, or a UV LED array, as the light source.
- To select the best luminant of the three light sources.
- To evaluate the impact of various operational conditions on the bleaching performance of these reactors.
- To evaluate the performance of various reagents (i.e. oxidants, photocatalysts, and photosensitizers, among others) in these reactors.
- To evaluate the extent of bleaching performance on various pulps.
- To determine how well photochemical bleaching, utilizing these technologies, would perform as an alternative to conventional thermal bleaching in multiple stage bleaching sequences.

1.6 *The structure of the thesis*

The thesis structure is as follows:

- An introduction is provided in Chapter 1 to outline the central hypothesis of the thesis that was tested.
- An extensive literature review is given in Chapter 2 containing an overview of all the basis of the literature on the topic; from the history of bleaching, to the overall structure of wood and plants, to an overview of bleaching technology today, to the basics of thermal and photochemistry, to an overview of most of the photochemical reactions associated with the pulp and paper industry, to an overview of the five possible sources of light (solar, mercury arc dark lamps, lasers, MDELs, and LED arrays), and the literature covering work around these sources.

- A material and methods chapter (Chapter 3) discussing the materials, reagents, analytical techniques and photochemical bleaching methods employed.
- A results and discussion chapter (Chapter 4) discussing the findings around the three light sources evaluated. This chapter also presents the outcome of two thermos-photochemical bleaching sequences for paper grade pulp and dissolving grade pulp respectively.
- A summary of the results, the conclusions drawn and proposed future work is found in Chapter 5.
- A reference section.
- Appendix A provides the Sappi specific methods employed.
- Appendix B lists all the raw data.
- Appendix C contains the personal communication from Jim Borsuk, and
- Appendix D contains the spectra of methylene blue and rose bengal.

LITERATURE REVIEW

This chapter is an extensive review of all the relevant, related and available literature on this thesis topic. This chapter also discusses the three proposed light sources and where they fit into the topic of the photobleaching of pulp.

2.1 *The history of bleaching in the pulp and paper industry*

Throughout most of recorded history, bleaching of material for writing and records purposes followed closely that of bleaching clothing material and linen. This was because, until about two centuries ago, both were generally based on the same fibre source; namely, fabric derived fibrous material. Only with the introduction of alternative fibre sources for paper making, based on new pulping technologies introduced during the industrial revolution, did the bleaching of paper and fabric diverge based on increasingly different bleaching techniques and goals [15, 16].

The bleaching of plant and fabric material has been practiced since ancient times and has been used in various locations around the globe; such as Egypt, Asia and Europe; since its inception [17, 18]. Although it is generally agreed that the bleaching process was preceded the pulping of plant material, the first true paper form is attributed to the Chinese, having been invented by Ts'ai Lun (or Cai Lun) [17, 19 to 21], of the imperial Ho Tin court, in about 105 AD. Prior this, the Pharaonic Egyptians employed sheets of combined papyrus (i.e. *Cyperus papyrus*) as a type of writing medium [17, 22]. The first specific mention of bleaching dates back 7000 years, in documentation from Pre Dynastic Egypt (5000 BC) [23 to 25]. The Egyptians were said to have been masters of producing white material from their bleaching techniques which typically involved prolonged exposure to sun light. During these earlier periods, the knowledge for bleaching techniques was generally maintained within specific families by passing it from one generation to the next, or within small related communities. Later on, these bleaching techniques were passed on more broadly from one society to the next, down time as the knowledge base became more wide spread.

The next recorded mention of bleaching in the historical records is by Theophrastus [16, 26], a Greek from the village of Eresos on the island of Lesbos, and whom was a successor to Aristotle in the Peripatetic school. In 300 BC, Theophrastus described how a wooden galley (a type of ocean going ship) was destroyed by its cargo of lime (i.e. calcium oxide or calcium hydroxide) after the lime was contaminated by a sizeable volume of sea water. This is followed by a third mention in the literature,

a few hundred years later, given by “Pliny the Elder” (23AD to 79 AD) [16, 27 to 31]. In his account, Pliny described the virtues of bleached linen in which he proceeds to describe the technique employed. The technique involved repeated steps of firstly scouring the linen with alkali, followed by washing with water and, lastly, laying out the linen in the open to be bleached by sun light.

Thereafter, the next significant mention of bleaching is in documentation from the Middle Ages, by which time bleaching had developed into a significant industry in Europe with the Dutch (i.e. the Netherlands) being among the foremost leaders therein [25, 32]. The Dutch had developed a method whereby which they were able to significantly reduce the detrimental impact of the lye (i.e. caustic soda or potassium hydroxide) on the strength of the fabrics and laundry treated therewith. This involved combining the lye with the sour milk (lactic acid) to “soften” the impact of the lye. By this approach, the Dutch were able to monopolize the bleaching industry while ensuring that the technique remained secret for a long time. Consequently, linen and fabric from all over Europe was sent to the Netherlands for bleaching. This included most of the manufactured linen in Europe (which was typically brown before bleaching), even from as far away as Scotland. The Dutch bleaching method was undertaken in stages. The first stage involved a week long initial soaking in a lye solution, followed by pouring further boiling potassium lye solution over the already soaked linen. The lye solution was then squeezed from the linen before it was washed of any residual lye. Next, the washed linen was then placed in wooden containers containing buttermilk and allowed to stand in the buttermilk dip for about a week. The final stage involved laying out the linen in open grassy fields (known as “grassing” in “bleaching greens”), exposed to the sun all the while keeping the linen moist. This entire process was repeated a number of times (five to six times) to ensure the linen was fully bleached at the end of the process and, often, the entire bleaching process could take all summer in Europe or as long as eight months. However, the downside of the Dutch process was that it was very lengthy and required considerable areas of land for prolonged sun exposure during “grassing”. Other documents from the period also describe the process of grassing in which processed fibre material was laid out in grassy meadows known as “Bleaching Greens”. One document proceeds to mention how the use of lime; by bleachers; was forbidden in some particular realms and dominions, by pain of death [16]. This was due to the strong alkalinity of the solution obtained by the dissolution of lime (i.e. calcium oxide and calcium hydroxide) in water which could cause serious physical injury to the user and significant damage to the environment. Theft from these Bleaching Greens also became a significant problem over time. Hence, those employing bleaching for a livelihood formed “Societies of Bleachers” to guard these meadows[33, 34]. On a number of occasions thieves, whom were caught, faced execution.

Chlorine was first discovered in 1774 by the Swedish chemist Carl Wilhelm Scheele [35 to 37], however, he did not recognize it as an element and named it “dephlogisticated marine acid gas” based on the premise of the predominant theory of chemistry of the time (The Dephlogiston Theory). It was

Sir Humphry Davy (a Cornish chemist and inventor) [35, 36, 38, 39], who actually recognized that chlorine was an element rather than a compound after repeating Scheele's experiment in 1810, giving it its present name of "chlorine" from the Greek meaning "green".

In 1785 the French chemist Claude Louis Berthollet [16, 40, 41] discovered that chlorine gas was soluble, in significant quantities, in alkali water. He used vegetable ash (sodium carbonate) as his alkali source, an expensive source for alkali. Berthollet [16] proceeded to produce Europe's first commercial bleaching solution of sodium hypochlorite in 1789 by passing chlorine gas through a solution of sodium carbonate, firstly, in his laboratory on the quay Javel in Paris (France) and, later, in a factory built at Javel for the same purpose in that same year [42]. The product was sold under the name "Eau de Javel" ("Javel water").

About the same time, a Scottish chemist and industrialist named Charles Tennant [43], upon hearing of Berthollet's work, developed an interest in combining both lime (whose use was illegal) and chlorine in an attempt to shorten the lengthy time periods associated with traditional grassing. Tennant had prior acquired bleaching fields at Darnley, near Barrhead, Renfrewshire (1788) for the purpose of bleaching after learning his bleaching craft in his youth. After a number of years of experimentation, he successfully managed to generate calcium hypochlorite by combining chlorine dissolved in water with lime in suspension, for which he was awarded a patent (patent#2209) on 23 January 1798. Further development lead to another patent (patent#2312) on 30 April 1799 for a purer more reliable grade of calcium hypochlorite which he called "bleaching powder" [16, 44, 45]. One of the advantages of "bleaching powder" was that lime was a much cheaper alkali source than vegetable ash (sodium carbonate used by Berthollet). Shortly after being awarded the second patent, Tennant and four partners (Dr William Couper, Alexander Dunlop, James Knox and Charles Macintosh) purchased land on the Monkland Canal, just north of Glasgow, to establish a factory which became known as St. Rollox Chemical Works for the production of bleach powder [16^b, 46 and 47]. The factory dominated the landscape at the time and was a major source of employment in the region. By the turn of the twentieth century, this had grown into the industrial giant "Imperial Chemical Industries" by 1926 [48].

Prior to about 1840, the primary source of fibre for paper making was cotton and fabric/linen rags. However, during the period of the industrial revolution, and thereafter, the demand for fibre for books quickly outstripped the supply possible by cotton and rags. Consequently, wood fibre began to replace cotton and linen rags as an alternative source of paper fibre [17, 49].

The first commercially and technically viable method for producing wood pulp from timber was discovered and proposed simultaneously by a German machinist and inventor, Friedrich Gottlob Keller, and a Canadian inventor, lumberman and farmer, Charles Fenerty, in 1844 without either being aware

of the others work [50 to 54]. Both of their processes were based on what is known today as mechanical pulping, or more specifically Stone Groundwood Mechanical Pulping/Refining (Figure 2.1 [54, 55]).

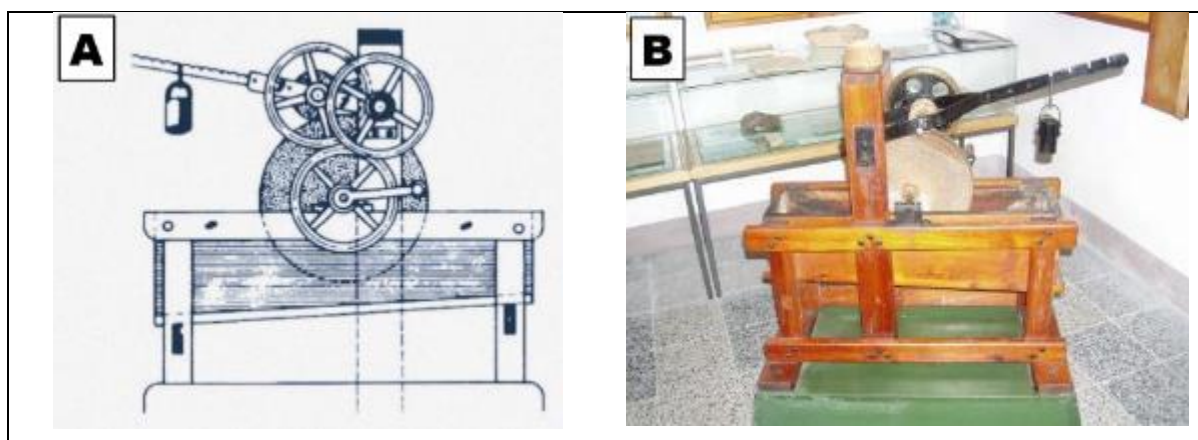


Figure 2.1: [A] Schematic and [B] photo of FG Keller's patented Wood Cutting Machine (Stone Groundwood mechanical refiner) [54, 55].

Keller developed an interest in machines in his youth and became interested in producing fibre from wood after reading a book by British paper maker, Matthias Koops, a concept which itself was based on an earlier idea by French mathematician, René Antoine Ferchault de Réaumur, who never pursued such an approach any further [49, 51^b]. In 1841, Keller started to put a concerted effort into developing his Wood Cutting Machine and by 1844 had successfully produced wood pulp with his device. However, Keller was unable to secure financial support from the German government and in 1845 he sold his invention to Heinrich Voelter (inventor and paper manufacturer), who took out a patent in both his and Keller's name [50, 51]. This allowed Voelter to produce the world's first commercial mechanical refiners/pulpers in 1848. When Keller couldn't pay his portion of the patent upon its relapse in 1852, Voelter became the sole owner of the patent and the Stone Groundwood mechanical refiner technology in Europe.

Fenerty, together with his two brothers, worked on their father's farmland near Halifax while growing up and would help clear cut the local forest during winter. This timber was then transported to the family's Springfield Lake lumber mill before transporting this lumber and the rest of the farm's produce to Halifax [50, 56]. Given the numerous similarities between the family's lumber mill and the local paper mills, Fenerty developed an interest in paper mill processes. In 1838, Fenerty started to experiment with making pulp from wood after learning about the fibrous nature of wood from the naturalist Titus Smith [57, 58]. In 1844, at the same time as Keller, Fenerty succeeded in producing wood pulp from timber using a mechanical pulping/refining process. However, although Fenerty approached at least one newspaper in Halifax (Acadian Reporter) he never applied for a patent for his invention, nor pursued it any further.

Following the introduction of Stone Groundwood Mechanical Pulping/Refining by Voelter (1848), improved methods for producing fibre from a wood source continued to be investigated with the first chemical pulping process being discovered shortly thereafter. The first successful chemical method of pulping was discovered by Julius Roth in 1857 who used sulfurous acid (i.e. " H_2SO_3 ") to treat wood, for which he subsequently took out a patent. This was followed by Benjamin Chew Tilghman who added a calcium base to the sulfurous acid giving a calcium bisulfite based process for which he obtained a patent in 1867 [59 to 62]. Use of a base allowed better control of the sulfurous acid ion during make up for the pulping process. However, in both of these cases, neither process was commercially used due to impurities within the sulfurous acid that produced pulp too weak for commercial application. The first commercial application of bisulfite pulping was by Carl Daniel Ekman, a Swedish chemical engineer, who used magnesium as base instead of calcium [60^b, 63]. In 1871, Ekman was hired to work as a chemist at Bergvik mill (Sweden) - a mill managed by his half brother. Ekman undertook his first experiments using the magnesium base bisulfite pulping process in the following year (1872). By 1874 the first commercial bisulfite pulping process was commercialized in Bergvik as part of a new plant based on Ekman's process. Ekman also helped set up mills in France, Italy, Russia, and Germany; and frequently travelled as a result. Furthermore, he also evaluated sugarcane, straw, aspen, birch, sycamore, esparto grass, linen, and hemp as alternative fibre sources. Sulfite pulping, being a more cost-effective chemical process than mechanical pulping, continued to grow in popularity with time and, consequently, by 1900, the sulfite pulping process surpassed mechanical pulping as the primary method of pulping wood globally.

Both the mechanical and sulfite pulping processes had the advantage of producing pulps of high brightness. This allowed the bleaching process to be completed in a single hypochlorite step or two hypochlorite steps at most. However, the disadvantage of these two processes was that they produced pulp that was significantly weaker than rag fibre used prior [64]. Hence, the search for a chemical pulping process that produced stronger pulp continued.

The first mention of a Kraft type pulping process (i.e. pulping with mainly caustic soda and some sulfur typically present as sodium sulfide) occurred in England during the Napoleonic wars (1803 – 1815) as a means of the soda pulping of straw with the first commercial operations undertaken by William Shryrock at the Honeywell mill near Chambersburg [19^b, 49, 65]. The first recognized Kraft process (also known as the sulfate pulping process) was discovered by Eaton in 1870 and 1871; who was awarded two US patents. Eaton [66, 67] found that the use of sodium sulfide together with the caustic soda primary base improved the level of delignification and strength of the resulting fibre. Carl F. Dahl [65, 66, 67] invented the world's first industrially applicable Kraft pulping process in Danzig Prussia/Germany in 1879. He found that the addition of sodium sulfate in the combustion furnace

during the Kraft pulping liquor chemical recovery process ensured complete recovery of the initial sodium sulfide content as the sulfate added was converted into sulfide via the reduction phase of the soda recovery system. This was key, as it allowed the Kraft pulping process, which used costly reagents, to economically compete with the sulfite process, which made use of much cheaper reagents and which, thus, did not require a chemical recovery system. Dahl was awarded a US patent (US patent 296,935) for his process in 1884 [49, 60]. The Kraft Process was almost immediately adopted for pulping coniferous wood in Sweden in 1890 after general recognition of its benefits in Scandinavia in 1885 [65].

Although Kraft pulping produced fibre that was significantly stronger than rag fibre and sulfite pulp, it was, however, significantly darker due to the use of large quantities of caustic soda and its associated strongly alkali conditions at elevated temperatures. This significantly darker pulp necessitated considerably more severe bleaching conditions and higher charges when relying on the old typical single stage and two stage hypochlorite bleaching processes. This was both costly and generated a much weaker pulp. These challenges served as an incentive to find much milder bleaching technologies and approaches. Experiment and trial showed breaking down the older typically bleaching process into multiple shorter stages using much lower hypochlorite charges with wash stages between each step improved the outcome giving stronger brighter pulps and significantly reduced production costs [68]. In addition, the inclusion of a pure caustic soda extraction stage (at temperature) between many of, or each, hypochlorite stage improved brightness gain further. Lastly, the use of dissolved elemental chlorine (Cl_2) in water (an acidic solution) in the sequence as an alternative bleaching reagent followed by an alkali extraction stage provided notable benefits in bleaching with little loss in pulp strength. These observations and trials led to new advances at the turn of the twentieth century, during the period 1900 to 1930, which helped improve the commercial paper making processes in general. Application of multi stage bleaching sequences with interstage washing such as -H-E-H-, -H-E-H-H- and -H-E-H-E-H- became common. Furthermore, the use of dissolved elemental chlorine often allowed for even shorter sequences such as -C-E-H- and -C-E-H-H-. Lastly, further evaluation of bleaching at higher consistencies with its improved efficiencies allowed paper makers to move to high consistencies during bleaching utilizing specialized reactors such as the Belmer reactor (3 to 6% consistency) and high density bleaching (~12% consistency).

A further significant improvement in the paper making process occurred during the 1930's with the introduction of the Kraft Recovery Boiler by G.H. Tomlinson [69 to 71]. This system allowed for the cocurrent recovery of all Kraft pulping liquors and the generation of electrical energy from high pressure steam generated inside the boiler using black liquor from the completed pulping process. This greatly contributed to paper mills being more energy independent and significantly reduced their dependence and reliance on coal and coal coke. The introduction of the Kraft Recovery Boiler resulted in most of

the industry switching from sulfite-based pulping processes to Kraft and Soda pulping processes by the 1940's.

Growing environmental concerns in the 1980's and 1990's around the impact of pulp and paper mills drove efforts to find more environmentally friendlier bleaching options. One of the key concerns was around the generation of dioxins, a key by product of elemental chlorine bleaching. Dioxins are stable long lived toxins which can persist in the environment and living complex organisms for years or decades [72, 73]. Hypochlorite was also known to be environmentally detrimental. These concerns drove the discontinued use of element chlorine (i.e. Cl_2) and hypochlorite (i.e. ClO^-) as bleaching reagents with alternative bleaching technologies falling into one of two categories Elemental Chlorine Free (ECF) and Total Chlorine Free (TCF). In Elemental Chlorine Free (ECF), elemental chlorine is replaced with chlorine dioxide (ClO_2) - a bleaching reagent that produces only one fifth the quantity of dioxins at the same equivalent charge. In Total Chlorine Free (TCF), all chlorine bleaching reagents (including chlorine dioxide) are replaced with other environmentally friendly bleaching reagents, such as oxygen, ozone and hydrogen peroxide. Consequently, elemental chlorine-based bleaching of bleached Kraft pulps dropped from 90% global capacity in 1990 to about 19 to 20% in 2005. Of this, 75% was ECF and the remainder (5 to 6%) was TCF by 2005 [74, 75]. By 2012, ECF made up 93% of global bleached Kraft production with TCF being a little less at just under 5% [76].

The world's first commercial oxygen bleaching process was the high consistency Saxopal process, introduced in 1970 by Sappi at Enstra mill [77, 78]. This was co-developed by Sappi and Air Liquide. Further technical development led to the development of the medium consistency Oxygen Delignification process which began to gain widespread use in the 1980/1990's period, to the complete exclusion of the high consistency Saxopal process. The introduction of medium consistency oxygen bleaching also led to the later practice of fortifying bleach alkali extraction stages (i.e. E_O -stage) with molecular oxygen in the 1980's.

One of the earlier commercial introductions of ozone bleaching of pulp was also by Sappi, at its Ngodwana pulp and paper mill in the 1980's [77]. As with Oxygen Delignification, further technical development eventually led to the introduction of the medium consistency high shear ozone bleaching process. However, unlike oxygen, bleaching with both the high consistency and medium consistency ozone bleaching processes continue to be used until the present, with suppliers specializing in one or the other technology.

During this same period (1980's and 1990's), further attempts to reduce the environmental footprint of certain ECF mills resulted in the inclusion of oxygen delignification, ozone or peroxide bleaching processes within their existing bleaching sequences. This gave sequences typical of the -O-D- E_OP -D-,

-Z-E_{OP}-D-D- and -D-E_{OP}-D-P- type and similar, with a reduced chlorine dioxide bleaching load/charge. In addition, the combination of both oxygen and ozone in the same sequence (e.g. -O-A-Z/D-E_{OP}-D- and -O-D-Z/E_P-D-) allowed for the chlorine dioxide bleaching load to be reduced even further. Lastly, on numerous occasions, a peroxide stage was attached to the end of these combined oxygen/ozone sequences (e.g. -O-A-Z/D-E_{OP}-P-). This approach, using much reduced chlorine dioxide bleaching loads, is termed “Lite ECF”. For TCF sequences, given the lower relative bleaching selectivity of hydrogen peroxide for wood lignin and chromophores, the inclusion of oxygen delignification, ozone bleaching, or both, was critical to achieving high target brightness values for most TCF sequences. Sequence such as -O-P-E_P-P-, -Z-E_O-P-P- and -O-Z-P-E_{OP}-P_O- were typical. Also, during this period, related technical advancements such as Twin Tower Two stage Oxygen Delignification processes, medium consistency high intensity pumps, medium consistency centrifugal pumps, and online sensors using optical as well as residual chemical measurements, led to improvements in bleaching and mill efficiency. It was also during this period that the concept of total mill closure, particular of the water circuit, was introduced. Considerable attempts were made at achieving this on an industrial scale.

However, at the turn of the twenty first century (i.e. 2000 – 2010), the significant shortcomings associated with TCF bleaching due to its lower bleaching selectivity and the enormous challenges associated with total mill closure started to drive a partial slow shift away from the use of these technologies, until at least their technical challenges could be adequately addressed. This is one reason why ECF and “Lite” ECF bleaching has not been entirely replaced with the more environmentally friendlier TCF approach.

Moving into the 2020’s and future 2030’s, presently there is a drive towards shortened bleach sequences using ozone, such as Metso’s Ze Trac system; however; the future prospects of this new technology are unclear [79, 80]. In addition, there have been moves closer to near complete closure of mill liquor and water circuits (some or all) [81 to 83]. Lastly, a number of new and developing pulping and bleaching technologies have begun to emerge, such as alternative milder OrganoSolv processes, wider use of purer ozone steams with a reduced or nil oxygen component (obtained by liquification separation of associated ozone/oxygen stream), wider use of various peracid reagents (e.g. Caro’s Acid and peroxyacetic acid), bleaching and delignification catalysts or additives, metal and transition metal based bleachers, and photocatalyzed/photoassisted/full photo-bleaching technologies applied at reduce or elevated temperatures. Exactly which of these, if any, will emerge as viable alternatives is still unknown; but, in general, photochemical based production processes are expanding rapidly in their commercial applications throughout all fields of industry.

2.2 The structure of wood and pulps

Aside from additives, binders, fluorescent agents and inorganic fillers, the key component employed for making products in the pulp and paper industry is the fibrous material extracted from plant matter in the form of plant pulp (i.e. the plant fibres). The main source of plant fibres in the pulp and paper industry is the pulped woody component extracted from felled timber [49, 51]. However, alternative sources for plant fibres are utilized in some mills (e.g. bagasse, hemp, kelp, cotton); but by far, most of the fibre used globally is derived from wood chips of the trunk section of trees/timber – or more specifically the mostly xylem component of trees found in the wood fibres (Figure 2.2) [84].

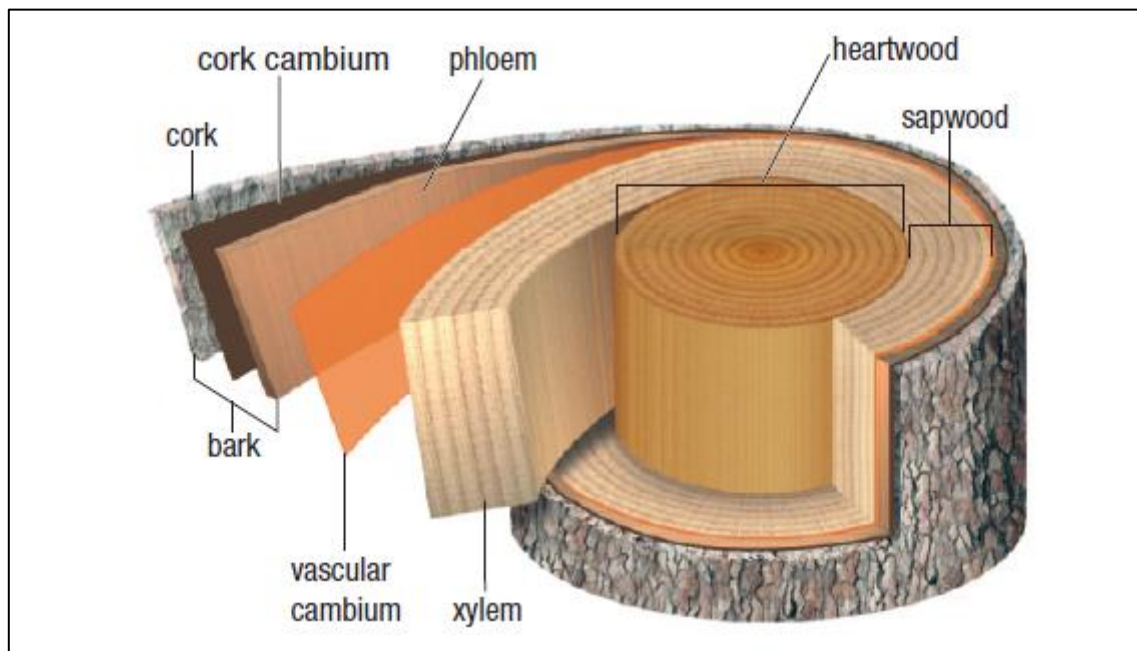


Figure 2.2: Cross section of Tree trunk showing various layers of tree tissue [84].

The only portion of a tree that is alive, aside from the leaf foliage, is a thin living layer on the outside of the tree trunk and the branches as well as portions of the root system, while the rest (which makes up the majority of the tree) is dead inert structural support material [85]. This living section on tree trunks includes a dead outer most bark layer for protection from the elements/outside vectors and a living inner bark (bark cambium) layer beneath that to grow the outer bark layer [86]. Below this is the living phloem vessel layer specialized for the transport of food, typically carbohydrates generated by the photosynthetic processes in the leaves, downwards to the rest of the tree [86^b and c]. Underneath this is the living xylem sapwood layer specialized to transport water and mineral nutrients up to the leaves from the roots for the photosynthetic process [86^d and e]. Between the living phloem and living xylem layers is a living cambium layer used to grow further living phloem and xylem as the tree expands in size [86^f]. Inwards of the living sapwood xylem layer (towards the core of the tree) is the dead heartwood xylem which is used to provide structural support and strength to the tree while also

constituting the bulk of the tree's mass. The xylem vessels of the sapwood consist of living cell vessels containing all the components of living plants cells: nucleus with DNA, cytoplasm with organelles and proteins, a large water vacuole, the cell membrane, and the cell wall [85^g and ^h]. The heartwood xylem is younger dead xylem vessels that have lost their living contents leaving behind only hollow vessels/wood fibres made up of a carbohydrate (cellulose/ hemicellulose) based cell wall. Often these vessels contain and are partially blocked by resins and woody waxes. For pulp and paper manufacturers, the most important component of the tree is the xylem wood fibre fraction. It is the xylem fibre that pulp and paper makers use as their source material during the pulp and paper making process. Consequently, the bark, phloem and cambiums are typically physically stripped away or chemically removed during the debarking and pulping processes, that precedes the bleaching of the pulp fibres. The pulping process also removes most of the resins and waxes typically found in the heartwood.

In general, tree species can be divided into two distinct groups: softwoods and hardwoods [86ⁱ]. This also allows for the classification of their wood fibres by the same system. Softwood species (e.g. conifers, etc.) tend to consist of longer larger fibres (approximately 2.0 to 4.0 mm in average length), while hardwood species (e.g. various Eucalyptus species, etc.) tend to have shorter smaller fibres (approximately 0.5 to 1.5 mm in average length) [87]. Typically, softwood fibres are used to afford paper and corrugated paper board strength, while hardwoods are typically used as a filler fibre and often make up the larger portion of the fibre material in paper products [88]. Chemical pulping processes (kraft and sulfite) typically attempt to design their conditions and charges to maximize the beneficial properties and strengths of both softwoods and hardwoods for the purpose they are usually employed for, but with an overall view on maximizing certain or all strength characteristics of the fibres. The only exception is dissolving pulps, where the main goal is to maximize the purity of the cellulose component of the fibre at the expense of the pentosan/hemicellulose fractions and pulping yield.

The cell wall of all plant fibres (including wood fibre) can be divided into three layers: the middle lamella on the outside, the thin primary cell wall (P) just below the middle lamella, and, lastly, the secondary cell wall (subdivided into S1 to S3 layers) on the inside (Figure 2.3) [89]. These three cell wall layers are all made from the same material components, but in moderately differing proportions, namely: cellulose, various hemicelluloses and lignin. Cellulose and various hemicelluloses make up the structural bulk of each fibre, while lignin is the natural adhesive/glue holding all the components in each fibre wall together in a complex matrix. Additional lignin present on the outside of the cell wall structure cements the individual fibres together in the bulk wood structure. Furthermore, the complex fibre matrix itself is constituted by a hierarchical ordered structure which can be subdivided at its various hierarchy levels, from large to small, within the cell wall of each plant fibre. At the largest

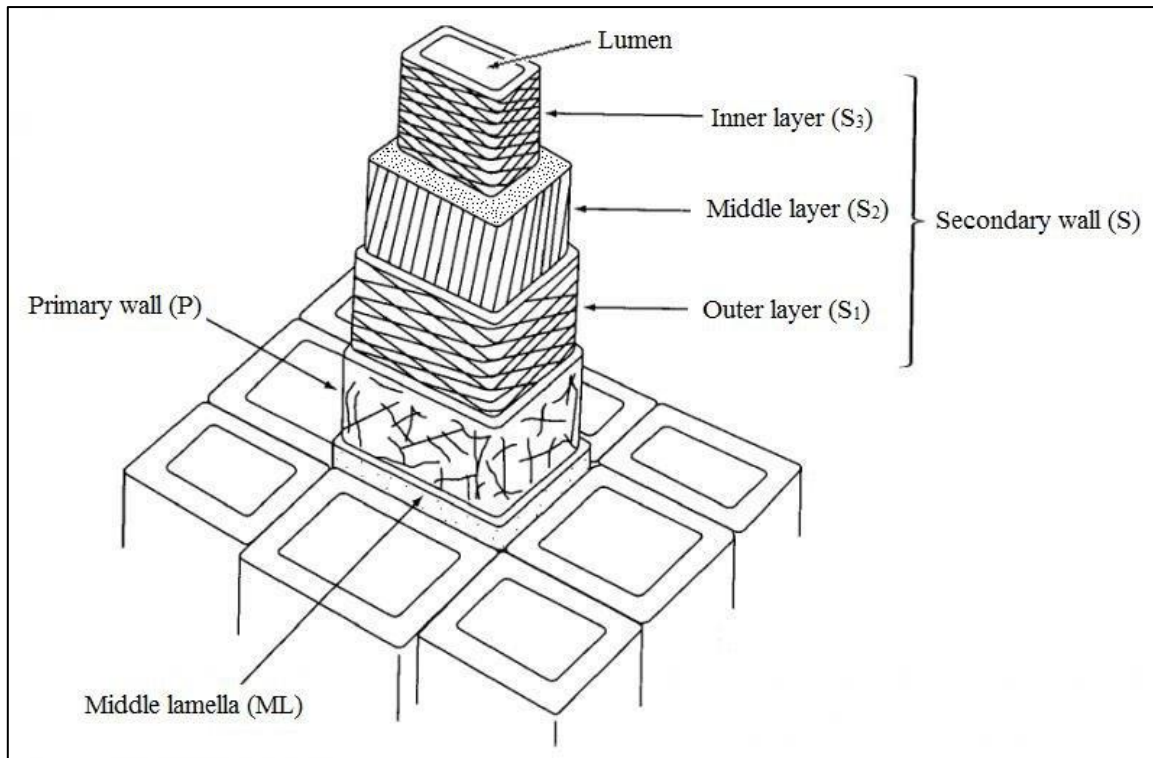


Figure 2.3: Cross section of xylem vessel fibre showing various cell wall sections [89].

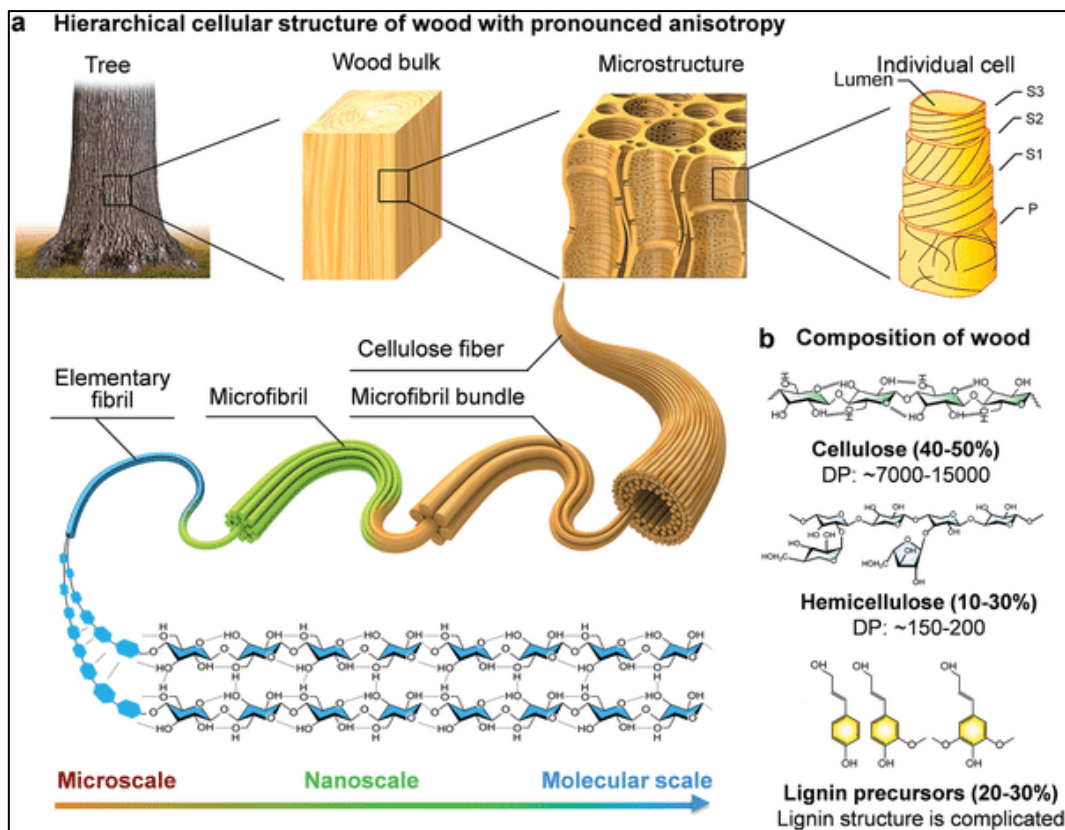


Figure 2.4: Hierarchical cellular structure of wood demonstrating wood fibre cell wall structure [90].

hierarchical level, the fibre cell wall is firstly composed of a collection of microfibril bundles (or macrofibrils). Each macrofibril is made up in turn of a collection of individual microfibrils, whom are themselves made up of a collection of elementary fibrils/nanofibrils, which in turn are made up of a collection of individual polymer chains of $\beta(1\rightarrow4)$ linked D glucose carbohydrate monomers (Figure 2.4) [90]. Each nanofibril is also typically surrounded or associated with chains of hemicellulose material which itself is typically linked to lignin polymer structures, that hold the whole structure together (Figure 2.5) [91]. The entire structure consists of highly ordered crystallized cellulose regions with regions of unstructured amorphous cellulose chains between each crystallized region. The amorphous cellulose regions are typically enriched with associated hemicellulose oligomer side chains.

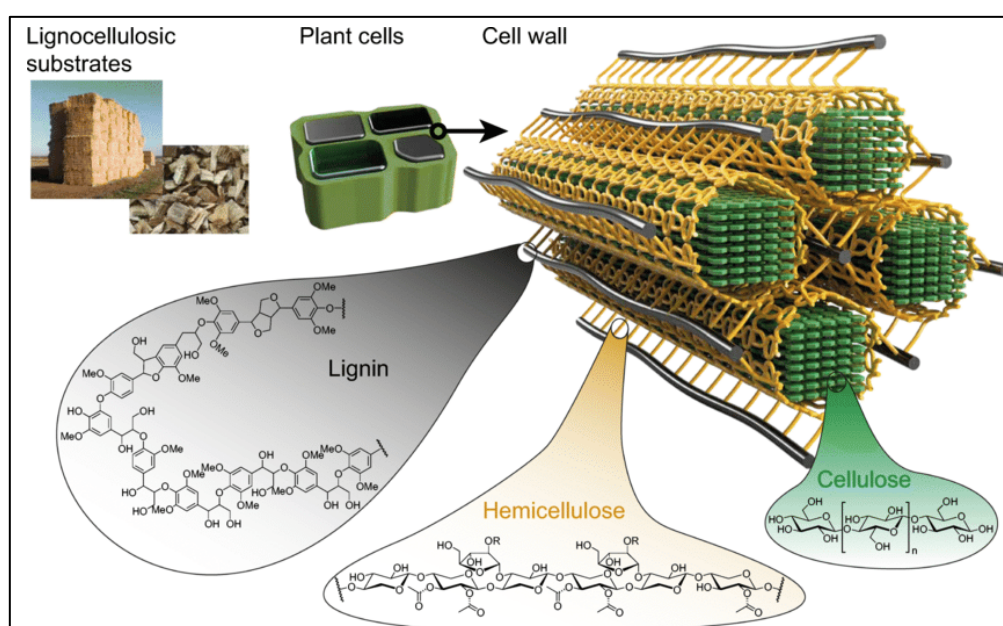


Figure 2.5: The complex cellulose/hemicelluloses/lignin structure of nanofibrils [91].

Typically, the middle lamella has the highest lignin content and lowest cellulose/hemicellulose fractions [92]. The primary cell wall always contains less lignin and more cellulose/hemicellulose as compared to the middle lamella,; while the secondary cell wall contains the lowest lignin to cellulose/hemicellulose proportion. In addition, the total cellulose, hemicellulose and lignin proportions vary between softwoods and hardwoods, species and even individual trees depending on type, species, conditions and climate, regional and global locations, and even hemisphere. Generally, softwoods (e.g. coniferous species) contain higher cellulose (40% to 45%) and lignin (26% to 34%) contents, but lower hemicellulose contents (7% to 14%) than hardwoods [93]. Conversely, hard woods generally have elevated hemicellulose contents (38% to 49% cellulose/23% to 30% lignin/19% to 26% hemicellulose).

In addition, the exact composition and structure of each cell wall layer is a reflection of its function at given times and when it was laid down. For example, the primary cell wall typically shows both elastic and plastic properties due to a highly hydrated architecture consisting of a high proportion of non orientated microfibrils interlocked by hemicellulose, pectins and structural proteins. These properties are essential during the growth and expansion phase of a cell wall fibre. On the other hand, the secondary cell wall is laid down later once the growth phase is completed, and is typically more structured and rigid in nature to ensure adequate structural support for the full grown fibre [94].

On a molecular level, the main components of the fibre cell wall (namely cellulose, hemicelluloses and lignin) are each made up of their respective monomers. Essentially, each component is nothing more than a polymer of its respective monomers.

The building block/monomer for cellulose is the six carbon D glucose carbohydrate monomer linked together via β -1,4-glycosidic bonds (Figure 2.6) [95]. Each glucose unit is orientated by a 180 degrees

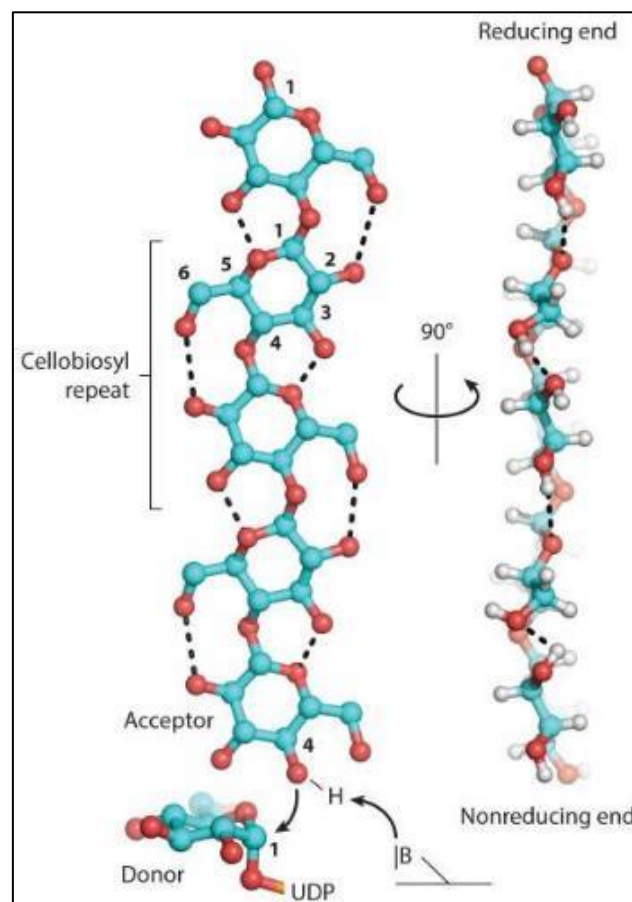


Figure 2.6: Molecular structure of cellulose illustrating the β -1,4-glycosidic bonds, hydrogen bonding (dashed lines) as well as reducing and nonreducing ends [95].

rotation relative to the adjacent unit and forms two hydrogens bonds with that adjacent unit. Consequently, the cellulose molecules form a stable elongated ribbon structure. Growth of the cellulose polymer generally occurs from the non reducing end via a nucleophilic substitution reaction involving the transfer of a glucose unit from uridine diphosphate glucose to the cellulose polymers C-4 hydroxyl group, facilitated by enzymes. Lastly, given the sheer mass of plant material globally, cellulose is the most abundant polymer on the planet.

Hemicellulose is a family of heterogeneous carbohydrate polymers containing many different five carbon and six carbon sugars (Figure 2.7) [96]. The five carbon sugar monomers include: xylose and arabinose; while the six carbon sugar monomers include: glucose, glucuronic acid, mannose and galactose, as well as the deoxy six carbon sugar rhamnose. General hemicellulose polymers include: xylan, glucuronoxylan, arabinoxylan, glucomannan, and xyloglucan [93 and 96]. Hemicelluloses form loose open amorphous chain networks, with little or no crystallinity or condensed structure. Hence, they are very easily broken down by acid hydrolysis. This fact serves as the basis for the acidic hydrolysis steps in all dissolving pulp production processes whether by acid-sulfite pulping or prehydrolysis kraft pulping.

Lignin is a broad heterogeneous polymer network of the two main p-coumaryl alcohol variants used by plants, crosslinked together at numerous positions using the various alcoholic functional groups on each monomer (Figure 2.8) [97]. These two main variants are guaiacyl lignol and syringyl lignol, both of which are based on the general p-coumaryl alcohol backbone (Figure 2.9) [98]. Hardwoods and grasses tend to contain significant proportions of both coniferyl and sinapyl alcohols, while softwoods are rich

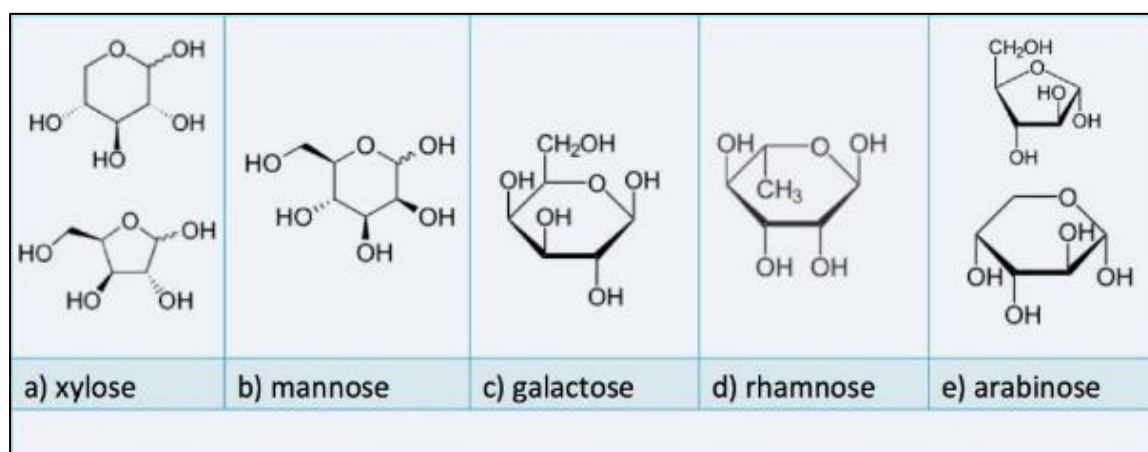


Figure 2.7: Molecular structure of important five carbon and six carbon hemicellulose carbohydrate monomers [96].

in coniferyl alcohols [99]. The lignin network is both aromatic and water insoluble in nature. Lignin is the second most abundant polymer on the planet, after cellulose.

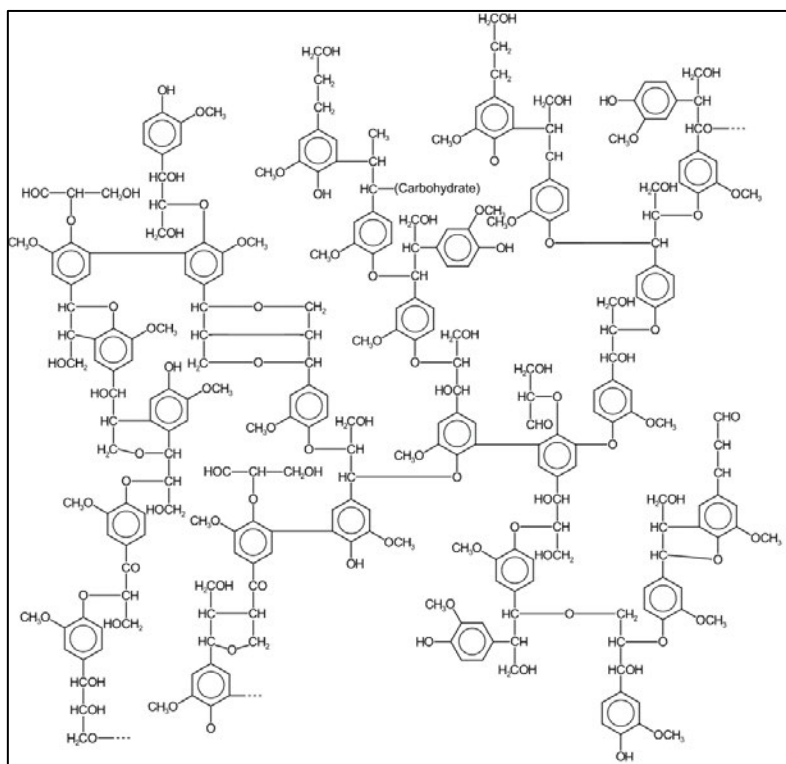


Figure 2.8: Lignin polymer network showing the various possible crosslinked alcoholic functional groups between different monomers [97].

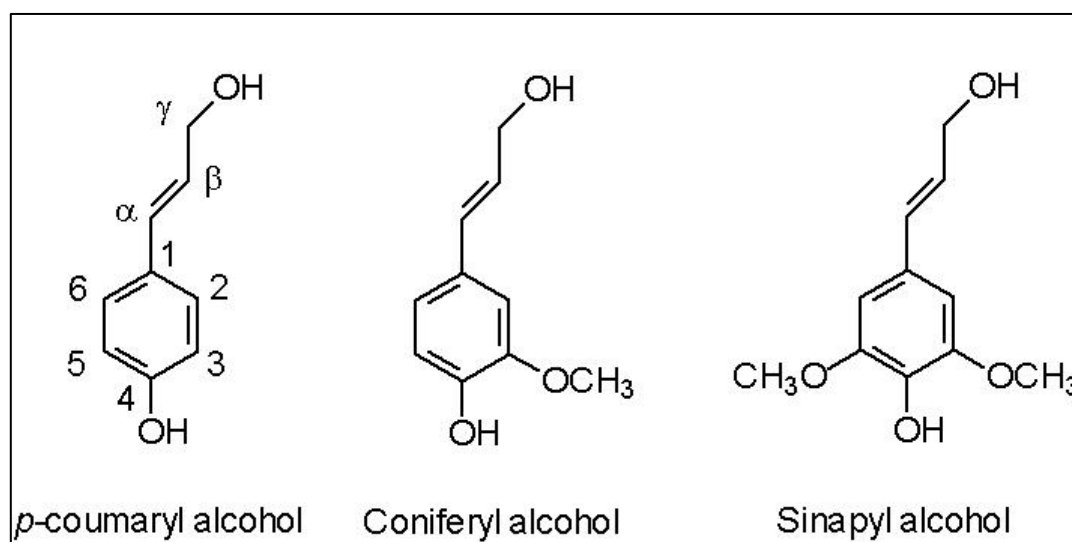


Figure 2.9: The two main lignin monomers of p-coumaryl alcohol: guaiacyl (coniferyl) lignol and syringyl (sinapyl) lignol [98].

2.3 *Basic chemistry of bleaching*

What follows in this section is a general overview of the modern bleaching of pulps and the various associated aspects thereof. These are divided into the basic chemistry and components of bleaching, the basics behind thermally driven chemical processes, and the basics behind photochemically driven processes.

2.3.1 *The basic chemistry, steps and components behind a Bleaching process*

Before pulp can be bleached, it must first be released from the wood timber matrix it is “trapped” in utilizing a variety of pulping processes. The two main chemical pulping processes are the soda/kraft process involving caustic soda (together with sodium sulfide in the kraft process) and the acid sulfite process involving sulfur dioxide attached to an alkali earth metal base such as calcium or magnesium. Pulping conditions and charges always are necessarily severe as this is the only viable method of breaking down the wood structure into pulp fibres (unless mechanical pulping is employed). Chemical pulping typically involves the pulping of wood chips in a batch or continuous digester, for paper grade pulp. However, batch digesters are employed almost exclusively for the generation of dissolving pulp cellulose. For the dissolving pulp process, an initial acidic breakdown of the hemicellulose content (using steam) proceeds the pulping process for the prehydrolysis kraft (PHK) process; while for the acid sulfite pulping process, the hemicellulose degradation and lignin degradation processes happen roughly simultaneously. [100, 101]. In addition, other fibre sources are also employed in a few processes as an alternative fibre source to timber, e.g. bagasse (crushed sugar cane), hemp and similar. Overall, bleaching then follows after pulping.

The basic chemistry around the bleaching of pulp consists of two sequential repeated steps, the first of which involves the chemical attack and degradation of the lignin matrix (typically by oxidation reactions) while the second consists of the subsequent dissolution and removal of the degraded lignin fractions under alkali conditions. These two sequential steps are repeated a number of times until the near target reduced lignin content (measured by the kappa number) and near target elevated brightness are reached. Then, the last bleaching step is undertaken and typically includes a final bleaching stage to give the pulp a final brightness boost before the pulp is forwarded to its end process - typically being made up into paper, wetlap or paper board [102 to 105]. However, if the lignin degradation step is undertaken under alkali conditions, then the degradation and dissolution steps can be combined into a single stage. A good example of this is the oxygen delignification process. In most mill operations, an alkali (caustic soda) pressurized oxygen stage is employed immediately after the pulping process as the first bleaching stage (while, chemically, the oxygen stage can actually be considered as a modified extension of the pulping process) [106]. Furthermore, individual bleaching steps/stages often are fortified with other bleaching agents, chelants and catalysts; and can also be pressurized with oxygen. Examples include alkali extraction stages fortified with hydrogen peroxide and an alkali peroxide stage

under pressurized oxygen [107]. In addition, beside the separate degradation and dissolution stages/steps in the bleaching process, each bleaching stage is also usually followed by a washing stage to remove residual bleaching reagents and as much lignin as possible before the next bleaching stage [108].

In addition to an alkali oxygen delignification stage, the lignin degradation step can be undertaken by a variety of methods and reagents. These include methods that are either acidic or alkaline in nature. The most common acidic methods/reagents employed are: chlorine, chlorine dioxide, and ozone; while the most common alkali methods/reagents employed are: oxygen, peroxide and hypochlorite. Other degradative methods/reagents employed are: Caro's acid (peroxysulfuric acid), peroxyformic acid and other peroxyorganics; but their application tends to be rare. In addition, reductive brightening of the lignin chromophores rather than degradation is also an option using dithionite (hydrosulfites) but is also rare for all pulps (except mechanical pulps) due to its strong brightness reversion upon pulp aging [109]. The dissolution step almost always involves a strong alkali solution usually using caustic soda as an alkali source due to its lower costs than other alkali sources, but other alkali sources such as potassium hydroxide are sometimes used (however, infrequently due to it being far more expensive). Other alkali sources are also available, such as sodium carbonate and calcium or magnesium hydroxide, but are not commonly used due to their weaker alkalinity and issues around scaling as well as poor water solubility.

All of these principles are employed in designing bleaching sequences with specific target parameters in mind (e.g. brightness, shade, kappa number and viscosity); however, all bleaching sequences can be divided into one of three general categories: elemental chlorine-based bleaching sequences, elemental chlorine-free bleaching sequences (ECF), and total chlorine-free bleaching sequences (TCF) [110 to 112]. The first category (elemental chlorine) are sequences that contain one or more degradative stages using elemental chlorine (Cl_2). The second category (elemental chlorine-free) are sequences that contain one or more degradative stages using chlorine-based bleaching reagents (e.g. chlorine dioxide and sodium hypochlorite) that are not elemental chlorine. The third category (total chlorine-free) are sequences that contain no chlorine-based reagent degradative stages at all (e.g. oxygen, peroxide and ozone). Although elemental chlorine-based bleaching was the only method employed globally for pulp bleaching for decades, environmental concerns associated with its use (particularly the generation of chlorinated organics such as the dioxins) drove its rapid replacement in the space of a decade or two with chlorine dioxide as an elemental chlorine-free alternative. At present, elemental chlorine-based bleaching is employed nowhere in the world on any significant industrial scale. However, chlorine dioxide is also not environmentally neutral and attempts to go with a completely "green" solution resulted in the development of the total chlorine-free option, but limitations associated with its lack of selectivity towards lignin as compared to chlorine dioxide has prevented it in displacing chlorine dioxide as an alternative with only about 5 to 6% of the present global market employing TCF instead

of ECF sequences. This lack of selectivity means that far more energy and effort is required to achieve similar brightness and residual lignin (i.e. kappa number) results as compared to ECF sequences, with the final pulp being typically significantly weaker. In addition, TCF sequences tend to require longer bleaching sequences than ECF sequences if the same pulp strength is to be maintained. These challenges continue to prevent ECF sequences from being replaced by TCF sequences, although a move to “lite” ECF is becoming more common. Thus, all bleaching sequences, regardless of type and source, fall into one of these three categories – although the first of these technically no longer commercially “exists”.

As a means to simplify bleaching descriptions for both individual bleach stages (i.e. steps) and entire bleaching sequences, the pulp and paper industry has, over the course of decades, introduced a short hand nomenclature (Table 2.1). Individual bleaching stages are typically represented by one or more

Table 2.1: Tabulation of individual bleaching stages and their associated short hand nomenclature.

Bleaching stage	Short hand Nomenclature	Active reagents
Acid wash	A	Sulfuric or hydrochloric acid
Chelant	Q	DTPA, EDTA, phosphonates, etc.
Chlorine	C	Elemental chlorine (i.e. Cl ₂)
Chlorine dioxide	D	Chlorine dioxide (i.e. ClO ₂)
Dithionite	Y	Sodium dithionite
Enzyme	X	Any enzyme (e.g. xylanase)
Extraction	E	Caustic soda
Hypochlorite	H	Sodium hypochlorite
Oxygen	O	Oxygen (typically alkali)
Ozone	Z	Ozone (typically acidic)
Peracids/Peroxyl acids	Paa	Caros acid, peroxy formic acid
Peroxide	P	Hydrogen peroxide
Pressurized Peroxide	PO	Hydrogen peroxide under oxygen pressure

capital alphabetic letters. A list of these short hand letters and their reagents are readily available in most literature on the topic. Where these stages are fortified or aided by other reagents, these are represented as subscript lower or capital letters to these short hand capital letters and typically come after the main letter/s, but in some cases are placed before. Examples may include an alkali extraction stage under pressurized oxygen (i.e. E_O), an extraction stage fortified with hydrogen peroxide (E_P), and an acid wash stage aided by a chelant (A_Q), among other examples. An example of multiple fortifications may include an oxygen pressurized alkali extraction stage fortified with hydrogen peroxide and aided with a chelant (i.e. _qE_{OP}). The washing stages between each bleaching stage are represented by a hyphen (i.e. “-”) and when no washing stage is present between individual bleaching stages, both are separated from each other by a back slash (i.e. “/”). Where more than one of a given type of bleaching stage exists, each is labelled with a subscript number in the sequence with the first number usually being zero (i.e. “0”). Thus, the first two chlorine dioxide stages in a sequence would be labelled: D₀ and D₁. The use of zero as the first number in a sequence is not universally applied and many mills used the number one (i.e. “1”) instead, considering the oxygen delignification stage upfront of the bleaching sequence as number “zero”. Also, the first extraction or peroxide stage after a D₀ stage is always labelled number one (i.e. E₁ or P₁). All bleaching sequences are represented using this systematic nomenclature, though there is some variation based on preferences and company history.

For illustrative purposes: an example of an elemental chlorine-based bleaching sequence would be the old former sequence for the Sappi Stanger mill which used to be: -C-E-H- [113]. This sequence used to consist of an elemental chlorine stage followed by a wash stage, then an alkali extraction stage followed by a washing stage, and, lastly, a hypochlorite stage with its own washing stage. The present Stanger sequence which now replaces that former elemental chlorine sequence is a good example of an ECF sequence: -D₀-E_P-P-. This newer sequence consists of a chlorine dioxide stage followed by a wash stage, followed by a hydrogen peroxide fortified alkali extraction stage and a washing stage, with a final alkali hydrogen peroxide stage with its own washing stage. Another example of an ECF sequence would be the one for the Sappi Cloquet mill with an ECF sequence: -O/O-Z/D₀-E_{OP}-D₁- [114]. This consists of a double oxygen stage upfront (directly after the post-digester washing) with its own wash stage, an ozone stage without a wash leading directly into a chlorine dioxide stage followed by a wash stage, a hydrogen peroxide fortified alkali extraction stage under oxygen pressure with its washing stage, and a final chlorine dioxide stage with its own wash. A good example of a TCF sequence is the present Sappi Gratkorn sequence: -E_{OP}-Q-P₁-P₂- [115]. The Gratkorn sequence consists of a hydrogen peroxide fortified alkali extraction stage under oxygen pressure with a subsequent wash stage, a chelation stage followed by a wash stage, and successive hydrogen peroxide stages each with their own wash stages. Further examples of mills using ECF bleaching sequences are: the Suzano/Stora Enzo joint venture Veracell mill in eastern Brazil/Bahia state (-O-A-D₀-E_{OP}-D₁-P-), and Altri’s Celbi PP ECF

mill (-D-PO-D-P-) [116 to 119]. Further examples of mills using TCF bleaching sequences are: the Bacell's Solucell mill (-O/O-A-Z-Q-P-) [120, 121].

2.3.2 *The energetics of thermal chemistry*

In general, any chemical reaction in nature can be considered as a three-legged pot or stool. Without all three legs, the pot or stool will fall over and not be workable. The three legs for any chemical reaction are thus: (1) energy/all chemical reactions are driven by energy (or the ability to do work). In many chemical reactions this is provided by thermal energy with the rate of reaction going up as the temperature is increased. However, thermal energy is not the only energy source with one readily and easily available alternative being photochemical energy. In the pulp and paper industry, thermal energy is the almost exclusive energy source typically supplied as steam. (2) Reactants/For any chemical reaction, all the different reactant components are required. In the pulp and paper industry, during bleaching operations, the reactants are the pulp material to be bleached and the different bleaching reagents as well as any associated chelants, catalysts, etc. (3) The mobile reaction phase/For all chemical reactions to take place, some form of mobile phase/matrix for suspending the different reactants is required to allow them to travel and reach each other. Without making contact with each other, no reaction can occur. In the pulp and paper industry, the mobile phase is always water with dissolution of degraded lignin fragments in it being a key reason for its use.

As energy, reactants and the mobile phase are the three key aspects around all chemical reactions, a discussion around the aspects of reaction mechanisms and their energy utilization is necessary at this point. All chemical reactions occur via a reaction mechanism known as an activated complex. Activated complexes may take the form of a combined collection of some or all of the different reactants or individual intermediates of the different reactants. Furthermore, the conversion from reactants to products may occur in a single step, through multiple steps, or by a radical chain reaction. In the case of most chemical reactions, thermal energy is the sole or main driver of the chemical reaction (as is the case with all commercial pulp bleaching operations in the pulp and paper industry); and for any chemical reaction to occur upon the formation of these activated complexes, the thermal energy of these complexes must be above a given threshold known as the activation energy (Figure-2.10) [122].

Only at or above this threshold, does the reaction mechanism have sufficient energy to break existing chemical bonds and form new bonds, thus "breaking down" the reactant molecules and "forming" the new product molecules. In terms of molecular orbital theory, the chemical reaction involves the "merging" of the existing reactants' molecular orbitals and their subsequent rearrangement into new molecular orbitals associated with the products. The product molecules are formed upon the

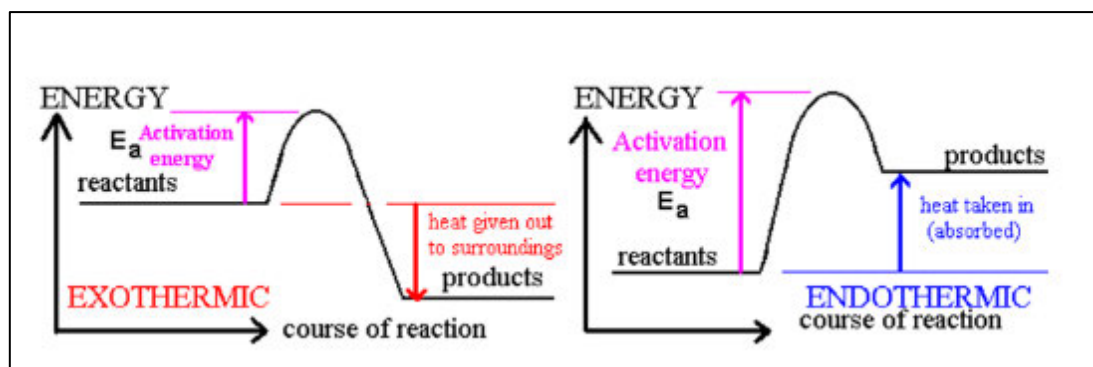


Figure 2.10: Generalized energy diagrams for exothermic and endothermic chemical reactions showing the activation energy barrier to chemical reaction [122].

redistribution of the electrons within these new molecular orbitals. Overall, the observed bulk effect is the conversion of the reactant materials into the product materials. However, during thermal reactions, only a small portion of the total reactant molecular population have enough thermal energy to reach or exceed the activation energy threshold. As the thermal energy of any chemical system is generally given by a Maxwell Boltzman distribution, the only molecules capable of undergoing reaction are those in the high energy “tail” of this distribution which may constitute significantly less than a single percent of the total material undergoing reaction at any one time (Figure 2.11).

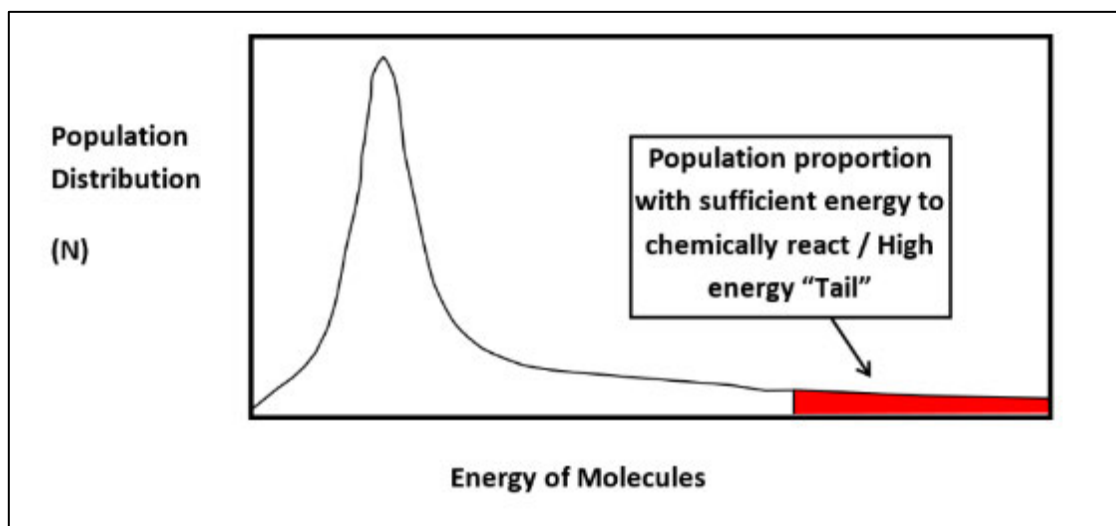


Figure 2.11: Generalized Maxwell Boltzman Distribution for the distribution of thermal energy within a molecular population (generated by thesis author).

Hence, for continued reaction, a constant input of thermal energy; whether from an internal (exothermic) or external (endothermic) source; is required to drive the reaction to completion or equilibrium. In addition, due to the nature of thermal chemistry, the breaking and formation of bonds is a purely random process with the resulting product materials being determined purely statistically by

thermodynamic, reaction rate kinetic, molecular orbital, and orbital energy properties and preferences. Thus, in thermal chemistry, the entire molecule can be considered as “activated” or “high energy” rather than selected chemical bonds/molecular orbitals. The result is that all thermal chemical reactions tend to produce a number of the more thermodynamically and/or kinetically stable final products at varying yields all of which are dependant on the nature of the above statistically random chemical processes; in other words, overall reduced chemical reaction and product selectivity. This is the category that modern pulp bleaching operations fall into.

2.3.3 The energetics of photochemistry

Energy on the smallest natural scale (i.e. quantum mechanical scale) is not a continuum, but is subdivided or apportioned into indivisible packets of discrete size known as quanta (quantum for singular). As indicated, these quanta cannot be further subdivided. Thus, all energy in the known universe, particularly that associated with chemistry, is quantized; but may appear continuous in nature to the casual average human observer as the energy gaps (quanta) are actual “subatomically” tiny. In addition, the distribution of energy can be categorised into distinct manifestations thereof, each with its own mechanism, which are often referred to as “energy types”; of which, every molecule has four distinct energy types that are relevant to chemical properties and chemical reactions. These four are the translational (i.e. motional), rotational, vibrational and electronic energy levels of an atom or molecule (Figures 2.12 and 2.13) [123]. The translational energy level of a molecule deals with the extent and speed of motion in three dimensional space and is key in thermal temperature. Rotational energy deals with the extent of rotation about common axes either through a molecule’s mass centre or about interatomic bonds and is of relevance to a material’s thermal capacitance and also (less so) temperature. Vibrational energy defines the extent of vibrational motion individual atoms experience; relative to each other; across a common chemical bond. Electronic energy deals with the energy electrons carry within molecules when in given orbitals. Electronic energy defines the present bonding status of the molecule as well as any additional chemical bonding options available as an electron’s energy determines which molecular orbital it occupies which in turn characterizes the molecules chemical properties. Quantum mechanics can be used to give specific solutions for each of these four energy types found in molecules based on models specific to each type [124]. Thus, translational energy solutions can be resolved using the particle-in-a-box model, rotational energy solutions are defined by the rigid-rotor model, vibrational energy by the balls-on-a-spring model, and electronic energy by wave functions derived from the Schrödinger equation for each atomic or molecular orbital [124^b].

Energy can also transfer between materials, and molecules can have energy imparted to or removed by a variety of methods; e.g. collision in chemical reactions. One common means of energy transfer is by the absorption or emission of electromagnetic radiation. As light also comes in discrete quanta known as photons; whose energy is given by the frequency ($E = h\nu$ where “h” is Planck’s constant and “v” is

the frequency of the light), or wavelength ($E = hc/\lambda$ where “c” is the constant for light speed and “λ” is the wavelength of the light); the absorption of specific wavelengths of electromagnetic radiation will increase the energy status or “activate” specific energy types within a molecule. Translational energy

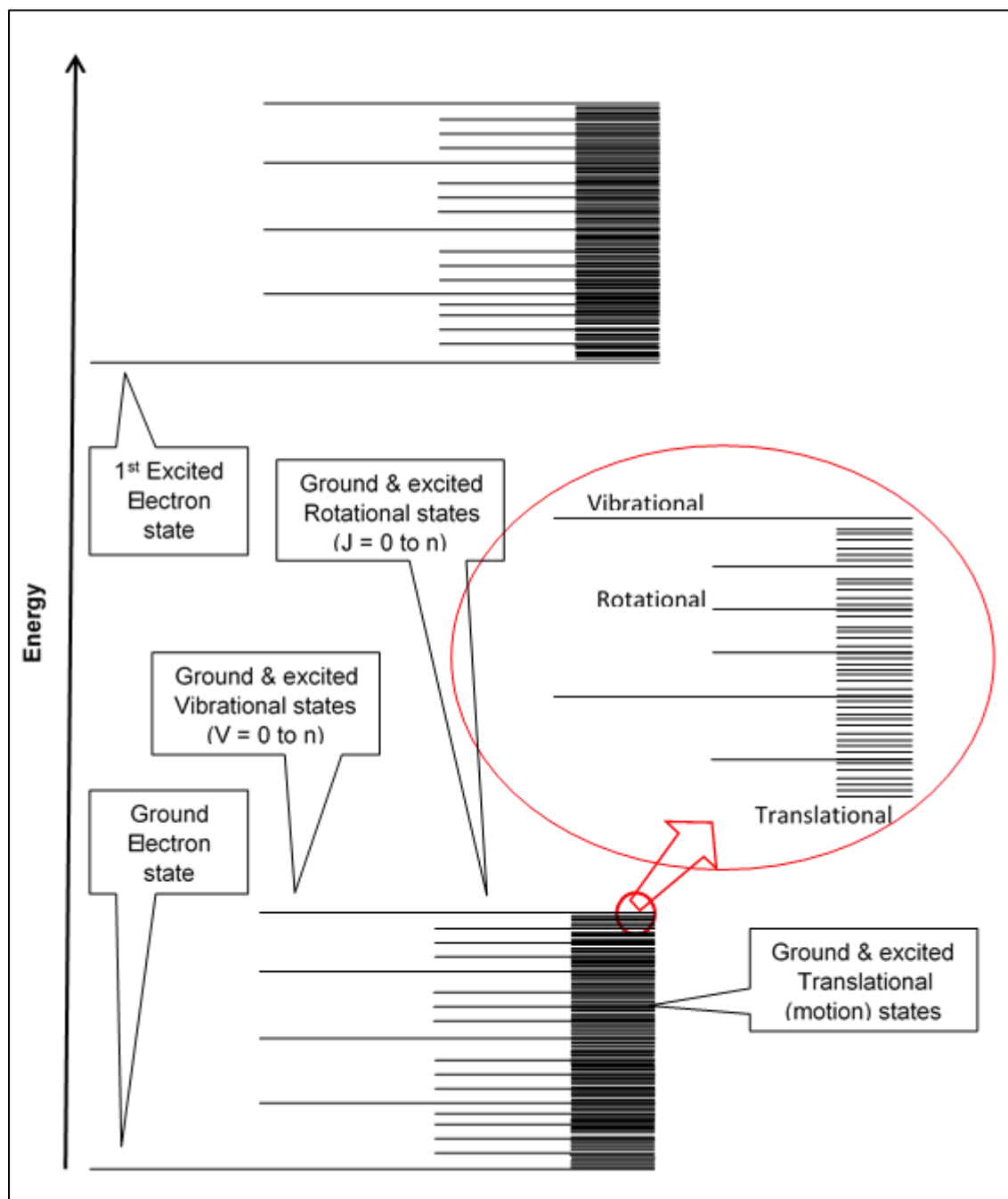


Figure 2.12: General diagram representing the quantified translational, rotational, vibrational and electronic energy levels and how they are typically arranged within an atom or molecule (generated by thesis author).

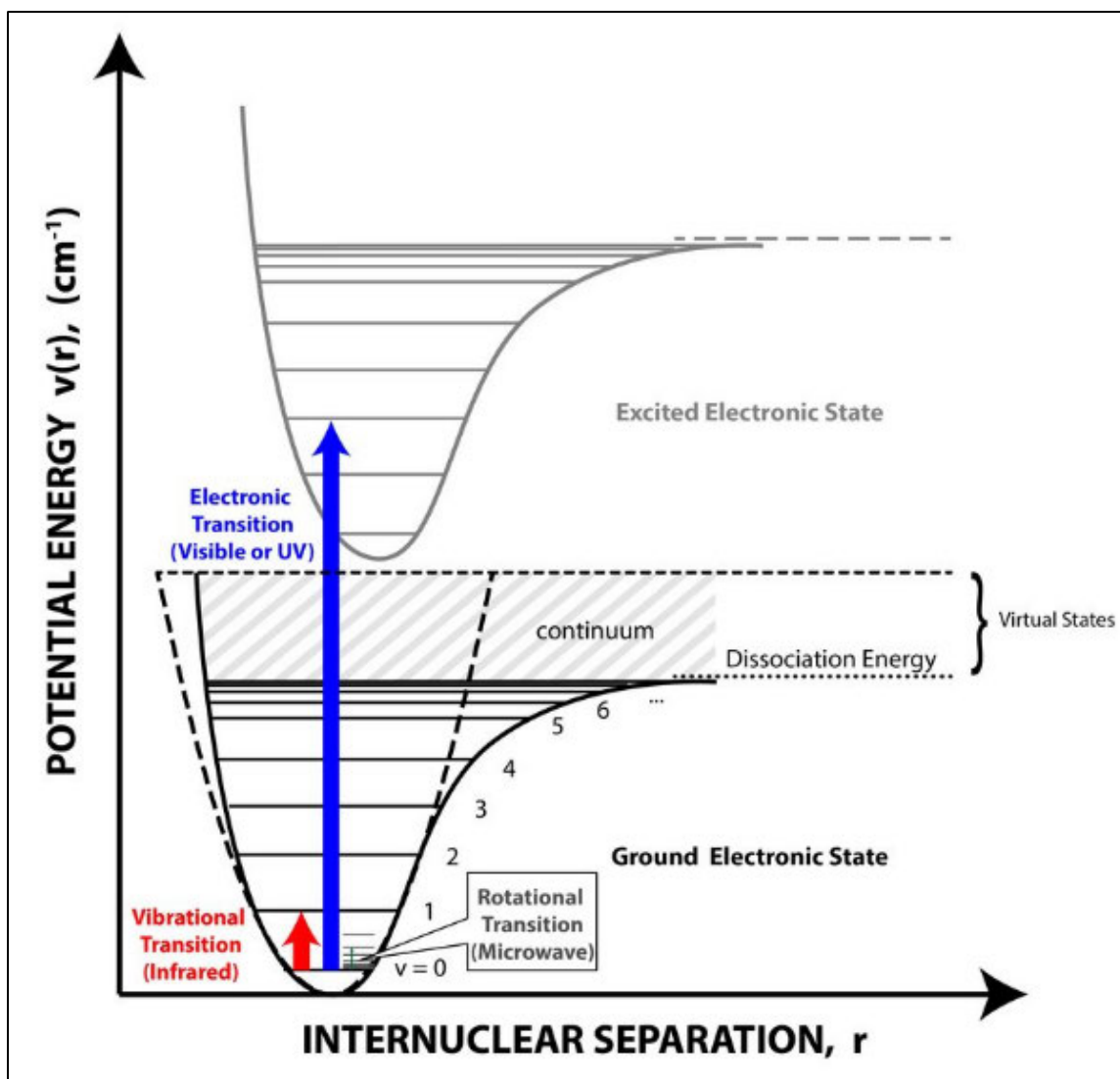


Figure 2.13: Diagram showing the ground and excited electronic states together with their respective vibrational and rotation energy states for a diatomic molecule [123].

can be affected by the absorption or emission of very low frequency waves typical of the sub radio range but typically emissions often span a broader range from the sub radio to near infra red; while rotational energy is affected by microwave radiation spanning the far radio and microwave range of frequencies; with vibrational energy is affected by infra red light; and electronic by visible and ultraviolet radiation (Figure 2.14) [125]. In addition to these molecular energy types, must be included transitions such as atomic nuclei and electron spins and alignments (radio and microwave), core electron transitions (X rays), and atomic and stellar nuclear events (gamma rays). Of all the energy types available, the only one of interest for photochemical bleaching of pulp is the electronic transitions associated with movement of electrons from one electronic orbital (typically in the ground state) to another electronic orbital (typically in an excited state) as only these are involved with chemical reactions.

In general, upon translational, rotational and vibrational excitation, the modes of motion of the whole molecule undergo transition. However, during electronic excitation, only the electrons in a specific chemical bond, rather than the atoms or molecule itself, undergo transition (although the entire molecule may be considered as in a higher energy state). These electrons jump from their ground state bonding orbital to a more energetic excited orbital by the absorption of a photon of specific wave length representing a precise quantity of energy. This absorption changes the electronic configuration within the existing molecular orbitals giving rise to a distinct new molecular species and can lead to new products generated by subsequent photochemical reactions as the newly filled orbitals of the intermediates are often nonbonding or anti bonding in nature. Furthermore, as these jumps are specifically quantized, it is also possible to target only given bond types within a reactant molecule as opposed to the general activation of the molecule as a whole that occurs within thermal chemical reactions. These photo excitations can occur as multi molecular activation complexes or singular

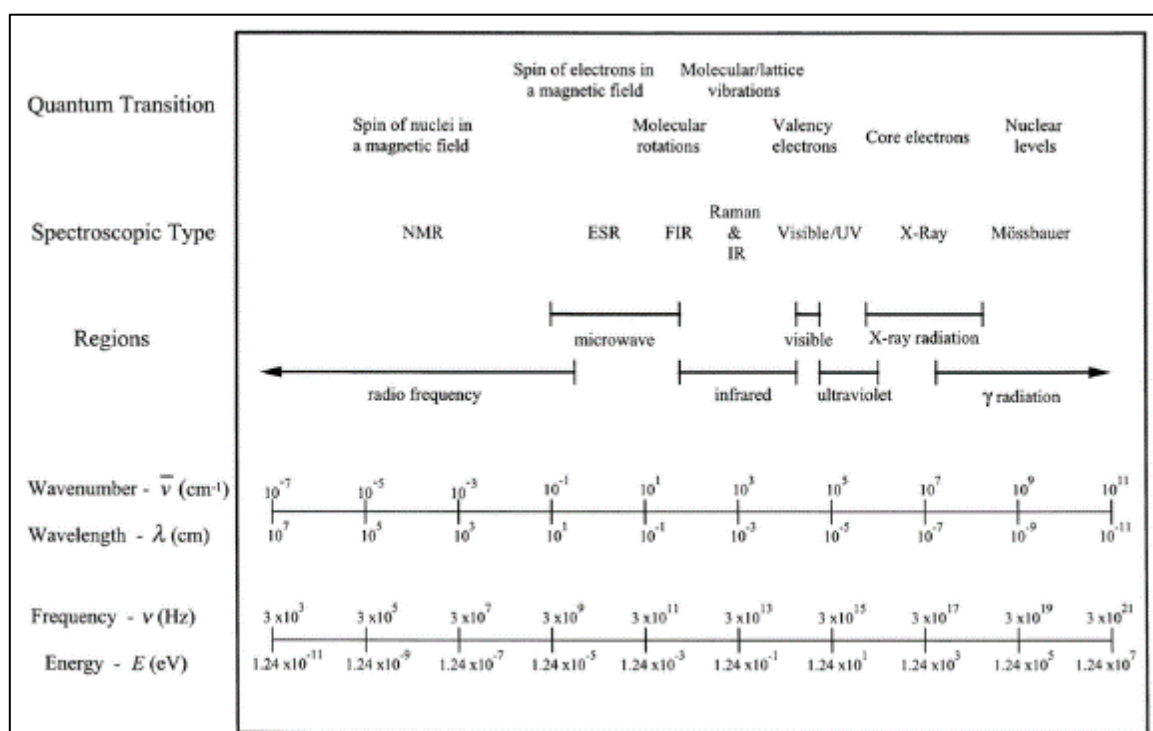


Figure 2.14: Electromagnetic spectrum showing the different frequencies, quantum mechanical transitions and different spectroscopic methods employed for analysis [125].

intermediate excited species which subsequently react further with other chemical reactant species often as activation complexes. Thus, photochemistry can induce specific given reaction types as well as targeting far more selectively than thermal reactions do. It is this ability of inducing specific chemical reactions within molecules upon absorbing UV/Visible light that is of interest in degrading lignin within pulps and which allows the possibility of photochemically bleaching pulps.

However, not all photoexcitation results in chemical reaction as there are more than one means of the excited molecule to return to an unexcited ground state without chemically reacting (Figure 2.15) [126]. One of the most common methods is to simply reemit the absorbed energy as a photon in a process called fluorescence. In most cases, the reemitted photon is less energetic than the initially absorbed photon as the initial absorption occurs while the molecule is in an excited Rotational and occasionally Vibrational state while being in the ground Electronic state (molecules are almost always at $v = 0$ vibrational state at room-temperature). Upon electronic excitation, much of the excited rotational and vibrational energy is retained, but, given that the molecule is energetically “unstable” after excitation the molecule undergoes rapid rotational and vibrational deexcitation to a ground rotation and vibrational state, in a process called internal conversion, while still being electronically excited. Vibrational relaxation ensures that all fluorescence takes place from the S1 electronic excitation level in almost all cases. Thus, once the fluorescence occurs thereafter, the energy remaining for release is slightly lower. The vibrational and rotational de excitation (internal conversion – i.e. IC) occur far more rapidly than the Electronic de excitation due to these two states having much shorter life spans than the electronic de-excitation due to the much smaller energy gaps associated with them (i.e. the shorter the energy gap the shorter the life span of the excited state). In all cases, electronic excitation after absorption retains the electron spin configuration which in many cases is singlet in configuration. Occasionally, after electronic excitation, the excited singlet state can convert into an excited triplet state via a process called intersystem crossing (i.e. ISC). This always involves a small loss of energy as the triplet state is always lower in energy than the related singlet state. From the triplet state, the molecule can also undergo a nonreaction deexcitation involving the re emission of a photon of significantly lower energy in a process known as phosphorescence. Besides these photophysical processes, the photoexcited molecules can also undergo selective photochemical reactions from both the singlet and triplet excited state. Thus, although photoexcitation does result in a higher selectivity, there is some loss in the hypothetical maximum selectivity due to these side phenomena, particularly rotational and vibrational de-excitation. Hence, although photochemical reactions are more selective than thermal chemical reactions, not all unwanted side-reactions are eliminated; but they are significantly reduced.

2.4 *Photochemical reactions of wood and correlations to yellowing of wood pulps [127]*

Much of the chemistry behind the photo yellowing of high yield/high lignin pulps as well as the brightness reversion of high brightness chemically bleached pulps, bear much in common with the chemistry behind the photochemical bleaching of pulps, often involving many of the same or similar chemical reactions and types; with the only differences being the extent of photochemical reaction.

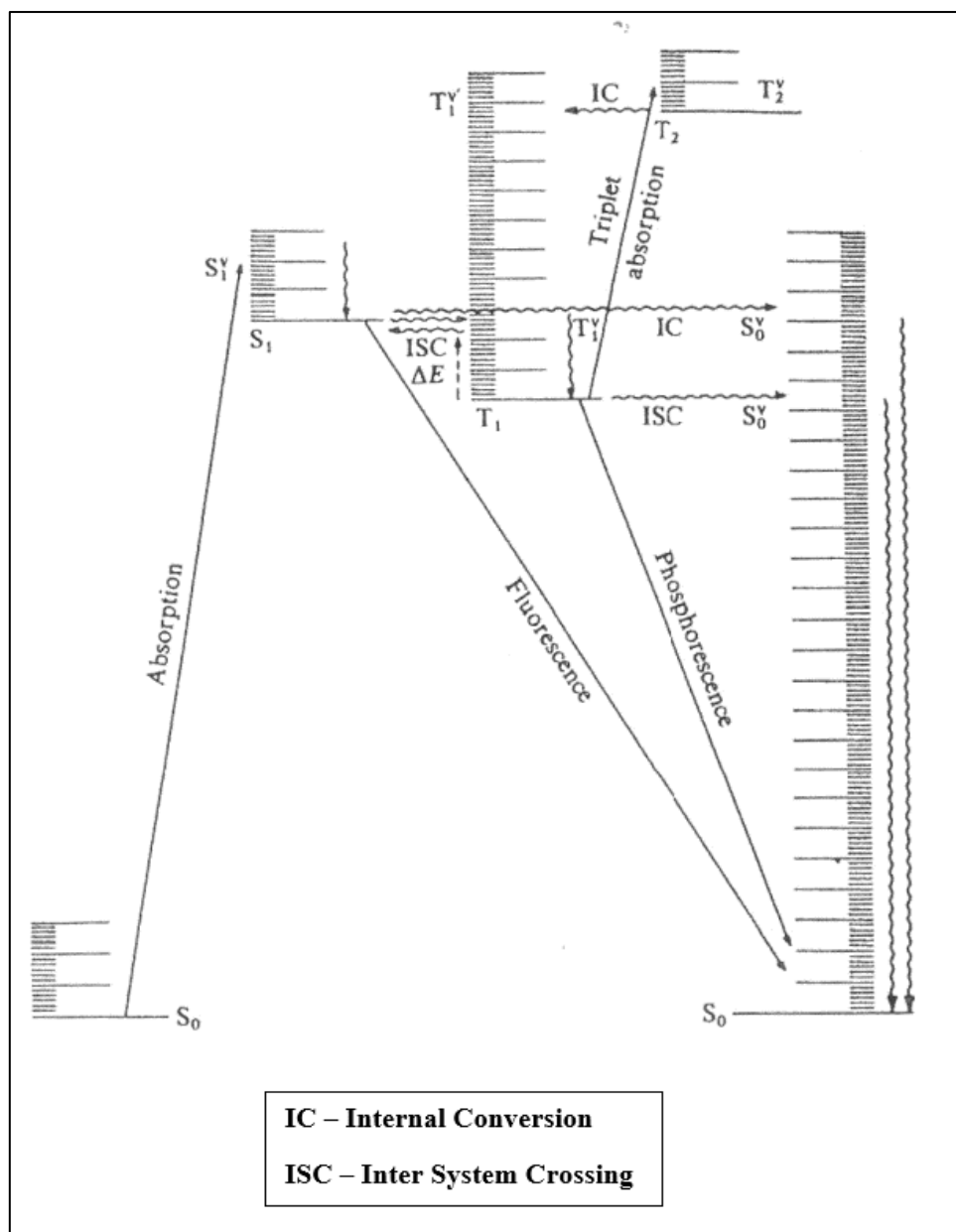


Figure 2.15: Modified Jablonski diagram giving the various non-chemical de-excitation options for a molecule after electronic excitation after absorption of a photon in the UV/visible part of the electromagnetic spectrum [126].

While photo yellowing and brightness reversion would involve a very limited extent of photochemical reactions producing a small amount of highly colour chromophores (e.g. quinones, etc.), the extent of photochemical bleaching is significantly greater often breaking up and destroying these chromophores, and degrading lignin and releasing it from its polymer matrix. It is thus relevant at this point to review past work around photo yellowing of pulp and pulp photochemical reactions in general.

2.4.1 Photo yellowing of high yield mechanical pulps and news print

The structure of lignin and the functional groups it contains has been investigated in wood, splutter wood, mechanical pulp (unbleached, semi bleached and “brightened”) and newsprint by a variety of analytical techniques. These include among others: FTIR, UV/Visible spectroscopy, Raman spectroscopy, X ray photoelectron spectroscopy and metastable induced electron spectroscopy. A study of the valence band spectra of lignin in wood clearly demonstrated the presence and helped classify the hydroxy, methoxy, and phenolic groups on the lignin surface as demonstrated by Klarhöfer et al. [128]. In earlier work, Andtbacka et al. [129] were able to evaluate the impact of photo yellowing at different wave lengths on high yield unbleached and semi bleached ground wood pulps. They were able to show that unbleached and semi bleached ground wood pulps respond differently upon photo yellowing of wood pulp. Unbleached pulp tended to yellow significantly less quickly than semi bleached ground wood, with some initial photobleaching at 396 to 420 nm (representing o-quinonic structures) which quickly reversed after more prolonged irradiation (2 h). For the conjugated α -carbonyl and *p*-quinonic structures, represented by the 360 and 350 nm bands, continuous and progressive photo yellowing was observed. For semi bleached ground wood pulp, photo yellowing across all wave lengths was observed and was particularly pronounced at 420 nm. The action of oxygen resulted in a strong yellowing effect, even when present in trace quantities, while moisture and pH were found to have almost no effect. The work by Andtbacka et al. was supported by similar findings by Fortsskåhl and Janson [130] in a later study. In an unrelated study, Scott and Goring [131] noted significant photolysis of lignin in very thin wood sections when viewed under a microscope utilizing an ultraviolet illumination source for prolonged periods. Illumination with a UV light source at 280 nm produced a 25% reduction in the UV absorption after 2 h of exposure.

Hemmingson et al. [132] utilized a CP/MAS carbon 13 NMR spectroscopic technique to study the impact of solar radiation on the photo yellowing of newsprint (ground wood). They noted that the newsprint pulp underwent changes in the functional groups within the structure of lignin resulting in the photo yellowing of the newsprint ground wood pulp. These changes included the formation of further carboxyl and ketone groups in lignin, demethoxylation of lignin aromatic groups, the removal or destruction of lignin aromatic groups, and general increased fragmentation and break down of the cellulose and hemicellulose chains. The generation of carboxylic groups came from the oxidative ring opening of aromatic rings as well as α and β aliphatic sidechain cleavage. Hemmingson et al. (1989) also noted that fragmentation of the hemicellulose structure occurred at a much greater extent than for the amorphous regions of the cellulose matrix. Lastly, they observed that most of the chromophores generated were carbonyl based.

Leary undertook a two part study of the impact of photo yellowing of wood in 1967 (Part I) [133] and 1968 (Part II) [134]. In Leary’s first study (Part I) the impact of monochromatic light at wave lengths

of 360 to 520 nm was evaluated. Leary observed that the newsprint yellowed when irradiated at wavelengths of 360 – 395 nm when oxygen was absent, but the yellowed newsprint pulp underwent photobleaching in the presence of oxygen when irradiated at 410 – 520 nm. He also observed that demethoxylation of the lignin methoxy side groups increased as the newsprint was photoyellowed. This relationship appeared to be linear in nature. In the second part of the study (Part II), he repeated the prior experimental design but with improved degassing and gas purification techniques. In the second set of experimental work, Leary clearly demonstrated that the presence of oxygen (even as a component of air) was essential in photo yellowing of newsprint, and that photo yellowing was avoided when no oxygen was present even under sustained photo illumination. The mechanism proposed for this photo yellowing was irradiation of photosensitizer type structures within the lignin leading to photo excitation of this specific lignin component, which in turn excited 3-methoxy-4-phenolic structures within lignin. The secondarily excited 3-methoxy-4-phenolic structures then underwent a hydrogen abstraction of the phenolic groups leading to the formation of phenolic radicals. These phenolic radicals in turn underwent demethoxylation and eventually formed the final *o*-quinonic structures that are highly coloured (Figure 2.16) [134].

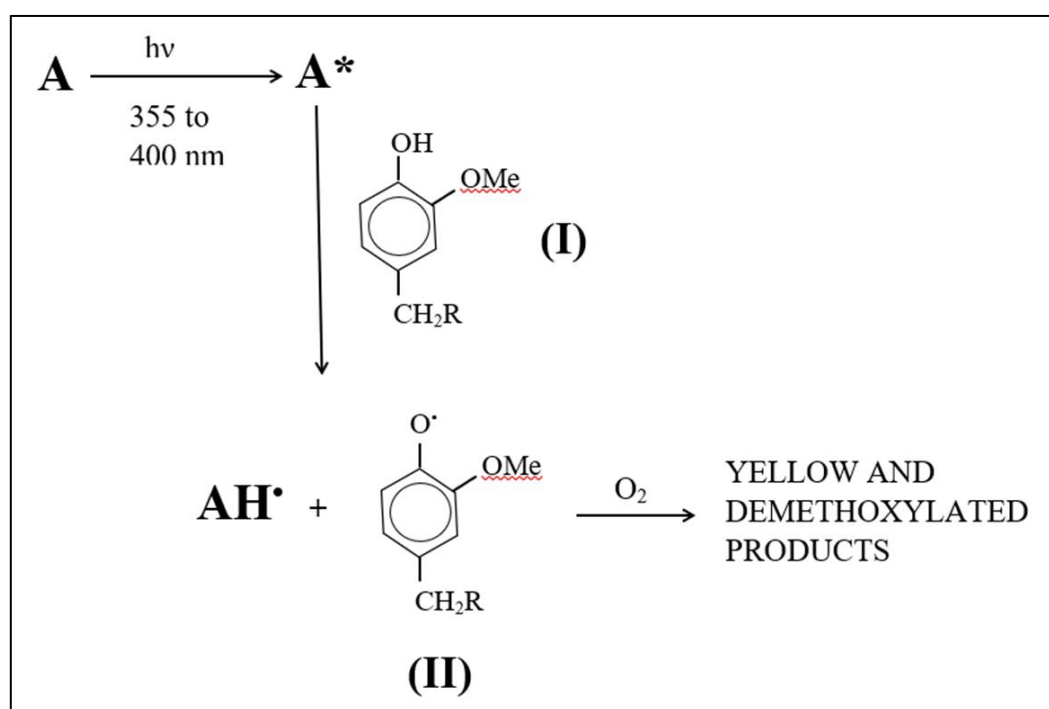


Figure 2.16 The proposed mechanism of photo yellowing of newsprint involving secondary excitation of 3-methoxy-4-phenolic structures utilizing lignin-based photosensitizer type structures [recreated from [134]]

Andrady and Torikia [135] investigated how mechanical pulp yellowed when exposed to monochromatic light within the 260 to 600 nm range. In their experimental work, they found that the

yellowing effect of mechanical pulps decreased as the wave length increased (i.e. as the individual photon became less energetic). This decrease followed a logarithmic relationship. In addition, Andradý and Torikia found that at similar luminant dosages, the yellowing was slightly more effective at longer wave lengths. Andradý and Torikia proposed that this finding suggests radical-radical interactions which work against the yellowing reaction initiation at longer wavelengths.

2.4.2 Direct irradiation

A significant quantity of research and experimental work has been done on the impact of direct photo irradiation of various lignin model compounds (LMCs) and the following section summarizes the most important work and findings thereof.

2.4.2.1 α -Carbonyl containing lignin model compounds

The α -carbonyl groups within LMCs are important for illustrating the photo yellowing and similar mechanisms occurring within pulps upon irradiation, despite their overall low chemical content within these pulps. This is illustrated by vanillin in work by Lin and Kringstad [127], which underwent changes in the UV spectrum similar to those observed in lignin, when irradiated at 350 nm. Similarly, in experimental work by Brunow and Eriksson [136], the degradation of 4-hydroxy-3-methoxybenzyl alcohol was accelerated when small quantities of acetoguaiacone (an α -carbonyl containing LMC) were present. The mechanism proposed from this experimental work was first the photo excitation of acetoguaiacone, followed by its inter system crossing (ISC) to an excited triplet state which then abstracted hydrogen from the phenolic group of the 4-hydroxy-3-methoxybenzyl alcohol leading to a ketyl and phenoxy radical pair (Figure 2.17, Pathway 1) [127]. Finally, quinones were generated from the phenoxy radicals.

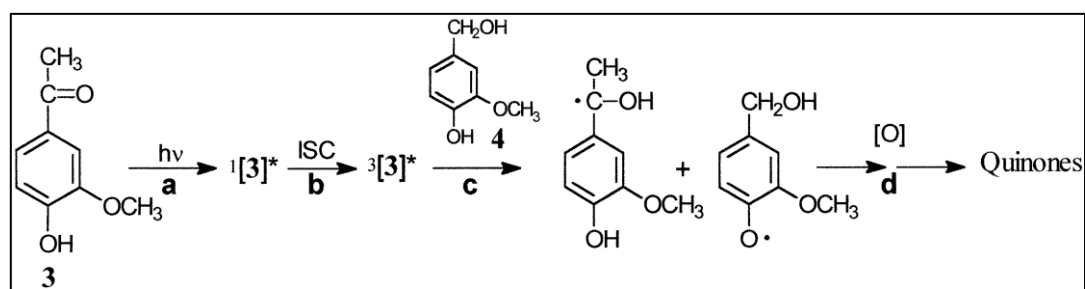


Figure 2.17: Pathway 1 - The photochemical reaction of the α -carbonyl phenolic LMC 4-hydroxy-3-methoxybenzyl alcohol and acetoguaiacone [127].

Phenolic groups in α -carbonyl LMCs also play an important role during α -carbonyl photo oxidation. This was illustrated by work conducted by Neumann and Machado [137], and Shkrob et al. [138] comparing the photo oxidative reactivity for vanillin (which served as a phenolic group) and 4-methoxyacetophenone (which did not have a phenolic group). During irradiation, only the vanillin

produced *p*-quinones while the 4-methoxyacetophenone did not. The proposed mechanism was based on phenoxyl radicals, although the mechanism for conversion of the radicals into coloured quinones was unknown; however, reactive oxygen species are known to play a role. Similarly, photo reduction of the lignin α -carbonyl groups via the interaction between the phenolic groups and the α -carbonyl groups play a key role in photo yellowing and degradation of LMCs and lignin. This process involves the reductive (rather than an oxidative) transfer of a hydrogen atom from the phenolic group within the molecule (generating a phenoxyl radical) to the α -carbonyl group. This, together with the generation of phenoxyl radicals by direct photo excitation of the phenolic group, constitute what is known as the phenol pathway [137, 139 to 141]. Castellan et al. [142] illustrated the Phenol pathway in their study of the impact of the solvent environment on the irradiation of 1-(4-ethoxy-3-methoxyphenyl)-8-hydroxy-8-(4'-hydroxy-3'-methoxyphenyl) octan-1-one. In non-polar or poor hydrogen-donating solvents, the intramolecular hydrogen atom was transferred from the phenolic group to the carbonyl group. However, in solvents that are good hydrogen donors with the above diphenyl hydroxyl octanone, when the molecule was incorporated into a 2-hydroxypropylcellulose matrix (to represented the constrained conditions within the lignin matrix), the hydrogen atom transfer occurred from the solvent instead. The results of this study supported and demonstrated the proposed mechanism of the phenol pathway [127, 136, 137, 142].

The inclusion of a β -ether-4 linkage (i.e. β -O-4) together with the α -carbonyl group opens the door for alternative photochemical pathways (Figure 2.18, Pathway 2) [127]. The work of a number of research groups showed that there are generally two main pathways, which are illustrated in the photochemical reaction of α -(2,6-dimethoxyphenoxy)acetophenone with R_1, R_2, R_3, R_5 = hydrogen; R_4, R_6 = methoxyl (Figure 2.18, molecule no. 7): (1) the β -cleavage of the excited singlet state molecule into a phenacyl and 2,6-dimethoxyphenoxy radical pair (path **b**), and (2) the inter system crossing of the singlet to a triplet state LMC followed by its reduction to an enol of acetophenone (path c and d) [143 to 147]. The β -cleavage of the singlet (path **b**) has also been observed for α -(4-methoxyphenoxy)-4-methoxyacetophenone (R_1, R_5 = methoxyl; R_2, R_3, R_4, R_6 = hydrogen) by Scaiano et al. [147]. For the α -(2,6-dimethoxy phenoxy)acetophenone, the phenacyl and phenoxyl radical pair underwent cage escape reactions leading to a 1,4-diphenyl-1,4-butanedione type dimer (path **i**) and 2,6-dimethoxyphenol via hydrogen abstraction (path **h**). Alternatively, the radical pair could undergo in cage recombination leading to cyclohexadienone products (path **f**) followed by protonic rearrangement into α -carbonyl- β -1 compounds (path **g**).

The research of a number of groups on the LMC: guaiacylacetoveratrone (R_1, R_2, R_4 = methoxy; R_3, R_5, R_6 = hydrogen), showed that the guaiacylacetoveratrone underwent similar reactions to α -(2,6-dimethoxyphenoxy)acetophenone upon irradiation producing guaiacoxyl and 3,4-dimethoxyphenacyl as the radical pair from the β -cleavage of a pathway 2 type process (Figure 2.18) [145, 148 to 155].

However, guaiacylacetoveratrone also illustrated that the radical pair could be recombined via C-O or C-C coupling leading back to the starting molecule (path **k**) as well as forming the isomeric α -carbonyl β -1 structures (path **g**). Experimental work by Argyropoulos and Sun [149] showed that when molecular oxygen was present, the phenacyl radical was oxidised to 1-(3,4-dimethoxyphenyl)-2-hydroxyethanone when X was ethanoxyl, and R₁ and R₂ was methoxyl in Figure 2.18 (molecule no. 10); as well as two C α -C β cleavage oxidation products: 3,4-dimethoxybenzaldehyde (X = hydrogen, R₁, R₂ = methoxyl) and 3,4-dimethoxybenzoic acid (X = hydroxyl, R₁, R₂ = methoxyl) in pathway **i** (Figure 2.18). Lastly, studies by Hurrell et al. [156], on α -aryloxy-3,4-dimethoxy-acetophenones have shown that a cellulose matrix imposed restrictions on the mobility of the radical pair seen in Figure 2.18. This was demonstrated when these acetophenones were adsorbed onto three solid supports: silica, zeolites and cellulose, and then irradiated. Silica gave singlet state β -cleavage products (Figure 2.18, β -1 dimers) while both the zeolites and cellulose gave very little photo degradation products at all (path **k**).

A comparison between the intermolecular transfer of a hydrogen atom from a phenolic group to the α -carbonyl triplet of a α -carbonyl- β -ether group LMC as opposed to the intramolecular β -cleavage of the phenacyl ether bond of the same LMC (pathway 1 in Figure 2.17 -vs- pathway 2 in Figure 2.18) has been well studied, with results showing that the intramolecular β -cleavage is favoured over the intermolecular hydrogen transfer. Fukagawa et al. [157] demonstrated this when both 4-hydroxy-3-methoxy- α -(2'-methoxy-phenoxy)acetophenone and 4-hydroxy-3-methoxy- α -(2'-methoxy-phenoxy)benzoyl ethan-3-ol were irradiated in ethanol as a solvent (a solvent that does not favour intermolecular hydrogen transfer in this case) as opposed to vanillin and acetoguaiacone. In the study, the two α -carbonyl- β -ether LMCs showed significant β -cleavage, while very little hydrogen atom transfer for the vanillin and acetoguaiacone was observed. In another earlier study by Castellan et al. [158], the four compounds: acetoguaiacone, acetosyringone, 4-hydroxy-3-methoxy- α -(2'-methoxy-phenoxy)acetophenone, and guaiacylacetoveratrone (two simple α -carbonyls LMCs and two more complex α -carbonyl- β -ether LMCs respectively) gave similar levels of yellowing when irradiated in ethanol. However, when these compounds were adsorbed onto a solid carbohydrate matrix, the two α -carbonyl- β -ether LMCs showed significantly more yellowing than the two simple α -carbonyl LMCs. The main mechanism for this more extensive yellowing was determined to be the intramolecular β -cleavage of the more complex α -carbonyl- β -ether LMCs (pathway-3 of Figure 2.19 / path **d**) as opposed to the far less extensive intermolecular hydrogen atom transfer from phenolic groups (pathway-3 in Figure 2.19 / path **a**). The intermolecular hydrogen atom transfer is followed by formation of a

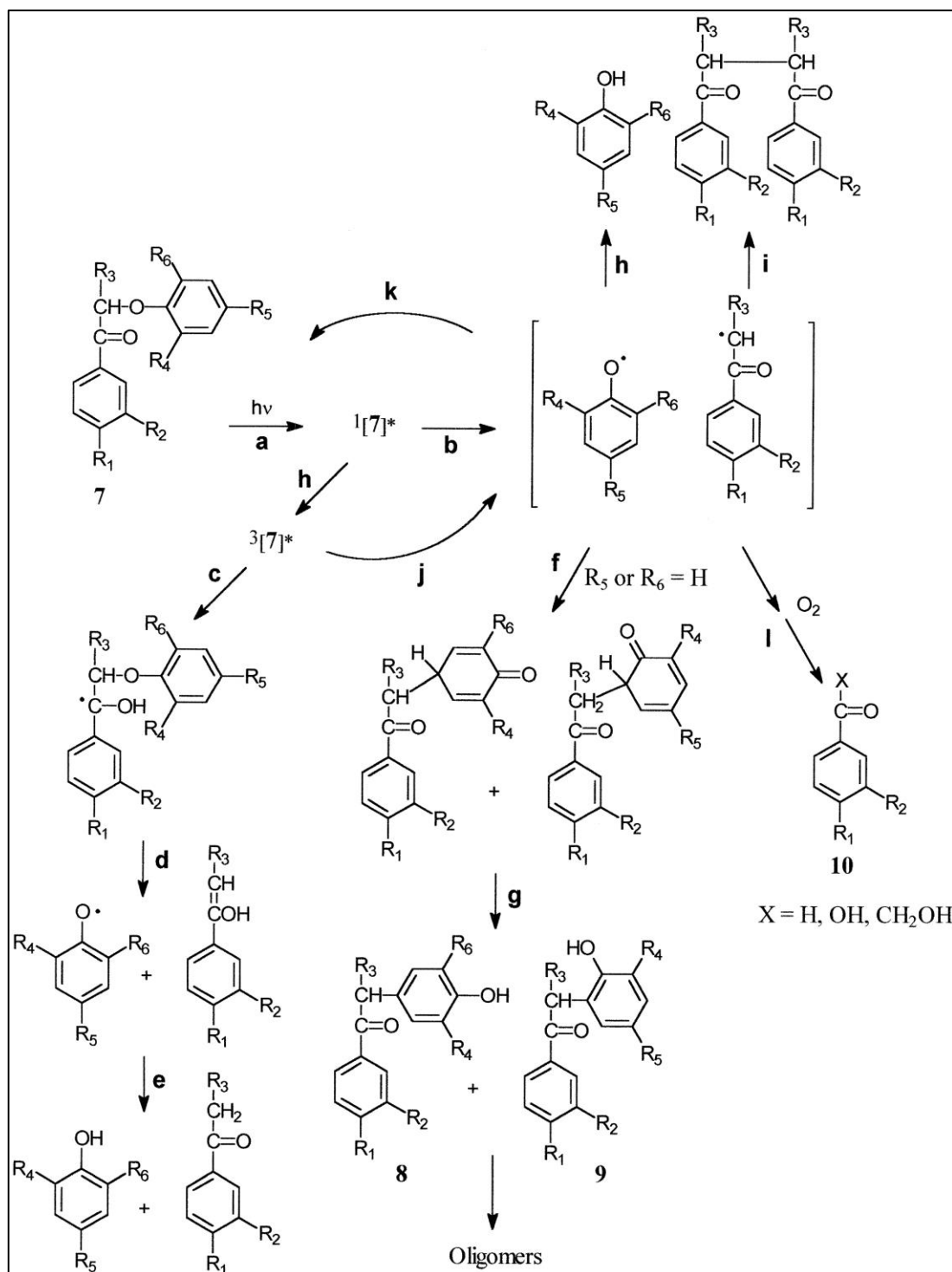


Figure 2.18: Pathway 2 - Photoirradiation alternative reaction pathways of various α -carbonyl β -ether typ-4 LMCs / [127].

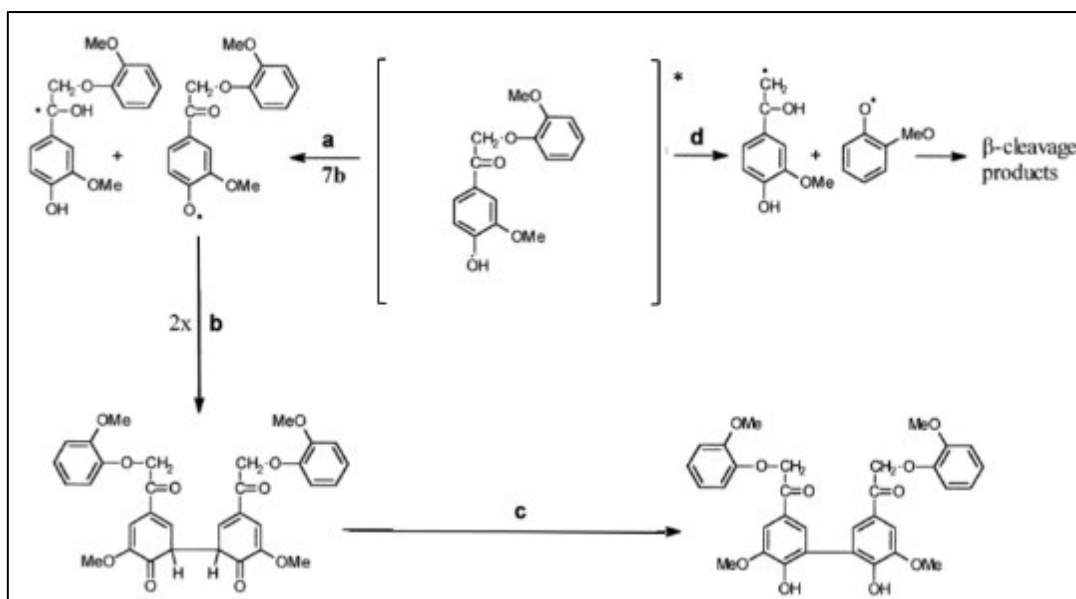


Figure 2.19: Pathway 3 - Reaction of α -carbonyl- β -ether LMCs upon photo irradiation via intermolecular hydrogen atom transfer -vs- intramolecular β -cleavage [127].

5-5'' dimer and then rearrangement to enols. The intermolecular hydrogen atom transfer accounts for about 10% of the total photoyellowing, while the homolytic β -cleavage accounts for about 30 – 40% of the yellowing and this homolytic β -cleavage represents what is known as the phenacyl pathway [152, 153].

In the absence of a phenolic alcohol (whether by exclusion from the LMC itself or the lack of a photosensitizer), α -carbonyl LMCs can undergo Norrish Type I cleavages of the α -carbonyl side chain or hydrogen atom reduction of the α -carbonyl moiety itself. This was illustrated by Castellan et al. [159] when 1,2-di(3',4'-dimethoxy-phenyl) ethanone was irradiated in solution or adsorbed to a lignin free fibre matrix (Figure 2.20). The benzoyl-benzyl caged radical pair formed from the Norrish Type I cleavage of the ethenone complex (Figure 2.20 / path **a**) could undergo either coupling leading to 3,4-dimethoxybenzaldehyde and 3,4-dimethoxytoluene; or hydrogen atom transfer leading to 3,3',4,4'-tetramethoxy-benzil and 1,2-bis(3',4'-dimethoxyphenyl)ethane. Alternatively, the ketyl and benzylic (i.e. desyl) radicals formed from the α -carbonyl reduction (Figure 2.20 / path **b**) could undergo dimerization leading to pinacol (Figure 2.20 / path **c**) and bidesyl (Figure 2.20 /path **d**) compounds; or benzylic alcohols by hydrogen atom transfer and disproportionation (Figure 2.20 / path **e**). In the presence of oxygen, the desyl radical produced veratric acid and strongly coloured oligomers via a Norrish type reaction (Figure 2.20 / path **f**); while the ketyl radical regenerated the starting LMC (Figure 2.20 / path **g**).

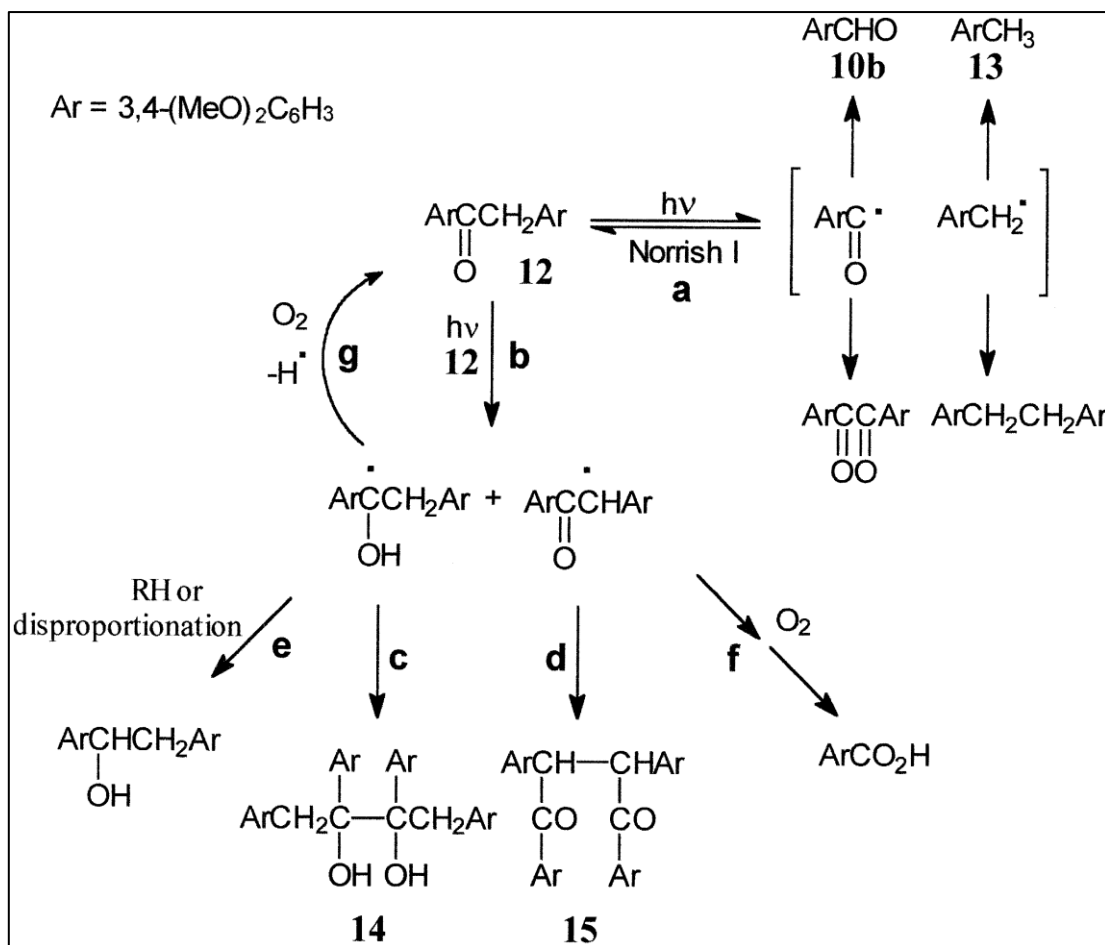


Figure 2.20: Pathway 4 - Photo irradiated reaction of 1,2-di(3',4'-dimethoxy-phenyl) ethanone via Norrish Type I -vs- α-carbonyl hydrogen atom reduction [127]

2.4.2.2 α-Hydroxy β-ether-4 containing lignin model compounds (α-OH β-O-4 LMC)

The α-hydroxy β-ether-4 LMCs are mostly photostable under irradiation, but their reaction rate significantly increases when irradiated in the presence of hydrogen atom abstractors such as α-carbonyls or peroxides. This is clearly illustrated in the study by Argyropoulos, and Sun [149] when guaiacylglycerol-β-guaiacyl ether was irradiated in the presence of an equimolar quantity of 3,4-dimethoxy-α-(4'-methyl-2'-methoxyphenoxy)acetophenone (Figure 2.21). Under irradiation, a hydrogen atom was abstracted from the α-C-H position of the guaiacyl ether to the α-carbonyl group of the acetophenone forming a ketyl radical in place of the α-C-H (Figure 2.21 / path **a**), which then underwent fragmentation into an enol and a phenoxyl radical (Figure 2.20 / path **b**). The enol finally tautomerized into the corresponding ketone giving 1-(4-hydroxy-3-methoxyphenyl)-3-hydroxy-1-propanone and guaiacol (Figure 2.21 / paths **c** and **b**). This cleavage of the ketyl radical formed from the α-C-H hydrogen atom abstraction of a α-hydroxy β-ether-4 LMC (Figure 2.21 / path **a** and **b**) together with the cleavage of the ketyl radical formed from photoreduction of a α-carbonyl of a α-carbonyl β-ether type-4 LMC (Figure 2.18 / path **c** and **d**) are an important source of phenoxyl radicals

which play an important role in yellowing of high lignin pulps; and together form what is known as the ketyl pathway [160, 161]. A variety of studies have shown the importance of the ketyl pathway, while the phenol pathway and phenacyl pathway account for less than half of the photo yellowing observed in high yield pulps [146, 160, 161].

However, in the presence of molecular oxygen, β -cleavage of the ketyl radical via the ketyl pathway is not the predominant source of photoyellowing, with α -phenoxyacetophenone being the primary product instead (Figure 2.21 / path **e**) – Huang et al. [162] study. This indicated that the ketyl radical reacted with the oxygen generating an α -carbonyl β -ether-4 LMCs instead allowing for further reaction via the phenacyl pathway which becomes the predominant chemical route in the presence of molecular oxygen. The secondary products were also found to be acetophenone and phenol.

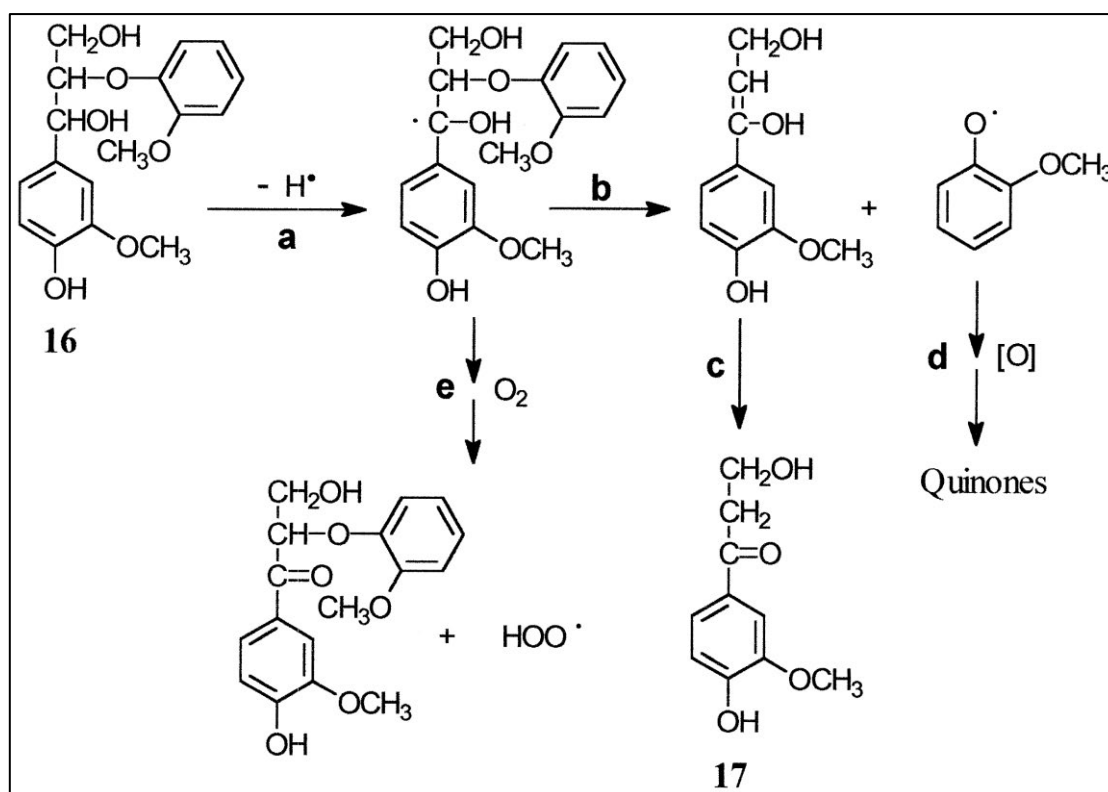


Figure 2.21: Pathway 5 - Photo irradiated reaction of guaiacylglycerol- β -guaiacyl ether in the presence of 3,4-dimethoxy- α -(4'-methyl-2'-methoxyphenoxy) acetophenone as a hydrogen atom abstracting species [127].

2.4.2.3 α -Ether-4 containing lignin model compounds (α -O-4 LMC)

The photo irradiation of α -ether-4 LMCs routinely leads to the homolytic cleavage of the α -Ether linkage giving a radical pair consisting of a phenoxyl and a benzyl pair. When α -(2',4',6'-trimethylphenoxy)-3,4-dimethoxytoluene was irradiated in protic or aprotic solvents, in a study by Castellan et

al. [163], the α -ether linkage was homolytically cleaved and gave 2,4,6-trimethylphenoxy and 3,4-dimethoxy-benzyl as a radical pair (path **a** of Figure 2.22 / pathway 6). This radical pair then undergo in cage and out of cage radical reactions resulting in the hydrogen atom transfer from the solvent (path **b**), radical to radical coupling (path **c**), and formation of methylene-quinones leading to phenolic derivatives which lead to highly coloured oligomers (path **d**).

2.4.2.4 Conjugated lignin model compounds

Conjugated Double Bond containing LMCs typically of the coniferyl type (e.g. cinnamyl alcohols and cinnamaldehydes), stilbenes and phenylcoumarans are strong light absorbers and often play key roles in photo yellowing and photolignin degradation. In addition, they are important structural components present in wood and pulp lignin matrices [127, 164 to 173]. As part of the investigation into the

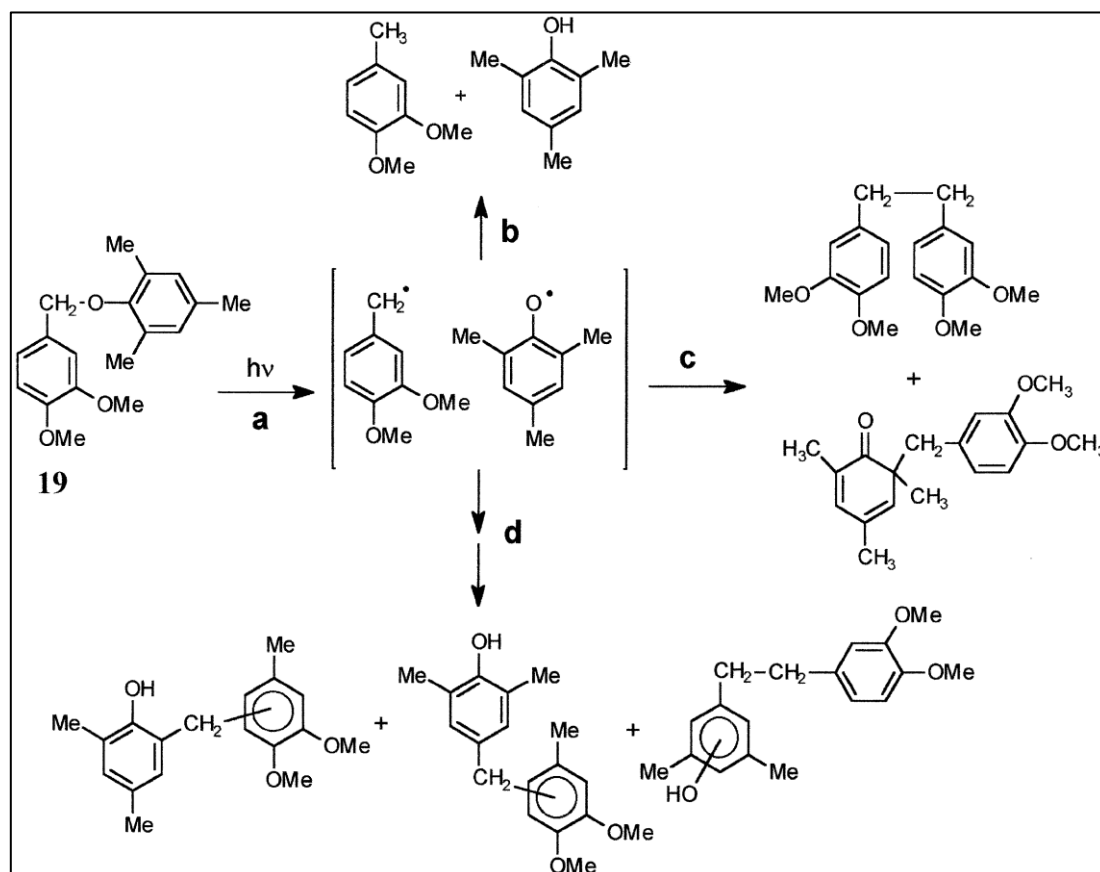


Figure 2.22: Pathway 6 - Photochemical reaction of α -(2',4',6'-trimethyl-phenoxy)-3,4-dimethoxytoluene in protic or aprotic solvents [127].

photochemistry of conjugated double bond containing LMCs, a number of studies were undertaken on *trans*-coniferyl alcohol, but differing results were obtained likely due to the varied experimental conditions employed, particularly whether the solvent used was organic or aqueous. As shown by Jaeger et al. [171], in organic solvents like dichloromethane (CH_2Cl_2) and methyl tert-butyl ether

(tBuOMe) the photo irradiation of *trans*-coniferyl alcohol yielded the *cis* or Z-isomer of coniferyl alcohol (path **a** of Figure 2.23, pathway 7) as well as other monomers produced from demethoxylation and oxidation (paths **b** and **c** of pathway 7), and a collection of oligomers due to coupling (path **e** of pathway 7). However, oxidation of the γ -alcohol group on the coniferyl alcohol to the aldehyde was not observed. In buffered aqueous solutions, only dimers, oligomers and polymers were observed; but not monomers as in the organic solvents. The primary photochemical mechanism was ionic in nature involving first protonation of the γ -alcohol group, followed by elimination of a water molecule and then a proton leading to a quinone-methide (path **f** of pathway 7). The quinone methide then underwent coupling leading to the dimers, oligomers and polymers observed [172, 173].

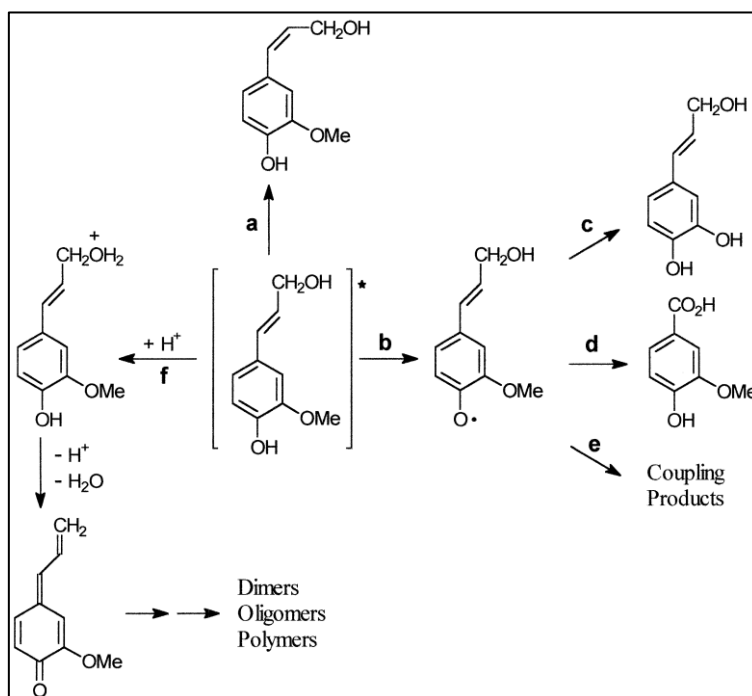


Figure 2.23: Pathway 7 - Various photochemical reactions of *trans*-coniferyl alcohol in organic and aqueous solvents upon irradiation [127].

Two possible mechanisms have been proposed for the photochemical reaction of stilbene type conjugated double bond LMCs. These are based on studies undertaken by multiple research groups on both *trans*-3,3',4'-trimethoxy-4'-hydroxystilbene and *trans*-4-hydroxy-3,3',4',5-tetramethoxystilbene [140, 164, 174]. For the first proposed photochemical mechanism involving irradiation by sunlight, various tetraphenylcyclobutanes were generated via a $[2\pi + 2\pi]$ cycloaddition between the excited state of one stilbene molecule and the ground state of another stilbene molecule (path **b** of Figure 2.24 / pathway 8). In addition, the primary mode of colour formation of this first photochemical mechanism was firstly the generation of phenoxyl and monohydrostilbene radical pairs via a sequential electron-

proton transfer between excited and ground state stilbene molecules (path **c** and **d** of pathway 8) followed by a one electron pathway oxidation of the phenoxyl radical generated which was then followed by water addition and methanol elimination to give the strongly coloured stilbene *ortho*-quinones (paths **e** to **g** of pathway 8) [164]. A possible competing reaction involving the reaction between the phenoxyl radical and monohydrostilbene radical giving a coupling product of the aryl ether type is also possible (path **h** of pathway 8).

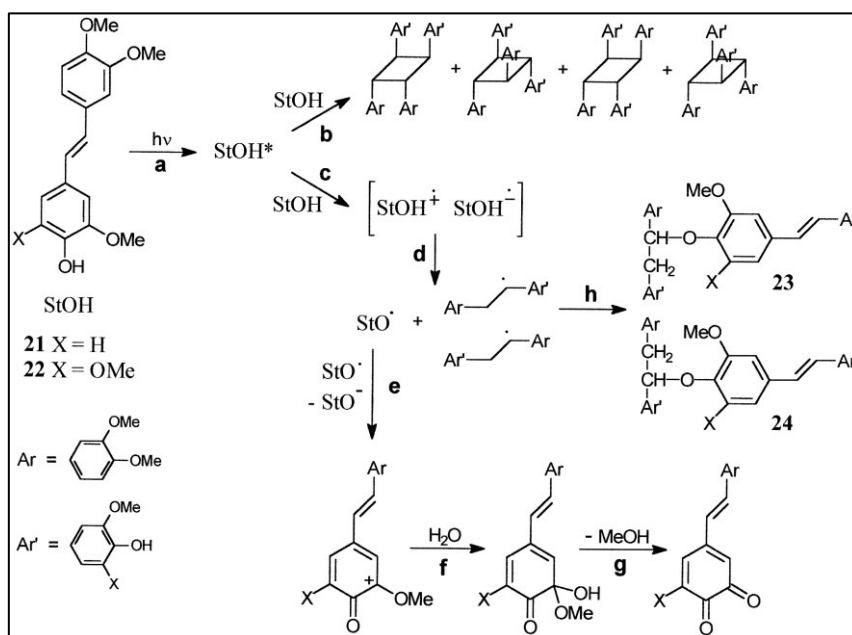


Figure 2.24: Pathway 8 - First proposed mechanism of reaction by sunlight irradiation for stilbenes trans-3,3',4'-trimethoxy-4'-hydroxystilbene and trans-4-hydroxy-3,3',4',5'-tetramethoxystilbene [127].

The second proposed photochemical mechanism involved the generation of a stilbene radical cation upon photo irradiation which then reacted with a ground state stilbene molecule to generate the cyclobutane products shown in the first photochemical mechanism (path **b** of Figure 2.25 / pathway 9) [175, 176]. In addition, phenoxyl radicals could be formed by the rapid deprotonation of the radical cation (path **c**) or direct photolysis of the stilbene molecule (path **d**) which then react with another ground state stilbene to generate the aryl ether type products also shown in the first photochemical mechanism (path **e**). This first proposed stilbene photochemical mechanism is the less likely process of the two proposed mechanisms. This is due to the photo ionization of the stilbene molecule being more likely (a well known and common process for olefins) than the electron transfer process from a ground state stilbene molecule to an excited state stilbene molecule.

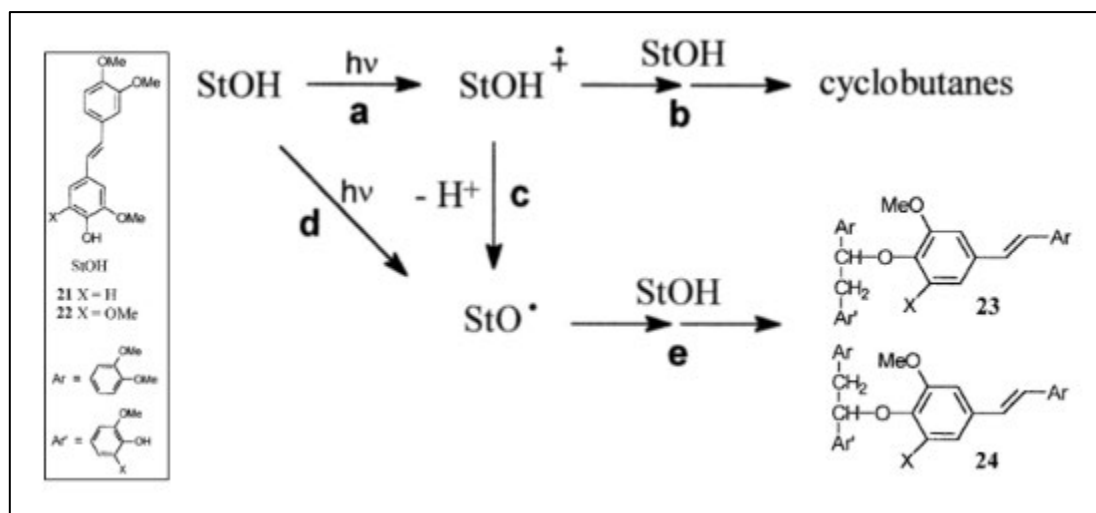


Figure 2.25: Pathway 9 - Second proposed mechanism of reaction by sunlight irradiation for stilbenes trans-3,3',4'-trimethoxy-4'-hydroxystilbene and trans-4-hydroxy-3,3',4',5-tetramethoxystilbene [127].

2.4.2.5 Lignin model compounds containing other chemical structures

Biphenyls are present in lignin in minor quantities and are photosensitive contributing to photo yellowing typically in high yield pulps, although their minor content allows them to have only a small impact on brightness reversion [140, 168]. Monophenolic biphenyl LMCs (R = Me / Figure 2.26) and biphenolic biphenyl LMCs (R = H / Figure 2.26) are strongly influenced by whether the biphenyl is in solution or adsorbed to a solid matrix, with the monophenolic biphenyl reacting more strongly than the biphenolic biphenyl when adsorbed onto a solid, while the biphenolic reacts more strongly when in solution (Figure 2.26). This is due to the conformational effect of the two phenolic groups of the biphenolic biphenyl when adsorbed to the solid matrix. Biphenyl structures can be formed by coupling of monomeric phenyl units under proto irradiation via a variety of mechanisms.

In addition, the derivatives formed from irradiation of coumarin and phenyl-coumaran type structures also play a role in emission of high yield pulps (Figures 2.27 and 2.28). There are a variety of mechanisms for forming these phenyl-coumarans which are characterised by extended conjugated systems. Examples include the phenyl-coumarans, dehydrodiisoeugenol (R = CH₃ / figure 2.28) and dehydroconirefyl alcohol (R = CH₂OH / figure 2.28) formed when α -hydroxy β -ether-4 LMCs are irradiated, while a phenyl-coumarone may be formed from the irradiation of the α -carbonyl β -1 LMC, 1,2-di(3',4'-dimethoxy-phenyl)ethenone, in the presence of a reducing agent – separate studies by Tylli et al. (1995), and Argyropoulos and Sun [149, 167]. The formed phenyl-coumarans would then derivatize to strongly light-absorbing structures upon further photo reaction with the main reaction likely being the conversion to light sensitive phenolic stilbene structures (Figure 2.29) – studies by Castellan et al. [140] and Cole et al. [177].

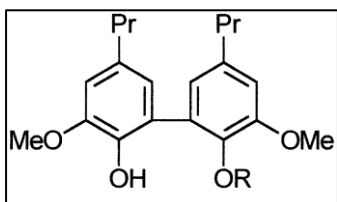


Figure 2.26: Monophenolic and biphenolic phenyl structures involved in photo yellowing of high yield pulps [127].

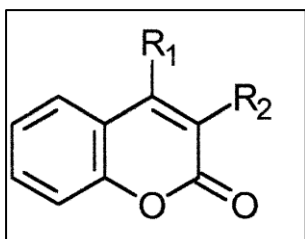


Figure 2.27: Coumarin ($R_1, R_2 = H$) and 4-hydroxy-3-(1-phenyl)-propylcoumarin ($R_1 = OH, R_2 = CH(CH_2CH_3)Ph$) as examples of coumarin types structures involved in the photo yellowing of high yield pulps [127].

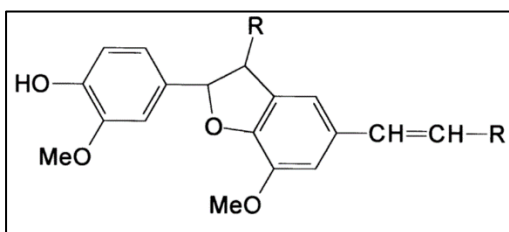


Figure 2.28: Dehydrodiisoeugenol ($R = CH_3$) and dehydroconirefyl alcohol ($R = CH_2OH$) as examples of phenyl-coumaran type structures involved in the photo yellowing of high yield pulps [127].

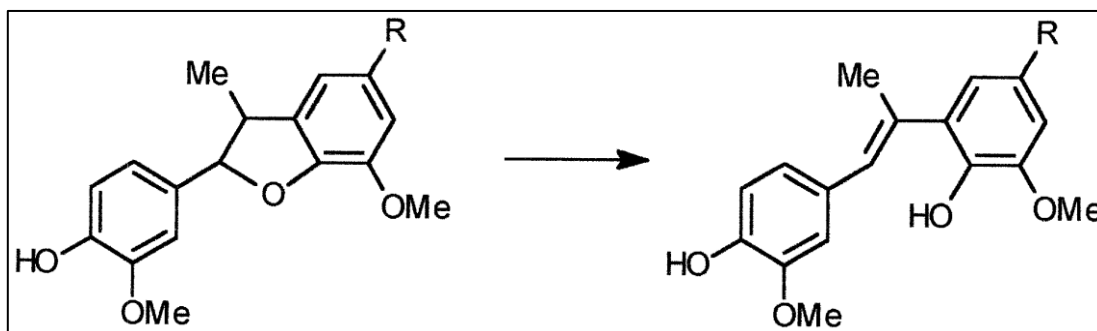


Figure 2.29: Derivatization of a phenyl-coumaran to a phenolic stilbene structure upon photo irradiation [127].

Other reactions that phenyl-coumarans can undergo were illustrated by two studies by Noutary et al. (1995) into the photo reaction of a phenolic phenyl-coumarone upon irradiation in both solution or a solid state (pathway 10 / Figure 2.30) [178, 179]. The excited singlet state formed by the initial irradiation led to a phenoxyl radical which could follow one of two paths: firstly an oxidative o-demethylation which led to catethol-type structures (path **a** / figure 2.30), and secondly coupling (involving a number of steps) with the parent compound which led to two dimeric stilbene compounds (path **b** / figure 2.30). The two coupling products were an α -carbonyl stilbenol and conjugated quinone methide which are strongly light-absorbing. There was no difference between reactions in solution or in the solid state.

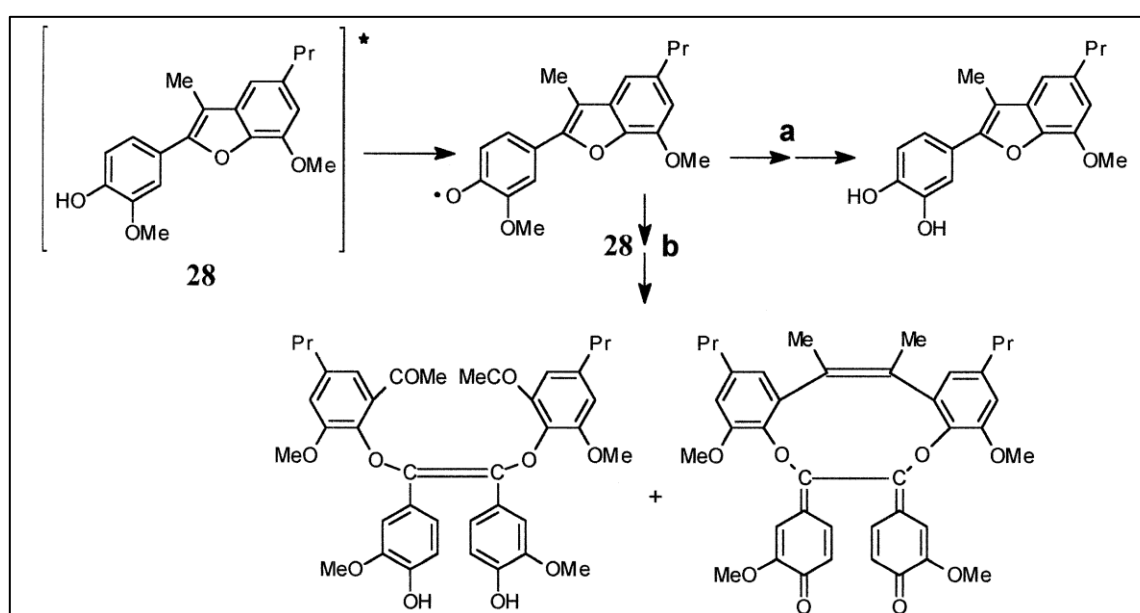


Figure 2.30: Pathway 10 - Two reaction mechanisms for the photo irradiation of a phenolic phenyl-coumarone in either solution or solid state [127].

2.4.3 Sensitized photo oxidations

As with studies into the impact of direct photo irradiation with various lignin model compounds (LMCs), a notable quantity of research has also been undertaken into photochemical reactions of various oxygen species with LMCs. A general overview of the behaviour of hydroxyl and superoxide radicals as well as singlet oxygen is required before a more specific discussion of selective experimental results is covered.

2.4.3.1 Overall behaviour of hydroxyl and super oxide radicals ($\text{OH}^\bullet$ and $\text{O}_2^{\bullet -}$)

Hydrogen peroxide and alkyl peroxides can be homolytically cleaved to generate the reactive hydroxyl radical (equation A in Figure 2.31) – study by Baxendale and Wilson [180]. In addition, the hydroxyl

radical so formed can also react with further peroxide (as hydrogen peroxide under acidic conditions, or the peroxide anion under alkali conditions) to generate the corresponding perhydroxyl radical (acidic conditions) or super oxide radical (alkali conditions) (equations B-1 and B-2 in Figure 2.31 respectively) – study by Bielski et al. [181].

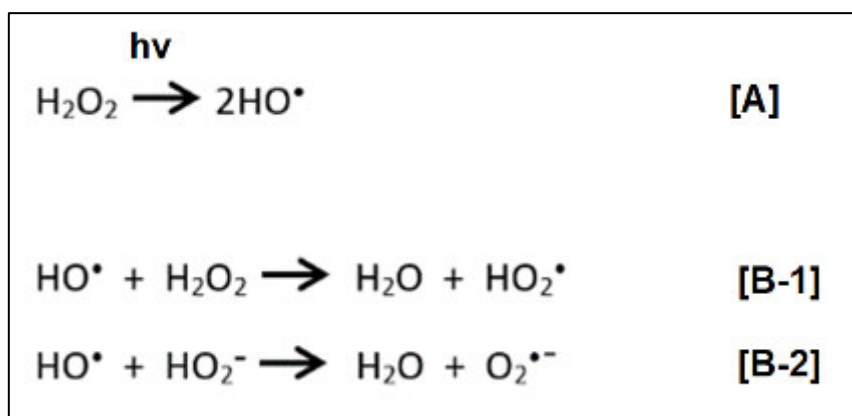


Figure 2.31: Homolytic cleavage of hydrogen peroxide under irradiation to hydroxyl radicals [A], and their subsequent reaction with further peroxide to generate perhydroxyl [B-1] / super oxide radicals [B-2] [127].

As shown in the studies by Schwarz and Dodson [182], and Steenken [183], the hydroxyl radical, despite being a strong oxidizing reagent with a large electronegativity allowing for a wide range of reactions, tends to react selectively with LMCs and lignin; with a preference to attach to aromatic rings and olefinic moieties of these lignin structures in addition to chemical reactions [182 and 183]. A less common reaction that was observed in those studies was hydrogen atom abstraction from saturated carbon atom centres. Under strong alkali conditions, the oxyl radical anion: $\text{O}^{\bullet-}$ (i.e. the conjugated based to the hydroxyl radical), tends to show a preference to hydrogen atom abstraction rather than addition to aromatics and olefins in the LMCs [184, 185]. The addition of the hydroxyl radical to the aromatic ring forms hydroxycyclohexadienyl radicals and is very position specific (Figure 2.32) [183].

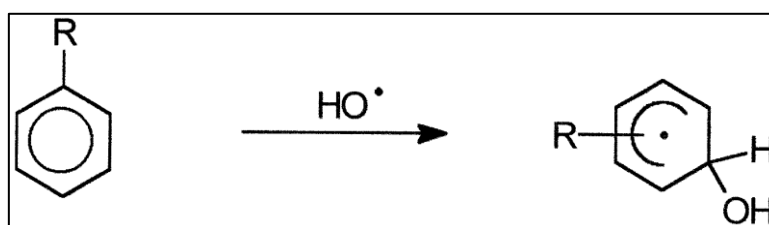


Figure 2.32: Addition of hydroxyl radical to aromatic ring generating a hydroxycyclohexadienyl radical. [127].

The ultimate fate of these hydroxycyclohexadienyl radicals was dependent on the electron density of the starting aromatic ring. If the starting aromatic ring was aryl (R = hydrogen atom in Figures 2.32 and 2.33), removal of the phenolic group via acid-catalysed dehydration was difficult and did not readily occur. However, if the starting aromatic ring was phenolic (R = hydroxyl group), dehydration occurred readily regardless whether the conditions are acidic, neutral or alkaline (Figure 2.34).

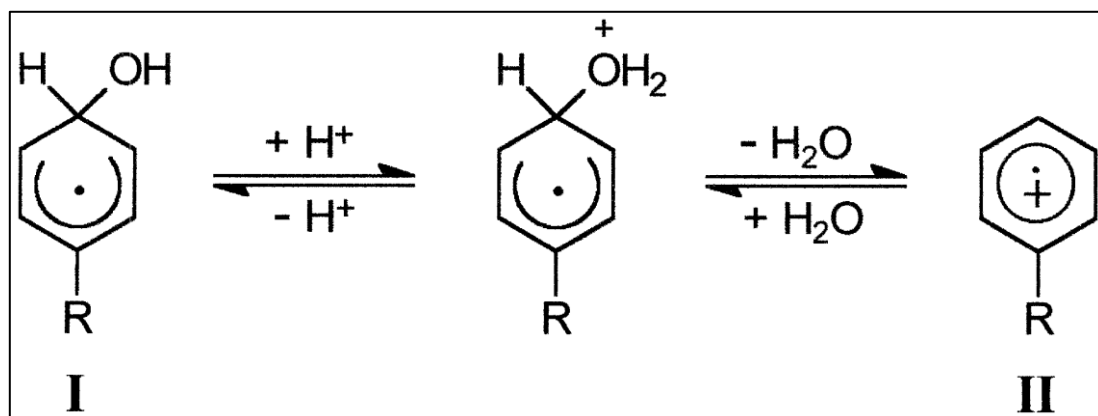


Figure 2.33: Acid-catalysed dehydration of hydroxycyclohexadienyl radical formed from the addition of a hydroxyl radical to an aryl aromatic ring (R = hydrogen atom) [127].

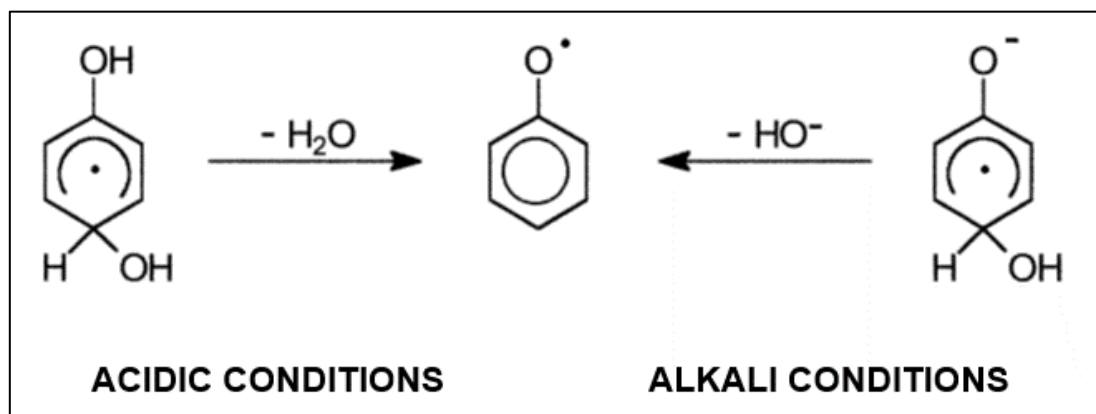


Figure 2.34: Acid catalysed dehydration of hydroxycyclohexadienyl radical formed from the addition of a hydroxyl radical to a phenolic aromatic ring [127].

During oxygen bleaching (i.e. O_2), the hydroxyl radical formed from molecular oxygen plays an essential role in the bleaching process. Due to the hydroxyl radical's electrophilic nature, it tends to selectively attack the electron rich aromatic ring of the lignin molecule. This process produces the primary hydroxycyclohexadienyl radicals formed which then allows for further modification and eventual degradation of the LMCs and lignin. A study by Gierer [185] showed that the hydroxycyclohexadienyl radical follows four possible main reaction pathways: firstly, hydroxylation (path A in Figure 2.35), secondly, demethoxylation (path B in Figure 2.35), thirdly, phenolic coupling (path C in Figure 2.35), and fourthly, (only for conjugated double bonded aromatics) cleavage of the

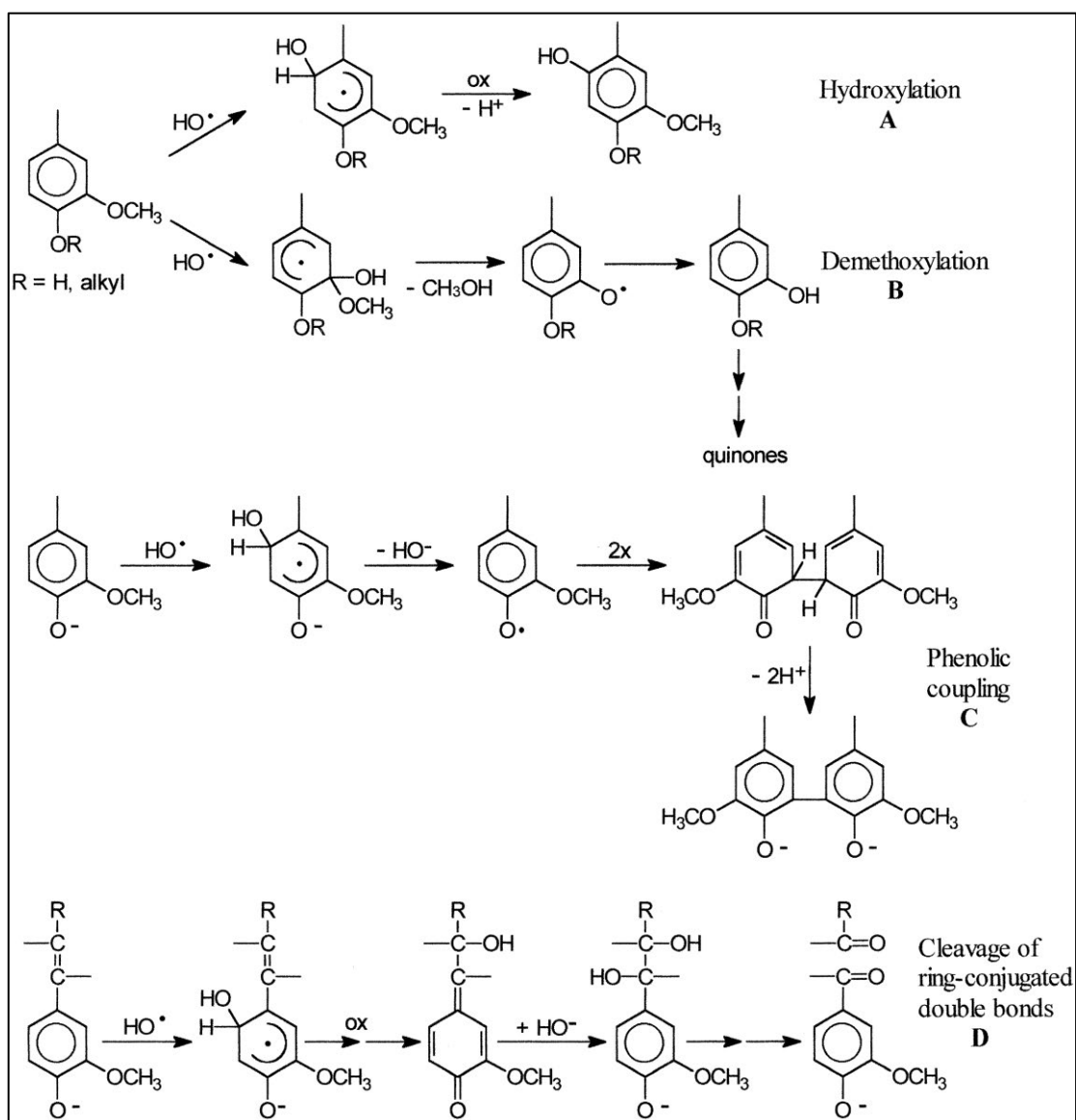


Figure 2.35: Pathway 11 - Four main reaction pathways for the hydroxycyclohexadienyl radical formed from the addition of a hydroxyl radical to lignin aromatic rings generated during bleaching with molecular oxygen (i.e. O_2) [127].

olefinic double bond (path D in Figure 2.35). Alternative oxygen bleaching reaction pathways that are less significant and often occur with less frequency are: firstly, deprotonation of the benzylic position or side-chain fragmentation, secondly, hydrogen atom abstraction from the aliphatic side chain resulting in a carbon radical centre (which converts to a peroxy in the presence of oxygen), and, thirdly, formation of a carbonyl from the carbon radical centre when it contains a hydroxyl group as given in pathway 5 for path **e** in Figure 2.21 (perhydroxyl radical elimination). The perhydroxyl/superoxide radicals degrade lignin only in co-operation and in the presence of hydroxyl radicals; they cannot degrade lignin on their own. The peroxy radicals (generated from reaction between the LMCs and

hydroxyl radicals) shown to react with super oxide radicals to generate intermediate peroxide anions, followed by an intramolecular nucleophilic attack leading to dioxetanes – study by Jonsson et al. [186]. In studies by Gierer [185], Jonsson et al. [186] and Sun et al. [187], these dioxetanes underwent rearrangement and resulted firstly in ring opening products (path A in Figure 2.36), secondly oxirane formation (path B in Figure 2.36), and thirdly cleavage of conjugated double bonds (path C in Figure 2.36).

2.4.3.2 Overall behaviour of singlet oxygen ($^1\text{O}_2$)

Singlet oxygen (i.e. $^1\text{O}_2$) is not formed by the direct absorption of radiation but rather through an initial photosensitizer such as rose bengal, methylene blue, the carbonyl groups (including quinones) and conjugated double bond structure of lignin / LMCs via means of inter system crossing (Figure 2.15) as seen by Frimer [188]. During the process the photosensitizer first absorbs the radiation exciting it to an excited state which then transfers this energy to triplet molecular oxygen in its ground state (i.e. $^3\text{O}_2$), exciting the oxygen to the singlet excited state (i.e. $^1\text{O}_2$). Singlet oxygen can also be formed during the irradiation of peroxides under alkali conditions, but does not persist for long rapidly being converted into super oxide and hydroxyl radicals upon reacting with hydroxide anions (i.e. OH^-). Due to its electrophilic nature, singlet oxygen tends to react with the electron rich centres of olefinic and aromatic

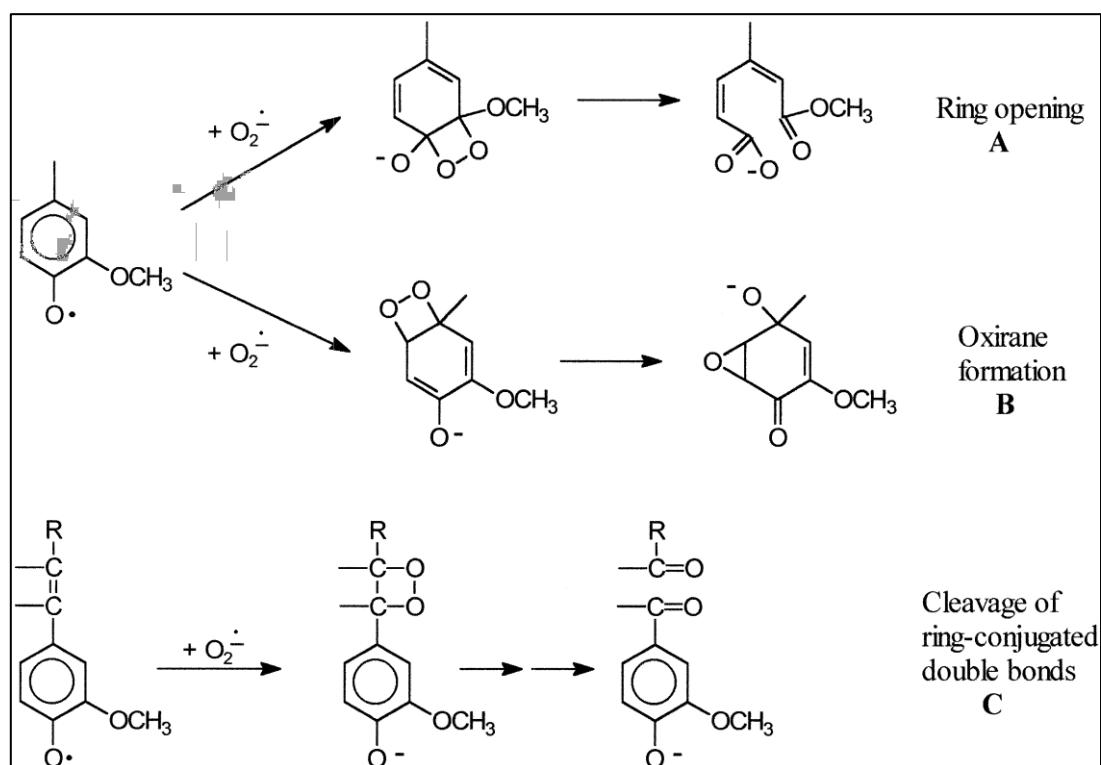


Figure 2.36: Pathway 12 - Three main pathways for co-operative reaction on LMCs / lignin between perhydroxyl / super oxide and hydroxyl radicals [127].

moieties of lignin and LMCs. Machado et al. [189] showed that these reactions tend to generate dioxitanes, endoperoxides and hydroperoxides; as well as carbonyls in some occasions. In multiple studies, reactions with phenolic groups formed phenoxyl and perhydroxyl radical pairs via hydroxyl group abstraction [161, 189].

2.4.3.3 General overview of reactions between reactive oxygen species and lignin model compounds

UV/peroxide bleaching of lignin has been demonstrated by studies of the degradation of LMCs in the presence of peroxides at alkali pHs while under UV irradiation with the main reactive agents formed being the super oxide ($O_2^{\bullet-}$) and hydroxyl radicals ($OH^{\bullet}$). Studies by Sun et al. (1997) comparing LMCs of the syringyl, guaiacyl, 3,4,5-trimethoxyphenyl and veratryl type LMCs with the same side chains have shown increased reactivity in the order: syringyl > guaiacyl > 3,4,5 - trimethoxyphenyl > veratryl. This indicated that LMCs with phenolic groups were more reactive than those with methoxy groups due to the greater electron-donating capacity of the phenolic anion [190]. Additionally, the same studies using varying side chains showed that these LMCs with alkyl side chains were more reactive than those with carbonyl and carboxylic groups. Analysis of the products from these studies showed some small conversions to aromatic oxidation products, but also a notable level of mono and dicarboxylic aliphatic ring opening products formed and rationalized from hydroxyl radicals acting on muconic-type structures together with super oxide radicals via path A for pathway 12 (Figure 2.36) – study by Sun et al. [187]. For non phenolic LMCs, the hydroxyl radical was found to first convert the LMCs into phenolic type LMCs before proceeding as described above. In acid conditions, the hydroxyl radical was found to be the predominant reactive reagent during UV/peroxide bleaching giving products as described by pathway 11 (Figure 2.35) as given by multiple studies [191 to 195].

Other multiple studies (Takagi et al. [196], Nimz and Turznik [197], and Gellerstedt and Pettersson [198]) involving the darkening of 1-(4-hydroxy-3-methoxyphenyl)ethanol coated to paper and exposed to singlet oxygen; studies involving the generation of singlet oxygen by reaction of hypochlorite with hydrogen peroxide; studies investigating the influence of singlet quenchers such as β -carotene and 2,6-di-*t*-butylphenol and the associated reduced yield in photo degraded LMCs; and, lastly, studies involving the impact of solutions such as $H_2O/tBuOH$, have shown the involvement of singlet oxygen in photo yellowing and lignin degradation.

2.4.3.4 α - Carbonyl containing lignin model compounds

The photo degradation of LMCs during irradiated alkali UV/peroxide and singlet oxygen bleaching processes was increased by the presence of α -carbonyls and phenolic groups on the LMCs. This was illustrated by Machado et al. [199] in studies of vanillin, guaiacylacetoveratrone, 1-(3,4-dimethoxyphenyl)-2-(4'-hydroxymethyl-2'-methoxyphenoxy)-1,3-propanediol, and 1-(4-hydroxy-3-methoxy-phenyl)-2-(2'-methoxyphenoxy)-1-propanone that showed a decrease in degradation when the

α -carbonyl groups were chemically reduced and phenolic groups were derivatized. During both the alkali UV/peroxide and singlet oxygen bleaching processes, the generation of phenoxyl radicals, which is usually achieved by reaction of the aromatic phenolate anionic groups with hydroxyl radicals or singlet oxygen respectively (Figure 2.35), resulted in the generation of phenoxyl/super oxide radical pairs via electron transfer and direct excitation of the phenolic group. These phenoxyl/super oxide radical pairs ultimately led to ring opening products, low molecular weight acids, and carbon dioxide typically via a final super oxide radical process (path A of pathway 12 / Figure 2.36). This was illustrated by the reaction of acteoguaiacone with hydrogen peroxide under alkali conditions with irradiation at 254 nm, leading to a process of demethoxylation and ring opening reactions based on the final products observed – two studies by Sun et al. [200, 201].

In their study on the use of the singlet oxygen quencher: 1,4-diazabicyclo[2.2.2]octane (i.e. DABCO) during the irradiation of vanillin and 4-hydroxybenzaldehyde in the presence of molecular oxygen, Neumann and Machado [137] showed no reduction in phenoxyl radical formation, but DABCO did disrupt and reduce the final photo product formation. This indicated that singlet oxygen was not involved in the initial photo degradation of α -carbonyl phenolics, but did impact the final product formation via secondary side chain reactions. Thus, quinones formed during the reaction, rather than the α -carbonyls present at the beginning of the process, appeared to be responsible for the formation of singlet oxygen in the photo irradiation process.

Machado et al. [189] showed that besides ring opening reaction processes, singlet oxygen also participated in the photo degradation of photosensitized α -carbonyl LMCs generating quinones as a final product. This was also demonstrated by Nimz and Turznik [202] and Forsska [203] in the photo reaction between vanillin (which served as both a reactant as well as a photosensitizer) and singlet oxygen in which two reaction paths are possible: firstly, the hydrogen atom abstraction from the vanillin phenolic group to the singlet oxygen (forming a super oxide/perhydroxyl radical and a phenoxyl radical) leading finally to *o*-quinonoid species (path a of pathway 13 / Figure 2.37); and, secondly, the addition of singlet oxygen to the aromatic ring forming an endoperoxide which finally leads to *p*-quinones (path b of pathway 13 / Figure 2.37). The above vanillin study showed that alkali conditions (which favour the phenolate anion) gave an increase in reactivity, but also a competition between physical and chemical singlet quenching with physical quenching being more dominant.

Besides only α -carbonyl LMCs, reactions between α -carbonyl- β -ether-4 LMCs and singlet oxygen also requires a photosensitizer. This is illustrated in the singlet oxygen induced photo degradation of 4-ethoxy-3-methoxyphenyl- α -(2'-methoxyphenoxy)-acetophenone in a molecular oxygen/rose bengal system (Figure 2.38) – two studies by Crestini and D'Auria, [204, 205]. In the presence of the quencher DABCO or the absence of the Rose bengal photosensitizer, no reaction was observed. However, when

rose bengal was present, singlet oxygen was generated leading to cleavage of the β -ether linkage (Figure 2.38/with R = hydrogen). A similar process was observed for the oxygen/rose bengal system for a closely related LMC, namely, 4-ethoxy-3-methoxyphenyl- α -(2,6-dimethoxyphenoxy)-acetophenone; but at a slower reaction rate (Figure 2.38/with R = methoxy).

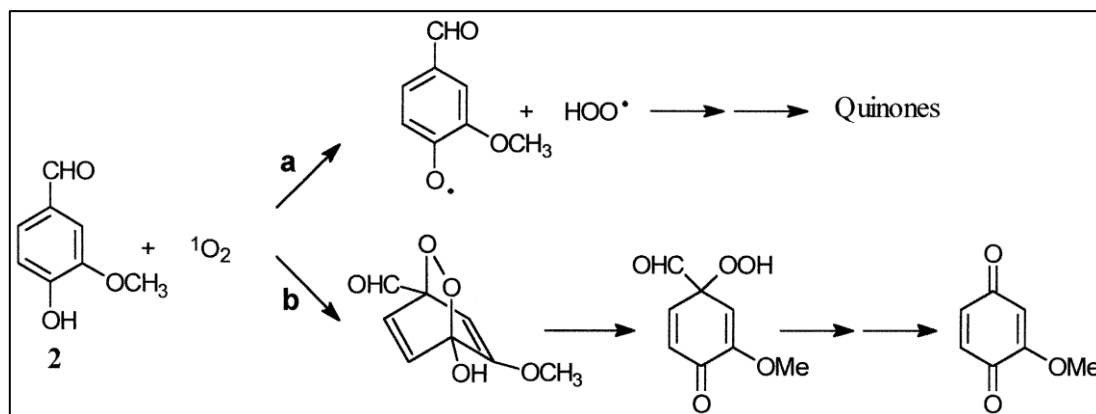


Figure 2.37: Pathway 13 - The two reaction pathways to quinonoid products from the photo reaction between vanillin and singlet oxygen. [127].

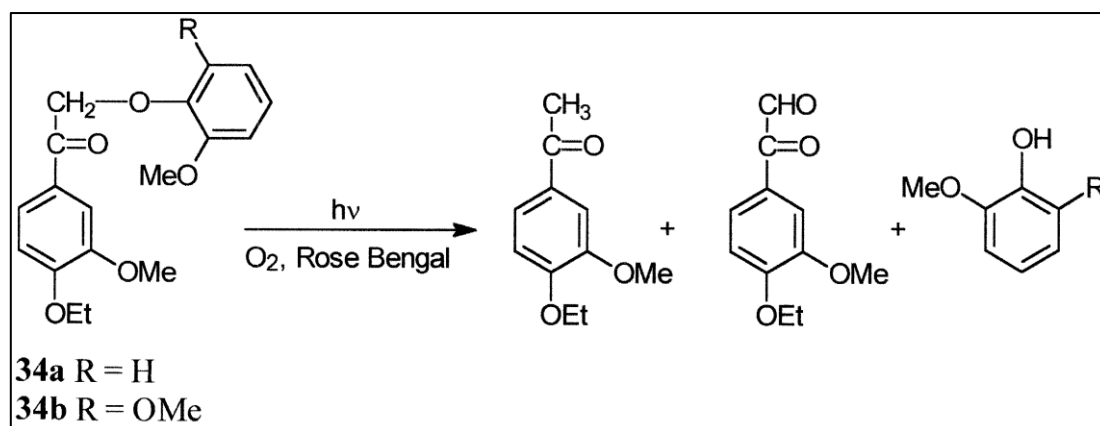


Figure 2.38: Pathway 14 - The oxygen/rose bengal photosensitizer reaction system for two known α -carbonyl- β -ether-4 LMCs [127].

2.4.3.5 α -Hydroxy β -ether-4 containing lignin model compounds (α -OH β -O-4 LMC)

Photo reactions with α -hydroxy β -ether-4 LMCs can be divided into two general types: firstly, reactions involving singlet oxygen generated from an oxygen/photosensitizer combination system, and then, secondly, triplet oxygen in an oxygen/photosensitizer combination system where the oxygen does not undergo an inter system crossing change from triplet to singlet state (i.e. not singlet oxygen generation). The reaction of guaiacylglycerol- β -guaiacyl ether in an oxygen/rose bengal system, giving guaiacol, acetoguaiacone and 1-(4-hydroxy-3-methoxyphenyl)-hydroxy-1-propanone as final products, is an example of the process in which singlet oxygen generated by such an oxygen/sensitizer system was

involved – study by Crestini and D’Auria, [204] (path A / Figure 2.39). In this photo reaction process, the singlet oxygen was added to the phenoxy moiety of the LMC via a 1,2-endoperoxide intermediate, while no proof of hydrogen atom abstraction from the phenolic hydroxy group via the singlet oxygen was evident. A different behaviour for the above oxygen/rose bengal system was observed when a more sterically hindered LMC is employed; namely, 1-(4-hydroxy-3-methoxyphenyl)-2-(2,6-dimethoxyphenoxy)-1,3-propanediol, in which the singlet oxygen reacted with the phenolic group instead of the phenoxy moiety giving products with no guaiacoxyl moieties (path B / Figure 2.39).

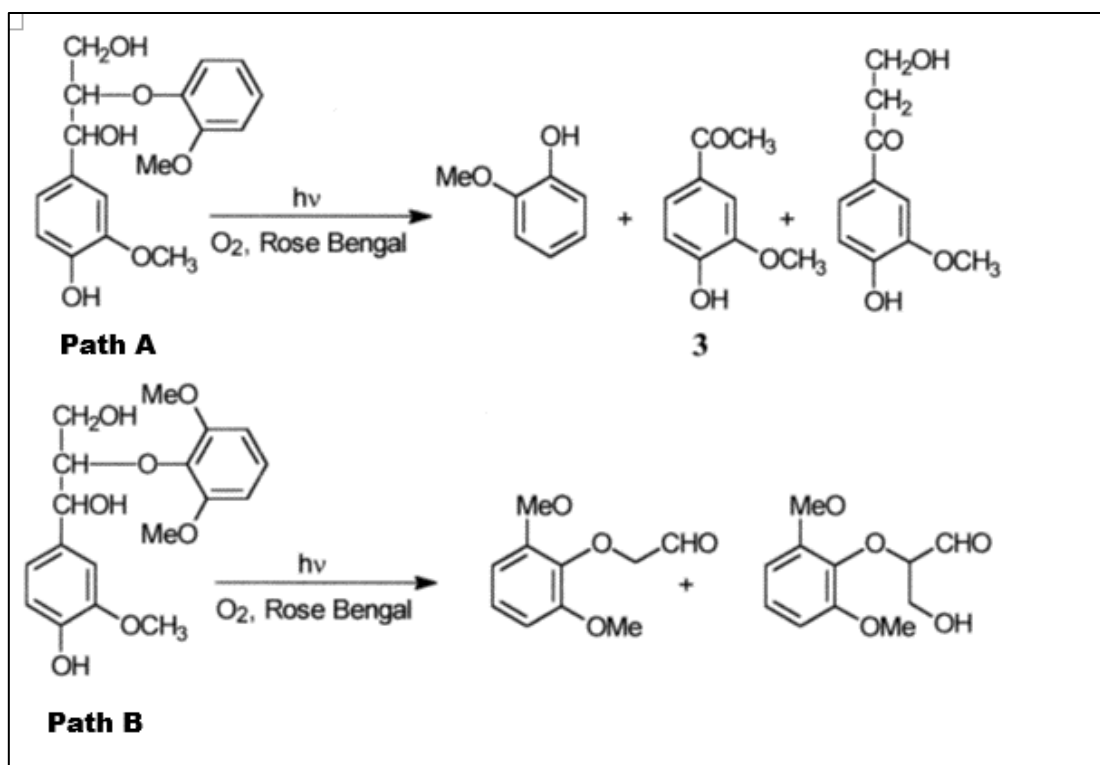


Figure 2.39: Pathway 15 / The oxygen/rose bengal photosensitizer reaction system for two known α -hydroxy- β ether-4 LMCs via generated singlet oxygen [127].

An example where singlet oxygen did not play a significant role but rather triplet oxygen was the main oxygen species, is illustrated by the reaction of 1-(3,4-dimethoxyphenyl)-2-(3'-methoxyphenoxy)-1,3-propanediol in an alkaline methanol solution in the presence of an oxygen/methylene blue system (pathway 16/figure 2.40) – study by Ruggiero et al. [161]. The three possible reaction paths were: firstly, the oxidation of the benzyl alcohol group to an α -carbonyl (path **a** / figure 2.40), secondly, the ring addition of hydroxymethyl radicals (i.e. $\cdot\text{CH}_2\text{OH}$ formed from hydrogen abstraction from the methanol solvent via a hydroxyl radical) followed by rearomatization (path **b** / figure 2.40), and thirdly the super oxide addition to the 2'-position of the phenoxy ring (path **c** / figure 2.40). Interestingly when the above LMC was irradiated in the presence of hydrogen peroxide, hydroxylation of either aromatic

ring was observed together with the products of hydroxymethyl and super oxide radical addition (path **d** / Figure 2.40).

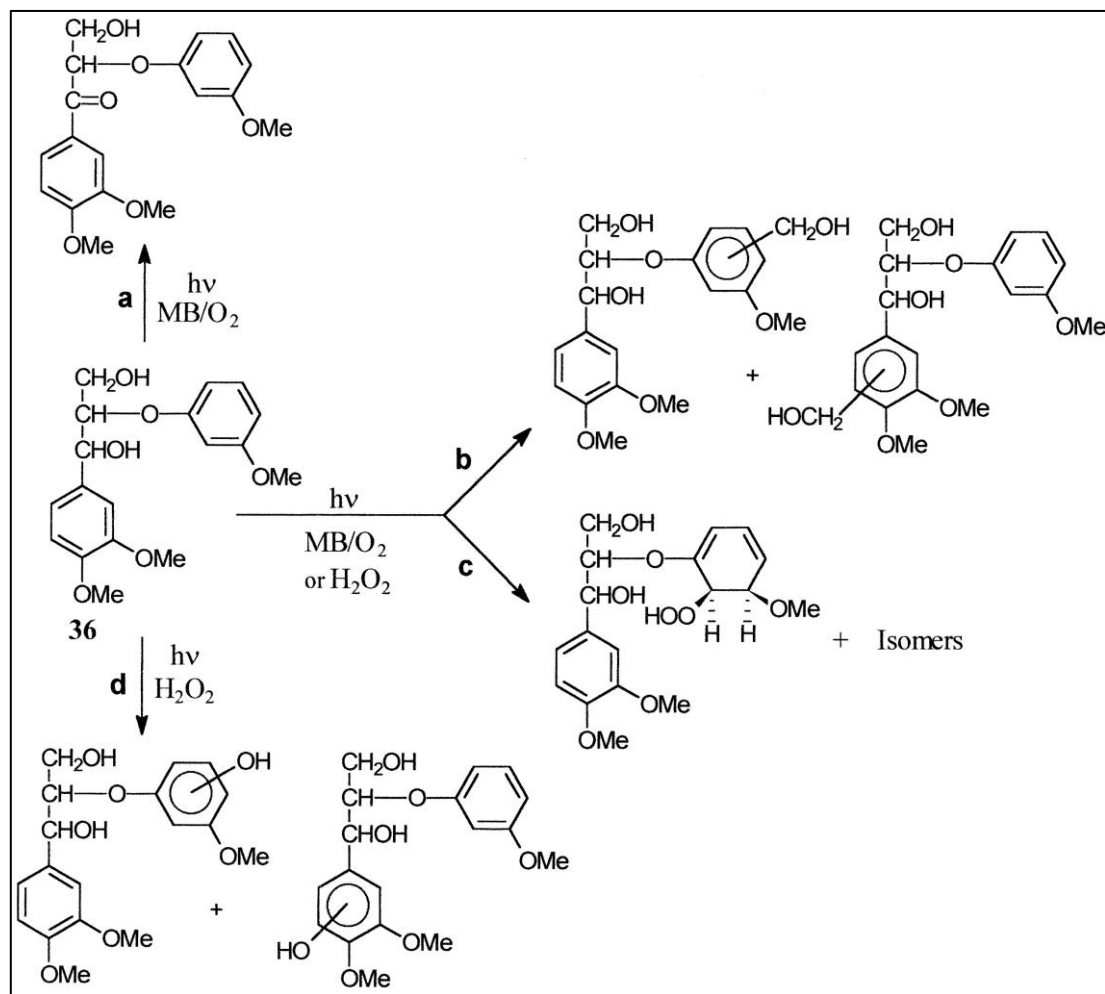


Figure 2.40: Pathway 16 - The reaction for a known α -hydroxy- β ether-4 LMC via an oxygen/methylene blue photosensitizer system via triplet oxygen or the LMCs reaction with hydrogen peroxide [127].

2.4.3.6 Lignin model compounds containing conjugated double bonds

In the presence of hydrogen peroxide (i.e. absence of molecular oxygen), the reaction of conjugated double bond aromatics was illustrated by the photo reaction of *trans*-ferulic acid in alkali UV/hydrogen peroxide conditions generating as products- fumaric acid, maleic acid, 4-hydroxybenzoic acid and the *cis*-ferulic acid isomer (Figure 2.41) – study by Sum et al. [200]. The reaction mechanisms involved included, firstly, formation of the *cis*-isomer via an excited triplet state (paths **a** to **c** / Figure 2.41), and secondly the generation of a phenoxyl radical intermediate from hydroxyl radicals (path **d** / Figure 2.21). Both the excited triplet states and the phenoxyl radical could then undergo oxidative ring opening reactions which led to the low molecular weight organic acids (fumaric acid and maleic acid) and carbon

dioxide (paths **e** and **f** / figure 2.41). The 4-hydroxybenzoic acid was formed by oxidative side chain cleavage and demethoxylation.

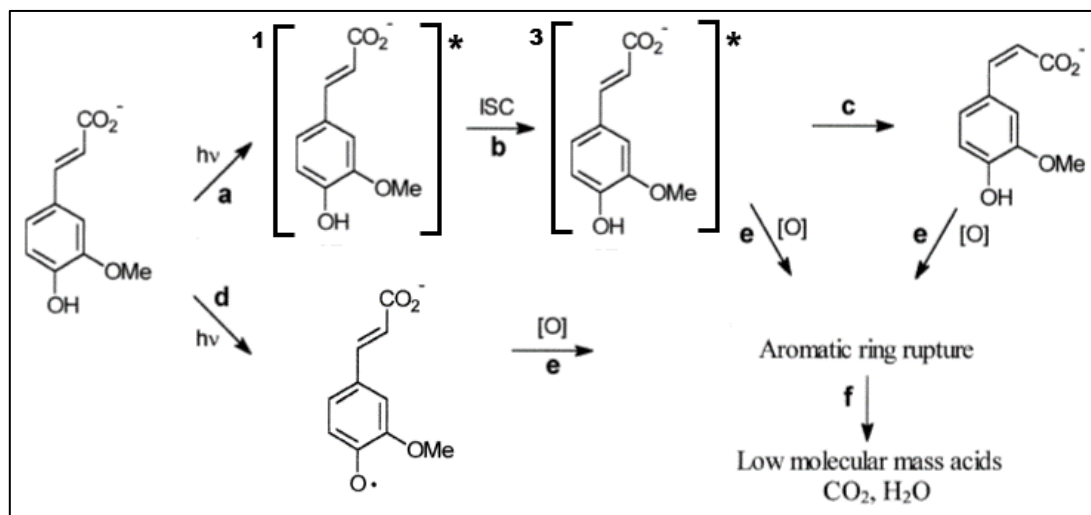


Figure 2.41: Pathway 17 - The photo reaction of the conjugated double bond aromatic *trans*-ferulic acid under alkali UV/hydrogen peroxide conditions [127].

In the presence of molecular oxygen, conjugated double bond LMCs could act as photosensitizers to convert triplet oxygen into singlet oxygen. This was illustrated by Gellerstedt and Pettersson [206] in the photo irradiation of *trans*-1-(3,4-dimethoxyphenyl)-1-propene in the presence of molecular oxygen, during which singlet oxygen (generated via photosensitization) was added across the side chain double bond resulting in a peroxirane intermediate (path **c** / Figure 2.42) which led finally to a glycerol type structure upon reaction with the solvent (whether water or an alcohol) (path **d** / Figure 2.42). Alternatively, the peroxirane generated could rearrange into an intermediary dioxetane which then underwent cleavage to two aldehydes followed by the oxidation to the final carboxylic acids (paths **f** and **g** / Figure 2.42).

The electron density of the double bonds in conjugated double bond LMCs plays an important role in their action as oxygen singlet photosensitizers, with decreased density leading to less reaction and greater photo stability of the initial LMCs. This was illustrated by Gellerstedt and Pettersson [206], and Omori et al. [207] with the LMCs: *trans*-3-(3,4-dimethoxyphenyl)-2-propen-1-ol and isoeugenol, as the lower electron density to their side chains made them both poor photosensitizers to oxygen. Finally, studies involving olefinic aromatic LMCs indicate that some of these olefinics could also serve as photosensitizers of oxygen, but the exact mechanism is still undetermined – study by Forsskåhl [203].

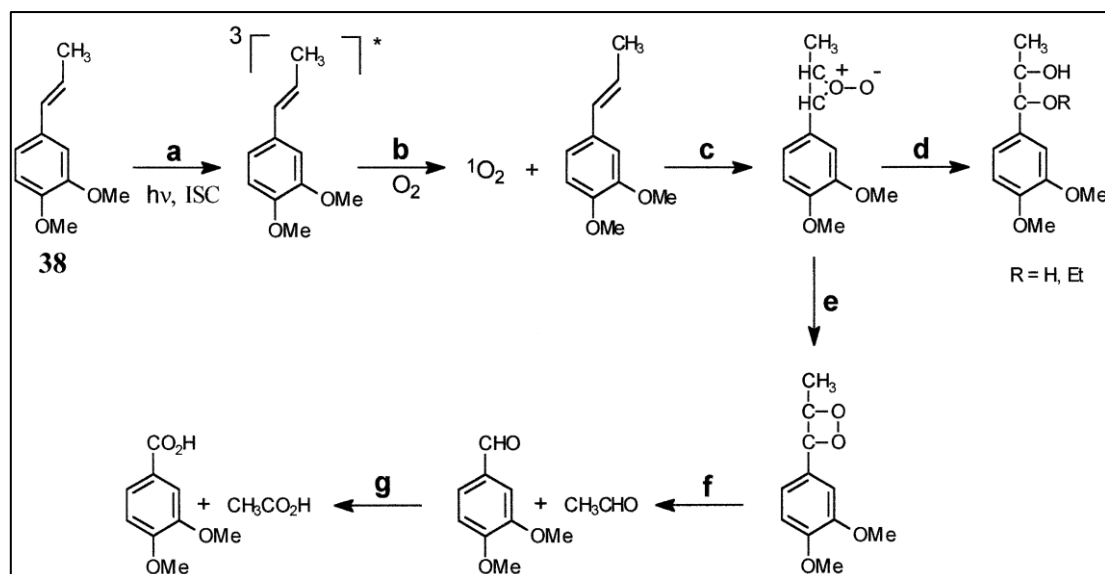


Figure 2.42: Pathway 18 - The photo reaction of the conjugated double bond LMC *trans*-1-(3,4-dimethoxyphenyl)-1-propene in the presence of molecular oxygen [127].

2.4.3.7 Photocatalysts and photosensitizers

Photocatalysis is a broad topic in photochemistry and photocatalysts themselves can be divided into three general types: firstly, heterogeneous catalysts in which the photocatalyst is in a different phase than the reactants (e.g. solid catalysts versus reactants in the liquid or gas phase), secondly, homogeneous catalysts in which both the catalyst and reactants are in the same phase, and, thirdly, plasmonic antenna reactor catalysts in which the photocatalyst is attached to an "antenna" that improves the catalyst's ability to absorb light. As with all catalysts, photocatalysts aid in the acceleration of selected chemical reactions by reducing the activation energy barrier for that reaction (Figure 2.10) [122]. For the bleaching of pulp and degradation of LMCs, heterogeneous catalysts are almost exclusively the most common photocatalysts used; typically being semiconductors of the oxides and sulfides of selected heavy metals (d-block and p-block elements); where the energy band gap (about 3.2 eV in size for titanium dioxide) between the filled valence electron orbitals and the empty first excited orbitals matches (either exactly or closely) the energy of the electromagnetic radiation it is being irradiated with. This radiation is almost always in the high frequency visible (i.e. green, blue and violet) and low to mid ultraviolet part of the electromagnetic spectrum. The mechanism of photocatalytic action is the excitation of a valence orbital electron (after absorption of an electromagnetic photon) from one of its ground state valence orbitals to an empty excited orbital creating a valence shell "hole"/excited electron pair (e.g. TiO_2 (h^+/e^-)) of the Langmuir-Hinshelwood model (Figure 2.43). Thereafter, either the valence "hole" or excited electron then interact with one or more of the reactants and/or solvents to catalyse the photochemical reaction via generating radicals of various selected types; while also regenerating the catalyst back in its ground state form. A general list of the most common semiconductor photocatalysts are: bismuth trioxide (Bi_2O_3), cerium dioxide (CeO_2), ferrous oxide

(Fe₂O₃), tin dioxide (SnO₂), titanium dioxide (TiO₂), tungsten trioxide (WO₃), vanadium pentoxide (V₂O₅), zirconium dioxide (ZrO₂), and zinc oxide (ZnO) for metal oxides; as well as cadmium sulfide (CdS), tungsten disulfide (WS₂), and zinc sulfide (ZnS) for metal sulfides [208].

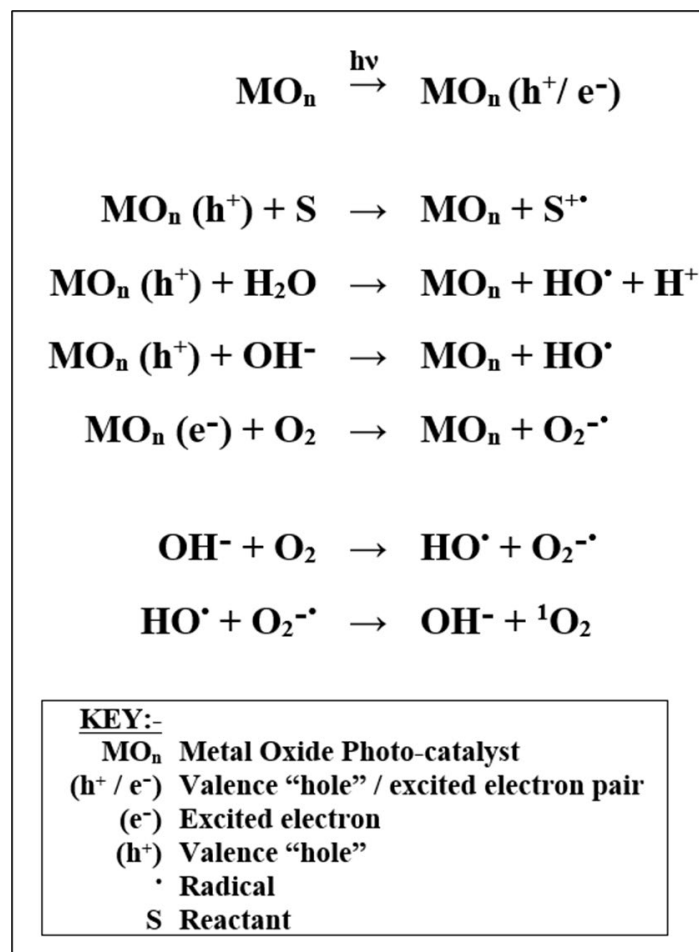


Figure 2.43: Generalized mechanism of photocatalytic action for a hypothetical metal oxide photocatalyst and possible direct and associated reactions (generated by thesis author).

The scientific literature on photocatalysed bleaching appears mostly focused on the treatment and remediation of waste streams; of which there are two general categories: waste water streams and waste/nauseous gas streams; with only a small selection of the literature aimed at the photocatalytic bleaching of pulp. The adequate treatment of waste water streams is an ongoing and serious problem to commercial industry in general due to their detrimental environmental and polluting nature (i.e. poisonous or toxic, carcinogenic, mutagenic, and environmentally persistent), with various industries such as cosmetics, dyeing and tanning, food (farms, wineries and commercial processors), plastic and polymers, pulp and paper, printing and press, pharmaceutical, and textile industries generating large quantities of these difficult to treat waste water streams. Present waste water treatment typically involves physical methods such as adsorption/settling/flotation/etc., biological degradation (aerobic and

anaerobic), chemical treatment/degradation, or any combination of these [209 to 212]. Waste/nauseous gaseous streams and their treatment is also another serious issue to industry given the large volumes generated and the serious impact of these streams as pollutants on air quality, particularly within the immediate area of the industry in question. Treatment methods for gaseous streams are more varied than waste water streams and include methods such as physical absorption and adsorption, various biological treatment options, condensation, chemical reaction and treatment, dust collection, thermal and catalytic incineration, separation by membranes, adjustment of physical properties, and a number of advanced oxidation processes (AOPs); and usually involve a combination of some of these in a sequential processes [213]. The application of photocatalytic semiconductors (with titanium dioxide being among the most common) is a novel and fairly effective method of treating these waste water and gaseous streams.

Dlamini et al. [209] evaluated the treatment of bromophenol blue in a waste water stream using titanium dioxide (TiO_2) chemically modified with fluorination and carbon nanotubes. Generally the use of unmodified pure TiO_2 in any photo treatment has some disadvantages: (a) a rapid recombination rate of electrons (e^-) and holes (h^+) on the catalytic surface lowering catalytic efficiency, and (b) a large band gap (3.2 eV) which excludes use of visible light for photo excitation while utilizing only UV light. Some of the more common means of addressing these include: (a) use of noble metal loading of the semiconductor photocatalyst (though disadvantages include reduced thermal stability while the metal centres can act as recombination centres for fast recombination), (b) anion doping which lowers the band gap of excitation allowing for the more readily use of visible light, and (c) dye sensitization of photocatalysts (though the disadvantages include the toxicity of most dyes and their chemical instability allowing for rapid degradation). The experimental work by Dlamini showed the highest activity was achieved by the fluorinated carbon nano tube titanium dioxide (CNT- TiO_2 -F) catalyst with a 98% bromophenol blue reduction in 20 minutes. Pure TiO_2 gave the lowest activity at 85% reduction in 120 minutes. The carbon nano tube titanium dioxide (CNT- TiO_2) and fluorinated titanium dioxide (TiO_2 -F) gave similar intermediate performance at approx. 94% reduction in 120 minutes. Reactions generally exhibited pseudo first order reaction mechanisms. The mechanisms proposed by Dlamini for these modified catalysts to improve over the unmodified TiO_2 were: (a) the extensive π orbital structure of carbon nano tubes of the CNT- TiO_2 which aided in conducting conductive band electrons away from electron/hole pair on the catalyst surface and so prevented recombination, (b) the fluorination of titanium dioxide in the TiO_2 -F photocatalysts aided the lowering of the band gap allowing for the use of light in the visible part of the spectrum, and (c) the CNT- TiO_2 -F photocatalyst employed a combination of both to achieve the maximum results achieved. Lastly results show the reduction of bromophenol blue is due to total mineralization and not just photobleaching.

Houas et al. [210] evaluated the treatment of methylene blue in a waste water stream using the photocatalysts titanium dioxide. Methylene blue is a commonly used dye in the textile industry, but it is also toxic and environmentally persistent. The experimental results by Houas showed that adsorption of methylene blue to the TiO_2 photocatalyst surface reached a steady state maximum in 1 h regardless of the concentration of the dye. The impact of plain photolysis (no TiO_2 catalyst) was negligible while total disappearance of methylene blue in the TiO_2 photocatalyzed process was completed in 60 minutes at 290 nm and 120 minutes at 340 nm, with complete mineralization achieved in 400 minutes producing carbon dioxide, ammonium, nitrate, and sulfate anions. The process was favoured by alkaline pH values. A complete degradation tree determined by Houas proposed that the dye degradation was initiated by opening of the methylene blue central aromatic ring via direct contact of the methylene blue cation functional group (i.e. $-\text{C}-\text{S}^+=\text{C}$) of the central aromatic ring with negative anion on the TiO_2 photocatalyst surface present under alkaline conditions. Based on the results, most of the reaction steps involved degradation by hydroxyl radicals, but the TiO_2 catalyst "holes" were also involved in degradation of the carboxylic acid groups to carbon dioxide. Houas et al. (2000) stated that the results demonstrated that the dye water stream could be successfully treated by a photocatalytic process. By extension, Houas proposed that the same technique could be used to treat dye water waste streams using visible solar light with titanium dioxide or similar photocatalysts; though this assumption needs proper vetting.

Aliabadi and Sagharigar [211] investigated the removal of rhodamine B, another dye common to the textile industry, from waste water streams also using the photocatalyst titanium dioxide while also evaluating the impact of dye concentration, level of catalyst loading, solution pH, and various UV light sources on the degradation process. Aliabadi and Sagharigar developed kinetic models which focused on reaction rate constants under specifically given conditions. All reactions followed pseudo first order kinetics. The experimental results showed that the degradation of rhodamine B could be increased with: (a) increased initial rhodamine B concentrations up to a maximum concentration of 10 mg.l^{-1} whereafter the reaction plateaued, (b) an increased level of catalyst loading to a maximum of 0.3 g.l^{-1} whereafter higher loadings amounts caused the reaction rate to drop due to increasing suspension opacity, (c) increased pH, and (d) shorter wavelength of the light in the order $\text{UVC} > \text{UVA} > \text{UV LED}$. Part of the UVC success was due to the much higher intensity of the UVC lamp, while the UV LED's better performance was due to much more electrical efficiency (>90% efficiency).

Wilhelm and Stephan [214] investigated the removal of rhodamine B from a waste water stream using titanium dioxide coated silica nanospheres with a light source that simulated solar radiation of equatorial regions at high noon. Although TiO_2 photocatalysts demonstrate promise in treating waste water streams, they have the disadvantage of being difficult to reclaim from a suspension due to the TiO_2 particles being very fine in size which prevents easy sedimentation and necessitates active filtration.

An alternative would be to bind the TiO₂ catalytic particles to a support in the form of an attached film allowing for easy and rapid reclamation. However, the disadvantage of this is the low surface area of the so supported photocatalyst resulting in reduced photocatalytic activity. Wilhelm and Stephan looked to employ TiO₂ particles attached to silica nanospheres (SiO₂@TiO₂) to take advantage of both approaches (i.e. high surface area and ease of reclamation). Wilhelm and Stephan made the silica nanospheres in three sizes: 220 nm, 470 nm, and 590nm. In their experimental results, they observed that the SiO₂@TiO₂ nanospheres showed significantly more activity than the near nil activity of the control without catalyst, with the rate of degradation decreasing with increased particle sphere size. Results showed that hydroxyl radicals were the main agent for dye degradation. These radicals were generated by direct TiO₂ excitation involving UV light, or indirect excitation involve visible light through the rhodamine B radical intermediate. Although the dye was completely removed, complete mineralization thereof did not occur. The total organic carbon content measured showed 20% retention of the full carbon content but no aromatic content. Wilhelm and Stephan proposed the carbon being retained as aldehydes and carboxylic acids.

Epling and Lin [215] evaluated the titanium dioxide photocatalytic degradation of various common commercial dyes (methylene blue, methylene green, dinitro methylene blue, eosin B, rose bengal, FD&C Red 2, D&C Green 5 and 6, FD&C Green 3, FD&C Blue 2, D&C Violet 2, FD&C Red 40, D&C Red 33, D&C Yellow 10, and D&C Green 8) using solar radiation and various simulated solar light sources. Overall, the photocatalytic degradation rates were found to be determined by the different functional groups of different dye families, the light source and the crystalline structure of the TiO₂ catalyst used. The experimental results showed that the impact of light source on the rate of photocatalytic degradation was given by the order: sunlight >> 90 W halogen lamp > 150 W spotlight; with the 150 W spotlight serving the chosen as light source for all subsequent experimental work, (although it was not the best performer). The photocatalytic degradation rate as determined by the crystalline structure of the TiO₂ photocatalyst was given by the order:-: anatase > amorphous > rutile. This order was consistent with the published literature. The photocatalytic degradation rate of the dye families was given by the order: indigo = phenanthrene > tri-phenylmethane > azo = quinoline > xanthene = thiazine > anthraquinone; with dyes containing electron withdrawing groups showing a slow rate of reaction and anionic dyes breaking down more quickly than cationic dyes in general. The photochemical mechanism proposed by Epling and Lin for the degradation of the various dyes followed three pathways: firstly, the photocatalytic oxidation of the dyes by hydroxyl radicals formed from the reaction of the “hole” (h⁺) component of the hole/electron pair on the excited TiO₂ photocatalyst’s surface with water; secondly, photocatalytic reduction where the visible light excited dyes transferred an electron to the TiO₂ catalyst’s conductive band generating super oxide radicals from selected oxygen species, and, thirdly, (exclusive to rose bengal) where visible light excited rose bengal to generate a

hole (h^+) on the TiO_2 catalyst's surface by abstracting an electron from the photocatalyst's valence band which in turn generated hydroxyl radicals from water.

Macedo et al. [216] evaluated the photocatalyzed electrolysis of dyes in the leather and tanning industry utilizing TiO_2 photocatalysts on supported indium tin oxide (ITO) glass. The leather and tanning industrial produces considerable quantities of waste water contaminated with various dyes and tanning colourants, which are toxic to life (as well as many of their breakdown products) and are also known to disrupt photosynthetic processes in natural bodies of water. Despite considerable industrial remediation efforts, significant quantities of these contaminants often still find their way into the water system creating considerable further environmental and remediation challenges. Macedo et al. have indicated that the photoelectrocatalysis of these streams holds promise to help resolve these issues. Macedo et al. employed TiO_2 /ITO as the working electrode in combination with a platinum sheet as the alternative electrode, 0.1 M potassium chloride as the electrolyte, and a ultraviolet/Visible mercury vapour lamp as the radiation source. In their experimental work, Macedo et al. (2006) tested and optimized the impact of solution pH, applied electrical potential, initial dye concentration, and temperature as operational parameters. The pH, applied potential and temperature were found to strongly impact the degradation performance of the photoelectrocatalysis with the optimal conditions being 0.2 V at pH 3.35 and 0.8V at pH 6.14 for the UV/ TiO_2 /ITO/KCl system. Degradation was also found to increase with temperature as mobility and intermolecular collisions of the dye molecules in solution increased. Overall, the UV/ TiO_2 /ITO/KCl system was shown to perform adequately for the mineralization and discolouration of a leather waste water stream with reductions of approximately 90% based on FT Raman and FTIR analysis.

Nakashima et al. [212] studied the photocatalytic degradation of dilute solutions of the estrogen species: 17 β -estradiol and estrone by titanium dioxide immobilized on polytetrafluoroethylene (PTFE) mesh sheets employing a reciprocating mode of motion for mixing/movement of the estrogen containing solution. Estrogens are a common pollutant in most released water streams, but tend to concentrate in the discharge streams of large sewage treatment plants. Estrogens are extremely difficult to treat and remove from waste streams, and given their endocrinal disruptive action are a concern at elevated levels. Experimental results by Nakashima et al. showed some degradation of both estrogens without irradiation in the PTFE mesh sheet reciprocating reactor, but ultraviolet irradiation significantly enhanced the degradation of the two estrogen species. The photocatalyzed degradation increased with the reciprocating rate and temperature. In addition, a waste water stream sampled from the Kitano sewage plant in Japan showed photocatalytic degradation of up to 90% in 4 minutes of the estrogen species in the ultraviolet reciprocating reactor system. Nakashima et al. (2003) proposed that photocatalytic degradation had been shown to be a viable and practical method for removal of estrogens from waste water streams, particularly with the reciprocating TiO_2 PTFE mesh sheet reactor design.

Machado et al. [217] investigated the treatment of a lignosulfonate lignin model compound (LMC) as well as waste effluent from a pulp and paper mill by photocatalytic (i.e. TiO_2) and photosensitization means. The mill effluent used in this study was from a mill employing an elemental chlorine-free bleaching sequence (-O-Z-D₀-E-P-) while the lignosulfonate LMC was obtained as a complex salt. In general, waste mill effluents contain various larger lignin fragments (many of which are sulfonated), various cationic and anionic trash salts, as well as chlorinated and oxidized smaller lignin fragments. Given the complex nature and multiple sources that make up mill effluents, the adequate treatment thereof is complex and particularly challenging for any mill. Experimental work from Machado et al. on the lignosulfonate composite was used to validate the photocatalytic degradation of mill lignin using TiO_2 as a photocatalyst. In the experimental work on the mill effluent, Machado showed that the photocatalytic degradation of the mill effluent content using a UVA light source was consistent with a process that appeared to strongly resemble TiO_2 degradation of phenol and related type structures. The photocatalytic degradation of the mill effluent gave an increasing chloride anion effluent concentration with a maximum reached at 40 minutes. This indicated that complete mineralization of the chloro organic components had taken place. Overall, temperature was found to not impact the photocatalytic degradative process; but pH, various additives (i.e. HPO_4^- phosphates as well as hydrogen peroxide) and catalysts morphology was shown to have a large impact on photocatalytic activity rates. The photocatalytic activity increased greatly above pH 4. This is likely due to the pH at the point of zero change (pH_{ZPC}) for TiO_2 ranging from 4.3 (P25 TiO_2) to 6.7 (anatase). Under these conditions the TiO_2 retained a localized "acidic" character which favoured reaction with alkali effluent organic components. All reactions took place at the catalyst liquid interface as typical of the Langmuir Hinshelwood model. In the addition of additives, the mono hydrogen phosphate (HPO_4^-) did not give a significant increase in activity, while peroxide increased activity by 173.5% for P25 and 354% for anatase. This was supported by total organic carbon (TOC) measurements which gave an 80% reduction in 60 minutes. The better photocatalytic activity of the P25 TiO_2 catalyst as opposed to that of anatase was likely due to its larger surface area of the P25 catalyst. Use of a TiO_2 photocatalyst together with zinc phthalocyanine (photosensitizer) gave positive results, the findings of which will be discussed in more detail later on in this chapter section of photocatalysts and photosensitizers (section 2.4.3.7.). In further work, Machado et al. used a compound parabolic collector for sunlight that allowed for the successful treatment and mineralization of a large quantity of the lignosulfonate LMC with TOC reaching zero in 150 minutes.

Raja et al. [218] investigated the TiO_2 photocatalysed degradation 3-methoxy-4-hydroxyphenyl methyl carbinol (3M-4HC) utilizing a medium pressure mercury vapour lamp. The aim of the study was to use 3M-4HC as a lignin molecular model (LMC) in the study of the TiO_2 semiconductor photocatalytic degradation of lignin with the view to determine the possible roles of singlet oxygen, as well as hydroxyl

and superoxide radicals in the photo degradative mechanism of dissolved lignin. In their experimental work, Raja et al. observed that the TiO₂ photocatalysed ultraviolet irradiation option (i.e. UV/TiO₂), in which all oxygen was purged with argon; showed clear evidence of the involvement of the hydroxyl radicals generated from the "holes" in the photoactivated TiO₂ surface. Complete removal of 3M-4HC based on high performance liquid chromatography (HPLC) analysis was achieved in 40 minutes utilizing the P25 Aeroxide Degussa TiO₂ as a photocatalyst, while 60 minutes was required when using the more conventional P25 Degussa TiO₂; with total mineralization of the 3M-4HC being achieved in 120 and 180 minutes respectively. Experimental work using the TiO₂ photocatalysed ultraviolet irradiation option with air or oxygen present (i.e. UV/TiO₂/air or oxygen) showed the involvement of superoxide radicals and singlet oxygen in the degradation of the lignin, with the process being strongly pH dependent (pH 3.0 favouring superoxide radicals and pH 6.0 favouring singlet oxygen generated from the superoxide radicals). Furthermore, in Raja et al.'s experiments the involvement of the three active species was confirmed by application of a hydroxyl scavengers (methanol and t-butanol), a superoxide scavenger (benzoquinone) and a singlet oxygen scavenger (sodium azide). Raja et al. (2004) proposed that the addition of hydrogen peroxide accelerated the UV/TiO₂/air degradation rate by scavenging valence shell electrons on the surface of the photo excited TiO₂ photocatalyst. The fact that the complete mineralization of 3M-4HC took much longer than LMC degradation suggested that long lived photo degradative intermediates were formed during the photo degradative process. In regards to kinetic studies of the process, the decomposition of 3M-4HC appeared to follow diffusion-controlled pseudo-first order kinetics, with the rate of reaction increasing with luminant intensity. In their characterization of the photocatalysts, Raja et al. found that the activity of TiO₂ catalysts was determined by (i) the ratio of anatase to rutile composition, (ii) the BET surface area, (iii) the crystalline structure, and (iv) the crystal radius. The P25 Degussa and P25 Aeroxide Degussa TiO₂ photocatalysts gave the highest reaction rate due to their larger surface area and elevated anatase : rutile proportion; with some rutile level still required to achieve these high reaction rates. The TiO₂ photocatalyst composed of mostly rutile TiO₂ gave very low reaction rates.

Cantau et al. [219] compiled a lengthy summary around the photocatalytic and photosensitized treatment of gaseous waste streams containing naseuous reduced sulfur compounds. The first half of their summary involved a review of work done by others on the treatment of reduced sulfur compounds utilizing photocatalysts. The second half of the summary reviewed their more recent work around the treatment of reduced sulfur compounds using various photosensitizers. Reduced sulfur compounds (where 'elemental' sulfur is present as a sulfide rather than sulfates, suphites, etc.) such as methanethiol (CH₃-SH or MSH), dimethylsulfide (CH₃-S-CH₃ or DMS), and dimethyldisulfide (CH₃-S-S-CH₃ or DMDS), etc., are aerial pollutants produced by a vast number of industrial processes in large quantities (including the pulp and paper industry) and offer serious challenges in their removal/processing given their strong smelling influences even at very low concentration in the environment. Cantau et al.'s

review of the photocatalytic literature on gaseous streams showed that, in general, the photocatalytic degradation of gaseous reduced sulfur compounds has broadly been investigated with both flow through and batch reactor systems, in which TiO_2 (in a variety of forms) served as the most common photocatalyst. With regards to mercaptans (thiols), their degradation has been investigated by catalytic oxidation, adsorption–oxidation on activated carbons, catalytic incineration, and also some alternative biological processes. Cantau et al. observed that Li studied the TiO_2 photocatalytic degradation of MSD in a batch reactor using cation and anion modified TiO_2 (P25). Li found that NH_4^+ doped TiO_2 had better photocatalytic activity than the pure P25 TiO_2 alone, while the SO_4^{2-} doped TiO_2 was the least active of all three. Li concluded that the NH_4^+ modified TiO_2 gave better TiO_2 reactivity due to its basic properties and enhanced specific surface area. Catalytic activity was affected by catalytic loading and relative humidity (RH) and followed pseudo-first order kinetics. Cantau et al. also observed that Kato studied the TiO_2 photocatalytic degradation of H_2S and MSH in a flow through reactor using silver metal deposition doped TiO_2 . The silver deposited TiO_2 significantly enhanced the degradation of both H_2S and MSH. For photocatalytic degradation of H_2S with pure TiO_2 , Cantau et al. observed that Canela demonstrated the need for oxygen to be present; while Kataoka et al showed that H_2S was oxidized to SO_4^{2-} without intermediates. Peral showed that the degradation of DMS was strongly influenced by the deactivation of the TiO_2 catalyst for a flow through reactor. Cantau et al. noted that Demeestere attempted to utilize visible light as opposed to ultraviolet light for DMS photocatalytic degradation by doping TiO_2 with anions. Demeestere investigated S doped TiO_2 ; prepared by a sol-gel (SG) method and simple physical mixing (PM); and found that the S- TiO_2 (PM) catalyst gave the highest photocatalytic activity. In addition, Canela also investigated the photocatalytic degradation of DMS and DSMS with $\text{SiO}_2/\text{TiO}_2$ catalysts. The DMS was completely degraded, while the DSMS was only 50% degraded. Overall, Cantau concluded that the optimal operational conditions (i.e. RH, residence time, inlet pollutant concentration, photocatalyst load/charge) for the photocatalytic degradation of reduced sulfur compounds with TiO_2 was strongly dependent of the reactor/experimental design of the research group involved and each photocatalytic reactor system needed be individually optimized. In addition, based on these individually optimal reactor performances, considerable variation in the intermediate and final products was observed for each research group. These final products included sulfoxides, sulfones, disulfides, aldehydes, CO_2 and SO_2 ; with sulfates and carboxylates adsorbed on the TiO_2 catalysts surfaces which served as poisons to these catalysts. The main disadvantage of TiO_2 observed overall, was its tendency to be deactivated by the surface poisons. Modification of the TiO_2 catalysts with metal doping and hetero atom doping (e.g. nitrogen, carbon and sulfur) often did improve their catalytic performance by either a greater kinetic rate or the shift to visible light activation rather than UV activation, but no clear conclusive way forward was shown. The more recent experimental work on photosensitized treatment of gaseous waste streams by Cantau et al. will also be discussed in more detail in this chapter section below on photosensitizers (section 2.4.3.7.).

Castellan et al. [220] and Perez et al. [221] all achieved beneficial use from the application of photocatalysts in the bleaching of pulp using mercury vapour lamps. Their findings are discussed in greater length in section 2.5.2. later in this chapter. In addition, Jamalia et al. [222] also obtained good results for the photocatalytic degradation of phenol using an ultraviolet light emitting diode (UV LED). Their findings are also discussed in more detail in section 2.5.5. in this chapter.

In the literature search for this thesis, the author found only a single article that covered the photo treatment and remediation of waste water streams, but without any form of photocatalyst or photosensitizer. In their study, Mokrini et al. [223] compared the ultraviolet photo degradation of phenol and benzoic acid against the more conventional advanced oxidation processes (AOPs) which utilized ozone and hydrogen peroxide. In general, aromatics are known for their high toxicity and low biodegradability in the water streams they contaminate. Given that they are often generated in significant quantities in industrial processes, this causes serious challenges in the aspect of treatment and remediation of waste and other contaminated water streams. In their study, Morkrini et al. used phenol and benzoic acid as their aromatic model molecules for their experimental work in which no photocatalyst or photosensitizer were employed with a low pressure mercury vapour lamp utilized as their UV radiant source. Mokrini et al. evaluated the operational parameters and conditions of the three degradative methods and found that pH had a strong impact with optimal conditions varying depending on the process employed. Acid pH values (pH 3 – 7) were favoured in the use of ozone for direct attack of the aromatic molecules via the process of ozonolysis which is favoured under acid conditions. Neutral and alkaline pH values (pH 7 and pH 9 – 12) were favoured by the UV photo degradative and peroxide methods, as generation and stabilization of hydroxyl radicals employed by both were favoured in alkaline conditions. The combination of two (O_3/H_2O_2) or all three methods ($O_3/UV/H_2O_2$) gave the speediest degradation results as compared to single methods as degradative contributions were made by the radicals and active reagents of both or all three.

As with photocatalysts, the topic of photosensitizers covers a very large field of study in chemistry; and includes both organic and inorganic materials many of which can also be classified as photocatalysts as well. In regards to studies involving the photochemical bleaching of pulp or the photo degradation of LMCs, photosensitizers can be narrowly defined as organic molecules (many being dyes). Some of these more common pulp and paper related photosensitizers include: methylene blue, rhodamine B and rose bengal. Generally, photosensitizers can be divided into two types: firstly, Type 1, in which the photosensitizer interacts with the reactant directly without generating an intermediary singlet oxygen species, and, secondly, Type 2 where the photosensitizer interacts with ground state triplet oxygen to generate singlet oxygen which then interacts with the reactant (Figure 2.44) [224]. In both cases, the organic photosensitizer; after being excited to an excited singlet state; undergoes inter system crossing to a slightly less energetic excited triplet state before interacting with the reactant (Type 1) or triplet

oxygen (Type 2). In Type 1, the final step down of the photosensitizer back to its ground state is via interaction with a ground state final recipient – almost always triplet oxygen, while in Type 2 this step down is usually via interaction with the triplet ground state oxygen (exciting it to an intermediary singlet oxygen species) which then reacts with the reactant as a final step.

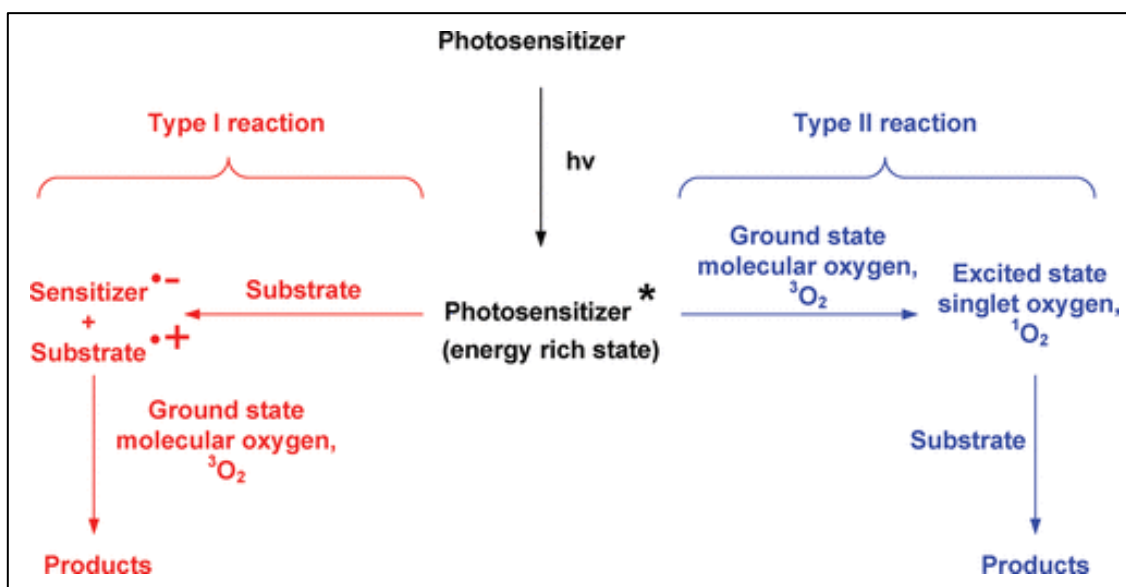


Figure 2.44: The two general types of photosensitizer action during irradiation [224].

Similar to photocatalysis, the majority of literature on photosensitizer bleaching focuses on the treatment and remediation of waste streams, specifically waste water streams and waste gas streams. The sources of these waste streams and the enormity of the challenge of dealing with the problem they present was discussed earlier in the section on photocatalysts (section 2.4.3.7.) and are the waste streams from the same industries. The amount of literature on the photosensitized bleaching of pulp is small (as observed with the photocatalysed bleaching of pulp). For photosensitizers, the aim is generally to facilitate photochemical reactions (usually involving inter system crossings with singlet and triplet electronic states) employing the visible light part of the spectrum rather than ultraviolet light; and often also involve the presence and actions of photocatalysts as part of that process.

As stated prior in this thesis, Machado et al. [217] studied the photocatalytic (TiO₂) and photosensitized treatment of a lignosulfonate model compound composite as well as pulp and paper mill effluent with reasonable success. The photocatalytic degradation of both lignin sources was successful using the TiO₂ catalyst. In regards to the photosensitization experimental work in this study, the combined use of the photocatalyst TiO₂ with the photosensitizer zinc phthalocyanine gave a small increase (6%) in reaction efficiency. The mechanism proposed by Machado et al. involved photo excitation of the photosensitizer (zinc phthalocyanine) with the light source which in turn excited the TiO₂ photocatalyst leading to the generation of radicals which then broke down the contents of the mill effluent. However,

the lower than expected increased activity for the photocatalyst/photosensitizer combination in this set of experiments was due to the lamp emission emitting at 660 nm (Q-band) versus the 360 nm band (Soret band) which is preferred by the photosensitizer. Regardless, using the photosensitizer to activate the photocatalysts at the correct wave length looks promising.

As stated prior also in this thesis, Cantau et al. [219] have compiled a lengthy summary around the photocatalytic and photosensitized treatment of gaseous waste streams containing reduced sulfur compounds. Literature reviewed by Cantau et al. also showed that photosensitizers had been employed with reasonable success to photochemically degrade reduced sulfur compounds in liquid solution (i.e. liquid water). The advantage of photosensitizers over photocatalysts is that they are activated by visible light (allowing for possible use of sunlight instead of a powered lamp) as opposed to ultraviolet light for photocatalysts (which require an active power supply). The photosensitizers commonly used in the research and literature Cantau et al. (2007) reviewed were: phthalocyanines, 9,10-dicyanoanthracene and benzophenone. As part of the experimental work undertaken in association with the literature review by Cantau et al., three photocatalysts/photosensitizers were generated and tested, but on gaseous waste streams. These included: titania on quartz ($\text{TiO}_2\text{-QZ}$) which served as a control photocatalyst using ultraviolet light, dicyanoanthracene incorporated in a sol-gel silica matrix (DCA-SG) as a novel supported photosensitizer, and an anthraquinone moiety covalently attached to silica beads (ANT-SB) as another novel supported photosensitizer. The two photosensitizers are aromatic based materials. The two photosensitizers tested (DCA-SG and ANT-SB) were shown to be efficient for the degradation of MDS and DSMS via an oxidative process taking place within a flow through reactor, along the gas solid support matrix interface. These supported photosensitizers have a few advantages over more traditional TiO_2 photocatalysts: firstly, they are transparent and do not attenuate the light passing through them, secondly, they are excited by visible light as opposed to ultraviolet light (allowing for solar applications), thirdly, they are generally stable, and fourthly, they operate with ease within a flow through gas phase reactor. The two photosensitizers operated via a different mechanism than the TiO_2 catalysts ($\text{TiO}_2\text{-QZ}$) in which the photosensitizers are involved in partial oxidation of the reduced-sulfur compounds utilizing singlet oxygen giving partial oxidation products that adhere to the silica matrix and photosensitizer strongly; a process that avoided complete mineralization of the starting reduced sulfur compounds. This was opposed to TiO_2 photocatalysts in general which tended to generate hydroxyl radicals via the Langmuir-Hinshelwood hole (h^+)/electron (e^-) mechanism which then completely mineralized the reduced sulfur compounds. However, in Cantau et al.'s study, the $\text{TiO}_2\text{-QZ}$ did not achieve completed mineralization of DMS and no DSMS mineralization at all under the conditions employed (low catalyst loading, absence of water, high GHSV) with a number of by products identified in both cases. The products suggested electron transfer from DMS and DSMS to the TiO_2 hole generated photocatalytically followed by a subsequent radical mechanism. For the silica attached

photosensitizers regeneration to full activity was easily achieved via desorption using polar solvents. This allowed for complete decontamination of such sensitizers.

Machado et al. [220] and Castellan et al. [225] all achieve success in using photosensitizers in the bleaching of pulp. Their findings are discussed in greater length in section 2.5.2. on mercury vapour lamps.

2.5 *Photochemical bleaching of wood and available light sources*

There are a variety natural and artificial light sources that emit radiation in the visible and ultraviolet portion of the electromagnetic spectrum (i.e. about 200 nm to 700 nm) which can be possibly employed for photochemistry in general. These same sources can also be used as illumination sources for the photobleaching of pulp as well as the photodegradation of LMCs by using the appropriate apparatus/reactor designs. These possible radiant sources can be listed as follows:

- Solar (exposure to sunlight or solar light simulators),
- Low, medium and high pressure mercury vapour lamps (i.e. dark light lamps),
- Lasers (various types),
- Micro-wave discharge electrodeless lamps (MDELs), and
- Light emitting diodes (LEDs) and LED arrays.

Each source has its own distinct advantages and disadvantages. A summarized review of each source and the associated work therewith is necessary at this point.

2.5.1 *Solar bleaching*

The advantages of solar radiation as a light source is that it is abundant, available at most external locations, limitless and completely free. The disadvantages are that it is uncontrollable, not as intense as many commercial sources, not available all the time (i.e. unavailable at night, early morning, late afternoon and in bad weather), has variable intensity depending on the time of day, and is available only outdoors. In addition, solar radiation is also a very “dirty” light source with its emission spectrum covering a near continuum from the infrared, through the entire visible spectrum into the ultraviolet and far ultraviolet (Figure 2.45) [226]. In addition, its intensity at given narrow band widths is variable as the wavelength changes across the spectrum’s range. These properties makes its application difficult and more favoured for selective use.

A review of the published scientific literature suggests that the majority of the work on solar bleaching and simulated solar bleaching appears to be focused on remediation of wastewater streams with a particular emphasis on photo-Fenton advanced oxidation processes (AOPs) or similar types of AOPs.

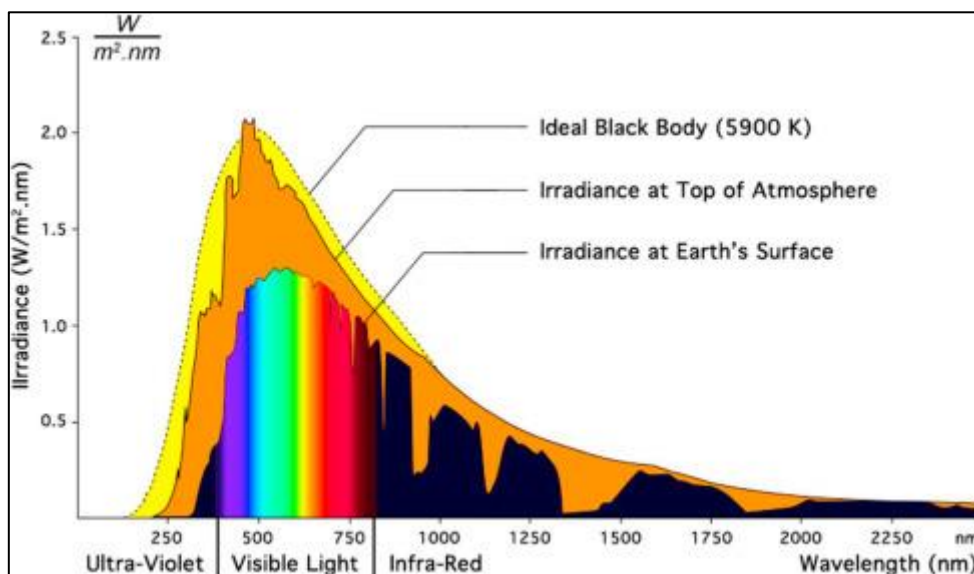


Figure 2.45: Solar radiation with irradiance intensities at various wavelengths [226].

Amat et al. [227] investigated the solar photocatalytic treatment of a paper mill wastewater effluent stream, as well as simulants thereof, utilizing both a photo-Fenton reagent/catalyst and a TiO_2 semiconductor photocatalyst. For irradiation, a xenon lamp (to simulate sunlight) and actual solar light were employed in all experiments on a benchtop-scale which were undertaken in open glass cylindrical reactors. For bulked up/pilot scale experiments, all experimental work was undertaken in a modified solar plant waste detoxification apparatus with all bulked up experimental work undertaken on actual paper mill wastewater effluent with sunlight as the light source. In their benchtop experimental design, Amat et al. investigated the following compounds representing certain effluent components: (i) *p*-toluene sulfonic acid to represent sulfonated pollutants, (ii) eugenol and guaiacol to represent degraded lignin, and (iii) a sodium acetate/sodium butyrate/D glucose mix to represent volatile fatty acids and saccharides coming from degraded starch. The results obtained showed a 47% reduction for the photo-Fenton reaction and 27% reduction for the TiO_2 photocatalyst for *p*-toluene sulfonic acid after 6 h, complete degradation of both lignin model compounds with reaction rates for the eugenol being larger than for the guaiacol, and only a 20% reduction for the degraded starch simulant for both photo-processes. On the bulked up scale, both the photo-Fenton and TiO_2 photocatalyst showed a significant reduction in the pollutant load for actual mill effluent.

Sarmet et al. [228] compared the degradation of 4-chloroguaiacol (4-CG) by a dark Fenton process as opposed to a solar photo-Fenton AOP utilizing hydrogen peroxide as an oxidant; while 4-CG was selected to serve as a simulant of a bleached mill effluent wastewater stream. In general, the Fenton process; whether dark or solar/photo; employs ferrous/ferric ions as a catalytic reagent to facilitate the

degradation of organic contaminants in aqueous solutions via hydroxyl radicals generated from the hydrogen peroxide. They noted that both the dark and solar photo-Fenton processes achieved reasonable degradation of the 4-CG with the solar photo-Fenton process having a significantly higher initial reaction rate. Evaluation of operational parameters showed that the rate of reaction also increased with: (i) increased $\text{H}_2\text{O}_2 : \text{Fe}^{3+}$ ratio, (ii) increased ferric ion concentration, (iii) increasing pH from pH of 2 to pH of 6, and (iv) increased temperatures up to 25 °C (whereafter no further increase was observed). Overall, Sarmet et al. proposed that the solar photo-Fenton AOP using sunlight was the most efficient of the two processes evaluated in this study.

Arslan-Alaton and Ferry [229] investigated the $\text{SiW}_{12}\text{O}_{40}^{4-}$ polyoxometalate ultraviolet/visible photocatalyzed degradation of the azo dye, acid orange 7 (AO7), utilizing a xenon lamp as a simulated solar light source. In general, the treatment and remediation of wastewater streams contaminated with dyes is a serious problem for the dyeing and textile industry given the toxic and non-biodegradable nature of almost all of these dyes, with azo dyes making up to about 15% of those used in the commercial textile industry. Arslan-Alaton and Ferry observed in their experimental work that $\text{SiW}_{12}\text{O}_{40}^{4-}$ polyoxometalate could successfully degrade the acid orange 7 azo dye completely in a few minutes provided that isopropanol was provided as a sacrificial electron donor to regenerate the $\text{SiW}_{12}\text{O}_{40}^{4-}$ polyoxometalate photocatalyst. The presence of oxygen was observed to reduce the efficiency of the photodegradative process serving as a competitor to the azo dye for the polyoxometalate catalyst. This was shown by the improved performance when the solution was deaerated with nitrogen gas. They proposed that the $\text{SiW}_{12}\text{O}_{40}^{4-}$ polyoxometalate photocatalyst could serve as an alternative to the more common TiO_2 photocatalyst given its similar ease of removal being a heterogeneous solid catalyst.

Fernandez et al. [230] evaluated the dark Fenton and photo-Fenton type bleaching of the azo dye Orange II utilizing Co^{2+} cations as initiators/catalysts together with potassium peroxymonosulfate (oxone) as an oxidant under irradiation by a xenon lamp to simulate solar light. Their experimental work showed that both the dark and photo-Fenton reactions displayed bleaching and mineralization of the Orange II azo dye, but that the photo-Fenton process was significantly faster. Typically photobleaching was observed to occur within about 15 seconds for these experiments. Fernandez et al. proposed that the photobleaching process generated peroxy containing Orange II radicals which aided the degradation of the azo dye giving the observed faster rate of degradation. The photo-Fenton type reaction trends suggested a branched chain radical mechanism. They also found that the reaction followed first-order reaction kinetics with regards to the cobalt concentration, but zero-order decay kinetics with regards to the Orange II dye. Results showed that the concentration of Co^{2+} required was 100 times less than the oxone concentration to achieve full mineralization of the Orange II dye. The presence of atmospheric oxygen in the reaction was found to facilitate the degradation process. Full mineralization and Total Organic Carbon (TOC) reduction was achievable under optimal conditions in about 70 minutes.

Mosteo et al. [231] investigated the photo-Fenton treatment of winery wastewater utilizing a sun chamber to simulate solar light together with hydrogen peroxide as an oxidant and diluted wine or grape juice as the winery waste stream simulant. They employed a two level factorial design to minimize the number of required experiments which evaluated the impact of: (i) hydrogen peroxide concentration, (ii) iron concentration (supplied as an iron rich clay), (iii) reaction time, and (iv) concentration of organic matter on the photo-Fenton process performance. The experimental results obtained indicated that the photo-Fenton treatment could achieve a maximum of 55% degradation on the waste streams. Results also indicated that level of organic matter removal was not impacted by either initial organic or clay concentration. Finally, Mosteo et al. were also able to develop a model that could successfully predict the best operational conditions for the desired parameters, organic concentrations, and required levels of degradation chosen.

As has already been discussed in Section 2.4.3.7., Machado et al. [217] employed sunlight (solar radiation) together with a compound parabolic collector to mineralize a large quantity of a solution of dissolved lignosulfonates using sunlight as their light source.

The main points that can be drawn from the review of the solar bleaching literature that are relevant to this study are: (i) Given that the light source is outdoors and outside of the control of the experimenter, care must be used in selecting the appropriate time of year and clear weather beforehand to ensure maximum solar radiation for the experiment. (ii) An appropriate location, and the correct type of glassware and container must be chosen for the experiment, also to maximize solar irradiation. (iii) Semiconductor photocatalysts may be used, but the extent of their benefit is unknown given that most solar radiation is in the visible part of the spectrum. (iv) The use of photosensitizers in conjunction with photocatalysts to promote photocatalyst excitation by visible light is proposed. (v) Solar radiation is low in intensity compared with most artificial sources, hence, prolonged periods of exposure are required to obtain any significant effect. Thus, sufficient time must be employed for solar experiments. (vi) It is necessary to evaluate various oxidants for the experimental work. This is valid for all light sources.

2.5.2 Low, medium and high pressure mercury vapour lamps (dark light lamps)

The general principle of operation for these “dark” lamps/mercury vapour lamps is that an electric discharge/electric arc is passed between two separated electrodes; through a near vacuum, a moderate pressure (1 bar) or high pressure (10 bars) mercury vapour for low, medium and high pressure lamps respectively. The electric discharge excites the mercury atoms in the vapour which then release blue/ultraviolet light as they return to their ground state. The advantages of low, medium and high pressure mercury lamps are that, unlike solar radiation, they are available all the time provided there is

an electrical power source. In addition, they can be used in any selected location (not being restrict to outdoors use only like solar radiation) and can be manipulated to fit any reasonable reactor design. They also have the advantage of being able to generate a narrow selected wavelength of light when low and medium pressure lamps are employed, or a board continuum of frequencies when high pressure lamps are employed. Furthermore, the addition of metal halide dopants to medium pressure lamps allows the narrow wavelength of irradiation to be manipulated/modified to specific bands. Medium and high pressure lamps are also very intense light sources. The disadvantages are that they are not very efficient light sources (10% to 20% conversion efficiency) generating considerable waste heat, particularly for high pressure lamps. This significant heat generation necessitates active cooling via an air fan or water jackets to keep the lamps functional and ensure a reasonable life span. Such cooling also has its own associated difficulties. Lastly, they require an external power source and do not operate for free.

As indicated prior, the majority of the literature on photobleaching appears to be focused on the treatment and remediation of waste streams (gaseous and water), and involves photocatalysts and photosensitizers in almost all cases. This treatment and remediation has been covered in Section 2.4.3.7. However, in more than half of these remediation treatments , the chosen source of light was a low, medium or high pressure mercury vapour lamp. Another type of lamp that makes up a large portion of the literature on treatment and remediation of waste streams is the microwave discharge electrodeless lamp (MDEL) which will be discussed in Section 2.5.4. of this chapter. As regards the photobleaching of pulps, which makes up only a small portion of the literature, the chosen light sources are mercury vapour lamps employing batch reactor designs in most cases.

Marcoccia [232], as part of his postgraduate thesis, investigated the photochemical delignification of softwood in the presence of molecular oxygen as an oxidizer. Marcoccia studied the impact of pH, temperature, consistency, lignin content/concentration, partial pressure of oxygen, and chemical modification to the pulp. He also studied the impact of the photo-enhanced oxygen delignification process on the properties of the bleaching filtrates obtained and their dissolved organic and inorganic contents. Lastly, Marcoccia also briefly evaluated the impact of including a photo-enhanced oxygen delignification stage into the full bleaching sequence: -UV/O-E-D-E-D- as opposed to a conventional -C-E-D-E-D- sequence (see Table 2.1 for a description of bleaching stage abbreviations). The thesis results demonstrated that irradiation of pulp with a high pressure mercury lamp (visible/ultraviolet light source) in the presence of oxygen at low consistency and room temperature was successful in achieving a significant level of delignification, while reactions without light achieved about 5 to 10% delignification. At the extremity of conditions and irradiation time, levels of delignification of up to 85% could be achieved. Thus, he showed that the photo-enhanced oxygen delignification process was viable. However, besides delignification being achieved by the photo-enhanced oxygen delignification

process, degradation of the pulp cellulose also occurred during irradiation. When compared to a conventional high pressure oxygen bleaching process at elevated temperature, the photo-enhanced oxygen delignification process gave a similar level of performance showing similar or better selectivity than the conventional process. Both the delignification and cellulose degradation appeared to follow pseudo-first-order rate kinetics. As regards the specific operational conditions and parameters Marcoccia evaluated, the rate of delignification and cellulose degradation was found to increase significantly at acidic and alkaline pH values, where the concentrations of hydronium and hydroxide ions were greatly increased. Marcoccia proposed that the photo-delignification process was both acid- and alkali-catalysed. However, the improved delignification under acidic conditions required the application of a hot alkali extraction stage after each acidic photo-enhanced oxygen delignification stage to achieve the improved delignification. The extraction was necessary to remove the degraded lignin from the pulp which was not solubilized under acidic conditions. The optimal pH conditions were mild acidic conditions (pH ranging from 2 to 4) and strongly alkaline conditions (pH above 12). The impact of temperature was observed to be usually small, while the rate of delignification and cellulose degradation showed an interactive behaviour between the temperature and the pH. This interaction was illustrated by the fact that for acidic conditions, the rate of delignification was unaffected by temperature, but cellulose degradation increased; while for alkaline conditions, both the rate of delignification and cellulose degradation increased with the delignification rate being strongly affected by the temperature. However, temperature did not appear to change the proportional selectivity of the one over the other as the temperature changed. The delignification rate was found to decrease with increased pulp consistency, while the rate of reaction was not impacted with oxygen partial pressures above 0.2 bars. Furthermore, some oxygen needed to be present in solution for any delignification to occur at all. This was demonstrated when the photo-enhanced delignification process was purged with nitrogen to remove any oxygen present. The effect with nitrogen purging was more significant under acidic than alkaline conditions. Adequate constant mixing of the pulp suspension was also necessary for proper photo-enhanced oxygen delignification to take place. Contrary to expectations, Marcoccia found that methylation and reduction (borohydride) of the starting pulp did not impact the delignification performance of the pulp. The photo-enhanced pulp gave similar pulp yields to pulp that was conventionally delignified/bleached to a similar extent. The kinetic rate constants for delignification and cellulose degradation both decreased with increased lignin concentration (as the lignin concentration increased with consistency and kappa number). However, when any variation in the starting kappa number was discounted for, the pulp always followed a similar delignification profile regardless of the starting kappa number with a pseudo-first-order appearance. The rising dissolved lignin concentration in solution resulted in an auto-inhibition of the photo-enhanced oxygen delignification process where the increasing dissolved lignin content gave an ever increasing inhibition of the process due to the increasing attenuation of the radiated light onto the pulp fibres. The photo-enhanced pulps did not significantly change in their cellulosic material make-up, retaining the same

proportional levels of their alpha, beta and gamma cellulose content as their starting unbleached pulp while also remaining similar to those levels in conventionally bleached pulps. However, the crystallinity of all the pulps increased with bleaching due to the removal of lignin which is amorphous in nature. He also developed a kinetic model based on the auto-inhibition, photon limited delignification process in which the dissolved lignin inhibits delignification due to the attenuation of the radiant light source. According to the model, the rate of delignification is zero-order with respect to the lignin in the pulp, and first-order in the amount of radiant power absorbed by lignin. Analysis of the bleach filtrates showed that not only lignin, but also cellulosic material was removed from the photo-enhanced oxygen delignified pulps. Chemical analysis of the lignin make-up in the bleach filtrates showed that it retained its aromaticity, which included aromatic aldehydes, carboxylic acids, alcohols, and ketones. The UV absorption spectra of the bleach filtrates were similar to those reported for isolated lignins, both on a qualitative and quantitative level. When compared to a the conventional chlorine based sequence (-C-E-D-E-D-), the photo-enhanced oxygen delignification sequence (-UV/O-E-D-E-D-) showed a similar level of bleaching performance (although its brightness was slightly lower) with comparable pulp strength. Specifically, the photo-enhanced sequence gave slightly lower tensile and burst values, but slightly higher tear values than the conventional sequence. A comparison of the relationships for tensile versus tear strengths showed that the pulp for the photo-enhanced sequence was only slightly weaker than the conventional sequence. This was expected as elemental chlorine-free bleaching sequences which include an oxygen stage tend to give pulp that is generally a little weaker than pulps from conventional chlorine sequences due to the highly selective and "gentler" bleaching characteristics of elemental chlorine on pulp. Marcoccia [233], in conjunction with Reeve and Goring, also published a later article in which they discussed some of the later part of this postgraduate thesis work.

Castellan et al. [220] undertook a study to investigate the two-stage photobleaching of organosolv bagasse pulp (peroxyformic acid pulping) in the presence of photocatalysts and photosensitizers. The conditions employed for the first photobleaching stage was the use of titanium dioxide as a photocatalyst (0.5%) in conjunction with a variety of photosensitizers: methylene blue (MB), 3,4,9,10-perylenetetracarboxylic acid (PCTA), or Fe(II) 4,4',4'',4'''-tetrasulfophthalocyanine {TSPC} all charged at about 50 μ M, with hydrogen peroxide charged at 2.0%, bubbling oxygen (atmospheric pressure), caustic soda (3.0%) and magnesium sulfate (0.5%) for pulp protection at 1 h and a 5% pulp consistency. The second photobleaching stage conditions included hydrogen peroxide (3.0%), bubbling oxygen, caustic soda (3.0%), sodium metasilicate for pulp protection, and methylene blue as the photosensitizer. The reasons chosen by them for evaluating the three photosensitizers were that: methylene blue is a known singlet oxygen sensitizer, while perylenetetracarboxylic acid has been shown to photosensitize semiconductor photocatalysts like TiO₂ using absorbed visible light, and the Fe(II) 4,4',4'',4'''-tetrasulfophthalocyanine promotes the thermal degradative oxidation of catechol and veratyl alcohol as well as serving as a potential photosensitizer. The light sources used were either a medium pressure

mercury ultraviolet/visible light lamp (400 W) with a strong UV component, or tungsten/iodine visible lamps (500 W) with a strong visible light component to simulate sunlight. Operational temperatures were 40 or 85 °C for both stages. The Pyrex wall of the reactor removed any wavelengths shorter than 300 nm that would detrimentally impact the cellulose matrix and pulp strength. Experimental results showed that the photobleaching of the bagasse pulp was strongly affected by temperature, with bleaching improving at elevated temperatures (85 °C versus 40 °C). Bleaching gave near fully bleached pulp at 85 °C, while very poor bleaching performance was achieved at 40 °C. Generally, pulp yield was about 90% across the two-stage process. Effective bleaching was obtained with the PTCA and MB photosensitizers with the UV/visible light mercury vapour lamp (1.2 to 1.3 kappa, brightness 86%, viscosity 510 to 550 ml.g⁻¹), and with MB for the visible light tungsten/iodine lamp (1.7 kappa, brightness 80%, viscosity 625 ml.g⁻¹). Near full bleaching of the pulp was achieved in all cases for all three two-stage sequences. MB also gave better viscosity retention, due to its generation of superoxide radicals which are more selective towards lignin than hydroxyl radicals. TSPC did not give any bleaching benefit, due to its thermal instability which allows it to rapidly breakdown within two minutes of starting the reaction process. Overall the UV/visible light source (mercury vapour lamp) always outperformed the visible light source (tungsten/iodine lamp) for the whole two-stage process, even though the visible light option across the TiO₂ photocatalytic/photosensitizer first stage gave better delignification and the UV/visible light control gave much better performance across the uncatalyzed/unsensitized second stage (i.e. a reverse in trend from first stage to second stage). The second stage tended to significantly boost brightness and delignification compared to the first, though any delignification improvements/lignin modification in the first stage tended to have a knockon effect in the second stage. UV/visible diffuse reflective spectroscopy showed that some chromophore groups remain in the pulp even after the two-stage photobleaching of the bagasse pulp.

Machado et al. [225] evaluated the photochemical bleaching of *Eucalyptus grandis* acesolv organosolv pulp looking at various one-stage, two-stage and three-stage photobleaching options. The photochemical reactor was a Pyrex cylinder utilizing two 400 W medium pressure mercury lamps. All experiments were undertaken under alkaline conditions to facilitate the photochemical chemical reactions involved and to promote the dissolution of degraded lignin fragments. Results from the work on various single-stage bleaching processes showed that, firstly, the ultraviolet/hydrogen peroxide option (-UV/P-) gave the best single stage bleaching performance with notably higher brightness development and a significantly higher rate of delignification over that of the dark (no light) control. These brightness results suggested destruction of the highly coloured chromophore groups. DRIFT IR spectra of pulps showed a near complete reduction at 1736 cm⁻¹ associated with carboxylic groups of lignin as well as similar groups found in certain carbohydrates, and for unconjugated carbonyl groups; but no change at 1646 cm⁻¹ associated with quinones and conjugated carbonyl groups, and (specific only to when the pulp was processed in the dark - lack of UV illumination) a partial reduction at 1250

cm⁻¹ associated with guaiacyl groups. Secondly, the ultraviolet/oxygen option (-UV/O-) in alkaline conditions did not give significant delignification, in contrast with work by Marcoccia who did get significant delignification with alkaline oxygen. This lack of delignification is likely due to acethylation of phenolic groups by the acetic acid/ethyl acetate organosolv pulping process. However, the -UV/O- did give significant changes to lignin structure and the DRIFT IR spectrum showed complete disappearance of lignin and carbohydrate carboxylic groups and unconjugated carbonyl groups peak at 1730 cm⁻¹, no change for quinones and conjugated carbonyls at the 1250 cm⁻¹ peak, and a reduction at 1250 cm⁻¹ for guaiacyl for the dark process. Thirdly, the use of the MB photosensitizer with ultraviolet/oxygen (-UV/O_{MB}-) to generate singlet oxygen did not significantly impact delignification or brightness directly. However, the lignin structure was significantly altered by the singlet oxygen process, particularly at the lower temperature (45 °C) where the 1740 cm⁻¹ peak (lignin and carbohydrate carboxylic groups and unconjugated carbonyl groups) was completely removed while 85 °C gave only a partial reduction, and the 1630 cm⁻¹ peak (quinones and conjugated carbonyls groups) was partially reduced at both temperatures. For the experimental work involving two photobleaching stages, the dark process (thermal bleaching only: -O-P-) gave good delignification and brightness development, while the overall (global) performance of the ultraviolet irradiated oxygen and hydrogen peroxide sequential stages (-UV/O-UV/P-) was significantly better than the dark process with very good brightness development. As regards the individual performances of each ultraviolet bleaching stage within the two-stage sequence, the brightness development by the hydrogen peroxide was much better than for the oxygen stage. The DRIFT IR spectra showed that the 1740 cm⁻¹ (lignin and carbohydrate carboxylic groups and unconjugated carbonyl groups) and 1646 cm⁻¹ peaks (quinones and conjugated carbonyls groups) had almost completely disappeared, while the 1250 cm⁻¹ peak (guaiacyl groups) showed some reduction as well. In addition, the ultraviolet irradiated oxygen and MB singlet oxygen sequential stages (-UV/O-UV/O_{MB}-) showed only a small improvement in brightness but a notable level of delignification (23%), though the low brightness development may have been due to retention of some of the MB photosensitizer/dye after washing. Furthermore, the lignin structure was significantly modified to allow for enhanced further bleaching as given by complete reduction of the 1740 cm⁻¹ (lignin and carbohydrate carboxylic groups and unconjugated carbonyl groups) and 1250cm⁻¹ (guaiacyl groups) peaks, as well as partial reduction of the 1640 cm⁻¹ peak (quinones and conjugated carbonyls groups). The outcome of the three-stage photobleaching process involving an ultraviolet irradiated oxygen, singlet oxygen with methylene blue photosensitizer, and hydrogen peroxide sequential bleaching sequence (-UV/O-UV/O_{MB}-UV/P-) , gave the best delignification (kappa number reduced from 65 to 8) and brightness development (70.9%) of all photobleaching options while retaining good viscosity (12 cP down from 19 cP). The third peroxide stage proved very effective at removing any residual methylene blue, achieving near complete delignification and brightening/whitening the pulp compared with the prior two stages; however, the prior two stages had prepared the pulp beforehand for the large peroxide bleaching effect by significantly modifying the lignin structure. These effects and

the contribution by each stage was easily tracked and demonstrated in the ultraviolet/visible diffuse reflectance spectra obtained.

Mirchin and Peled [234] investigated the photobleaching of chlorophyll-a in a 95% ethanol solution utilizing a broadband ultraviolet fiber lamp (Dr. Hohme Co./Model Blue Point) with a non-bleaching helium/neon laser as an analytical probe. In their experimental work they noted a strong bleaching effect of the chlorophyll-a upon UV irradiation and a white precipitate formed during the photobleaching. All photobleaching appeared to be completed after 3 to 10 minutes of irradiation depending on the radiation power level. The optical absorption cross-section of the chromophores in the solutions was measured to be approximately 10^{-15} cm, which they proposed was due to the photobleaching mechanism that was occurring on the molecular level for chlorophyll-a.

Nascimento et al. [235] investigated the photochemical bleaching of *Eucalyptus grandis* pulp generated via the acetic acid/ethyl acetate organosolv (acesolv) pulping method. There is a strong environmental and regulatory impetus for pulp and paper manufacturers to move away from chlorine based bleaching processes which produce large quantities of chlorinated organics, to environmentally friendlier bleaching technologies involving agents such as oxygen, ozone and hydrogen peroxide. They evaluated the application of an ultraviolet/hydrogen peroxide bleaching process as one such option. In the experimental work the impact of pH, peroxide concentration, temperature and the application of a pulp peroxide stabilizer (sodium silicate) were investigated. The following observations from this work were made: firstly, increased pH gave better delignification rates, a higher viscosity and shorter reaction time. Below a pH of 6, delignification was poor and a large drop in viscosity was observed. Above a pH of 6, the extent of delignification and viscosity losses started to noticeably improve. At pH 10, the level of delignification and viscosity retention was near its maximum which was achieved at pH 11. At pH 11, the lowest retention time was achieved (100 minutes). Secondly, the retention time could be decreased with increasing peroxide concentration to achieve a similar bleached kappa number in each case. The optimal peroxide charge was determined to be 0.47 M peroxide without any stabilizer. Thirdly, an increase in temperature caused a reduction in the retention time and improved pulp viscosity due to the greater selectivity of peroxide for lignin with the increased generation of perhydroxyl radicals. However, there was a small drop in the extent of delignification at these shorter times. With regards to pulp strength properties, the breaking length (traction), deformation and burst (explosion) indices of the photochemical bleached pulp were similar to a kraft *Eucalyptus grandis* pulp chemically bleached to a similar extent (similar kappa number); however, the brightness of the photobleached pulp was significantly lower. This lower brightness was expected for a pulp bleached with a bleaching sequence involving only one stage. The use of sodium silicate to stabilize the hydrogen peroxide allowed the use of a much lower hydrogen peroxide concentration (15% odp) while retaining good pulp

viscosity. The pulp lignin content also decreased with increased sodium silicate charges, but brightness development was significantly lower than at the higher peroxide charges.

Perez et al. [221] investigated the photochemical bleaching of various pulps from differing pulping processes (acesolv on *Eucalyptus grandis*; kraft on *Eucalyptus grandis*, *Pinus pinaster*, and *Picea mariana*; peroxyformic acid with and without reflux on *Eucalyptus grandis*) utilizing a two-stage photobleaching sequence involving an oxygen stage followed by a peroxide stage (-UV/O-UV/P-). The photobleaching oxygen stage employed titanium dioxide as a photocatalyst (1.0%) together with caustic soda (3.0%) and magnesium sulfate for pulp protection (0.5%); while the photobleaching peroxide stage (6.0% H_2O_2 /3.0% NaOH) was undertaken using metasilicate (3.0%) and magnesium sulfate (0.5%) as pulp protectors. Oxygen was bubbled through the pulp suspension during the entire oxygen stage process. Both stages were undertaken at 85 °C and 5% consistency for 1 h while under constant agitation. The experimental work showed that the TiO_2 photocatalyst significantly enhanced the degree of delignification in the oxygen stage while maintaining viscosity, even though no increase in brightness was observed. Irradiation of the TiO_2 photocatalyst in the oxygen stage tended to generate the classic hole (h^+)/electron (e^-) separation in the valence/conduction orbitals on the surface of the photocatalyst (Langmuir-Hinshelwood model). They proposed a mechanism in which the valence holes on the catalyst surface would generate hydroxyl radicals from reaction with the water/hydroxide anions while also interacting directly with the lignin itself generating lignin cation radicals. They also proposed that the electrons in the conduction band would generate superoxide radical with oxygen which then formed peroxide, which could subsequently be photolyzed into further hydroxyl radicals. The superoxide radicals could also react with the lignin radical cations ultimately generating organic peroxides (Figure 2.46). The pulping process (acesolv, kraft, and peroxyformic acid) clearly impacted the performance of the subsequent bleaching process. Peroxyformic acid pulping gave a better bleaching response due to the generation of additional phenolic groups as opposed to acesolv and kraft. The peroxide stage bleaching also relied predominantly on hydroxyl and superoxide radicals for its bleaching mechanism, but was critical for much of the observed brightness gain. An elevated temperature did increase the bleaching performance of both stages. The TiO_2 photocatalyst in combination with the MgSO_4 also provided certain benefits: reduced reaction time, increased selectivity, retention of viscosity (pulp strength), and decreased bleaching reagent consumption. UV/visible reflectance and FTIR spectroscopic studies showed that chromophores (particularly carbonyl groups) were degraded by the TiO_2 photocatalysed process in the two-stage sequence although the changes were not always evident in the oxygen stage. Perez et al. [221] proposed that the better delignification in the peroxide stage was due to modification of the lignin in the oxygen stage which made it easier to bleach more extensively with the subsequent peroxide stage. The absence of TiO_2 gave an increased level of carbonyl groups, while the presence of TiO_2 tended to decrease them.

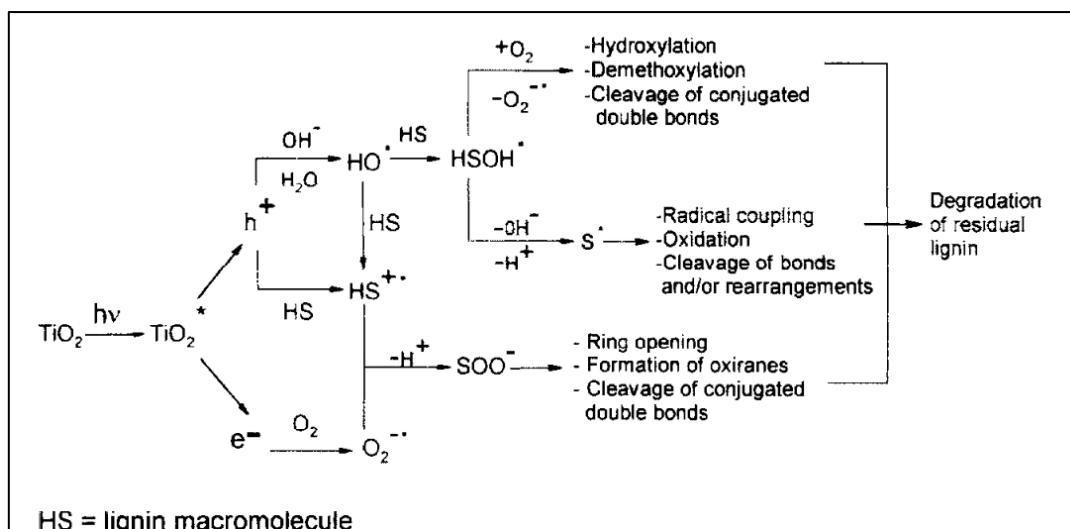


Figure 2.46: Reaction mechanism proposed by Perez et al. for photobleaching of various pulps involving a two-stage sequence (-UV/O-UV/P-) [221].

The main points that can be drawn from the reports on the use of low, medium and high pressure mercury lamps that are relevant to this study are: (i) Selection between a narrow frequency band for irradiation (typically involves selection of low and medium pressure mercury lamps) as opposed to a broad band of frequencies (high pressure mercury lamps). (ii) Selection of the exact frequency for a narrow frequency band by using lamps containing the correct dopant for that band. The exact dopant of such lamps will determine the frequency where that narrow band is emitted from. (iii) To adequately address any issues around adequate cooling of the lamp in use. (iv) Selection of the correct reactor design and conditions to accommodate the chosen lamp.

2.5.3 Lasers

The word LASER is an acronym for the phrase: “light amplification by stimulated emission of radiation” [236]. In general, any laser device consists of three main components:

- The lasering medium/gain medium is the material which emits the laser light at a given wavelength upon excitation by a light source/“pump”. This medium can be a gas, a liquid or a solid; and its composition determines the wavelength emitted during the lasering process.
- The energy source or energy “pump” which “pumps” energy‘ usually as light‘ into the lasering medium to continuously excite the medium’s contents. The pump varies depending on the type of laser and can be an electric discharge, a chemical reaction, a flash lamp, a laser diode, or another laser.
- The resonator is the reflector that surrounds the lasering medium; usually at either end of the laser device (typically two mirrors). Its purpose is to concentrate the light in the lasering medium and helps increase the optical gain of the laser as intensity builds with each reflection or “pump”. The

resonator can be mirrors (solid state lasers), Bragg reflectors (fibre lasers), or cleaved/coated facets (laser diodes).

There are a significant variety of lasers and their design (which determines their type) is typically dictated by what purpose they are used for. However, lasers can be broadly divided into five overall types:

- Gas lasers
- Solid state lasers
- Fibre lasers
- Liquid lasers (dye lasers)
- Semiconductor lasers (laser diodes)

Gas lasers use a specified gas or gas mixture (e.g. carbon dioxide, helium, neon, argon, or krypton) as the lasering medium and generate light at a given wavelength via an electrical discharge through that gas medium. Their fairly simple design allows for a wide range of applications. These include bar code scanning, air pollution monitoring, material processing (e.g. laser cutting and welding), laser surgery, spectroscopy and holography [236]. Another important application of gas lasers are as exciplex lasers (excimer lasers) which find application in high resolution ultraviolet photolithography for the production of micro-devices and micro-circuits in the production of microchips.

Solid state lasers use a solid lasering medium; usually a crystal or some type of glass; which has been doped with certain selected rare earth elements (e.g. chromium, erbium, neodymium, thallium, or ytterbium). This solid lasering medium is usually “pumped” by another light source (e.g. flash lamp). The first solid state laser ever built was the ruby laser, but the Nd:YAG laser (neodymium doped yttrium aluminum garnet) laser has found widespread use today. Applications include various medical applications (e.g. tatoo and hair removal, tissue ablation, and kidney stone removal), material processing and LIDAR applications [236 and 237].

Fibre lasers are solid state lasers whose properties as a group are sufficiently unique as to warrant their own separate category/type. The lasering medium for fibre lasers is a silica glass optical fibre that has been doped with a rare earth element (see solid state lasers above). The unique properties of optical fibres allow for complete internal reflection of the light within meaning that the fibre need not be of a straight linear design as with simpler solid state lasers. This imparts certain benefits to fibre lasers typically not common in other solid state lasers, such as being far more compact and smaller. Other benefits from this are a straighter and more narrow beam which allows it to be more precise than other laser types. Applications include medical applications, material processing (e.g. laser cleaning, texturing, marking, cutting, and welding), and directed energy weapons [236].

Liquid lasers (i.e. dye lasers) use an organic dye dissolved in a liquid (aqueous or organic) as their laser medium, and are typically pumped by short pulse small flash lamps, as well as continuous wave and pulsed lasers as light sources [238]. One of the benefits of dye lasers is that they produce light over a much broader spectrum of wave lengths, when processed through a prism or grating, allows for the selection of a chosen narrow wavelength band width giving a tuneable laser as a result. This affords dye lasers certain unique benefits, such as application in isotope separation. Other applications include medical applications, birth mark removal, and spectroscopy [236]. Another characteristic unique to dye lasers is that the dye can be constantly replenished/replaced by circulation with a larger dye reservoir attached to the laser. This has the benefit of ensuring a “fresh” laser medium, cooling the laser and is often necessary to prevent dye degradation and singlet-triplet conversion events.

Semiconductor lasers (diode lasers) have a very different design to the aforementioned laser types, with a design closer to a standard diode but with a P-I-N junction. The light is emitted from the intrinsic layer (that is highly polished on all but one side) which is sandwiched between the positive and negative P-N zones of the semiconductor. As “holes” and electrons, flowing in opposite directions when under electrical bias, recombine at the intrinsic layer they create a runaway snow balling effect of released photons eventually resulting in a coherent beam. Diode lasers have found uses in a large number of applications including barcode readers, laser pointers, laser printers, and laser scanners [236]. Diode lasers are also used as energy sources to “pump” other laser types. Diode lasers are also combined into laser diode arrays allowing for an increased radiation intensity and the quick firing of multiple quick pulses from the array.

Lasers show many of the advantages of mercury vapour lamps (i.e. low, medium and high pressure lamps). These include being available at all times when a power source is available, high level of direct control (internal and external use within various reasonable reactor designs) – unlike solar radiation, and generation of an extremely narrow frequency of light as a source. In addition, they produce light that is focussed into a very narrow point and that is also completely coherent at the time (i.e. no or minimal destructive interference or sideways diffraction) as compared with all other sources. The disadvantages include the requirement of a power source as well as the losses in radiation power (as heat) if the focussed beam requires dispersal over a large area via means of mirrors or a grating.

Of the scientific literature published around laser bleaching, the majority appears to be focused on the dental industry and the whitening of teeth enamel as well as associated issues [239 to 244]. Almost all of the remainder of the published literature on laser bleaching covers the remediation of wastewater streams. The author of this thesis found only one article covering the laser bleaching of wood or chemical pulps.

Gondal and Sayeed [245] studied the photodegradation of phenol in solution by utilizing a Nd:YAG laser and zinc oxide as a photocatalyst. In general, phenol is highly toxic and a carcinogen, with water contaminated with it not being fit for human or animal consumption. It is also not fit for irrigation of crops when so contaminated. Moreover, large quantities of phenol and phenolic type waste products are generated in many industrial processes covering a wide field of applications. Hence, the remediation of waste waterstreams contaminated with phenol and similar aromatics is an ongoing challenge to industry. In the experimental work, Gondol and Sayeed employed a harmonic generator (the third harmonic for frequency “tripling”) to stepup the infra red wavelength of the Nd:YAG laser to the shorter ultraviolet wavelength of 355 nm (Figure 2.47). A beam diameter controller and selected reactor lenses were employed to disperse the laser beam to an approximately one centimetre diameter to prevent degradation of the phenol in solution via thermal photo-shock. Based on their results, they observed that a 70% mineralization of the phenol in solution was achieved for their experimental setup with the hydroxyl radical serving as the main active agent. The in process pH was found to increase with the use of the ZnO photocatalyst as the photodegradation of the phenol proceeded by what appeared to be the Langmuir-Hinshelwood reaction mechanism (i.e. h^+ / e^-) around activity on the ZnO photocatalyst’s surface. Reaction kinetics followed a pseudo first order process with a measured reaction rate decay constant of 0.0088 min^{-1} for phenol. Gondol and Sayeed have proposed that their Nd:YAG laser-based system is more efficient than the more conventional photocatalytic degradation systems for phenol which use mercury vapours lamps and a TiO_2 photocatalyst.

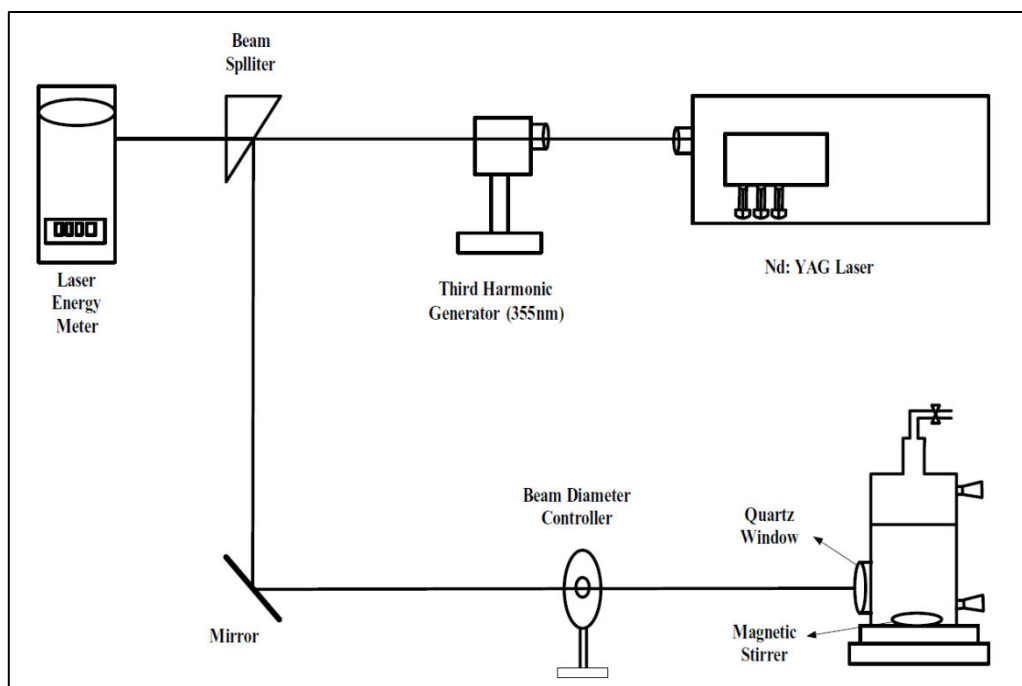


Figure 2.47: The Nd:YAG laser system design evaluated by Gondol and Sayeed for the photodegradation of phenol in solution utilizing a ZnO photocatalyst [245].

Polat et al. [246] investigated the photodegradation of metoprolol tartrate (MPT) utilizing an ultraviolet semiconductor laser diode. The increasing use of bioactive pharmaceuticals in the global population is leading to a rapid buildup in wastewater streams of many water treatment plants, where their concentration is resulting in growing problems in remediating these wastewater streams due to their non-biodegradable stability. Disposed water soluble drugs such as metoprolol, atenolol, antibiotics, β -blockers, mood stabilizers, and other waste drugs are among this growing problem. In their studies, Polat et al. evaluated three reactor designs: (i) their first laser flow system (LFS) design in which the MPT solution was subjected to the UV laser light shone onto a ultraviolet transparent glass tube in a closed circulation loop in which MPT solution was pumped from and back to the bulk solution in a beaker, (ii) their second laser flow system (LFS-2) which had the same design and circulation loop as the first; except that the laser was aimed at the bulk beaker itself, and (iii) a fixed bed system (FBS) in which the MPT solution was stirred in a beaker with a magnetic stirrer with the laser aimed at the beaker (no external circulation circuit) (Figure 2.48). In this study, MPT degradation was achieved via photo-generated hydroxyl radicals. They firstly optimized conditions around the operational parameters of H_2O_2 concentration, iron oxide catalyst concentration (hematite- Fe_2O_3 + magnetite- Fe_3O_4 clay), time and irradiation power. Secondly, they performed mathematical modelling to study the impact of thermal and solution flow outcomes which were then employed in the final kinetic studies. What Polat et al. observed was that the first laser flow system (LFS) gave the best photodegradation performance of the three reactor designs (giving an 87.6% and 45.5% reduction in MPT based on UV spectroscopic

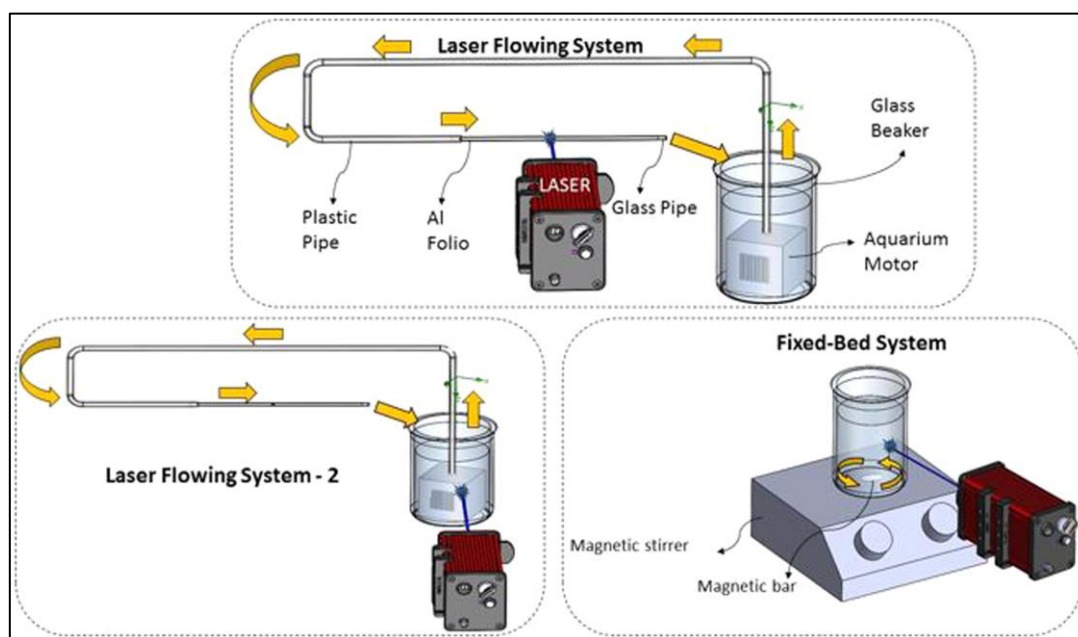


Figure 2.48: The three reactor designs evaluated by Polat et al. for the photodegradation of metoprolol tartrate utilizing an ultraviolet semiconductor laser diode [246].

and COD analyses respectively), followed by the fix bed system (FBS), with the second laser flow system (LFS-2) performing the worst. For the first laser flow system, the optimal conditions were found to be 0.1 M H_2O_2 , 40 mg catalyst, 0.3 W laser diode power, and 5 h retention time. The impact of thermal inputs and solution flow outcomes to the laser diode reactor system were found to be negligible. Kinetic modelling showed that the MPT photodegradation process was a combination of zero-order and first-order kinetics, with the zero-order kinetics predominant during the first 30 minutes, and then the first-order kinetics during the remaining 4.5 h. The experimental relationship of the MPD degradation showed good correlation with the mathematical models developed with 97.7% and 96.8% agreement for the zero-order and first-order kinetic studies respectively. Polat et al. proposed that their first laser flow system utilizing a laser diode (i.e. laser diode aimed at the external circulation loop) would serve as a good design for future industrial scale water remediation systems in the medical, textile and chemical wastewater recovery facilities.

Ouchi [247] evaluated the photobleaching of two different Kraft pulp combinations utilizing various oxidative bleaching agents irradiated by different light sources with the view to avoid any form of halogen-based bleaching reagent. Generally, the bleaching process is used to generate higher brightness and white pulps from unbleached pulp made from the breakdown of wood via the kraft pulping process. Early bleaching employed elemental chlorine (i.e. Cl_2) or its alkali equivalent of hypochlorite (i.e. ClO^-), but this has been replaced recently by the environmentally friendlier reagent chlorine dioxide (elemental chlorine free) or non-halogen-based reagents such as oxygen, ozone and hydrogen peroxide (total chlorine free). Ouchi utilized two kraft pulp types in his studies: (i) post-oxygen softwood kraft pulp (semi-bleached), and (ii) a 1:1 mix of unbleached hardwood kraft and fully bleached softwood kraft (the softwood component providing only strength to the hardwood component). The experimental work was undertaken initially on dried pulp sheets and then as pulp suspensions. The light sources employed were three excimer lasers (KrF for 248 nm, XeCl at 301 nm, and XeF at 351 nm), a low pressure mercury vapour lamp, and a long wavelength black light blue fluorescent lamp; as well as various oxidative bleaching reagents: (i) hydrogen peroxide - H_2O_2 , (ii) sodium peroxocarbonate - $\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}_2$, (iii) sodium peroxide - Na_2O_2 , (iv) sodium peroxoborate - NaBO_3 , and (v) urea hydrogen peroxide - $\text{H}_2\text{NCONH}_2 \cdot \text{H}_2\text{O}_2$. In the initial experimental work, he employed both the excimer lasers and pulp sheets to evaluate and optimize for the type of bleaching reagents, light wavelength, the type of light source, the reaction pH, and irradiation time. He found that the peroxocarbonate performed the best and it was employed in most of the subsequent pulp sheet experiments. By using the three excimer lasers at their three different wavelengths, he found that the level of interaction between the laser light and lignin generally increased as the wavelength shortened. The aim of the excimer laser experiments was to evaluate which wavelength would interact with the lignin component of the pulp only without interacting with the pulp cellulose (to avoid cellulose breakdown) or the bleaching reagents

themselves (degradative loss or overlap of photo-excitation wavelengths). As regards pH, Ouchi found that the ideal pH for alkaline hydrogen peroxide (instead of peroxocarbonate) was a pH 11 as the photobleaching activity increased with pH from 10 to 12, but that excessive cellulose degradation occurred above pH 11. Overall, the photobleaching with lasers generally achieved brightness and yellowness index levels (on the side of the photo-sheets that were irradiated) which were similar or better than conventional thermal bleaching involving an ECF two-stage bleaching sequence using a chlorine dioxide stage followed by a hydrogen peroxide stage. This photobleaching, however, did not extend through the entire pulp sheet width. Once the optimal conditions were determined utilizing pulp sheets, the photobleaching was repeated using pulp suspensions which were irradiated by the low pressure mercury vapour lamp and the long wavelength black light blue fluorescent lamp as a UV light source with alkaline hydrogen peroxide (pH 11) as the oxidative bleaching reagent. As with the pulp sheets, the mercury vapour and black light fluorescent lamps achieved brightness/yellowness index values and pulp strength properties equivalent to the two staged ECF bleaching process for both the softwood and hardwood combination pulps in suspension. UV-Visible spectroscopy indicated that the observed photobleaching changes occurred across the entire UV and visible portion of the electromagnetic spectrum which is consistent with removal/destruction of the coloured chromophoric aromatic moieties of the lignin phenolic phenylpropane functional groups in the lignin structure (i.e. hydroquinonic and catechol types). The mercury vapour lamp achieved these brightness targets more quickly than the black light fluorescent lamp due to the greater luminant intensity of the mercury vapour lamp.

The main points that can be drawn from review of the laser literature that are relevant to this study are: (i) Selection of the correct laser and laser type. Selection of the laser and laser type would determine the frequency of the laser as a light source, the frequency band width of the light emitted, and the output power of the laser. Selection would also impact the reactor design and type of cooling system required for the laser (if necessary). (ii) As lasers generate a concentrated point of light, many reactor designs would require a means of beam dispersal throughout the reaction medium. This would impact on the type of lenses and mirrors required for this dispersal. (iv) Dye lasers employ a photo-luminant to operate. Thus, dye lasers require additional support equipment to operate. The need for such supportive equipment is a disadvantage, though, dye lasers have the advantage of being “tuneable”. (v) Diode lasers have the advantage of being able to be assembled in an array of multiple diode lasers as a method of boosting power output, though such arrays will require a method of active cooling.

2.5.4 Microwave discharge electrodeless lamps

Microwave discharge electrodeless lamps (MDELs) are simply enclosed glass/quartz tubes that contain mercury vapour at extreme low pressures/near vacuum, at pressures of about 700 Pa [248 to 250]. MDELs have also been made up with fillers other than mercury (e.g. nitrogen gas), but mercury is by

far the most common filler. They have no electrical elements, no wiring, no cathodes or anodes, and are completely disconnected from any electrical circuit. When MDELs are subjected to microwave radiation from a continuous source, the mercury within the lamps is excited as the valence electrons jump from the ground state to an excited orbital heating the lamp until its inner walls reach about 800 °C, at which point “ignition” occurs. During ignition, light (typically ultraviolet) is generated as the mercury vapour atoms de-excite back down to their ground state emitting photons in the process. As the lamp continues to “burn” with continued microwave irradiation, a continuous stream of emission radiation is generated requiring slightly less energy to sustain than the initial ignition. The light emitted is typically medium to high intensity and consists of a few narrow bands of wavelengths characteristic of multiple excited mercury states. These band wavelengths can be “shifted” or replaced by other bands via dopants added to the mercury. Common dopants include iodide, potassium iodide and sulfur [251]. The ignition and sustained burning of MDELs can be improved by the addition of glass/quartz encased tungsten wire/antennae at either end of the lamp [252]. These antennae MDELs (w-MDELs) increase the absorption of microwave radiation, driving the process with greater ease requiring significantly lower energy levels to ignite and even less energy to sustain. MDELs have found widespread use in certain commercial applications such as curing of labels and polymers, generation of light for illumination, and treatment of some waste streams. Their application in research is moderately common and growing. The advantages of MDELs are that they can be produced in almost any shape with few limits on the size (except for extremely small or large) and shape allowing for a large range of reactor designs, have no electrical connections (which can wear out with use), and produce intense light as a source. They are reasonably compact as compared to mercury vapour lamps and are available at all times for use with microwave magnetrons as a power source. Due to their long lifespan, MDELs require less frequent replacement than the average luminant bulb/lamp. In addition, the simultaneous exposure to both microwave and ultraviolet radiations appears to have a synergistic effect on many chemical processes. The disadvantages are that they easily suffer thermal quenching (particularly when immersed in water) which can prevent ignition and sustained burning; as well as typically requiring a well designed microwave chamber with good microwave resonance to operate properly. A final disadvantage is that MDELs are very difficult to make up and require particularly stringent manufacturing requirements [248, 249 and 253]. These are typically beyond the scope and ability of most glass blowing artisans and facilities. Although MDELs and their variants have found widespread scientific and commercial application, they have not been used or studied for photochemical bleaching of pulp or photodegradation of LMCs. All the scientific literature that is published on MDELs, is focused on remediation of waste streams – both water and gas streams.

Horikoshi, Abe and Serpone [252] have published a good overall summary on MDELs covering most topics associated with these lamps. The first aspect that this summary covered was an introduction on what MDELs are and how they function as well as a historic review on the topic. The second aspect

was how MDELs fulfil the need for novel ultraviolet and visible light sources within industry and science, and the benefits they offer over more traditional light sources - particularly in the field of AOPs. They also discussed how the benefits from the microwave thermal component and their ultraviolet light component are synergistic in producing an outcome that is more than the sum of their individual contributions. Thirdly, they evaluated the various applications (both potential and existing) of MDELs in both industry and the sciences. These include the remediation of waste gaseous and volatile streams (e.g. destruction of acetaldehyde and toluene as volatile organic compounds), wastewater streams (e.g. 2,4-D herbicides and bisphenol-A as an endocrine disruptor), and fly ash streams contaminated with dioxins. Included in these examples was the topic of excitation of semiconductor photocatalysts such as titanium dioxide. The fourth aspect covered was how the emission spectra of MDELs can be modified and tailored to their needs by the addition of dopants of various elements. The fifth and final aspect of this summary was the use of tungsten-wire antennae MDELs (w-MDELs), and how the tungsten antennae allows for the ignition and sustained "burning" of w-MDELs at much lower microwave power levels than the simpler plain MDEL design. A similar summary was also published about the same time by Horikoshi and Serpone [254]. It covered all the points raised and described in the first summary discussed.

In some of their earlier work, Horikoshi et al. [255] investigated the use of a modified domestic microwave oven to treat a wastewater stream containing 2,4-dichlorophenoxyacetic acid (2,4-D) using a Teflon batch reactor surrounded by a unique double glass cylindrical plasma lamp (DGCPL); i.e. a cylindrically spaced MDEL. The microwave-powered DGCPL reactor gave enhanced degradation of the 2,4-D herbicide over the simpler system using photodegradation only. Horikoshi et al. proposed that a continuous reactor system of this type utilizing the domestic microwave oven together with a DGCPL type lamp would hold many commercial advantages as well as being considerably cost-effective.

Horikoshi et al. published a multiple article series, numbering more than ten articles, covering various aspects of their investigation into MDELs, over the period of 2007 to 2018. What follows in this paragraph is a brief review of six of the more than ten articles in roughly date order. In the first article reviewed, Horikoshi et al. [256] evaluated the use of MDELs to degrade 2,4-dichlorophenoxyacetic acid (2,4-D) herbicide in an advanced oxidation process. They believed that this offered a novel means to remediate this herbicide in a risk-free method. In addition, the benefit of including the photocatalyst TiO_2 was also studied. The experimental work investigated various options such as: (i) microwave irradiation alone, (ii) MDEL outside reactor, (iii) Hg lamp/ TiO_2 , (iv) Hg lamp/microwave/ TiO_2 , (v) MDEL outside reactor/ TiO_2 , (vi) MDEL inside reactor, and (vii) MDEL inside reactor/ TiO_2 . Results showed that the best combination was the MDEL inside the reactor while utilizing the TiO_2 photocatalyst, followed by the MDEL inside the reactor without the photocatalyst. In the second article

reviewed, Horikoshi et al. [257] evaluated the photodegradation of acetaldehyde using a MDEL in conjunction with a TiO_2 photocatalyst. The results showed good degradation of the acetaldehyde in solution over a reasonable timeframe. The synergistic effects between microwaves and ultraviolet light were observed in this set of experiments, with the key processes being desorption of the acetaldehyde from the catalytic surface, thermal pyrolysis, degradation of the acetaldehyde by photogenerated reactive oxygen species, and direct photodegradation of the acetaldehyde. In the third article, Horikoshi et al. [258] evaluated the photodegradation of bisphenol-A (BPA) and the herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) using a novel tungsten wire antennae MDEL (w-MDEL). Both BPA and the 2,4-D herbicide are water soluble pollutants with BPA being a xenoestrogen and 2,4-D being an endocrine disruptor. In the experimental work, the optimal conditions for the make-up and charging of the w-MDEL were successfully undertaken. Ignition and "burning" were shown possible at much lower power levels than a simpler MDEL, even when immersed in water, from a focused microwave source. The w-MDEL was more than adequate in achieving good photodegradation of the BPA and 2,4-D, and performed significantly better than the Hg lamp/ TiO_2 control. The degradation with the w-MDEL was achieved without the need of the photocatalyst TiO_2 . In the fourth article reviewed, Horikoshi et al. [259] investigated the use of a metallic microwave condensing cone as part of a novel self-ignition system for the MDEL treatment of wastewater streams containing 4-chlorophenol (4-CP), 2,3-dichlorophenoxyacetic acid (2,4-D), and bisphenol-A (BPA). They were able to achieve ignition and keep selected MDELs "burning" at much lower power levels with the metallic concentrating cone positioned within the microwave's waveguide than without the cone (i.e. 75 W with the cone and 650 W without). A reasonable level of degradation of the three pollutants tested (4-CP, 2,4-D and BPA) was also achieved with MDELs fired and maintained by the concentrating cones. The proposed chemical mechanism was both the direct photodegradation of pollutants and the generation of degrading hydroxyl radicals. Horikoshi et al. proposed that such concentrating cones would serve as one of a number of useful tools for the future commercial treatment of wastewater streams using MDELs. In the fifth article of the six reviewed, numbered Part VI, Horikoshi et al. [260] investigated the performance of miniaturized MDELs, called microwave discharge granulated electrodeless lamps (MDGELs), in the photo assisted defluorination of perfluoroalkoxy acids. The MDGELs were utilized in a collective batch of twenty (20) at the focal point of the microwave generator employing a metallic concentrating cone. Each MDGEL was as bulb of about 5 to 10 mm in length. The initial part of the experimental work on the MDGELs indicated that the MDGELs required a minimal level of energy to ignite and to sustain their "burn" as opposed to the standard MDEL (80 W versus 650 W for the standard MDEL). The performance of the MDGELs in the photo-assisted defluorination of trifluoroacetic acid (TFA), heptafluorobutyric acid (HFBA) and perfluorooctanoic acid (PFOA) was shown to be significantly better than for a single large MDEL lamp or a mercury vapour lamp under a variety of pH conditions. A full mechanistic pathway for the complete defluorination, degradation and mineralization of PFOA was also proposed by them. In the sixth and final article reviewed in Horikoshi

et al. multiple article series, Horikoshi et al. [261] investigated the photo-isomerization of trans-urocanic acid using a novel MDEL called a microwave discharge thermally insulated electrodeless lamp (MDTIEL). The MDTIEL consisted of a standard MDEL (in this case filled with low pressure nitrogen rather than mercury vapour as nitrogen is more environmentally friendly) which was physically enclosed and suspended within a larger tubular bulb that had been evacuated to a complete vacuum to ensure maximum thermal insulation between the inner MDEL and the outside environment. This thermal isolation of the MDEL from the surrounding environment would ensure nil to minimal transfer of heat between the MDEL and the surroundings which should ensure an easier ignition and more stable "burn" of the MDEL allowing it to operate at low microwave energy levels. In addition, the isomerization of trans-urocanic acid to its cis-isomer is adversely affected by heat, and Horikoshi et al. proposed that employing thermally isolated MDEL would significantly improve the rate and yield of the trans to cis isomerization process. In the results obtained, the MDTIEL demonstrated significantly better isomerization of the trans-urocanic acid to its cis-form over both a standard MDEL process as well as a control process based on a mercury vapour lamp. The MDEL and MDTIEL both performed better than the vapour lamp control due to the electrodeless lamps being in direct contact with the urocanic acid solution, while the MDEL was disadvantaged over the MDTIEL due to thermal conduction between the surface of the standard MDEL and the urocanic acid solution.

Klan et al. evaluated the performance of a custom made MDEL reactor based on a combination of a commercial microwave oven containing a custom reactor vessel and a standard MDEL. The study also evaluated the impact of the combination of ultraviolet and microwave energies on the photo-efficiency of the process, their synergies, as well as the reactor's usefulness as a future tool. Klan et al. discussed the results of this investigation on the custom MDEL reactor in a five article series. In their experimental work for the first article (Part 1), Klan et al. [262] evaluated certain aspects of their custom build MDEL reactor including: (i) the influence of microwave power level and temperature on the MDEL, (ii) the influence of polarity of the solvent, (iii) the influence of the heating capacity of the MDEL, and (iv) the influence of the microwave power output on the photochemical reaction efficiency of the MDEL. They found that the MDEL emitted sufficient heat to quickly heat any solvent to boiling point even in solvents that are microwave transparent. In the photo-fragmentation of valerophenone via Norrish Type II reactions, they found that the generation of acetophenone (a product of the Type II reaction) followed an almost linear relationship to the microwave power levels. Klan et al. also found that the reaction efficiency was favoured by solvents that were less polar (benzene versus acetonitrile). In the second article (Part 2), Klan and Literák [263] continued to evaluate the usefulness of their custom MDEL reactor. As part of this study, they evaluated five common types of photoreactions for their custom MDEL reactor as compared to the more conventional mercury vapour lamp based reactors. The five reactions evaluated included: (i) Norrish Type II reaction of valerophenone and its p-methyl derivative, (ii) photo-Fries reactions, (iii) acetophenone photoreduction, (iv) phenacyl-ester photolysis,

and (v) a nucleophilic radical substitution of chlorobenzene in methanol as a solvent. When compared to the more conventional photoreactors with various mercury vapour lamps, the custom MDEL reactor performed similarly for all five common photoreactions. They proposed that their custom MDEL reactor would thus be useful as a tool for future photoreactions and synthesis work. In the third article (Part 3) of the five part series, Klan et al. [264] discussed in detail the construction, various experimental setups (single or double reflux reactor vessels, reactor arrangements for solid state reactions), applications and safety precautions for their custom MDEL reactor based on a commercial kitchen microwave oven. They proposed that their custom MDEL reactor would be a cheaper and useful tool for chemistry laboratories investigating a broad range of various microwave photochemistry reactions and syntheses. Klan et al. [265] undertook further experimental work to clarify and optimize the operational conditions and parameters of their custom MDEL reactor. This extended investigation was reported in the fourth article (Part 4). In the fourth article, Klan et al. discussed their investigation into: (i) the MDEL emission characteristics as a function of temperature over the spectral range of 250 to 600 nm, (ii) the microwave power output of the reactor, (iii) the impact of the MDEL envelope material, and (iv) the impact of the solvent properties. The experimental results showed that the intensity of the emission peak was clearly impacted by rising temperature, particularly for shorter wavelengths. Solvents that absorbed microwave radiation were found to also significantly attenuate peak intensities. Thus, they concluded the right choice of MDEL envelope material and reaction conditions was important for achieving the maximal effect for the custom MDEL reactor. In the fifth and final article (Part 5), Klan et al. [251] undertook an evaluation of the impact of various MDEL fillers/dopants and envelope material (quartz versus pyrex) for their custom MDEL reactor. The various fillers and dopants investigated were: mercury, mercury iodide, cadmium, calcium iodide, iodine, potassium iodide, phosphorus, selenium, and sulfur. Klan found that the fillers/dopants: mercury, mercury iodide, cadmium iodide and phosphorus gave spectra with distinct spectral emission lines; while iodine, potassium iodide, selenium and sulfur gave continuous spectra with numerous band peaks. The continuous spectral characteristics of the sulfur MDEL were very similar to solar light and could be used to investigate certain solar and environmental related photochemical queries. The envelope material was also important in regards what wavelengths the MDEL would be transparent to over the range studied (250 to 600 nm). They concluded that the correct choice of filler/dopant and envelope material was critical to the type of application the customized MDEL could be used for.

Kunz et al. [266] investigated the photodegradation of ethylenediaminetetraacetic acid (EDTA) using hydrogen peroxide in a batch reactor illuminated by a MDEL. They optimized their process for pH and reagent charge ratio using a two-factorial experiment design. In their experimental work, Kunz et al. were able to achieve a near complete breakdown of the EDTA (90%) in a short period of time (6 minutes). They noted that this is considerably better than 12 days required when treating the EDTA

solution via active sludge. They also hypothesized that the recent introduction of low cost continuous photoreactors make this a potentially economically viable alternative.

Lan-Yan et al. [267] evaluated the photodegradation of hydrogen sulfide (H_2S) in a continuous flow reactor. In their experimental work, Lan-Yan et al. found that the H_2S was photodegraded more efficiently with higher initial H_2S concentrations and residence times, but more slowly with a larger reactor pipe diameter. They were able to successfully reduce the H_2S contaminant in a gas stream passing through their continuous photoreactor by 56% in a single pass using a MDEL.

Sun et al. [268] investigated the photodegradation of hydrogen sulfide (H_2S) in a flow through continuous photoreactor utilizing a MDEL that was interior or exterior to the reactor. They showed that the best results for photodegradation occurred with a photoreactor with an internal MDEL light source (IMDEL) than with an exterior MDEL light source (EMDEL). They were able to achieve a 91% removal of H_2S in a gaseous waste stream through a continuous flow through reactor employing an interior MDEL (IMDEL) and microwave generator with residence times in the reactor of only 1.5 seconds. Sun et al. were able to demonstrate that the efficiency and rate of photodegradation of H_2S (or potentially any gas contaminant) with a MDEL will be strongly dependent on the reactor design.

Zabova and Cirkva [269] studied the preparation of MDELs coated with a thin film of various transition metal cation doped TiO_2 photocatalysts and their application in the photodegradation of mono-chloroacetic acid. As part of the preparatory aspect of this study, they evaluated the ultraviolet mercury vapour lamp photocatalytic degradation of Rhodamine B using similarly doped TiO_2 microscope slides (iron, cobalt, nickel, vanadium, chromium, manganese, zirconium, and silver). The prepared thin film microscope slides and the thin film coated MDELs were all characterized by Raman spectroscopy, ultraviolet/visible spectroscopy, X-ray photoelectron spectroscopy, electro-microprobe analysis, and atomic force microscopy which were used to certify that the thin films were successfully prepared. In their experimental work, Zabova and Cirkva (2009) showed that the thin film doped vanadium, zirconium, and silver microscope slides demonstrated greater photodegradation of the dye rhodamine B over the plain undoped TiO_2 slides when under UV mercury vapour lamp irradiation. This information was employed to select the doped TiO_2 thin film MDELs that were to be prepared for the subsequent experimental work. The vanadium, zirconium, and silver ion doped TiO_2 MDEL's showed increased absorption of light in the visible part of the spectrum for the photocatalysts allowing for possible enhanced photocatalytic activity by utilizing a larger portion of the electromagnetic spectrum. For the thin film vanadium, zirconium, and silver doped MDELs, a significant increase in the photocatalytic degradation of mono-chloroacetic acid was observed. The best measured degradation rate constant was for the 3% Ag doped thin film TiO_2 coated MDEL with a value of 0.0125 min^{-1} which was 1.7 times faster than the pure TiO_2 coated MDEL.

Zhao et al. [270] investigated the photodegradation of butyl acetate in a gaseous stream using a continuous flow reactor with a MDEL. In their experimental results, they were able to achieve a 78% photodegradation of butyl acetate in the gaseous stream using their continuous flow reactor with an internal MDEL under the experimental conditions they employed. Zhao et al., using hydrogen sulfide and carbon disulfide, also found that using a segregated MDEL in which the MDEL is fired by microwave energy but the gas stream is subjected only to the ultraviolet light, but not the microwave radiation simultaneously, gave reduced performance to the photodegradation process as opposed to when the gas stream is subjected to both forms of radiation together. Thus, they were able to show that a MDEL light source internal to the gas stream (i.e. interior of photoreactor) performed better than an external MDEL light source.

The main points that can be drawn from the review of the MDEL literature that are relevant to this study are: (i) Unless the reaction medium/solvent is microwave transparent, the microwave/MDEL combination will boil any solvent in a short space of time. A condenser will likely be required to recondense any evaporated solvent to prevent significant solvent loss. (ii) To make proper use of the MDEL, the microwave oven and MDEL need to be properly “coupled”/tuned to each other to obtain good performance from the MDEL. (iii) The microwave oven must produce sufficient power to ignite and maintain the MDEL. (iv) The use of a microwave concentrating cone must be considered to facilitate successful MDEL use. (v) The use of a w-MDEL must also be considered to facilitate MDEL use, particularly at reduced power levels. (vi) MDELs with fillers other than mercury must be considered for environmental reasons (eg. nitrogen). (vii) The application of various dopants to the MDEL must be evaluated to modify the principle frequencies of MDEL emission. (viii) The use of various photocatalysts and photosensitizers should be investigated.

2.5.5 Light emitting diodes

Light emitting diodes (LEDs) operate on a similar principle to semiconductor lasers [271, 272]. As with laser diodes, LEDs generate light from the Intrinsic layer of a P-I-N junction where the “holes” and electrons (travelling in opposing direction when under electrical bias) from the positive and negative P and N zones of the semiconductor crystal combine emitting light, except that (unlike laser diodes) the light LEDs generate is not a coherent beam. The first visible light LEDs were commercially introduced in the 1960s although the first working LED were demonstrated as far back as the 1920s (infrared). These first visible light LEDs generated only red light of low intensity. Continued research and development during the later 1960s and through the 1970s led to LEDs of increasingly shorter wavelengths. Orange, yellow and then green LEDs were successively introduced into the market during the 1970s as a result. Nakamura et al. demonstrated the first blue light LED in 1993, which became commercially available in 1996. Development of the first high powered LED of about one Watt was

demonstrated and introduced in 1999. As with laser diodes, LEDs can be assembled into an array to ensure a greater radiation intensity. The applications for LED and LED arrays include curing of labels and polymers, lighting for buildings and homes, and experimental research. LEDs share many of the advantages and disadvantages of laser diodes. These include high energy conversion efficiency (i.e. 90% to 99%), high intensity, and compact size. They are also available at all times, both for inside and outside use, wherever there is a power source. In addition, they have extremely long lifespans (with LED arrays having more than 20 000 h without loss of intensity and up to 40 000 to 50 000 h lifespan). LEDs are also robust and highly compact which gives greater freedom in designs in which they are employed. The one disadvantage is that the operation is not free, it requires an external power source. Furthermore, all LEDs and LED arrays generate heat, although considerably less than other light sources. The means of cooling of LED's include conduction to mount, convection, forced air movement via fans, and liquid cooling. The exact method of cooling is dependent on the power input, design and requirements of the LED system. Consequently, LED arrays almost always require cooling with air or water media.

A review of the literature on bleaching with LEDs appears focused mostly on the photo-remediation of wastestreams, and photochemical synthesis. There appear to be no publications on the photobleaching of pulps.

Chen et al. [273] evaluated the TiO_2 photocatalytic degradation of perchloroethylene (PCE or C_2Cl_4) in an air waste stream for a single pass flow through reactor utilizing multiple ultraviolet LEDs as a light source. A schematic of their reactor design is given in Figure 2.49. At even the lower irradiation power levels for the single pass flow through reactor ($49 \mu\text{W cm}^{-2}$), the reactor was still able to achieve a 43% conversion efficiency for PCE utilizing Degussa P25 TiO_2 as a photocatalyst. Chen et al. postulated that if the price for UV LEDs continued to drop, that UV LED would eventually replace mercury vapour lamps as the preferred luminant for future photocatalytic degradation studies.

Griebenow et al. [274] studied the use of a customized ultraviolet LED batch reactor for the thiol-yne click reaction in a bioconjugation type process. Bioconjugation (i.e. the conjugation of small molecules with bioactive moieties) is a field of growing interest. However, despite the significant number of conventional conjugation techniques available (metal-catalyzed and metal-free), there are few photoconjugation methods available as alternatives. The photochemical thiol-yne click technique, in which thiols are conjugated to a functionalized alkyne, are one of these few photochemical options. In the experimental work, Griebenow et al. evaluated and optimized the operational conditions for the thiol-yne click reaction involving N-benzyloxycarbonyl cysteine as the thiol precursor together with

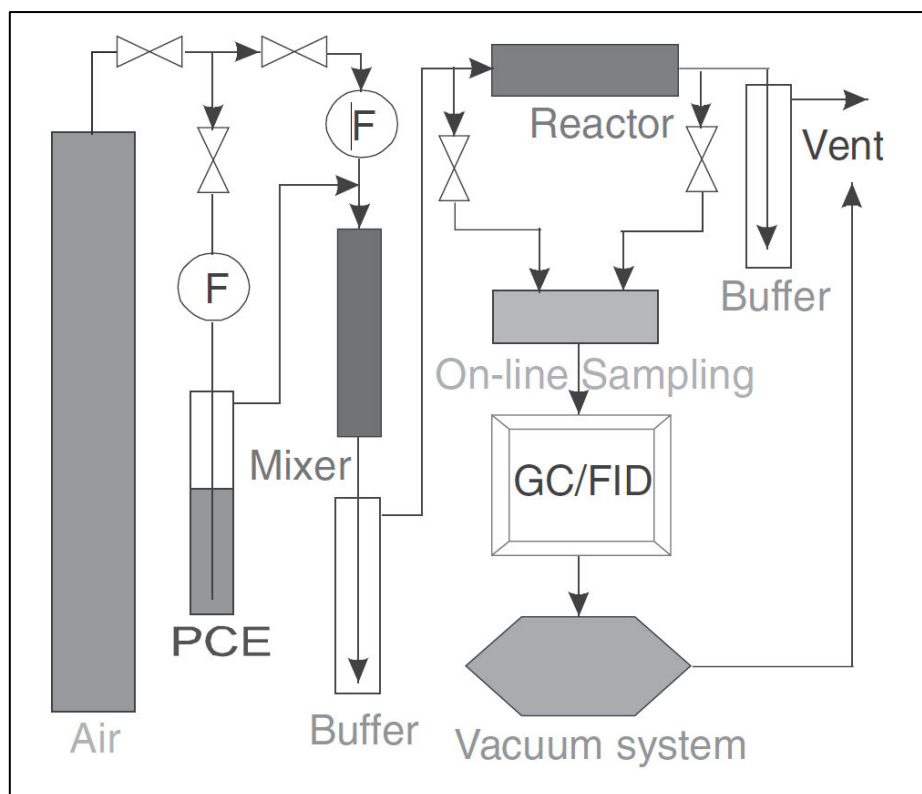


Figure 2.49: Schematic of Chen et al. single pass flow through reactor utilizing multiple ultraviolet LEDs as a light source for the photodegradation of perchloroethylene in an air waste stream [273]

various alkyne precursors and initiators for their UV LED batch reactor. They also optimized the concentration and stoichiometric ratios of the two precursors. They found that the final products and the proportional ratios in which they were generated were strongly influenced by the stoichiometric ratio and initiators used, and that higher conversion yields could be achieved by the correct choice of stoichiometry and initiator. In addition, the correct choice of stoichiometry and initiator could be employed to achieve a high conversion efficiency for preferably the mono-adduct, the bis-adduct, or disulfide adduct. In a final set of experiments, they evaluated a reduction reaction followed by the photochemical thiol-yne click reaction to insert 10-undecynoic acid into the disulfide bond of tris(2-carboxyethyl) phosphine (TCEP) via a one-pot insertion process. Conversion efficiencies of 49% were achieved. Overall, Griebenow et al. suggested that the photochemical thiol-yne click process using a UV LED batch reactor was viable and controllable.

Hölz et al. [275] investigated the proposed replacement of mercury vapour lamps (arc lamps) with a high powered UV LED (365 nm) for photolithography of DNA microarrays. In general, LEDs offer many benefits as an alternative light source over the more traditional luminants such as incandescent and mercury vapour lamps. However, the requirements for photolithography are considerably more

complex and stringent than for more general photochemical processes (e.g. waste stream remediation). Photolithography requires a very concentrated light source with high spatial resolution for whatever mask/pattern onto whichever solid substrate media it illuminates. The light generated by the compact electric arc of high pressure mercury arc lamps provides such a compact light source making such lamps the favoured luminant for photolithography. However, Hölz et al., proposed that the recent introduction of high powered gallium nitride UV LED's may provide an alternative to these high pressure mercury arc lamps. This is advantageous given the many disadvantages high pressure mercury arc lamps have. In experimental work undertaken by them, they were able to build a custom high powered UV LED lamp together with its power supply and control circuits. Although the high pressure mercury arc lamp has a higher power output than the UV LED (20 W for the mercury lamp versus 4 W for LED), the more compact UV LED ensured that higher proportions of its UV light (about 3% of luminant power) reached the DNA microarray than the high pressure mercury arc lamp (about 0.6% of luminant power). Thus the UV LED operated more efficiently as a light source. As regards the management of the power supply and control, the computer-regulated control circuit ensured that no excessive current passed through the LED, as well as a short controlled steady power up when energized and near instant shut down; both of which prevented damage to the LED. As regards heat management of the LED lamp, the options tested (conventional cooling with no fan, continuous operation of the fan, and Peltier thermoelectric control of the fan) showed that thermocouple-controlled cooling performed the best, but that the option of the fan continuously running was sufficient for the present lithographic operations. In subsequent work, the UV LED lamp served as the ultraviolet light source together with a digital micromirror device (DMD) as the key components in a precision optical imaging photolithography system employing a maskless array synthesis (MAS) process for the generation of the test DNA microarrays. The synthesis of the DNA microarray using 2-(2-nitrophenyl)propoxycarbonyl (NPPOC) and thiophenyl-2-(2-nitrophenyl)propoxycarbonyl (SPh-NPPOC) with the UV LED as the light source gave similar photolithographic performance during the synthesis as for the high pressure mercury arc lamp. For both lamp types, the optimal synthesis illumination intensity for NPPOC was 6 J cm^{-2} , and 0.5 J cm^{-2} for the SPh-NPPOC. Results showed this to be the case in both the ultraviolet (365 nm) part of the spectrum and the blue violet (400 nm) part of the spectrum. Thus, Hölz et al. proposed that the high powered gallium nitride UV LED was a viable alternative for high pressure mercury arc lamps. They also stated that UV LED offer advantages over high pressure mercury arc lamps such as better illumination efficiency, easier cooling, lower installation and operational costs, faster DNA microarray synthesis, much longer lifespans of the UV LEDs, a more than 85% reduction in electricity consumption, and the elimination of toxic mercury as a waste upon lamp disposal.

Jamali et al. [276] investigated the use of a batch reactor with a single ultraviolet LED lamp in the TiO_2 photocatalytic degradation of phenol. The aim of the study was to determine whether a UV LED lamp could replace mercury vapour lamps that are typically employed for such photocatalytic processes. In

this study, they evaluated the impact of the operational parameters of catalyst loading, catalyst type, phenol/hydrogen peroxide charge ratio and control of radiation power by pulse width modulation (PWM). They found that optimal conditions for their UV LED reactor design were: (i) 0.7 g l^{-1} for TiO_2 (with TiO_2 chosen over other semiconductor photocatalysts based on the research work of others), (ii) a molar H_2O_2 :phenol ratio of 100:1 with lower and higher ratios showing significantly less photocatalytic degradative performance, and (iii) an optimal pH of 4.8. The excessively "large" H_2O_2 :phenol ratio was due to peroxide serving the roles of both electron scavenger from the TiO_2 conductive band and phenol radical oxidant. Jamali et al. also found a near linear relationship between the radiant power level of their UV LED reactor and the rate of photocatalytic degradation. However, Jamali et al. have stated, other researchers have observed that when the radiant power is sufficiently excessive, recombination of the conduction band electrons and valence band holes becomes favoured [276]. Since this was not observed in this work, Jamali et al. proposed that their UV LED reactor is of low enough radiant intensity to avoid this detrimental effect. Lastly, Jamali et al. also found that increasing the distance between the UV LED and the phenol solution significantly reduced the efficiency of the photocatalytic degradation process. Under optimal conditions, Jamali et al. were able to achieve 42% photocatalytic degradation in 4 h employing a 120 degrees beam width. When the beam width was reduced to 40 degrees, the photocatalytic degradation increased to 87%. Thus, Jamali et al. proposed that UV LED lamps could be employed as alternatives to mercury vapour lamps in similar such remediation processes. In their concluding remarks, Jamali et al. indicated that further optimization of the reactor system was required.

Rajesh et al. [277] studied the use of a group of five supported ultraviolet LEDs for the photocatalytic degradation of methylene blue with TiO_2 . The UV LEDs were evaluated as an alternative to mercury vapour lamps that are commonly used in this role. In their experimental work, Rajesh et al. evaluated the impact of catalyst loading, initial dye concentration, pH, and the addition of hydrogen peroxide. Results demonstrated that for their UV LED reactor design the following observation could be made: (i) photocatalytic degradative efficiency increased with TiO_2 photocatalyst loading up to 1.2 g l^{-1} whereafter it decreased (due to excessive solution opaqueness and light scattering), (ii) photocatalytic degradative efficiency remained unchanged as the initial methylene blue concentration increased up to $31.2 \text{ }\mu\text{M}$ whereafter it decreased, (iii) degradative efficiency increased with pH value above a neutral $\text{pH} = 7.0$ with a maximum at a pH of 8.84 (negatively charged/biased surface of the TiO_2 photocatalysts formed under alkali conditions favour methylene blue adsorption to the catalyst surface facilitating photo reaction), and (iv) that the addition of hydrogen peroxide significantly increased degradative efficiency. At a peroxide concentration of 5 mM complete degradation was achieved within 2 h, while 10 mM allowed complete degradation to occur within 1 h; but no further improvement was observed at H_2O_2 concentrations above 10 mM. These results were also confirmed by COD and UV visible spectroscopy analysis. Rajesh et al. proposed that UV LED's could serve as viable alternatives to

mercury vapour lamps for the remediation of an aqueous stream contaminated with methylene blue within a reasonable load.

Wang and Ku [278] investigated the photocatalytic degradation of the dye reactive red 22 (RR22) utilizing a continuous flow through reactor circulating from a solution reservoir with an ultraviolet LED array as a light source and TiO_2 as the photocatalyst (which was coated onto a quartz pane which made up the one of the two quartz pane walls of the photoreactor). In general, given the large quantity of organic dyes used in multiple industries, the treatment and remediation of contaminated wastewater streams is a significant problems as such dyes are typically toxic and non-biodegradable in nature. In addition, RR2 is also known as a reactive dye, meaning that it is designed to actively covalently bond to the textile, etc., that it is dying to improve its colour fastness. This reactivity, further enhances its toxicity. A schematic of the reactor design employed by Wang and Ku is given in Figure 2.50 as well as the internal design of the reactor itself and its component layers in Figure 2.51. As part of their experimental work, they evaluated and optimized the operational parameters of: (i) initial dye concentration, (ii) luminant intensity, (iii) continuous versus periodic illumination, and (iv) arrangement of TiO_2 coating. In the experimental results they obtained, Wang and Ku observed that increased radiation intensity resulted in greater photodegradative activity. However, the reaction rate constant and photonic efficiency decreased as the initial dye concentration increased due to a larger portion of

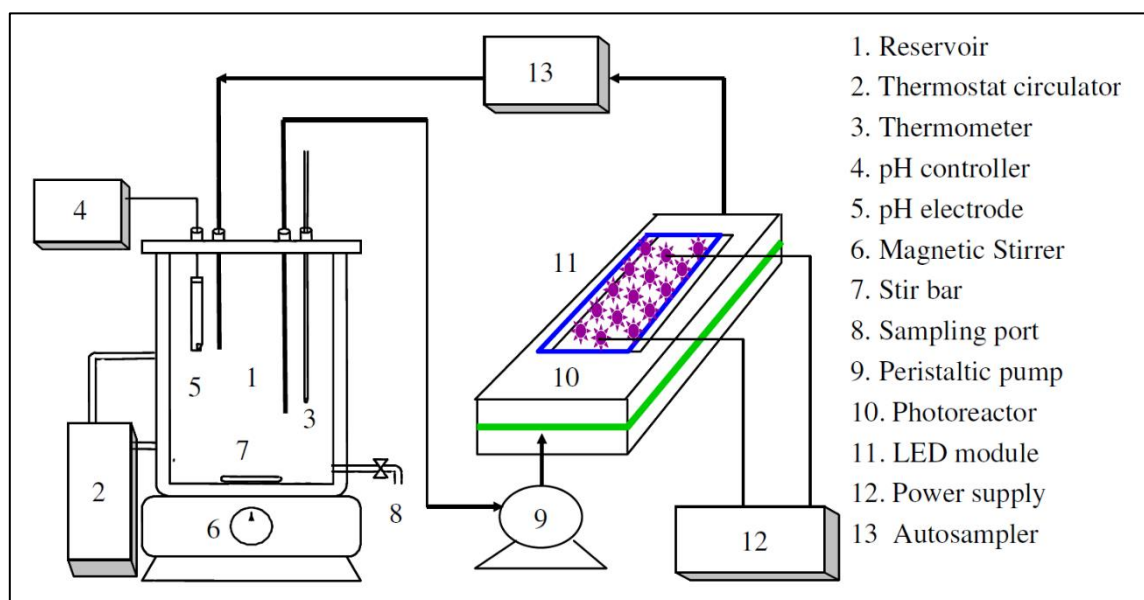


Figure 2.50: Schematic of Wang and Ku's continuous flow through UV LED array reactor with circulating solution reservoir for investigating the TiO_2 photocatalytic degradation of the dye reactive red 22 [278].

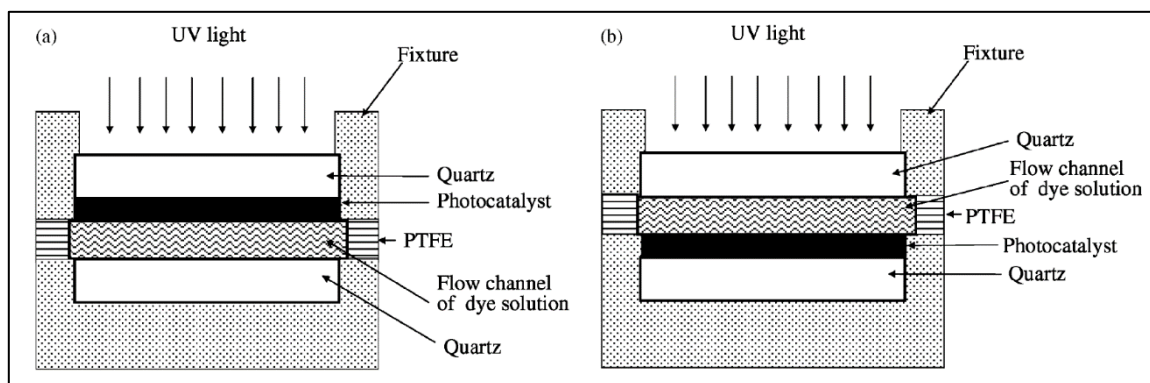


Figure 2.51: Internal design and components of Wang's and Ku's reactor vessel used to investigating the TiO_2 photocatalytic degradation of the dye reactive red 22 [278]

the catalyst surface became overloaded with dye. Application of periodic irradiation gave less photodegradation than continuous irradiation, though the periodic illumination was more photonic efficient than the continuous illumination. They found that the photonic efficiency of the quartz-catalyst-liquid reactor arrangement (radiant light struck the photocatalyst before reaching the dye solution) was lower than the opposing quartz-liquid-catalyst reactor arrangement (radiant light struck the dye solution before reaching the photocatalyst) at low luminant intensity, however, both arrangements showed not real differences at high luminant intensity. Overall, Wang and Ku were able to successfully degrade RR2 with their reactor design, with the reaction kinetics following a pseudo-first-order process based on a Langmuir-Hinshelwood mechanism (i.e. "hole"/electron pairs on the TiO_2 photocatalyst surface).

The main points that can be drawn from the LED literature that are relevant to this study are: (i) To consider the use of a LED array (i.e. multiple LEDs in a single array) over a single LED due the much higher power output of the former. The higher power output may be required to obtain significant bleaching in a reasonable length of time. (ii) Selection of the correct frequency of emission (typically in the near UV range of about 350 nm where the majority of photochemical reactions occur). (iii) Selection of the correct reactor design and experimental conditions to maximize irradiation during experiments. (iv) Adequate cooling of any LED array. (v) Evaluation of various photocatalysts and photosensitizers to facilitate photochemical reactions during experiments.

An overview of the available literature on the five light sources discussed prior: solar, mercury vapour lamps, lasers, MDELs, and LEDs shows that these five light sources have found notable application within many commercial fields with some of these types becoming widespread in application; as well as their use in a significant number of studies reported in the scientific literature. However, with high

powered UV LEDs and associated LED arrays having been made commercially widely available only recently from a number of suppliers, studies of their application for the photodegradation of LMCs and photochemical bleaching of pulps is almost completely lacking. The one purpose of this thesis was to address this lack.

MATERIALS AND METHODS

This chapter contains a description of the materials, the analytical techniques, the equipment and methods used in this post graduate thesis. It also lays out the design of experiment for each study and set of experiments undertaken.

3.1 *Methods for the analysis of test samples*

The lignin content of all pulps and their viscosities were both measured using the ISO international standard methods: ISO 302 (kappa number) and ISO 5351 (CED viscosity) respectively. The residual peroxide content in all filtrates was determined via an iodometric titration with sodium thiosulfate [279]. The residual peroxide was also used to calculate the peroxide consumption from the full charge employed. The brightness of pulps was measured by variants of the international standard methods: ISO 2469 and ISO 3688. The variants of this brightness method involve measuring at 457 nm (blue/violet parts of the spectrum) on hand sheets formed on the Rapid Köthen hand sheet former in the 2 degrees/C-filter mode, at 680 nm (red part of the spectrum) in the 2 degrees/C-filter mode on the same type of hand sheets, and on pulp hand sheets formed on a 15 cm Büchner funnel that were pH adjusted to 4.5 – 5.5 at 457 nm in the 2 degrees/C-filter mode. The shade parameters of the L, a, and b-values were measured on the same brightness hand sheets using the same instrument and instrument settings. The L-value is a measure of the luminance factor of the pulp, the a-value of the red to green shade factor, and the b-value of the yellow to blue shade factor. The carbohydrate makeup of the pulps and their alkali solubility analyses were also undertaken by methods based on international standards: SCAN-CM 71:09 and Tappi T235. The pulp testing handsheets formed by Papirindustriens Forskningsinstitut (PFI) pulp mill beating (Tappi T248), hand sheet forming (ISO 5269-2), and hand sheet conditioning (ISO 187), were tested using international standard methods: ISO 536 (grammage, bulk and thickness), ISO 1924 (total energy absorption, tensile, stretch and breaking length), ISO 2758 (burst), ISO 1974 (tear), ISO 5636-3 (porosity) and ISO 2417 (opacity) at variable Canadian Standard Freeness (Tappi T227). The viscose reactivity index was determined by the in house developed quick reactivity method [280] utilised by the Saiccor Centre of Excellence. The fibre morphology was determined using the Lorentzen and Weltre FT Plus fibre tester [281]. The pH was measured with an Ohaus starting series 3100 with a 3 in 1 combined pH and temperature probe. All sodium thiosulfate titrations were undertaken using a Titronic auto titrator. All consistencies were determined with an Ohaus MB25 moisture balance. Most weighing of pulps was done on a Mettler PM6000-F rough

balance, whereas all fine weighing was undertaken on a Ohaus Pioneer fine mass balance. Copies of the methods for the Fibre morphology and the Sappi quick reactivity index are given in Appendix A.

A more detailed description of the analytical methods mentioned above is given below:

Kappa Number

The lignin remaining within any pulp can be measured at any point of the pulping and bleaching process via the kappa number parameter utilizing the kappa number method. The kappa number is defined as: “... number of millilitres of 0.02 mol l⁻¹ potassium permanganate solution consumed under the specific conditions by one gram of pulp (calculated on an oven dry basis) ...” and is reported as a unitless number [282 and 283]. In the kappa number method, the lignin within the pulp was first completely consumed by reaction with a given excess of added permanganate over a specific period of time (10 minutes) for a given quantity of pulp. Thereafter, the remaining permanganate was converted into iodine (i.e. I₃⁻) by the addition of potassium iodide, and the iodine generated was back-titrated with a 0.2000 mol l⁻¹ sodium thiosulfate solution; which (together with a back-titrated permanganate blank with no pulp) was used to calculate the kappa number of the pulp (i.e. the quantity of permanganate consumed by the pulp).

Viscosity

The viscosity of pulp samples was measured by its dissolution within a cupriethylenediamine (CED) solution of known concentration [284]. After dissolution, under set conditions, the viscosity was measured and calculated using the efflux time of the dissolved pulp/CED solution out of a precalibrated custom CED capillary tube viscometer. This viscosity can be used to estimate the average level of polymerization of the carbohydrate chains within the pulp which gives a relative indication of the strength of that pulp. Thus, the higher a pulp's CED viscosity, the stronger the pulp is relative to others of the same type.

Brightness

The brightness and shade parameters of the pulp samples were measured on dry formed hand sheets of those pulps using a Technidyne Colour Touch attached to a PC for data storage. The Technidyne was calibrated according to the ISO international standard method: ISO 2469 [285]. The hand sheets used for testing kappa number were formed on either a Rapid Köthen hand sheet former (formed without pH adjustment of the pulp suspension) or a 15.0 cm Büchner funnel under suction using fast filter paper (formed with pH adjustment of the pulp suspension to a pH range of 4.5 to 5.5 to ensure maximal brightness performance for the pulp), before being air dried overnight under standard conditions of 23 ± 1 °C with relative humidity of 50 ± 2%, according to the ISO international standard methods: ISO187, ISO 3688, and ISO 5269-2 [286 - 288]. Unless specified, all brightness and shade measurements were

undertaken on the kappa number hand sheets formed on a Rapid Köthen hand sheet former (referred to as “R457 brightness”). When specified, the brightness and shade were measured on hand sheets formed specifically on a 15.0 cm Büchner funnel (referred to as “ISO brightness” in Sections 4.3.12 and 4.3.13). The brightness and shade parameters were measured at 457 nm (unless specified otherwise in the results) employing the CIE illuminant C filter, rather than the CIE illuminant D65 filter [289, 290].

Hand sheet properties

Pulp samples to be tested for hand sheet strength and other pulp properties (Section 4.3.12) were first weighed into four equal portions of known mass (i.e. 24.0 ± 0.25 g oven dry equivalent) and then beaten on a PFI mill at selected beating levels (nil, 2000, 4000, and 6000 revolutions) after which these beaten pulps were formed into hand sheets on the Rapid Köthen hand sheet former according to the International Standard methods: Tappi T248 and ISO 5269-2 [288 and 291]. After being formed, the hand sheets were conditioned overnight at 23 ± 1 °C with relative humidity of $50 \pm 2\%$ according to the ISO International Standard method: ISO 187 [286]. During hand sheet forming, the Canadian Standard Freeness at each beating point for each pulp was measured before being formed into hand sheets according to Tappi international standard method: Tappi T227 [292]. After forming, drying and conditioning of the hand sheets, the hand sheets were subjected to hand sheet testing at each beating point for the methods: moisture content (after conditioning); grammage, bulk and thickness; tensile, stretch, burst and tear strength; porosity; as well as selected optical properties.

- Canadian Standard Freeness

The Canadian Standard Freeness (CSF) is a measurement of the drainage properties of a pulp using the CSF Freeness Tester [292]. A given volume of a pulp suspension (three grams of pulp in 1000 ml of water) was added to the sealed Freeness Tester and its top lid closed and sealed. The air entrance valve on the top of this lid was opened whereafter the bottom of the tester was opened to allow the pulp suspension to drain through the fine sieve screen at the bottom of the tester. The drained water fell into the tester’s separation funnel landing on top of the inner separation cone. The water was drained out of the two exit tubes (one on the bottom and one on the side of the funnel below the cone). The water from the side tube was collected and measured as the Canadian Standard Freeness value (CSF) in millilitres. The drainage of a pulp suspension is characterized by its level of beating, temperature, inherent pulp characteristics, and condition of the tester (which is maintained in all tests). The CSF is typically employed as the defining parameter (i.e. the independent axis) for all hand sheet properties (i.e. the dependant axes) instead of the beating revolutions used at each beating point.

- Moisture content

The moisture was measured by first cutting the hand sheets into pieces of a given size and weighing the hand sheet pieces before being dried in an oven at 105 °C for 120 minutes according to the ISO international standard method: ISO 638 [293]. After drying, the oven dry/bone dry pieces were reweighed and the masses before and after drying were used to calculate the handsheet moisture content.

- Grammage, thickness and bulk

The grammage was measured by cutting a stack of multiple hand sheets of the pulp sample to a specific size using a pre-existing mask. The stack of cut pulp samples was then weighed to calculate the grammage when the area of the mask and the number of sheets are accounted for according to the ISO international standard method: ISO 536 [294]. The grammage is reported on the basis of both the conditioned mass (about 5% moisture) and oven dry/bone dry mass (nil moisture). The thickness and bulk of the hand sheets was calculated using a micrometer for thickness and a balance for mass according to the ISO international standards method: ISO 534 [295].

- Tensile, stretch, breaking length and total energy absorption

The tensile, stretch, breaking length, and total energy absorption strength properties of the handsheets of a pulp sample were all determined using the Testometric Tensile Tester No. PT/E 301B according to the ISO international standard method: ISO 1924 [296 and 297]. By definition: the tensile strength is "... The maximum force per unit width that a paper strip tested under prescribed conditions will stand before breaking ...", the stretch is "... The ratio of the measured elongation at the moment of rupture of a paper specimen, when extended under the prescribed conditions, to the initial test length ...", the breaking length is "... the ratio of the measured elongation at the moment of rupture of a paper specimen ...", and the total energy absorption is "... The work done when a paper specimen is broken under prescribed conditions ..." [298]. A test hand sheet piece (having been cut to precise dimensions) was placed between the two clamp jaws of the tensile tester and clamped into place. During testing the distance of separation between the two clamps increased at the same given rate until the piece of hand sheet physically failed/broke. Upon failure of the piece of hand sheet, the tester provided the tensile, stretch, breaking length, and total energy absorption as read-out results.

- Burst

The burst strength properties of handsheets of a pulp sample were determined using a Burst Tester according to the ISO international standard method: ISO 2758 [299]. By definition, the burst strength is "... maximum pressure developed by the hydraulic system in forcing an elastic

diaphragm through a circular area of the paper ...” [299]. During testing of the burst strength, a sample hand sheet was first clamped into place after the rubber bladder has been deflated. The bladder was then inflated until the paper failed/burst with the pressure at which the burst occurred used to calculate the burst strength of the paper.

- Tear

The tear strength properties of hand sheets of a pulp sample was determined using a Elmendorf type tear tester according to the ISO international standard method: ISO 1974 [300]. By definition, the tear strength is “... The mean force required to continue the tearing started by an initial cut in a single sheet of paper (or board)...” [300]. For tear strength testing, the hand sheets were cut into precise dimensions and secured in the two clamps of the tear tester after the plane quarter circle pendulum had been moved back into its starting position. Thereafter, a small cut was made in the hand sheet pieces where the tear action was to initiate from. Upon starting the actual tear strength test, the pendulum was released to swing freely from its starting position and perform the tearing action while the work done to tear the paper was measured as the loss in the pendulum’s potential energy. This was used to calculate the tear strength of the pulp hand sheet.

- The mean flow of air through paper (i.e. porosity)

The mean flow of air through paper (porosity) was measured using the Bendtsen apparatus according to the ISO international standard method: ISO 5636-3 [301]. Before testing, the hand sheet was cut into given precise dimensions and clamped into position in a circular gasket with a flat annular surface below it. Compressed air that was slightly above atmospheric pressure was passed through the hand sheet piece at a controlled rate and the measured flow rate through the hand sheet piece was used to calculate the porosity of the pulp hand sheet.

- Diffuse blue reflectance and opacity

This was exactly as the same method used to measure the R457 brightness on the kappa number hand sheets, but used the PFI mill hand sheets and the Technidyne ColorTouch colorimeters employed by the Paper Science department, the sister department at Sappi (Pretoria), to whom this analysis was outsourced too. For opacity, the same equipment setup for the R457 brightness on PFI mill hand sheets was employed, however, the opacity measurement of the hand sheets with and without the specifically supplied “black box” black cavity container behind the hand sheet was employed according to the ISO international standard method: ISO 2471 [302]. The opacity was calculated as the ratio of these two opacity factors.

Alkali solubility

The combined content of degraded cellulose and hemicellulose, and the mostly hemicellulose only content of a pulp can be separately determined via the alkali solubility method in which these pulp fractions are specifically dissolved out of the pulp using 10% (S_{10}) and 18% (S_{18}) caustic soda solutions respectively according to Tappi international standard method: TAPPI T235 [303]. Both the S_{10} and S_{18} determinations employ the exact same analytical technique, except that the S_{10} method uses 10% caustic soda and the S_{18} method uses 18% caustic soda to dissolve their respective fractions. For the analysis, the pulp samples were incubated for about 60 minutes at about 20 °C in either caustic soda solution separately before being filtered through G3 filter funnels under vacuum. The filtrates from both caustic soda filtrations were then treated with a given excess of potassium dichromate solution to oxidize the carbohydrate contents before the remaining dichromate was converted into iodine (I_3^-) by the addition of excess potassium iodide. The iodine generated was then back-titrated with a 0.2000 mol l^{-1} sodium thiosulfate solution, which (together with back-titrated caustic soda blanks with no pulp) was used to calculate the alkali solubilities (S_{10} and S_{18} values) for the pulp.

Carbohydrate content determination

The carbohydrate content of the pulp samples was determined by a high performance anion exchange chromatography method with a pulsed amperometric detector (HPAEC-PAD) [304]. The first step in the process was the hydrolysis/“digestion” of the pulp into its monosaccharide sugars using 72% sulfuric acid in crimped sealed serum bottles in an autoclave at 121 °C for 60 minutes [304]. Immediately after the digestion, the samples in crimped sealed serum bottles were removed, allowed to cool to 90 °C, and then diluted further (1:9 suggested) to prevent further breakdown of the monosaccharide sugars into smaller molecular fragments. The final dilute and digested pulp monosaccharide samples were then introduced into the HPAEC-PAD to determine and calculate the carbohydrate content of the pulps using prior run internal standards of certified reference materials of the monosaccharide sugars of interest.

Fibre morphology

The fibre morphology of the pulp samples was determined using a Lorentzen and Woltre FT Plus fibre tester [281]. The pulp sample were first diluted to a 0.1% consistency using the pulp consistency (i.e. equivalent dry mass content) before being feed to the Lorentzen and Woltre FT Plus fibre tester which provided the fibre morphology and the fibre distribution of its fibre population.

Quick reactivity index

The quick reactivity index is used to measure the quantity of recovered fibre content within a viscose grade dissolving pulp by simulating the commercial viscose dope making process [280, 305]. A high recovery of the fibre from the pulp indicates a poor performing dissolving pulp which is reflected in an

elevated quick reactivity index. In the first step, the mercerisation process was simulated by steeping the pulp in a 18% caustic soda solution for 60 minutes at room temperature. Thereafter, any excess 18% NaOH solution was removed by draining and squeezing the pulp to a given narrow range of pulp masses which were crumbled into pulp bits. This was followed by the xanthation process (the second commercial step) in which the pulp was dissolved in 14% caustic soda solution in the presence of carbon disulfide (CS₂) with continuous shaking for 3 h; giving a xanthate type dope. In the third step, the xanthate was transferred to a dilute caustic soda solution (1 mol l⁻¹) and washed using serial dilutions in conjunction with a centrifuge, producing a clear viscose dope as the removed supernatant. In the fourth step (the commercial viscose fibre reconstitution step), the clear viscose dope was treated with 10% acetic acid and allowed to age for 1 h. In the last step of the analytical method, the recovered fibres were filtered on a G3 filter, washed and dried. The measured recovered fibre mass in the G3 filter was then used to calculate the quick reactivity index.

3.2 *Statistical methods*

Statistical methods of the comparative T-test (T_c or t_c) and the analysis of variance (ANOVA) were employed to review parts of the data obtained [306, 307]. In addition, in view of undertaking these analyses on certain data obtained, which could not be so analysed due to having significant different starting positions, the statistical method of linear transformation or Z-score transformation was employed to "normalize" the data around its z score parameters for the raw data obtained and so allow the subsequent aforementioned statistical analyses [308].

3.2.1 *The comparative T-test method*

The Student T-test is a statistical method employed to determine whether two sets of data are significantly different or not from each other based on a given null hypothesis. When comparing two sets of independent data, a given variant of the T-test known as the comparative T-test is employed. This operates under the assumption that if the standard deviations of both independent data sets are not too different, then the estimated standard deviation of the two pooled means can be estimated for the global population by the Equation (1) where "σ_i" is the global standard deviation, "n_i" is the sample size, and "x̄_i" is the global mean for data set "i":

$$\sigma_{\bar{x}_1 - \bar{x}_2} = \sqrt{\frac{\sigma_1^2}{n_1} + \frac{\sigma_2^2}{n_2}} \quad (1)$$

However, given that the standard deviations of neither global populations are known, then the standard deviations of both sample populations can be employed instead to estimate the standard deviation of

the two pooled sample means by Equation (2) where “ S_i ” is the sample population standard deviation, “ n_i ” is the sample population sample size, and “ $\bar{x}_i$ ” is the sample population mean for data set “i”:

$$S_{\bar{x}_1 - \bar{x}_2} = \sqrt{\frac{S_1^2}{n_1} + \frac{S_2^2}{n_2}} \quad (2)$$

This then allows the comparative T-test value/Tc-value for the pooled data sets to be calculated according to Equation (3):

$$t_c = \frac{(\bar{x}_1 - \bar{x}_2)}{\sqrt{\frac{S_1^2}{n_1} + \frac{S_2^2}{n_2}}} \quad (3)$$

The T-test score replaces the Z-score value when comparing two sets of data for being significantly different employing T-tables for student T distributions.

3.2.2 Analysis of variances

The analysis of variance (i.e. ANOVA) is a broad grouping of statistical methods used to analyse the statistical differences between the means of different sample groups with a view to determine whether they are significantly different from each other or not based on a given null hypothesis. Although both the Student T-test and the ANOVA methods can be used to determine whether two sets of data are significantly different or not from each other, the ANOVA method also has the benefit of being able to provide considerably more useful information. A full ANOVA analysis is typically undertaken in two steps: in the first step a one way ANOVA F test compares the grand means for both sample populations to determine whether both sample populations are generally significantly different or not, and in the second step (assuming that the one way ANOVA F test or similar shows both populations to be significantly different) an analysis via a multiple comparison procedure is undertaken (of which the Tukey analysis is one such method). The Tukey analysis separately compares pairs of means of both populations (i.e. $\bar{x}_i$ versus x_j) across both specified ranges of data collection to determine where the two sample populations are significantly different and where they are not. This provides additional useful information about both sample populations when so comparing both.

- One way ANOVA F test

The one way ANOVA F test uses the sum-of-squares and the mean-of-squares of its factor (treatment) and error components of the sample populations to determine the statistical differences between the

means of the sample populations. The parameters of the sum-of-squares of treatments/factors (SSTr), the sum-of-squares of errors (SSE), the mean-of-squares of treatments/factors (MSTr), and the mean-of-squares of errors (MSE); as well as the grand mean ($\bar{\bar{x}}$) can be calculated by Equations (4 to 8):

$$SSTr = n_1(\bar{x}_1 - \bar{\bar{x}})^2 + n_2(\bar{x}_2 - \bar{\bar{x}})^2 + n_3(\bar{x}_3 - \bar{\bar{x}})^2 + \dots + n_k(\bar{x}_k - \bar{\bar{x}})^2 \quad (4)$$

$$SSE = \sum_{f=1}^{n_1} (x_{1f} - \bar{x}_1)^2 + \sum_{f=1}^{n_2} (x_{2f} - \bar{x}_2)^2 + \dots + \sum_{f=1}^{n_k} (x_{kf} - \bar{x}_k)^2 \quad (5a)$$

or

$$SSE = (n_1 - 1)S_1^2 + (n_2 - 1)S_2^2 + (n_3 - 1)S_3^2 + \dots + (n_k - 1)S_k^2 \quad (5b)$$

$$MSTr = \frac{SSTr}{(k-1)} \quad (6)$$

$$MSE = \frac{SSE}{(n-k)} \quad (7)$$

$$\bar{\bar{x}} = \left(\frac{n_1}{n}\right)\bar{x}_1 + \left(\frac{n_2}{n}\right)\bar{x}_2 + \left(\frac{n_3}{n}\right)\bar{x}_3 + \dots + \left(\frac{n_k}{n}\right)\bar{x}_k \quad (8)$$

These equations typically are employed to complete the details of a variance table for ease of analysis (Table 3.1). The variance table components are then used to calculate the F factor Equation (9) of the sample populations which, based on a given confidence level (α value), are used to estimate the probability factor (P value) from the associated F tables employing the related degrees of freedom for factors/treatments ($k - 1$) and errors ($m = n - k$) with “n” being the total sample population size, and “k” being the number of factors/treatments.

$$F = \frac{MStr}{MSE} \quad (9)$$

Table 3.1: Variance table generated by the sum-of-squares and mean-of-squares of treatments/factor and errors of sample populations.

Source of variation	Degrees of freedom	Sum-of-Squares	Mean-of-Squares	F factor	P factor
Factors (between samples)	$k - 1$	SSTr	MSTr	MSTr / MSE	P
Error (within samples)	$m = n - k$	SSE	MSE	-	-
Total variation	$n - 1$	SST	-	-	-

If the F factor value is found to be larger than the P factor value, then the null point hypothesis is considered to not be valid, and the sample population means are considered to be significantly different.

- Tukey: multiple components

When comparing pairs of means within the sample populations, the Tukey analysis is used to determine which pair of sample population means are significantly different from each other, and which are not. The Tukey analysis does this by comparing the size of the difference between the two mean pairs (i.e. absolute difference) to a threshold value (T value) at a given confidence level (α value). The threshold T value can be calculated from the mean-of-square for the error components and sample sizes Equation (10) with “ n_i ” being the sample size, and “ q_α ” being the value drawn from the studentized range distribution.

$$T = q_\alpha \sqrt{\frac{MSE}{n_i}} \quad (10)$$

Where the mean difference (i.e. $\bar{x}_i - \bar{x}_j$) is larger than the threshold value (i.e. T value) the two means are considered to be significantly different.

As regards physically representing the findings of a Tukey analysis in a graph or similar, a common technique used is to represent the means that are not significantly different as linked by a horizontal bar in the figure with the individual means (given on the independent x axis) arranged in an ascending or descending order.

3.2.3 *Linear transformation (Z-score transformation)*

Linear transformation or Z-score transformation is a statistical technique used to “normalize” two sets of raw data measured for two completely different analytical parameters or the same analytical parameter from two significantly different starting positions. The technique involves converting each data set to its Z-score values using each data set’s mean and standard deviation in conjunction with the simple linear equation: $y = mx + c$ as its basis. In the conversion, values must be employed for each data set’s line equation variables (i.e. m and c variables) such that each data sets’ mean gives a value of zero (i.e. 0) and each data sets’ standard deviation gives a value of one (i.e. 1). In the case where the same analytical parameter is measured, but at significantly different starting positions, the slope of the line equations (i.e. variable m) assume a value of 1.0 (provided that both data sets have the same response coefficient for the same analytical parameter) while the intercept points of the line equations (i.e. variable c) assume the starting value of their respective data sets. This technique is known as standardizing or reducing to z-scores. In this thesis, to complete the “normalization” process for both data sets, the starting values for each sample population were subtracted from the respective data sets to give a relative starting value for both of zero. An example of this “normalization” are the batch 1 and batch 2 of the unbleached starting pulp used in much of this thesis which had starting kappa numbers of 12.01 and 10.98 respectively, but were both normalized to relative starting kappa numbers (“normalized”) to zero where relevant in this thesis.

3.3 *Materials*

A variety of starting pulps were employed during the experimental work, with specific pulps used for the investigation of selected topics and sets of experiments.

For the study on solar bleaching, the starting pulp was a semi-bleached Kraft Aspen furnish, taken after the double-stage oxygen delignification reactor at the Sappi Cloquet mill (USA) during a paper grade run. This pulp was washed with deionized water as well as being made pH neutral at the Sappi Technology Centre in Pretoria, before being spun in a SV-10 pilot Rouselette centrifuge, whereafter it was crumbled. The kappa number and viscosity of this starting pulp was 8.02 and 997 ml g⁻¹ respectively.

For the studies which employed a MDEL and UV LED array as light sources, the starting pulp was unbleached Aspen kraft hardwood pulp (i.e. post-pulping digester) sampled from the Sappi Cloquet mill during later paper grade swing runs. This pulp was sampled twice in two separate batches from the Cloquet mill about a year apart, as the first pulp batch was exhausted before the planned experimental work was completed. Both batches were washed with deionized water at the Sappi Technology Centre in Pretoria upon arrival, before being spun in a SV-10 pilot Rouselette centrifuge, whereafter they were separately crumbled. The kappa number and viscosity of the first unbleached

batch of starting pulp was measured as 10.84 and 1096 ml g⁻¹ respectively, while the kappa number and viscosity of the second batch was measured as 12.03 and 1102 ml g⁻¹. The first pulp batch was employed in studying the use of MDELs for photobleaching; and the use of UV LEDs for the topics of peroxide bleaching, oxygen bleaching, impact of pH, impact of temperature, impact of power levels, and the initial evaluation of selected photocatalysts and photosensitizers. The second batch was employed to complete a more in-depth study of a selection of these photocatalysts and photosensitizers as well as the impact of variable photobleaching consistency.

The second Cloquet Aspen batch was also employed in studying a full thermophotobleaching sequence for paper grade pulps in a comparison to a conventional bleaching sequence. For the study of bleaching a dissolving viscose grade pulp via a full thermophotobleaching sequence, unbleached acid sulfite dissolving viscose-grade pulp from Sappi Saiccor mill, sampled during one of their viscose grade dissolving pulp runs, was employed. This pulp was washed with deionized water at the Sappi Technology Centre in Pretoria, before being spun in a SV-10 pilot Rouselette centrifuge, whereafter it was crumbled. The kappa number and viscosity of the unbleached starting pulp were measured as 8.24 and 722 ml g⁻¹, respectively after washing.

The starting pulps for the study of photobleaching of various different pulps were the aforementioned Cloquet unbleached Aspen kraft from the first batch sampled (hardwood paper grade), a Ngodwana pre-hydrolysis kraft (PHK) pulp (sample ID: Demo Cook 146 B), a Stanger bagasse mill pulp, a Saiccor dissolving viscose-grade mill pulp, a Gratkorn mill pulp, and a Somerset mill pulp. The starting kappa number and viscosities are given in Table 3.2. All pulps were unbleached out of their respective mill digesters which represented the following pulping technologies: kraft pulping of Aspen (Cloquet), prehydrolysis Kraft dissolving pulping (Ngodwana), soda pulping (Stanger), acid sulfite pulping (Saiccor), magnefite pulping (Gratkorn), and continuous digester kraft pulping of a mostly hardwood blend (Somerset), respectively. These different pulps were selected due to the different starting fibre sources and pulping processes they represent, so as to provide an approximate broad collection of the various fibre sources available globally. The Saiccor pulp in the variable starting pulp study was not the one used in the study on the thermophotobleaching sequence. The Ngodwana and Stanger mill pulps were screened and washed to remove the large residual cooking liquor left in the pulps after pulping. The Cloquet, Saiccor, Gratkorn and Somerset pulps were used as supplied by the respective mills given that they were mostly already washed clean when supplied by those mills. All pulp storage was undertaken in a cold room at about 3.0 °C.

Table-3.2: Kappa number and viscosity of various different starting pulps for the UV LED photobleaching study.

Sample Pulp designation	Pulping Process	Kappa Number	Viscosity / CED (ml g ⁻¹)
Cloquet Aspen kraft	Batch kraft (paper grade / first batch)	10.84*	1096*
Ngodwana PHK pulp	Pre-hydrolysis kraft (dissolving pulp)	6.63	900
Stanger bagasse mill pulp	Soda (paper grade)	14.07	710
Saiccor dissolving viscose grade mill pulp	Acid sulphite (dissolving pulp)	5.47	694
Gratkorn mill pulp	Magnefite (paper grade)	23.20	987
Somerset mill pulp	Continuous kraft (paper grade)	16.19	1078

NOTE: *Starting kappa number and viscosity (CED) as for unbleached Aspen kraft hardwood pulp sampled from Sappi Cloquet mill during paper grade swing runs at the mill

The reagents used: caustic soda (sodium hydroxide), hydrogen peroxide, potassium permanganate, sodium thiosulfate, starch (indicator), potassium iodide, cupriethylenediamine (CED), and sulfuric acid were all analytical grade reagents as supplied by Merck/NT and Rochelle Chemicals. The oxygen was supplied in large gas cylinders by Air Products as commercial grade oxygen. The semiconductor photocatalysts (i.e. titanium dioxide/TiO₂, cerium dioxide/CeO₂, bismuth trioxide/Bi₂O₃, tungsten trioxide/WO₃, and zinc oxide/ZnO) and photosensitizers (i.e. rose bengal and methylene blue) were supplied by Sigma Aldrich as chemically pure (>99%) reagents. Filter paper was supplied by Commercial Papers SA (fast filter paper Grade F-60WS).

All glassware and laboratory equipment were standard laboratory grade as supplied by Chembiz, Merck/NT, Rochelle Chemicals and Sigma Aldrich. The MDEL was a Primarc MDEL purchased from Primarc UV curing lamps. The UV LED array was a 365 nm 8 W cm⁻² UV LED array purchased from the Hong Kong UVet Company. For the conventional thermal bleaching stages, the oxygen delignification and pressurized alkali extraction stages were undertaken in a Quantum Mixer from Quantum Technologies, while the ozone stage was performed in a modified rotary evaporator reactor attached to an ozone generator, and the bleaching stages for the thermal elemental chloride free (thermal ECF) and total chlorine free (TCF) sequences (Sections 4.3.12 and 4.3.13) were undertaken in thick-walled polypropylene plastic bottles with the use of a water bath.

3.4 *Solar bleaching of pulps*

All controls and experiments were performed at 0.5% consistency and room temperature ($\sim 25\text{ }^{\circ}\text{C}$) with a caustic soda charge of 15.0 kg t^{-1} [309]. The mass of pulp employed was 10.0 g in each experiment, but was reduced to about 7.0 g in later experiments to save on the total mass of pulp used. The contents of each experiment were constantly stirred with a magnetic stirrer and follower (i.e. magnetic stirrer bar) at a moderate speed to prevent the ingress of small air bubbles (to avoid unwanted diffraction or refraction in solution). Each set of controls and experiments were placed together, side by side, on a laboratory window. The controls were not exposed to sunlight due to being completely covered over with thick brown paper, while the experiments were exposed to sunlight as a light source due to being uncovered. This side by side approach also minimized any temperature differential between the controls and experiments. However, this resulted in each photochemical experiment being separated from its light source (i.e. sun) by two layers of glass, which would have filtered out a significant portion of the light at wavelengths below about 300 nm (i.e. ultraviolet range), and the extent of this attenuation was unknown. As sunlight at sea level, has wavelengths down to 295 nm , some of the most energetic wavelengths of sunlight would have been filtered out in this trial. All controls were performed exactly as the experiments, but completely darkened from any light source, while all experiments were undertaken in clear Pyrex glass conical flasks. The experimental conditions that were varied during these parallel runs were retention time (0.0 to 5.0 days), hydrogen peroxide charges (0.0 or 60.0 kg t^{-1}) and the use of different additives (nil or 5.0 kg t^{-1} as Al_2O_3 , CaCO_3 , MgO or TiO_2). At the end of a run, the pulps were separated from their bleach solutions before being washed and prepared for pulp analysis. All pulp suspensions remained alkaline throughout the investigation, regardless of charge or retention time (i.e. $\text{pH} > 9.5$).

3.5 *Microwave discharge electrodeless lamps*

Various MDEL reactor designs were considered and evaluated for their general performance and operational effectiveness in this extended qualitative study [310]. During this study, all testing of ignition times were undertaken in triplicate. Generally, ignition times that were notably different from the other repeats (i.e. outliers) in the triplicate analyses were not retested, but were excluded from the final discussion around the data obtained to avoid clear experimental error-based bias.

3.5.1 *Primarc commercial UV curing lamp: General performance and operational testing of unattached and unshielded (“naked”) MDEL*

To evaluate the general performance and operation of the Primarc MDEL (Figure 3.1) on its own, testing was undertaken using the Roto SYNTH microwave oven with the MDEL placed inside a 250 ml glass breaker while on top of a Teflon block inside the oven cavity. During testing, the sustained ignition times to a maximum of 70 s at variable microwave power levels, from 100 W to 1200 W , were recorded.

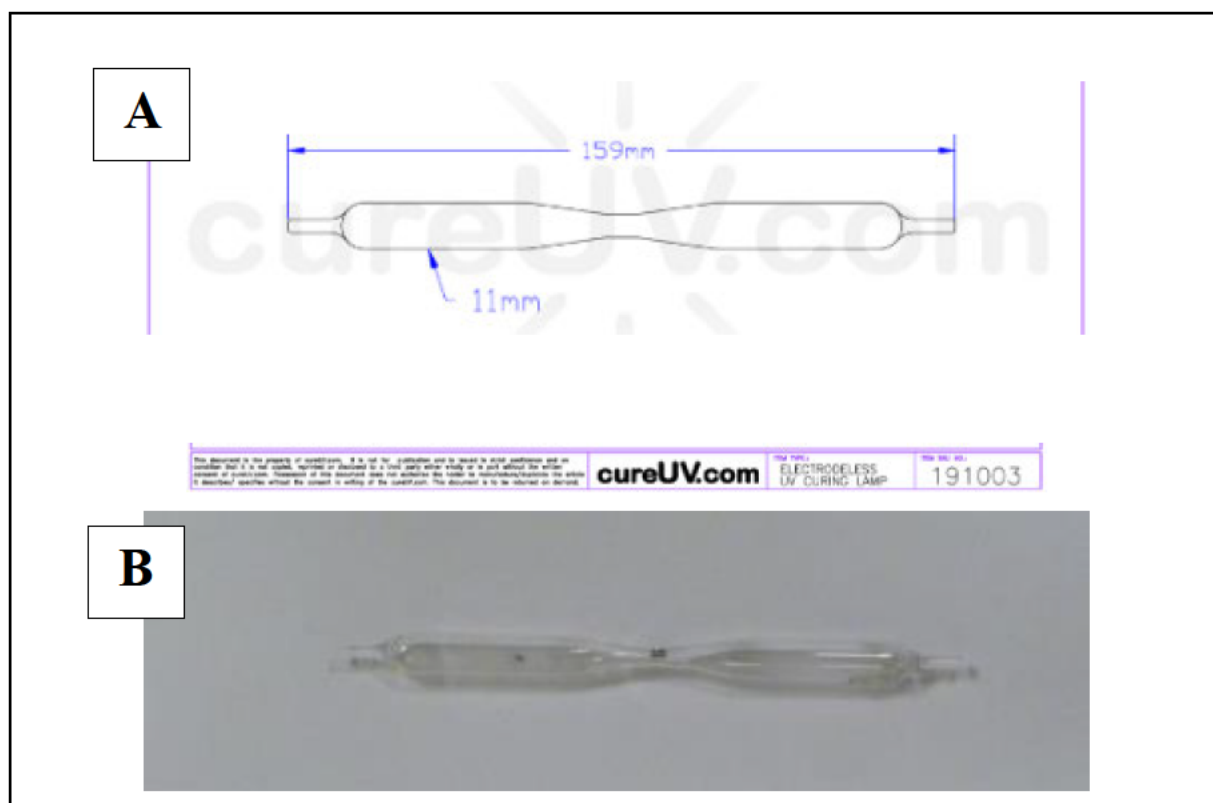


Figure 3.1: [A] Schematic and [B] photograph of a Primarc UV curing lamp containing mercury iodide (MDEL) [16].

3.5.2 Reactor design: Roto SYNTH, MDEL, round flat-bottomed flask combination

The first MDEL reactor design tested was a Roto SYNTH/MDEL/round flat-bottomed flask combination [311] (Figure 3.2). The Primarc MDEL used was secured within the Roto SYNTH/MDEL/round flat-bottomed flask combined reactor via a custom made Plexiglass MDEL cradle which was held in place with a screw on a GL25 open plastic cap. The Primarc MDEL was evaluated for first sustained ignition over an irradiation period of no more than 70 s within the Roto SYNTH/MDEL/round flat-bottomed flask combined reactor at a continuous microwave power level of 1200 W at variable levels of water content.

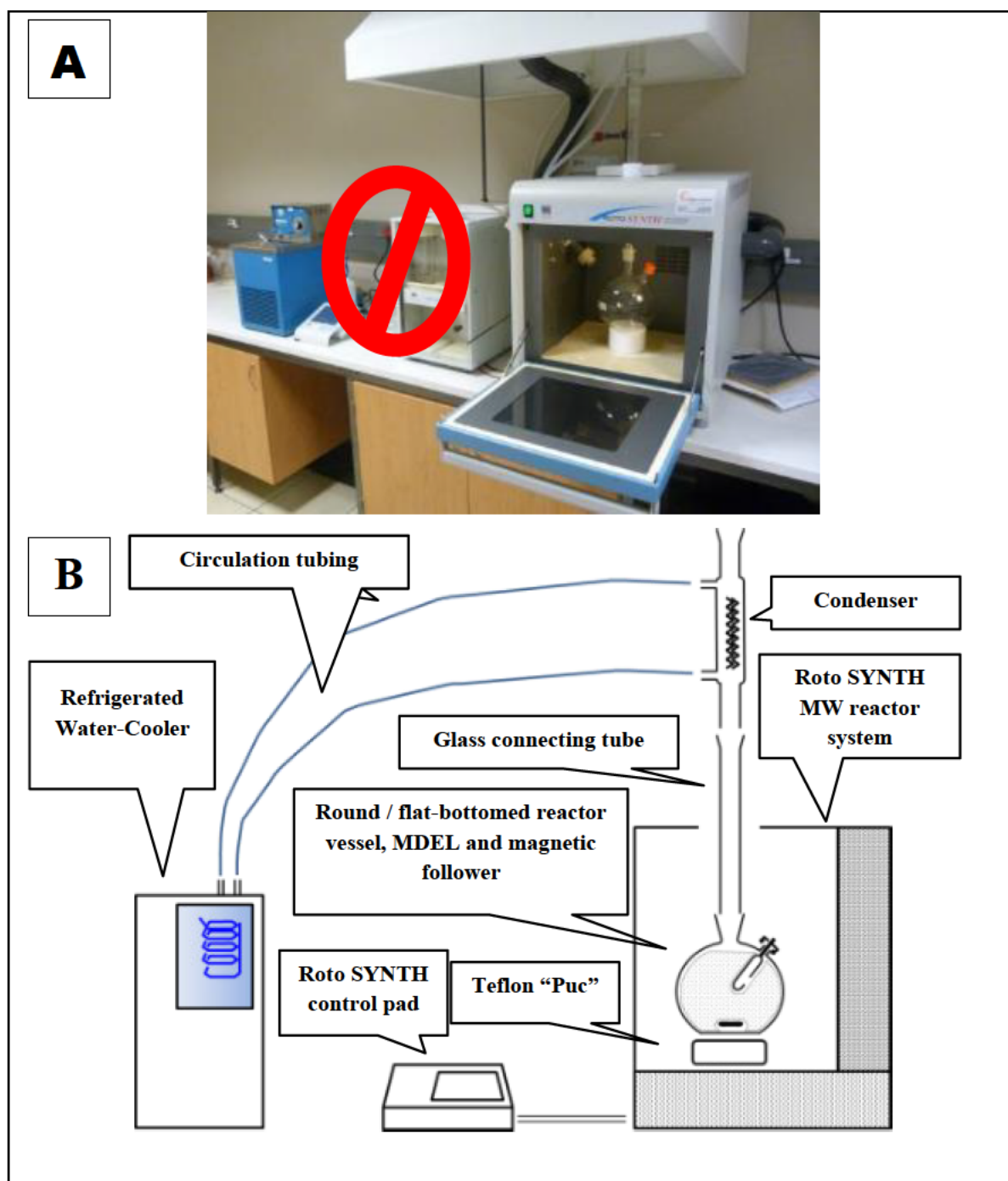


Figure 3.2: [A] Photograph and [B] schematic of the Roto SYNTH microwave MDEL apparatus setup used in this study. *The gas trap (crossed out in Figure 3.2A), although attached to the apparatus, was not used in this study.*

3.5.3 Reactor design: Immersed sleeve

Observations around the performance of the aforementioned Roto SYNTH/MDEL/round flat-bottomed flask combined reactor (specifically problems around lamp ignition) led to a subsequent qualitative investigation into the shielding effects of water surrounding a Primarc MDEL in an immersed sleeve reactor design (Figure 3.3). Two glass beakers of variable diameter were used (40.0 mm and 80.0 mm)

in combination with a test tube of fixed size (20.0 mm) for the immersed sleeve reactor. The MDEL was placed within the test tube once it had been secured in the relevant beaker filled with water. Microwave power levels were 1200 W for a maximum of 70 s. The sustained ignition times were recorded upon microwave irradiation.

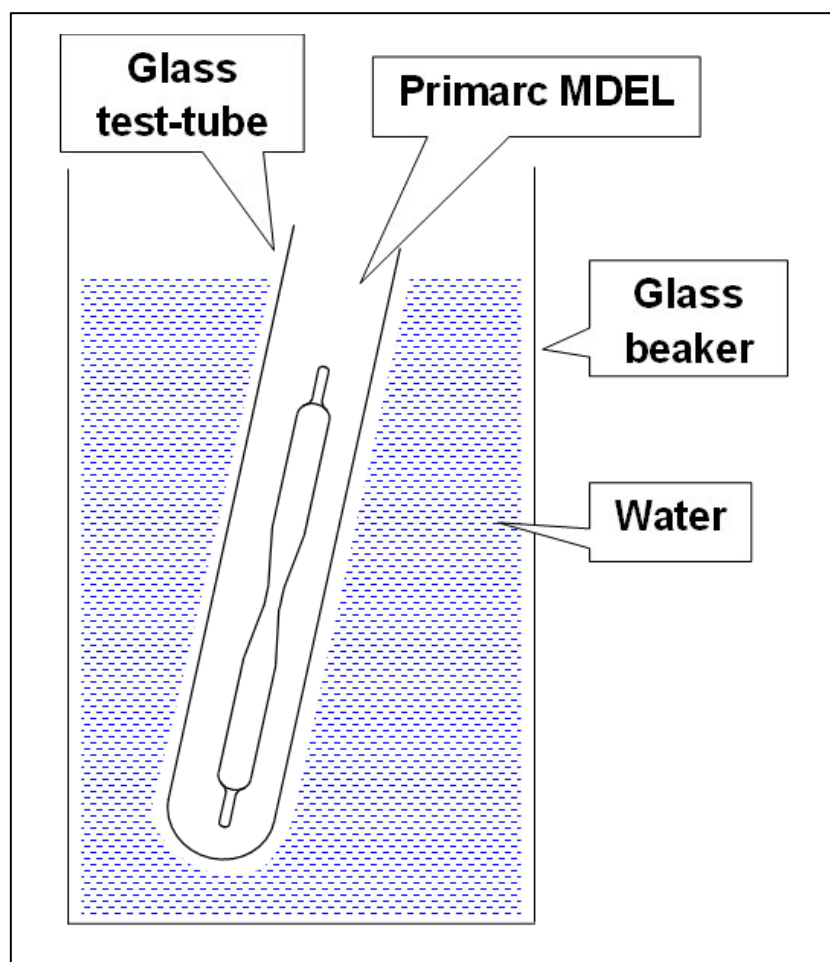


Figure 3.3: Schematic of Primarc MDEL within an immersed sleeve reactor design.

3.5.4 Reactor design: MDEL core, tubular coil combination

Previous observations around the performance of the Roto SYNTH/MDEL/round flat-bottomed flask combined reactor also led to a further investigation involving the use of a proposed MDEL core/tubular coil combination reactor design (Figures 3.4 and 3.5). For this investigation, a glass tube for the MDEL core/tubular coil combination reactor within which the MDEL core was secured, was 200 mm in length with a 30 mm diameter. The silicone tube, used in the qualitative investigation, that was wrapped around this glass tube had an outer diameter of 12.5 – 13 mm with an inner diameter of 10 mm, and

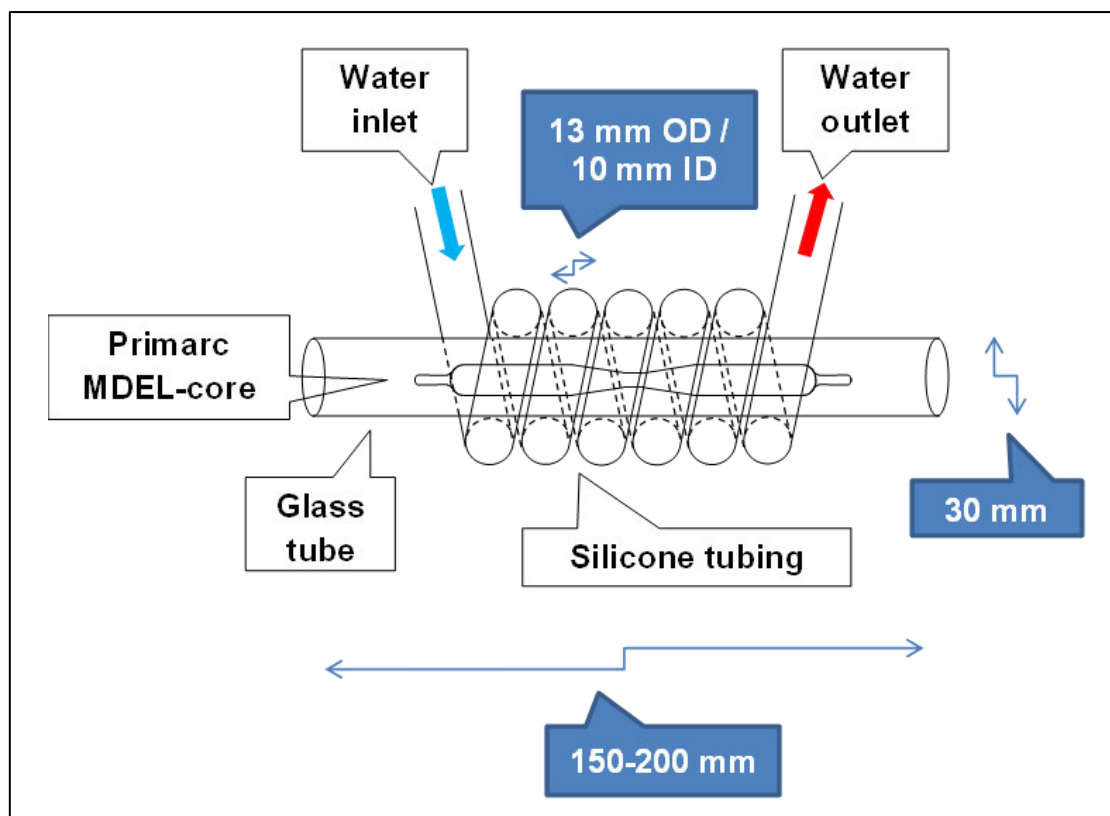


Figure 3.4: Schematic of proposed MDEL core/tubular coil reactor design.

was held in place with small cable ties. Chilled water, supplied by a refrigerated water cooler, was passed through this tube during microwave irradiation. The sustained ignition times to a maximum of 70 s at microwave power levels of 1000 W to 1200 W were recorded at a variable number of full coil turns of the silicone tubing around glass tube of the MDEL core/tubular coil combination reactor.

If the performance for the MDEL core/tubular coil combination reactor was shown to be adequate in this trial, future work envisaged replacing the silicone tubing with a shaped coiled quartz glass tube of similar dimensions through which the pulp suspension for photobleaching would be pumped. This coiled quartz glass tube would have included the most efficient number of full coils as determined within this set of experiments.

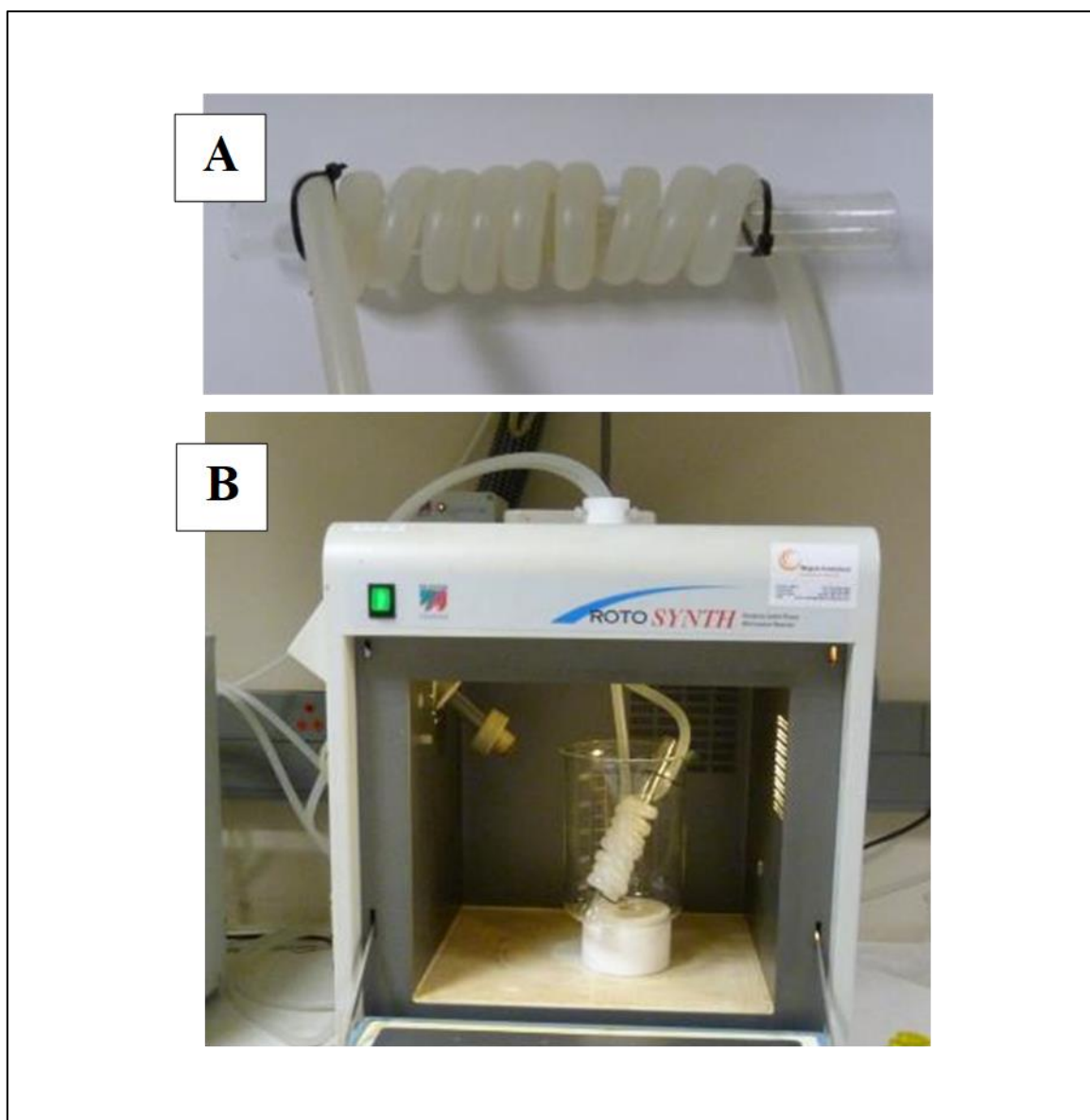


Figure 3.5: [A] Close-up view and [B] overall view in RotoSYNTH microwave oven of simulated MDEL core/tubular coil reactor.

3.5.5 Reactor design: *Suspended MDEL, “bucket” combination*

Previous observations around the evaluation of the Roto SYNTH/MDEL/round flat-bottomed flask combined reactor’s performance also led to a another investigation into the use of a suspended MDEL/“bucket” combination reactor design (Figures 3.6). A glass tube, 215.0 mm in length and 20.0 mm in diameter (which was used to hold the Primarc MDEL), was secured in a 5.0 l beaker through holes in the sides of the beaker. The junction between the holes in the beaker and the glass tube holding the MDEL was made watertight for the experiment using a malleable sticky rheological gel

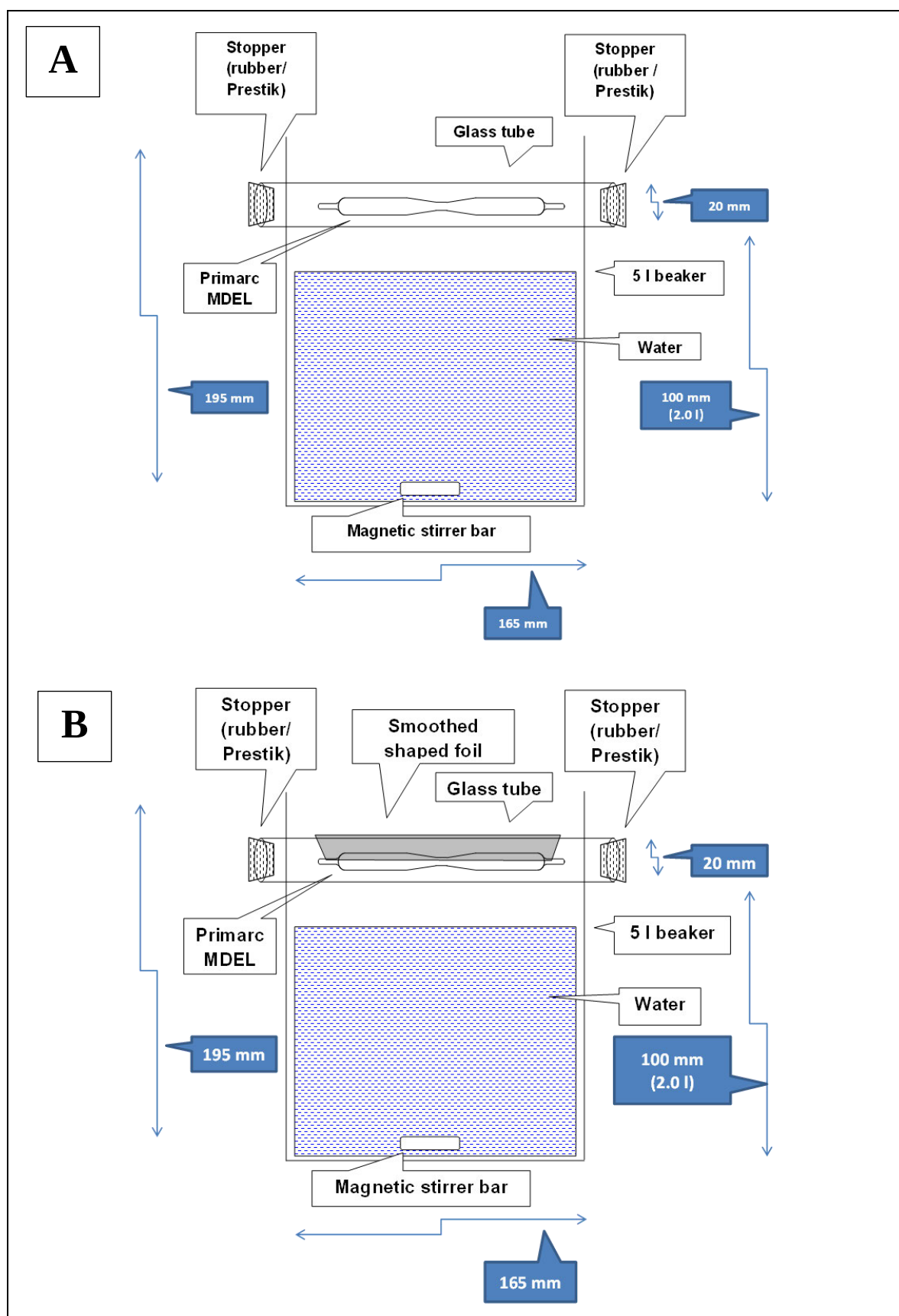


Figure 3.6: [A] Schematic without foil mirror and [B] schematic with smoothed shaped foil mirror of suspended MDEL/“bucket” reactor.

(i.e. "Prestik"). The bottom of the tube was 20.0 mm above the water level of the beaker when filled to 2.0 l. An aluminium foil mirror, was evaluated in some of the experimental work. It was attached and secured over the top of the glass tube. This aluminium foil mirror was cut from heavy aluminium foil. It had no sharp edges and was kept as smooth as possible to avoid any possible arcing during microwave irradiation. The sustained ignition times to a maximum of 70 s at a microwave power level of 1200 W were recorded at variable water levels in the suspended MDEL/"bucket" combination reactor.

3.5.6 Photobleaching of pulp utilizing the suspended MDEL, "bucket" combination

The starting pulp used in this study was the unbleached paper grade Kraft Aspen hardwood pulp from the Sappi Cloquet mill (North America) sampled for the first batch [312]. All experimental work was undertaken in the Roto SYNTH microwave reactor/suspended Primarc MDEL "bucket" combination system and was performed in triplicate (Figure 3.7). The Roto SYNTH microwave reactor was run from its control pad using a customised experimental recipe based on the controller's programmable software [313 - 315]. The rotational speed of the magnetic stirrer was set at 50% of maximum and the microwave cyclotron was operated at a continuous power setting of 1200 W and at variable reaction times of 1 to 240 minutes. The total suspension volume was 2000 ml with a pulp charge of 16.0 g oven dry equivalent, at a 0.70% consistency. Caustic soda and hydrogen peroxide charges of 18.0 and 80.0 kg t⁻¹ were employed respectively. During runs of the control set, the Primarc MDEL was removed from the reactor; while it was present (returned) during runs of the experimental set. For run times of 60 minutes and above, the water volume lost to evaporation was replaced at every 30 minute interval (i.e. 60 and 90 minutes). At the end of each experiment, any final water loss was also replaced before measurements of pH and residual peroxide were undertaken. The initial and final pH value of each experiment was also measured. The temperature of the pulp suspension was measured using the external infrared probe of the Roto SYNTH microwave reactor. Lastly, all experiments were undertaken in such a manner as to prevent any thermal energy transfer from prior experiments to the next.

3.6 UVet UV LED array

The experimental work for the UVet UV LED array was subdivided into three general categories: (i) testing and validation of the UV LED array reactor design, (ii) testing of various operational parameters and options for the UV LED array reactor design. These included various photobleaching oxidants, various operational conditions (i.e. pulp suspension pH, temperature, consistency, photocatalysts, photosensitizers, and array power level), and (iii) various photochemical bleaching options used in various full thermophotochemical bleaching sequences [316 - 329].

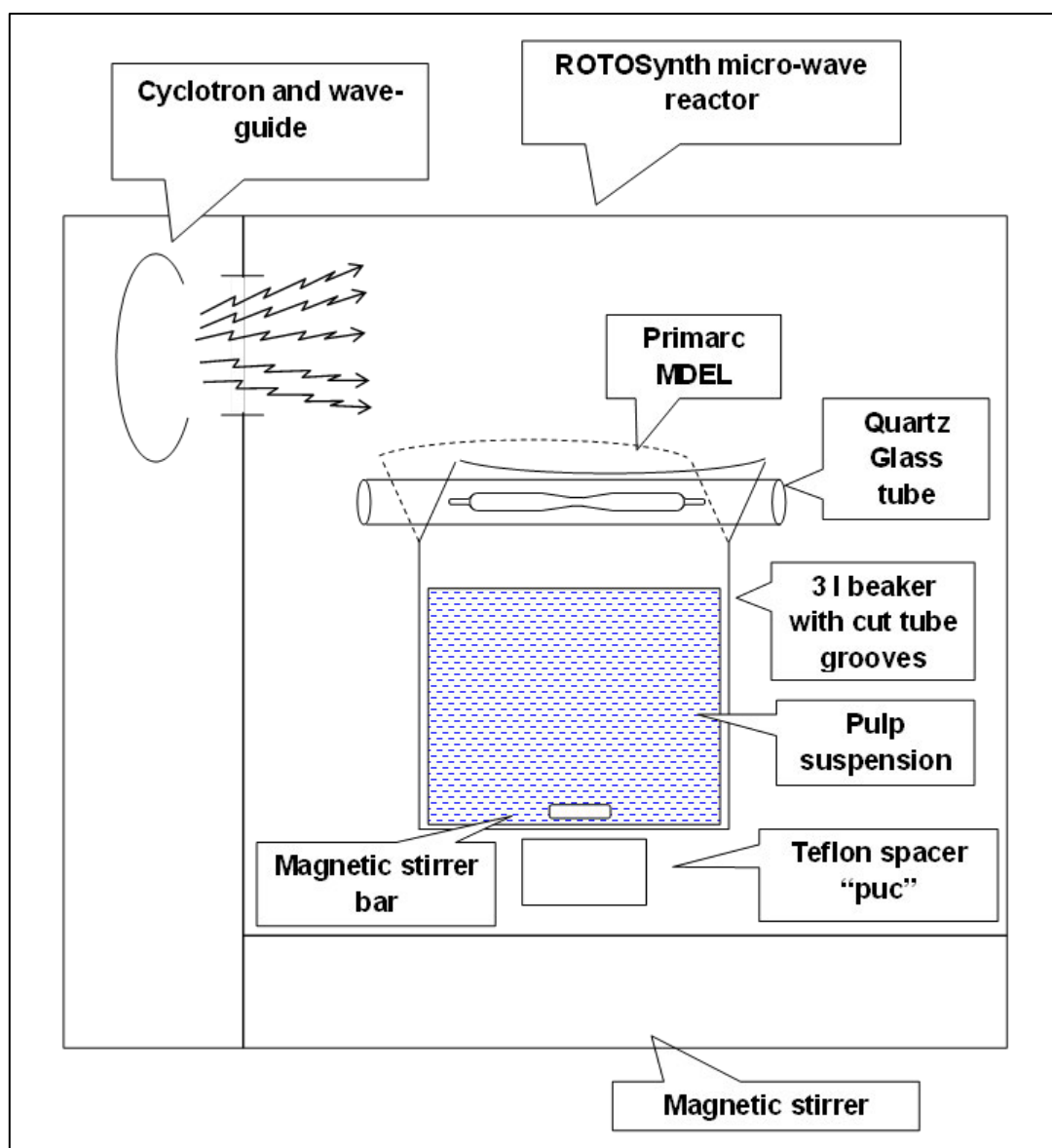


Figure 3.7: Schematic showing the combined photobleaching system consisting of the Roto SYNTH microwave oven and the “bucket” reactor with a suspended Primarc MDEL.

3.6.1 Photochemical pulp bleaching with UV LED array: Establishing control blanks for pulp and alkali peroxide solutions

The initial objective of the study into a reactor design based on the UV LED array was, firstly, to determine the changes to the pulp (bleaching, degradation, etc.) from all sources/agents/effectors except the ultraviolet irradiation, and, secondly, to validate the design and operation of the UV LED array reactor when employing the powered up UV LED array [316, 317]. The starting pulp used in this study was the unbleached paper grade Kraft Aspen hardwood pulp from the Sappi Cloquet mill (North America) sampled for the first batch. All experiments were undertaken at room temperature either with

the pulp or with only deionised water (20 to 25 °C). A schematic of the UV LED array reactor used is given in Figure 3.8; while images of the full reactor are given in Figures 3.9 and 3.10.

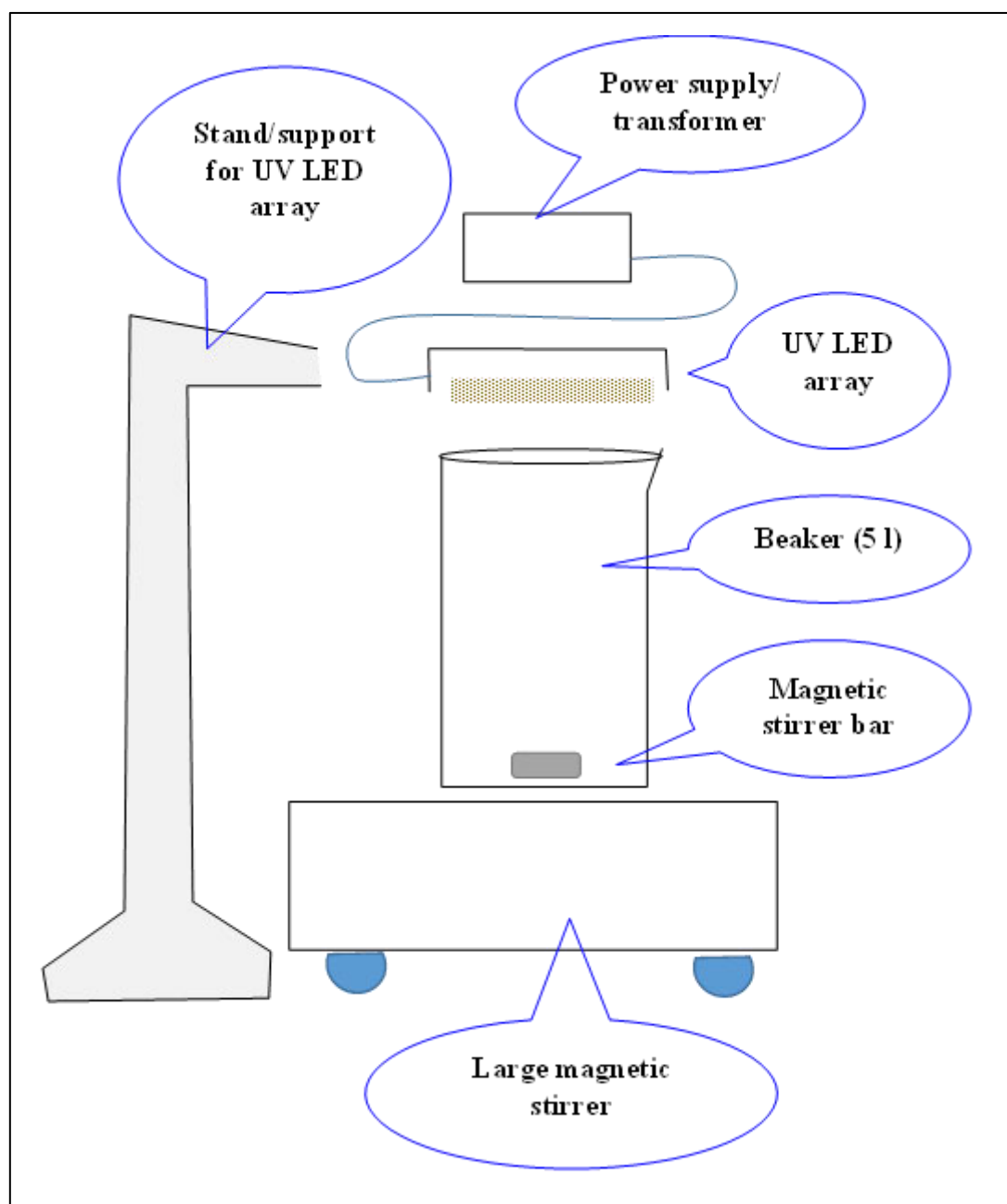


Figure 3.8: Schematic of proposed full photoreactor system employing an UV LED array for photochemical bleaching of a low consistency pulp suspension.

The rotational speed of the magnetic stirrer was set at 50% of maximum and the total suspension volume was 4000 ml with a pulp charge of 20.0 g oven dry equivalent at a 0.50% consistency, or nil for the water only runs (i.e. alkali peroxide solutions). Caustic soda and hydrogen peroxide charges of 18.0 and 80.0 kg t⁻¹ were employed respectively based on a 20.0 g pulp mass regardless whether the pulp was present or only water was employed. Run times spanning 1 to 120 minutes were evaluated. All

experiments were undertaken in triplicate and analysed as separate samples. The power level was set to nil (zero/switched off) for the UV LED array for all experiments with pulp suspensions and the first experimental set with water only (i.e. alkali peroxide); while being set to full power for experiments with the second set of the alkali peroxide solutions only. These pulp and peroxide solutions without power served as control blanks for all subsequent experimental work giving the level of delignification and viscosity loss for all effects besides the impact of photobleaching via the UV LED array illumination. The experiments with full UV LED power for only the alkali solutions served to validate the UV LED reactor design when under illumination.



Figure 3.9: UVet UV LED array photochemical reactor system showing UV light protective reactor chamber, shield and window cover. These items were present to minimize the exposure of any non-participants to the UV light generated by the UV LED array source.

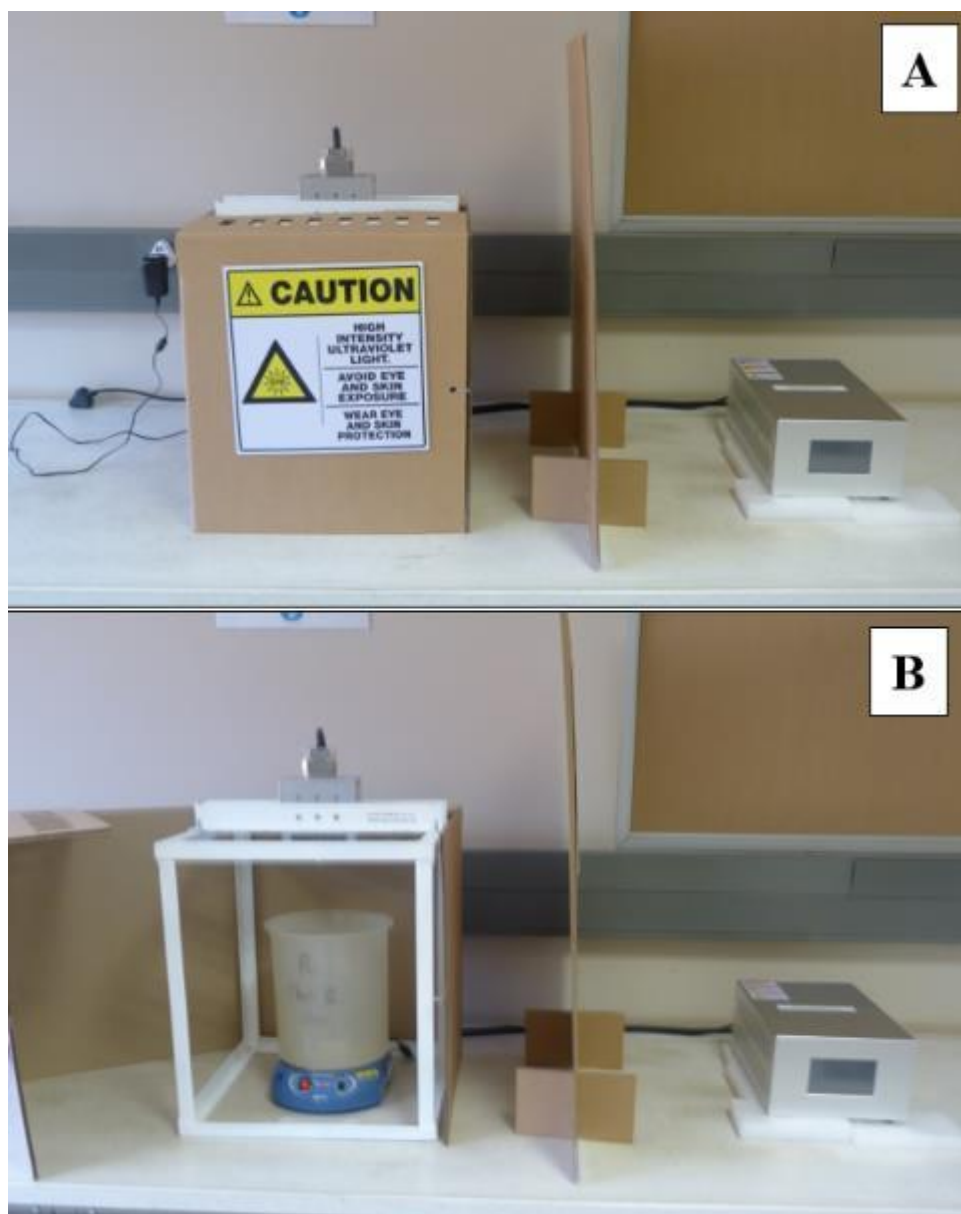


Figure 3.10: UVet UV LED array photochemical reactor system showing (A) all components enclosed by the reactor chamber, and (B) the opened reactor chamber revealing the magnetic stirrer, reactor beaker, support rig, and UVet UV LED array.

3.6.2 Photochemical bleaching of pulp with UV LED array: Photobleaching effect on pulp in the presence and absence of hydrogen peroxide (Variable 1)

The aim of this study was to determine whether pulp could be photobleached using an alkali peroxide solution under UV LED array irradiation [318]. The starting pulp used in this section was the unbleached paper grade Kraft Aspen hardwood pulp from the Sappi Cloquet mill (North America) sampled for the first batch. Schematics and images of the full UV LED array reactor system are given in Figures 3.8, 3.9 and 3.10. The UVet UV LED array operates at a wavelength of 365 nm and a power intensity of 8.0 W cm^{-2} with a power conversion ratio of approximately 85 to 95% when operated at

full power (100% power level). In this study all experiments were undertaken at room temperature (20 to 25 °C) using 20.0 g oven dry equivalent pulp mass at an experimental consistency of 0.5%. The caustic soda and hydrogen peroxide (when added) were charged at 18.0 kg t⁻¹ and at 80.0 kg t⁻¹ respectively and made up to a total volume of 4000 ml with deionised water. The rotational speed of the magnetic stirrer was set at 50% of maximum with run times spanning from nil to 120 minutes at 1, 2, 5, 10, 15, 30, 45, 60, 90 and 120 minute intervals, and the UV LED array was powered to 100% of total power capacity/output in all cases. All experiments were undertaken in triplicate and analysed as separate samples.

3.6.3 Photochemical pulp bleaching with UV LED array: Impact of pH on the photobleaching of pulp (Variable 2)

The aim of this study was to determine the impact of the pH of a pulp suspension on the photobleaching of that pulp under UV LED array irradiation [319]. The starting pulp used in this section was the unbleached paper grade Kraft Aspen hardwood pulp from the Sappi Cloquet mill (North America) sampled for the first batch. Schematics and images of the full UV LED array reactor system are given in Figures 3.8, 3.9 and 3.10. In this section, all experiments, including the control, were undertaken at room temperature (20 to 25 °C) using 20.0 g oven dry equivalent pulp mass at an experimental consistency of 0.5%. The hydrogen peroxide was charged at 80.0 kg t⁻¹ while the pH was varied by a range of incremental charges of sulfuric acid and caustic soda (30.0 kg t⁻¹ sulfuric acid to 30.0 kg t⁻¹ caustic soda). The pulp solution was made up to a total volume of 4000 ml with deionised water. The rotational speed of the magnetic stirrer was set at 50% of maximum with a run time of 120 minutes in all cases and with the UV LED array powered to 100% of total power capacity/output. All experiments were undertaken in triplicate and analysed as separate samples.

3.6.4 Photochemical pulp bleaching with UV LED array: Impact of UV LED array power levels on the photochemical bleaching of pulp (Variable 3)

The aim of this study was to determine how the power level of the UV LED array would impact the photobleaching of pulp under UV LED array irradiation [320]. The starting pulp used in this section was the unbleached paper grade Kraft Aspen hardwood pulp from the Sappi Cloquet mill (North America) sampled for the first batch. Schematics and images of the full UV LED array reactor system are given in Figures 3.8, 3.9 and 3.10. All treatments were undertaken at room temperature (20 to 25 °C) using 20.0 g (oven dry equivalent) pulp at a consistency of 0.5%. The caustic soda and hydrogen peroxide were charged at 18.0 kg t⁻¹ and 80.0 kg t⁻¹, respectively and made up to a total volume of 4 000 ml with deionised water. The pulp suspension was adequately stirred for a run time of 120 minutes in all cases. However, the power levels of the UV LED array (wavelength: 365 nm) were varied from 0.8 W cm⁻² to 8.0 W cm⁻² at 0.8 W cm⁻² increments (i.e. 10% to 100% at 10% intervals) of the total

power capacity/output for each treatment of the 120 minute treatment period. All experiments were undertaken in triplicate and analysed as separate samples.

3.6.5 Photochemical pulp bleaching with UV LED array: Molecular oxygen gas as oxidant (Variable 4)

The aim of this study was to determine the performance of oxygen as an oxidant during the photobleaching of pulp under UV LED array irradiation [321]. The starting pulp used in this section was the unbleached paper grade Kraft Aspen hardwood pulp from the Sappi Cloquet mill (North America) sampled for the first batch. Schematic illustrations of the UV LED array reactor used with oxygen is given in Figure 3.11, while that of the oxygen gas aspirator rig is given in Figure 3.12. Images

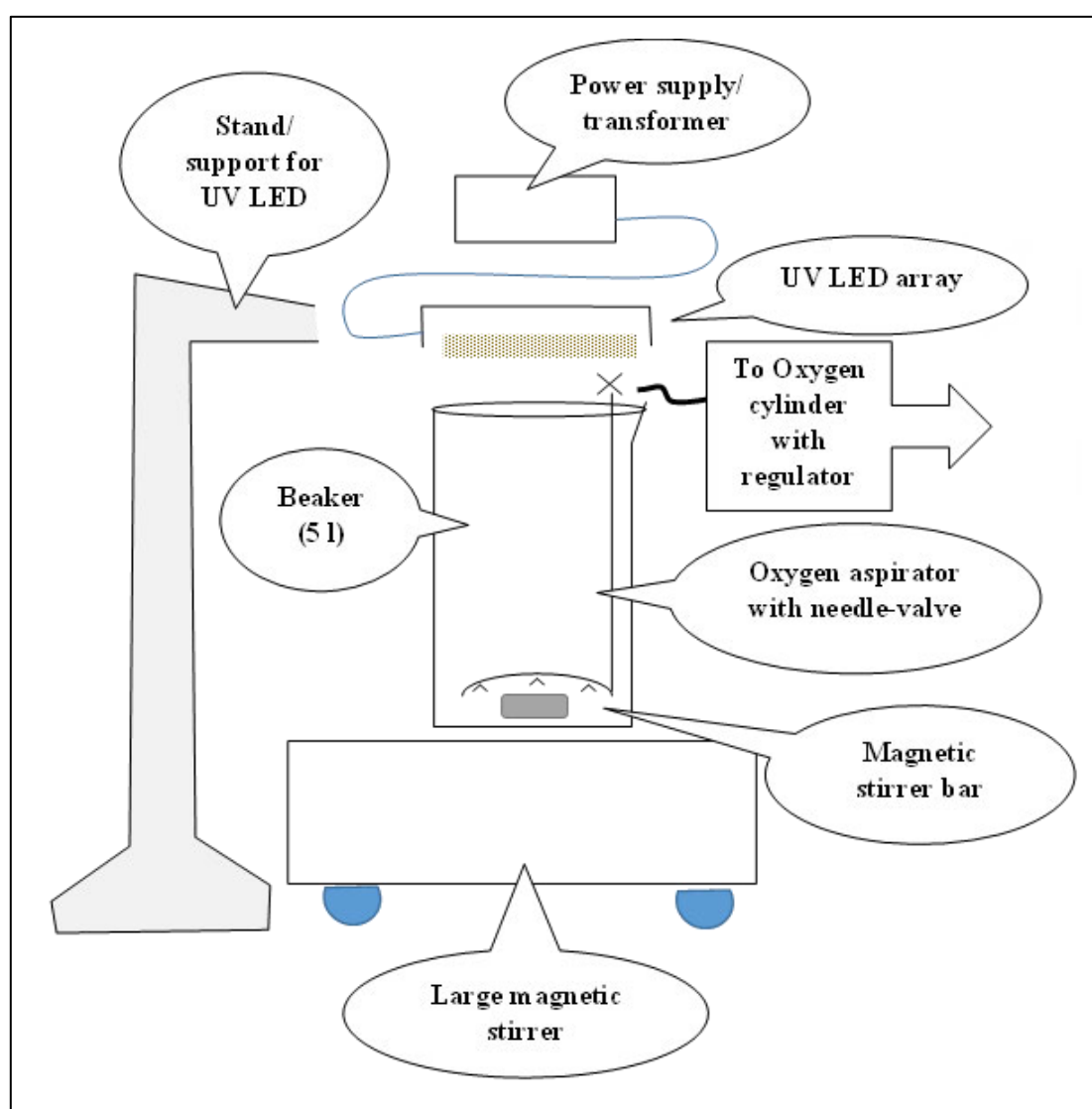


Figure 3.11: Schematic illustration of the full photochemical reactor system employing UVet UV LED array with an oxygen gas aspirator for photochemical bleaching of a low consistency pulp suspension employing molecular oxygen as an oxidant.

of the full reactor and its oxygen connection are given in Figures 3.13 and 3.14. All treatments were undertaken at room temperature (20 to 25 °C) using 20.0 g (oven dry equivalent) pulp at a consistency of 0.5% in the reactor system [6,7,8]. The caustic soda was charged at 18.0 kg t⁻¹ and made up to a total volume of 4 000 ml with deionised water. Oxygen was introduced into the suspension by bubbling it through the aspiration rig attached to the reactor system with the oxygen pressure set at 400 kPa on the regulator attached to the oxygen cylinder. The needle value was employed to ensure an adequate, gentle and continuous flow of oxygen to the aspirator rig. The pulp suspension was adequately stirred for run times ranging from 1 to 120 minutes. The power level of the UV LED array (wavelength 365 nm) was set at 8.0 W cm⁻² (i.e. 100%) for all treatments. All experiments were undertaken in triplicate and analysed as separate samples.

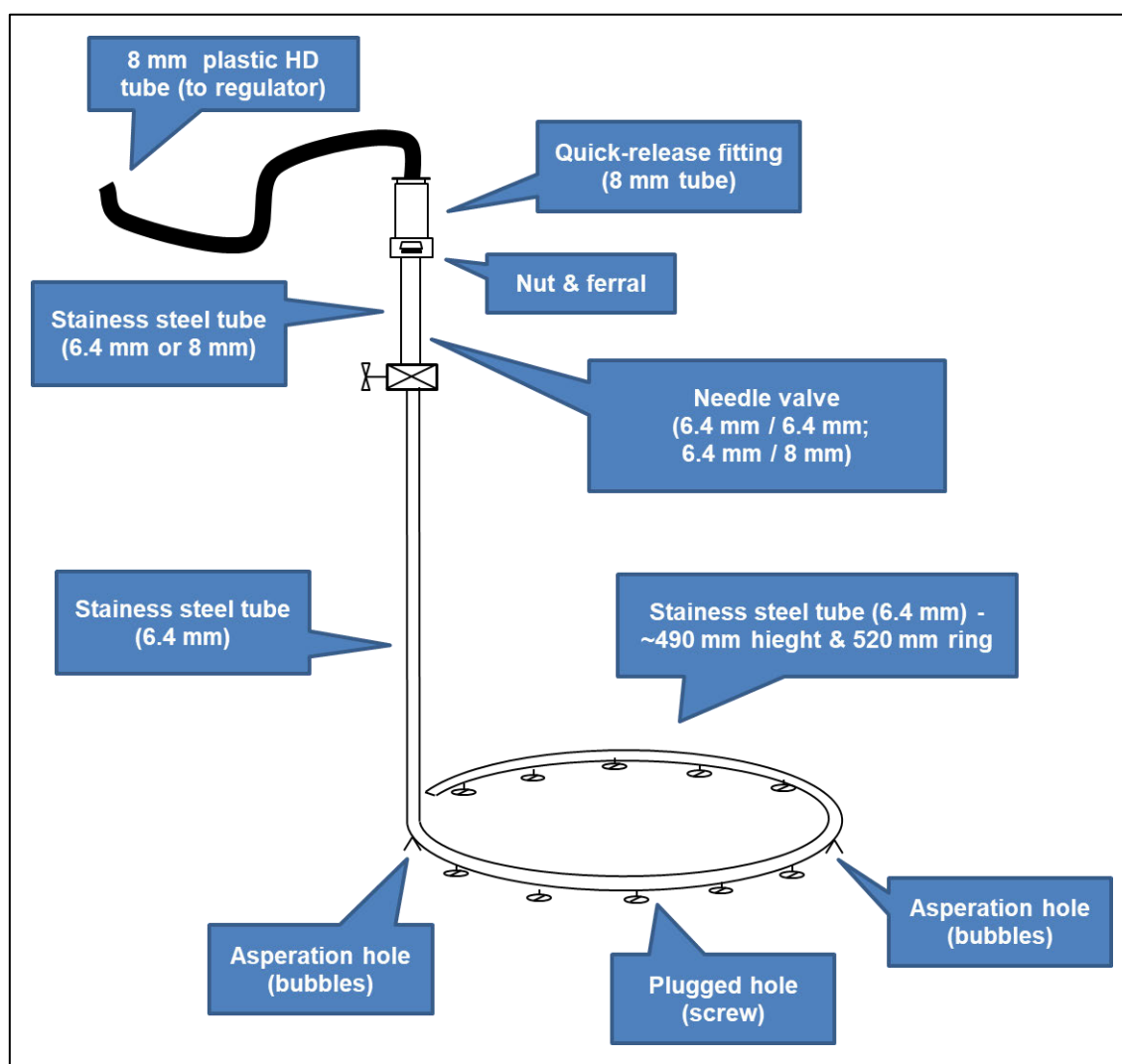


Figure 3.12: Schematic illustration of the oxygen aspirator rig used for introduction of molecular oxygen to UV LED array reactor system when employing molecular oxygen as an oxidant.

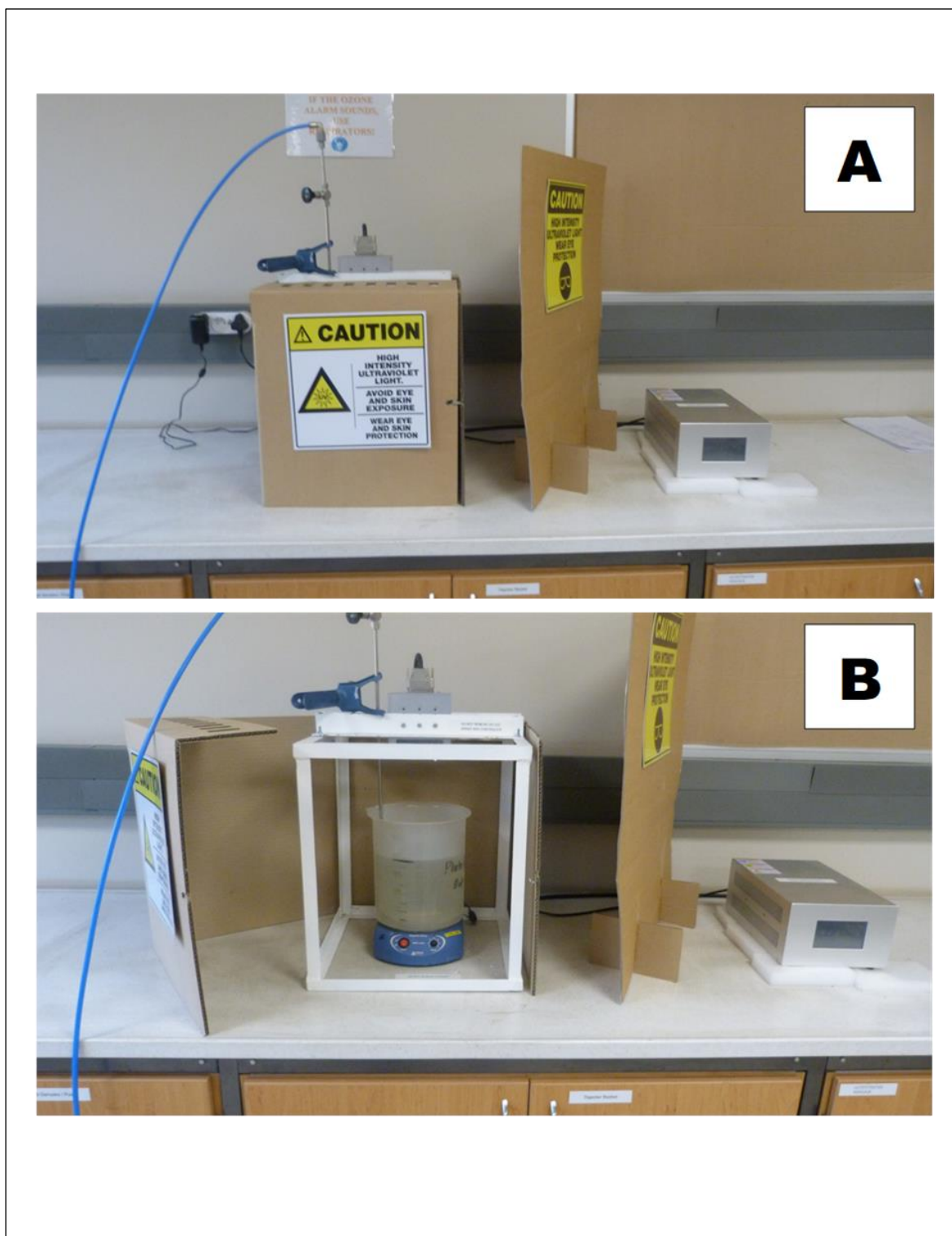


Figure 3.13: UVet UV LED array photochemical reactor system with oxygen aspirator showing (A) all components enclosed by the reactor chamber, and (B) the opened reactor chamber revealing the magnetic stirrer, reactor beaker, support rig, UVet UV LED array, and oxygen aspirator rig.

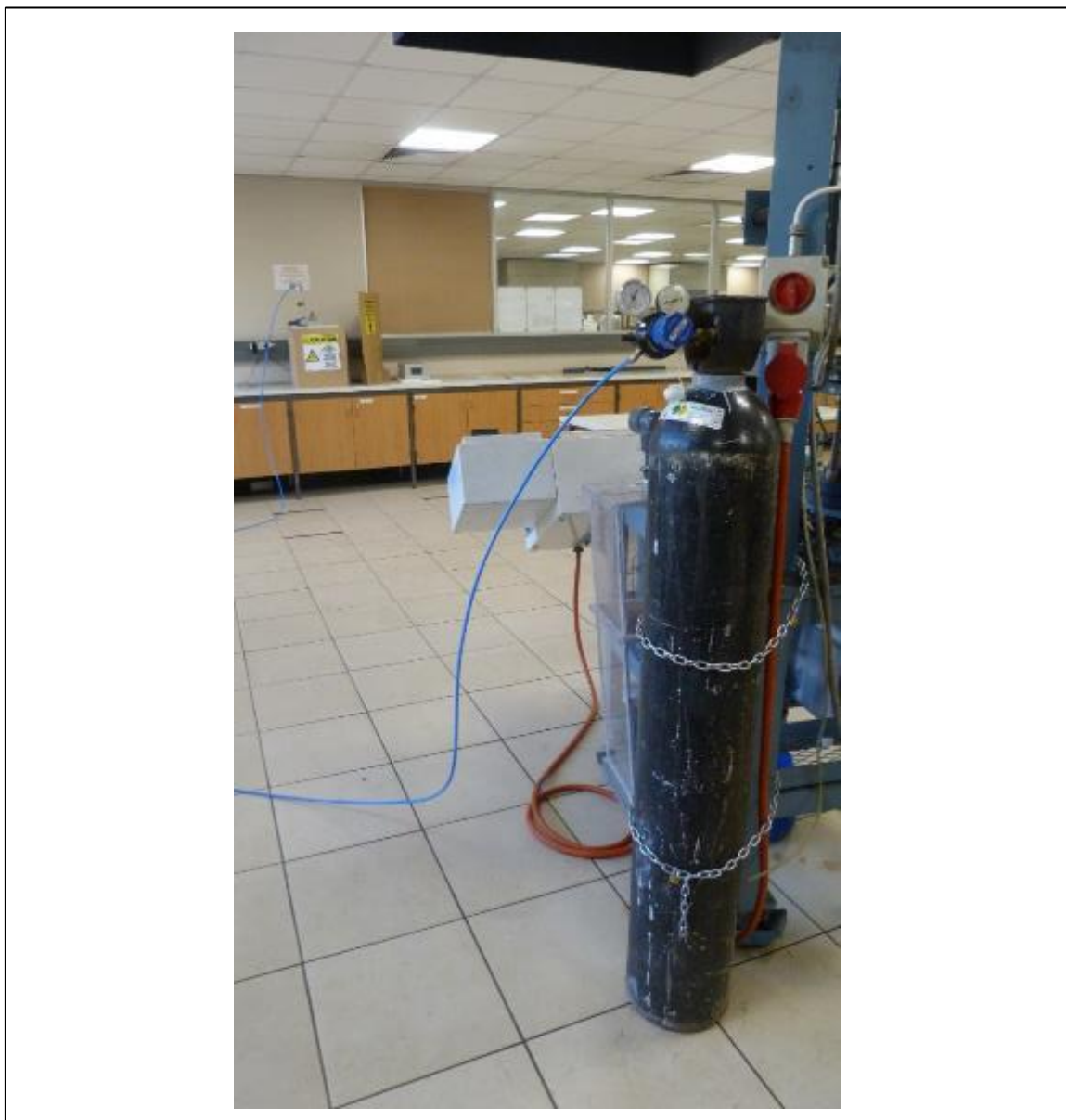


Figure 3.14: Chain-secured oxygen cylinder with regulator attached to the UVet UV LED array photochemical reactor system with oxygen aspirator (covers closed).

3.6.6 Photochemical pulp bleaching with UV LED array: Impact of temperature on the photochemical bleaching of pulp (Variable 5)

The aim of this study was to determine the impact of temperature on the photochemical bleaching of pulp under UV LED array irradiation [322]. The starting pulp used in this section was the unbleached paper grade Kraft Aspen hardwood pulp from the Sappi Cloquet mill (North America) sampled for the first batch. Schematics and images of the full UV LED array reactor system are given in Figures 3.8, 3.9 and 3.10. In this study, all treatments were undertaken at aimed starting temperatures ranging from about 50 °C to 80 °C using 20.0 g (oven dry equivalent) pulp at a consistency of 0.5%. The caustic

soda and hydrogen peroxide were charged at 18.0 kg t⁻¹ and 80.0 kg t⁻¹, respectively and made up to a total volume of 4000 ml with deionised water. The pulp suspension was stirred for run times of 1 to 120 minutes for experiments run at 70 °C, and 60 minutes only for all other temperatures (50, 60 and 80 °C). The power level of the UV LED array (wavelength of 365 nm) was maintained at 8.0 W cm⁻² (i.e. 100%). All experiments were conducted in triplicate and analysed as separate samples. The control experiments with UV irradiation were taken from prior experimental work conducted at room temperature (i.e. 25 °C).

3.6.7 Photochemical pulp bleaching with UV LED array: Initial calibration and optimization of photocatalysts and photosensitisers (Variables 6 and 7)

The aim of this study was to undertake a preliminary investigation into various photocatalysts and photosensitizers during photobleaching pulp under UV LED array irradiation [323]. The starting pulp used in this section was the unbleached paper grade Kraft Aspen hardwood pulp from the Sappi Cloquet mill (North America) sampled for the first batch. The experimental work around the photocatalysts was divided into two phases, while that for the photosensitisers was undertaken separately. Schematics and images of the full UV LED array reactor system for the photocatalyst study are given in Figures 3.8, 3.9 and 3.10; while schematic and images for the photosensitizer study (with oxygen) are given in Figures 3.11, 3.12, 3.13 and 3.14. In the first phase for the photocatalysts, various photocatalysts were evaluated to determine their effect on the photochemical degradation of a hydrogen peroxide solution without pulp. The photocatalysts evaluated were (as more input variables): anatase titanium dioxide (TiO₂), cerium dioxide (CeO₂), bismuth trioxide (Bi₂O₃), tungsten trioxide (WO₃), and zinc oxide (ZnO); while alumina (Al₂O₃) was used as a non-photocatalytic control. The average and varied particle size of each photocatalyst was: titanium oxide (< 25 microns), cerium oxide (< 5 microns), bismuth oxide (approx. 10 microns), tungsten oxide (approx. 10 microns) and zinc oxide (< 5 microns); with the alumina non-catalyst (approx. 10 microns). The variable dosage of each photocatalyst used ranged from 0.02 to 1.20 g, while the caustic soda and hydrogen peroxide quantities charged were 0.36 g and 1.60 g respectively per experiment (applied as concentrated solutions) and made up to a total volume of 4000 ml. This would have been a photocatalyst charge ranging from 1.0 kg t⁻¹ to 60.0 kg t⁻¹, as well as caustic soda and hydrogen peroxide charges of 18.0 and 80.0 kg t⁻¹ respectively, if a 20.0 g oven dry equivalent pulp mass had been used at an experimental consistency of 0.5%. The hydrogen peroxide solution was well stirred for a run time of 60 minutes for all experiments run at room temperature (approximately 25 °C). The power level of the UV LED array (wavelength 365 nm) was maintained at 8.0 W cm⁻² (i.e. 100%). All experiments were undertaken as single experimental runs. The residual peroxide content was determined via an iodometric titration with sodium thiosulfate.

In the second phase for the photocatalysts, the photocatalysts selected from the first phase (i.e. titanium dioxide and cerium dioxide) underwent optimization to obtain their optimal catalytic charge for the

photochemical bleaching of pulp. All treatments were undertaken at a starting temperature of approximately 25 °C using 20.0 g (oven dry equivalent) pulp at a consistency of 0.5%. The caustic soda and hydrogen peroxide were charged at 18.0 kg t⁻¹ and 80.0 kg t⁻¹, respectively and made up to a total volume of 4000 ml with deionized water. The power level of the UV LED array (wavelength 365 nm) was maintained at 8.0 W cm⁻² (i.e. 100%) in all cases. The pulp suspension was adequately stirred for a run time of 30 minutes with the photocatalyst being charged in the ranges of 2.5 to 60.0 kg t⁻¹. All experiments were undertaken as single experiments and so analysed. All photocatalytic pulps were subjected to two specialized wash/filtration stages with deionized water to aid in the complete removal of the metal oxides. This was done to avoid any artificial impact on the pulp brightness these solid metal oxides might have. In the first wash/filtration stage, the pulp suspension was filtered over a 150 mm Büchner funnel using fast filtering filter paper (Commercial Papers SA/Grade F-60WS) and rinsed with large quantities of deionized water. Thereafter, the pulp was resuspended in about 2500 to 3500 ml of deionized water before being drained on a 150 to 200 micron fine steel mesh screen. Finally, the pulp was sprayed with a jet of water, while still on the screen, under moderate tap pressure (less than 4 bars) to mobilize any last metal oxide particulates before being hand squeezed after fully draining.

The two photosensitizers evaluated (i.e. methylene blue and rose bengal) were optimized to obtain their optimal charge in the photochemical bleaching of pulp. All treatments were undertaken at a starting temperature of approximately 25 °C using 20.0 g (oven dry equivalent) pulp at a consistency of 0.5%. The caustic soda was charged at 18.0 kg t⁻¹ and made up to a total volume of 4000 ml with deionised water. Oxygen was introduced into the suspension by bubbling it through an aspiration rig attached to the reactor system with the oxygen pressure set at 400 kPa on the regulator attached to the oxygen cylinder. The power level of the UV LED array (wavelength 365 nm) was maintained at 8.0 W cm⁻² (i.e. 100%) in all cases. The pulp suspension was adequately stirred for a runtime of 30 minutes with the photosensitisers being charged in the range of 0.25 to 10.0 kg t⁻¹. All experiments were undertaken as single experiments and so analysed. All photosensitizer pulps were subjected to a set of organic rinses before being thoroughly washed with deionised water to maximize the removal of the photosensitizers and to minimize the dying of the pulps by these photosensitizing dyes. This was done as follows: (i) the pulp containing the aqueous photosensitizer was dewatered under vacuum on a 150 mm Büchner funnel using fast filtering filter paper (Commercial Papers SA/Grade F-60WS) before being washed with portions of deionized water (approximately 1000 ml) to maximize the removal of the photosensitizer from the pulp, (ii) for the first organic solvent rinse, 250 ml of glacial acetic acid was then added to the pulp mat, still under vacuum, (iii) the pulp mat was then subsequently washed with an approximately 250 ml volume of 98% methanol for the second organic solvent rinse, and (iv) lastly, the pulp mat was thoroughly washed with large portions of deionized water (> 2000 ml) before being hand squeezed after fully draining.

3.6.8 Photochemical pulp bleaching with UV LED array: Application of photocatalysts in the photochemical bleaching of pulp (Variable 6)

The aim of this study was to perform a more in-depth investigation into selected photocatalysts during the photobleaching of pulp under UV LED array irradiation [324]. The starting pulp used in this section was the unbleached paper grade Kraft Aspen hardwood pulp from the Sappi Cloquet mill (North America) sampled for the second batch and not the first. Schematics and images of the full UV LED array reactor system are given in Figures 3.8, 3.9 and 3.10. The two photocatalysts selected from the prior study for further experimental testing and quantification (titanium dioxide and cerium dioxide) were evaluated for their ability to catalyse the photochemical bleaching of pulp over a variable time range (15 to 120 minutes) under set conditions and charges. All treatments were undertaken at a starting temperature of approximately 25 °C using 20.0 g (oven dry equivalent) pulp at a consistency of 0.5%. The caustic soda and hydrogen peroxide were charged at 18.0 kg t⁻¹ and 80.0 kg t⁻¹, respectively and made up to a total volume of 4000 ml with deionized water. The power level of the UV LED array (wavelength 365 nm) was maintained at 8.0 W cm⁻² (i.e. 100%) in all cases. For all experimental work, the pulp suspension was stirred for run times of 15 to 120 minutes. The photocatalysts were charged at 5.0 kg t⁻¹ and 20.0 kg t⁻¹ for the titanium dioxide and cerium dioxide respectively. All experiments were undertaken in triplicate and analysed as separate samples. All pulps were subjected to two wash/filtration stages with deionized water as done in the prior section (Section 3.6.7) to aid in the complete removal of the metal oxides. This was done to avoid any artificial impact on the pulp brightness these solid metal oxides might have.

3.6.9 Photochemical pulp bleaching with UV LED array: Application of photosensitizers in the photochemical bleaching of pulp (Variable 7)

The aim of this study was to perform a more in-depth evaluation into selected photosensitizers during the photobleaching of pulp under UV LED array irradiation [325]. The starting pulp used in this section was the unbleached paper grade Kraft Aspen hardwood pulp from the Sappi Cloquet mill (North America) sampled for the second batch and not the first. Schematics and images for the UV LED reactor with oxygen are given in Figures 3.11, 3.12, 3.13 and 3.14. The two photosensitizers (i.e. methylene blue and rose bengal) were further evaluated for their ability to facilitate the photochemical bleaching of pulp over a variable time range (15 to 120 minutes) under set conditions and charges. All treatments were undertaken at a starting temperature of approximately 25 °C using 20.0 g (oven dry equivalent) pulp at a consistency of 0.5%. The caustic soda was charged at 18.0 kg t⁻¹ and made up to a total volume of 4 000 ml with deionised water. Oxygen was introduced into the suspension by bubbling it through an aspiration rig attached to the reactor system with the oxygen pressure set at 400 kPa on the regulator attached to the oxygen cylinder. The power level of the UV LED array (wavelength 365 nm) was maintained at 8.0 W cm⁻² (i.e. 100%) in all cases. For all experimental work, the pulp suspension was adequately stirred for run times of 15 to 120 minutes. The photosensitizers

were charged at 2.0 kg t⁻¹ and 7.2 kg t⁻¹ for the methylene blue and rose bengal respectively. All experiments were undertaken in triplicate and analysed as separate samples. All photosensitizer pulps were subjected to a set of organic rinses before being washed with deionised water as before (see Section 3.6.7) to maximize the removal of the dyes. In addition, single experimental runs were undertaken, without irradiation (i.e. UV LED array switched off), of both photosensitizers at the given charges of 2.0 kg t⁻¹ and 7.2 kg t⁻¹ for methylene blue and rose bengal respectively at 15, 30 and 45 minute run times to quantify the impact of the organic solvent rinse on the brightness and kappa number of the pulp.

3.6.10 Photochemical pulp bleaching with UV LED array: Impact of variable consistency on the photochemical bleaching of pulp (Variable 8)

The aim of this study was to evaluate the impact of variable pulp consistency on the photochemical bleaching of pulp under UV LED array irradiation [326]. The starting pulp used in this section was the unbleached paper grade Kraft Aspen hardwood pulp from the Sappi Cloquet mill (North America) sampled for the second batch. A schematic of the UV LED array reactor system used is given in Figure 3.15. All experiments were undertaken at room temperature (20 to 25 °C) with mixing of the pulp suspension undertaken by an overhead mixer with a small broad four blade impellor. The consistency of the pulp suspension was varied from 0.5 to 4.0% consistency, with the speed of the mixer dictated by the consistency. At pulp consistencies of 1.5% and below, a mixer speed of 5 out of a maximum setting of 10 was employed. At pulp consistencies of 2.0%, the speed was increased to 8/10; while at 2.5% consistencies and above, the maximum speed of 10/10 was employed. This was in an attempt to ensure adequate continuous mixing of the pulp suspension during the process. The UV LED array was operated at 100% power throughout all experiments, except for the two control experiments where it was not employed at all (i.e. switched off and disconnected). The total suspension volume was 4000 ml with the pulp charge varying from 20 to 160 g oven dry equivalent depending on the consistency. Caustic soda and hydrogen peroxide charges of 18.0 and 80.0 kg t⁻¹ were employed respectively with their volumes increasing as the mass of pulp increased. Run times were 90 minutes. Furthermore, the two controls without UV LED irradiation were undertaken at 0.5% and 2.5% consistency respectively.

3.6.11 Photochemical pulp bleaching with UV LED array of various Sappi mill pulps (Variable 9)

The aim of this study was to observe how various different pulps, selected based on their pulping processes, photobleached [327]. The various pulps used in this study were the Cloquet unbleached Aspen kraft – first batch (hardwood paper grade), a Ngodwana prehydrolysis Kraft pulp (sample ID: Demo Cook 146 B), a Stanger bagasse mill pulp, a Saiccor dissolving viscose grade mill pulp, a Gratkorn mill pulp and a Somerset mill pulp. Schematics and images of the full UV LED array reactor

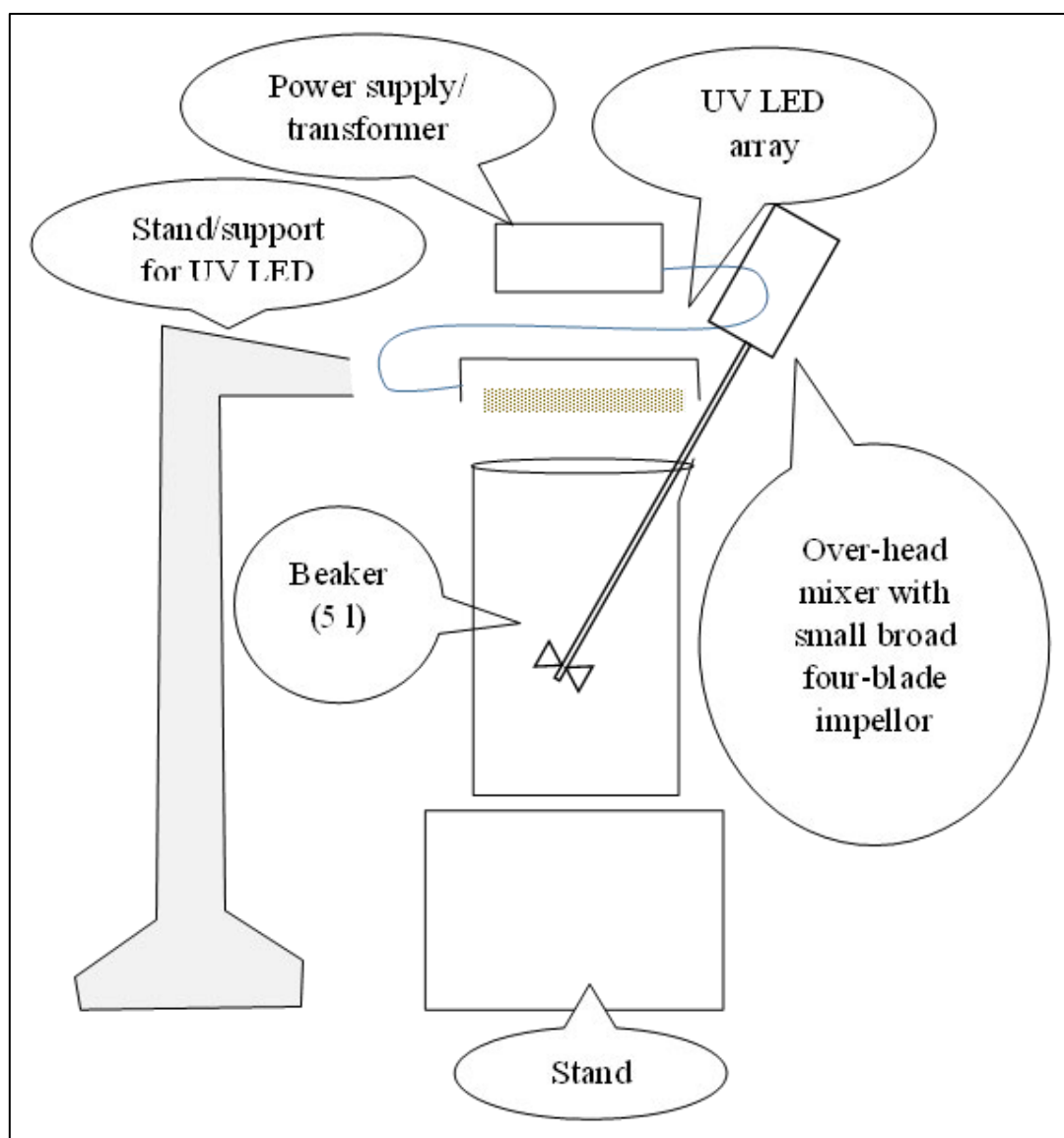


Figure 3.15: Schematic of full photoreactor system employing a UV LED array with external mixing for photochemical bleaching at variable pulp suspensions.

system are given in Figures 3.8, 3.9 and 3.10. All experiments were undertaken at room temperature (20 to 25 °C) using a 20.0 g oven dry equivalent pulp mass at an experimental consistency of 0.5%. The caustic soda and hydrogen peroxide were charged at 18.0 kg t⁻¹ and 80.0 kg t⁻¹ respectively, and made up to a total volume of 4000 ml with deionised water. The rotational speed of the magnetic stirrer was set at 50% of maximum with the exceptions of the Ngodwana and Gratkorn pulps, where the magnetic stirrer speed needed to be increased to 60% and 70% of its maximum speed to ensure adequate mixing of the pulp suspension. The UV LED array was run at 100% of total power capacity/output in all cases with run times of 120 minutes. Due to this being a brief study, all experiments were undertaken only once.

3.6.12 Evaluation of various combined thermophotochemical and thermal bleaching sequences for paper grade pulp

The objective in this investigation was to compare a thermophotochemical based bleaching sequence against conventional sequences for paper grade pulp [328]. The starting pulp used in this study was the unbleached paper grade Kraft Aspen hardwood pulp from the Sappi Cloquet mill (North America) sampled for the second batch. Schematics and images of the full UV LED array reactor system using caustic soda and hydrogen peroxide are given in Figures 3.8, 3.9 and 3.10; while schematic and images for the UV LED array reactor system with oxygen are given in Figures 3.11, 3.12, 3.13 and 3.14. The thermally driven elemental chlorine free (ECF) control sequence used in this study is a hypothetical sequence based on similar paper grade sequences typically used within the pulp and paper industry, while the thermally driven total chlorine free (TCF) control sequence is another hypothetical sequence, based on the same first hypothetical sequence, but using its proposed equipment with a few additions and modifications. The thermophotochemically based total chlorine free (TCF) bleaching sequence is a hypothetical sequence based on the findings made in this study. The charges and conditions for the three sequences are given in Table 3.3. The pulps from the photochemical oxygen stages were subjected to two specialized wash/filtration stages with deionized water to aid in the complete removal of the titanium dioxide photocatalyst (as given in Section 3.6.7). This was done to avoid any artificial impact on the pulp brightness the TiO_2 might have.

Given that each photochemical bleaching stage only delivered 20 g oven dry equivalent of pulp per experiment, every photochemical bleaching stage was repeated multiple times whereafter the pulp from that bleaching stage was collectively crumbled, processed and tested as a single pulp sample. This was to ensure adequate pulp mass for each stage, from 360 g for the first photochemical oxygen stage (i.e. oxygen_{UV}-stage) to 200 g for the final photochemical peroxide stage (i.e. $\text{P}_{2/\text{UV}}$ stage).

3.6.13 Evaluation of various combined thermophotochemical and thermal bleaching sequences for dissolving/chemical grade pulp

The goal in this investigation was to compare a thermophotochemical based bleaching sequence against a conventional sequence for dissolving viscose-grade pulp [329]. The starting pulp used in this section was the unbleached acid sulfite dissolving viscose grade pulp from Sappi Saiccor mill. Schematics and images of the full UV LED array reactor system using caustic soda and hydrogen peroxide are given in Figures 3.8, 3.9 and 3.10; while schematic and images for the UV LED array reactor system with oxygen are given in Figures 3.11, 3.12, 3.13 and 3.14. The thermally driven elemental chlorine free (ECF) control sequence used in this study a hypothetical sequence based on those typical employed for Sulfite dissolving pulps, while the photochemically based total chlorine free (TCF) bleaching sequence is a

Table 3.3: Experimental conditions and charges for comparison of thermophotochemically based TCF bleaching sequence against thermally-driven paper grade ECF control and TCF sequences.

THERMAL PAPER GRADE ECF CONTROL				
Oxygen-stage	Ozone-stage	D ₀ -stage	E _{OP} -stage	D ₁ -stage
33.0 kg t ⁻¹ NaOH; 85 °C / 95 °C; 20 / 50 min.; 10.0% cons.; 760 / 275 kPa O ₂	3.8 / 6.5 kg t ⁻¹ O ₃ / H ₂ SO ₄ ; < 25 °C; ~10 min.; 12.0% cons.	11.0 kg t ⁻¹ ClO ₂ ; 70 °C; 60 min.; 11.0% cons.	17.0 / 4.5 kg t ⁻¹ NaOH / H ₂ O ₂ ; 77 °C; 120 min.; 11.5% cons.; 380 kPa O ₂	3.5 kg t ⁻¹ ClO ₂ ; 80 °C; 240 min.; 11.5% cons.
THERMAL PAPER GRADE TCF PROPOSED				
Oxygen-stage	Ozone-stage	Acid-Wash stage	P ₀ -stage	P ₁ -stage
33.0 kg t ⁻¹ NaOH; 85 °C / 95 °C; 20 / 50 min.; 10.0% cons.; 760 / 275 kPa O ₂	3.8 / 6.5 kg t ⁻¹ O ₃ / H ₂ SO ₄ ; < 25 °C; ~10 min.; 12.0% cons.	6.0 kg t ⁻¹ H ₂ SO ₄ ; 65 °C; 30 min.; pH < 3.0; 11.0% cons.	15.0 / 10.0 kg t ⁻¹ NaOH / H ₂ O ₂ ; 85 °C; 60 min.; 11.0% cons.	12.0 / 14.0 kg t ⁻¹ NaOH / H ₂ O ₂ ; 80 °C; 210 min.; 11.5% cons.
PHOTOCHEMICAL TCF EXPERIMENT				
Oxygen-UV-stage	P ₀ / UV-stage	E _{P / Δ} -stage (thermal)	P ₁ / UV-stage	P ₂ / UV-stage
18.0 / 2.0 kg t ⁻¹ NaOH / Mg ²⁺ †; 65 °C*; 120 min.; 0.5% cons.; 400 kPa O ₂	18.0 / 80.0 / 5.0 kg t ⁻¹ NaOH / H ₂ O ₂ / TiO ₂ #; 65 °C*; 90 min.; 0.5% cons.	15.0 / 9.0 kg t ⁻¹ NaOH / H ₂ O ₂ ; 85 °C; 45 min.; 10.0% cons.	18.0 / 80.0 / kg t ⁻¹ NaOH / H ₂ O ₂ ; 65 °C*; 120 min.; 0.5% cons.	18.0 / 45.0 / kg t ⁻¹ NaOH / H ₂ O ₂ ; 65 °C*; 60 min.; 0.5% cons.

NOTE:- † Magnesium added as magnesium sulfate solution. Starting temperature of photochemical bleaching stage.

* Temperature not maintained at starting value by active heating, cooling allowed with atmosphere.

Photocatalyst employed (titanium dioxide).

hypothetical sequence based on the findings made in this study. The charges and conditions for the two sequences are given in Table 3.4. Given that each photochemical bleaching stage only delivered 20 g oven dry equivalent of pulp per experiment, every photochemical bleaching stage was repeated multiple times whereafter the pulp from that bleaching stage was collectively crumbled, processed and tested as a single pulp sample. This was to ensure adequate pulp for each stage, from 180 g for the first photochemical oxygen stage (i.e. oxygen_{UV} stage) to 80 g for the final photochemical peroxide stage (i.e. P_{1/UV} stage).

Table 3.4: Experimental conditions and charges for comparison of photochemically based TCF bleaching sequence against thermally-driven sulfite dissolving pulp ECF control sequence.

THERMAL SULFITE DISSOLVING PULP ECF CONTROL				
Oxygen stage	D ₁ stage	E _O stage	D ₂ stage	H stage
23.0 kg t ⁻¹ NaOH 90 °C ; 60 min 10.0% cons. 680 kPa O ₂	8.0 kg t ⁻¹ ClO ₂ 60 °C ; 60 min 10.0% cons.	34.0 kg t ⁻¹ NaOH 100 °C ; 120 min 10.0% cons. 350 kPa O ₂ .	7.0 kg t ⁻¹ ClO ₂ 65 °C ; 180 min 10.0% cons.	2.0 / 5.0 kg t ⁻¹ NaOH / NaClO 60 °C; 120 min 10.0% cons.
PHOTOCHEMICAL TCF EXPERIMENT				
Oxygen _{UV} stage	P _{0/UV} stage	E _{O/Δ} stage (<i>thermal</i>)	P _{1/UV} stage	
18.0 / 2.0 kg t ⁻¹ NaOH Mg ²⁺ †, 65 °C* 90 min, 0.5% cons. 400 kPa O ₂	18.0 / 80.0 kg t ⁻¹ NaOH / H ₂ O ₂ , 65 °C*, 90 min, 0.5% cons.	34.0 kg t ⁻¹ NaOH 100 °C, 120 min, 9.0% cons. 350 kPa O ₂	18.0 / 55.0 kg t ⁻¹ NaOH / H ₂ O ₂ 65 °C*, 60 min 0.5% cons.	

NOTE: † Magnesium added as magnesium sulfate solution at 100g l⁻¹.

* Temperature not maintained at starting value by active heating, cooling allowed with atmosphere.

The results of each of these experiments are presented and evaluated in chapter 4.

RESULTS AND DISCUSSION

This chapter discusses the investigations into the three proposed light sources for the photochemical bleaching of pulp: (i) solar, (ii) microwave discharge electrodeless lamps, and (iii) ultraviolet light emitting diode arrays [309 - 329]. This chapter also discusses the application of an ultraviolet light emitting diode array in photobleaching sequences. All raw data is given in Appendix B .

4.1 *Solar bleaching of pulps*

The objective of this study was to evaluate the solar bleaching of pulp under constant mixing in pure caustic soda or an alkaline peroxide solution while sitting on the windowsill over five days. A description of the experimental work is given in Section 3.4 [309]. An improved level of delignification of the Aspen pulp was observed upon irradiation with visible/UV light (solar) in both the pure alkali and the alkali peroxide pulp suspensions as compared to their controls (Figure 4.1). This clearly demonstrates the occurrence of solar photobleaching of the pulp. The only exception is the anomalous kappa number result for the pure alkali control at five days, which is likely an analytical error. The exact contribution from solar versus the fluorescent indoor building lights is unknown, but given that the sun is a much stronger luminant source, the UV contribution from the fluorescent lights is expected to be minor. The kappa number results also demonstrated that some thermal bleaching had occurred, but that much of the bleaching process was photochemically driven. In addition, the impact of thermal bleaching appears to level off after two days, upon its completion, and any further reduction in the kappa number appears solely photochemical in nature. Furthermore, the application of hydrogen peroxide to the process also gave improved bleaching for both the control and solar experiments as compared to their respective pure caustic soda experiments. This was expected, as the addition of hydrogen peroxide gives a significant reservoir of oxidative potential for bleaching not available for the pure caustic soda experiments. As regards viscosity, both the pure caustic soda control and solar experiment showed almost no loss in viscosity, while the alkaline peroxide control and solar experiment gave a viscosity that decreased with time (Figure 4.1). However, these losses in viscosity with alkaline peroxide were moderately small in size giving only an approximate 5 to 10% loss in viscosity. As the length of the pulp cellulose chain can be determined from the viscosity, and the length of the polymer chain is an indication of pulp strength; the loss in viscosity for the alkaline peroxide control and solar experiment over time suggests a loss in pulp strength over the same period. However, this loss in strength was small.

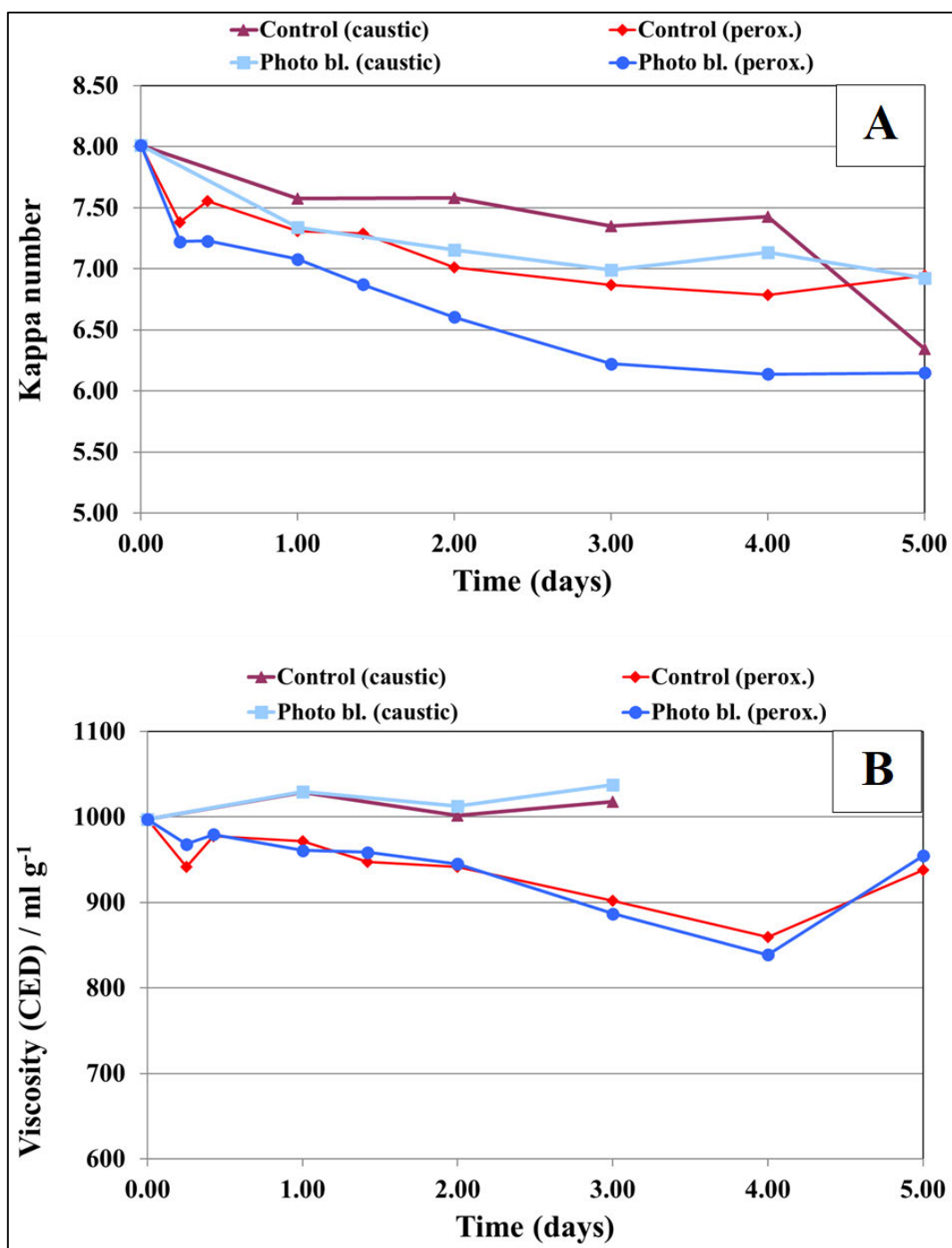


Figure 4.1: Variation of the [A] kappa number and [B] viscosity of solar bleached Cloquet Aspen pulp with retention time in the presence or absence of hydrogen peroxide.

Conditions: 15.0 kg t⁻¹NaOH, 60.0 kg t⁻¹ H₂O₂; 10.0 g pulp (pH neutralized); 25.0 °C (Room temperature); 0.5% consistency ; sunlight as light source.

The use of titanium dioxide, alumina, calcium carbonate and magnesium oxide, as photocatalysts or additives, did not improve the extent or efficiency of pulp solar bleaching (Figures 4.2 and 4.3). In most cases, the extent of solar bleaching was reduced. This is likely due to the attenuated level of

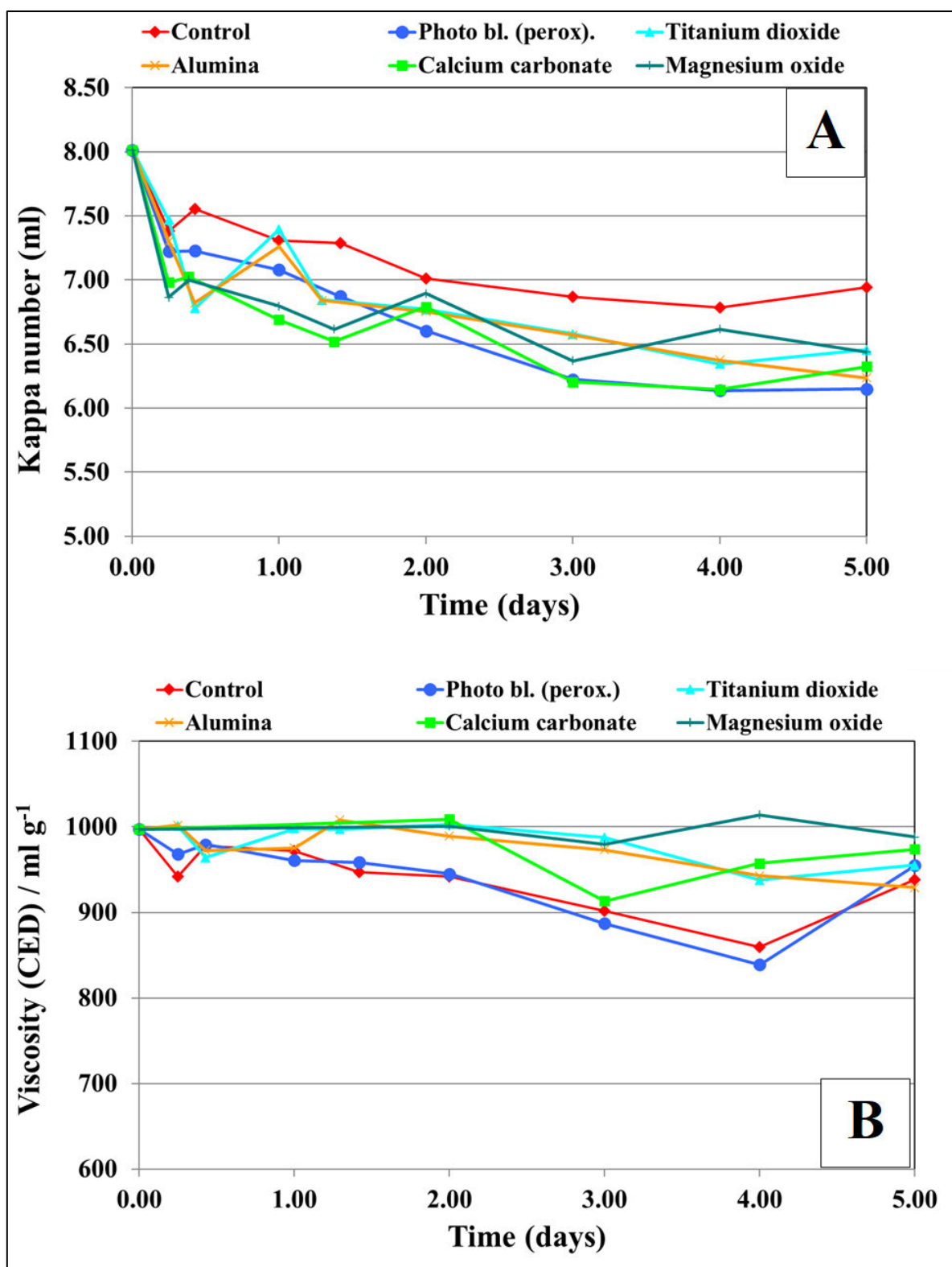


Figure 4.2: Variation in [A] kappa number and [B] viscosity of solar bleached Cloquet Aspen pulp with retention time for various photocatalysts or additives.

Conditions: 15.0 kg t⁻¹NaOH, 60.0 kg t⁻¹ H₂O₂, 5.0 kg t⁻¹ for TiO₂, Al₂O₃, CaCO₃ and MgO where relevant; 10.0 g pulp (pH neutralized); 25.0 °C (Room temperature); 0.5% consistency ; sunlight as light source.

irradiation of the pulp suspension as the added materials significantly increased the suspension's opacity. The control gave a higher kappa than all other experiments due to it not being exposed to

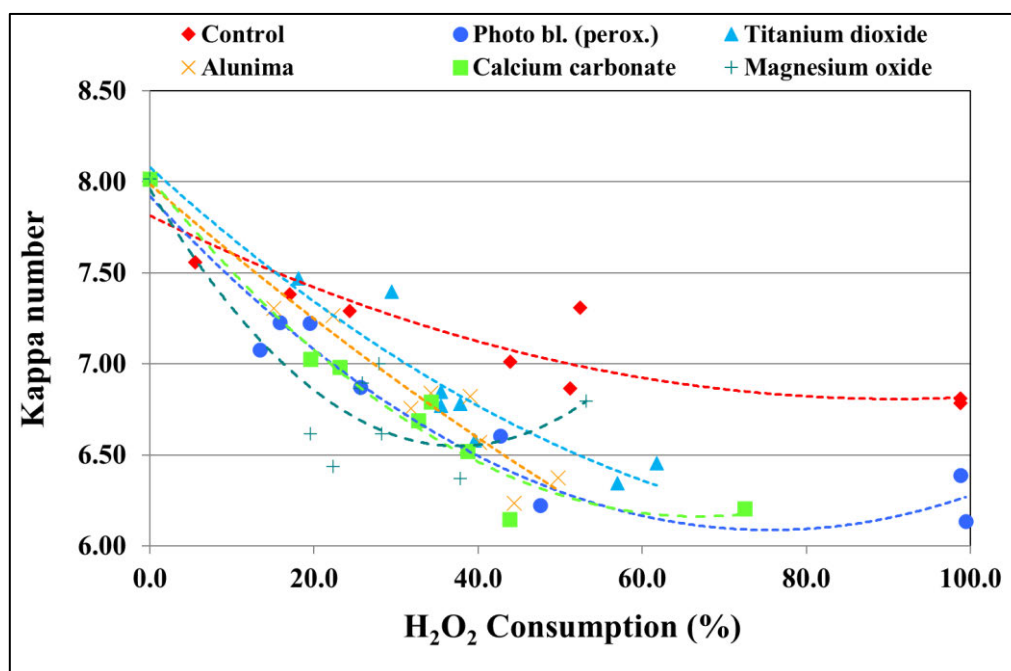


Figure 4.3: Variation of kappa number of solar bleached Cloquet Aspen pulp with hydrogen peroxide consumption in the presence of various photocatalysts and additives.

Conditions: 15.0 kg t⁻¹NaOH, 60.0 kg t⁻¹ H₂O₂, , 5.0 kg t⁻¹ for TiO₂, Al₂O₃, CaCO₃ and MgO where relevant; 10.0 g pulp (pH neutralized); 25.0 °C (Room temperature); 0.5% consistency ; sunlight as light source.

sunlight. This was also illustrated in that the peroxide experiments gave similar kappa number profiles as the photocatalysts and additives at similar levels of peroxide consumption (Figure 4.3). In addition, the photocatalysts and additives did not cause any notably reduction in the pulp viscosity either as shown by their viscosities being higher than both the control and peroxide experiments, and, thus, suggesting better pulp strength (Figure 4.2). Moreover, these additives did protect the fibres from cellulose degradation giving stronger pulps at given kappa numbers (Figure 4.4). This is shown by the higher viscosity results (i.e. approximately 5% improvement) achieved with the addition of these photocatalysts and additives at similarly kappa numbers as compared to the control and solar bleached alkaline peroxide pulps. As viscosity is an approximate indication of pulp strength, the higher viscosity indicates stronger pulps, and, hence protection of the pulps when these materials are added [284]. This suggested that the improved strength was not due solely to attenuated irradiation intensity, but also due to the protection against photogenerated hydroxyl and other damaging radicals as well as other unstable reaction intermediates [106, 225, 247]. The reduced attenuation also appeared to reduce the extent of peroxide utilization and possible waste.

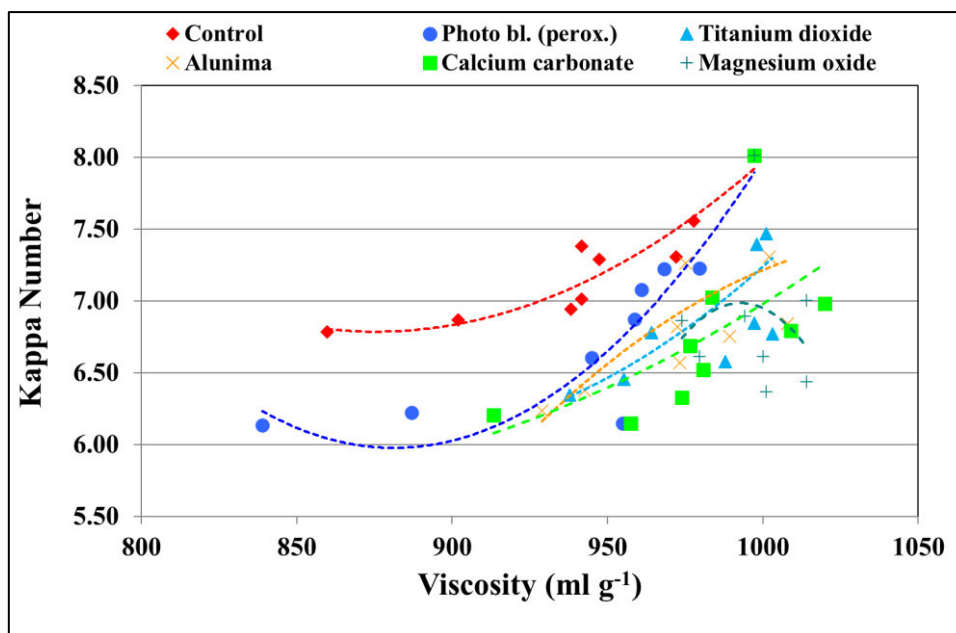


Figure 4.4: Variation of kappa number with viscosity of solar bleached Cloquet Aspen pulp in the presence of various photocatalysts and additives.

Conditions: 15.0 kg t⁻¹NaOH, 60.0 kg t⁻¹ H₂O₂, , 5.0 kg t⁻¹ for TiO₂, Al₂O₃, CaCO₃ and MgO where relevant; 10.0 g pulp (pH neutralized); 25.0 °C (Room temperature); 0.5% consistency ; sunlight as light source.

In summary, solar bleaching under pure alkali and alkali peroxide conditions was observed to occur with improvements in delignification beyond those observed for thermal bleaching and increased Brownian motion due to heating with sunlight. The hydroxyl radical was the active agent in the solar photobleaching mechanism [106, 182 - 185]. These hydroxyl radicals are likely generated in two methods: (i) from the photolysis of water molecules and hydroxide anions (OH⁻) in the pure alkali only solution likely with phenolics and α -carbonyl phenolics serving as photosensitizer-type reagents, and (see Sections 2.4.2.1 and 2.4.2.2) (ii) from the direct photolysis of the hydrogen peroxide in the alkali peroxide solutions [180, 190]. Given that the pure alkali solution generates hydroxyl radicals solely from the less favoured water photolysis mechanism, while the alkali peroxide would have two mechanisms for hydroxyl radical generation (photolysis of H₂O₂ and water), the alkali peroxide solar bleaching experiments are thus expected to outperform the pure alkali process – an outcome borne out by the experimental results. The use of metal oxides and carbonates, common to the pulp and paper industry, or commonly used photocatalysts and additives (TiO₂, Al₂O₃, CaCO₃, MgO), did not improve the solar bleaching efficiency. However, these materials did improve pulp strength under solar bleaching conditions. Lastly, approximately five days was required in this trial to achieve even a small drop in kappa number upon solar bleaching with hydrogen peroxide. Given that the thermally-driven bleaching processing in the pulp and paper industry (e.g. a hot alkaline peroxide bleaching stage: 85 °C) requires only an hour or two to achieve far more significant reductions in the kappa number, the application of solar radiation as a light source for the photobleaching of pulp was impractically long.

The impractically long process time observed in this experimental work was reflected in the work of both Machado et al. and Amat et al., who required a solar parabolic collector and about 6 hours respectively to achieve any significant photochemical bleaching effect in either of their solar experiments using dissolved lignin simulants [217, 227]. However, in contrast, Sarmet et al. required as little as 24 minutes for a 80 – 89% degradation of 4-chloroguaiacol (i.e. a lignin simulant) with hydrogen peroxide and TiO_2 as a photocatalyst when exposed to sun light [228].

4.2 Microwave discharge electrodeless lamps

For the Primarc MDEL to be adequately evaluated as a light source for the photochemical bleaching of pulp, the following aspects were tested: (i) the impact of power levels and time on the ignition and burning profiles of the Primarc MDEL, (ii) the impact of reactor design on the Primarc MDEL performance, and (iii) the bleaching performance of the Primarc MDEL for unbleached pulp [310, 312].

4.2.1 Primarc commercial UV curing lamp: General performance and operational testing of unattached and unshielded (“naked”) MDEL

In this study, the Primarc MDEL was placed inside an empty 250 ml glass beaker in the Roto SYNTH microwave reactor and subjected to microwave power levels from 100 – 1200 W over 70 s period to evaluate the ignition and burn properties of the MDEL over a variable power range. A description of the experimental work is given in Section 3.5.1. Under microwave irradiation, the time to ignition of the unattached and unshielded (“naked”) Primarc MDEL increases exponentially with lower irradiation power levels (Figure 4.5). However, there was considerable variation in the ignition time for most triplicate analyses. The exact cause is unknown, but was likely due to the varied extent of cooling between ignition trials, the total burn time, possible disturbance or physical movement of the MDEL between trials, and other random events. However, it was not possible to quantify the exact effect of each of these individual variables. The proper optimization and calibration of the microwave oven cavity for this MDEL was not possible, likely also contributing to the varied ignition and burn.

Evaluation of the sustainability of the burn of the Primarc MDEL inside the Roto SYNTH microwave reactor, after ignition, was considerably intermittent and random in nature (Figure 4.6). The Primarc MDEL was not able to continuously produce UV visible light for more than a few seconds as the Primarc MDEL was ignited and extinguished every few seconds in a random pattern when irradiated with microwaves within the Roto SYNTH microwave oven. Rolling the MDEL over between each run to help ensure a more uniform distribution of the mercury therein (i.e. “rotated”) also did not produce any improvement.

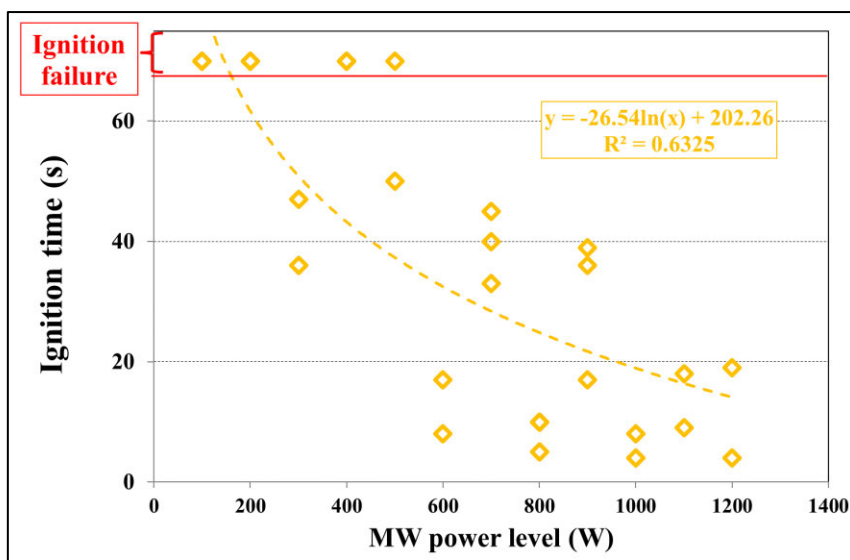


Figure 4.5: Ignition time of the commercial Primarc MDEL at variable power levels of the Roto SYNTH microwave oven during general performance and operational testing.

Conditions: Primarc MDEL placed in empty 250 ml beaker on Teflon “puc” inside Roto SYNTH microwave reactor; 25.0 °C (Room temperature); microwave at 100 – 1200 W; 70 s.

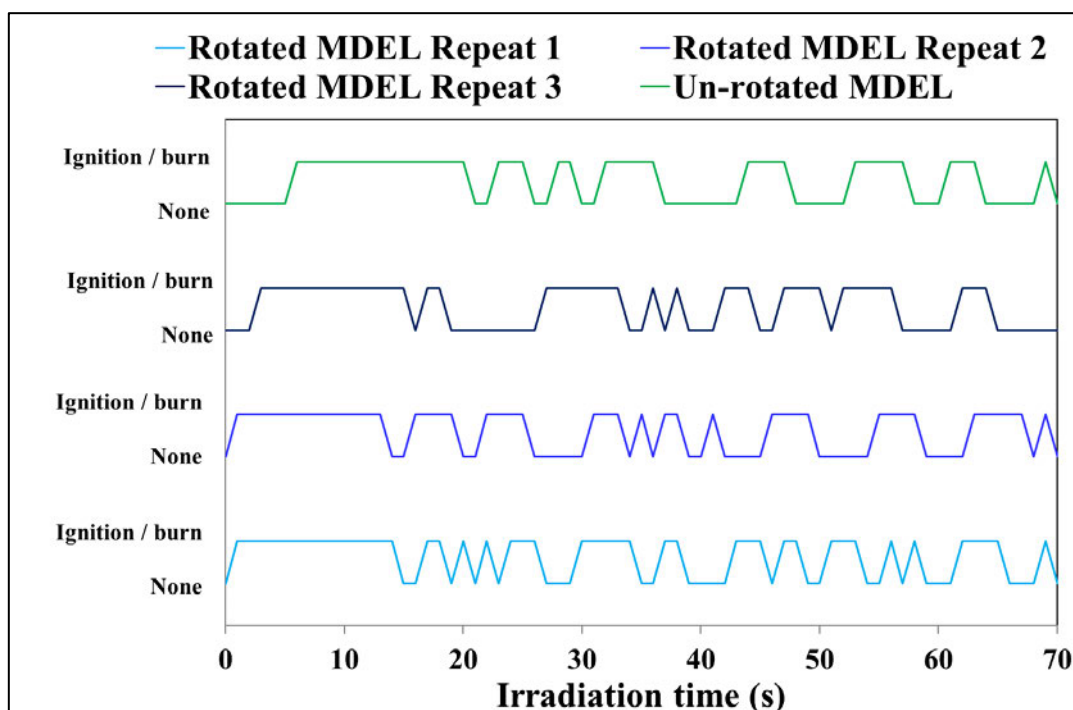


Figure 4.6: Ignition/burn profile of Primarc MDEL over time in a Roto SYNTH microwave oven at 1200 W power level.

Conditions: Primarc MDEL placed in empty 250 ml beaker on Teflon “puc” inside Roto SYNTH microwave reactor; 25.0 °C (Room temperature); microwave at 1200 W; 70 s.

The intermittent ignition and burn was likely due to insufficient microwave flux/intensity aimed directly at the MDEL, as well as the oven cavity not being properly calibrated and optimized for the MDEL used. Sustained and continuous burning can be achieved only if the microwaves are focussed/concentrated on the MDEL rather than being allowed to diffuse outwards upon entering the more “spacious” volume of the large microwave cavity. Under these circumstances only a small fraction of the microwave radiation impinges on the MDEL, which may result in ignition due to an initial excitation, but no sustained burn. This is clearly evident from information communicated by Nordson (the company who made the microwave oven in which the Primarc MDEL are used) as given by the personal communication in Appendix C [310]. In that communication, the paramount importance of properly coupling the microwave radiation to the MDEL was strongly emphasized. This is accomplished by a careful calibration and tuning of the microwave cavity, the magnetron and the MDEL. This is necessary to ensure that sufficient energy is pumped into the mercury in the MDEL to heat it to its evaporation point and then convert it into a plasma. The plasma then emits the UV and visible light required. Without that coupling, sustained burning is not possible, though some initial slight intermittent reaction may be observed. The communication also indicated the importance of adequate cooling of the MDEL with air to avoid melting of the quartz glass. Lastly, the communication did suggest approaching tertiary education institutions for help with such tuning and coupling, putting the university of Michigan as one possibility.

4.2.2 Reactor designs: Roto SYNTH, MDEL, round flat-bottomed flask combination

In this study, the Roto SYNTH, MDEL, round flat-bottomed flask combination was subjected to 1200 W microwave power levels for 70 s to evaluate the viability of the reactor design. A description of the experimental work is given in Section 3.5.2. Direct contact or near proximity of water appeared to have a severe deactivating/shielding impact on the Primarc MDEL for the Roto SYNTH/MDEL/round flat-bottomed flask combination reactor (Table 4.1). The ignition time increased as more of the MDEL was

Table 4.1: Ignition time for the Roto SYNTH/MDEL/round flat-bottomed flask combination and immersed sleeve reactors at variable water content levels.

Parameter	Roto SYNTH/MDEL/round flat-bottomed flask					Immersed sleeve	
Water volume [coverage] (ml)	No water [0%]	1000 [25%]	1200 [33%]	1500 [45%]	1900 [Total]	40 mm [Thin diameter]	80 mm [Thick diameter]
Ignition time – triplicate results (s)	8, 8, 10	15, 12, 16	>70, >70, >70	32, 24, 38	>70, >70, >70	>70, >70, >70	>70, >70, >70

covered or surrounded with water. Short ignitions times were observed only for zero to little MDEL coverage (none to one quarter of MDEL covered) as the water content of the round flat-bottomed flask was increased from nil to 1000 ml with the total reactor vessel being 1900 ml. At 1200 ml no ignition was observed (one third of MDEL coverage), while at 1500 ml (45% coverage of MDEL) ignition time was moderately long (approximately 30 s). When the round flat-bottomed flask was full (MDEL mostly covered), ignition did not occur.

The lack of ignition with rising water content levels is due two possible causes:

- a) Thermal quenching of the MDEL. To operate properly, the internal temperature within the MDEL needs to reach adequately high levels for ignition and sustained burning – typically above 500 °C. When the MDEL is in direct contact with water, a significant portion of this heat (injected by the microwave radiation) is removed by direct contact conduction. As previously reported [259], the use of a microwave concentrating cone or a properly optimized microwave cavity is necessary to resolve such problems, however, in this study, this was not available for this experimental design.
- b) Shielding of the MDEL from microwave electromagnetic radiation by the large dipole vector of water molecules in close proximity or covering the MDEL. Water molecules are known to have a dipole vector due to the molecular orbital configuration [330]. It is this dipole that is responsible for the heating of water with microwave radiation due to the interaction of these dipoles with the microwave electromagnetic radiation. In the process, the microwave field is progressively attenuated as it propagates through the water surrounding the MDEL. If adequately attenuated, the microwave field strength reaching the MDEL is too weak to adequately heat and ignite the MDEL. This is particularly relevant for a MDEL surrounded by a large volume of water as in the Roto SYNTH/MDEL/round flat-bottomed flask combination reactor design.

Overall, the Roto SYNTH/MDEL/round flat-bottomed flask combination reactor did not appear to be a viable reactor design for the use of a MDEL in the photobleaching of pulp. In addition, all attempts to modify a commercial kitchen micro-wave oven to employ a custom made aluminium microwave concentrating cone for the Primarc MDEL resulted in severe electrical arcing around the cone, the cone attachments to the oven, and the cyclotron itself, resulting in severe damage to all these items [331]. These attempts were completely unsuccessful.

4.2.3 Reactor design: Immersed sleeve

In this study, the MDEL/immersed sleeve design was subjected to 1200 W microwave power levels for 70 s to evaluate the viability of the reactor design as well as quantifying the “shield” effect of the water around the sleeve. A description of the experimental work is given in Section 3.5.3. Experimental results for the immersed sleeve reactor design showed that when the MDEL was placed within an immersed sleeve reactor with water surrounding it, ignition was not observed with beakers of both diameters, namely: 40.0 mm and 80.0 mm (Table 4.1). This suggested that shielding of the MDEL by water, when in sufficiently close proximity, prevented the MDEL from igniting. The impact of thermal quenching cannot be dismissed for this design either, but is expected to be of less significance. Thus, the immersed sleeve reactor was also not a viable reactor design for the use of a MDEL.

4.2.4 Reactor design: MDEL core, tubular coil combination

In this study, the MDEL core, tubular coil combination was subjected to 1200 W microwave power levels for 70 s to evaluate the viability of the reactor design. A description of the experimental work is given in Section 3.5.4. The MDEL core/tubular coil combination reactor showed quick ignition for no coils, i.e., nil coverage around the MDEL core, to moderate ignition times for ten full coils, i.e. complete coverage around the MDEL core (Figure 4.7A). During ignition, the visual illuminant intensity was significant (Figure 4.7B). However, variability in some of the repeats was considerable, which gave a low coefficient of correlation for the visually observed ignition times ($R^2 = 0.081$). When the microwave irradiation power level was reduced from 1200 W to 1100 W, there appeared to be a significant increase in the ignition time (Figure 4.8). However, this observation was based on a single analysis at 1100 W as the cable ties holding the silicone tubing in place failed towards the end of the ignition time of the first repeat at 1100 W. This failure was likely due to excessive heat of the cable ties and, consequently, no further repeat analyses were undertaken at 1100 W due to potential safety issues at the time of experiment.

In summary, the MDEL core/tubular coil combination reactor was a possible viable reactor design for the use of a MDEL in photobleaching of pulp. However, the effort needed to successfully build and use a working version of such a design made solely out of quartz glass is considerable.

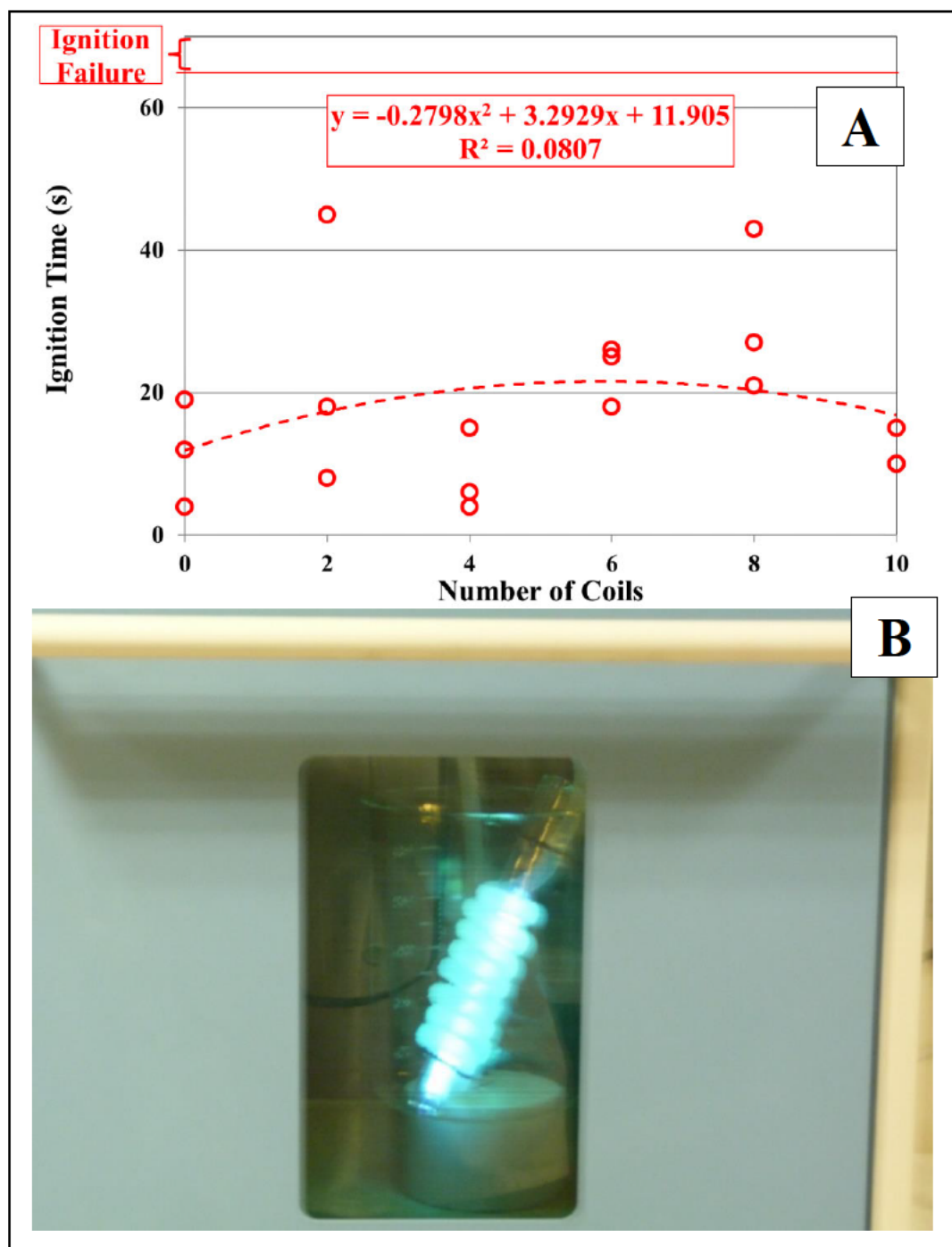


Figure 4.7: [A] Ignition time and [B] photograph during ignition of MDEL core/tubular coil combination reactor at variable coil rotations.

Conditions: Primarc MDEL with tubular/coil combination reactor placed in empty 250 ml beaker on Teflon "puc" inside Roto SYNTH microwave reactor; 25.0 °C (Room temperature); microwave at 1200 W; 70 s.

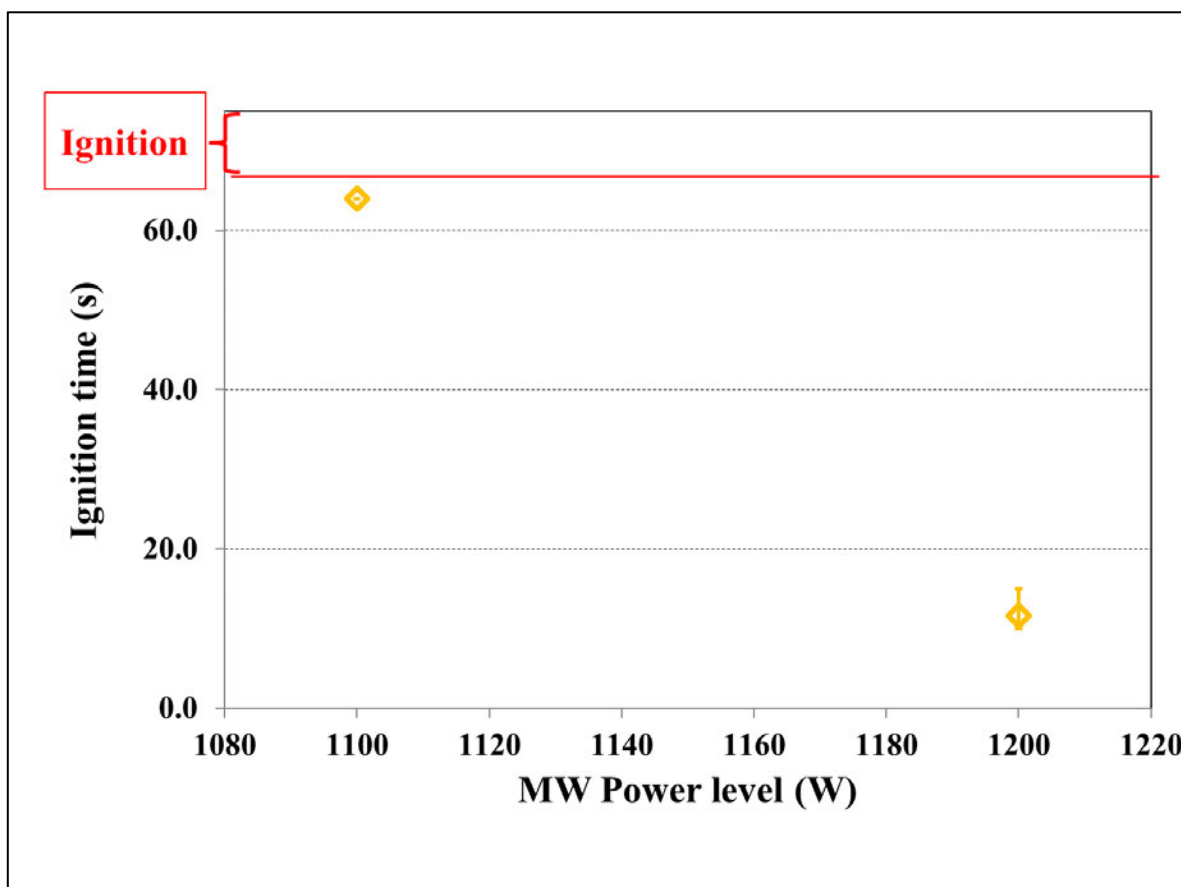


Figure 4.8: Ignition times at 1100 W and 1200 W of MDEL core/tubular coil combination reactor.

Conditions: Primarc MDEL with tubular/coil combination reactor placed in empty 250 ml beaker on Teflon “puc” inside Roto SYNTH microwave reactor; 25.0 °C (Room temperature); microwave at 1100 and 1200 W; 70 s.

4.2.5 Reactor design: *Suspended MDEL, “bucket” combination*

In this study, the suspended MDEL, “bucket” combination reactor design was subjected to 1200 W microwave power levels for 70 s to evaluate the viability of the reactor design. A description of the experimental work is given in Section 3.5.5. The application of an aluminium foil mirror to the upper surface of the glass tube holding the MDEL core resulted in severe arcing around the periphery of the foil despite the best care taken to avoid/remove initiation points (crinkles and sharp edges/points). Hence, it was removed from subsequent experimental work. The suspended MDEL, “bucket” combination reactor design showed quick to moderate ignition times when the water level was kept at 20.0 mm (2.0 cm) below the glass tube holding the MDEL core (Figure 4.9A). As with the MDEL core/tubular coil reactor, ignition intensity with the suspended MDEL/“bucket” combination reactor

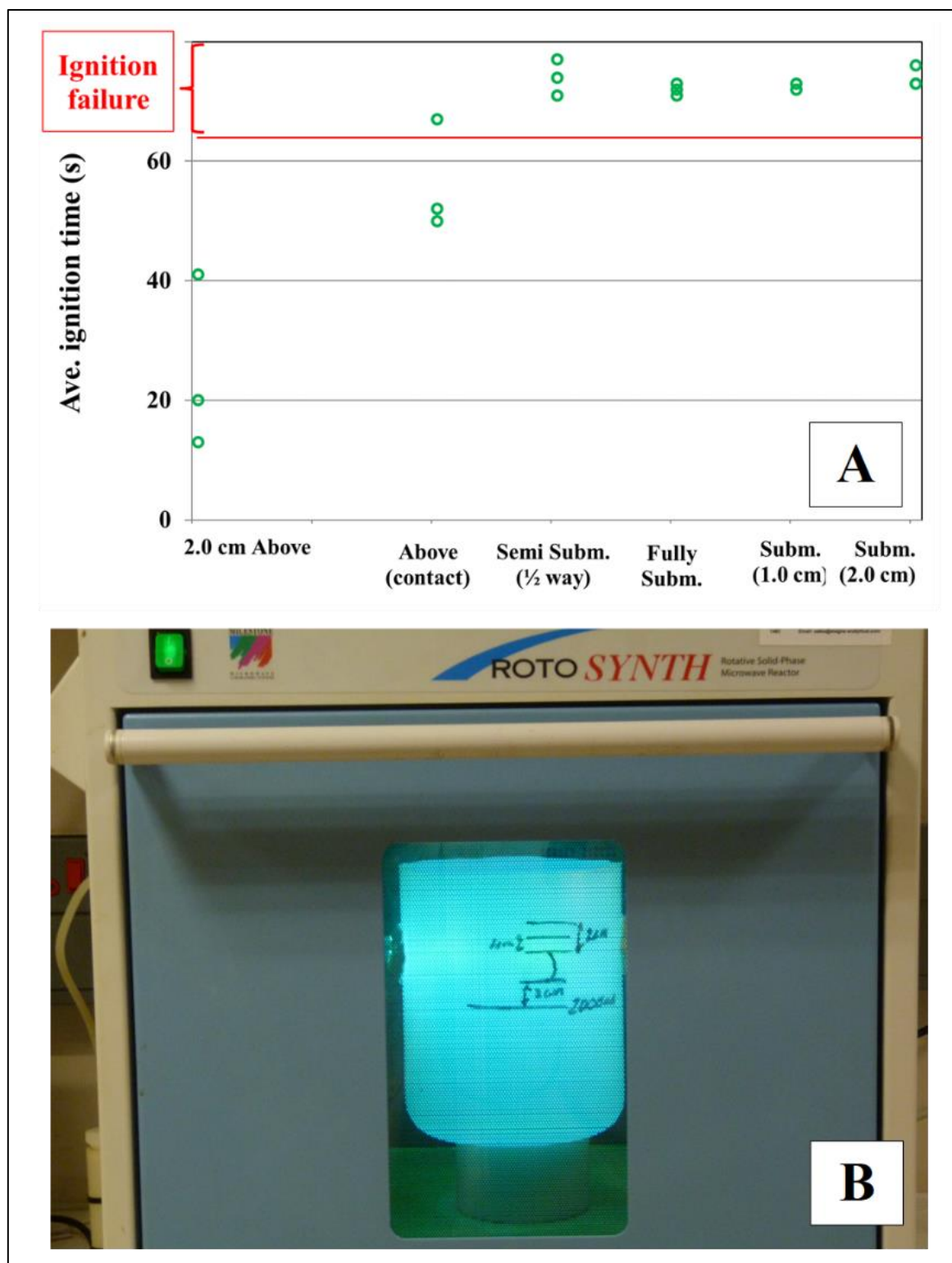


Figure 4.9: [A] Ignition time and [B] photograph during ignition of suspended MDEL/'bucket' combination at variable water content levels.

Conditions: Primarc MDEL in glass tube of suspended 'bucket' combination Teflon 'puc' inside Roto SYNTH microwave reactor; 25.0 °C (Room temperature); microwave at 1200 W; 70 s.

was visually notable (Figure 4.9B). However, once the water level was raised to be just in contact with the bottom of the glass tube holding the MDEL, the ignition time was markedly higher or ignition did not occur. As the water level was further raised (i.e. partial submersion to full submersion and above), ignition was not observed in all cases.

In summary, the overall speed of ignition of the Primarc MDEL did appear to increase with the ROTO synth microwave oven power levels, however, both ignition and “burning” of the MDEL was irregular and random in pattern. As regards the reactor design, the suspended MDEL, “bucket” combination reactor appeared to be a possible viable reactor design for the Primarc MDEL, and the most promising of all MDEL reactor designs tested in this work.

4.2.6 Photobleaching of pulp utilizing the suspended MDEL, “bucket” combination

Since the suspended MDEL, “bucket” combination appeared to be the most promising reactor design for the MDEL Primarc light source, experimental photobleaching was undertaken with this reactor design to gauge its performance [312]. A description of the experimental work is given in Section 3.5.6. The Primarc MDEL gave a small improvement in delignification/bleaching over the control suggesting that some low level of photochemical bleaching with UV light may have occurred (Figure 4.10). The small difference in kappa number steadily grew over the period of 10 to 90 minutes. This is noteworthy given that the ignition and burning of the Primarc MDEL would likely have been erratic and brief in duration involving numerous ignition/burn “bursts”. Overall the kappa reduction was inversely exponential in relationship with a moderate statistical fit (R^2 function) for the control and Primarc MDEL curves respectively (see equations in Figure 4.10).

Analysis of variances (i.e. single factor ANOVA) showed that none of the results for the Primarc MDEL were significantly different from the control (Table 4.2). However, the P values showed a general improvement at the longer times (i.e. 45 minutes and after) with P values about 0.3 or less, and with the results for 45 minutes almost achieving the 95% confidence level. Overall, although not statistically different, this reflects positively on the results. Furthermore, this also demonstrates the exceptional difficulties associated with achieving successful photochemical bleaching using the MDEL/microwave oven combination reactor system.

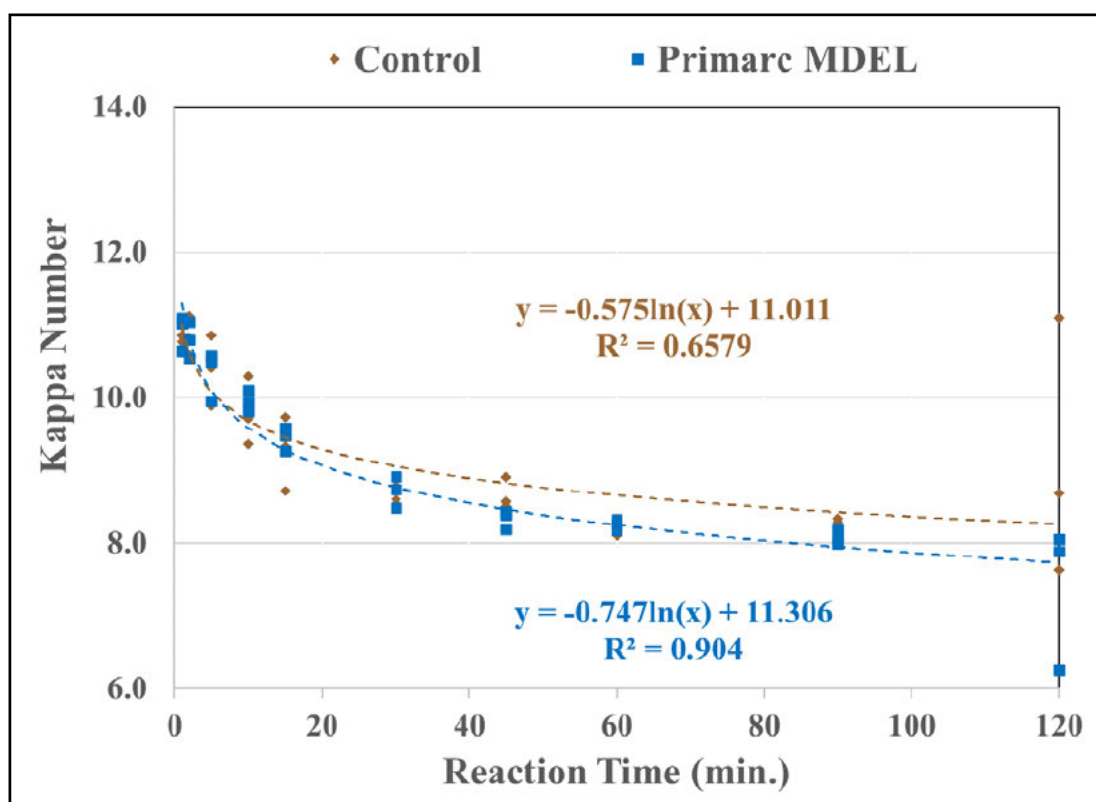


Figure 4.10: Kappa number of Cloquet unbleached HW pulp at variable times after photobleaching in the combination Roto SYNTH/MDEL “bucket” reactor.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂; 14.0 g pulp; 25.0 °C (Room temperature); 0.7% consistency ; suspended MDEL, “bucket” combination.

Table 4.2: P values from single factor analysis of variances (ANOVA) of kappa number of Cloquet unbleached HW pulp at variable times after photobleaching in the combination Roto SYNTH/MDEL “bucket” reactor.

Time (minutes)	P value
1	0.8407
2	0.7814
5	0.2172
10	0.9532
15	0.8552
30	0.8424
45	0.0527
60	0.2422
90	0.3206
120	0.2831

The viscosities of the Primarc MDEL bleached pulp generally appeared to be lower than those of the control, but the differences between the two were small and not likely significant (Figure 4.11). Absolute losses in viscosity for both the Primarc MDEL and the control pulps were moderate in

magnitude (about 300 ml g⁻¹ units) and increased with reaction time with most of the viscosity loss occurring within the initial 60 minutes of reaction. Similar to the kappa number, the viscosity followed an inverse exponential relationship. Statistical agreement was moderate to good based on the R² function for the absolute viscosity (see equations shown in Figure 4.11).

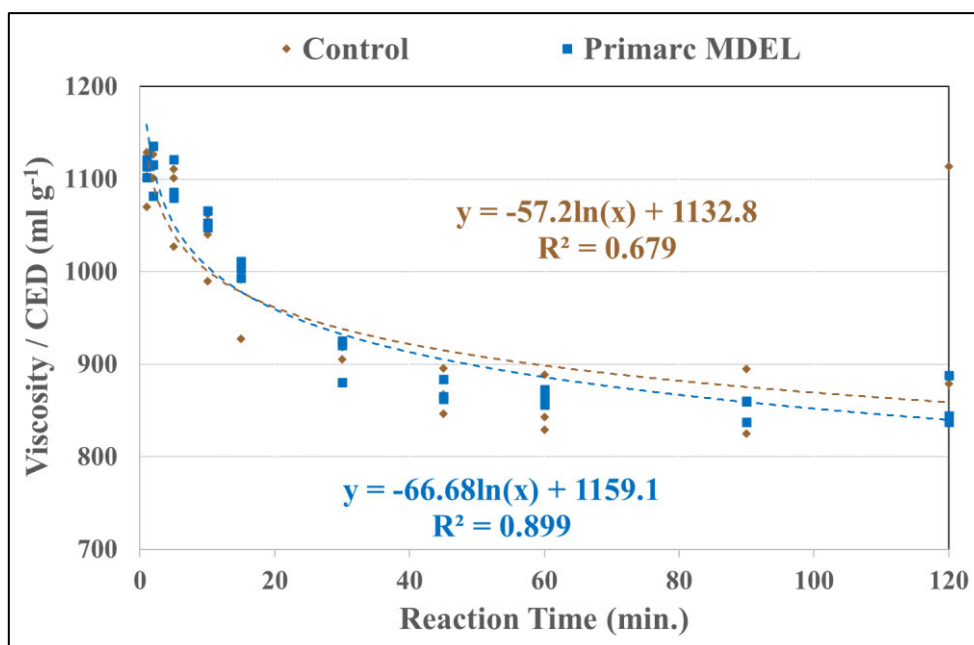


Figure 4.11: Viscosity of Cloquet HW pulp at variable times after photobleaching in the combination Roto SYNTH/MDEL “bucket” reactor.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂; 14.0 g pulp; 25.0 °C (Room temperature); 0.7% consistency ; UV LED suspended MDEL, “bucket” combination.

The residual peroxide content for both the control and the Primarc MDEL bleached pulps followed notably similar exponential curves, suggesting that much of the peroxide consumed utilised similar chemical mechanisms, namely, the thermal peroxide bleaching of the pulp and the wasteful thermal degradation at low consistency (Figure 4.12). This is supported by the observation that the boiling point was reached in less than 15 minutes while it took about 60 minutes for most of the peroxide to be consumed (Figure 4.13). The near nil residual peroxide at 100 to 110 minutes suggests that any kappa number reduction after 100 minutes is likely due to purely caustic soda extraction of degraded lignin. However, the small but increasing difference in kappa number between the control and the Primarc MDEL pulps in the period from 10 to 90 minutes suggested that some of the peroxide utilised was due to photo-bleaching utilizing the Primarc MDEL (via photolysis of peroxide to hydroxyl radicals) [127, 266].

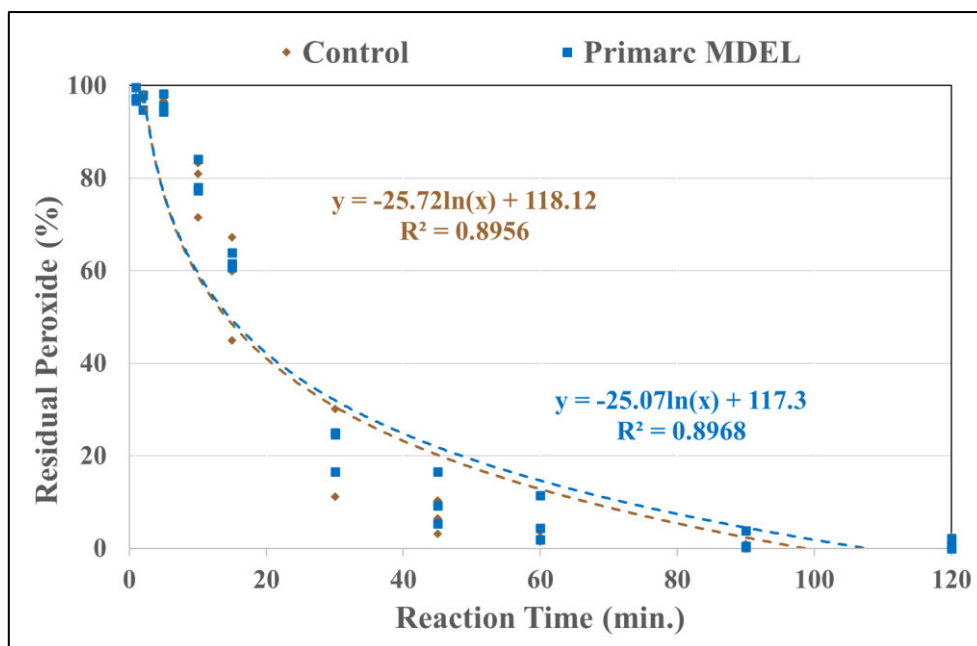


Figure 4.12: Residual peroxide of Cloquet HW pulp at variable times after photobleaching in the combination Roto SYNTH/MDEL “bucket” reactor.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂; 14.0 g pulp; 25.0 °C (Room temperature); 0.7% consistency ; suspended MDEL, “bucket” combination.

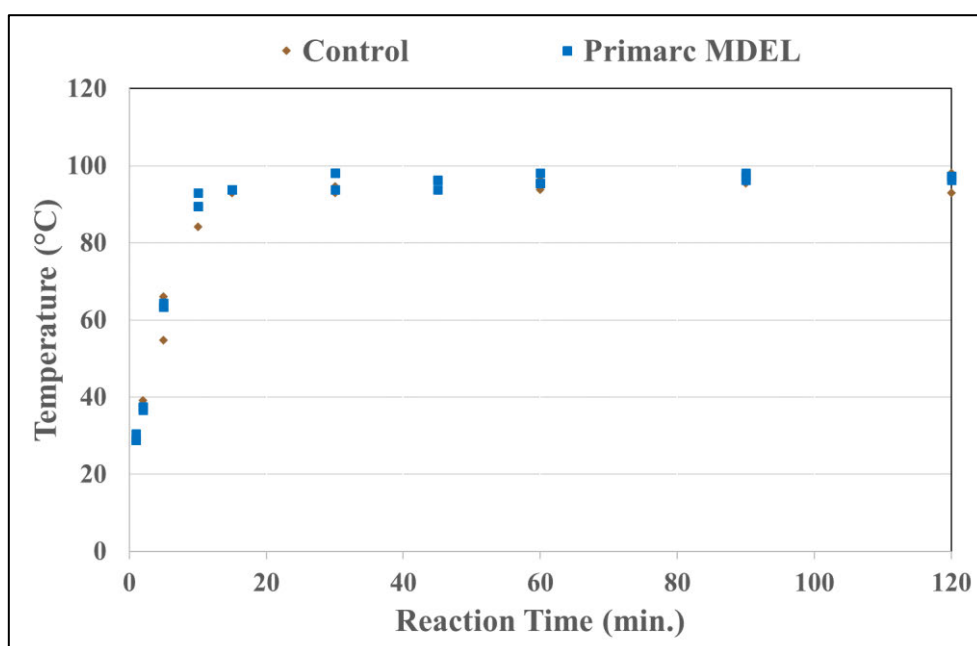


Figure 4.13: Temperature of Cloquet HW pulp at variable times during photo bleaching in the combination Roto SYNTH/MDEL “bucket” reactor.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂; 14.0 g pulp; 25.0 °C (Room temperature); 0.7% consistency ; suspended MDEL, “bucket” combination.

In all experiments, both the control and the Primarc MDEL bleached pulps, gave initial and final pH values above the pH 9.0 minimum needed for proper peroxide bleaching (Table 4.3). Thus, in all cases, the experiments were under appropriate control and performing adequately as expected.

Table 4.3: Average pH value of Cloquet pulp suspension at variable times for the control and Primarc MDEL experimental sets before and after photobleaching in the combination Roto SYNTH/MDEL “bucket” reactor.

Time (min)	1	2	5	10	15	30	45	60	90	120
Control										
Initial pH	10.14	9.36	9.60	9.94	10.55	10.40	10.15	10.26	9.88	9.28
Final pH	9.66	9.41	9.34	9.64	9.83	9.87	9.43	9.51	9.54	9.42
MDEL										
Initial pH	10.29	9.86	10.17	10.39	10.58	10.33	10.33	10.12	10.20	10.10
Final pH	10.00	9.51	9.82	9.76	9.84	9.75	9.68	9.68	9.48	9.29

In summary, although a small degree of photochemical bleaching utilizing the Primarc MDEL was qualitatively apparent, the control and MDEL results were not statistically different based analysis of variances (ANOVA). Most of the bleaching appears thermally-driven as given by both the kappa number and viscosity. In addition, even if qualitative observations are taken on their own, it would not be possible to mathematically separate out the small benefit from the MDEL from the solely microwave heat and other effects, particularly, given the random pattern of ignition and “burning” of the Primarc MDEL in the Roto SYNTH microwave oven reactor. If the Roto SYNTH microwave oven cavity was better calibrated and tuned, the photobleaching using the Primarc MDEL may have performed better in a uniform, consistent and continuous manner.

A review of the experimental work of other researchers, including the multiple articles by Horikoshi et al. [255 – 261] and Klan et al. [251, 262 – 265], the topic summaries written by Horikoshi, Abe and Serpone [252, 254], as well as short-term work by others [266 – 270], indicated that MDELs could be employed as possible light sources under specific conditions, including the possible photochemical bleaching of pulp. However, these specific conditions include properly calibrated microwave resonant chambers, properly designed reactors, custom built MDELs, and microwave wave-guides/focusing-

cones. Without most of these specific conditions, proper ignition and sustained burning of the MDELs would not be possible. In addition, such precise and specific conditions may not be able to survive a harsh commercial mass-production environment, making MDEL based bleaching of pulp impractical. A possible, more practical, alternative to MDELs may be radio frequency DELs (see Appendix C).

4.3 UVet UV led array

For the UV LED array to be properly evaluated as a light source, the following topics were investigated: (i) the viability of the UV LED array reactor design, (ii) the use of various reagents and bleaching oxidants, (iii) the impact of various operational conditions (i.e. pH, temperature, UV radiation intensity, and consistency of Cloquet Aspen pulp), and (iv) the application of various photocatalysts and photosensitizers [316 - 327]. Once evaluated as a light source, the UV LED array was investigated in the photochemical bleaching of various starting pulps, as well as the use of the UV LED array as a light source in various paper grade and dissolving pulp grade photobleaching sequences [328, 329].

4.3.1 Photochemical pulp bleaching with UV LED array: Establishing control blanks for pulp and alkali peroxide solutions

As stated, this study which evaluated a reactor design based on a UV LED array, aimed to quantify the contribution of changes to the pulp (bleaching, degradation, etc.) from all sources/agents/effects except the ultraviolet radiation (i.e. switched off/nil power), and to validate the general design and operation of the UV LED array reactor design [316, 317]. A description of the experimental work is given in Section 3.6.1. The overall investigation into the utilization of an UV LED array for the photobleaching of pulp required the establishment of these control blanks for the pulp and alkali peroxide solutions. These blanks for the pulp and alkali peroxide solutions were then used as the necessary controls for all subsequent experimental work employing the UV LED array as an illuminant. In all cases, whether using a pulp or alkali peroxide solution, the initial and final pH results of the blanks/controls remained above a value of ten (i.e. 10.0) indicating that conditions were correct for peroxide bleaching and/or degradation (Table 4.4). This indicated that, with regards to pH values, the UV LED array reactor was operating properly without experimental anomalies.

The kappa number for the unirradiated pulp with alkali peroxide showed a general downward trend with increased reactor time, but the decrease was small amounting to approximately 8% of the starting kappa number (Figure 4.14). This was likely due partially to alkali extraction of the soluble degraded lignin fraction from the pulp, via swelling of the pulp fibres, over prolonged periods. The contribution of peroxide bleaching giving the observed kappa number reduction is minor given the low reaction temperature. The individual triplicate kappa number results for each time interval show a variable

Table 4.4: Average initial and final pH values of pulp with deionised water, and pure alkaline peroxide solution for UV LED array reactor control blanks (nil power).

Conditions: 18.0 kg t⁻¹NaOH , 80.0 kg t⁻¹ H₂O₂; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency ; UV LED array (unpowered – no light source).

Time (min.)	1	2	5	10	15	30	45	60	90	120
PULP WITH DE-IONIZED WATER										
Initial pH	10.96	10.88	10.94	10.91	11.00	10.98	11.05	10.99	11.02	11.03
Final pH	11.01	11.01	10.91	11.09	10.96	11.03	11.09	11.07	11.15	11.13
PURE ALKALINE PEROXIDE SOLUTION										
Initial pH	11.05	11.05	11.09	11.05	11.06	11.05	10.94	10.79	10.83	10.70
Final pH	10.77	11.07	11.06	11.08	11.02	11.04	11.04	11.02	10.99	11.04

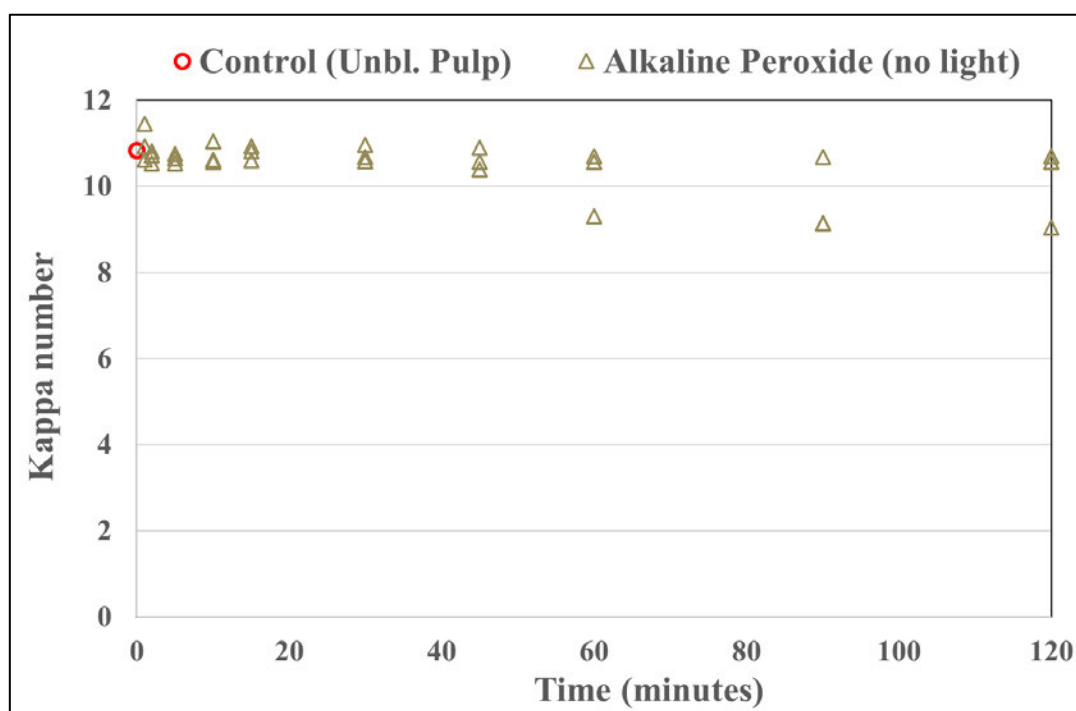


Figure 4.14: Kappa number of pulp suspensions for UV LED Array reactor at variable reaction times with UV light source unpowered.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency ; UV LED array (unpowered – no light source).

spread among triplicates with no discernible pattern. The approximate variation for triplicate raw data of the kappa number was 0.6. This is about 5.5% of the starting kappa number , which suggests that

the variation within the triplicates of both was small; and variation in the kappa number data may account for about as much as half the kappa number reduction (8% of starting kappa) observed over the 120 minutes evaluated.

For the viscosity, there was no reduction over the same time scale (Figure 4.15). As with the kappa number, the individual triplicate viscosity results also show a variable spread among triplicates with no discernible pattern. The approximate variation in the viscosity was 50 ml g⁻¹. This is about 4.5% of the starting viscosity, and suggests that the variation within the triplicates was small. Given the relationship between the viscosity of the pulp and its strength discussed earlier, the alkaline peroxide bleaching of the pulp without a powered UV LED array gave no loss in pulp strength.

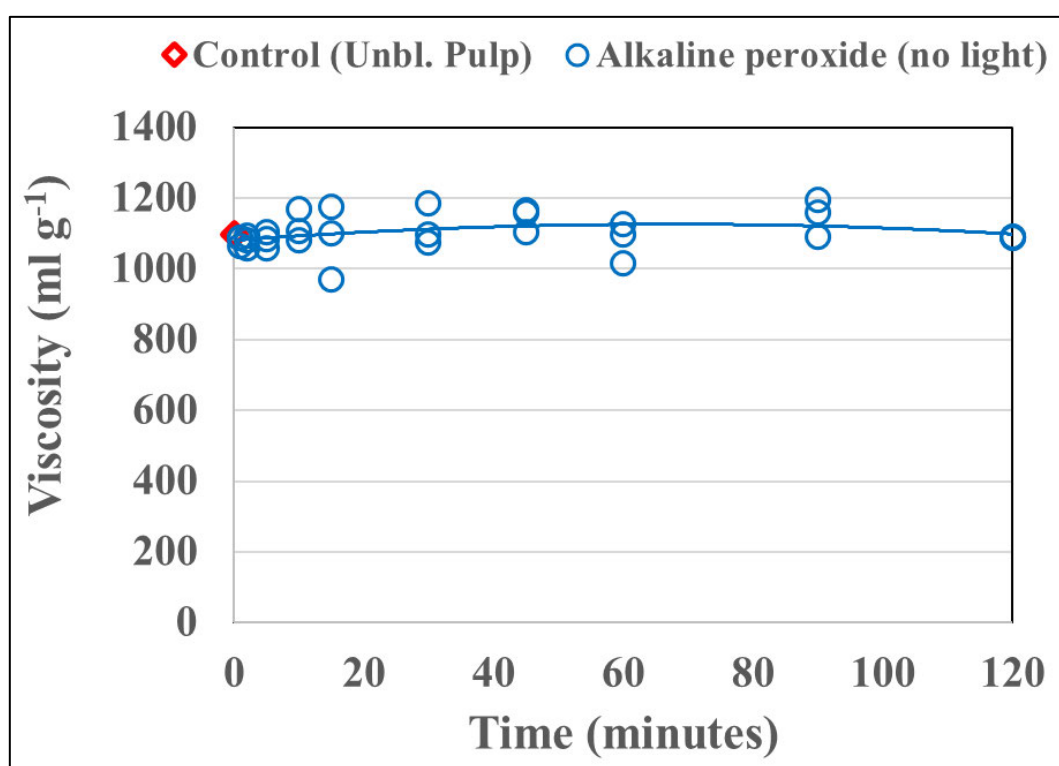


Figure 4.15: Viscosity of pulp suspensions for UV LED array reactor at variable reaction times with UV light source unpowered.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency ; UV LED array (unpowered – no light source).

Pulp yield showed a minor variation over time (Figure 4.16). This upward trend is likely an experimental error as a gain in yield makes no sense, and it is more reasonable to assume that there was nil to very little loss in pulp yield. The approximate variation for triplicate raw data was estimated at 2.6%, suggesting that the variations within triplicate raw data results were minor.

The residual peroxide showed no peroxide degradation with the pulp suspension, and some small steady loss over time with the deionised water only (Figure 4.17). Thus, the pulp appears to “protect” the peroxide from degrading over time at low temperatures, preventing the steady drop observed for the deionised water only. As indicated in the insert (Figure 4.17), approximately 10% of the peroxide charge is lost over the 120 minutes period for the deionised water only. The standard deviations for triplicate raw data of the pulp suspension and deionised water only were estimated at 2.83% and 3.47% respectively, suggesting minimal variation within the triplicates of both residual peroxide measurements.

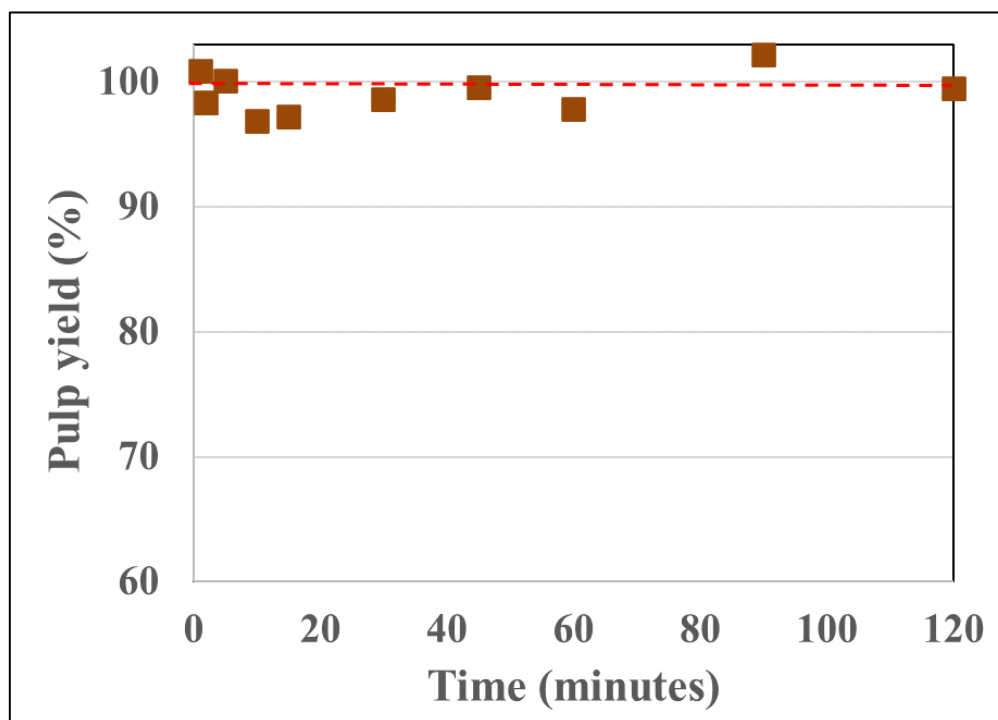


Figure 4.16: Pulp yield for UV LED Array reactor at variable reaction times with UV light source. Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹H₂O₂; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency ; UV LED array (unpowered – no light source).

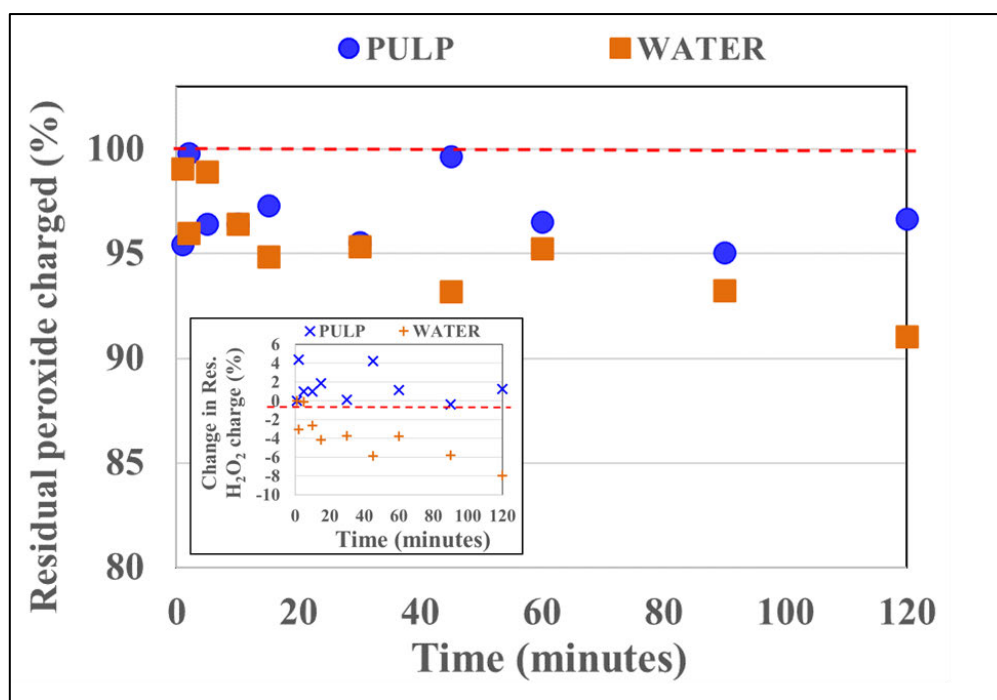


Figure 4.17: Residual average peroxide charged of pulp suspensions or only deionised water for UV LED Array reactor at variable reaction times with UV light source unpowered. Insert: Change in peroxide residual as for main figure.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency ; UV LED array (unpowered – no light source).

Having established the control blanks for the pulp and alkali peroxide solution without UV LED irradiation, the next step was to validate the UV LED array reactor system by investigating the photodegradation of an alkali peroxide solution (without pulp) while under UV LED irradiation. For this control, the residual peroxide content of the peroxide solution decreased from 97.1% to 92.7% of the original charge over the two-hour period that the experiments were run with the unpowered UV LED array, i.e. in the “OFF” position (Figure 4.18). This demonstrated that the peroxide, although it did decompose in the presence of caustic soda as expected, did so extremely slowly with most of it still present after two hours. However, when the UV LED array was powered up, i.e. in the “ON” position, the residual peroxide content dropped from the full initial charge to 13.1% in an hour. Thus, in half the time observed for the control experiment, most of the peroxide had degraded when exposed to the high intensity UV light from the UV LED array. This decomposition of the residual peroxide was due to direct photolysis of the hydrogen peroxide in solution to eventually form oxygen gas and water. The UV exposure experimental set was nonlinear in nature. In summary, this photolysis indicates that the reactor system and its UV LED array are fully operational and ready for use. These results validate the UV LED array reactor system.

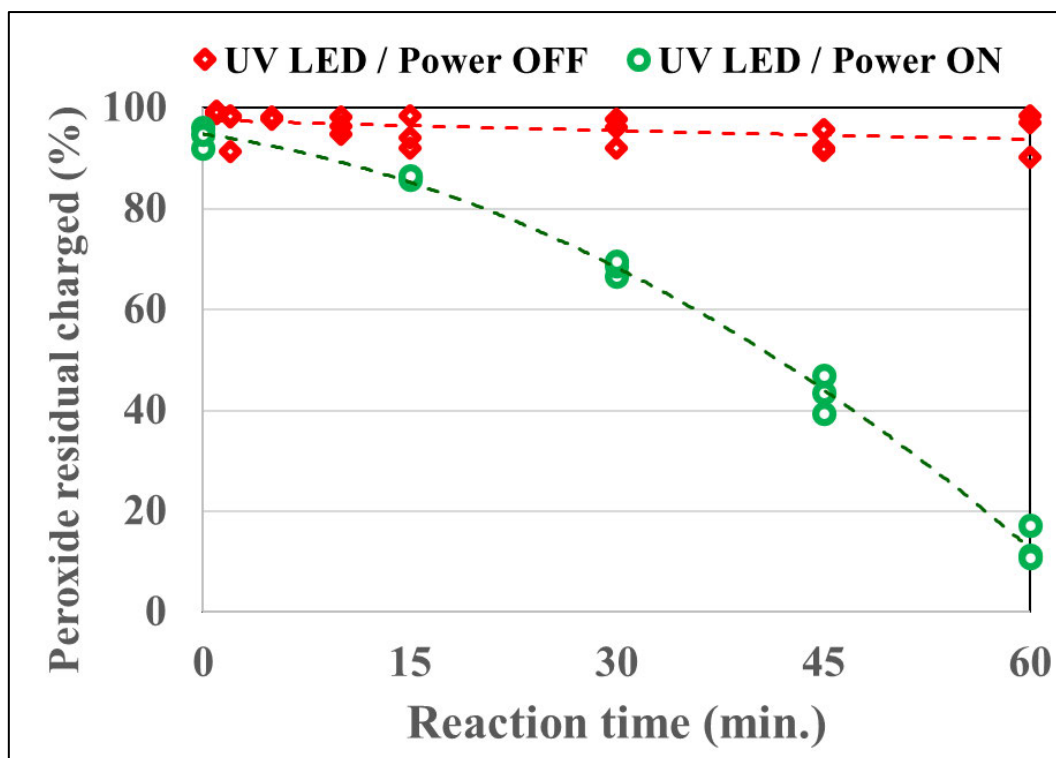


Figure 4.18: Residual peroxide charge for peroxide solution for UV LED Array reactor at variable reaction times with UV LED array either unpowered or powered up.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂; no pulp; 25.0 °C (Room temperature); UV LED array (full power).

The pH value of the solution showed almost no change between the start and final pH values (Figure 4.19). This indicated that most of the decomposition of the peroxide was not due to reaction with caustic soda, which would have lowered the final pH value, but rather due to direct photolysis of the hydrogen peroxide itself.

The increase in temperature with exposure to high intensity UV light was small, amounting to a 6.2 °C change at most (Figure 4.20). Given that the rate constant of thermally-driven chemical reactions can be approximated by the Arrhenius equation: $k = Ae^{(-E_a/RT)}$ where the rate of reaction approximately doubles for every 10 °C change, a temperature rise of only 6.2 °C amounts to no more than a 60% increase in the thermal degradation of the peroxide in the presence of caustic soda [124]. This is minimal and its contribution to the total rate of peroxide decomposition under intense UV light exposure is insignificant.

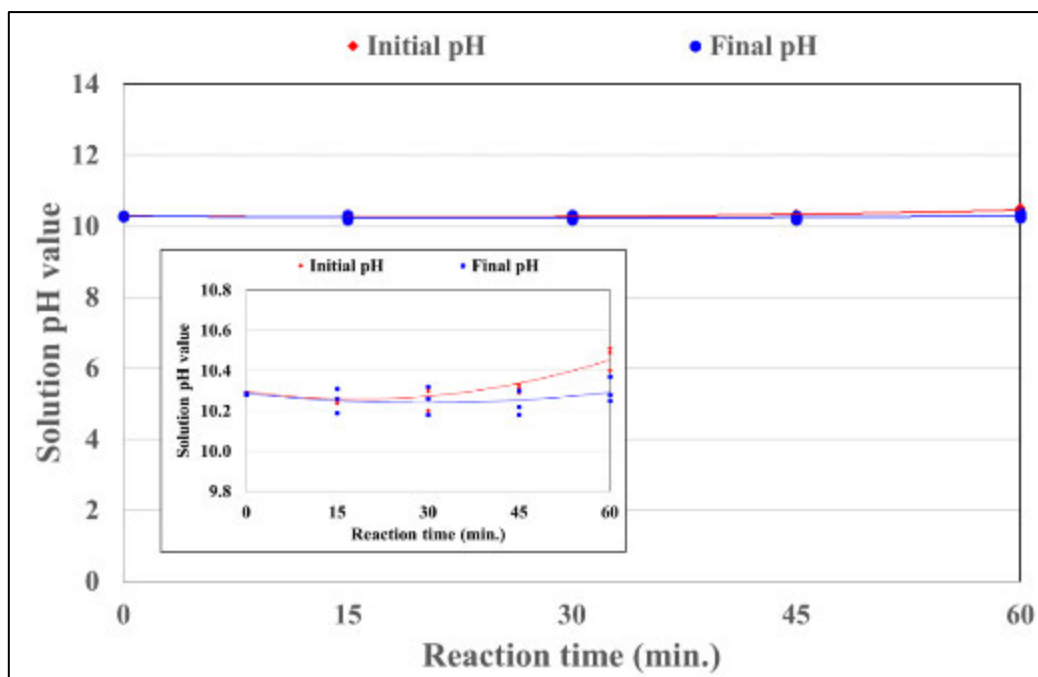


Figure 4.19: Start and final pH values of peroxide solution for UV LED array reactor at variable reaction times with UV light source powered up. Insert: As main, i.e. start and final pH, but viewed at a narrower pH scale.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂; no pulp; 25.0 °C (Room temperature); UV LED array (full power).

In summary, the control blank curve for the UV LED array reactor (i.e. no UV light irradiation) showed no loss in viscosity for the Cloquet paper grade pulp over the 120 minutes of reaction time, while the kappa number showed a small decrease of about 8% due to extraction of the smaller soluble degraded lignin fractions under alkali conditions as the fibre walls swelled and “opened up” above a pH of nine; with about half of that kappa reduction likely due to experimental variation in the multiple analyses. There was no degradation of the peroxide charge to the reactor in the presence of the pulp while an approximately 10% degradation in the peroxide charge occurred when only deionised water was used. The pulp appeared to “protect” the peroxide when not being irradiated with the UV LED array. Pulp yield losses were minimal or nil. In general, the control blanks showed that (when there is no UV irradiation) the changes in kappa number, viscosity, peroxide content and pulp yield were nil to minimal. Thus, any enhanced changes in these parameters upon UV LED irradiation can be attributed to the photobleaching effect when under UV LED irradiation. As regards UV LED irradiation of the pure alkali peroxide solution, exposure of a solution of caustic soda and hydrogen peroxide to high intensity UV light gave almost complete decomposition of the peroxide component in 60 minutes. The results obtained indicate that the UV LED array reactor system is fully operational and ready for use. Thus, the UV LED array reactor system had been successfully validated for use.

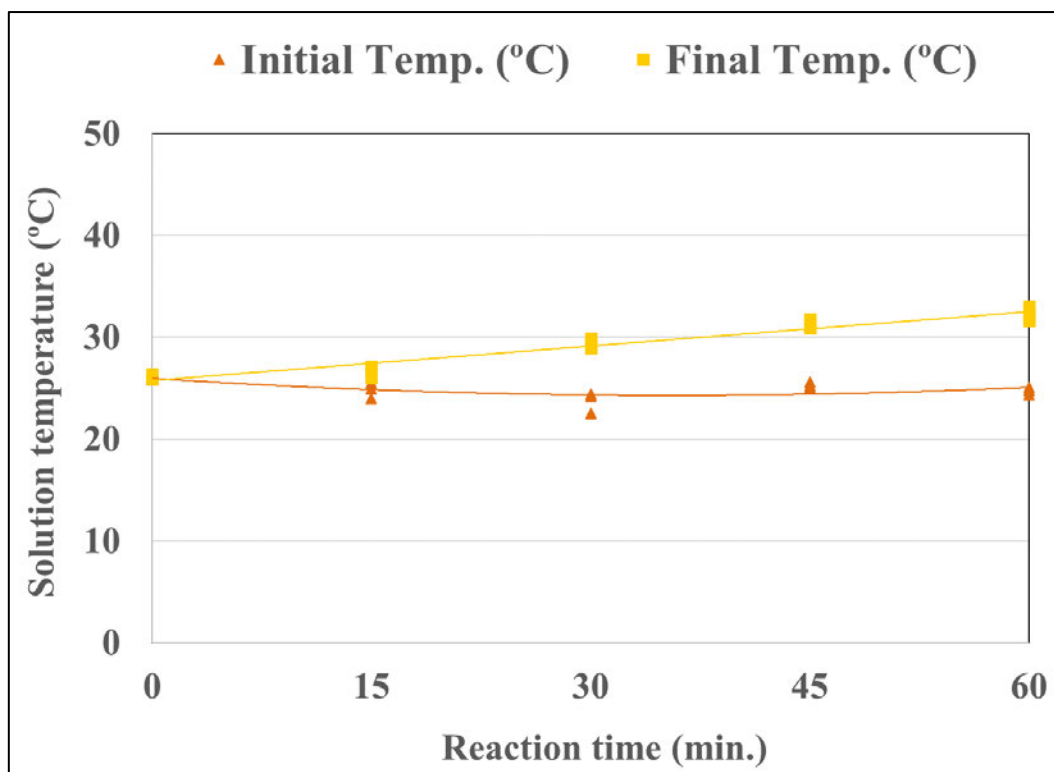


Figure 4.20: Initial and final temperatures of peroxide solution for UV LED array reactor at variable reaction times with UV light source powered up.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂; no pulp; 25.0 °C (Room temperature); UV LED array (full power).

4.3.2 Photochemical bleaching of pulp with UV LED array: Photobleaching effect on pulp in the presence and absence of hydrogen peroxide (Variable 1)

In this study the aim was to determine how an alkali peroxide solution would perform in the photobleaching of pulp under UV LED array irradiation [318]. A description of the experimental work is given in Section 3.6.2. The reduction in the kappa number over a two-hour period for a pulp suspension charged with caustic soda and hydrogen peroxide but without any UV light irradiation (i.e. the control) was minimal, about a single kappa unit from a kappa of about eleven down to ten (Figure 4.21). However, when under UV irradiation with the UV LED array, a far larger reduction for the same pulp suspension was achieved, of about five units from eleven down to six. When using only caustic soda (i.e. pure caustic soda), a higher kappa reduction than without UV irradiation was still observed, but, less than when peroxide was present (about three and half units from eleven down to seven and half). Overall, these results clearly demonstrated that photochemical bleaching in pure alkali and alkali peroxide solutions had occurred.

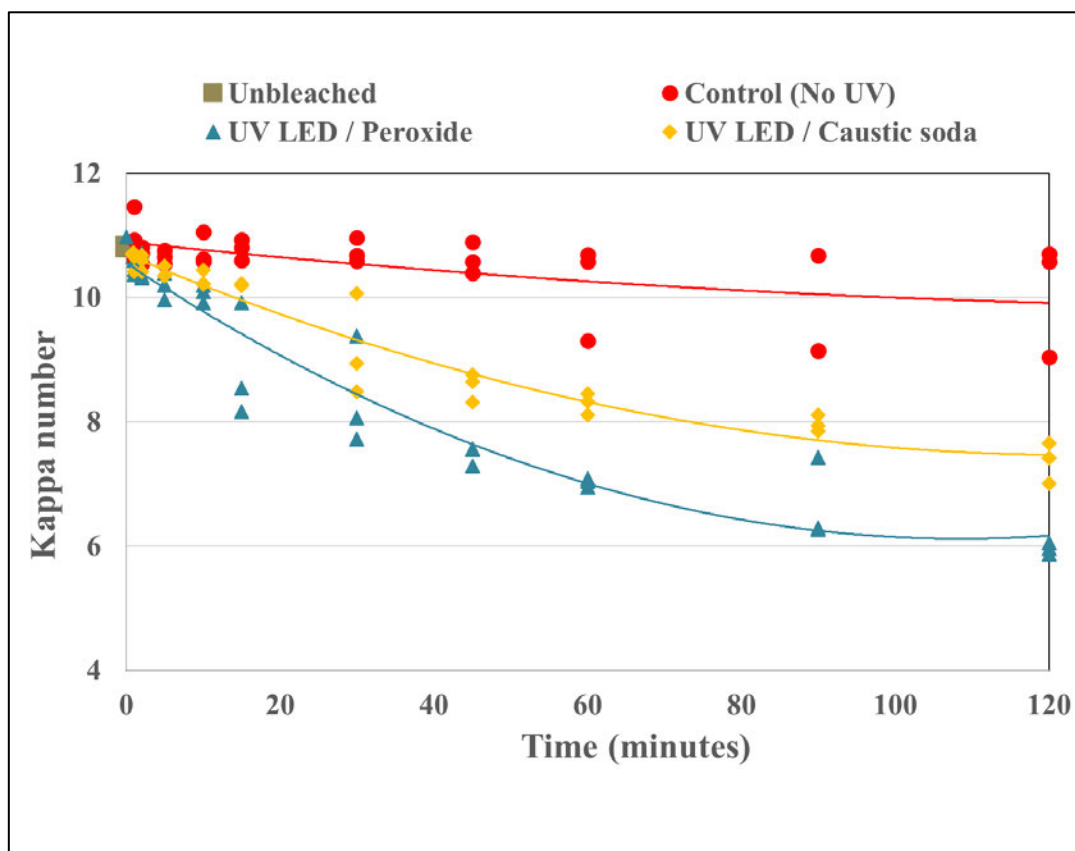


Figure 4.21: Kappa number for various alkaline pulp suspensions bleached in a UV LED array reactor, with or without peroxide, at variable reaction times with array either unpowered or powered up.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂ where relevant; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency; UV LED array (full power).

The brightness followed a similar but opposite trend to the kappa number for the two UV-irradiated pulp suspensions (Figure 4.22). The peroxide irradiation curve increased brightness by about twenty four units over the two-hour period, while the curve for the use of caustic soda only increased brightness by seven units only over the same period. The inclusion of peroxide greatly increased brightness development.

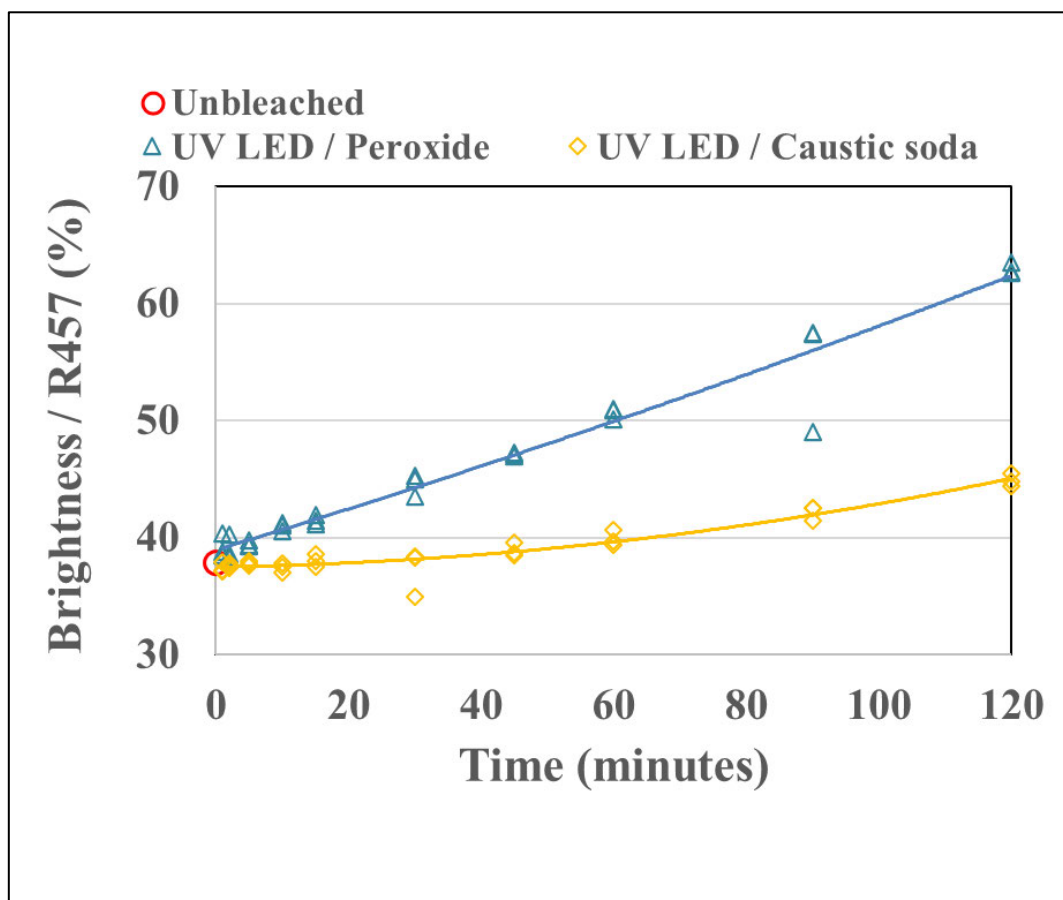


Figure 4.22: Brightness (R457) for various alkali pulp suspensions bleached in a UV LED array reactor, with or without peroxide, at variable reaction times.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂ where relevant; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency; UV LED array (full power).

A fourth- and third-order polynomial relationship between their kappa numbers and their brightness was observed for both the peroxide and pure caustic soda pulps respectively (Figure 4.23). The peroxide pulp gave a correlation coefficient of about 0.98 (fourth-order polynomial), while the pure caustic soda pulp gave a lower correlation coefficient value of about 0.84 (third-order polynomial). However, the peroxide and caustic soda experiments appear to be based on very different mathematical models, meaning that using mathematic models of the brightness number to predict the kappa number would be difficult for a generalized formula. In addition, a combined universal model for both peroxide and pure caustic soda would contain far too little data to model its prediction accurately. Consequently, all future experimental work continued to measure both parameters.

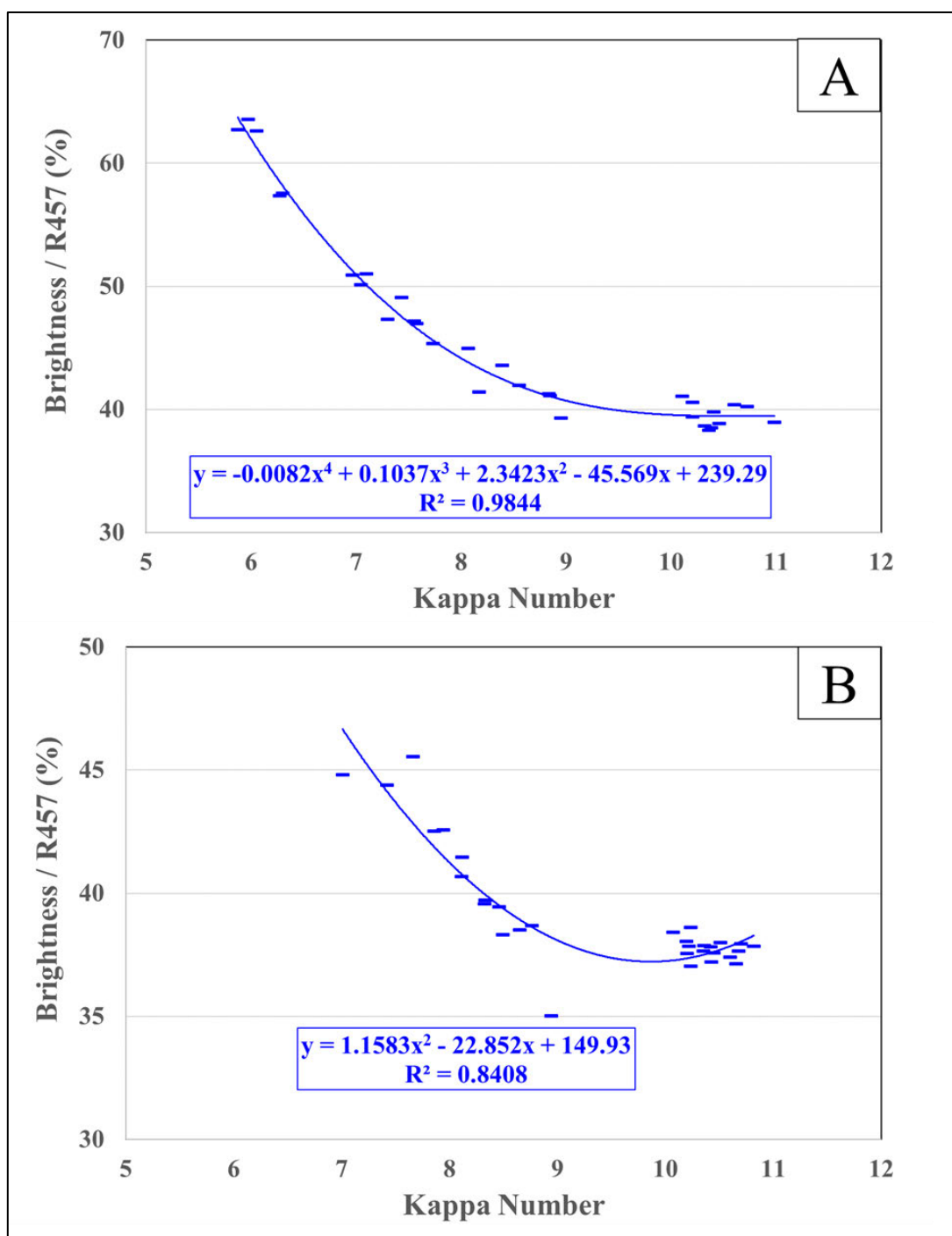


Figure 4.23: Kappa number versus brightness curves for UV LED array reactor for [A] peroxide and [B] caustic soda only pulp suspensions.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂ where relevant; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency; UV LED array (full power).

A visually-based estimate of the extent of UV light penetration by the UV LED array as given by the observed scattered and reflected light indicated that less than one eighth (approximate 500 ml depth of penetration in 4000 ml) of the pulp was subjected to UV/visible irradiation at any one instant (Figure 4.24). The opacity of any pulp suspension is a well known obstacle in their photobleaching, even at

low consistencies, yet despite of this, significant photochemical bleaching of the Cloquet pulp was still achieved.



Figure 4.24: Visually observed extent of penetration given by scattered blue reflected light produced from UV irradiation using the UV LED array reactor.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂ where relevant; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency; UV LED array (full power).

Overall, losses in viscosity were small, suggesting little damage to the cellulose of the fibre during photochemical bleaching with irradiation by the UV LED array (Figure 4.25). The peroxide pulp gave an approximate 100 ml g⁻¹ reduction, while the pure caustic soda pulp gave a 50 ml g⁻¹ reduction. The control gave no significant reduction. These small reductions were due to the low temperature employed in the process (about room temperature rising to about 35 °C (see Table 4.6) and the likely selectivity of the UV light to lignin's unsaturated aromatic structure over that of the saturated carbohydrates of cellulose and hemicellulose (via direct interaction with the lignin or the selectivity of the radicals generated from the peroxide and water itself).

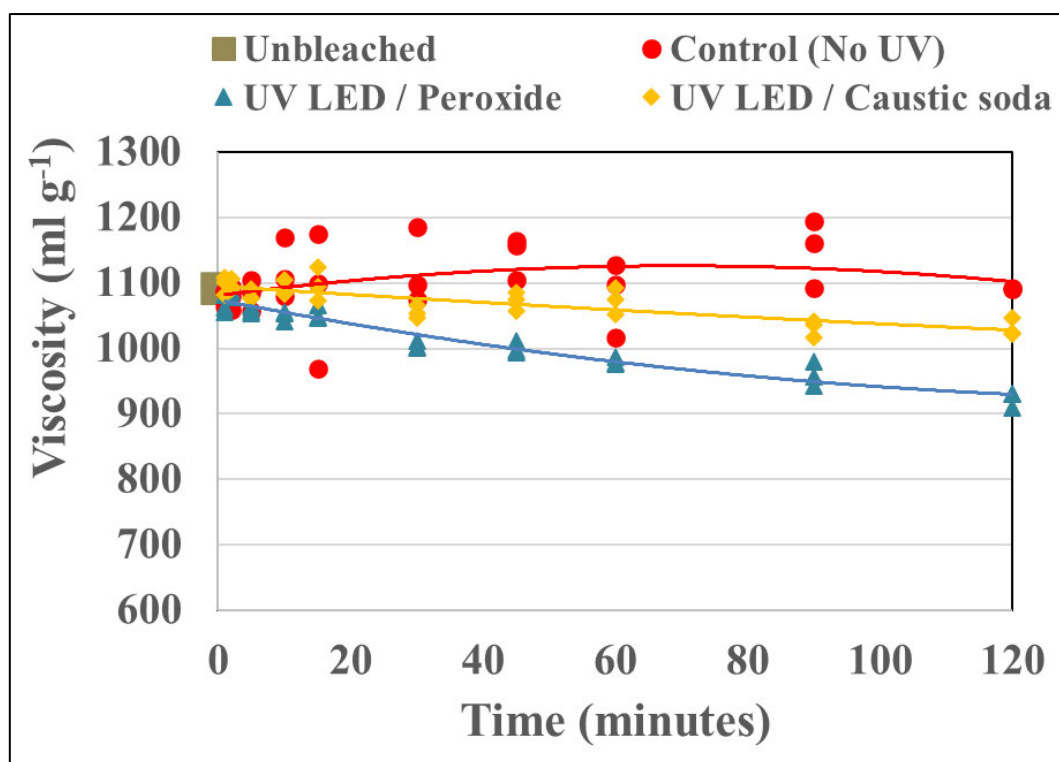


Figure 4.25: Viscosity for various alkaline pulp suspensions bleached in a UV LED array reactor, with or without peroxide, at variable reaction times with array either unpowered or powered up.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂ where relevant; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency; UV LED array (full power).

The initial pH was always above 10.0 for both the peroxide or pure caustic soda, but increasingly decreased for longer reaction times with reductions of about half a pH unit after the full 120 minutes (Table 4.5). Some pH reduction was due to the slow diffusion of the caustic soda into the fibre to neutralize imbedded acid groups (e.g. phenolics and carboxylic acids) or the diffusion out of the fibre of any residual acidic cations. However, it also may be an indication of the type of chemical mechanism involved during the photochemical reaction.

For both UV irradiated pulps (i.e. alkali peroxide and pure caustic soda), the temperature increased by about 13 °C from room temperature to about 37 °C in almost cases (Table 4.6). Given that the preferred temperature for peroxide bleaching is typically above 80 °C and that the reaction rate, as given by the Arrhenius equation: $k = Ae^{(-E_a/RT)}$, suggests an approximate doubling of reaction rates for every 10 °C rise for all first-order kinetics, the thermal contribution to the bleaching effect observed in these experiments, given that the temperature never rose above 37 °C, is likely small. This is further supported by the fact that the fastest thermal reaction kinetics and the greatest proportion of the thermal

Table 4.5: Average initial and final pH values of UV LED array reactor for peroxide and caustic soda pulp suspensions at variable reaction times.

Time (min.)		1	2	5	10	15	30	45	60	90	120
Alkali Perox.	In. pH	10.4	10.4	10.4	10.4	10.4	10.4	10.4	10.44	10.3	10.4
	Fin. pH	10.4	10.3	10.34	10.3	10.3	10.2	10.2	10.1	9.92	9.80
Caustic Soda (only)	In. pH	11.1	11.0	11.0	10.9	10.9	10.9	11.0	11.0	11.1	11.1
	Fin. pH	11.1	11.0	10.9	10.9	10.8	10.7	10.7	10.6	10.6	10.5

Table 4.6: Average initial and final temperatures of UV LED array reactor for peroxide and caustic soda pulp suspensions at variable reaction times.

Time (min.)		1	2	5	10	15	30	45	60	90	120
Alkali Peroxide	In. Temp.	24.1	23.8	24.2	24.3	24.1	24.1	23.4	23.8	23.5	24.7
	Fin. Temp.	24.3	24.5	24.9	25.9	26.6	28.8	30.8	33.0	35.4	38.2
Caustic Soda (only)	In. Temp.	23.8	25.5	24.3	25.0	24.3	24.7	23.8	23.7	24.2	24.4
	Fin. Temp.	24.0	25.2	25.4	26.3	26.8	29.6	31.3	32.5	35.7	37.9

contribution to the bleaching was present only for a small portion of the total photobleaching period usually towards the end of each experiment when the temperature was at its highest and the overall bleaching reaction rate (at the same period) was at its lowest as evident in the kappa curves (Figure 4.21). This small thermal contribution to kappa reduction is further illustrated in equations derived from fitted kappa number versus temperature curves for both UV irradiated pulps (Figure 4.26). Both curves showed an exponential decrease with correlation coefficients of $R^2 = 0.9294$ and $R^2 = 0.8684$ for the alkali peroxide and pure caustic soda pulps respectively, showing good correlations for both. What these curves and their equations show is that the reduction in kappa number is reduced exponentially as the temperature is increased, showing very small contributions to the kappa number reduction at the high temperatures required for adequate thermal peroxide bleaching. These three lines of evidence all suggest that the thermal contribution to the total pulp bleaching effect for both pulps under UV LED array irradiation was minimal.

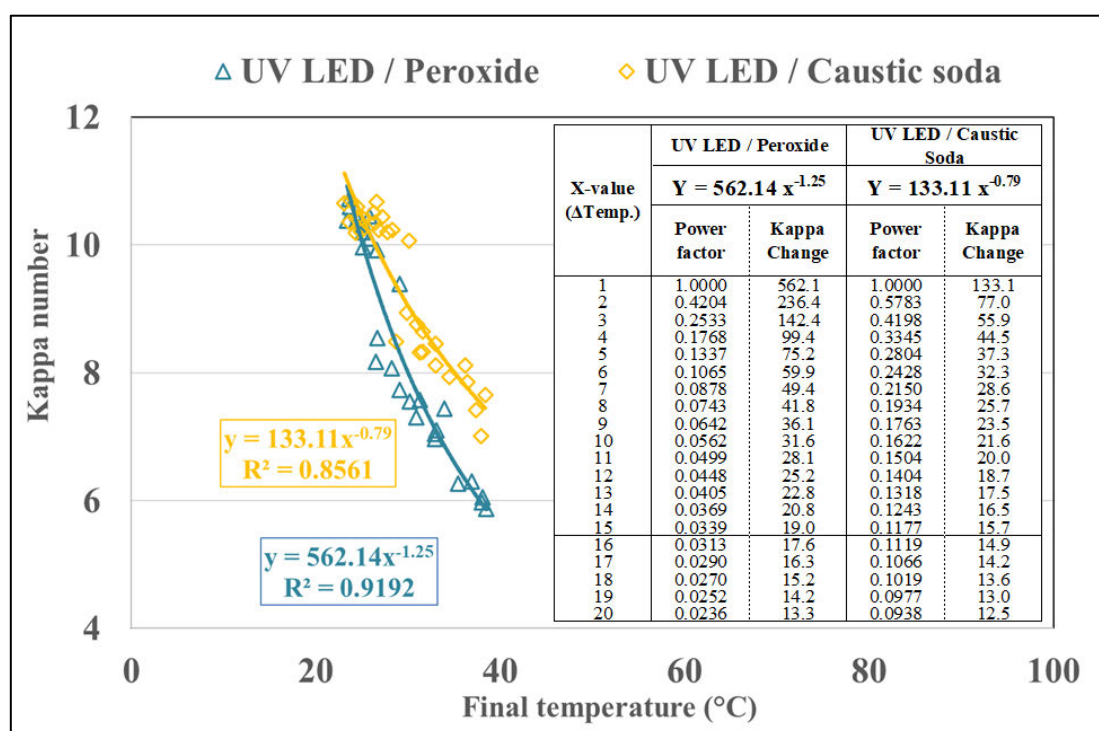


Figure 4.26: Kappa number vs. final temperature for various alkaline pulp suspensions bleached in a UV LED array reactor, with or without peroxide.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂ where relevant; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency; UV LED array (full power).

Pulp yields tended to show little or no loss in material with yields typically above 95% (Figure 4.27).

For the two pulp suspensions charged with peroxide (i.e. control and irradiated peroxide), peroxide consumption was minimal to small, but increased with reaction time for the irradiated peroxide (Table 4.7). The control typically gave an approximate 1.0% reduction on average (if any) after 120 minutes, while the irradiated peroxide gave an approximately 6.0% reduction over the same period. These results show that the peroxide is being used in excess and future work (outside of the scope of this thesis) should also aim to further optimize the peroxide charge for whatever experimental conditions are employed.

In summary, the photochemical bleaching of unbleached Cloquet paper grade pulp using the UV LED array reactor system, with pure caustic soda, was successful, giving increases in brightness and reductions in kappa number, while ensuring minimal losses in pulp viscosity and pulp yield. The

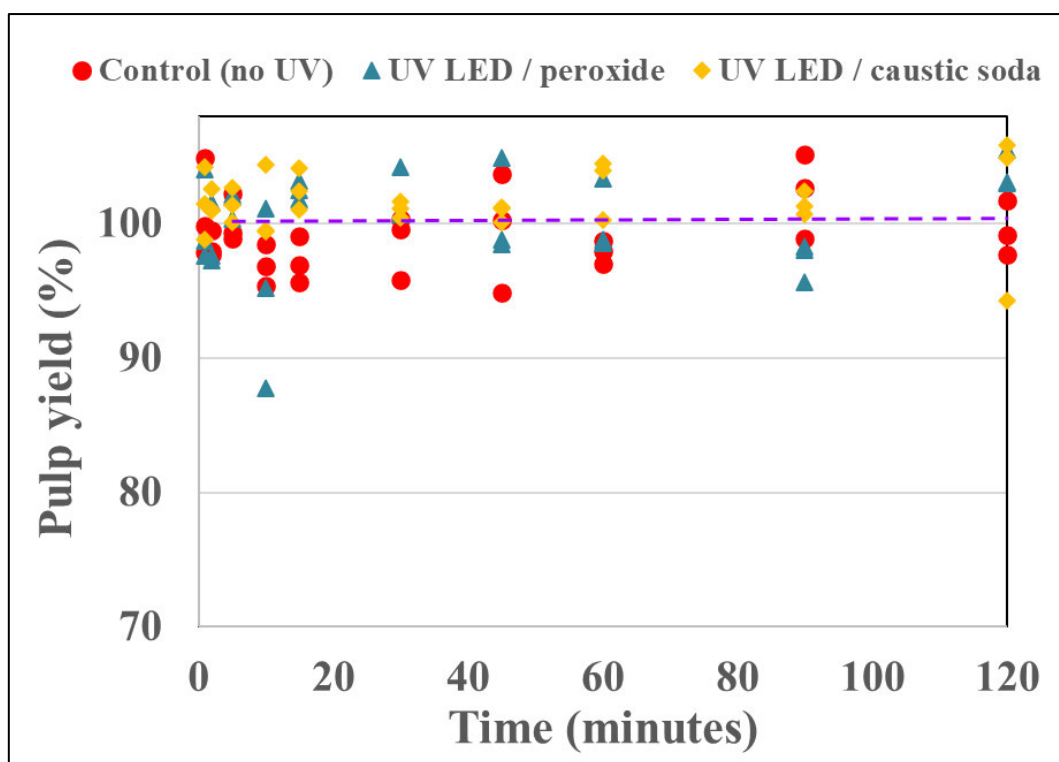


Figure 4.27: Pulp yields for various alkaline pulp suspensions bleached in a UV LED array reactor, with or without peroxide, at variable reaction times with the array either unpowered or powered up.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂ where relevant; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency; UV LED array (full power).

Table 4.7: Change in residual peroxide for peroxide control (no UV LED irradiation) and UV LED irradiated alkaline peroxide pulps suspensions.

Time (min.)	1	2	5	10	15	30	45	60	90	120
Control (%)	95.4	99.8	96.4	96.4	97.3	95.6	99.7	96.6	95.1	96.7
Irradiated (%)	101.6	101.9	100.9	97.5	100.0	100.9	100.5	98.7	94.0	96.3

addition of hydrogen peroxide significantly improved the bleaching effect for all parameters with greater increases in brightness and improved reductions in kappa number, with a small loss in viscosity while still maintaining pulp yield. Photochemical bleaching, for both the alkali peroxide and pure caustic soda pulps, appeared to be more efficient earlier in the process than later with the efficiency decreasing slowly over time. This is evident from the shape of the irradiation bleaching curves for the kappa numbers which were exponential in nature rather than linear. In addition, only a small portion of the hydrogen peroxide charged was consumed during the photochemical bleaching as the peroxide was deliberately being used in excess. The contribution of thermally-driven peroxide bleaching at elevated temperatures to the total bleaching effect on the pulp was minimal as evident from the

evaluation of the kappa number versus temperature curves. Thus, the majority of the bleaching effect was due to photochemical bleaching of the pulp while under UV LED array irradiation. The photochemical mechanisms involved in this experimental work were likely both: (i) the photolysis and electron abstraction of water and hydroxide anions respectively for the pure caustic soda pulps; (ii) and a combination of water and hydroxide photolysis and electron abstraction respectively and the photolysis of hydrogen peroxide in the alkali peroxide pulps. The active bleaching agent formed from these processes was the hydroxyl radical. Part of the small reduction in the pH of the pulp suspensions for both alkali peroxide and pure caustic soda pulps with time was due to loss in hydroxide anions during the hydroxyl radical generation by electron abstraction. Another reagent that may have played a minor role was dissolved molecular oxygen (O_2), however it would not have been directly involved in the photobleaching as indicated in earlier reports (see Section 2.4.3.1). The most likely mechanism for oxygen's action would have been the generation of peroxy radicals/superoxide anion radicals ($OOH^\bullet / O_2^{\bullet-}$), which would have served as a source for hydrogen peroxide generation, which itself would serve as a source of hydroxyl radicals for pulp bleaching. Lastly, the results obtained suggested that the hydroxyl radicals have a clear selectivity towards lignin's unsaturated aromatic structure over that of the saturated carbohydrates of cellulose and hemicellulose. These findings are supported broadly by the work of others, such as Chem et al., Griebenow et al., Hölz et al., Jamali et al., Rajesh et al., Wang and Ku, in that the high emission intensity of light emitting diodes favoured a significant photochemical effect [273 – 278].

4.3.3 Photochemical pulp bleaching with UV LED array: Impact of pH on the photobleaching of pulp (Variable 2)

The aim here was to determine the impact of the pH of a pulp suspension on the photobleaching with alkali peroxide while under UV LED array irradiation [319]. A description of the experimental work is given in Section 3.6.3. The kappa number showed significant reductions (from 11.0 down to a range of 6.0 to 8.0) for photochemical bleaching of Sappi Cloquet paper grade pulp across the entire 2.5 to 11.0 pH range tested, performing better than the control triplicate without UV irradiation in all cases (Figure 4.28). However, the kappa number remained mostly constant in value at about 8.0 for pH values less than 7.0 but showed a steadily decreasing kappa from 8.0 down to 6.0 as the pH rose from 7.0 to 11.5. This is expected, as sufficiently alkaline pH values favour the formation and stability of hydroxyl radicals when formed at alkali pH values. The kappa number of about 8.0 over the pH range of 2.5 to 7.0 is closer in value to the results obtained for the prior experiments for the pure caustic soda pulps (see Section 4.3.2.).

The viscosity showed little difference across the pH range of 2.5 to 11.0 evaluated, with a small increase for more alkaline experiments above pH values of 7.0 (Figure 4.28). This small increase was likely due

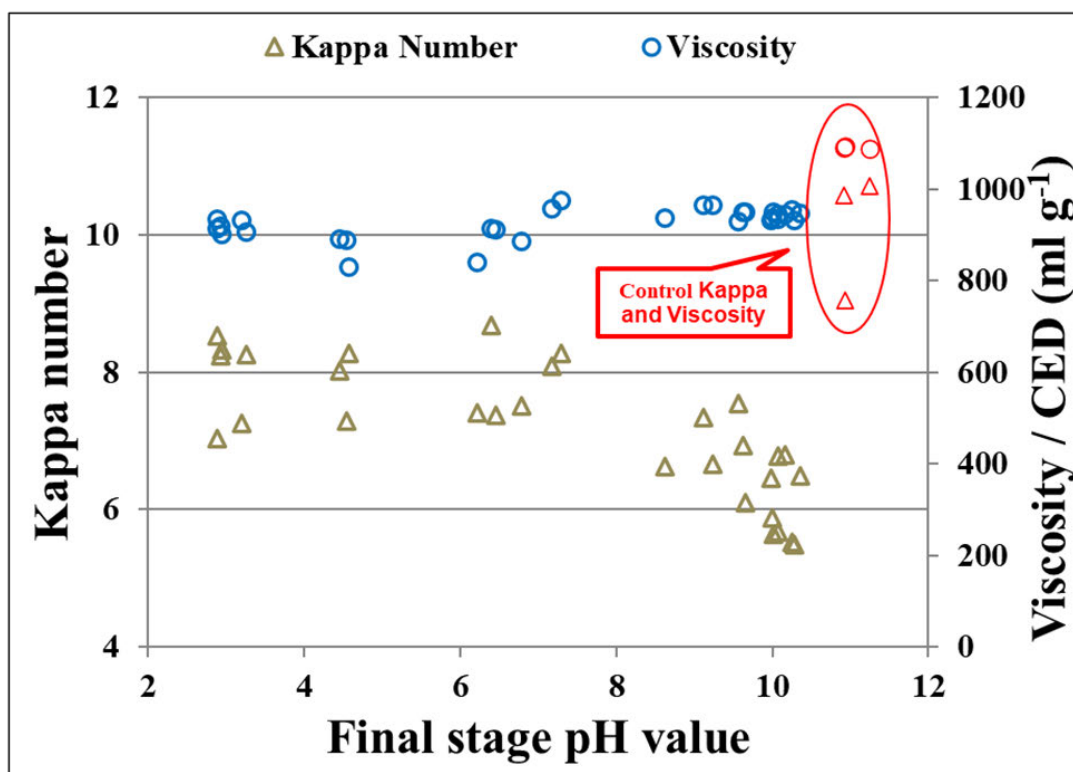


Figure 4.28: Kappa number and viscosity for various pulp suspensions bleached in a UV LED array reactor at variable starting pH values.

Conditions: 30.0 kg t⁻¹ H₂SO₄ - 30.0 kg t⁻¹NaOH (variable pH), 80.0 kg t⁻¹ H₂O₂ where relevant; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency; UV LED array (full power).

to removal of any small fibre fractions (carbohydrate oligomers) under alkaline conditions as the alkali solution swelled the fibres, opening them up for the small fibre fractions to be removed by dilution into solution. In addition, there was a small but notable reduction in the viscosity from the starting value of 1090 ml g⁻¹ down to the final values in the range of 900 to 950 ml g⁻¹ across the entire pH range. Thus, the peroxide supported photochemical bleaching did cause some small damage to the starting fibre material giving a small viscosity drop across all pH values, but the pH did not significantly alter the chemical mechanism behind the photochemical attack on the fibres.

The brightness followed the trend in kappa number with steadily increasing brightness values at pH values above 7.0 (Figure 4.29). Below pH 7.0, the brightness was not responsive to changes in pH.

A plot of kappa number versus brightness across the entire pH range showed the data can be grouped into two localised locations (Figure 4.30). Below pH 7.0, the data shows a flat response between the changing kappa number and the mostly unchanging brightness. For pH values above 7.0, the brightness decreased with increasing kappa number. Alkaline pH values favour the generation and stabilization of bleaching hydroxyl radicals.

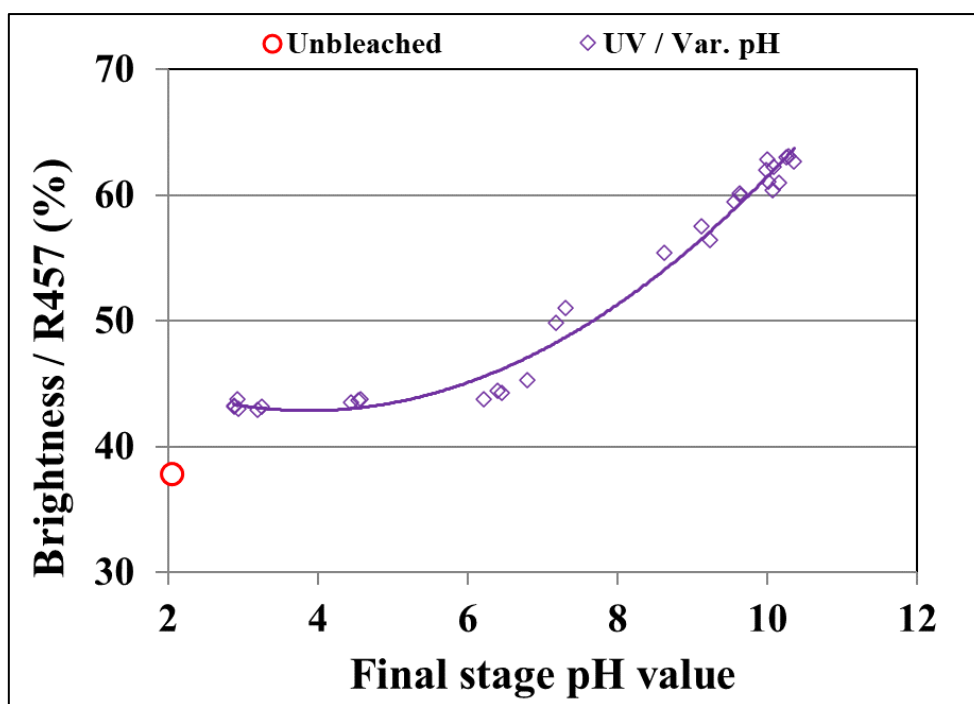


Figure 4.29: Brightness (R457) for various pulp suspensions bleached in a UV LED array reactor at variable starting pH values.

Conditions: 30.0 kg t⁻¹ H₂SO₄ - 30.0 kg t⁻¹NaOH (variable pH), 80.0 kg t⁻¹ H₂O₂ where relevant; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency; UV LED array (full power).

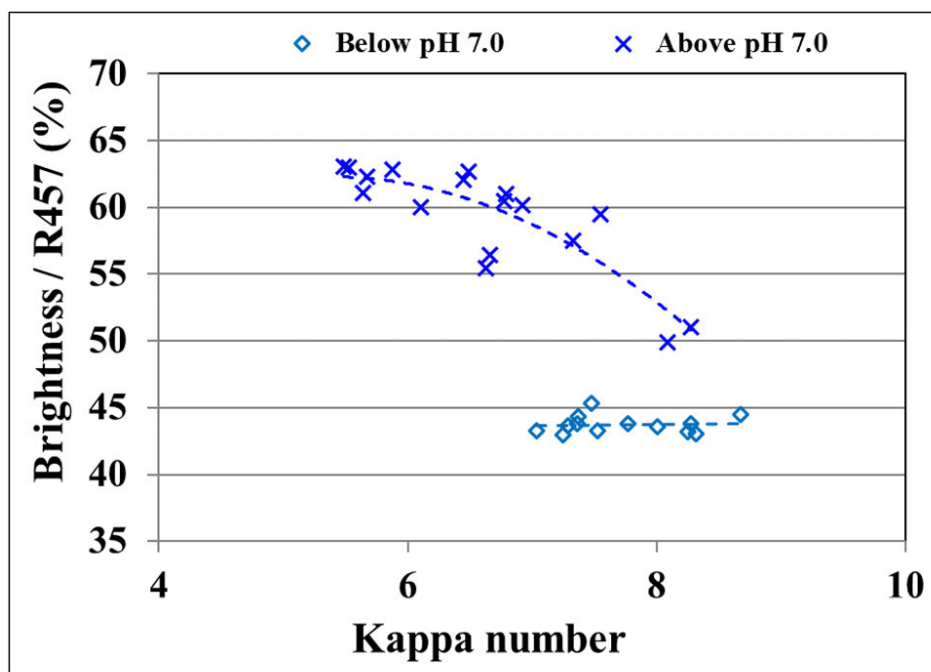


Figure 4.30: Kappa number versus brightness curves of various pulp suspensions bleached in a UV LED array reactor at pH values segregated at pH 7.0.

Conditions: 30.0 kg t⁻¹ H₂SO₄ - 30.0 kg t⁻¹NaOH (variable pH), 80.0 kg t⁻¹ H₂O₂ where relevant; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency; UV LED array (full power).

The initial and final pH values at each pH did not show significant departure from each other or among the triplicate experiments (Figure 4.31). Above pH 7.0, the expected small decrease in pH was observed due to loss of hydroxide content in the photogeneration of hydroxyl radicals. The increase in pH for pH values below 7.0 was likely due to diffusion out of the fibre cell walls of any residual alkali content still within the fibre. A buffering effect was observed at the strongly acidic and strongly alkaline pH values which was likely due to a large excess of conjugated acid or conjugated base functions groups respectively on the lignin structure such as alcohols, phenols/phenolics and carboxylic acids/carboxylates at these pH values.

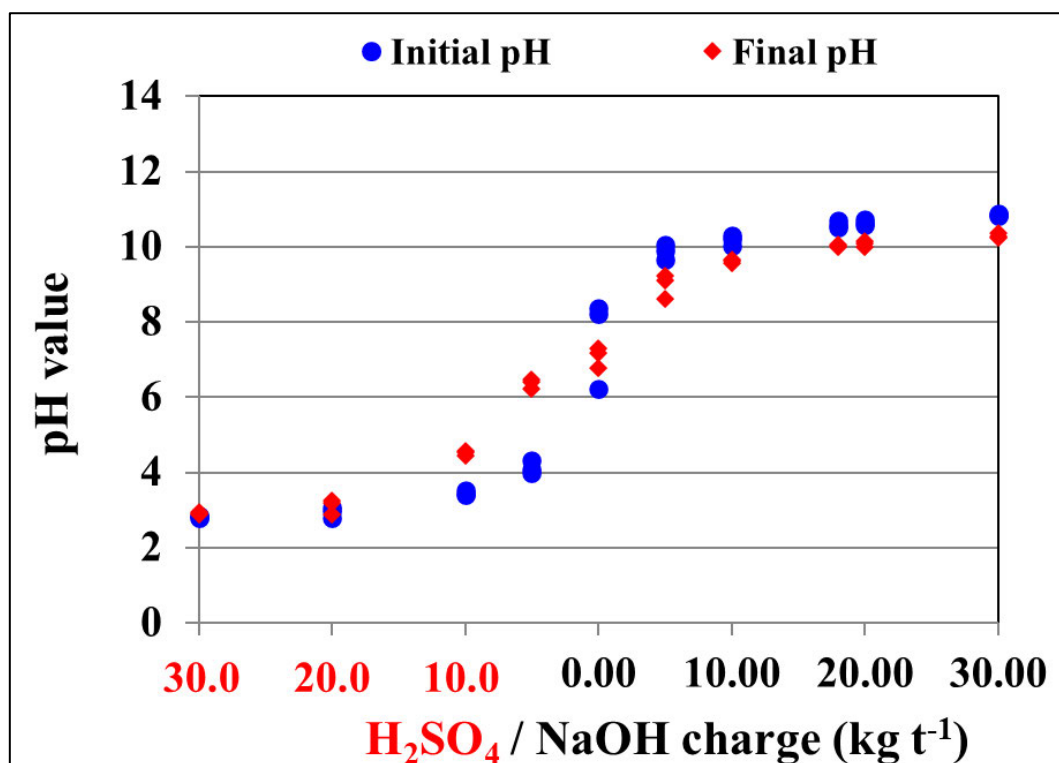


Figure 4.31: Variation between initial and final pH values for various pulp suspensions bleached in a UV LED array reactor at variable starting pH values.

Conditions: 30.0 $kg\ t^{-1}$ H_2SO_4 - 30.0 $kg\ t^{-1}$ NaOH (variable pH), 80.0 $kg\ t^{-1}$ H_2O_2 where relevant; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency; UV LED array (full power).

Similarly, the temperature profiles did not show any significant departure from each other or among the triplicate experiments (Table 4.8). In general, the experimental temperatures did not rise above 37 °C suggesting that the thermal contribution to the bleaching effect was minimal as observed in earlier work for alkali peroxide and pure caustic soda pulp study (see Section 4.3.2).

Table 4.8: Average initial and final temperatures for various pulp suspensions bleached in a UV LED array reactor at variable pH values.

In. Temp. (°C)	21.5	22.1	21.4	21.2	21.7	20.9	22.1	21.0	21.3	21.7
Fin. Temp. (°C)	34.8	35.0	35.3	35.5	35.4	34.8	34.8	34.2	35.2	35.7
Final pH	2.92	3.11	4.52	6.36	7.09	8.99	9.61	10.03	10.08	10.30

Pulp yield losses across the entire pH range appear minimal (Table 4.9). The spread of triplicate yield results appeared to be small.

Table 4.9: Average triplicate pulp yields for various pulp suspensions bleached in a UV LED array reactor at variable final pH values.

Pulp Yield (%)	97.4	99.5	101.1	101.5	101.7	100.7	100.3	99.9	100.1	101.7
Final pH	2.92	3.11	4.52	6.36	7.09	8.99	9.61	10.03	10.08	10.30

The residual of the hydrogen peroxide charged showed almost nil consumption below a pH value of 7.0, while peroxide consumption increased steadily with increased pH above a pH of 7.0 (Table 4.10). This appeared to follow the trends in kappa number and brightness at above and below pH values of 7.0. However, overall the extent of peroxide loss was minimal.

Table 4.10: The residual peroxide for various pulp suspensions bleached in a UV LED array reactor at variable final pH values.

Residual Peroxide (%)	99.2	100.5	103.3	103.4	104.7	100.9	98.0	97.2	99.0	94.0
Final pH	2.92	3.11	4.52	6.36	7.09	8.99	9.61	10.03	10.08	10.30

In summary, the photochemical bleaching effect employing alkali peroxide was significant across the entire pH range evaluated (pH 2.5 to 11.0) as given by the overall reduction in kappa number and associated increase in brightness. A notable increase in the photochemical bleaching was observed at pH values above 7.0 as given by a steadily decreasing kappa number and steadily increasing brightness as the conditions became progressively more alkaline. However, at pH values below 7.0 the extent of photobleaching was similar at all pH values, but significant in value. The proposed reaction mechanism for better photobleaching above a pH of 7.0, which steadily improved as the pH became more alkaline,

was the improved extraction of degraded lignin under alkaline conditions after hydroxyl degradation as proposed by Marcoccia's study [232]. The increased peroxide consumption at pH values above 7.0 was also consistent with this mechanism of improved hydroxyl radical formation and stabilization under alkaline conditions. There was minimal loss in pulp yield across the entire pH range of 2.5 to 11.0, while there was some small loss in pulp viscosity across the entire pH range but no distinction in those losses based on pH values was observed. Thermal contribution to the total bleaching effect was observed to be minimal with most of the bleaching being photochemical in nature.

4.3.4 Photochemical pulp bleaching with UV LED array: Impact of UV LED array power levels on the photochemical bleaching of pulp (Variable 3)

This section of the study aimed to determine how the power level of the UV LED array would impact the photobleached pulp [320]. A description of the experimental work is given in Section 3.6.4. The kappa number followed a strong linear relationship from a high kappa (average of 7.95) at 10% UV LED power level down to a low kappa (average of 5.95) at full UV LED power over the 120 minutes runtime (Figure 4.32). Even at the lowest power level of 10%, there was a noticeable reduction in kappa number from the starting pulp. The kappa numbers obtained in this experimental set at the 100% UV LED power level were similar to those obtained earlier for the alkali peroxide at 120 minutes when under UV LED irradiation (Section 4.3.2.) (Figure 4.32). In contrast, the blank control with no power to the UV LED array (Section 4.3.2.) gave a kappa number decrease from a starting value of 11.0 down to a final kappa of 10.1 after 120 minutes. The data for variable power (Section 4.3.4.), and Section 4.3.2. on alkaline peroxide and pure caustic soda photobleaching show good agreement between each other and add credence to both sets of data.

The viscosity of the pulp showed a minimal steady reduction (1010 ml g⁻¹ at 10% UV LED power level down to 950 ml g⁻¹ at 100% UV LED power level) as the power level was increased (Figure 4.32). There was also a small, but noticeable drop in viscosity from the starting pulp. As with the kappa number, the viscosity at 120 minutes at full power was similar in value to the viscosity results discussed earlier for alkaline peroxide at the same time scale (Section 4.3.2.). This adds credence to both sets of viscosity data. As viscosity can be employed to approximate a pulp's strength and cellulose polymer chain length, the minimal viscosity losses suggested that losses in the pulp strength due to UV LED irradiation were minimal at all power levels. This is also consistent with observations for viscosity losses made in the earlier work on alkali peroxide pulp discussed earlier (Section 4.3.2.).

As with the kappa number, the brightness followed a linear curve (Figure 4.33). Overall, the increasing brightness with rising power levels appeared to follow the trend in decreasing kappa number across the same power level range.

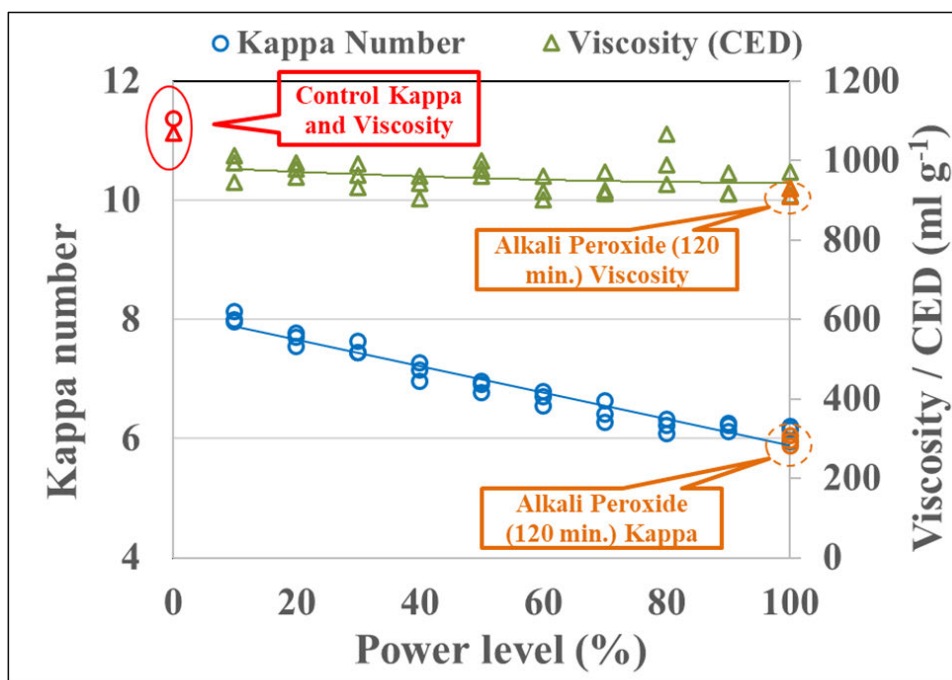


Figure 4.32: Kappa number and viscosity for an alkaline peroxide pulp suspension bleached in a UV LED array reactor at variable UV LED array power levels.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency; UV LED array (10% - 100%).

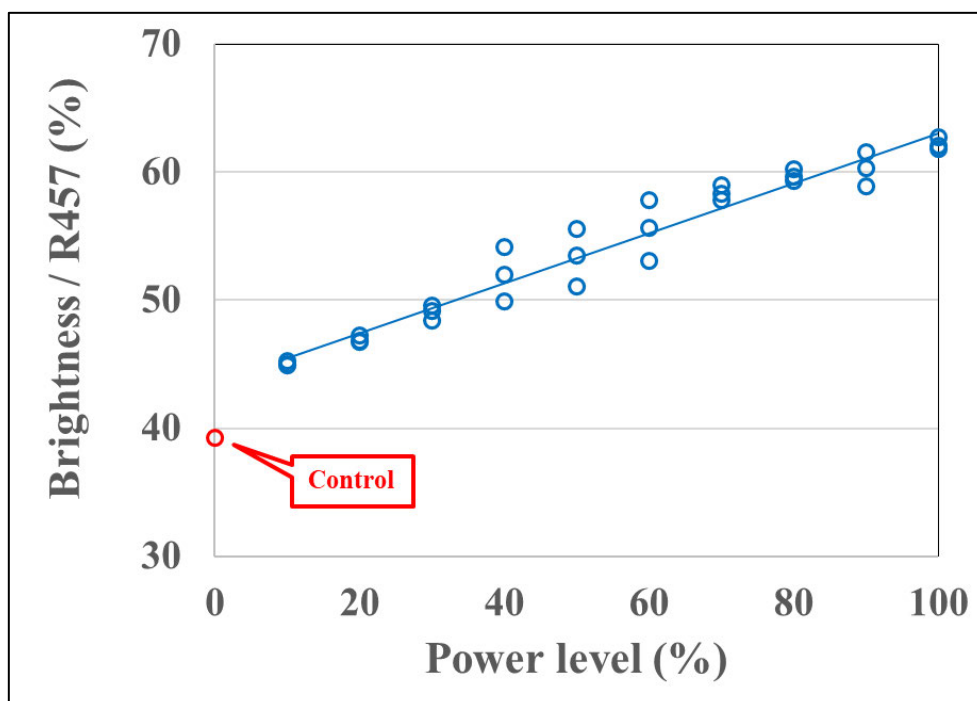


Figure 4.33: Brightness (R457) for an alkaline peroxide pulp suspension bleached in a UV LED array reactor at variable UV LED array power levels.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency; UV LED array (10% - 100%).

The initial and final pH values at various power levels were close to 10.0 and above, showing that the photochemical bleaching process was operating as expected, with no noticeable anomalies (Table 4.11). This is also the favoured pH range for the formation and stabilization of hydroxyl radicals which are the active agent in the photobleaching process for these series of experiments. The final temperature of the pulp suspensions increased, from similar starting temperatures, with the increased power levels (Table 4.11). This is expected given the larger energy input with high power levels. However, as the final temperature never increased above 36 °C from a starting average of about 21 °C, the contribution of the thermal bleaching component to the total bleaching effect was minimal as based on the Arrhenius equation $k = Ae^{(-E_a/RT)}$ and discussed earlier (Sections 4.3.1, and 4.3.2). Pulp yield losses appeared to be minor with no clear pattern evident (Table 4.11). However, the spread of results among the triplicate analyses is quite broad with ranges of about 97% to 104%. This sizeable spread in the triplicate results for pulp yield is due to the small quantity of pulp used in each experimental run as well as the precision of the weighing and moisture balances.

Table 4.11: Average initial and final pH, initial and final temperature, and pulp yield for an alkaline peroxide pulp suspension bleached in a UV LED array reactor at variable UV LED array power levels.

Power levels (%)	10	20	30	40	50	60	70	80	90	100
Initial pH	10.26	10.40	10.44	10.35	10.35	10.40	10.50	10.39	10.45	10.32
Final pH	10.17	10.09	10.10	10.06	10.06	9.98	10.01	9.96	9.86	10.02
In. Temp. (°C)	21.8	21.0	21.2	20.6	21.1	21.2	21.1	22.1	20.5	21.3
Fin. Temp. (°C)	24.5	24.8	26.8	27.2	28.3	30.5	31.4	33.2	33.1	35.2
Pulp yield (%)	101.1	101.4	100.0	99.6	101.8	102.3	102.4	100.3	98.8	99.4

The measured proportional residual peroxide was “normalized” by subtracting 5% from the measured results. This was to avoid any residual giving more than 100%. The residual peroxide showed a small drop of about 7% with an increase in UV LED power levels from 10% to full power (Table 4.12). The poor correlation among triplicate analyses is due to the larger spread among the triplicates. Similar residual values and trends were observed in the earlier results discussed in Section 4.3.2. As with the prior work, hydrogen peroxide was employed in excess.

Table 4.12: Average measured residual peroxide, and normalised residual peroxide (100% average for the 10% power level) for an alkaline peroxide pulp suspension bleached in a UV LED array reactor at variable UV LED power levels.

Power levels (%)	10	20	30	40	50	60	70	80	90	100
H ₂ O ₂ Conc. (%)	103.2	103.9	104.1	104.6	101.0	100.4	98.5	99.9	97.6	99.1
Norm. H ₂ O ₂ Conc.* (%)	98.2	98.9	99.1	99.6	96.0	95.4	93.5	94.9	92.6	94.1

NOTE: * The measured peroxide residual (H₂O₂ Conc.) was “normalized” by subtracting 5% units to give the normalized peroxide residual (Norm. H₂O₂ Conc.) to avoid residual exceeding 100%.

In summary, a linear relationship exists between the intensity of the UV light irradiation (as given by the UV LED power levels employed) and the efficiency of photochemical bleaching. This was strongly supported by the high degree of correlation between the kappa number and brightness against the power levels of the UV LED array. Expressed in another way: the amplitude of the UV wave front (i.e. the number of photons at 365 nm) is linearly related to the extent of photochemical bleaching (i.e. the more UV light or the higher the number of photons, the more the pulp is bleached). In addition, the viscosity of the pulp and pulp yield appeared to be minimally affected by the UV LED array power level or not at all. However, the residual peroxide did show some small loss with increasing UV LED array power with levels similar to earlier experimental work. The thermal contribution to bleaching at all power levels appeared to be minimal with the majority of the bleaching effect being photochemical in nature. The main active bleach agent was likely the hydroxyl radical. These observations raise a few interesting questions:

- Question 1: How much can the photobleaching be sped up with a more intense ultraviolet light source (i.e. a UV LED of greater power output than 8 W cm⁻²)?
- Question 2: At what irradiated intensity level would the linear relationship between the power level and the degree of photobleaching breakdown due to saturation of the process with photonic events?
- Question 3: At the point of saturation, would the fundamental photochemical mechanics significantly change, e.g. changes due to multiple photonic absorptions by the same molecule?

These questions could possibly be answered as follows:

- Question 1: By using a UV LED array in the power output range of 20 - 50 W cm⁻², but of similar physical dimensions to the 8 W cm⁻² array. Measuring the kappa number, brightness and

viscosity results at UV LED array power levels above 8 W cm^{-2} , to full power, the relationship between photobleaching and irradiation intensity can be determined at higher power levels (i.e. $> 8 \text{ W cm}^{-2}$).

Question 2: As stated for Question 1, using a UV LED of higher power output range. At sufficiently high power levels, the breakdown in the relationship between photobleaching and irradiation intensity would become evident.

Question 3: Also as stated for Question 1, using a UV LED of higher power output range. This would be more complicated to answer and would involve kinetics studies, likely around pseudo-order reaction rates, looking for markers associated with such multi-photon events (i.e. reactions only possible due to multiple photon absorptions).

4.3.5 Photochemical pulp bleaching with UV LED array: Molecular oxygen gas as oxidant (Variable 4)

The objective with these experiments was to determine the performance of oxygen as an oxidant during the photobleaching of pulp under UV LED array irradiation [321]. A description of the experimental work is given in Section 3.6.5. The use of molecular oxygen gas (i.e. O_2) as an oxidant gave a significant level of delignification which increased with time for the photochemical bleaching of unbleached Cloquet paper grade pulp using an UV LED array, with the kappa number decreasing from about 10.5 down to about 6.5 over 120 minutes (Figure 4.34). However, the viscosity of the pulp showed only a small decrease over the same time scale, dropping from about 1090 ml g^{-1} down to about 1000 ml g^{-1} ; which suggested that the pulp retained much of its strength.

The oxygen (i.e. O_2) as an oxidant showed bleaching performance slightly below that of the peroxide, but significantly better than pure caustic soda, as well as the control without UV LED illumination (Figure 4.35). The four experimental sets gave kappa reductions of about 5.0, 4.5, 3.5 and 1.0 for peroxide, oxygen, pure caustic soda, and control respectively. A similar comparison of viscosity for these four experimental sets showed almost zero loss for the control, but, a similar small loss for both the pure caustic soda and peroxide (Figure 4.36). Thus, as a bleaching oxidant driven by UV LED array irradiation, oxygen gas was almost as effective as hydrogen peroxide as an oxidant for pulp bleaching. The likely reaction mechanism for oxygen involved the conversion of the oxygen dissolved in solution into peroxy ($\text{OOH}^\bullet$) or superoxide ($\text{O}_2^{\bullet-}$) radicals which then served as a source to generate hydrogen peroxide (see Sections 2.4.3.1 and 2.4.3.2). The hydrogen peroxide, so generated, subsequently photolyzed into hydroxyl radicals which were the active bleaching agent in the oxygen

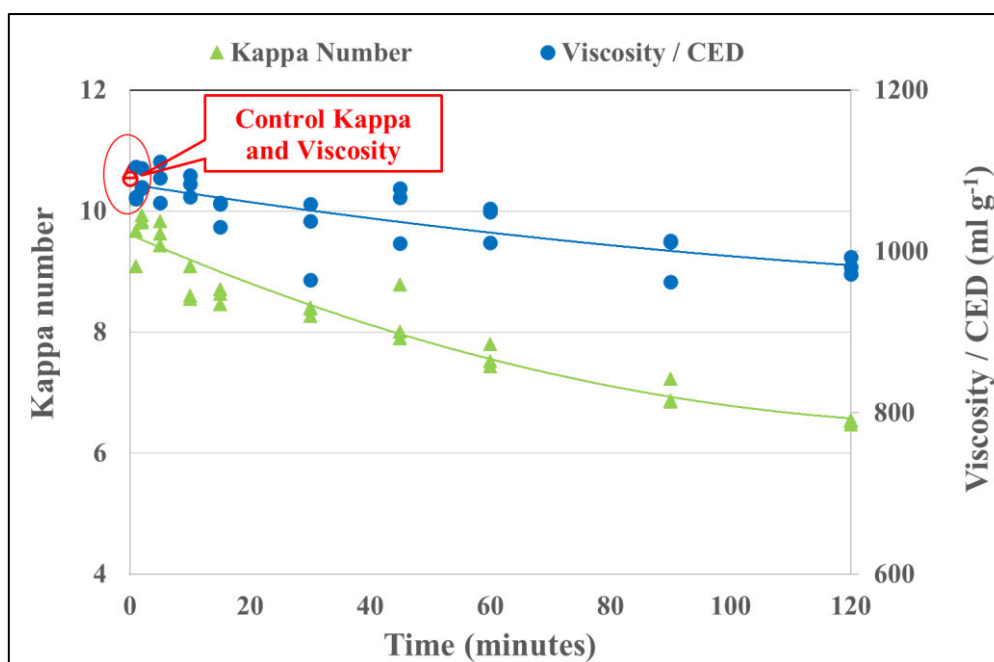


Figure 4.34: Kappa number and viscosity for UV LED array bleached Cloquet paper grade pulp suspension using oxygen as an oxidant at variable irradiation times.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂ where relevant; oxygen bubbled into suspension through needle valve, cylinder 400 kPa where relevant; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency; UV LED array (full power).

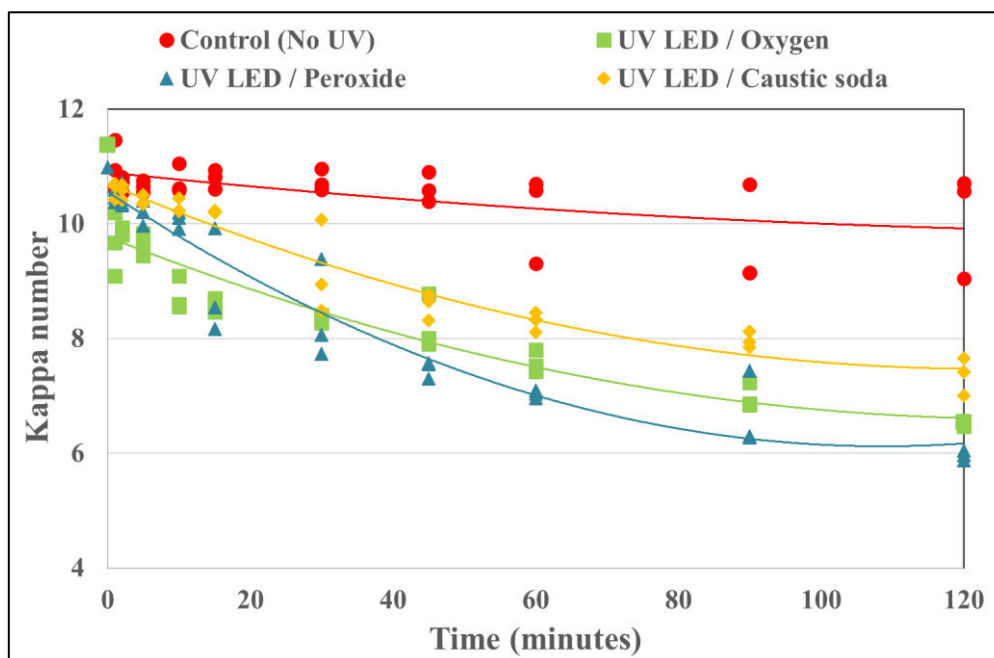


Figure 4.35: Kappa number for UV LED array bleached Cloquet paper grade pulp with pure caustic soda, hydrogen peroxide and oxygen gas at variable irradiation times.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂ where relevant; oxygen bubbled into suspension through needle valve, cylinder 400 kPa where relevant; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency; UV LED array (full power).

photobleaching process. Certain functional groups within the lignin would likely have served as photosensitizers to aid the generation of peroxy and superoxide radicals. This mechanism is proposed by the reviewed literature.

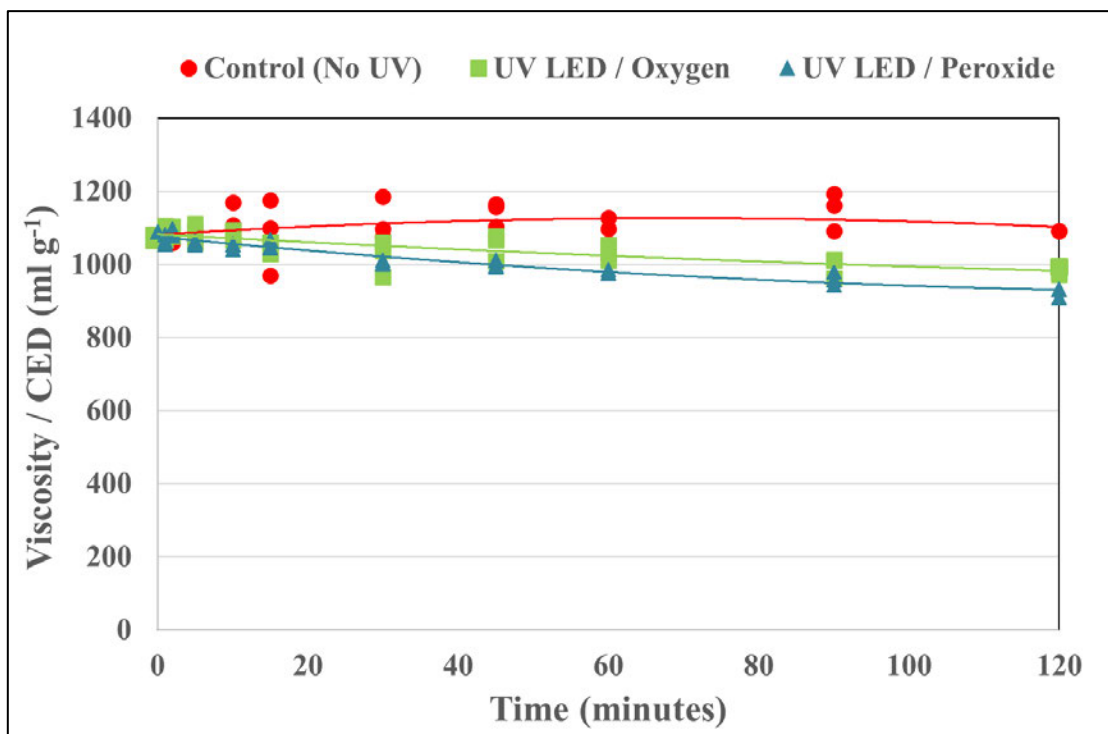


Figure 4.36: Viscosity (CED) for UV LED array bleached Cloquet paper grade pulp with hydrogen peroxide and oxygen gas at variable irradiation times.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂ where relevant; oxygen bubbled into suspension through needle valve, cylinder 400 kPa where relevant; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency; UV LED array (full power).

The use of oxygen as an oxidant gave good brightness development for the photochemical bleaching of the pulp which increased from about 39 to about 54%. However, oxygen underperformed relative to peroxide which increased the brightness to as much 62% (Figure 4.37). The oxygen did outperform pure caustic soda which gave a final brightness of only 46%.

The initial and final pH values were as expected, all measurements being above 10.0 (Table 4.13). There did appear to be an overall minor decrease in pH for all time intervals up to 60 minutes. The exact cause is unknown but may be due to neutralization of acidic groups deep within the fibre walls as the hydroxide anions migrated inwards over time, or normal experimental error. The final temperature showed a steady increase over the initial temperature with increasing time, however,

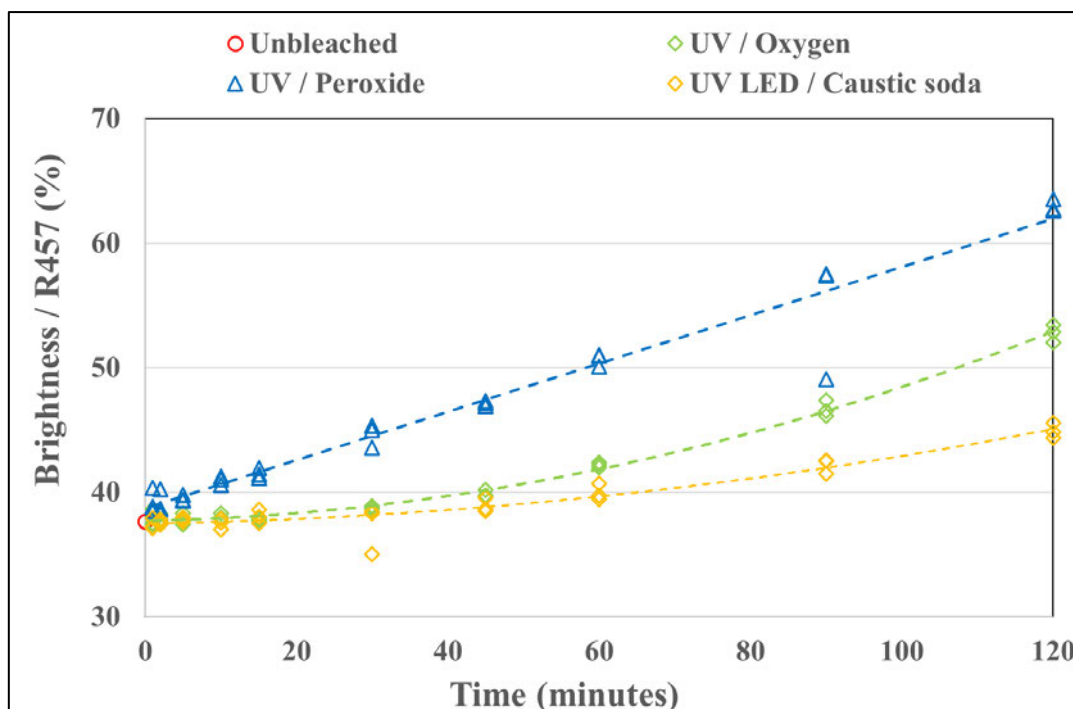


Figure 4.37: Brightness (R457) for Cloquet paper grade pulp suspension bleached in a UV LED array reactor using peroxide and oxygen as oxidants at variable irradiation times.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂ where relevant; oxygen bubbled into suspension through needle valve, cylinder 400 kPa where relevant; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency; UV LED array (full power).

Table 4.13: Average initial and final pH, initial and final temperature, and pulp yield for an alkaline oxygen pulp suspension bleached in a UV LED array reactor at variable time.

Time (min.)	1	2	5	10	15	30	45	60	90	120
Initial pH	11.00	10.85	10.81	10.92	11.06	11.01	11.32	11.25	11.28	11.27
Final pH	10.82	10.85	10.64	10.84	10.97	10.88	10.75	10.77	10.78	10.72
In. Temp. (°C)	25.8	25.7	27.0	24.8	24.7	24.8	23.5	24.4	25.0	24.8
Fin. Temp. (°C)	25.7	25.9	27.6	26.8	27.1	29.7	30.2	33.5	36.1	37.1
Pulp Yield (%)	100.9	102.5	101.6	102.8	99.7	98.9	100.6	100.6	100.6	97.6

the increases were generally small at about 10 degrees at the most (Table 4.13). As noted for prior experimental work for the alkaline peroxide photobleaching of pulp, the contribution from the thermal bleaching of the pulp to the total bleaching effect would be minor at the temperatures observed. The

pulp yield showed a steady but small decrease with increased time with a total yield loss of about 3% (Table 4.13). This is expected as more material is lost and liberated the further the bleaching process progresses as progressively more material (mostly lignin) is oxidatively degraded.

Visually, graphs of the brightness (R457) versus kappa number for prior and present data sets show that all experiments using peroxide as an oxidant (alkaline peroxide at variable time, variable power, and variable pH) all fell on similar curves grouped in the same area of the graph regardless of the variation in experimental conditions employed, while the use of oxygen as an oxidant or no oxidant (i.e. pure caustic soda) fell on similar shaped but different curves in a second grouping (Figure 4.38).

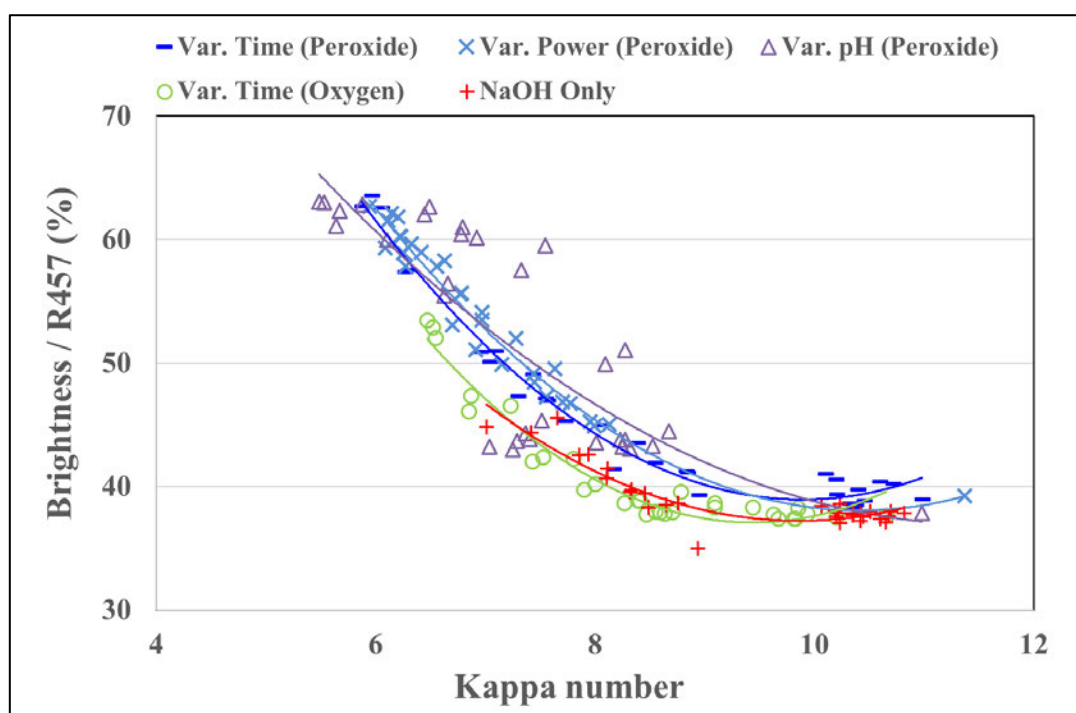


Figure 4.38: Kappa number versus brightness for Cloquet paper grade pulp suspension bleached in a UV LED array reactor using various experimental conditions.

Conditions: $18.0 \text{ kg t}^{-1} \text{NaOH}$, $80.0 \text{ kg t}^{-1} \text{H}_2\text{O}_2$ where relevant; oxygen bubbled into suspension through needle valve, cylinder 400 kPa where relevant; 20.0 g pulp; 25.0°C (Room temperature); 0.5% consistency; UV LED array (full power).

Lastly, both groupings visually show some overlap at the higher kappa numbers/lower brightness values where bleaching has been minimal or small.

A comparative T-test (Tc-test) for kappa numbers indicated that the alkaline peroxide at variable time (1 to 120 minutes) was significantly different from the control set where the UV LED was unpowered over the same time scale for run times larger than 5 minutes at a 95% confidence level (Table 4.14). In

addition, the T_C -test showed that the same experimental set for the alkaline peroxide at variable time (1 to 120 minutes) was significantly different from the set without an oxidant (pure caustic soda) over the same time scale for run times larger than 10 minutes at a similar confidence level (i.e. 95%). However, a similar T_C -test for the same variable time peroxide set against the experimental set using oxygen as an oxidant only showed a consistent significant difference at the 90% confidence level after 5 minutes. Alternatively, a comparative T-test of the ratio of brightness (R457) to kappa number for the same data sets indicated that the alkaline peroxide at variable time was significantly different from the pure caustic soda (no oxidant) and oxygen at variable time after 15 and 10 minutes respectively at a 95% confidence level (Table 4.15). Given that the photobleaching using alkaline peroxide and oxygen as oxidants are statistically different, it was evident that both photobleaching processes employed different reaction mechanisms (see Sections 2.4.2.1 and 2.4.2.2, versus Sections 2.4.3.1 and 2.4.3.2). For both mechanisms, hydroxyl radicals are the active photobleaching agent [180, 181, 185, 188]. However, for alkaline peroxide these radicals are generated by direct peroxide photolysis [180, 181], whereas for oxygen the peroxide for reaction is first generated from photo-excited triplet oxygen (singlet oxygen) before it can be utilized [185, 188]. The mechanism for pure caustic soda utilized a third photochemical mechanism, namely, the photolysis of water/hydroxide to hydroxyl radicals which occurs at a significantly slower rate than peroxide photolysis.

In summary, the use of molecular oxygen (i.e. O_2) as an oxidant gave a similar kappa reduction to the alkaline peroxide (i.e. 6.5 for oxygen versus 6.0 for peroxide from a starting kappa of 10 to 11) with only a minor reduction in viscosity over the run time range of 1 to 120 minutes (1000 ml g^{-1} for oxygen against 950 ml g^{-1} for peroxide from a starting viscosity of 1100 ml g^{-1}). This indicated that, generally, the pulp strength was mostly maintained with oxygen as an oxidant. However, while the oxygen gave good brightness development, its brightening performance was poorer than that for alkaline peroxide (54% for oxygen versus 62% for peroxide from a starting brightness of 39%). A comparison of the brightness versus kappa number suggested that there were two general groupings for all experimental work for the alkaline photobleaching of pulp utilizing a UV LED array, with alkaline peroxide at variable time, variable power levels and variable pH pulps in the first grouping, and oxygen and pure caustic soda pulps in the second grouping. The comparative T-tests undertaken suggested that the alkaline peroxide, pure caustic soda and oxygen processes as well as the control without UV LED irradiation were all statistically different from each other, and each of the three processes employed different reaction mechanisms. In all three cases, the common photobleaching active agent was the highly reactive hydroxyl radical. For the pure caustic soda process, the reaction mechanism involved the generation of hydroxyl radicals via the photolysis and electron abstraction of water and hydroxide anions respectively. These two mechanisms tend to be the least favoured to occur of the three and

Table 4.14: Comparative T-test (Tc) for differences between kappa numbers for Cloquet paper grade pulp suspensions bleached in a UV LED array reactor using various experimental conditions.

Time (minutes)	1	2	5	10	15	30	45	60	90	120	STD	n _x
KAPPA NUMBERS												
Control (No UV LED)	11.01	10.69	10.65	10.75	10.78	10.75	10.63	10.20	9.66	10.11	0.579	30
Peroxide (Var. Time)	10.48	10.47	10.19	10.07	8.88	8.40	7.48	7.03	6.67	5.96	1.693	30
Caustic Soda Only	10.59	10.57	10.40	10.30	10.21	9.17	8.58	8.30	7.97	7.36	1.202	30
Oxygen	9.65	9.87	9.63	8.75	8.60	8.36	8.23	7.59	6.98	6.51	1.122	30
T _C (Control / Peroxide) α (<0.05 / 95% confidence)	1.63	0.69	1.42	2.08	5.83	7.20	9.65	9.69	9.17	12.69		
	FALSE	FALSE	FALSE	TRUE	TRUE	TRUE	TRUE	TRUE	TRUE	TRUE		
T _C (Peroxide / Caustic Soda) α (<0.05 / 95% confidence)	0.30	0.26	0.57	0.59	3.50	2.03	2.91	3.34	3.44	3.69		
	FALSE	FALSE	FALSE	FALSE	TRUE	TRUE	TRUE	TRUE	TRUE	TRUE		
T _C (Peroxide / Oxygen) α (<0.05 / 95% confidence) α (<0.10 / 90% confidence)	2.22	1.62	1.50	3.57	0.75	0.11	2.04	1.50	0.85	1.48		
	TRUE	FALSE	FALSE	TRUE	FALSE	FALSE	TRUE	FALSE	FALSE	FALSE		
	TRUE	TRUE	TRUE	TRUE	FALSE	FALSE	TRUE	TRUE	FALSE	TRUE		
T _C (Caustic Soda / Oxygen) α (<0.05 / 95% confidence)	3.12	2.33	2.57	5.16	5.35	2.70	1.15	2.37	3.28	2.83		
	TRUE	TRUE	TRUE	TRUE	TRUE	TRUE	FALSE	TRUE	TRUE	TRUE		

Table 4.15: Comparative T-test (Tc) for differences between ratios of brightness values (R457) to kappa numbers for Cloquet paper grade pulp suspensions bleached in a UV LED array reactor using various experimental conditions.

Time (minutes)	1	2	5	10	15	30	45	60	90	120	n_x
Peroxide (Var. Time) / Kappa	10.600	10.721	10.400	10.200	8.548	8.067	7.553	7.095	7.433	6.053	30
Brightness (R457)	40.38	40.25	39.79	40.58	41.94	44.98	47.17	51.00	49.07	62.60	
Bri/Kappa	3.809	3.754	3.826	3.978	4.906	5.576	6.246	7.189	6.602	10.342	
AVE (Bri/Kappa)	3.74	3.73	3.88	4.07	4.71	5.36	6.31	7.21	8.30	10.56	
										STD 2.265	
Caustic Soda Only / Kappa	10.700	10.600	10.507	10.443	10.232	8.941	8.650	8.457	8.117	7.658	30
Brightness (R457)	37.94	37.41	37.99	37.57	38.6	35.02	38.51	39.44	41.47	45.55	
Bri/Kappa	3.546	3.529	3.616	3.598	3.772	3.917	4.452	4.664	5.109	5.948	
AVE (Bri/Kappa)	3.53	3.56	3.64	3.64	3.73	4.08	4.54	4.82	5.29	6.11	
										STD 0.8611	
Oxygen / Kappa	9.673	9.937	9.439	8.550	8.706	8.412	7.904	7.803	7.232	6.470	30
Brightness (R457)	37.41	37.78	38.32	37.96	37.93	38.8	39.73	42.25	46.55	53.45	
Bri/Kappa	3.867	3.802	4.060	4.440	4.357	4.612	5.027	5.415	6.437	8.261	
AVE (Bri/Kappa)	3.93	3.83	3.93	4.35	4.40	4.64	4.85	5.57	6.69	8.11	
										STD 1.3489	
Tc(Peroxide / Caustic Soda)	0.48	0.39	0.54	0.96	2.21	2.89	3.99	5.41	6.78	10.05	
α (<0.05 / 95% confidence)	FALSE	FALSE	FALSE	FALSE	TRUE	TRUE	TRUE	TRUE	TRUE	TRUE	
Tc(Peroxide / Oxygen)	0.39	0.21	0.11	0.59	0.65	1.49	3.03	3.41	3.34	5.09	
α (<0.05 / 95% confidence)	FALSE	FALSE	FALSE	FALSE	FALSE	FALSE	TRUE	TRUE	TRUE	TRUE	
Tc(Caustic Soda / Oxygen)	1.36	0.92	1.00	2.44	2.28	1.91	1.06	2.57	4.76	6.84	
α (<0.05 / 95% confidence)	FALSE	FALSE	FALSE	TRUE	TRUE	FALSE	FALSE	TRUE	TRUE	TRUE	

account for the lowest photobleaching performance of the three processes. The same hydroxyl generation from water and hydroxide anions also occurs with the hydrogen peroxide process, but the main source of hydroxyl radicals was the direct photolysis of hydrogen peroxide. As the most thermodynamically favoured of the three mechanisms, the photobleaching of pulp with peroxide as an oxidant gave the best performance. For oxygen, the direct interaction between the lignin in the pulp and oxygen for bleaching did not occur. Upon photo-excitation of triplet oxygen to excited singlet oxygen, the oxygen was converted into peroxy or superoxide radicals which served as a source of peroxide. It was this generated peroxide that became the source for hydroxyl radicals. This indirect process together with the same hydroxyl generation from water and hydroxide anions as the pure caustic soda and alkali peroxide allowed the oxygen process to achieve a performance similar to that of the alkaline peroxide process.

4.3.6 Photochemical pulp bleaching with UV LED array: Impact of temperature on the photochemical bleaching of pulp (Variable 5)

The objective of this study was to observe the impact of temperature on the photochemical bleaching of pulp under UV LED array irradiation [322]. A description of the experimental work is given in Section 3.6.6. For experimental work undertaken at variable times (1 to 120 minutes) and an aimed temperature of 70 °C, the actual initial temperature was usually lower than that aimed for with an average starting temperature of 60 °C while also showing considerable variability in each triplicate for many of the experiment time intervals (Figure 4.39). The lower actual starting temperature and observed large variability was due equipment restrictions, at the time of experimentation, used to heat the water beforehand (i.e. two old water baths) which gave frequent differences in the temperature of the water before addition to the pulp during experiments. The final temperature (aimed initial temperature of 70 °C) decreased with increased time and showed less variation. This was expected given that there was no further active heating of the pulp suspension after the hot water was added to the pulp at the beginning of each experiment, and the pulp's temperature was allowed to equalize with the environment over time. For the experiments evaluating variable initial temperatures (25 °C to 80 °C) at a constant time of 60 minutes, the initial temperatures showed little variability between the triplicate results, but were usually below (about 5 to 8 °C) the aimed starting temperatures above those at 25 °C (Figure 4.40). In addition, the final temperatures similarly showed little variability between the individual triplicate results.

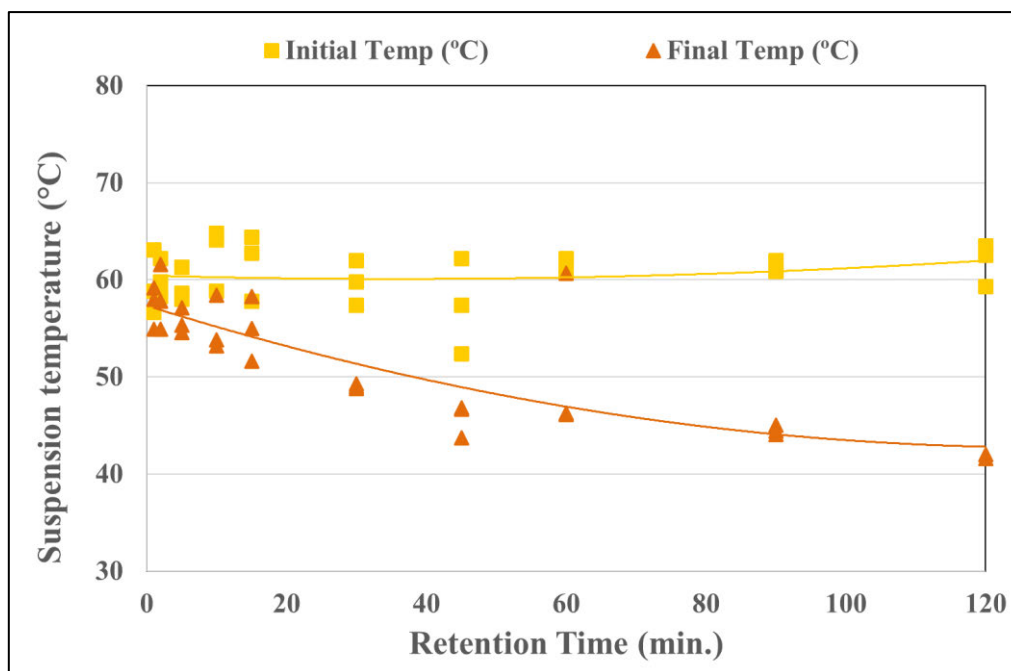


Figure 4.39: Start and final temperature for an alkaline peroxide pulp suspension bleached in a UV LED array reactor at 70 °C for variable time.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂; 20.0 g pulp; 70 °C (aimed temperature); 0.5% consistency; UV LED array (full power).

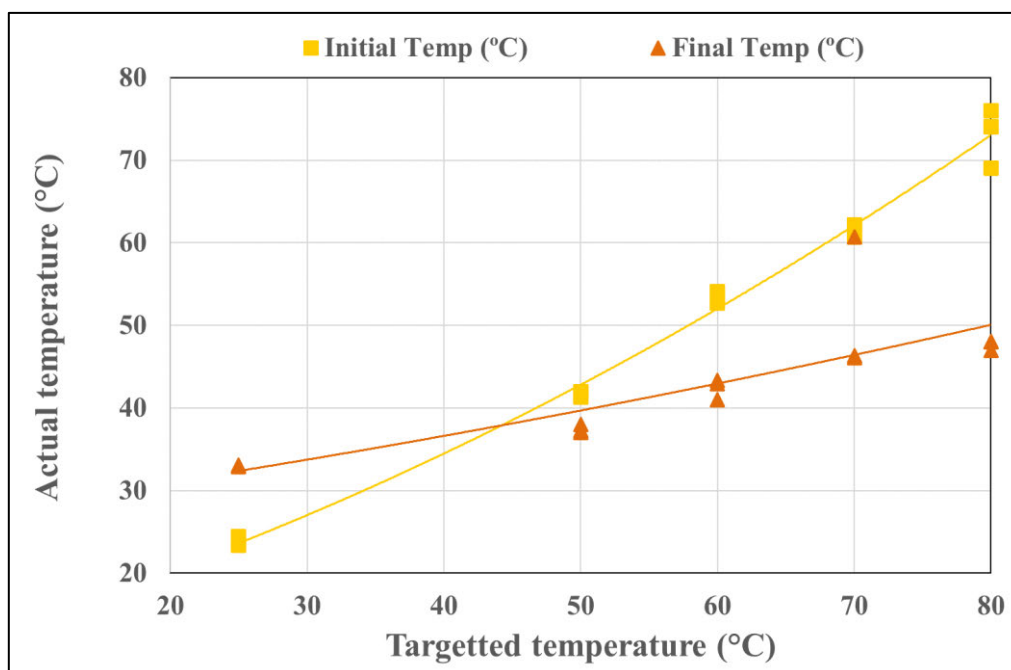


Figure 4.40: Start and final temperature for an alkaline peroxide pulp suspension bleached in a UV LED array reactor at variable temperature.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂; 20.0 g pulp; 25 - 80 °C (aimed temperature); 60 minutes; 0.5% consistency; UV LED array (full power).

At an aimed starting temperature of 70 °C (60 °C actual) for the photochemical bleaching process (using an UV LED array), there was a progressive improvement in the brightness development over the same process at room temperature from 1 to 75 minutes, whereafter, no further improvements over the room temperature process were observed (Figure 4.41). The 70 °C aimed (60 °C actual) process was about 8 units brighter than the room temperature process after the full 120 minutes.

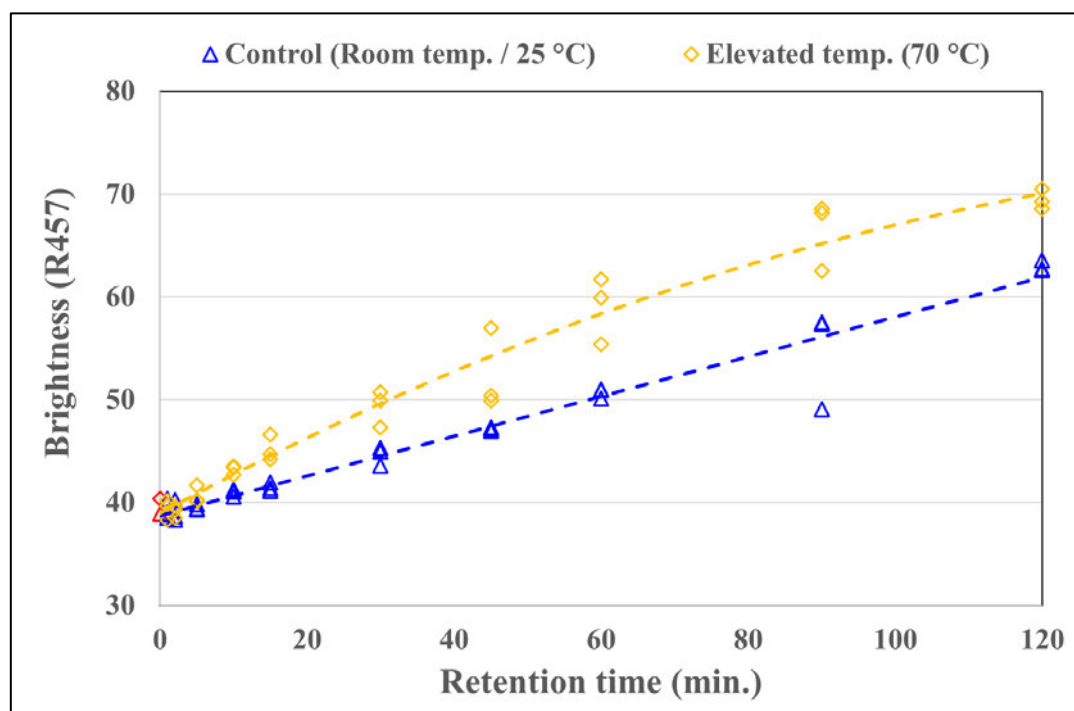


Figure 4.41: Brightness (R457) for an alkaline peroxide pulp suspension bleached in a UV LED array reactor at temperatures of 25 °C (control) and 70 °C for variable time.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂; 20.0 g pulp; 25 °C , 70 °C (aimed temperature); 0.5% consistency; UV LED array (full power).

An evaluation of the impact of variable temperature (at 60 minutes) gave an increase for brightness, which increased from 55% to 64%, as the aimed starting temperature was increased from 50 °C to 80 °C (43 °C to 75 °C actual) (Figure 4.42). These were all higher than the room temperature process with a brightness value of 52%. Furthermore, above 60 °C, there was some plateauing of the relationship between brightness and temperature. In addition, there was also considerable variation among the triplicate brightness results for some of the temperatures evaluated.

The kappa number for the pulp at an elevated starting temperature of 70 °C aimed (60 °C actual) was notably lower than the control at all times from 1 to 120 minutes (Figure 4.43). Contrary to expectation, there was a near constant offset in the kappa number of about 2.0 units between the control (25 °C) and

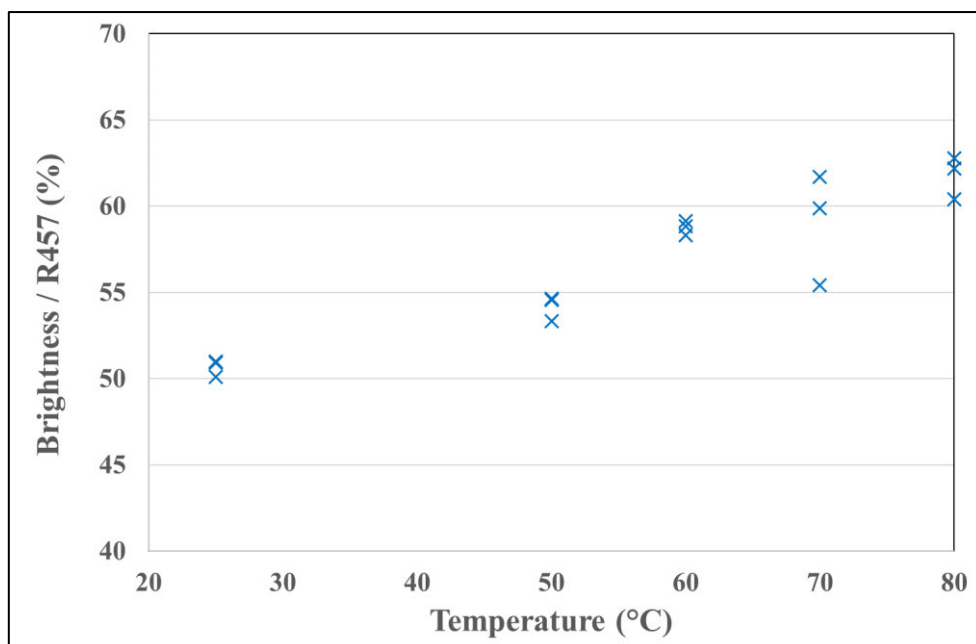


Figure 4.42: Brightness (R457) for an alkaline peroxide pulp suspension bleached in a UV LED array reactor at variable temperature.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂; 20.0 g pulp; 25 - 80 °C (aimed temperature); 60 minutes; 0.5% consistency; UV LED array (full power).

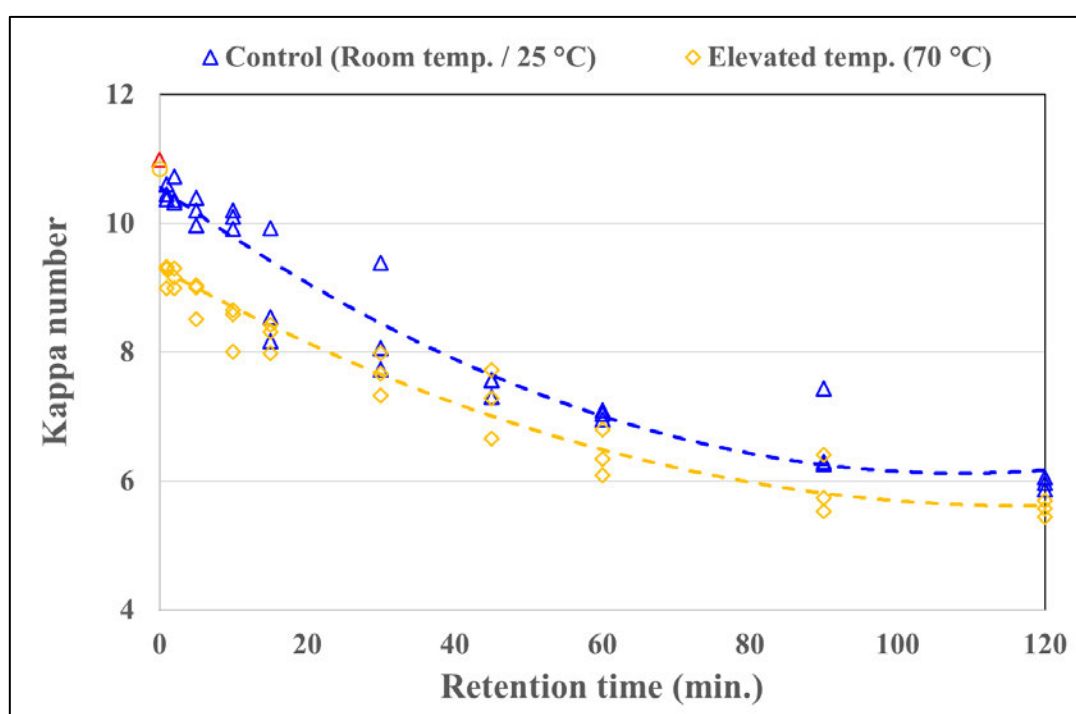


Figure 4.43: Kappa number for an alkaline peroxide pulp suspension bleached in a UV LED array reactor at temperatures of 25 °C (control) and 70 °C for variable time.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂; 20.0 g pulp; 25 °C, 70 °C (aimed temperature); 60 minutes; 0.5% consistency; UV LED array (full power).

the 70 °C aimed (60 °C actual) temperature curves. It was expected that the offset at the beginning of the photobleaching process (1 to 15 minutes) would be near nil and would have steadily increased to a maximum over a period of time. The exact cause of the offset at the beginning of the study is unknown, but was likely due an analytical error, or that the much higher starting temperature (70 °C aimed/60 °C actual) aided the dissolution and removal of degraded lignin fractions trapped within the fibre walls over even a very short period of time. A comparison of the effect of temperature for brightness and kappa suggested that the elevated temperature likely gave elevated brightening of the pulp's optical properties even if not much difference in the lignin was observed. This is a characteristic of peroxide bleaching of pulps frequently observed at elevated temperatures.

An elevated starting temperature (70 °C aimed/60 °C actual) gave slightly lower viscosity results from the control at all evaluated times of 1 to 120 minutes with differences of about 50 ml g⁻¹ in viscosity being typical (Figure 4.44). The triplicate viscosity results showed wide variability. As with the kappa number, an offset to lower viscosity results was observed at all times (1 to 120 minutes) between the control pulps (25 °C) and those at elevated temperature (70 °C aimed/60 °C actual). For an increasing starting temperature (50 to 80 °C aimed/43 to 75 °C actual), a lower kappa number (approximately 6.5 to 6.0 respectively) at 60 minutes was obtained than for to the control at 25 °C which had a final kappa number of approximately 7.0 (Figure 4.45). The viscosity of the pulp decreased with the increasing temperature showing a small reduction of about 100 ml g⁻¹. Overall, an increased temperature gave a greater kappa reduction and brighter pulp, but also notably lowered the viscosity.

Generally, both the initial and final pH of the pulp suspensions remained above the minimum targeted value of 9.0 across all times and temperatures (Tables 4.16 and 4.17). In all cases, no anomalous results were observed from any of the experiments being undertaken under alkaline conditions. No significant yield losses were observed at a temperature of 70 °C aimed (60 °C actual) over variable time (1 to 120 minutes); and at variable temperatures (50 °C to 80 °C aimed/43 °C to 75 °C actual) at a constant time of 60 minutes (Tables 4.16 and 4.17). The peroxide residual at a temperature of 70 °C aimed (60 °C actual) for variable time (1 to 120 minutes) showed an excessive spread in results for each set of triplicates measurements (Table 4.16). This spread was likely due to a moderate spread in the actual starting temperature over the aimed starting temperature of 70 °C (60 °C actual). For variable temperatures (50 to 80 °C aimed/43 to 75 °C actual) at a constant time of 60 minutes, no discernible pattern was apparent (Table 4.17). Overall, the peroxide residual decreased with increasing temperature, as was expected. However, even at the maximum temperature, there was still a significant quantity of residual peroxide after 60 minutes.

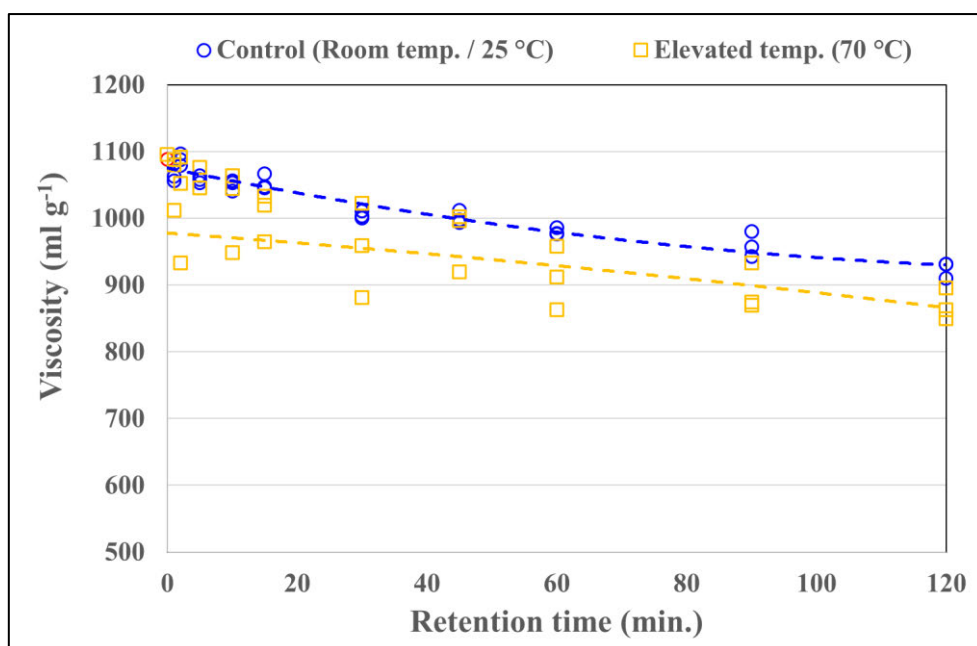


Figure 4.44: Viscosity for an alkaline peroxide pulp suspension bleached in a UV LED array reactor at temperatures of 25 °C (control) and 70 °C for variable time.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂; 20.0 g pulp; 25 °C, 70 °C (aimed temperature); 0.5% consistency; UV LED array (full power).

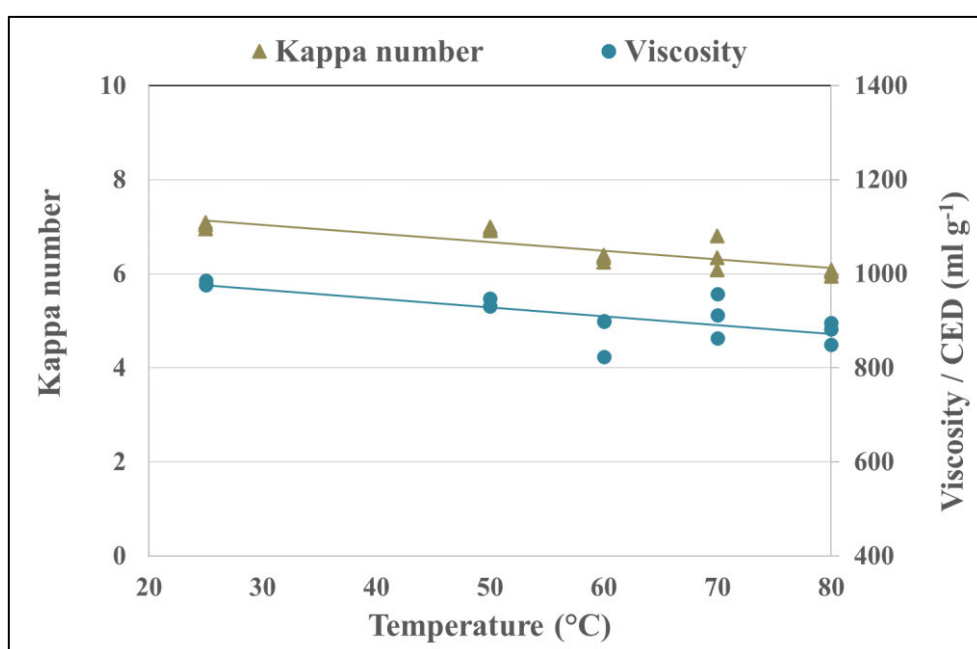


Figure 4.45: Kappa number and viscosity for an alkaline peroxide pulp suspension bleached in a UV LED array reactor at variable temperature.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂; 20.0 g pulp; 25 - 80 °C (aimed temperature); 60 minutes; 0.5% consistency; UV LED array (full power).

Table 4.16: Initial and final pH, residual peroxide and range, and pulp yield for an alkaline peroxide pulp suspension bleached in a UV LED array reactor at 70 °C for variable time.

Time (min.)	1	2	5	10	15	30	45	60	90	120
Initial pH	9.71	9.88	9.91	9.78	9.74	9.83	9.86	9.85	9.82	9.83
Final pH	9.94	9.89	9.98	9.95	10.00	9.94	9.86	9.78	9.78	9.61
Res. Peroxide (%)	88.1	86.8	82.1	71.8	85.2	67.7	83.1	60.5	65.8	79.3
Range (± value %)	14.4	2.1	16.4	32.9	9.3	36.8	15.7	28.1	18.4	1.9
Pulp Yield (%)	99.8	99.3	100.6	100.1	100.0	101.8	99.7	99.5	102.5	100.4

Table 4.17: Initial and final pH, residual peroxide and range, and pulp yield for an alkaline peroxide pulp suspension bleached in a UV LED array reactor at variable temperature (i.e. 25 to 70 °C).

In. temp. / aimed (actual) (°C)	25 (25)	50 (43)	60 (54)	70 (62)	80 (75)
Initial pH	10.41	10.21	10.10	9.85	9.82
Final pH	10.10	10.12	10.05	9.78	9.84
Pulp yield (%)	100.3	100.6	101.6	99.5	102.2
Res. peroxide (%)	97.0	87.9	69.1	60.5	55.3
Range (±value %)	5.6	4.0	6.1	28.1	15.2

A comparative Student T-test (Tc-test) for kappa numbers indicated that the data set at 70 °C aimed (60 °C actual) and variable time (1 to 120 minutes) was significantly different from the data set at 25 °C across most times for a 90% confidence level, and for most of the shorter times at the 95% confidence level (Table 4.18). The unexpected statistical difference between the two curves for time periods less than 15 min was likely due to the aforementioned analytical error and elevated starting temperature. However, as expected, the comparative T-test for the ratio of brightness (R457) to kappa number (i.e. Bri / kappa) for this data set was significantly different from the data set at 25 °C for times only above 45 minutes at both confidence levels (Table 4.19). Overall, these results showed that increasing the starting temperature of the pulp suspension affected the rate and extent of photochemical bleaching of the pulp with greater delignification occurring at an elevated temperature and longer times (i.e. 70 °C and more than 45 minutes).

Table 4.18: Comparative student T-test (T_c) for differences between kappa numbers of Cloquet paper grade pulp suspensions bleached in a UV LED array reactor at an elevated temperate (70 °C) for variable time (1 to 120 minutes).

Time (minutes)	1	2	5	10	15	30	45	60	90	120	STD	n_x
KAPPA NUMBERS												
Control (No UV LED)	11.01	10.69	10.65	10.75	10.78	10.75	10.63	10.20	9.66	10.11	0.579	30
Peroxide (Var. Time)	10.48	10.47	10.19	10.07	8.88	8.40	7.48	7.03	6.67	5.96	1.693	30
Temp. (70°C)	9.20	9.15	8.85	8.42	8.24	7.66	7.22	6.41	5.89	5.57	1.202	30
$T_{C(\text{Control} / \text{Peroxide})}$	1.63	0.69	1.42	2.08	5.83	7.20	9.65	9.69	9.17	12.69		
α (<0.05 / 95% confidence)	FALSE	FALSE	FALSE	TRUE	TRUE	TRUE	TRUE	TRUE	TRUE	TRUE		
$T_{C(\text{Peroxide} / \text{Temp.: 70 °C})}$	3.36	3.48	3.53	4.37	1.68	1.94	0.67	1.64	2.04	1.05		
α (<0.05 / 95% confidence)	TRUE	TRUE	TRUE	TRUE	FALSE	FALSE	FALSE	FALSE	TRUE	FALSE		
α (<0.1 / 90% confidence)	TRUE	TRUE	TRUE	TRUE	TRUE	TRUE	FALSE	FALSE	TRUE	FALSE		

Table 4.19: Comparative student T-test (Tc) for differences between ratios of R457 brightness to kappa numbers of Cloquet paper grade pulp suspensions bleached in a UV LED array reactor at an elevated temperate (70 °C) for variable time (1 to 120 minutes).

Time (minutes)	1	2	5	10	15	30	45	60	90	120	n _x
Peroxide (Var. Time) / Kappa	10.600	10.721	10.400	10.200	8.548	8.067	7.553	7.095	7.433	6.053	30
Brightness (R457)	40.38	40.25	39.79	40.58	41.94	44.98	47.17	51.00	49.07	62.60	
Bri/Kappa	3.809	3.754	3.826	3.978	4.906	5.576	6.246	7.189	6.602	10.342	
AVE (Bri/Kappa)	3.74	3.73	3.88	4.07	4.71	5.36	6.31	7.21	8.30	10.56	
										STD 2.265	
Temp. (70 °C) / Kappa	9.292	9.296	9.005	8.588	8.319	7.989	7.287	6.800	6.410	5.690	30
Brightness (R457)	39.65	39.27	40.25	43.38	44.66	47.31	50.39	55.41	62.5	68.58	
Bri/Kappa	4.267	4.224	4.470	5.051	5.368	5.922	6.915	8.149	9.750	12.053	
AVE (Bri/Kappa)	4.28	4.28	4.60	5.14	5.48	6.45	7.31	9.24	11.34	12.48	
										STD 2.945	
Tc (Peroxide / Temp.: 70 °C)	0.79	0.80	1.06	1.58	1.15	1.81	1.47	3.00	4.49	2.84	
α (<0.05 / 95% confidence)	FALSE	FALSE	FALSE	FALSE	FALSE	FALSE	FALSE	TRUE	TRUE	TRUE	
α (<0.1 / 905% confidence)	FALSE	FALSE	FALSE	FALSE	FALSE	FALSE	FALSE	TRUE	TRUE	TRUE	

Table 4.20: Tukey and ANOVA analysis of kappa number for an alkaline peroxide pulp suspension bleached for 60 minutes in a UV LED array reactor at variable temperatures (25 to 80 °C) at a 90% and 95% confidence level.

Temp. (°C)	25	50	60	70	80
Rep 1	7.095	7.000	6.390	6.800	5.950
Rep 2	6.960	6.920	6.240	6.343	6.040
Rep 3	7.041	6.940	6.340	6.090	6.090
n_i	3	3	3	2	3
n	14				
k	5				
$m = (n-k)$	9				
Average	7.032	6.953	6.323	6.217	6.027
Std Dev.	0.06772	0.04163	0.07638	0.17890	0.07095
TREAT $n_i * (\bar{x}_i - \bar{\bar{x}})^2$	0.752	0.534	0.130	0.198	0.764
GRAND $(n_i/n) * x_i$	1.507	1.490	1.355	0.888	1.291
ERROR $(n_i-1) * s_i^2$	0.0092	0.0035	0.0117	0.032	0.0101
			$= (\sum x_i)/n$		
Grand Average	6.531		6.531		
SSTr	2.378		F-Value	80.6	P-Value 3.63
SSE	0.0664		The P-value (df = 4,9) from F= 80.6 is far below $\alpha = 0.05$ for H_0 point to be valid. Therefore the temperature effect on kappa is significantly different.		
MSTr	0.5945				
MSE	0.0074				
T value					
$\alpha =$	0.05	0.1			
$q_{\alpha} (5,9)$	4.755	4.084			
$T = q_{\alpha} * (MSE/n_i)$	0.2358	0.2025			
$ (\bar{x}_i - \bar{x}_j) $					
Temp. (°C)	25	50	60	70	80
	$ (\bar{x}_i - \bar{x}_j) $	$H_1 : \mu_i \neq \mu_j >$			
				0.2358	0.2025
25 / 50	0.079			FALSE	FALSE A
25 / 60	0.709			TRUE	TRUE B
25 / 70	0.815			TRUE	TRUE B
25 / 80	1.005			TRUE	TRUE B
50 / 60	0.630			TRUE	TRUE B
50 / 70	0.737			TRUE	TRUE BC
50 / 80	0.927			TRUE	TRUE BC
60 / 70	0.107			FALSE	FALSE BC
60 / 80	0.297			TRUE	TRUE BC
70 / 80	0.190			FALSE	FALSE C
			$\alpha =$	0.05	0.1

NOTE: Replicate at 70 °C not included in Tukey analysis as excessively different from other two replicates.

An one way ANOVA F test and a Tukey ANOVA analysis of the impact of elevated temperatures showed that there was a significant difference in the kappa number obtained from the UV LED array reactor at elevated temperatures (50 to 80 °C aimed/43 to 75 °C actual) as compared to room temperature at 25 °C (Table 4.20 and Figure 4.46). Furthermore, a significant difference was also observed for 50 °C as compared to higher temperatures between 60 to 80 °C. Above 50 °C, any differences at elevated temperatures (60, 70 and 80 °C aimed) became statistically insignificant. This was true for both a 90% and 95% confidence level, with both trends in confidence levels behaving similarly.

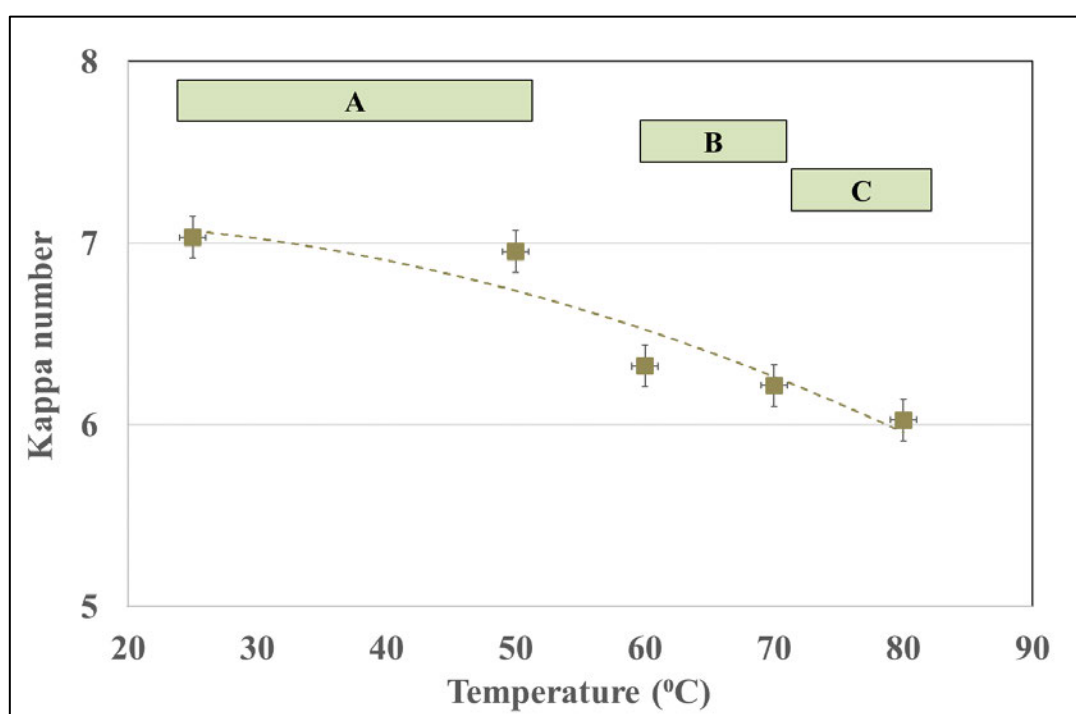


Figure 4.46: Averaged kappa number for UV LED array bleached alkaline peroxide pulp at variable temperature with error bars and groupings given by Tukey ANOVA.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂; 20.0 g pulp; 25 - 80 °C (aimed temperature); 60 minutes; 0.5% consistency; UV LED array (full power).

The same pattern was observed for an one-way ANOVA F test and a Tukey ANOVA analysis for the R457 brightness at elevated temperatures (50 to 80 °C aimed/43 to 75 °C actual) as compared to room temperature (Table 4.21 and Figure 4.47). As with the kappa number, this was true for all results at both a 90% and 95% confidence level. Overall, within the temperature range of 25 to 80°C, an increased temperature increased the rate and extent of photochemical bleaching of a pulp suspension, but was only statistically significant between 25 and 50°C.

Table 4.21: Tukey and ANOVA analysis of R457 brightness for an alkaline peroxide pulp suspension bleached for 60 minutes in a UV LED array reactor at variable temperatures (25 to 80 °C) at a 90% and 95% confidence level.

Temp. (°C)	25	50	60	70	80
Rep 1	51.000	54.660	59.140	55.410	62.790
Rep 2	50.930	54.580	58.860	59.890	60.410
Rep 3	50.110	53.340	58.330	61.700	62.190
n_i	3	3	3	3	3
n	15				
k	5				
$m = (n-k)$	10				
Average	50.680	54.193	58.777	59.000	61.797
Std Dev.	0.49487	0.74009	0.41138	3.23807	1.23779
TREAT $n_i * (\bar{x}_i - \bar{x})^2$	115.667	21.805	10.686	13.365	72.246
GRAND $(n_i/n) * x_i$	10.136	10.839	11.755	11.800	12.359
ERROR $(n_i-1) * s_i^2$	0.4898	1.0955	0.3385	20.97	3.0643
			$=(\sum x_i)/n$		
Grand Average	56.889		56.995		
SSTr	233.769		F-Value	10.0	P-Value 3.48
SSE	25.958		The P-value (df = 4,10) from F= 10.0 is far below $\alpha = 0.05$ for Nul point to be valid. Therefore the temperature effect on brightness is significantly different.		
MSTr	25.974				
MSE	2.5958				
T value					
$\alpha =$	0.05	0.1			
$q_{\alpha(5,9)}$	4.654	4.018			
$T=q_{\alpha} * (MSE/n_i)$	4.3292	3.7375			
$ (\bar{x}_i - \bar{x}_j) $					
Temp. (°C)	25	50	60	70	80
$ (\bar{x}_i - \bar{x}_j) $				4.3292	3.7375
25 / 50	3.513			FALSE	FALSE
25 / 60	8.097			TRUE	TRUE
25 / 70	8.320			TRUE	TRUE
25 / 80	11.117			TRUE	TRUE
50 / 60	4.583			TRUE	TRUE
50 / 70	4.807			TRUE	TRUE
50 / 80	7.603			TRUE	TRUE
60 / 70	0.223			FALSE	FALSE
60 / 80	3.020			FALSE	FALSE
70 / 80	2.797			FALSE	FALSE
			$\alpha =$	0.05	0.1

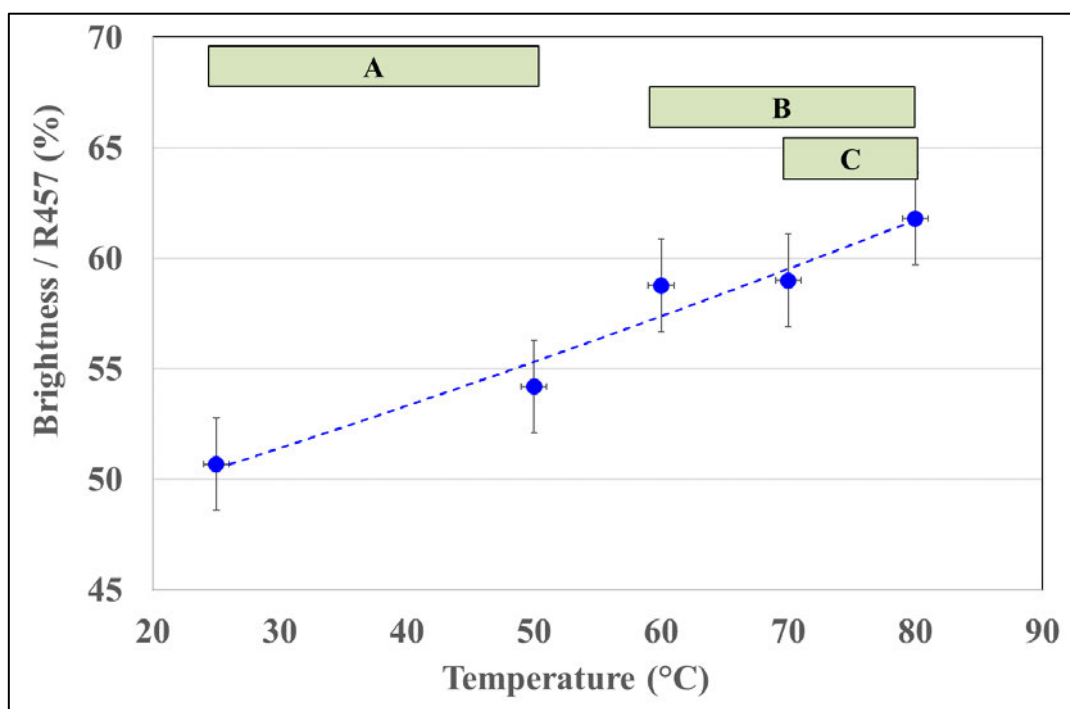


Figure 4.47: - Average brightness for UV LED array bleached alkaline peroxide pulp at variable temperature with error bars and groupings given by Tukey ANOVA.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂; 20.0 g pulp; 25 - 80 °C (aimed temperature); 60 minutes; 0.5% consistency; UV LED array (full power).

A plot of R457 brightness values against their kappa numbers showed that the results at room temperature (25 °C) and those at elevated temperatures (50 to 80 °C aimed/43 to 75 °C actual), essentially fell visually on the same curve (Figure 4.48). Overall, this observation would suggest that the reaction mechanism of the photochemical bleaching was not significantly altered by the larger quantity of thermal energy, but just accelerated by the heat instead.

In summary, the starting temperature of the pulp suspension significantly impacted the rate and extent of photochemical delignification/bleaching of the process by accelerating the bleaching process but without changing the reaction mechanism itself. This gave a significantly larger than expected brightness improvement for the given increased kappa reduction obtained, and is a known effect of high temperature peroxide bleaching. The general trend was that the higher the temperature, the more extensive the bleaching effect – particularly at longer times. However, statistical treatment of the data showed that even though higher brightness values and lower kappa numbers were observed at higher temperatures, at aimed temperatures above 50 °C the differences became statistically insignificant. Both the room temperature (25 °C) and elevated temperatures (50 to 80 °C aimed/43 to 75 °C

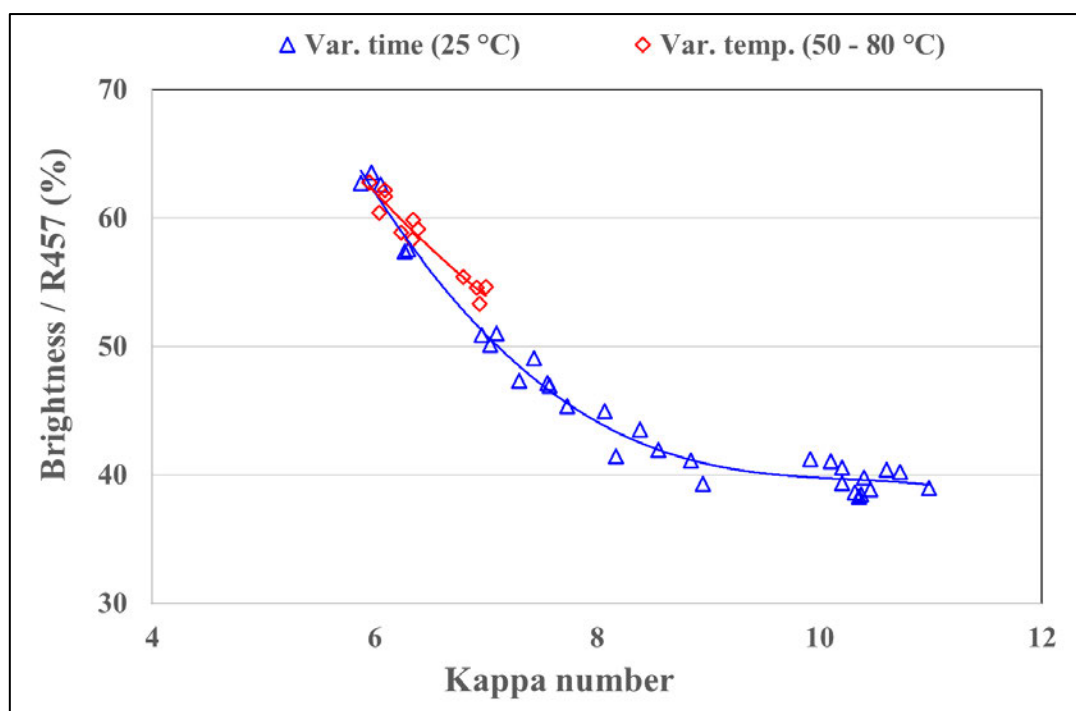


Figure 4.48: Brightness versus kappa number for alkaline peroxide pulp suspensions bleached in a UV LED array reactor at room temperature (25 °C) and elevated temperatures (50 to 80 °C).

Conditions for Var. time: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂; 20.0 g pulp; 25 °C (aimed temperature); 1 - 120 minutes; 0.5% consistency; UV LED array (full power).

Conditions for Var. temp: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂; 20.0 g pulp; 25 - 80 °C (aimed temperature); 60 minutes; 0.5% consistency; UV LED array (full power).

actual) plots of their brightness versus kappa curves were not statistically different from each other, suggesting no change to the reaction mechanisms involved at higher temperatures, but rather only acceleration. Overall, higher temperatures did give small reductions in the pulp viscosity, but, this had no impact on the yield of the pulp.

4.3.7 Photochemical pulp bleaching with UV LED array: Initial calibration and optimization of photocatalysts and photosensitisers (Variables 6 and 7)

These experiments were a preliminary investigation into the use of various photocatalysts and photosensitizers during the photobleaching of pulp under UV LED array irradiation [323]. A description of the experimental work is given in Section 3.6.7. Generally, all the metal oxides evaluated, both the semiconductor photocatalysts and the alumina control, showed a slightly increased hydrogen peroxide degradation at the lowest oxide charge levels (increasing with the oxide charge levels) equivalent to 1.0 to 5.0 kg t⁻¹ (0.02 to 0.10 g per experiment) whereafter (at oxide charges above these

lowest charge levels) the various metal oxides proceeded to show divergent trends in peroxide degradation specific to each catalyst from the charges equivalent of 10.0 – 60.0 kg t⁻¹ (Figure 4.49).

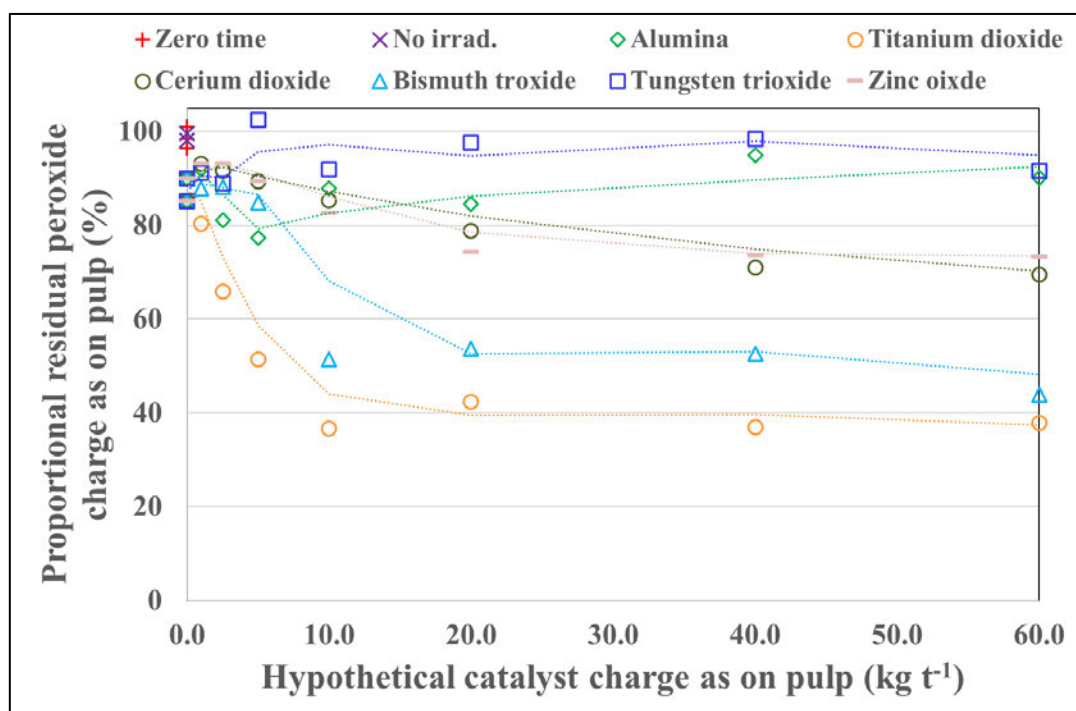


Figure 4.49: The impact of variable catalytic charge for various photocatalysts on the degradation of hydrogen peroxide solution irradiated in a UV LED array reactor system.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂, 1.0 – 5.0 kg t⁻¹ photocatalyst/additive (all equivalent to hypothetical 20.0 g pulp); no pulp; 25 °C; 60 minutes; UV LED array (full power).

This general increase in degradation for all oxide charges up to 5.0 kg t⁻¹ equivalent is likely due to the increased reflectance from the white and pale yellow metal oxide surfaces in the clear alkali peroxide solution, which increased the interaction between the peroxide and UV light resulting in a higher level of peroxide degradation. Above 5.0 kg t⁻¹ equivalent, the increased metal oxide charges made the alkali peroxide solution adequately opaque as regards reflectance so that any catalytic activities of the metal oxides began to dominate over the impact of pure reflectance producing the divergent trends which reflected primarily the photocatalytic properties specific to each metal oxide/photocatalyst. Above 5.0 kg t⁻¹ equivalence, the increased charge for the alumina control showed a slight decrease in peroxide degradation with almost nil total degradation of the peroxide throughout the 60 minute run. This was expected given that alumina is not a semiconductor and, thus, cannot catalyse the degradation of peroxide. Conversely, the semiconductor tungsten oxide also showed almost nil peroxide degradation. This was unexpected and was likely due to the tungsten oxide appearing to visually agglomerate during the process. This agglomeration prevented the tungsten oxide catalyst from adequately dispersing through the alkali peroxide solution during stirring, thus preventing photocatalytic activity to any notable degree, which was the cause of the poor activity observed rather than any lack of photocatalytic

activity of the tungsten oxide itself. In addition, the tungsten oxide settled at the bottom of the reactor (once stirring had stopped) while retaining its initial intense yellow shade of colour. Hence, overall, tungsten oxide would not be a viable photocatalyst for the photochemical bleaching of pulp. The cerium oxide and zinc oxide photocatalysts showed a steady increase in the photodegradation of peroxide with increased catalytic charge, however, the degradation never exceeded 30% of the initial peroxide charged to the solution. This lower activity together with the yellow precipitated cerium oxide residual present at the end of the photodegradative run also indicated that neither cerium oxide or zinc oxide would serve as viable photocatalysts for the photochemical bleaching of pulp. The zinc oxide also showed some mild greying of the catalyst on occasion. Both the bismuth oxide and titanium oxide showed good photocatalytic degradation of the peroxide with maxima reached at relatively low charges of 10.0 to 20.0 kg t⁻¹, whereafter activity plateaued at higher charges likely due to increased opacity of the solution. However, the bismuth oxide left behind a black solid bismuth oxide residue while the titanium oxide did not. Overall, the particulate size of each of the two photocatalysts did not appear to have a detrimental impact on their overall performance over the size range employed (5.0 to 25.0 microns). Thus, of all the catalysts evaluated, only titanium dioxide would serve as a viable photocatalyst. Nevertheless, given their high activity at low charges and lack of dark precipitate, both titanium dioxide and cerium dioxide were further evaluated for their catalytic activity in the photochemical bleaching of pulp. Furthermore, the residual peroxide with no exposure to irradiation, but at the 60 minute runtime, showed no notable loss in peroxide charge as compared to the zero time experiments. Both gave close to 100% of the initial peroxide charge applied as expected. Lastly, the difference in performance of the various photocatalysts tested does raise the question of whether UV light at 365 nm is adequately energetic to successfully activate each of the photocatalysts. Given that UV light at 365 nm provides the equivalent of 3.4 eV, the wavelength of 365 nm is, hence, adequate to successfully activate each of the photocatalysts tested given that the photocatalysts' bandgaps range from 1.8 - 3.4 eV (Table 4.22) [332 - 334].

Table 4.22: Energy equivalent or additive bandgap for various materials tested in the photodegradation of hydrogen peroxide using an UV LED array.

UV frequency or additive	Energy equivalent of bandgap (eV)
UV light at 365 nm	3.4
Titanium dioxide	3.0
Cerium dioxide	3.2
Bismuth trioxide	1.8
Tungsten trioxide	2.7
Zinc oxide	3.4
Alumina	N / A (not a semiconductor)

The titanium dioxide photocatalyst gave the highest delignification (i.e. kappa number reduction) and best brightness development at a charge of 10.0 kg t⁻¹, with the charge at 5.0 kg t⁻¹ being close to this maximum catalytic efficiency for kappa reduction (Figure 4.50). Changes in both brightness (R457) and kappa number demonstrated similar trends. At higher titanium dioxide charges, both delignification and brightness development steadily dropped off as the suspension became progressively more opaque with more photocatalyst addition. A titanium dioxide charge of 5.0 kg t⁻¹ was selected for subsequent experimental work on titanium dioxide with a view to achieve close to maximum catalytic promotion of the reaction, while avoiding the opaquing out effect of too high a photocatalyst charge. The cerium dioxide photocatalyst gave the highest delignification and best brightness development at a charge of 31.0 kg t⁻¹ with these pulp properties beginning to plateau from a charge of 20.0 kg t⁻¹, whereafter (at 31.0 kg t⁻¹) both delignification and brightness development decreased progressively more as the suspension became increasingly opaque with more photocatalyst addition (Figure 4.51). Changes in both brightness (R457) and kappa number were typically small for cerium dioxide, particularly at the higher charges, making analysis of the observed trends difficult. A cerium dioxide charge of 20.0 kg t⁻¹ was selected for subsequent experimental work on cerium dioxide with a view to achieve close

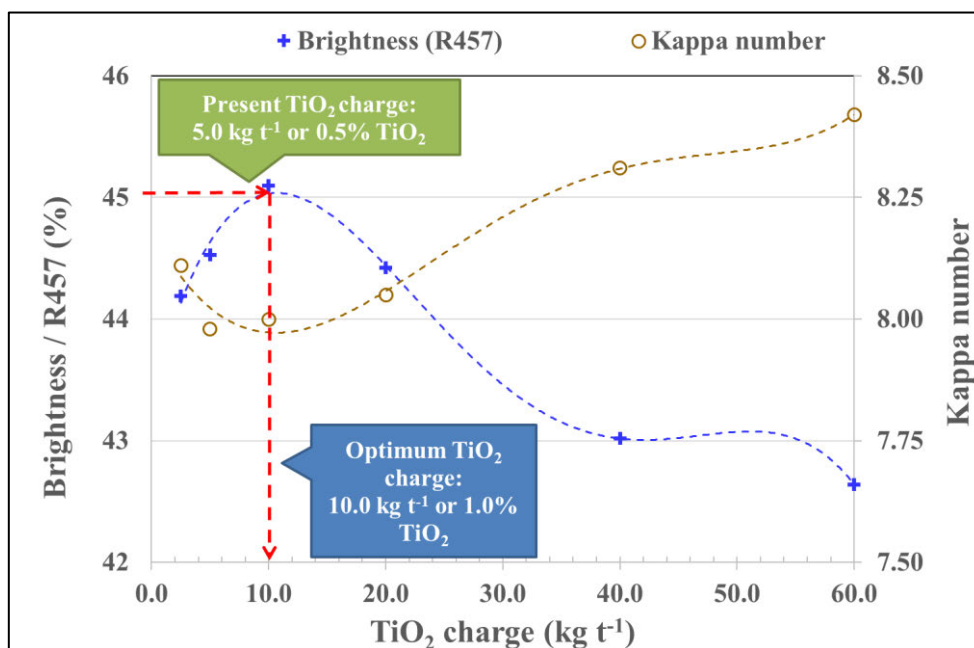


Figure 4.50: Brightness (R457) and kappa number of Cloquet paper grade pulp at variable titanium dioxide photocatalytic charges to determine optimal photocatalytic charge in a UV LED array reactor system.

Conditions: 18.0 kg t⁻¹, NaOH, 80.0 kg t⁻¹ H₂O₂, 2.5 – 60.0 kg t⁻¹ titanium dioxide; 20.0 g pulp; 25 °C; 30 minutes; UV LED array (full power).

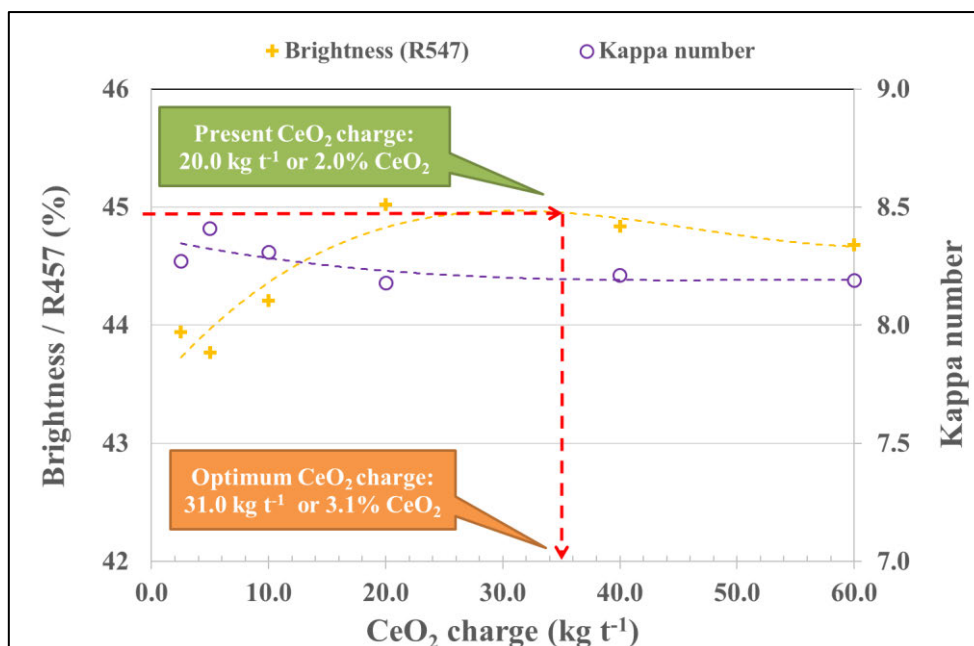


Figure 4.51: Brightness (R457) and kappa number of Cloquet paper grade pulp at variable cerium dioxide photocatalytic charges to determine optimal photocatalytic charge in a UV LED array reactor system.

Conditions: 18.0 kg t⁻¹, NaOH, 80.0 kg t⁻¹ H₂O₂, 2.5 – 60.0 kg t⁻¹ cerium dioxide; 20.0 g pulp; 25 °C; 30 minutes; UV LED array (full power).

to maximum catalytic promotion of the reaction, while avoiding the opaquing out effect of too high a photocatalyst charge.

The photosensitizer, methylene blue, gave the highest delignification (i.e. kappa number reduction) and best brightness development at a charge of 2.0 to 2.2 kg t⁻¹ (Figure 4.52). At higher methylene blue charges, both delignification and brightness development steadily dropped off as the suspensions became progressively darker and more opaque with the addition of increasing quantities of photosensitizer. A methylene blue charge of 2.0 kg t⁻¹ was selected for subsequent experimental work with a view to achieve close to maximum promotion of the reaction, while avoiding the darkening effect of too high a dye charge. The rose bengal photosensitizer gave the highest delignification (i.e. kappa number reduction) and best brightness development at a charge of 7.2 to 8.0 kg t⁻¹ (Figure 4.53). At higher rose bengal charges, both delignification and brightness development showed some small reduction and trends at the higher charges were not easily apparent. A rose bengal charge of 7.2 kg t⁻¹ was selected for subsequent experimental work with a view to achieve close to maximum promotion of the reaction, while avoiding the darkening out effect of too high a dye charge. Overall, the methylene blue gave better delignification than the rose bengal.

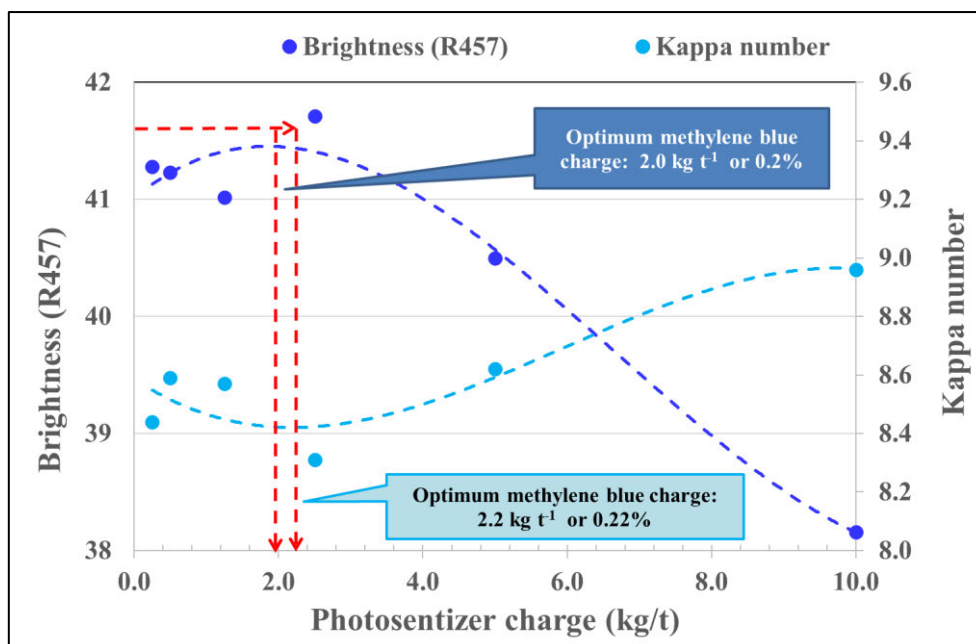


Figure 4.52: Brightness (R457) and kappa number of Cloquet paper grade pulp at variable methylene blue photosensitiser charges to determine optimal photosensitiser charge in a UV LED array reactor system.

Conditions: 18.0 kg t⁻¹, 0.25 – 10.0 kg t⁻¹ methylene blue; oxygen bubbled into suspension through needle valve, cylinder 400 kPa; 20.0 g pulp; 25 °C; 30 minutes; UV LED array (full power).

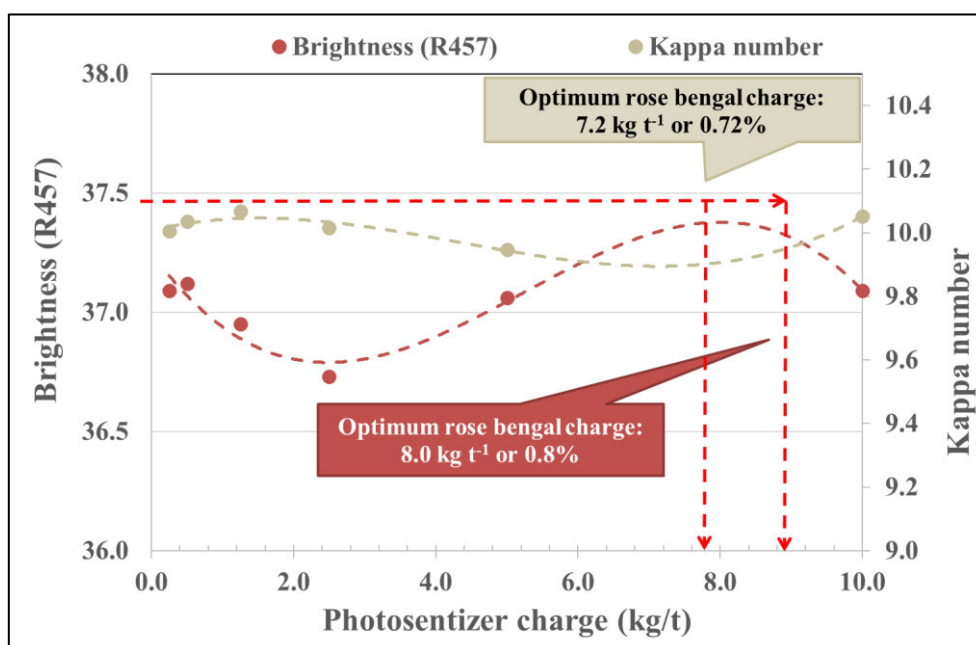


Figure 4.53: Brightness (R457) and kappa number of Cloquet paper grade pulp at variable rose bengal photosensitiser charges to determine optimal photosensitiser charge in a UV LED array reactor system.

Conditions: 18.0 kg t⁻¹, 0.25 – 10.0 kg t⁻¹ rose bengal; oxygen bubbled into suspension through needle valve, cylinder 400 kPa; 20.0 g pulp; 25 °C; 30 minutes; UV LED array (full power).

The dyeing/discolouration of the pulp, even after extensive washing, was clearly apparent for methylene blue with the green shaded pulp becoming visually darker and greener as the photosensitiser charge was increased (Figure 4.54). Rose bengal demonstrated considerably less of the dyeing effect as the organic rinse/deionised water wash appeared to visually remove considerably more of the attached dye, while any residual red shade was easily masked by the red/green shade factor of the brown semi-bleached final pulp.

In summary, based on the parameters of catalytic performance (brightness development and kappa reduction) as well as catalyst discolouration, only titanium dioxide (TiO_2) and cerium dioxide (CeO_2), were found to be potential viable photocatalysts from the original list of semiconductors tested (titanium dioxide, cerium dioxide, bismuth trioxide, tungsten trioxide, and zinc oxide). The charges chosen for both titanium oxide and cerium oxide for further experimental work were 5.0 kg t^{-1} and 20.0 kg t^{-1} respectively. These charges were chosen to be near their maximum performance, but also to avoid making the suspension excessively opaque. The alumina control (aluminium trioxide) did not show

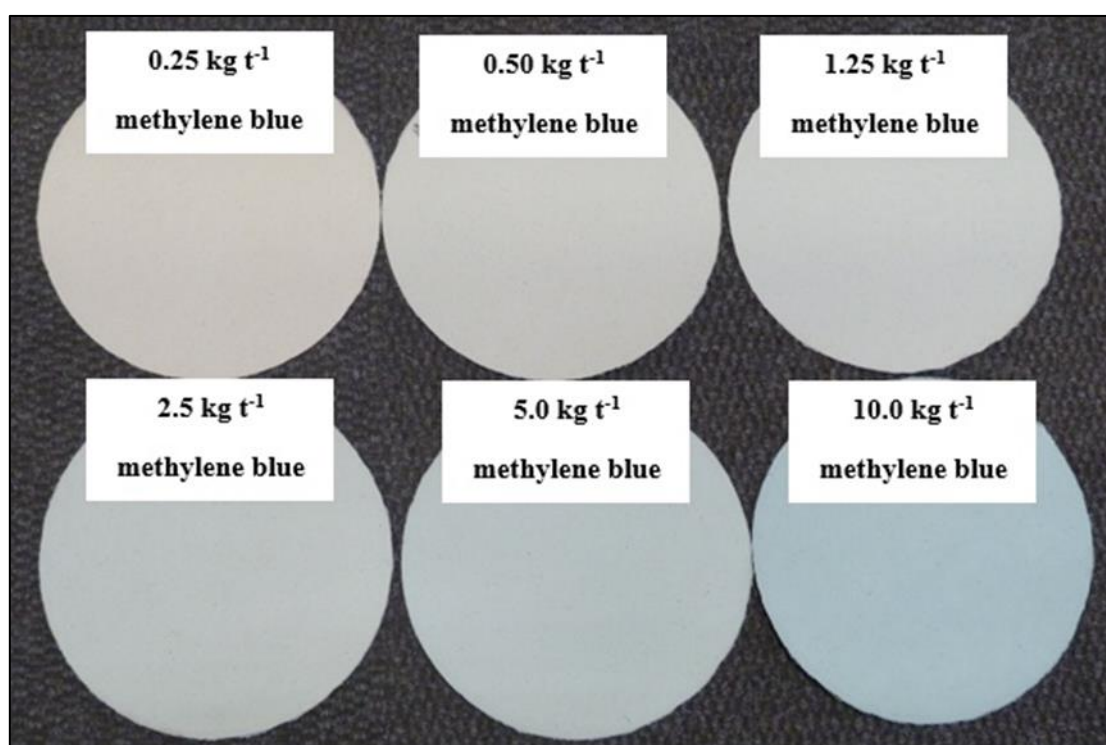


Figure 4.54: Images of Cloquet paper grade pulp at variable methylene blue photosensitiser charges to determine optimal photosensitiser charge in a UV LED array reactor system.

Conditions: 18.0 kg t^{-1} , $0.25 - 10.0 \text{ kg t}^{-1}$ methylene blue; oxygen bubbled into suspension through needle valve, cylinder 400 kPa; 20.0 g pulp; 25°C ; 30 minutes; UV LED array (full power).

any photocatalytic activity which is consistent with what is expected given that it is not a semiconductor. Both photosensitisers (methylene blue and rose bengal) showed some photo-activity, with methylene blue performing better of the two. The optimal photosensitizer charges chosen for further experimental work were 2.0 kg t^{-1} for methylene blue and 7.2 kg t^{-1} for rose bengal. The next step was to quantify the bleaching performance of both photocatalysts and photosensitisers while photochemically bleaching pulp over a variable time range.

4.3.8 Photochemical pulp bleaching with UV LED array: Application of photocatalysts in the photochemical bleaching of pulp (Variable 6)

This study was a more extensive investigation on the selected photocatalysts during the photobleaching of pulp under UV LED array irradiation [324]. A description of the experimental work is given in Section 3.6.8. The photocatalyst titanium dioxide, at a charge of 5.0 kg t^{-1} , catalysed a steadily increased brightness development after 30 minutes as compared to the control pulp without the catalyst (Figure 4.55).

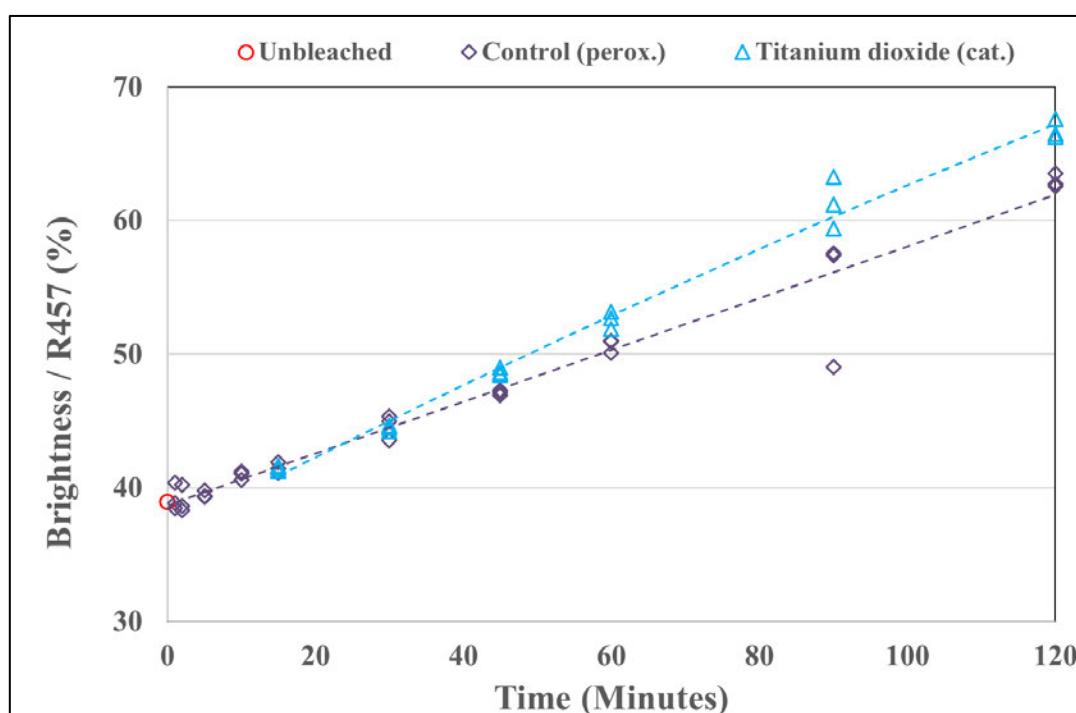


Figure 4.55: Brightness (R457) for a Cloquet paper grade pulp suspension bleached in a UV LED array reactor with a titanium dioxide photocatalyst at variable irradiation times.

Conditions: 18.0 kg t^{-1} , NaOH, $80.0 \text{ kg t}^{-1} \text{ H}_2\text{O}_2$, 5.0 kg t^{-1} titanium dioxide; 20.0 g pulp; 25°C ; 1 - 120 minutes; UV LED array (full power).

As the cerium dioxide catalysed pulps and the control pulps were sampled about a year apart (unbleached Cloquet paper grade batch 1 and batch 2) with different starting brightness values (34.26%

and 38.96% respectively) and kappa numbers (12.01 and 10.98), both sets of brightness values needed to be “normalized” with their respective unbleached starting brightness values serving as each pulp’s respective zero point before a comparative analysis could be made. The normalization undertaken is based on partial application of a technique known as linear transformation or Z-score transformation [308]. Linear transformation/Z-score transformation involves converting each set of data to its Z-score values using each data set’s mean and standard deviation in conjunction with the simple line equation: $y = mx + c$ as its basis. In this study, to allow for some reasonable comparison to other earlier bleaching data, the constant (i.e. c) in the linear equation was taken as the unbleached brightness instead of the mean; while the slope (i.e. m) was taken as the value of one (1) instead of the standard deviation giving a one to one relationship between any two brightness values obtained for two different pulps. Consequently, each data set had the brightness value of its unbleached starting pulp subtracted from each data point to allow a viable comparison between the two sets of data from the two different starting pulps. The photocatalyst cerium dioxide, at a charge of 20.0 kg t^{-1} , did not showed any benefits over the control without catalyst for normalized brightness values (Figure 4.56). Conversely, the cerium dioxide brightness curve demonstrated a minor drop in brightness over the control within the 30 to 90 minute time range.

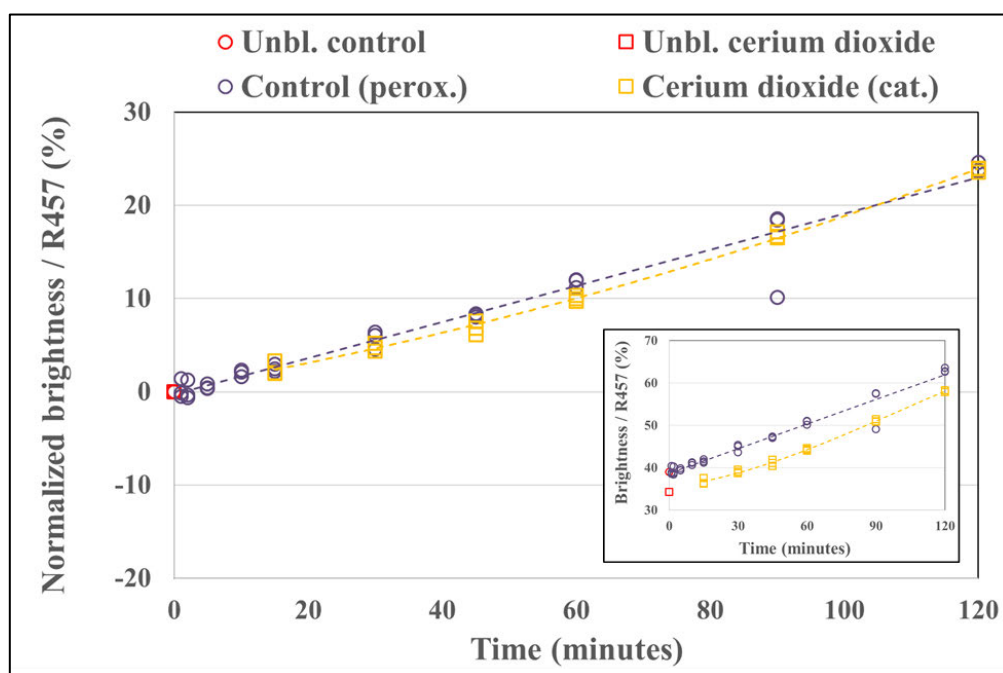


Figure 4.56: Normalized brightness (R457) for two different Cloquet paper grade pulps both bleached in a UV LED array reactor with a cerium dioxide photocatalyst at variable irradiation times. Insert shows the absolute brightness (R457) for the same cerium dioxide data set.

Conditions: 18.0 kg t^{-1} , NaOH, $80.0 \text{ kg t}^{-1} \text{ H}_2\text{O}_2$, 20.0 kg t^{-1} cerium dioxide; 20.0 g pulp; 25°C ; 1 - 120 minutes; UV LED array (full power).

The titanium dioxide photocatalyst gave a small improvement in delignification as given by the kappa number within the 15 to 30 minute time range, as well as at 120 minutes; but with no benefit within the 45 to 90 minute time range (Figure 4.57). The exact cause of this lack of benefit in the 45 to 90 minute time range is unknown.

As indicated prior, given that the cerium dioxide catalysed and the control pulps were sampled on different dates (batch 1 and batch 2), both sets of kappa numbers values needed to be “normalized” with their respective unbleached starting kappa numbers serving as each pulp’s respective zero point before a comparative analysis could be made via the technique of linear transformation or Z-score transformation [308]. As with the titanium dioxide, the cerium dioxide photocatalyst gave a small improvement in delignification within the 15 to 30 minute time range, as well as at 120 minutes; but with no benefit within the 45 to 90 minute time range (Figure 4.58). For both photocatalysts (titanium dioxide and cerium dioxide), there appeared to be a drop off in their catalytic performance with the time range of 45 to 90 minutes. The exact cause of this drop off in catalytic performance within this time range is unknown, though it is likely due to both the pulp suspensions being made too opaque by either photocatalyst or degraded solubilize lignin. Why there is improved delignification at 120 minutes for both photocatalysts is unknown.

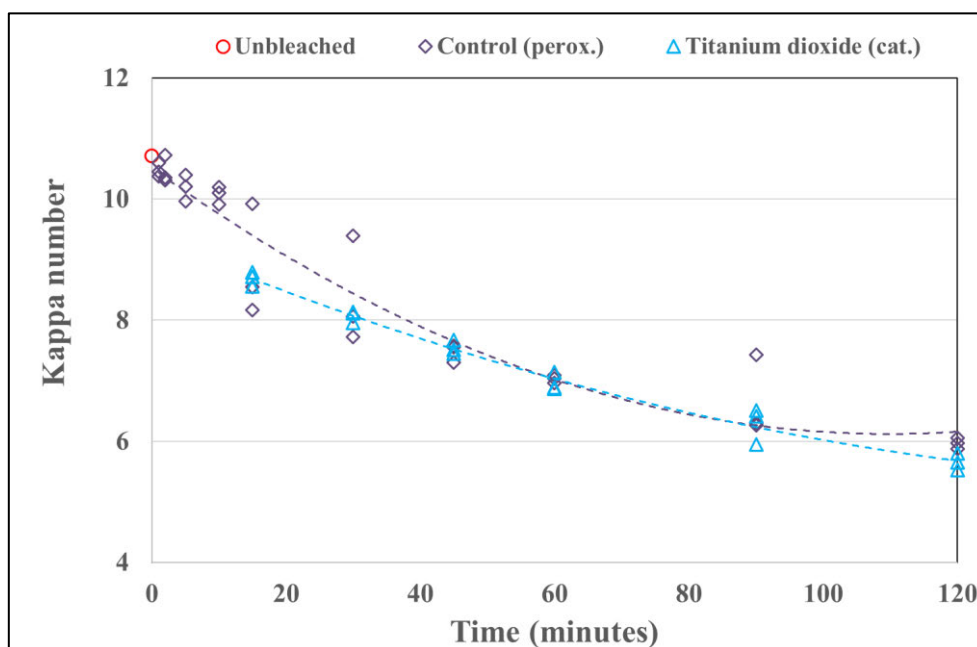


Figure 4.57: Kappa number for a Cloquet paper grade pulp suspension bleached in a UV LED array reactor with a titanium dioxide photocatalyst at variable irradiation times.

Conditions: 18.0 kg t⁻¹, NaOH, 80.0 kg t⁻¹ H₂O₂, 5.0 kg t⁻¹ titanium dioxide; 20.0 g pulp; 25 °C; 1 - 120 minutes; UV LED array (full power).

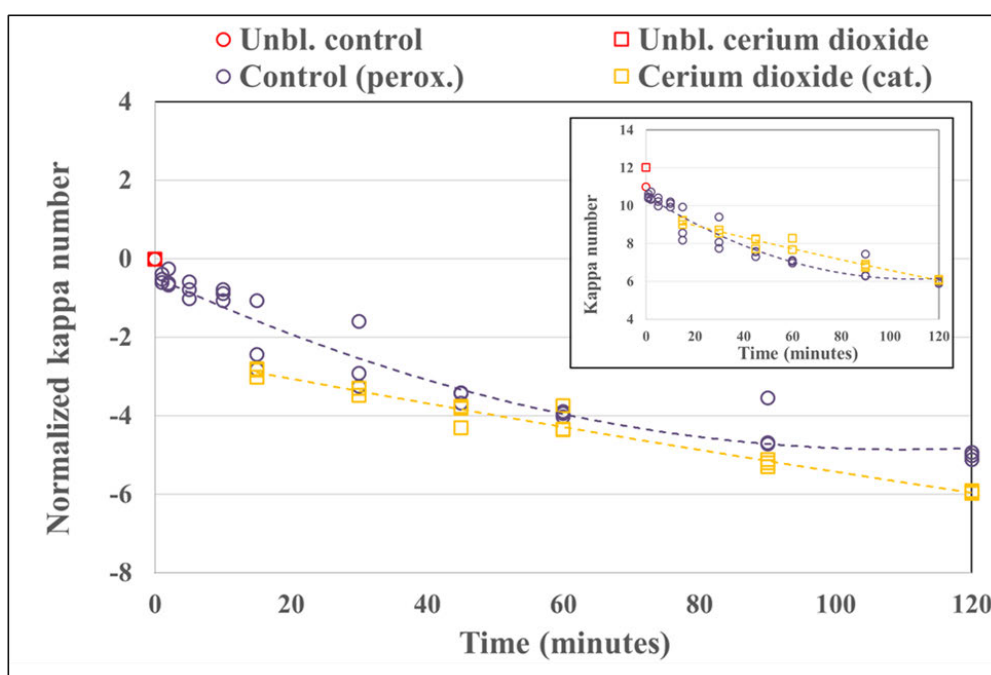


Figure 4.58: Normalized kappa number for a Cloquet paper grade pulp suspension bleached in a UV LED array reactor with a cerium dioxide photocatalyst at variable irradiation times. Insert shows the absolute kappa number for the same cerium dioxide data set. Conditions: 18.0 kg t⁻¹, NaOH, 80.0 kg t⁻¹ H₂O₂, 20.0 kg t⁻¹ cerium dioxide; 20.0 g pulp; 25 °C; 1 - 120 minutes; UV LED array (full power).

The pulp catalysed with titanium dioxide showed increased viscosity losses compared to the control at increased time (Figure 4.59). This is likely due to the photocatalysed generation of larger quantities of active hydroxyl radicals giving an increased level of photobleaching with increased brightness and reduced kappa. The pulp catalysed with cerium dioxide only showed a lower viscosity compared to the control at 90 and 120 minutes (Figure 4.60). This lower viscosity is also likely due to a similar reason as for titanium dioxide.

Both photocatalysts gave initial and final alkaline pH values above pH 10.0 for their respective pulp suspensions as expected (Table 4.23). These results suggest that there was no unexpected deviation in both photocatalysts' outcomes due to strongly varying or uncontrolled pH changes. Both photocatalysts gave initial temperatures of about 25 °C across the entire time range evaluated (15 to 120 minutes) while both photocatalyst pulp suspensions showed increasing temperatures up to about 35 °C across the same time range (Table 4.23). This is expected and demonstrates that the photochemical bleaching process was under control and performing without any thermal anomalies. Thus, the thermal

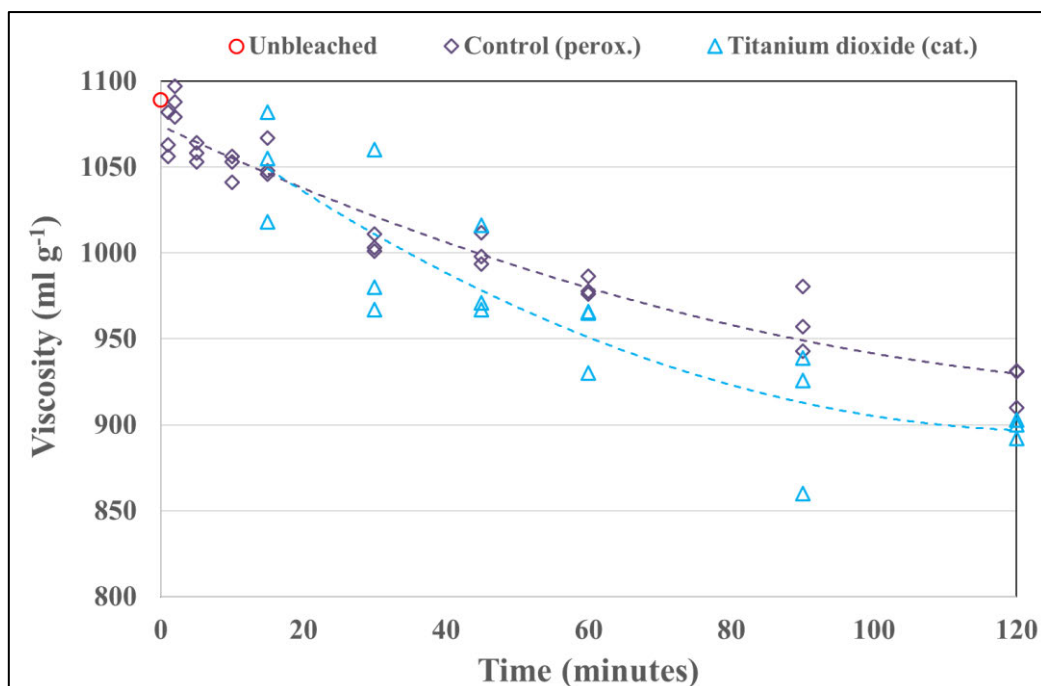


Figure 4.59: Viscosity (CED) for a Cloquet paper grade pulp suspension bleached in a UV LED array reactor with a titanium dioxide photocatalyst at variable irradiation times.
Conditions: 18.0 kg t⁻¹, NaOH, 80.0 kg t⁻¹ H₂O₂, 5.0 kg t⁻¹ titanium dioxide; 20.0 g pulp; 25 °C; 1 - 120 minutes; UV LED array (full power).

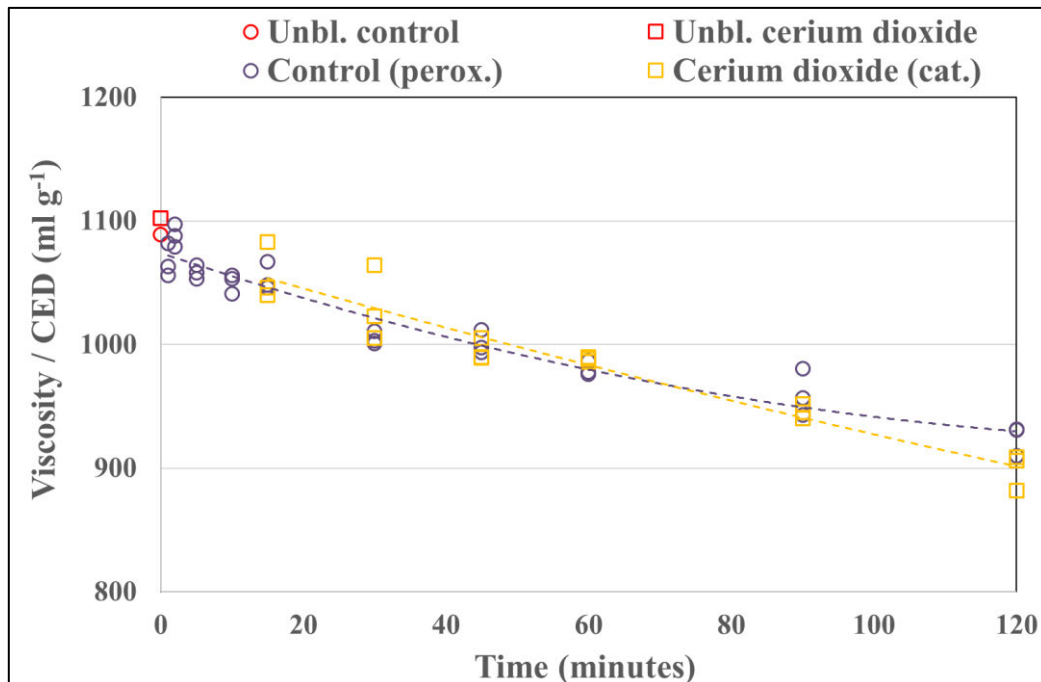


Figure 4.60: Viscosity (CED) for a Cloquet paper grade pulp suspension bleached in a UV LED array reactor with a cerium dioxide photocatalyst at variable irradiation times.
Conditions: 18.0 kg t⁻¹, NaOH, 80.0 kg t⁻¹ H₂O₂, 20.0 kg t⁻¹ cerium dioxide; 20.0 g pulp; 25 °C; 1 - 120 minutes; UV LED array (full power).

contribution to either photocatalytic process was minimal. Both the titanium dioxide and cerium dioxide showed significantly greater peroxide degradation over time than the control (Table 4.23). This is likely due to the photocatalytic activity of both catalysts and the increased direct photolysis of peroxide to hydroxyl radicals by both catalysts. The residual for the cerium dioxide tended to be lower than that for the titanium dioxide over the same time scales. This difference was likely due to analytical or experimental error. Both the titanium dioxide and cerium dioxide show little change in their pulp yield over the time scale of 15 to 120 minutes evaluated, suggesting that neither photocatalyst facilitated any significant material loss from degradation in pulp material (Table 4.3). Overall, there were no indications of anomalous occurrences during either photocatalyst experimental runs.

Table 4.23: Initial and final pH, initial and final temperature, peroxide residual and range, and pulp yield for a Cloquet paper grade pulp suspension bleached in a UV LED array reactor with either a titanium dioxide or cerium dioxide photocatalyst at variable irradiation times.

Time (min.)	15	30	45	60	90	120
Control						
Res. peroxide (%)	100.0	100.9	100.5	98.7	94.0	96.3
Range ($\pm$ value)	0.8	1.7	1.2	3.0	4.1	0.3
Titanium dioxide						
Initial pH	10.98	10.81	10.80	10.78	10.61	10.78
Final pH	10.93	10.69	10.58	10.50	10.43	10.29
Initial temperature (°C)	20.6	21.1	20.2	20.2	19.7	20.2
Final temperature (°C)	23.0	25.6	27.5	28.5	28.3	33.3
Res. peroxide (%)	95.6	89.5	85.9	76.4	65.6	41.1
Range ($\pm$ value)	3.9	6.9	5.6	10.8	24.3	29.5
Pulp Yield (%)	97.4	97.8	96.2	98.2	99.0	96.4
Cerium dioxide						
Initial pH	10.56	10.80	10.36	10.78	10.70	10.83
Final pH	10.39	10.70	10.43	10.39	10.48	10.48
Initial temperature (°C)	21.2	22.1	21.1	23.0	22.0	21.3
Final temperature (°C)	23.5	26.9	28.4	31.5	33.9	35.3
Res. peroxide (%)	90.3	81.6	74.2	67.5	45.3	30.6
Range ($\pm$ value)	3.7	2.1	3.0	2.2	1.1	2.6
Pulp yield (%)	95.1	95.9	93.9	94.8	95.1	96.1

A plot of the brightness (R457) against the kappa number showed that both the control and the titanium dioxide catalyzed pulps fell visually on the same general curve with a high level of correlation for each (Figure 4.61). This suggested that the titanium dioxide photocatalyst did not employ a different photochemical reaction mechanism from that observed with the control, but rather simply accelerates it by the Langmuir-Hinshelwood photocatalytic mechanism. This was consistent with the observations made for the brightness values and kappa numbers at variable times (15 to 120 minutes) given in Section 4.3.7.

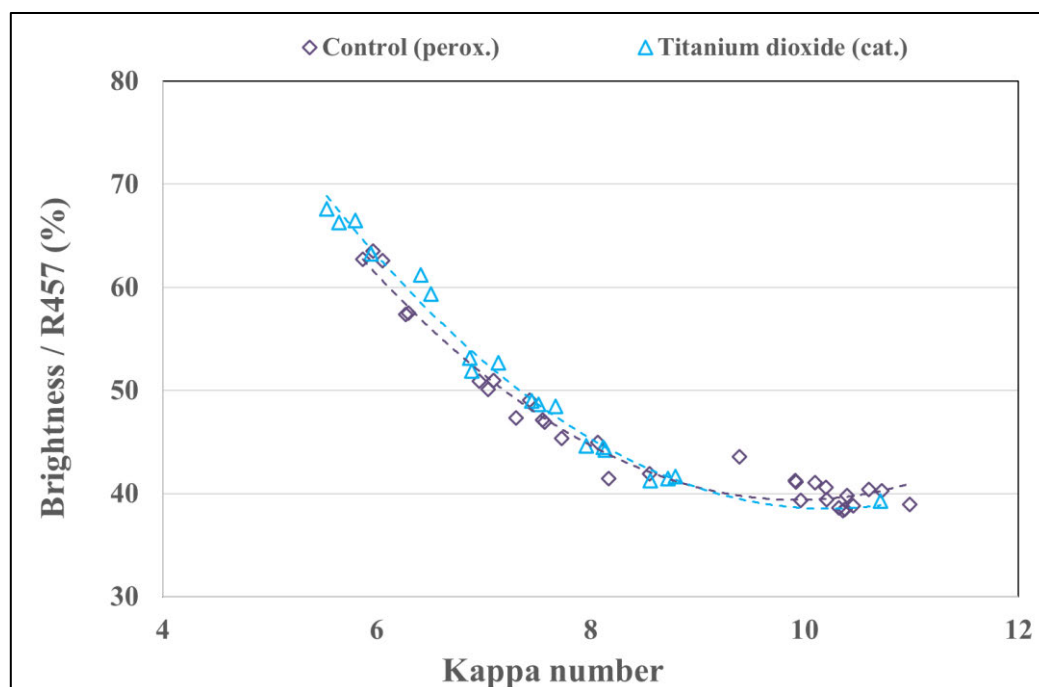


Figure 4.61: Brightness (R457) versus kappa number for a Cloquet paper grade pulp suspension bleached in a UV LED array reactor with a titanium dioxide photocatalyst at variable irradiation times.

Conditions: 18.0 kg t⁻¹, NaOH, 80.0 kg t⁻¹ H₂O₂, 5.0 kg t⁻¹ titanium dioxide where relevant; 20.0 g pulp; 25 °C; 1 - 120 minutes; UV LED array (full power).

A comparative Student T-test (T_C-test) for kappa numbers indicated that the titanium dioxide photocatalyst pulp at variable time (15 to 120 minutes) was not significantly different from the control at 25 °C across all times for both a 90% and 95% confidence level (Table 4.24). This is consistent with the kappa number curve for both across the same time range given in Figure 4.57, where the titanium dioxide pulp gave a slightly lower kappa number at 15 to 30 minutes, was similar at 45 to 90 minutes, and was slightly lower again at 120 minutes as compared to the control. Similarly, the comparative T-test for the ratio of brightness (R457) to kappa numbers (i.e. Bri / kappa) showed that the titanium dioxide photocatalyst pulp was not significantly different from the control (25 °C) at and below 60 minutes; however, was significantly different at and above 90 minutes for both a 90% and 95%

confidence level (Table 4.25). Overall, this suggests that the benefits of the titanium dioxide catalyst only become apparent at longer time scales (longer than 60 minutes). This is consistent with the observations around the brightness values for the titanium dioxide photocatalyst (Figure 4.55).

Table 4.24: Comparative student T-test (Tc) for differences between kappa numbers of a Cloquet paper grade pulp suspension bleached in a UV LED array reactor with a titanium dioxide photocatalyst at variable irradiation times.

Time (minutes)	15	30	45	60	90	120	STD	n_x
Control (No UV LED)	10.78	10.75	10.63	10.20	9.66	10.11	0.579	30
Peroxide (Var. Time)	8.88	8.40	7.48	7.03	6.67	5.96	1.693	30
Photo-cat. (TiO ₂)	8.69	8.07	7.54	6.97	6.29	5.66	1.127	18
Tc (Control / Peroxide)	6.92	8.54	11.45	11.50	10.89	15.06		
α (<0.05 / 95% confidence)	TRUE	TRUE	TRUE	TRUE	TRUE	TRUE		
Tc (Peroxide / TiO ₂ Photo-Cat.)	0.47	0.79	0.17	0.16	0.93	0.75		
α (<0.05 / 95% confidence)	FALSE	FALSE	FALSE	FALSE	FALSE	FALSE		
α (<0.1 / 90% confidence)	FALSE	FALSE	FALSE	FALSE	FALSE	FALSE		



INCREASED BRIGHTNESS

Table 4.25: Comparative student T-test (Tc) for differences between ratios of R457 brightness to kappa numbers of a Cloquet paper grade pulp suspension bleached in a UV LED array reactor with a titanium dioxide photocatalyst at variable irradiation times.

Time (minutes)	15	30	45	60	90	120	n _x
Peroxide (Var. Time) / Kappa	8.548	8.067	7.553	7.095	7.433	6.053	30
Brightness (R457)	41.94	44.98	47.17	51.00	49.07	62.60	
Bri/Kappa	4.906	5.576	6.246	7.189	6.602	10.342	
AVE (Bri/Kappa)	4.71	5.36	6.31	7.21	8.30	10.56	STD 2.265
Photo-Cat. (TiO ₂) / Kappa	8.558	7.960	7.450	6.870	5.950	5.530	18
Brightness (R457)	41.28	44.64	48.97	53.15	63.25	67.59	
Bri/Kappa	4.824	5.608	6.573	7.737	10.630	12.222	
AVE (Bri/Kappa)	4.77	5.51	6.46	7.55	9.77	11.81	STD 2.541
INCREASED BRIGHTNESS							
Tc (Peroxide / TiO ₂ Photo-Cat.)	0.09	0.20	0.20	0.47	2.02	1.72	
α (<0.05 / 95% confidence)	FALSE	FALSE	FALSE	FALSE	TRUE	FALSE	
α (<0.1 / 90% confidence)	FALSE	FALSE	FALSE	FALSE	TRUE	TRUE	

As indicated, given that the cerium dioxide catalyzed pulps and the control pulps were sampled on different dates (batch 1 and batch 2), both sets of brightness (R457) and kappa numbers values needed to be normalized with their respective unbleached starting kappa numbers serving as each pulp's

respective zero point before a comparative analysis could be made. Consequently, a plot of the normalized brightness (R457) against the normalized kappa number showed that both the control and the cerium dioxide catalysed pulps fell visually on different, but similar, curves with a high level of correlation for each (Figure 4.62). The small difference in the two curves is not large enough to suggest a different photochemical bleaching mechanism for both the control and cerium dioxide pulps.

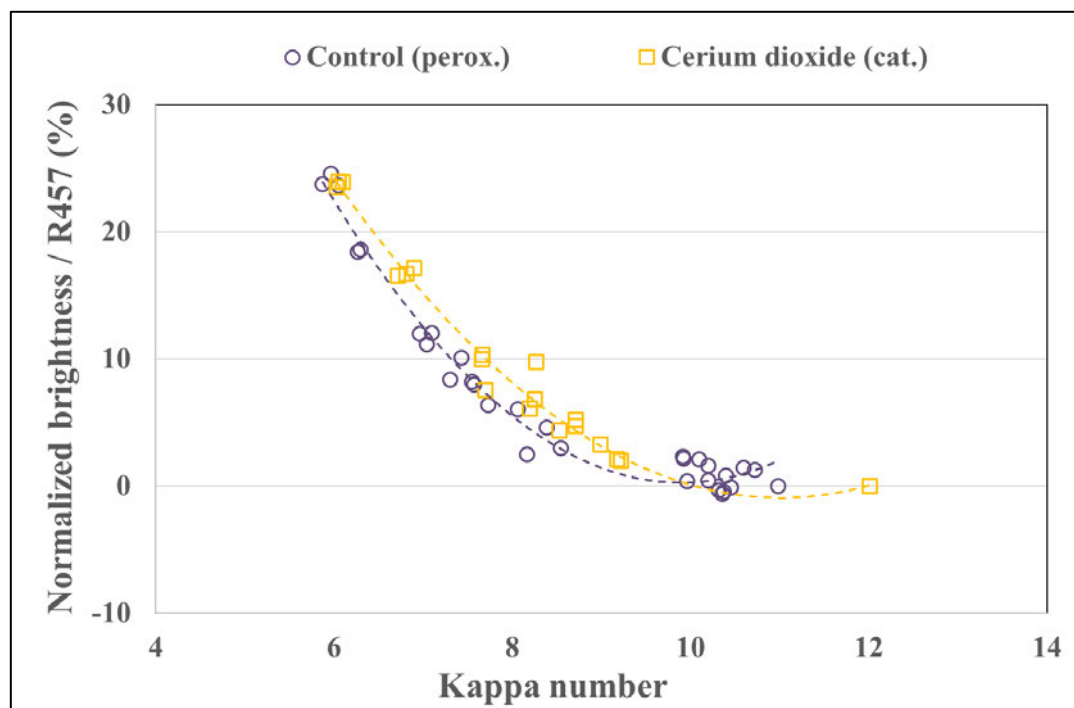


Figure 4.62: Normalized brightness (R457) versus normalized kappa number for a Cloquet paper grade pulp suspension bleached in a UV LED array reactor with a cerium dioxide photocatalyst at variable irradiation times.

Conditions: 18.0 kg t⁻¹, NaOH, 80.0 kg t⁻¹ H₂O₂, 20.0 kg t⁻¹ cerium dioxide where relevant; 20.0 g pulp; 25 °C; 1 - 120 minutes; UV LED array (full power).

The comparative Student T-test (Tc-test) for normalized kappa numbers indicated that the cerium dioxide photocatalyst pulp at variable time (15 to 120 minutes) was significantly different from the control (25 °C) at times of 15 and 30 minutes and at 90 to 120 minutes for a 90% confidence level, but only significantly different at 90 minutes and above at a 95% confidence level (Table 4.26). The comparative T-test for the ratio of normalized brightness (R457) to normalized kappa numbers (i.e. Norm. Bri / Norm. kappa) showed that the cerium dioxide photocatalyst pulp at variable time (15 to 120 minutes) was significantly different from the control at times of 30 minutes and 120 minutes for a 90% confidence level and significantly different at 30 minutes at a confidence level of 95% (Table 4.27). These observations are consistent with the normalized kappa number curve for both the cerium dioxide and control across the time range of 15 to 120 minutes given in Figure 4.58, where the

Table 4.26: Comparative student T-test (Tc) for differences between kappa numbers of a Cloquet paper grade pulp suspension bleached in a UV LED array reactor with a cerium dioxide photocatalyst at variable irradiation times.

Time (minutes)	15	30	45	60	90	120	STD	n_x
Control (No UV LED)	-0.20	-0.24	-0.36	-0.79	-1.32	-0.87	0.579	30
Peroxide (Var. Time)	-2.10	-2.59	-3.51	-3.95	-4.31	-5.02	1.693	30
Photo-cat. (CeO ₂)	-2.88	-3.36	-3.96	-4.15	-5.20	-5.95	1.145	18
Tc(Control / Peroxide)	5.83	7.20	9.65	9.69	9.17	12.69		
α (<0.05 / 95% confidence)	TRUE	TRUE	TRUE	TRUE	TRUE	TRUE		
Tc (Peroxide / CeO ₂ Photo-Cat.)	1.90	1.89	1.11	0.48	2.17	2.28		
α (<0.05 / 95% confidence)	FALSE	FALSE	FALSE	FALSE	TRUE	TRUE		
α (<0.1 / 90% confidence)	TRUE	TRUE	FALSE	FALSE	TRUE	TRUE		
INCREASED BRIGHTNESS								

Table 4.27: Comparative student T-test (Tc) for differences between ratios of normalized R457 brightness to kappa numbers of a Cloquet paper grade pulp suspension bleached in a UV LED array reactor with a cerium dioxide photocatalyst at variable irradiation times.

Time (minutes)	15	30	45	60	90	120	n_x
Per. (Var. Time) / Norm. Kappa	-2.434	-2.916	-3.430	-3.888	-3.549	-4.929	30
Norm. Brightness (R457)	2.98	6.02	8.21	12.04	10.11	23.64	
Norm. Bri/Norm. Kappa	-1.224	-2.065	-2.394	-3.097	-2.849	-4.796	
AVE (Norm. Bri/Norm. Kappa)	-1.38	-2.30	-2.34	-2.97	-3.58	-4.78	STD 1.665
Photo-Cat. (CeO ₂) / Norm. Kappa	-3.023	-3.303	-4.313	-4.353	-5.203	-5.963	18
Norm. Brightness (R457)	3.28	5.23	7.56	9.98	16.67	23.97	
Norm. Bri/Norm. Kappa	-1.085	-1.583	-1.753	-2.293	-3.204	-4.020	
AVE (Norm. Bri/Norm. Kappa)	-0.84	-1.42	-1.72	-2.42	-3.23	-4.00	STD 1.117
INCREASED BRIGHTNESS							
Tc (Peroxide / CeO ₂ Photo-Cat.)	1.35	2.19	1.53	1.36	0.87	1.95	
α (<0.05 / 95% confidence)	FALSE	TRUE	FALSE	FALSE	FALSE	FALSE	
α (<0.1 / 90% confidence)	FALSE	TRUE	FALSE	FALSE	FALSE	TRUE	

cerium dioxide pulp gave a slightly lower kappa number at 15 to 45 minutes, was similar at 60 minutes, and was slightly lower again at 90 to 120 minutes as compared to the control. A similar to the titanium dioxide photocatalyst, the cerium dioxide photocatalyst only appears beneficial at prolonged time scales (120 minutes). Lastly, although the plot of the normalized brightness (R457) against the normalized kappa number may have suggested similar but slightly different reaction mechanisms with and without the cerium dioxide photocatalyst, the lack of significant differences for the comparative Student Tc tests for the normalized kappa number at 45 to 60 minutes and similar lack of difference for the ratio of normalized brightness (R457) to normalized kappa numbers (i.e. Norm. Bri / Norm. kappa) at 45 to 90 minutes favoured the overall argument for there being no difference in the reaction mechanism with the use of the cerium dioxide photocatalyst as compared to the control, and for the titanium dioxide photocatalyst, but rather on acceleration of hydroxyl radical based bleaching.

In summary, the semiconductor photocatalysts titanium dioxide and cerium dioxide showed some photocatalytic activity at longer bleaching times of 90 to 120 minutes at the optimum charge levels of 5.0 kg t^{-1} and 20.0 kg t^{-1} respectively. Also, neither photocatalyst appears to suffer from darkening or discolouration during the process. The titanium dioxide and cerium dioxide photocatalysts retain their white and pale yellow shades respectively. However, there is still some concern around the possible loss of photocatalytic bleaching efficiencies in the 45 to 60 minutes time range likely due to both opaquing out the pulp suspension by either photocatalyst and the significant loss in peroxide residual due to the catalysts' activities in that time range (less peroxide to drive reaction). In addition, the titanium dioxide appeared to cause some additional loss in pulp viscosity upon use as compared to the control. In conclusion, titanium dioxide would be ideal for photocatalyzing the bleaching of pulp to a fully bleached level where maximum whiteness and brightness are critical (given that titanium dioxide remains white); while cerium dioxide would be ideal for photocatalysing the bleaching of pulp to a semi-bleached level where a golden brown shade is typically favoured (given that cerium dioxide remains pale yellow). However, further photocatalytic bleaching optimization is required.

4.3.9 Photochemical pulp bleaching with UV LED array: Application of photosensitizers in the photochemical bleaching of pulp (Variable 7)

This evaluation was a more extensive investigation on the selected photosensitizers during the photobleaching of pulp under UV LED array irradiation [325]. A description of the experimental work is given in Section 3.6.9. As the starting pulps for both photosensitisers and their oxygen control were sampled about a year apart (batch 1 and batch 2) with different starting brightness values (34.26% and 38.96% respectively) and kappa numbers (12.01 and 10.98), the brightness values and kappa numbers typically needed to be normalized with their respective unbleached starting brightness and kappa numbers serving as each pulp's respective zero point via the technique of linear transformation/Z-score

transformation before a comparative analysis could be made in many cases [308]. Overall, the two photosensitizers gave improved brightness development (normalized brightness values) over the oxygen control at shorter time ranges (i.e. 15 to 45 minutes), but showed reduced ability at longer time ranges (90 to 120 minutes) when subjected to irradiation from a UV LED array using oxygen as an oxidant (Figure 4.63). Based on the brightness results alone, it is uncertain whether this initial brightness improvement at the shorter time ranges is due to photo-activity of the photosensitisers or enhanced lignin/chromophore removal by the organic solvent rinse stage of the pulp washing process, and further data (beyond brightness results) was required to draw a conclusion regarding this. It was also noted that without the solvent rinses both pulps would have been considerably darker and intensely shaded (navy blue for methylene blue and intensely red for rose bengal).

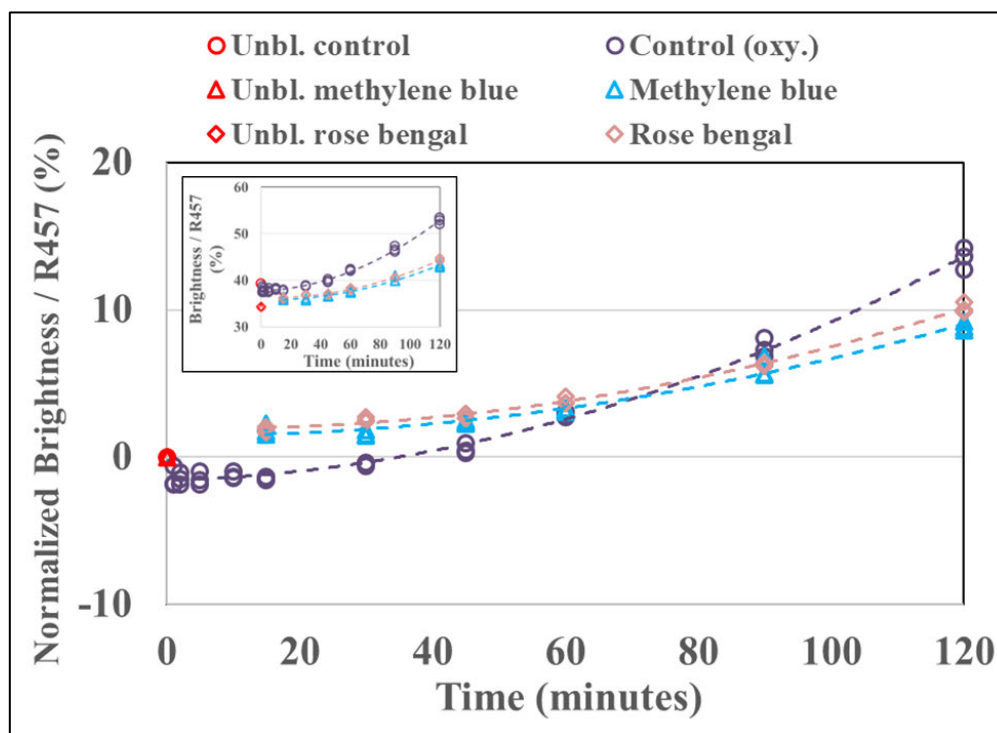


Figure 4.63: Normalized brightness (R457) for a Cloquet paper grade pulp suspension bleached in a UV LED array reactor with methylene blue and rose bengal photosensitizers at variable irradiation times. Insert shows the absolute brightness (R457) for the methylene blue and rose bengal photosensitizers.

Conditions: 18.0 kg t⁻¹, 2.0 kg t⁻¹ methylene blue or 7.2 kg t⁻¹ rose bengal where relevant; oxygen bubbled into suspension through needle valve, cylinder 400 kPa; 20.0 g pulp; 25 °C; 15 - 120 minutes; UV LED array (full power).

The luminance factors (L-value) of both the oxygen control and rose bengal pulps showed a general increase with runtime, while their red (a-value) and yellow (b-value) shade factors started at similar values and decreased similarly as the pulp became whiter with time (Figure 4.64). Of the two pulps,

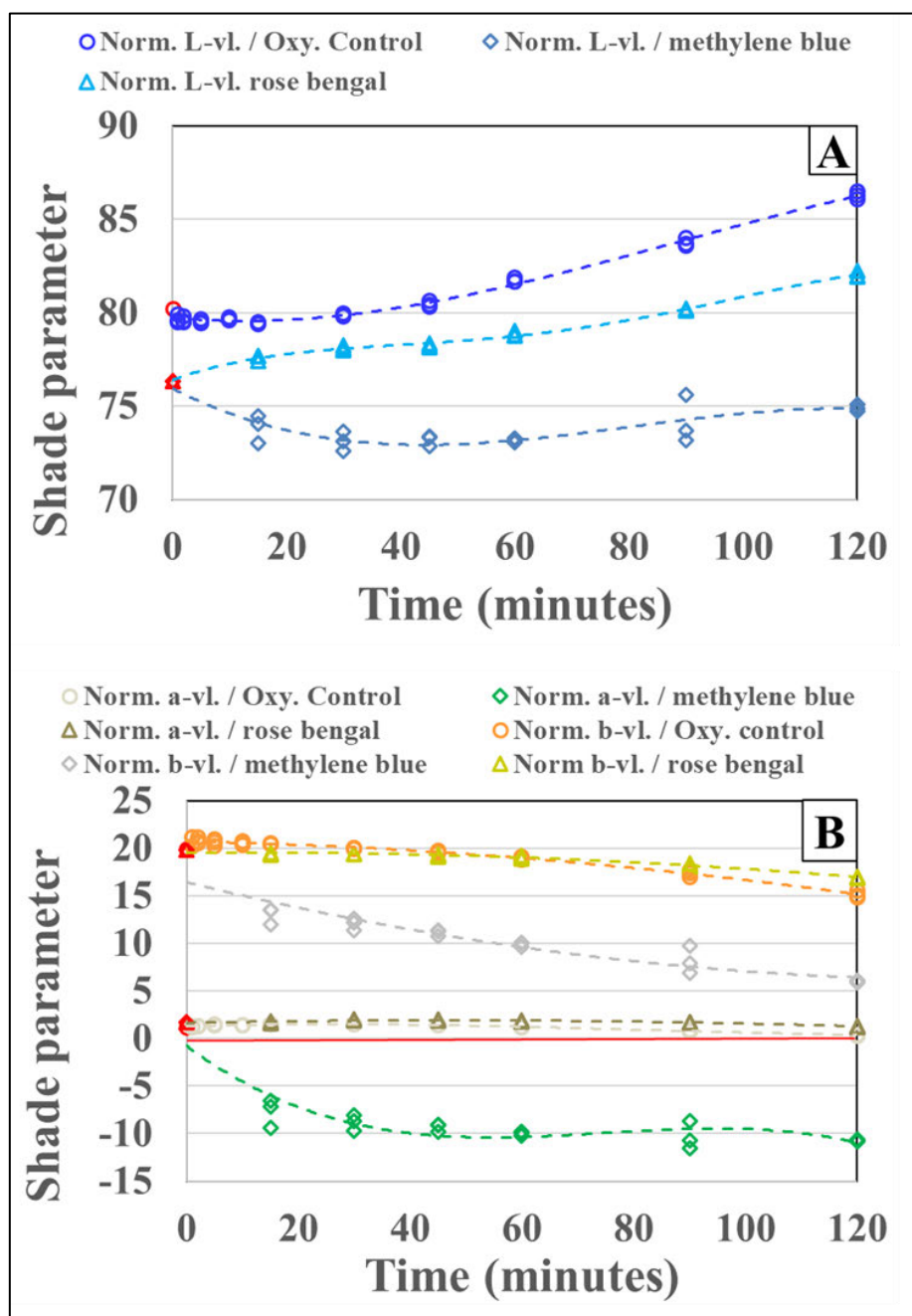


Figure 4.64: [A] Shade L-values and [B] shade a- and b-values for a Cloquet paper grade pulp suspension bleached in a UV LED array reactor with either methylene blue or rose bengal photosensitizers at variable irradiation times.

Conditions: 18.0 kg t⁻¹, 2.0 kg t⁻¹ methylene blue or 7.2 kg t⁻¹ rose bengal where relevant; oxygen bubbled into suspension through needle valve, cylinder 400 kPa; 20.0 g pulp; 25 °C; 15 - 120 minutes; UV LED array (full power).

the oxygen control showed a visually slightly better reduction in shade than the rose bengal photosensitizer. However, the luminance factor of the methylene blue pulp was significantly lower than its starting pulp or both the oxygen control and rose bengal pulps over most of the 120 minute time range. In addition, the methylene blue pulp's red/green shade factor (a-value) showed that the pulp was strongly green in shade and that its yellow shade factor (b-value) showed a large progressive reduction over the 120 minute time range. The results suggest that the solvent rinse stage of the solvent rinse/water washing process was effective in removing most of the rose bengal dye, but that a reasonable portion of the methylene blue dye was not removed and remained attached/fixed to the pulp fibre in a modified form (giving the green shade). Given that both pulps were intensely dyed by their respective photosensitizers being fixed in the fibres (i.e. red for rose bengal and navy blue for methylene blue) without the inclusion of an organic solvent rinse stage, the results suggest that neither water soluble photosensitisers would be practical additives in any proposed photobleaching scheme or sequence unless much lower charges could be employed or the dye was oxidized/destroyed and removed in a subsequent peroxide stage.

As with the brightness results, the normalization undertaken for kappa number was also based on application of the linear transformation technique. Consequently, each data set had the kappa number value of its unbleached starting pulp subtracted from each data point to allow a viable comparison between the two sets of data from the two different starting pulps (batch 1 and batch 2). Contrary to the brightness results, the normalized kappa number showed a poorer delignification for both photosensitizers over the initial 15 to 30 minute time range as compared to the oxygen control, but these detriments were not visible after the 45 minute time range (Figure 4.65). These initial differences in the normalized kappa numbers for rose bengal compared to the oxygen control were far smaller than the differences for methylene blue.

The oxygen control, methylene blue, and rose bengal pulps showed a steady reduction in viscosity over time with both photosensitizers showing a larger reduction than the control (Figure 4.66). These differences were likely real changes in viscosity for the control pulp as compared to the two photosensitizers pulps given that batch 1 and 2 pulps had very similar starting viscosities (1096 ml g^{-1} and 1102 ml g^{-1} for batch 1 and 2 respectively). Overall viscosity losses were small in size.

Both methylene blue and rose bengal showed initial and final pulp suspension pH values within the expected range above 10.0 (Table 4.28). In addition, both photosensitizers also had starting temperatures for their pulps of about 25°C , while their final temperatures never rose above 37°C even

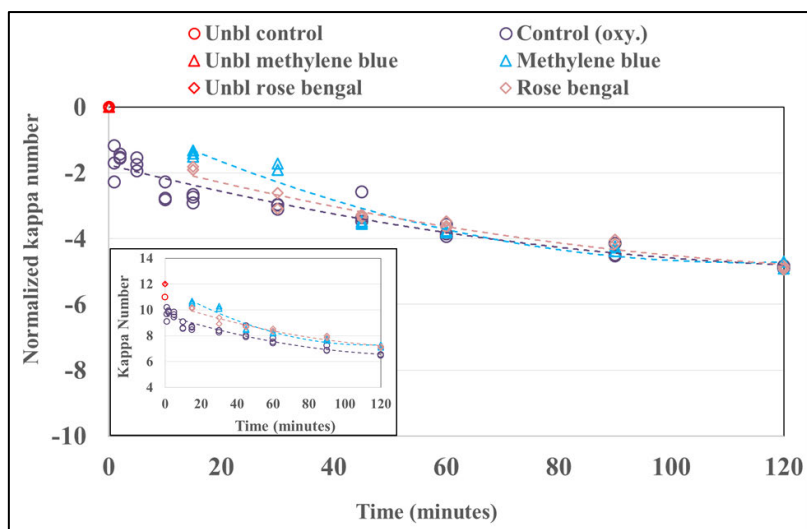


Figure 4.65: Normalized kappa number for a Cloquet paper grade pulp suspension bleached in a UV LED array reactor with either methylene blue or rose bengal as photosensitizers at variable irradiation times. Insert shows the absolute kappa number for the methylene blue and rose bengal photosensitizers.

Conditions: 18.0 kg t^{-1} , 2.0 kg t^{-1} methylene blue or 7.2 kg t^{-1} rose bengal where relevant; oxygen bubbled into suspension through needle valve, cylinder 400 kPa; 20.0 g pulp; 25°C ; 15 - 120 minutes; UV LED array (full power).

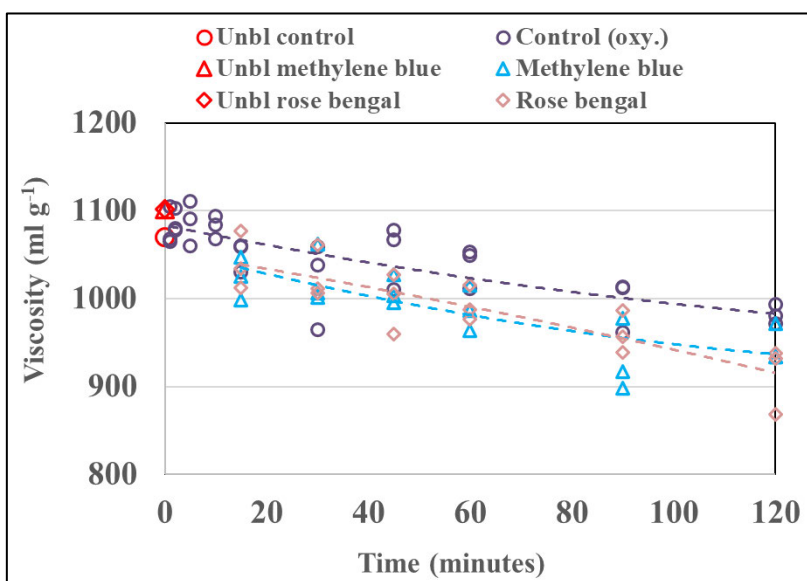


Figure 4.66: Viscosity (CED) for a Cloquet paper grade pulp suspension bleached in a UV LED array reactor with either methylene blue or rose bengal as photosensitizers at variable irradiation times.

Conditions: 18.0 kg t^{-1} , 2.0 kg t^{-1} methylene blue or 7.2 kg t^{-1} rose bengal where relevant; oxygen bubbled into suspension through needle valve, cylinder 400 kPa; 20.0 g pulp; 25°C ; 15 - 120 minutes; UV LED array (full power).

though the temperature did increase with time (Table 4.28). Thus, the thermal contribution to either photosensitizer process was minimal. Overall, both the pH values and temperatures would suggest that all experimental runs went as expected without any unwanted or anomalous side issues. The pulp yields for the two photosensitizers were similar across the entire time range of 15 to 120 minutes, with no notable losses over time (Table 4.28).

The poor photosensitizing performance of both methylene blue and rose Bengal raises the question whether irradiation at 365 nm is appropriate for either photosensitizer. Both methylene blue and rose bengal show little absorption at 365 nm (See Figures A and B in Appendix D), suggesting that both photosensitizers would likely experience very little excitation by the UV LED array used. This likely accounts for at least part of the poor methylene blue and rose bengal performance observed [335 – 336].

Table 4.28: Initial and final pH, initial and final temperature, and pulp yield for a Cloquet paper grade pulp suspension bleached in a UV LED array reactor with either methylene blue or rose bengal as photosensitizers at variable irradiation times.

Time (min.)	15	30	45	60	90	120
Methylene Blue						
Initial pH	10.70	10.80	10.56	10.71	10.63	10.72
Final pH	10.54	10.45	10.12	10.04	10.23	10.33
Initial Temperature (°C)	22.7	23.4	23.1	23.4	23.4	23.2
Final Temperature (°C)	25.1	27.8	29.1	31.6	34.9	36.8
Pulp Yield (%)	97.8	98.2	98.6	99.6	98.5	98.9
Rose Bengal						
Initial pH	10.91	10.58	11.40	11.32	11.40	10.83
Final pH	10.55	10.49	11.12	11.08	10.91	10.33
Initial Temperature (°C)	23.7	23.5	23.0	23.4	23.3	23.5
Final Temperature (°C)	26.5	27.4	30.0	31.7	33.9	35.0
Pulp Yield (%)	98.7	96.5	100.9	96.9	99.1	97.0

The two photosensitizers (methylene blue and rose bengal) visually fell on a different curve than the oxygen control for a plot of the normalized brightness versus the normalized kappa number (Figure 4.67). This suggested that the delignification for the two photosensitizer pulps occurred via a different photochemical process than for the oxygen control pulp, with the two possibilities being: (a) photo-activity of the photosensitizers through a triplet electronic state, or (b) enhanced lignin/chromophore removal by the organic solvent rinse stage of the pulp washing process. The experimental runs

undertaken to evaluate the impact of the organic solvent rinse on the delignification of the pulp (i.e. photosensitizers methylene blue and rose bengal without UV LED array irradiation) gave results that sat close to the curve observed for the two photosensitizers rather than on the control curve in Figure 4.67. This indicated that the improvements observed for the two photosensitizers for the normalized brightness versus the normalized kappa number plots were due solely to the organic solvent effect and improved enhanced lignin/chromophore removal rather than actual photo-activity, i.e. option (b) above. In addition, it was concluded that both photosensitizers darkened the pulp suspension at the given charge levels used, such as to significantly attenuate the passage of UV light through the suspension, reducing any benefit the photosensitisers may have actually provided.

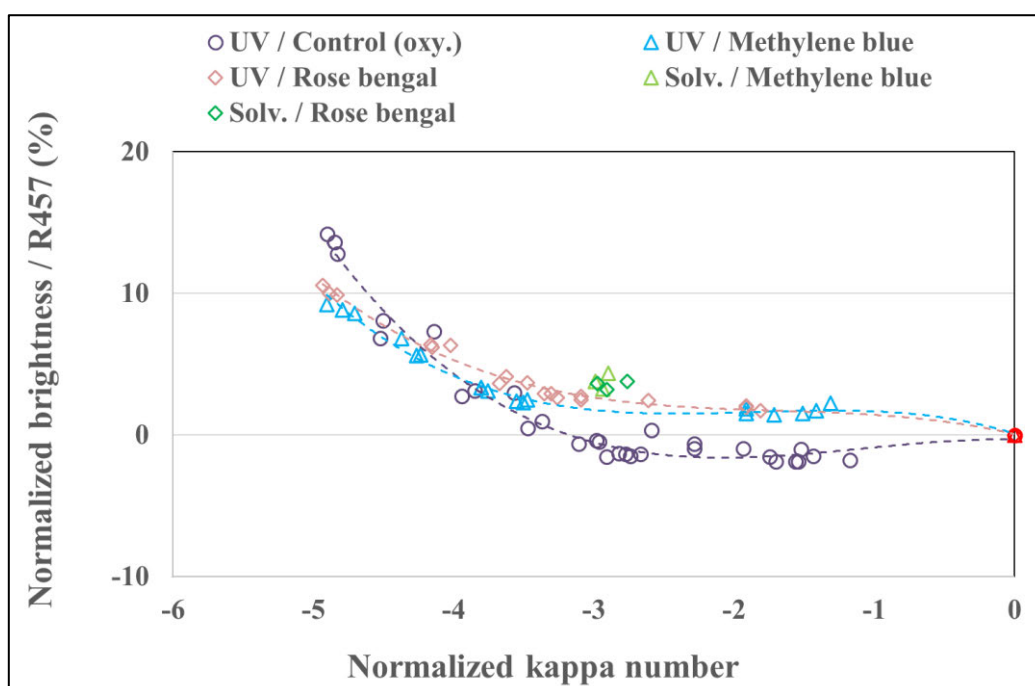


Figure 4.67: Normalized brightness (R457) versus normalized kappa number for a Cloquet paper grade pulp suspension bleached in a UV LED array reactor with either methylene blue or rose bengal as photosensitizers at variable irradiation times.

Conditions: 18.0 kg t⁻¹, 2.0 kg t⁻¹ methylene blue or 7.2 kg t⁻¹ rose bengal where relevant; oxygen bubbled into suspension through needle valve, cylinder 400 kPa; 20.0 g pulp; 25 °C; 15 - 120 minutes; UV LED array (full power).

The comparative Student T-test (Tc-test) for normalized kappa numbers indicated that the methylene blue photosensitiser was significantly different from the oxygen control (25 °C) at only initial times of 15 and 30 minutes for both a 90% and a 95% confidence level (Table 4.29). For the rose bengal photosensitizer, the comparative Student T-test (Tc-test) for normalized kappa numbers indicated that rose bengal was not significantly different from the oxygen control (25 °C) across the entire time range for both a 90% and a 95% confidence level (Table 4.30). This is as expected for both photosensitizers

given the kappa results obtained and represented by the normalized kappa number curves in Figure 4.65.

Table 4.29: Comparative student T-test (Tc) for differences between normalized kappa numbers of a Cloquet paper grade pulp suspension bleached in a UV LED array reactor with a methylene blue photosensitizer at variable irradiation times.

Time (minutes)	15	30	45	60	90	120	STD	n_x
Control (No UV LED)	-0.20	-0.24	-0.36	-0.79	-1.32	-0.87	0.579	30
Oxygen (Var. Time)	-2.77	-3.02	-3.14	-3.79	-4.39	-4.86	1.122	30
Photo-sen. (methylene bl	-1.41	-1.85	-3.51	-3.79	-4.29	-4.80	1.355	18
Tc (Control / Oxygen)	10.79	11.67	11.69	12.59	12.88	16.73		
α (<0.05 / 95% confidence)	TRUE	TRUE	TRUE	TRUE	TRUE	TRUE		
Tc (meth. blue Photo-Sen.)	3.57	3.08	0.97	0.00	0.26	0.15		
α (<0.05 / 95% confidence)	TRUE	TRUE	FALSE	FALSE	FALSE	FALSE		
α (<0.1 / 90% confidence)	TRUE	TRUE	FALSE	FALSE	FALSE	FALSE		



Table 4.30: Comparative student T-test (Tc) for differences between normalized kappa numbers of a Cloquet paper grade pulp suspension bleached in a UV LED array reactor with a rose bengal photosensitizer at variable irradiation times.

Time (minutes)	15	30	45	60	90	120	STD	n _x
Control (No UV LED)	-0.20	-0.24	-0.36	-0.79	-1.32	-0.87	0.579	30
Peroxide (Var. Time)	-2.10	-2.59	-3.51	-3.95	-4.31	-5.02	1.122	30
Photo-sen. (rose bengal)	-1.88	-2.93	-3.31	-3.59	-4.11	-4.88	1.026	18
Tc (Control / oxygen)	7.99	9.87	13.23	13.28	12.58	17.40		
α (<0.05 / 95% confidence)	TRUE	TRUE	TRUE	TRUE	TRUE	TRUE		
Tc (rose bengal Photo-Sen.)	0.70	1.09	0.63	1.14	0.64	0.42		
α (<0.05 / 95% confidence)	FALSE	FALSE	FALSE	FALSE	FALSE	FALSE		
α (<0.1 / 90% confidence)	FALSE	FALSE	FALSE	FALSE	FALSE	FALSE		



INCREASED BRIGHTNESS

The comparative T-test for the ratio of normalized brightness (R457) to normalized kappa numbers (i.e. Norm. Bri / Norm. kappa) showed that both the methylene blue and rose bengal photosensitizer pulps at variable time (15 to 120 minutes) were significantly different from the oxygen control at times of 15 to 45 minutes and 120 minutes for both a 90% and a 95% confidence level (Tables 4.31 and 4.32). This

Table 4.31: Comparative student T-test (Tc) for differences between ratios of normalized R457 brightness to normalized kappa numbers of a Cloquet paper grade pulp suspension bleached in a UV LED array reactor with a methylene blue photosensitizer at variable irradiation times.

Time (minutes)	15	30	45	60	90	120	n _x
Oxygen (Var. Time)/Norm. kappa	-2.666	-2.960	-3.468	-3.569	-4.140	-4.902	30
Brightness (R457)/Norm.	-1.35	-0.48	0.45	2.97	7.27	14.17	
Norm. bri/Norm. kappa	0.506	0.162	-0.130	-0.832	-1.756	-2.891	
AVE (Norm. bri/Norm. kappa)	0.53	0.17	-0.17	-0.78	-1.69	-2.78	
							STD 1.229
Photo-sen. (meth. blue)/Norm. kappa	-1.313	-1.713	-3.473	-3.803	-4.373	-4.793	18
Brightness (R457)/Norm.	2.25	1.44	2.46	3.33	6.82	8.81	
Norm. bri/Norm. kappa	-1.714	-0.841	-0.708	-0.876	-1.560	-1.838	
AVE (Norm. bri/Norm. kappa)	-1.31	-0.87	-0.68	-0.86	-1.40	-1.85	
							STD 0.436
INCREASED BRIGHTNESS							
Tc (methylene blue)	7.44	4.18	2.03	0.33	1.15	3.78	
α (<0.05 / 95% confidence)	TRUE	TRUE	TRUE	FALSE	FALSE	TRUE	
α (<0.1 / 90% confidence)	TRUE	TRUE	TRUE	FALSE	FALSE	TRUE	

Table 4.32: Comparative student T-test (Tc) for differences between ratios of normalized R457 brightness to normalized kappa numbers of a Cloquet paper grade pulp suspension bleached in a UV LED array reactor with a rose bengal photosensitizer at variable irradiation times.

Time (minutes)	15	30	45	60	90	120	n _x
Oxygen (Var. Time)/Norm. kappa	-2.666	-2.960	-3.468	-3.569	-4.140	-4.902	30
Brightness (R457)/Norm.	-1.35	-0.48	0.45	2.97	7.27	14.17	
Norm. bri/Norm. kappa	0.506	0.162	-0.130	-0.832	-1.756	-2.891	
AVE (Norm. bri/Norm. kappa)	0.53	0.17	-0.17	-0.78	-1.69	-2.78	
							STD 1.229
Photo-sen. (r. bengal)/Norm. kappa	-1.813	-2.613	-3.303	-3.673	-4.023	-4.933	18
Brightness (R457)/Norm.	1.69	2.44	2.91	3.64	6.32	10.54	
Norm. bri/Norm. kappa	-0.932	-0.934	-0.881	-0.991	-1.571	-2.137	
AVE (Norm. bri/Norm. kappa)	-1.00	-0.87	-0.85	-1.06	-1.53	-2.08	
							STD 0.454
Tc (Rose Bengal)	6.16	4.18	2.72	1.15	0.62	2.84	
α (<0.05 / 95% confidence)	TRUE	TRUE	TRUE	FALSE	FALSE	TRUE	
α (<0.1 / 90% confidence)	TRUE	TRUE	TRUE	FALSE	FALSE	TRUE	

was consistent with the normalized brightness versus normalized kappa number curve given in Figure 4.67. Given the limited data available on the extent of delignification of pulp by the organic solvent rinse, no reasonable statistical analysis could be made as to whether improvements observed for the two photosensitizers were due to the solvent effect or actual photo-activity based on a similar statistical analysis. However, prior qualitative analysis based on Figure 4.67 would suggest a solely solvent-based effect.

In summary, both the methylene blue and rose bengal photosensitizers showed only limited and selected improved delignification (i.e. brightness and normalized kappa number) within a narrow time range of 15 to 45 minutes. However, a review of the normalized brightness and normalized kappa number results for both photosensitizers (i.e. methylene blue and rose bengal) as well as the impact of the organic solvent rinse in the pulp washing process on the delignification of the pulp (i.e. photosensitizers methylene blue and rose bengal without UV LED array irradiation) showed that the observed improvements were likely due solely to an organic solvent effect (i.e. improved enhanced lignin/chromophore removal) and not any actual photo-activity effect. Pulp yield appeared unaffected for both photosensitizers. Lastly, as prior indicated, both the methylene blue and the rose bengal photosensitizers required an organic solvent rinse in their organic rinse/water wash process to facilitate their removal from the pulp, while the methylene blue pulp remained shaded green even after the organic solvent rinse. Given the need for such an organic solvent rinse stage for both photosensitizers, neither are likely to be viable options for practical use within any pulp bleaching process, unless they could be destroyed in latter peroxide bleaching stages. Consequently, dying of the pulp as well as avoiding the organic solvent wash stage would require application of the photosensitizers at a much lower charge level followed by a peroxide bleaching stage.

4.3.10 Photochemical pulp bleaching with UV LED array: Impact of variable consistency on the photochemical bleaching of pulp (Variable 8)

The aim of this part of the study was to evaluate the impact of variable pulp consistency on the photochemical bleaching of pulp under UV LED array irradiation [326]. A description of the experimental work is given in Section 3.6.10. The increase in brightness (R457) due to photochemical bleaching, was decreased by about 50%; from 58.19% to 49.10%; with increasing consistency from 0.5% to about 1.5% consistency (indicating an increase in pulp mass from 20.0 g to 60.0 g), whereafter it remained unchanged at higher consistencies up to 3.0%, which represented a pulp mass of 120 g (Figure 4.68). No further reductions were observed up to the highest working consistency of 3.0% at which effective continuous mixing of the pulp suspension occurred. Results at 4.0% consistency gave a dual brightness outcome due to the lack of any mixing of pulp at this consistency, with the top layer of pulp being exposed to continuous irradiation resulting in a high brightness (56.85%) and the lower

layers having a low brightness (44.71%) due to no irradiation at all (i.e. total internal attenuation). Given the inability to physically separate the two layers perfectly and the resulting cross contamination of both pulp layers, the difference between the two may have been larger, as was noted by the initial visual observation in which the top pulp layer appeared almost completely white. The two control pulps at 0.5% and 2.5% consistency gave brightness values a little above the unbleached pulp at 38.83% and 40.90%. This was likely due to minor peroxide bleaching and alkali extraction of soluble lignin fragments when under constant active mixing for a prolonged period (i.e. 90 minutes). Overall, photochemical bleaching at higher consistencies appears to be a potentially viable option, provided adequate mixing of the pulp suspension and sufficient light intensity was in effect.

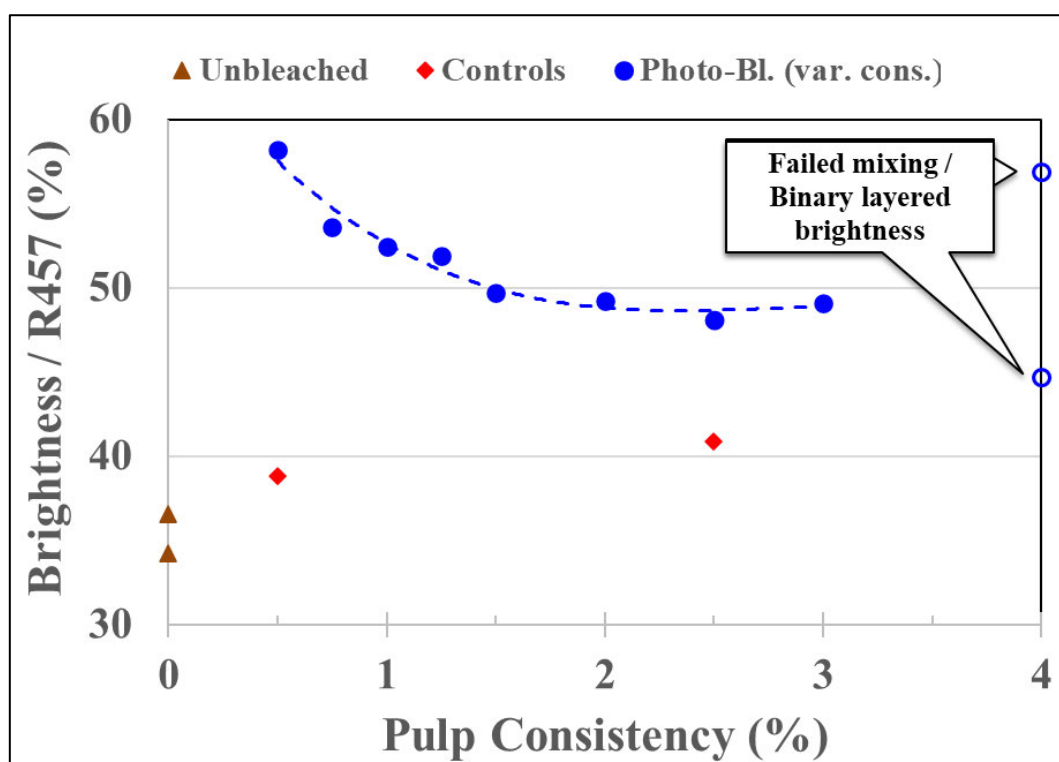


Figure 4.68: Brightness (R457) for an alkaline peroxide pulp suspension bleached in a UV LED array reactor at variable pulp consistency.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂; 20.0 - 160.0 g pulp; 25.0 °C (Room temperature); 0.5 – 4.0% consistency; UV LED array (full power).

The kappa number followed the brightness closely, with the reduction in kappa number plateauing at consistencies above 1.5% (Figure 4.69). The two controls showed some reduction in kappa number (likely due to prolonged alkali extraction of residual degraded lignin), but these reductions were significantly smaller than the reduction observed under photochemical bleaching at all tested consistencies. Photochemical bleaching gave a level of delignification ranging from about 40% to 25% in the consistency range of 0.5% to 3.0% with the plateau point being at 1.5% consistency, while both controls gave a delignification level of about 15%. This represented a maximum equivalent loss for

photochemical bleaching efficiency of about 30% as the consistency increased from 0.5% to 3.0%. The dual brightness layered pulp gave two kappa numbers, with the “unbleached” pulp giving a kappa number close to the starting pulp (8.24 versus 10.31) and the “bleached” pulp giving a kappa close to the photochemically bleached pulp at 0.5 % consistency (6.19 versus 6.10).

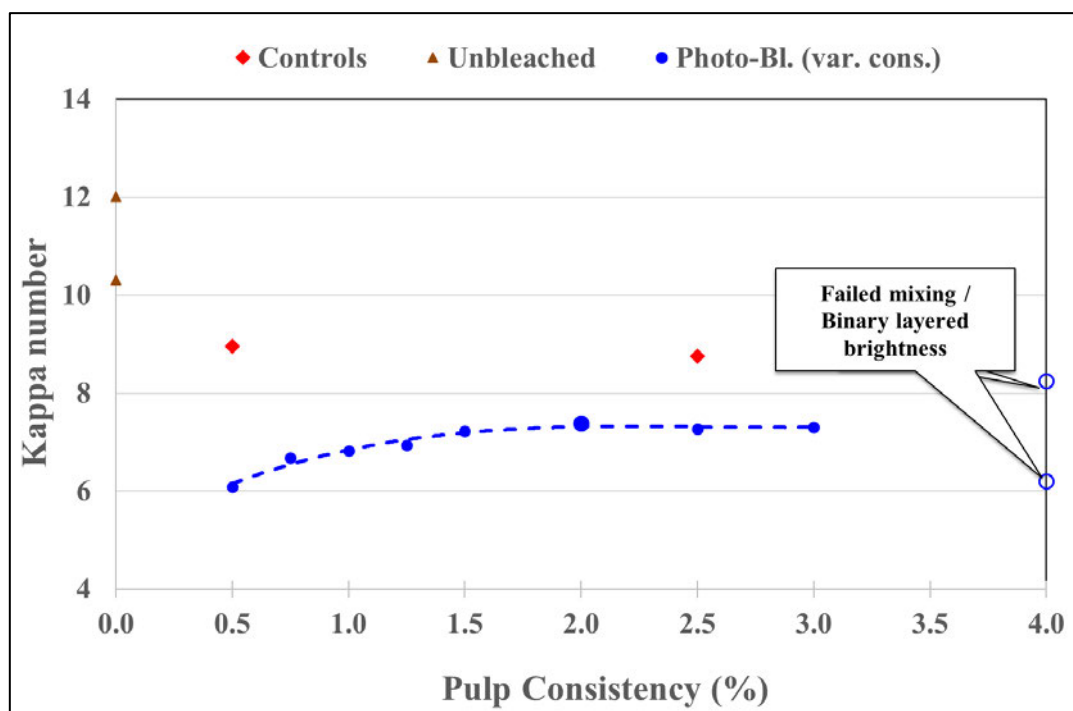


Figure 4.69: Kappa number for an alkaline peroxide pulp suspension bleached in a UV LED array reactor at variable pulp consistency.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂; 20.0 - 160.0 g pulp; 25.0 °C (Room temperature); 0.5 – 4.0% consistency; UV LED array (full power).

The two controls showed no change in viscosity as compared to the starting pulp used in this study (Figure 4.70). The photochemical bleaching experiments gave a small reduction in viscosity as compared to the starting pulp, with the reduction in viscosity decreasing slightly at the higher consistencies. The dual brightness pulps at 4.0% consistency gave divergent viscosities with the “unbleached” pulp giving a viscosity slightly less than the starting pulp, while the pulp subjected to constant irradiation showed a significant loss in viscosity of over 200 units. This latter significant loss was likely due to the constant chemical attack by hydroxyl radicals when exposed to constant UV irradiation.

A review of the initial and final pH, initial and final temperature, proportional peroxide residual, and pulp yields at variable consistencies indicated that none of the experiments showed anomalies during their experimental runs, with all experiments operating within acceptable limits (Table 4.33). The final pH values never dropped below 9.5, while final temperatures typically rose from room temperature to

about 36 °C or less upon irradiation with the UV LED array. For the unirradiated control, pH and temperature remained almost unchanged. Thus, overall, any thermal bleaching contribution of the pulp was minimal. This was also true for the unirradiated controls. There was no clear relationship between the consistency at which the photochemical bleaching was conducted and pulp yield obtained, with the lowest yield never dropping below 96%. Moreover, any loss in pulp yield appeared to be minor and within the analytical limits of the methods. The residual peroxide for these two controls showed only nil to minor losses, while the residual peroxide at variable consistency was usually about 90% with the lowest being 86% at 2.0% consistency due to general analytical and experimental variation and error. Overall, all experiments were under adequate control.

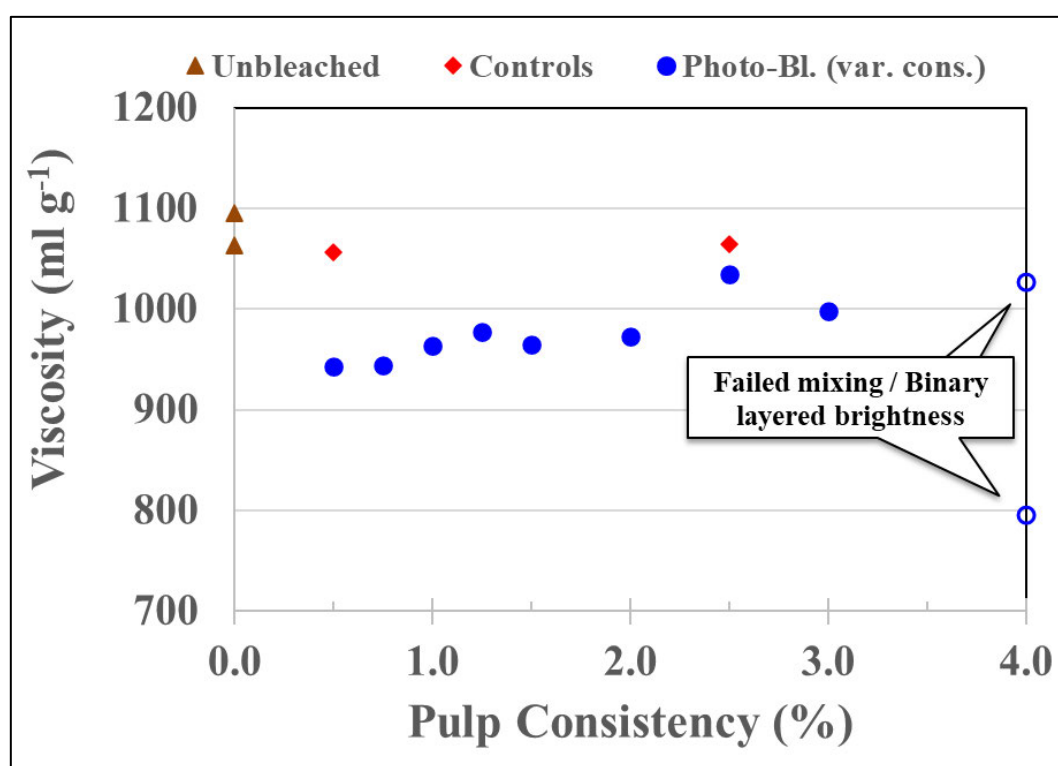


Figure 4.70: Viscosity (CED) for an alkaline peroxide pulp suspension bleached in a UV LED array reactor at variable pulp consistency.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂; 20.0 - 160.0 g pulp; 25.0 °C (Room temperature); 0.5 – 4.0% consistency; UV LED array (full power).

final pH values never dropped below 9.5, while final temperatures typically rose from room temperature to about 36 °C or less upon irradiation with the UV LED array. For the unirradiated controls, pH and temperature remained almost unchanged. Thus, overall, any thermal bleaching contribution of the pulp was minimal. This was also true for the unirradiated controls. There was no clear relationship between the consistency at which the photochemical bleaching was conducted and pulp yield obtained, with the lowest yield never dropping below 96%. Moreover, any loss in pulp yield appeared to be minor and

within the analytical limits of the experimental methods. The residual peroxide for the two controls showed only nil to minor losses, while the residual peroxide at variable consistency was usually about 90% with the lowest being 86% at 2.0% consistency due to general analytical and experimental variation and error. Overall, all experiments were under adequate control.

Table 4.33: Initial and final pH and temperature of an alkaline peroxide pulp suspension bleached in a UV LED array reactor at variable pulp consistency.

	Unirrad. (control)		UV LED Array Irradiated								
Cons. (%)	0.5	2.5	0.5	0.75	1.0	1.25	1.5	2.0	2.5	3.0	4.0
Final pH	9.9	10.1	9.71	9.86	9.89	9.96	9.87	9.95	9.9	9.88	9.88
Initial pH	10.2	10.0	10.3	10.6	10.5	10.2	10.4	10.2	10.1	10.7	10.2
Final Temp. (°C)	23.5	26.7	35.4	35.5	35.6	34.4	35.6	33.6	33	32.5	33.2
Initial Temp. (°C)	24.7	23.9	24.5	25.3	23.8	23.1	24.8	24.6	24	24.8	25.3
Res. H₂O₂ (%)	101	94.0	91.8	90.8	92.9	91.8	91.4	86.3	92.4	88.9	89.1
Pulp Yield (%)	97.9	99.4	96.6	97.7	101	97.7	92.5	98.8	99.4	96.3	99.0

In summary, the efficiency of photobleaching of pulp in an alkali peroxide suspension using a UV LED reactor system decreased as the consistency increased from 0.5% to 1.5%, whereafter no further reduction in the efficiency was observed as the consistency was increased further. A known difficulty with any photochemically-driven reaction involving a suspension (including pulps) is that as the suspension becomes thicker it becomes increasingly more opaque reducing photochemical efficiency. A point is eventually reached where the suspension is sufficiently thick, that the light does not penetrate beyond the top layer of the suspension. For paper grade pulps, including the unbleached Cloquet paper grade pulp used, this happened at about 1.5 – 2.5% consistency whereafter no further reduction in the efficiency was observed. A significantly more intense light source may have helped partially mitigate this, but only to a limit extent when it comes to the suspension's opacity. Overall, photobleaching of pulp can occur at higher consistencies with little loss to pulp strength or yield provided the suspension is adequately and continuously mixed.

4.3.11 Photochemical pulp bleaching with UV LED array of various Sappi mill pulps (Variable 9)

The aim of this study was to observe how various different pulps, selected based on their pulping processes, photobleached under UV LED irradiation [327]. A description of the experimental work is given in Section 3.6.11. All pulps showed a reduction in their kappa numbers upon photochemical bleaching, except for the control without UV irradiation, where the kappa reduction was minimal as expected (Figure 4.71). The reductions for the Cloquet kraft, Ngodwana PHK, Stanger bagasse and Saiccor viscose pulps were significant, reflecting their different pulping processes and fibre sources, and this was borne out in that the extent of delignification for these four pulps was above 40% (Figure 4.72). The extent of delignification for Gratkorn was the lowest (i.e. 25.1%) with Somerset slightly higher than Gratkorn (30.8%). Even so, these later two kappa number reductions were notable being about five kappa units in size. The extent of delignification for the control (without UV irradiation) was much smaller at less than 8%. The brightness followed the trend in kappa number with all pulps showing a significant increase in brightness, with the exception of Gratkorn mill where the brightness increase was minimal (Figure 4.73). As based on their different pulping processes and fibre sources, this was due to Gratkorn mill pulp being a high brightness magnefite pulp with a high lignin content, as well as an ageing effect on the pulp brightness observed prior for Gratkorn mill pulp when stored under cold conditions (approximately 5 °C) for extended periods of time (6 months +). Overall, all pulps showed a reasonable level of photochemical bleaching indicating that the photochemical bleaching process was applicable across a wide range of unbleached pulps of reasonable kappa number.

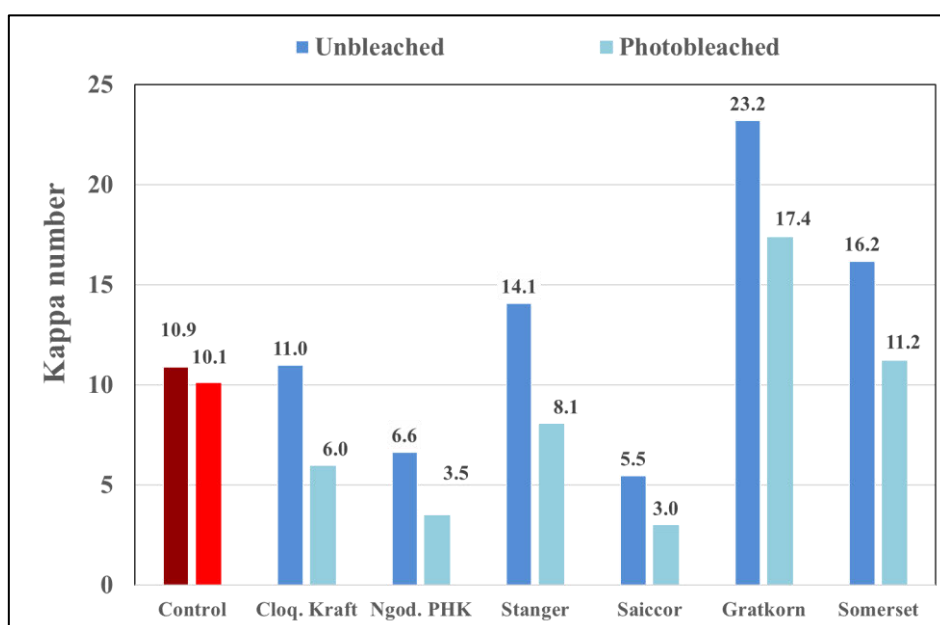


Figure 4.71: Kappa number of pulp suspensions from different Sappi mills bleached in a UV LED array reactor.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂; 20.0 g pulp; 25.0 °C (Room temperature); 120 minutes; 0.5% consistency; UV LED array (full power).

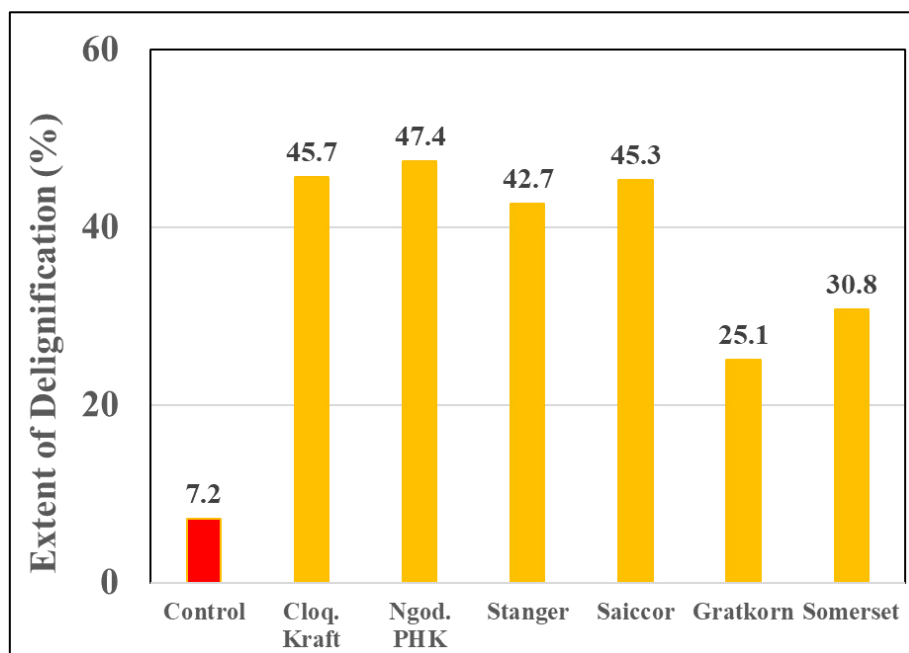


Figure 4.72: Extent of delignification of pulp suspensions from different Sappi mills bleached in a UV LED array reactor.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂; 20.0 g pulp; 25.0 °C (Room temperature); 120 minutes; 0.5% consistency; UV LED array (full power).

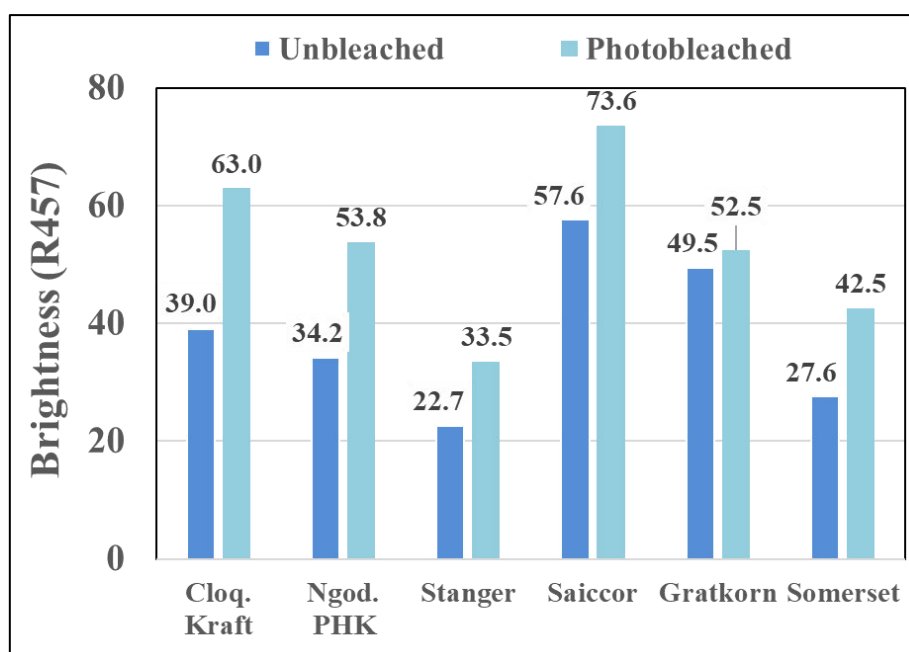


Figure 4.73: Brightness (R457) of pulp suspensions from different Sappi mills bleached in a UV LED array reactor.

Conditions: 18.0 kg t⁻¹NaOH, 80.0 kg t⁻¹ H₂O₂; 20.0 g pulp; 25.0 °C (Room temperature); 120 minutes; 0.5% consistency; UV LED array (full power).

The control pulp showed no viscosity reduction, while the unbleached kraft pulps (i.e. Cloquet kraft and Somerset kraft) showed a small reduction in their viscosity of about 100 to 150 ml g^{-1} units (Figure 4.74). This is not unexpected given that both are unbleached kraft pulps. The other pulps (i.e. Ngodwana PHK, Stanger bagasse, Saiccor viscose, and Gratkorn magnefite) showed only minimal losses in viscosity. This is particularly notable for Ngodwana PHK which gave a minor viscosity loss of about a 50 ml g^{-1} compared with the expected 150 ml g^{-1} drop observed for the same starting kappa number and kappa reduction during mill operations (i.e. Ngodwana oxygen stage). The viscosity losses observed for Saiccor viscose pulp were similar to those observed during mill processes (i.e. 30 ml g^{-1} drop compared to a small gain across the Saiccor mill oxygen stage due to the dissolution of small chain cellulose oligomers). Overall, given that the viscosity gives some indication of pulp strength and strength loss, damage to the various mill fibres and their associated viscosity losses tended to be small.

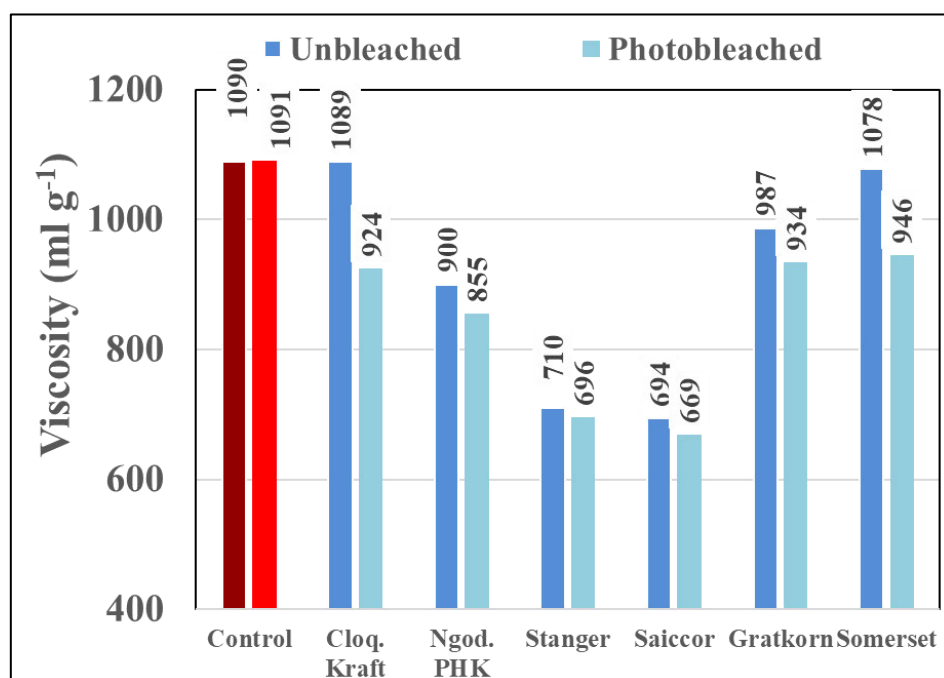


Figure 4.74: Viscosity of pulp suspensions from different Sappi mills bleached in a UV LED array reactor.

Conditions: 18.0 kg t^{-1} NaOH, 80.0 kg t^{-1} H_2O_2 ; 20.0 g pulp; 25.0 °C (Room temperature); 120 minutes; 0.5% consistency; UV LED array (full power).

Pulp yield losses were small, suggesting no serious fibre degradation or material losses (Table 4.34). This corresponded with the observations made around the viscosity results. The level of peroxide degradation, as suggested by the peroxide residuals, was small to moderate and varied considerably (i.e. 97% to 80%) depending on the pulp type (Table 4.34). In addition, the initial peroxide charge of 80.0 kg.t^{-1} was based on findings from earlier work around microwave discharge electrodeless lamps (MDEL) in the Roto SYNTH microwave reactor and are excessively large for work based on the UV

LED array. Thus, further optimization around these charges is required to obtain a more cost-efficient charge.

Table 4.34: Pulp yields of pulp suspensions from different Sappi mills bleached in a UV LED array reactor.

Sample Pulp designation	Res. peroxide (%)	Pulp yield (%)
Control (No UV)	96.7	99.5
Cloquet Aspen kraft	96.3	103.9
Ngodwana PHK pulp	86.8	102.0
Stanger bagasse mill pulp	89.8	94.0
Saiccor dissolving viscose grade mill pulp	97.4	103.6
Gratkorn mill pulp	90.8	99.8
Somerset mill pulp	80.5	98.7

In summary, the UV LED array reactor system employed to photobleach unbleached Cloquet paper grade pulp using an alkali peroxide suspension was also successfully used to photobleach a variety of other pulps from Sappi mills. Significant delignification (brightness development and kappa reduction) were achieved for all pulps evaluated with the exact extent dependant on the starting pulp itself. The loss in pulp strength, as given by the pulp viscosity, and pulp yield were generally minimal to small.

4.3.12 Evaluation of various combined thermophotochemical and thermal bleaching sequences for paper grade pulp

The aim of this investigation was to compare a photochemically based bleaching sequence against a conventional sequence for paper grade pulp [328]. A description of the experimental work is given in Section 3.6.12. Both the thermal ECF control and the thermophotochemical TCF bleaching sequences gave similar final brightness values (both 90.6% respectively) which were above the specified target limit of 89% (Figure 4.75). The thermal TCF proposed sequence performed poorly giving a final brightness value that was below the specified target limit (i.e. 85.02%) despite having utilized two further bleaching stages than both the thermal ECF and photochemical TCF sequences. In all cases, brightness reversion was small at about four units. Generally, results suggested that the photochemical TCF sequence was a viable alternative option to the thermal ECF sequence presently employed at the mill and performed as well. However, given that the photochemical sequence relied on stages that mostly employed low consistency (i.e. 0.5% consistency), it was not a practical alternative unless a similar performance can be achieved for photochemical bleaching stages at a higher consistency (i.e. 5 to 10% consistency).

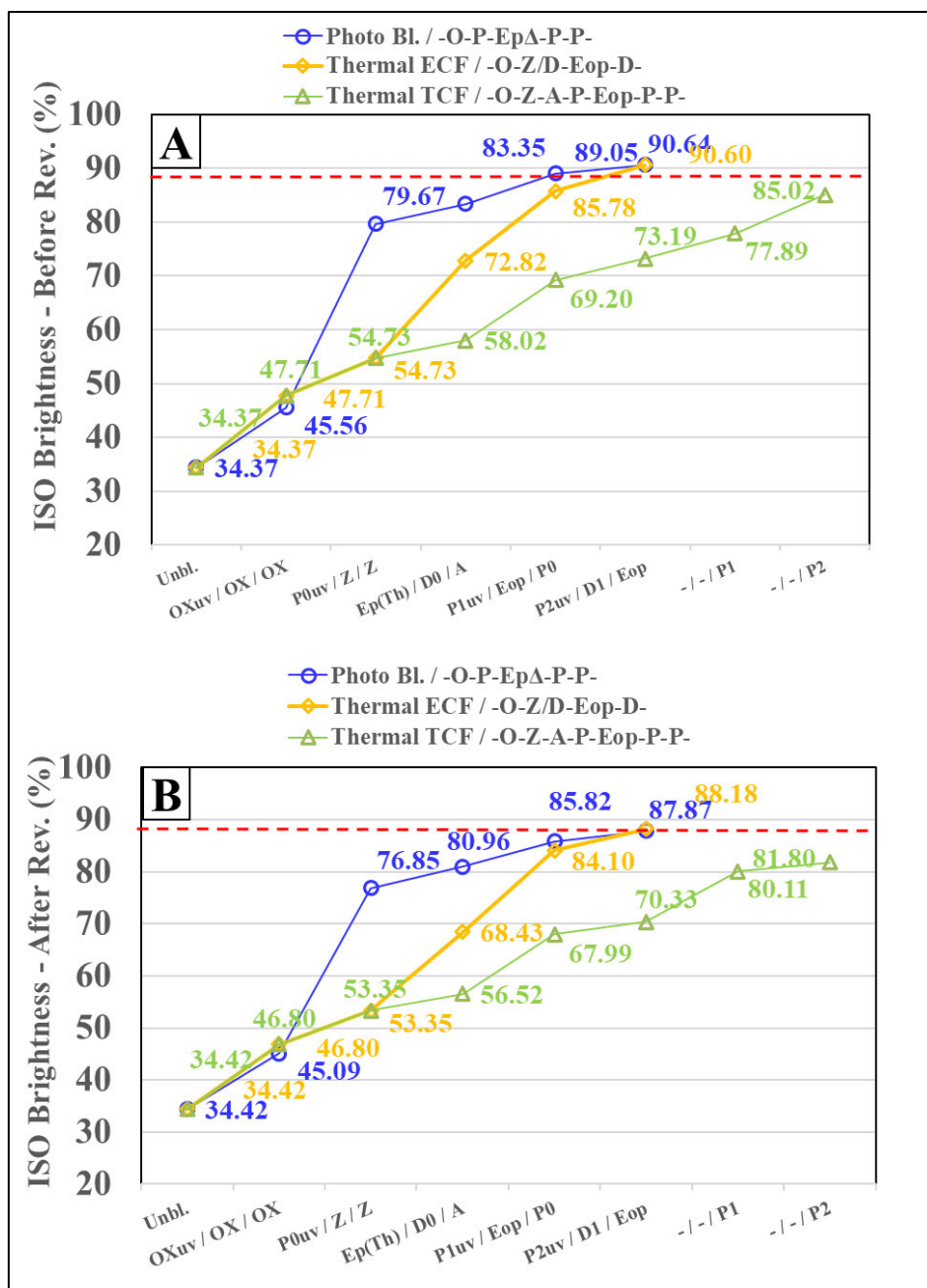


Figure 4.75: ISO brightness [A] before and [B] after reversion for the present control ECF sequence, and the proposed thermal TCF and photochemical TCF based sequences.

Conditions:

- Photo Bl. Charges (kg t⁻¹): 18.0 NaOH + 2.0 Mg²⁺ + 400 kPa O₂ (bubbling), 18.0 NaOH + 80.0 H₂O₂ + 5.0 TiO₂, 15.0 NaOH + 9.0 H₂O₂, 18.0 NaOH + 80.0 H₂O₂, 18.0 NaOH + 45.0 H₂O₂; temperature (°C): 65*, 65*, 85 (thermal stage), 65*, 65* (* starting temperature of photobleaching stage); time (minutes): 120, 90, 45, 120, 60; consistency (%): 0.5, 0.5, 10.0, 0.5, 0.5; Pulp mass (g): 360.0, 320.0, 280.0, 240.0, 200.0.
- Thermal ECF. Charges (kg t⁻¹): 33.0 NaOH + 760 / 275 kPa O₂, 3.8 O₃ + 6.5 H₂SO₄, 11.0 ClO₂, 17.0 NaOH + 4.5 H₂O₂ + 380 kPa O₂, 3.5 ClO₂; temperature (°C): 95, < 25, 70, 77, 80; time (minutes): 20 / 50, 10, 60, 120, 240; consistency (%): 10.0, 12.0, 11.0, 11.5, 11.5; Pulp mass (g): 2000.0, 1500.0, 360.0, 320.0, 220.
- Thermal TCF. Charges (kg t⁻¹): 33.0 NaOH + 760 / 275 kPa O₂, 3.8 O₃ + 6.5 H₂SO₄, 6.0 H₂SO₄, 15.0 NaOH + 11.0 H₂O₂, 17.5 NaOH + 5.0 H₂O₂ + 380 kPa O₂, 12.0 NaOH + 14.0 H₂O₂, 15.0 NaOH + 20.0 H₂O₂; temperature (°C): 95, < 25, 65, 85, 70, 80, 85; time (minutes): 20 / 50, 10, 30, 60, 120, 210, 210; consistency (%): 10.0, 12.0, 11.0, 11.0, 11.5, 11.5, 11.5; Pulp mass (g): 2000.0, 1500.0, 495.0, 360.0, 320.0, 240.0, 200.0.

The thermal ECF control sequence gave the expected kappa number trend across its bleaching stages with the final kappa number dropping to less than half a kappa number unit (i.e. <0.5) for a final brightness of 90.6%, or 88.2% after reversion (Figure 4.76). However, the photochemical TCF sequence gave a smaller kappa number reduction with an elevated final kappa number of 3.75 for a similar brightness of 90.6% (87.9% reverted). This was unexpected and suggested that less thermally-driven chromophores and coloured quinonics were generated by the photochemically-driven bleaching mechanism, or more of these chromophores and coloured quinonics were selectively destroyed, than for the thermal ECF control stages. The thermal TCF sequence gave an elevated final kappa number of 2.79, which is consistent with its lower final brightness 85.0% (81.8% reverted). This trend for the

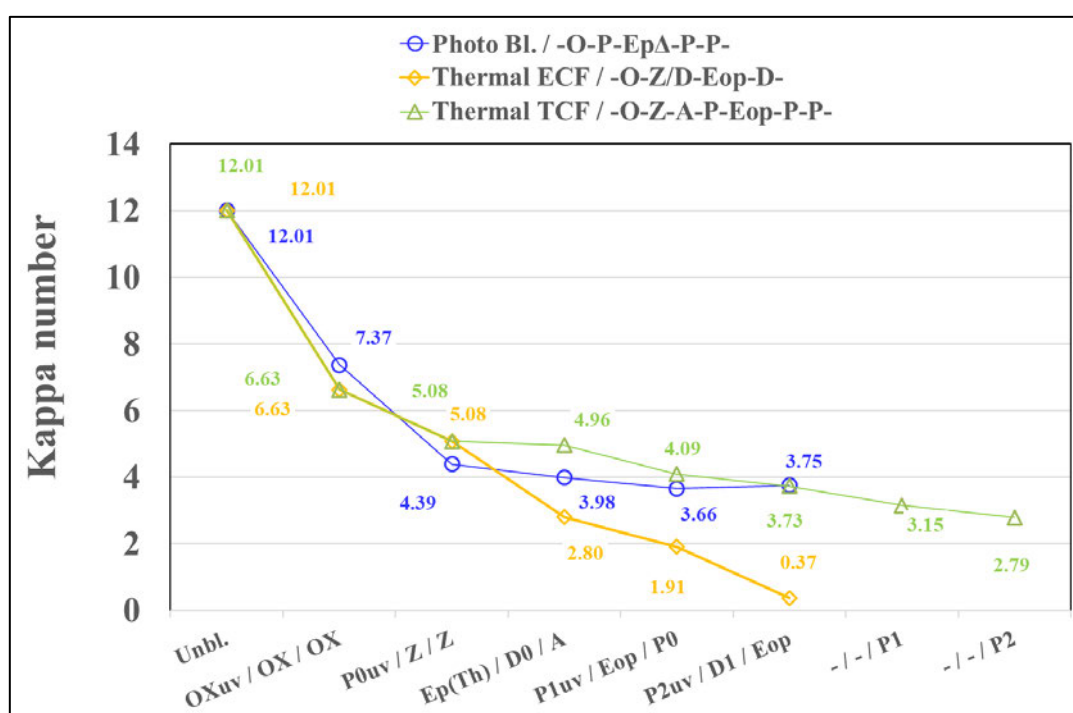


Figure 4.76: Kappa number for the present control thermal ECF sequence, and the proposed thermal TCF and photochemical TCF based sequences.

Conditions:

- Photo Bl. Charges (kg t⁻¹): 18.0 NaOH + 2.0 Mg²⁺ + 400 kPa O₂ (bubbling), 18.0 NaOH + 80.0 H₂O₂ + 5.0 TiO₂, 15.0 NaOH + 9.0 H₂O₂, 18.0 NaOH + 80.0 H₂O₂, 18.0 NaOH + 45.0 H₂O₂; temperature (°C): 65*, 65*, 85 (thermal stage), 65*, 65* (* starting temperature of photobleaching stage); time (minutes): 120, 90, 45, 120, 60; consistency (%): 0.5, 0.5, 10.0, 0.5, 0.5; Pulp mass (g): 360.0, 320.0, 280.0, 240.0, 200.0.
- Thermal ECF. Charges (kg t⁻¹): 33.0 NaOH + 760 / 275 kPa O₂, 3.8 O₃ + 6.5 H₂SO₄, 11.0 ClO₂, 17.0 NaOH + 4.5 H₂O₂ + 380 kPa O₂, 3.5 ClO₂; temperature (°C): 95, < 25, 70, 77, 80; time (minutes): 20 / 50, 10, 60, 120, 240; consistency (%): 10.0, 12.0, 11.0, 11.5, 11.5; Pulp mass (g): 2000.0, 1500.0, 360.0, 320.0, 220.
- Thermal TCF. Charges (kg t⁻¹): 33.0 NaOH + 760 / 275 kPa O₂, 3.8 O₃ + 6.5 H₂SO₄, 6.0 H₂SO₄, 15.0 NaOH + 11.0 H₂O₂, 17.5 NaOH + 5.0 H₂O₂ + 380 kPa O₂, 12.0 NaOH + 14.0 H₂O₂, 15.0 NaOH + 20.0 H₂O₂; temperature (°C): 95, < 25, 65, 85, 70, 80, 85; time (minutes): 20 / 50, 10, 30, 60, 120, 210, 210; consistency (%): 10.0, 12.0, 11.0, 11.0, 11.5, 11.5, 11.5; Pulp mass (g): 2000.0, 1500.0, 495.0, 360.320.0, 240.0, 200.0.

thermal TCF sequence was as expected with higher kappa numbers giving lower brightness results. Thus, generally, the thermal sequences appeared to follow the expected brightness versus kappa number trends while the photochemical TCF sequence did not and performed better. This was evident in the ISO brightness versus kappa number curves of the three sequences (Figure 4.77). Furthermore, the dissimilar brightness versus kappa number curve for the photochemical TCF bleaching sequence suggested different chemical reaction mechanism as compared to the thermal bleaching sequences. This difference in photochemical- and thermal-driven reaction mechanism was expected, with the energy used in the thermal sequences giving broad general activation of all chemical processes, but,

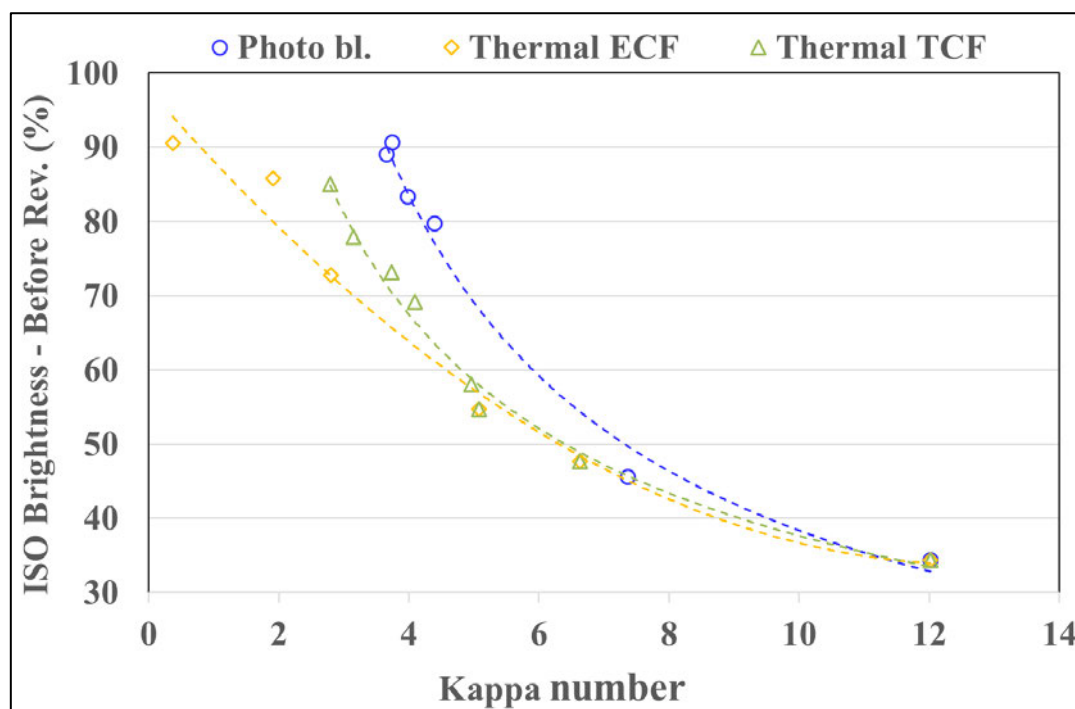


Figure 4.77: ISO brightness versus Kappa number for the present control thermal ECF sequence, and the proposed thermal TCF and photochemical TCF based sequences.

Conditions:

- Photo Bl. Charges (kg t^{-1}): 18.0 NaOH + 2.0 Mg^{2+} + 400 kPa O_2 (bubbling), 18.0 NaOH + 80.0 H_2O_2 + 5.0 TiO_2 , 15.0 NaOH + 9.0 H_2O_2 , 18.0 NaOH + 80.0 H_2O_2 , 18.0 NaOH + 45.0 H_2O_2 ; temperature ($^{\circ}\text{C}$): 65*, 65*, 85 (thermal stage), 65*, 65* (* starting temperature of photobleaching stage); time (minutes): 120, 90, 45, 120, 60; consistency (%): 0.5, 0.5, 10.0, 0.5, 0.5; Pulp mass (g): 360.0, 320.0, 280.0, 240.0, 200.0.
- Thermal ECF. Charges (kg t^{-1}): 33.0 NaOH + 760 / 275 kPa O_2 , 3.8 O_3 + 6.5 H_2SO_4 , 11.0 ClO_2 , 17.0 NaOH + 4.5 H_2O_2 + 380 kPa O_2 , 3.5 ClO_2 ; temperature ($^{\circ}\text{C}$): 95, < 25, 70, 77, 80; time (minutes): 20 / 50, 10, 60, 120, 240; consistency (%): 10.0, 12.0, 11.0, 11.5, 11.5; Pulp mass (g): 2000.0, 1500.0, 360.0, 320.0, 220.
- Thermal TCF. Charges (kg t^{-1}): 33.0 NaOH + 760 / 275 kPa O_2 , 3.8 O_3 + 6.5 H_2SO_4 , 6.0 H_2SO_4 , 15.0 NaOH + 11.0 H_2O_2 , 17.5 NaOH + 5.0 H_2O_2 + 380 kPa O_2 , 12.0 NaOH + 14.0 H_2O_2 , 15.0 NaOH + 20.0 H_2O_2 ; temperature ($^{\circ}\text{C}$): 95, < 25, 65, 85, 70, 80, 85; time (minutes): 20 / 50, 10, 30, 60, 120, 210, 210; consistency (%): 10.0, 12.0, 11.0, 11.0, 11.5, 11.5, 11.5; Pulp mass (g): 2000.0, 1500.0, 495.0, 360.0, 320.0, 240.0, 200.0.

more selective specific activation associated with the absorption of electromagnetic radiation in a given narrow distribution of wavelengths for the photochemical bleaching process. In general, the photochemical approach tended to greatly reduce or negate any unwanted side reactions; however, energy transfer processes such as molecular thermal, rotation and vibrational deactivation of the photochemically excited state did reduce the selectivity of photochemical reactions to some small extent. Overall, much of this greater selectivity is a known advantage and characteristic of photochemically-driven reaction processes.

Both the thermal ECF control and the photochemical TCF sequences gave similar final viscosity results of 577 ml g⁻¹ and 546 ml g⁻¹ respectively showing only a thirty viscosity unit difference (Figure 4.78).

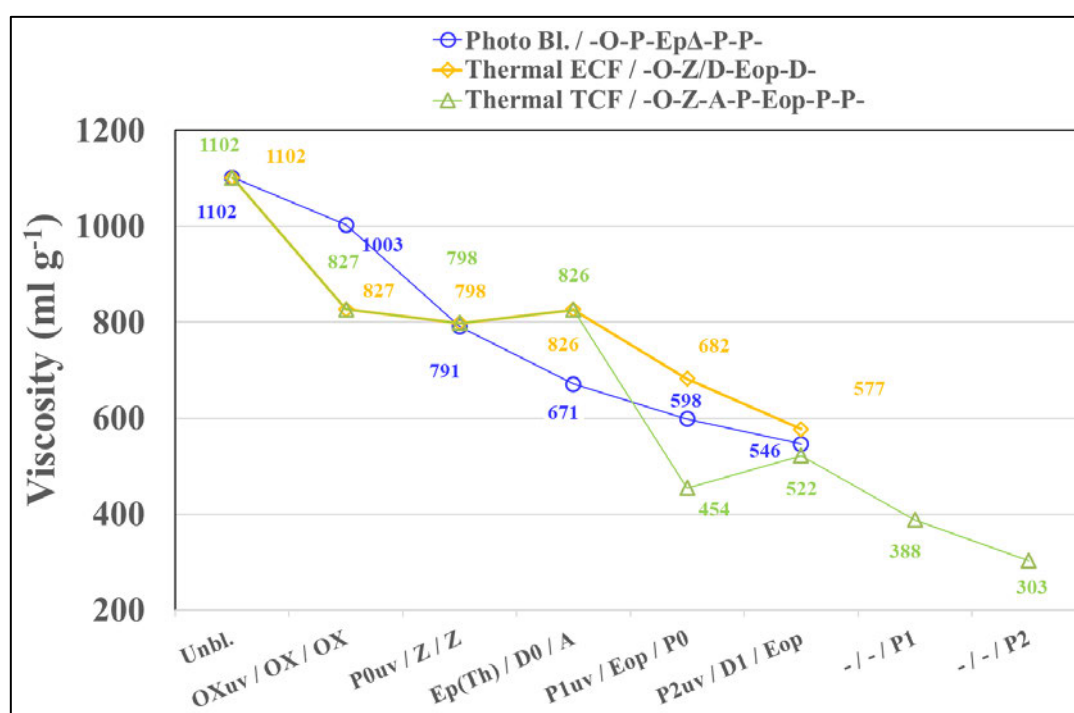


Figure 4.78: Viscosity (CED) for the present control thermal ECF sequence, and the proposed thermal TCF and photochemical TCF based sequences.

Conditions:

- Photo Bl. Charges (kg t⁻¹): 18.0 NaOH + 2.0 Mg²⁺ + 400 kPa O₂ (bubbling), 18.0 NaOH + 80.0 H₂O₂ + 5.0 TiO₂, 15.0 NaOH + 9.0 H₂O₂, 18.0 NaOH + 80.0 H₂O₂, 18.0 NaOH + 45.0 H₂O₂; temperature (°C): 65*, 65*, 85 (thermal stage), 65*, 65* (* starting temperature of photobleaching stage); time (minutes): 120, 90, 45, 120, 60; consistency (%): 0.5, 0.5, 10.0, 0.5, 0.5; Pulp mass (g): 360.0, 320.0, 280.0, 240.0, 200.0.
- Thermal ECF. Charges (kg t⁻¹): 33.0 NaOH + 760 / 275 kPa O₂, 3.8 O₃ + 6.5 H₂SO₄, 11.0 ClO₂, 17.0 NaOH + 4.5 H₂O₂ + 380 kPa O₂, 3.5 ClO₂; temperature (°C): 95, < 25, 70, 77, 80; time (minutes): 20 / 50, 10, 60, 120, 240; consistency (%): 10.0, 12.0, 11.0, 11.5, 11.5; Pulp mass (g): 2000.0, 1500.0, 360.0, 320.0, 220.
- Thermal TCF. Charges (kg t⁻¹): 33.0 NaOH + 760 / 275 kPa O₂, 3.8 O₃ + 6.5 H₂SO₄, 6.0 H₂SO₄, 15.0 NaOH + 11.0 H₂O₂, 17.5 NaOH + 5.0 H₂O₂ + 380 kPa O₂, 12.0 NaOH + 14.0 H₂O₂, 15.0 NaOH + 20.0 H₂O₂; temperature (°C): 95, < 25, 65, 85, 70, 80, 85; time (minutes): 20 / 50, 10, 30, 60, 120, 210, 210; consistency (%): 10.0, 12.0, 11.0, 11.0, 11.5, 11.5, 11.5; Pulp mass (g): 2000.0, 1500.0, 495.0, 360.320.0, 240.0, 200.0.

However, the thermal TCF sequence gave a final viscosity considerably lower at 303 ml.g⁻¹. The viscosity of the first peroxide stage (i.e. P₀ stage) for the thermal TCF sequence did appear to be excessively low and out of trend with the other viscosities of the same sequence. The exact cause is unknown. Given that the viscosity of a pulp is determined by the polysaccharide chain length and provides a rough indication of fibre damage during the bleaching process, the photochemical sequence did not appear to damage the fibre more than the thermal ECF control sequence, while the pulp for the thermal TCF sequence appeared to be subjected to significantly more fibre damage. This was expected given the harsher treatment of any pulp fibre required to get a similar brightness performance for any TCF sequence compared to an ECF sequence.

The control thermal ECF control and photochemical TCF sequences gave similar total pulp yields (90.6% and 89.7% respectively) with the thermal ECF control being slightly higher (Figure 4.79).

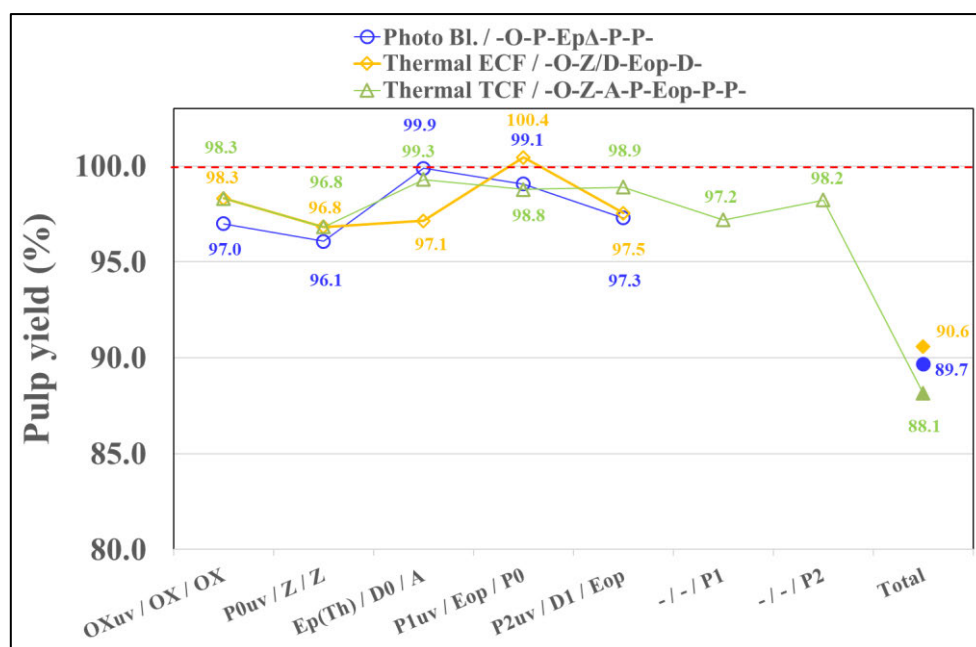


Figure 4.79: Pulp yield for the present control thermal ECF sequence, and the proposed thermal TCF and photochemical TCF based sequences.

Conditions:

- Photo Bl. Charges (kg t⁻¹): 18.0 NaOH + 2.0 Mg²⁺ + 400 kPa O₂ (bubbling), 18.0 NaOH + 80.0 H₂O₂ + 5.0 TiO₂, 15.0 NaOH + 9.0 H₂O₂, 18.0 NaOH + 80.0 H₂O₂, 18.0 NaOH + 45.0 H₂O₂; temperature (°C): 65*, 65*, 85 (thermal stage), 65*, 65* (* starting temperature of photobleaching stage); time (minutes): 120, 90, 45, 120, 60; consistency (%): 0.5, 0.5, 10.0, 0.5, 0.5; Pulp mass (g): 360.0, 320.0, 280.0, 240.0, 200.0.
- Thermal ECF. Charges (kg t⁻¹): 33.0 NaOH + 760 / 275 kPa O₂, 3.8 O₃ + 6.5 H₂SO₄, 11.0 ClO₂, 17.0 NaOH + 4.5 H₂O₂ + 380 kPa O₂, 3.5 ClO₂; temperature (°C): 95, < 25, 70, 77, 80; time (minutes): 20 / 50, 10, 60, 120, 240; consistency (%): 10.0, 12.0, 11.0, 11.5, 11.5; Pulp mass (g): 2000.0, 1500.0, 360.0, 320.0, 220.
- Thermal TCF. Charges (kg t⁻¹): 33.0 NaOH + 760 / 275 kPa O₂, 3.8 O₃ + 6.5 H₂SO₄, 6.0 H₂SO₄, 15.0 NaOH + 11.0 H₂O₂, 17.5 NaOH + 5.0 H₂O₂ + 380 kPa O₂, 12.0 NaOH + 14.0 H₂O₂, 15.0 NaOH + 20.0 H₂O₂; temperature (°C): 95, < 25, 65, 85, 70, 80, 85; time (minutes): 20 / 50, 10, 30, 60, 120, 210, 210; consistency (%): 10.0, 12.0, 11.0, 11.0, 11.5, 11.5, 11.5; Pulp mass (g): 2000.0, 1500.0, 495.0, 360.320.0, 240.0, 200.0.

However, given the elevated kappa number of the final photochemical TCF pulp, a higher total pulp yield might have been expected for the photochemical TCF sequences. The thermal TCF sequence was lower than either of these at 88.1%. The pulp yields for the control thermal ECF control and photochemical TCF sequences gave results close to those expected for commercial operations for paper grade mills using a similar type of paper grade pulp.

Overall, the pH values and temperatures showed that the bleaching stages for all three sequences proceeded as expected without any significant anomalies (Table 4.35). Only the P₀ stage of the

Table 4.35: Initial and final pH, initial and final temperatures, and percentage residual of chemical charges obtained across bleaching stages for the present thermal ECF sequence, and the proposed thermal TCF and photochemical TCF based sequences.

Photobleaching sequence							
	OX _{UV}	P0 _{UV}	E _{P(Th)}	P _{1/UV}	P _{2/UV}	-	-
Final pH	10.31	10.15	11.30	10.85	10.81	N / A	N / A
Initial pH	10.12	9.97	11.91	10.18	10.21		
Fin. Temp. (°C)	42.7	42.7	67.4	36.8	43.3		
Init. Temp. (°C)	57.4	57.7	42.8	58.4	59.3		
Res. chrg (%)	N / A	54.4	0.0	0.1	0.5		
Thermal ECF sequence							
	OX	Z	D ₀	E _{OP}	D ₁	-	-
Final pH	12.27	4.66	2.17	10.85	1.36	N / A	N / A
Initial pH	-	-	3.03	-	1.96		
Fin. Temp. (°C)	85/95*	<25	70*	120*	80*		
Init. Temp. (°C)	85/95*	<25	70**	120*	80*		
Res. chrg (%)	N / A	N / A	-	0.0	0.0		
Thermal TCF sequence							
	OX	Z	A	P ₀	E _{OP}	P ₁	P ₂
Final pH	12.27	4.66	2.39	11.94	12.64	-	11.65
Initial pH	-	-	2.64	11.34	-	-	10.99
Fin. Temp. (°C)	85/95*	<25	65*	85*	70*	80*	85*
Init. Temp. (°C)	85/95*	<25	65*	85*	70*	80*	85*
Res. chrg (%)	N / A	N / A	-	0.5	0.9	0.0	0.2

NOTE: * Temperature maintained at set point by active temperature control and heating.

photochemical TCF sequence gave any significant residual at 54.4% for the three sequences evaluated, while all other measured residuals were minimal (i.e. < 0.1%). In addition, although the initial temperature of the individual photochemical stages were elevated by the use of heated water (approximately 65 °C) at the start of each bleaching stage, the temperature dropped by the end of each stage (i.e. < 50 °C) due to the lack of any active heating and temperature control during all photochemical bleaching. The temperatures for all bleaching stages of both thermal sequences and the single thermal E_p stage in the photochemical TCF sequence were maintained at their operational settings by active temperature control in the pilot oxygen bleach reactor and temperature-controlled water baths.

Of the three sequences tested, the photochemical TCF sequence generally gave the highest pulp strength properties at 425 ml Canadian Standard Freeness (Table 4.36). These included tensile strength (tensile index and breaking length), burst strength (burst index), tear strength (tear index) and tensile energy absorption (TEA). Although the photochemical TCF sequence performed more poorly than the control thermal ECF control sequence for stretch, the differences between the two were small. The thermal TCF sequence gave the best performance with regards to bulk and porosity, and was significantly higher than the control thermal ECF control and photochemical TCF sequences. For bulk and porosity, the photochemical TCF sequence had the lowest results at 425 ml CSF which would cause deterioration of drainage properties on a running commercial paper machine. The brightness results at 425 ml CSF in the red part of the spectrum (brightness 680 nm) and blue part of the spectrum (brightness/R457) showed the greatest reduction of the red factor, but strongest improvement in the blue factor for the photochemical TCF sequence. This would be beneficial for the photochemical TCF sequence by removing the unwanted visually “red/brown” shade of the paper and increasing the more desired “blue/apparent whiteness” of the pulp for fully bleached pulp. However, the differences between the three sequences for both colour factors tended to be minimal to small in size. In addition, the photochemical TCF sequence also gave the best opacity results of the three sequences tested. Of the two thermal sequences, the ECF control sequence tended to outperform the TCF sequence in all pulp strength properties, as expected. Only small differences were observed for brightness, optical properties and bulk between these two sequences. When evaluating the difference from the unbleached starting pulp, the photochemical TCF sequence tended to give improvements of the starting pulp for most parameters except for the bulk, opacity and particularly the porosity (Table 4.36 – percentage differences given in parentheses). The two thermal sequences tended to give reductions as compared to the starting pulp, with the exception of stretch and brightness measurements.

Table 4.36: Hand sheet testing properties at 425 ml Canadian Standard Freeness for the present control thermal ECF sequence, and the proposed thermal TCF and photochemical TCF based sequences.

	Unbl. Aspen	Photo Bl.*	Thermal ECF*	Thermal TCF*
Bulk specific (cm³ g⁻¹)	1.96	1.69 (-13.8)	1.77 (-9.7)	1.83 (-6.6)
Tensile Index (Nm g⁻¹)	57.5	61.5 (7.0)	47.0 (-18.3)	35.5 (-38.3)
Stretch (%)	2.43	3.08 (26.7)	3.14 (29.2)	2.83 (16.5)
Breaking Length (m)	5920	6135 (3.6)	4900 (-17.2)	3300 (-44.3)
Burst Index (kPa m² g⁻¹)	3.13	3.85 (23.0)	2.85 (-8.9)	2.35 (-24.9)
Tear Index (mN m² g⁻¹)	7.27	7.32 (0.7)	7.27 (0.0)	5.20 (-28.5)
TEA (J m⁻²)	58.5	81.5 (39.3)	66.0 (12.8)	48.0 (-17.9)
Porosity (ml min.⁻¹)	1670	940 (-43.7)	1600 (-4.2)	2700 (61.7)
Brightness 680 nm (%)	69.2	92.7 (34.0)	93.5 (35.1)	93.0 (34.4)
Brightness R457 (%)	38.4	86.0 (124.0)	85.0 (121.4)	82.2 (141.1)
Opacity (%)	94.5	86.0 (-9.0)	84.7 (-10.4)	76.2 (-19.4)

NOTE: * The percentage difference from unbleached pulp in 425 ml CSF hand sheet testing properties for the present control thermal ECF sequence, proposed thermal TCF and photochemical TCF based sequences is given in parentheses after the analytical results.

The photochemical TCF sequence showed little change in the distribution of its fibre length fractions and retained a distribution similar to the unbleached starting fibre (Figure 4.80). However, the two thermal sequences (i.e. thermal ECF control and thermal TCF) showed a shift in fibre length distribution to shorter fibre lengths, particularly in the 600 to 900 µm and 900 to 1500 µm length ranges. The shortening of fibre length with the thermal sequences was due to fibre and cellulose damage that typically occurs with bleaching at temperature. These observations were consistent with the findings on hand sheet properties and strength for the three bleaching sequences with the photochemical TCF sequence typically giving the highest strength properties, while the two thermal sequences showed poorer pulp strengths. Based on results from the Lorentzen and Wettre Fibre Tester Plus, the fibres from all three bleaching sequences retained a similar fibre length and width as compared to the unbleached starting Aspen pulp (Table 4.37). However, the photochemical TCF sequence showed a significantly thicker fibre wall thickness. This suggested that less damage was done to the fibre walls

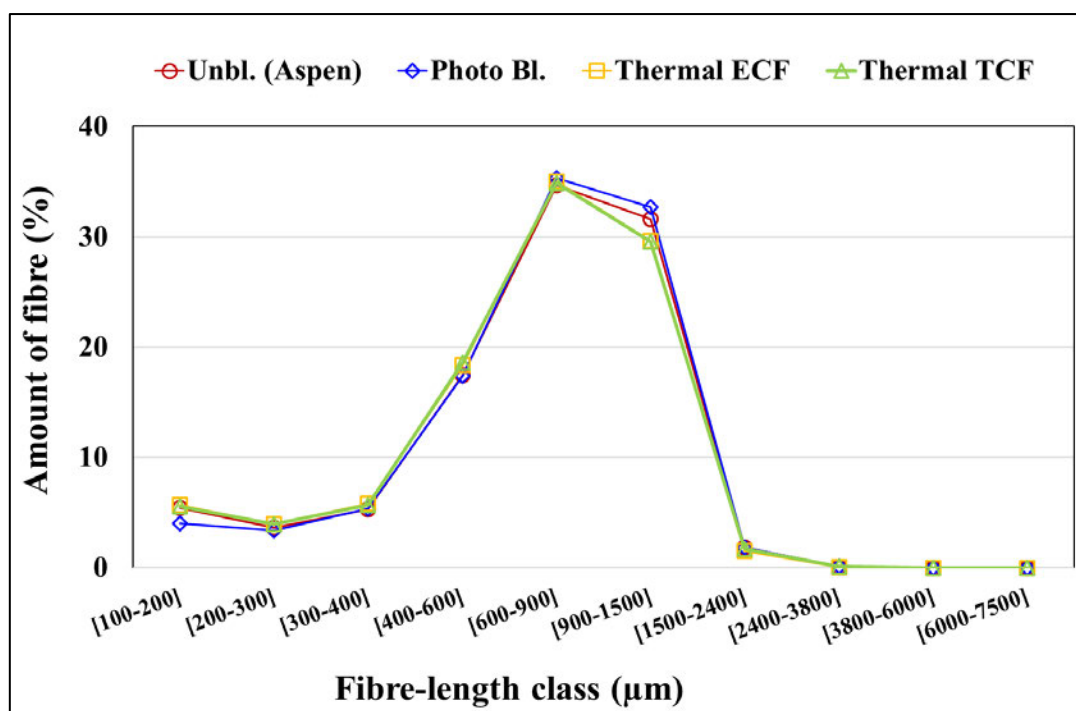


Figure 4.80: Lorentzen and Wettre Fibre Tester Plus L and W fibre morphology for the present control thermal ECF sequence, and the proposed thermal TCF and photochemical TCF based sequences.

Conditions:

- Photo Bl. Charges (kg t⁻¹): 18.0 NaOH + 2.0 Mg²⁺ + 400 kPa O₂ (bubbling), 18.0 NaOH + 80.0 H₂O₂ + 5.0 TiO₂, 15.0 NaOH + 9.0 H₂O₂, 18.0 NaOH + 80.0 H₂O₂, 18.0 NaOH + 45.0 H₂O₂; temperature (°C): 65*, 65*, 85 (thermal stage), 65*, 65* (* starting temperature of photobleaching stage); time (minutes): 120, 90, 45, 120, 60; consistency (%): 0.5, 0.5, 10.0, 0.5, 0.5; Pulp mass (g): 360.0, 320.0, 280.0, 240.0, 200.0.
- Thermal ECF. Charges (kg t⁻¹): 33.0 NaOH + 760 / 275 kPa O₂, 3.8 O₃ + 6.5 H₂SO₄, 11.0 ClO₂, 17.0 NaOH + 4.5 H₂O₂ + 380 kPa O₂, 3.5 ClO₂; temperature (°C): 95, < 25, 70, 77, 80; time (minutes): 20 / 50, 10, 60, 120, 240; consistency (%): 10.0, 12.0, 11.0, 11.5, 11.5; Pulp mass (g): 2000.0, 1500.0, 360.0, 320.0, 220.
- Thermal TCF. Charges (kg t⁻¹): 33.0 NaOH + 760 / 275 kPa O₂, 3.8 O₃ + 6.5 H₂SO₄, 6.0 H₂SO₄, 15.0 NaOH + 11.0 H₂O₂, 17.5 NaOH + 5.0 H₂O₂ + 380 kPa O₂, 12.0 NaOH + 14.0 H₂O₂, 15.0 NaOH + 20.0 H₂O₂; temperature (°C): 95, < 25, 65, 85, 70, 80, 85; time (minutes): 20 / 50, 10, 30, 60, 120, 210, 210; consistency (%): 10.0, 12.0, 11.0, 11.0, 11.5, 11.5, 11.5; Pulp mass (g): 2000.0, 1500.0, 495.0, 360.320.0, 240.0, 200.0.

during photochemical bleaching. The two thermal sequences had thinner fibre cell walls than the unbleached Aspen starting pulp, with the thermal TCF have the thinnest of the two cell walls due to harsher bleaching conditions and the longer bleaching sequence associated with the thermal TCF sequence. The photochemical TCF sequence pulp had a lower kinked fibre index than the two thermal sequences or the starting pulp, likely due to the increase in fibre wall thickness which suggests less fibre damage. However, the photochemical TCF sequence pulp also had the highest curled fibre fraction and was the most coarse. This was likely due to retained curl latency from the pulping process and the subsequent milder bleaching conditions associated with photochemical bleaching. This

Table 4.37: Fibre characteristics for present the control thermal ECF sequence, and the proposed thermal TCF and photochemical TCF based sequences.

Fibre characteristics	Unbl. Aspen	Photo Bl.	Thermal TCF	Thermal ECF
Mean length weighted fibre length (μm)	765	778	747	745
Mean fibre width (μm)	22.7	22.2	21.7	21.7
Fiber Wall Thickness (μm)	2.000	2.367	1.533	1.933
Shape factor [Curl] (%)	87.5	89.2	86.6	87.3
Mean kink index (%)	2.647	2.231	2.978	2.804
Fibrillation index (area based) %	1.200	1.300	1.433	1.567
Fibrillation index (perimeter based) %	3.300	3.067	3.500	3.500
Primary (coarse) fines (%)	6.733	4.833	6.467	6.600
Secondary (fine) fines (%)	15.333	9.467	14.500	15.867
Mean fines content %	22.067	14.333	21.000	22.467
Coarseness (mg m^{-1})	0.077	0.088	0.059	0.072

increased photochemical bleaching curl latency was expected given that bleaching at elevated temperatures allows for any fibre latency to be “relaxed” which may help improve a fibre’s strength later in the paper making process. The photochemical TCF sequence showed less fibrillation of the cell wall than the two thermal bleaching sequences. Furthermore, the photochemical TCF sequence also contained less fines than the two thermal bleaching sequences. The two thermal sequences showed increased fibrillation over the unbleached Aspen starting pulp but had similar fines content to the to the unbleached Aspen pulp. It is unknown why the photochemical bleached sequence had significantly less fines than both the two thermal bleaching sequences and the unbleached Aspen starting pulp, although the significantly milder bleaching conditions and removal of the smallest fine fractions during washing is the most likely cause. Overall, the results for fibre characteristics from the Lorentzen and Wettre Fibre Tester Plus showed that the photochemical TCF sequence was significantly gentler on the Aspen pulp than either thermal bleaching sequences, giving better fibre properties as a result.

In summary, the photochemical bleaching sequence was shown to be a viable alternative to the thermal ECF and TCF bleaching sequences save for its low comparative operational consistency (i.e. 0.5% versus about 10%). The photochemical TCF bleaching sequence achieved final brightness values above the bleached brightness target of 89% giving similar results to the thermal ECF control for the control sequence (both about 90.6% respectively), both of which outperformed the thermal TCF sequence

(85.0%). The photochemical TCF bleaching sequence accomplished this at an elevated final kappa number as compared to both thermal sequences, which suggested that it generated significantly less and selectively destroyed more of the chromophoric lignin and quinonic components due to its more selective photochemical reaction mechanism. It also gave a final viscosity (546 mg l^{-1}) similar to the thermal ECF control sequence (577 ml g^{-1}), while the thermal TCF sequence gave a much lower final viscosity (303 ml g^{-1}) due to the needed for a harsh extended bleaching sequence necessary to improve its final brightness. Pulp yields were generally similar for the photochemical TCF and thermal ECF control sequences. The photochemical TCF sequence generally gave improvements in the hand sheet strength properties over both thermal sequences at 425 ml Canadian Standard Freeness save for bulk and drainage. In addition, the photochemical TCF sequence tended to retain the longer fibre distribution of the unbleached starting pulp, while the two thermal sequences gave a reduction in the proportion of longer fibre lengths. The photochemical TCF sequence tended to give better fibre characteristics with less fibrillation and fines, as well as a smaller kinked fibre fraction. However, the photochemical sequence did show a greater retention of curl latency due to its milder conditions which would cause some difficulties later in the paper making process, with fibres being more coarse. This experimental work for thermophotochemical bleaching sequences, for paper grade pulp, was supported by the work of Castellan et al. and Machado et al. who demonstrated that significant levels of photochemical bleaching of pulp could be achieved using multi stage photochemical bleaching sequences [220, 225].

4.3.13 Evaluation of various combined thermophotochemical and thermal bleaching sequences for dissolving/chemical cellulose grade pulp

The goal in this investigation was to compare a thermophotochemical based bleaching sequence against a conventional sequence for dissolving viscose grade pulp [329]. A description of the experimental work is given in Section 3.6.13. Both the thermal ECF control (95.5% before reversion) and photochemical TCF (91.2% before reversion) sequences gave brightness values above the 91.0% target. The thermal ECF control exceeded the target by about 5 brightness units and this value was significantly higher than values achieved in commercial operations and laboratory experiments (91.0 to 91.5% on average) for the same charges, and is excessively high (Figure 4.81). The excessively high final brightness for the ECF control appears to stem from an above average brightness obtained out of the oxygen stage (77.9% before reversion) for the thermal control as compared to typical commercial operations (71% on average), being about seven brightness units above what was expected and representing an excessive degree of delignification of the pulp for the thermal ECF sequence. This elevated brightness was then passed forward through the control bleaching sequence, giving the much elevated final brightness. The exact cause of the elevated oxygen stage brightness in the ECF control is unknown, but, is likely due to an excessive caustic soda (NaOH) charge or excessive temperature. Brightness reversion appears to be small and uniform for both the ECF control and photochemical TCF experiment.

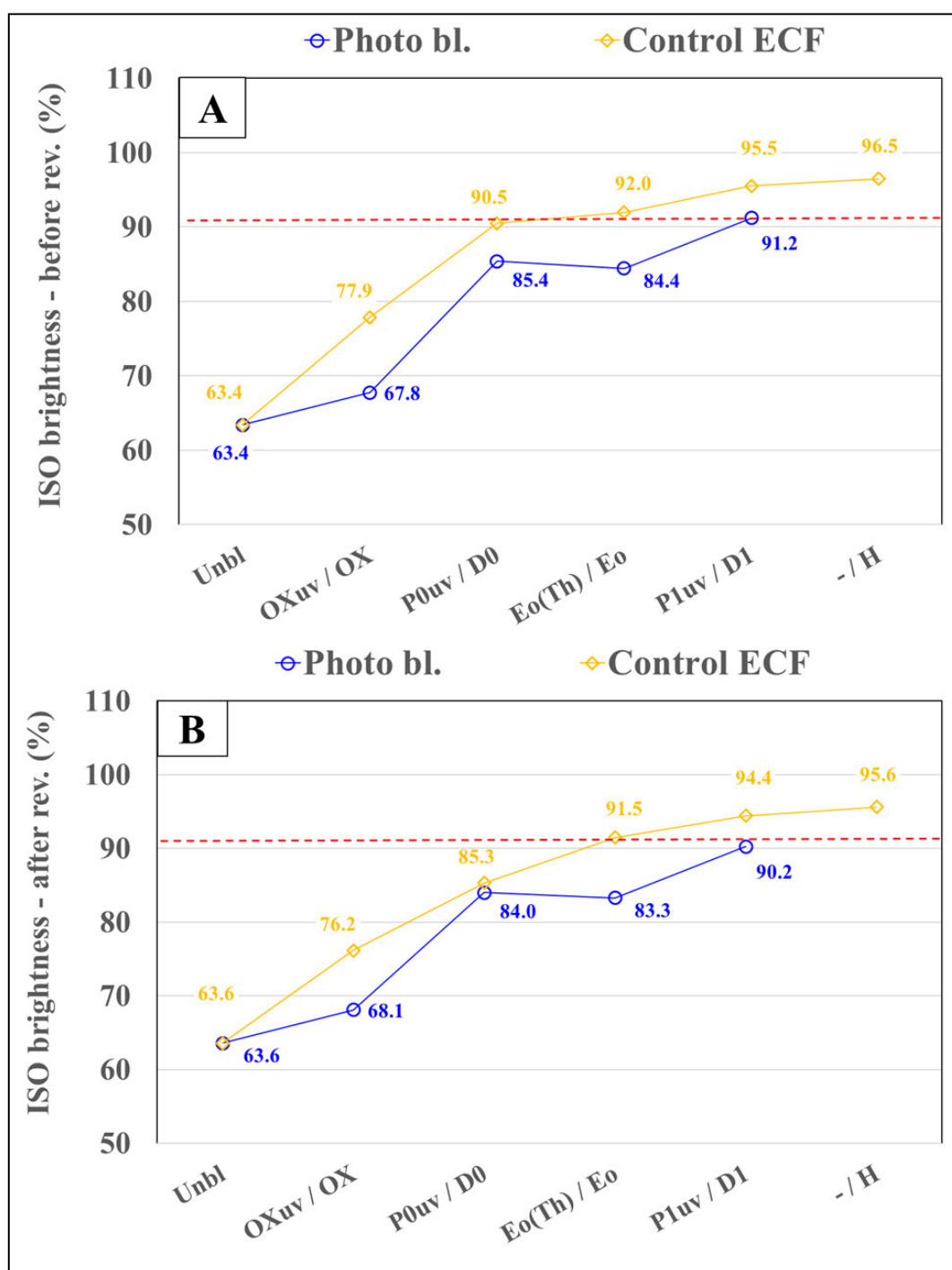


Figure 4.81: ISO brightness [A] before and [B] after reversion for the present thermal ECF control and the photochemical TCF based sequences.

Conditions:

- Photo Bl. Charges (kg t^{-1}): 18.0 NaOH + 2.0 Mg^{2+} + 400 kPa O_2 (bubbling), 18.0 NaOH + 80.0 H_2O_2 , .0 NaOH + 350 kPa O_2 , 18.0 NaOH + 55.0 H_2O_2 ; temperature ($^{\circ}\text{C}$): 65*, 65*, 100 (thermal stage), 65* (* starting temperature of photobleaching stage); time (minutes): 90, 90, 20, 60; consistency (%): 0.5, 0.5, 9.0, 0.5; Pulp mass (g): 180.0, 140.0, 120.0, 100.0.
- Thermal ECF. Charges (kg t^{-1}): 23.0 NaOH + 680 kPa O_2 , 8.0 ClO_2 , 34.0 NaOH + 350 kPa O_2 , 7.0 ClO_2 , 2.0; NaOH + 5.0 NaClO; temperature ($^{\circ}\text{C}$): 90, 60, 100, 65, 60; time (minutes): 60, 60, 120, 180, 120; consistency (%): 10.0, 10.0, 10.0, 10.0, 10.0; Pulp mass (g): 310.0, 200.0, 160.0, 40.0, 80.

The kappa number for both the thermal ECF control and photochemical TCF sequences generally followed the expected kappa number trends based on their respective brightness bleaching profiles (Figure 4.82). However, the kappa number out of the photochemical oxygen stage of the photochemical sequence was higher than typically obtained by the control sequence for their oxygen delignification process (about 0.5 higher). This is likely due to the milder conditions employed in the photochemical sequence and due to the photochemical oxygen stage not being a pressurised process such as the conventional oxygen stage employed for the thermal ECF sequence. The use of these milder conditions in the photochemical oxygen stage hold significance as the harsh conditions in oxygen stage of the ECF sequence are employed to help “chemically refine” the dissolving pulp by removing/dissolving cellulose oligomers and some of the residual hemicellulose fractions. In addition, as observed with the photochemical TCF sequence evaluated for paper grade pulp, the photochemical TCF sequence for viscose grade dissolving pulp tended to give higher kappa numbers across all stages than the ECF control at similar brightness values (see Section 4.3.12). The kappa number out of the oxygen stage

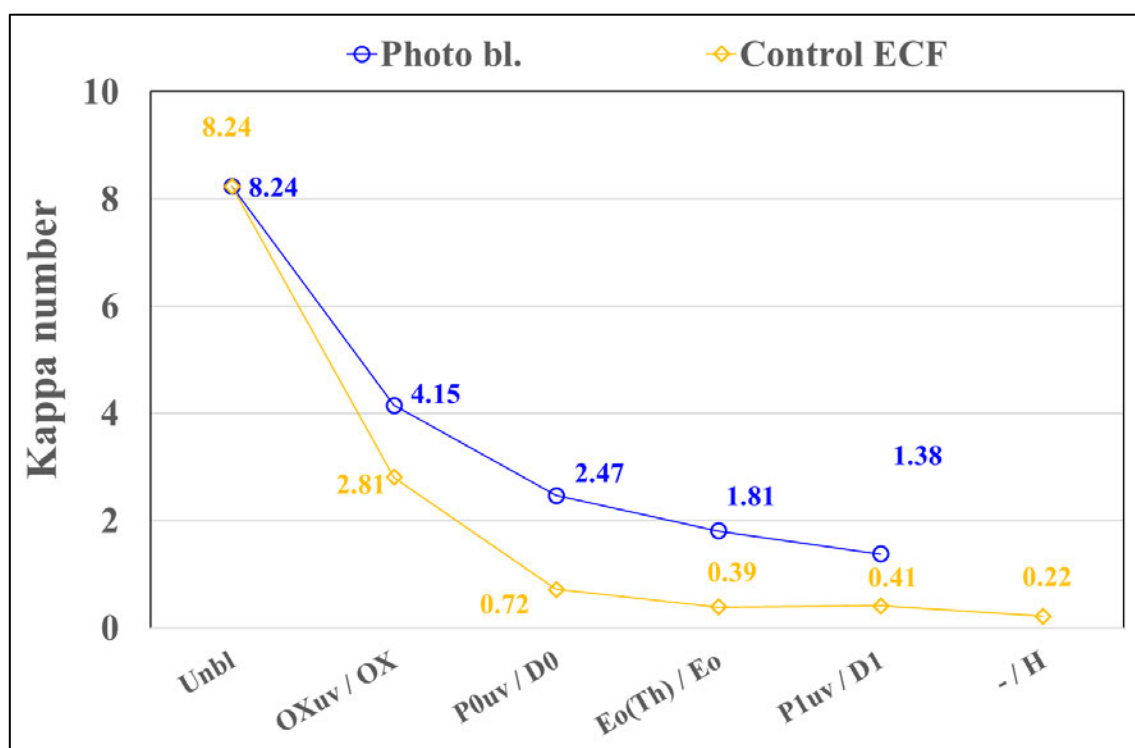


Figure 4.82: Kappa number for the present thermal ECF control and the photochemical TCF based sequences.

Conditions:

- Photo Bl. Charges (kg t^{-1}): 18.0 NaOH + 2.0 Mg^{2+} + 400 kPa O_2 (bubbling), 18.0 NaOH + 80.0 H_2O_2 , .0 NaOH + 350 kPa O_2 , 18.0 NaOH + 55.0 H_2O_2 ; temperature ($^{\circ}\text{C}$): 65*, 65*, 100 (thermal stage), 65* (* starting temperature of photobleaching stage); time (minutes): 90, 90, 20, 60; consistency (%): 0.5, 0.5, 9.0, 0.5; Pulp mass (g): 180.0, 140.0, 120.0, 100.0.
- Thermal ECF. Charges (kg t^{-1}): 23.0 NaOH + 680 kPa O_2 , 8.0 ClO_2 , 34.0 NaOH + 350 kPa O_2 , 7.0 ClO_2 , 2.0; NaOH + 5.0 NaClO; temperature ($^{\circ}\text{C}$): 90, 60, 100, 65, 60; time (minutes): 60, 60, 120, 180, 120; consistency (%): 10.0, 10.0, 10.0, 10.0, 10.0; Pulp mass (g): 310.0, 200.0, 160.0, 40.0, 80.

for the ECF control was lower than expected by about 0.5 to 1.0 kappa number units. This was consistent with the observation made for the elevated brightness values of the oxygen stage of the ECF pulp and represents a level of delignification of 66% across the oxygen stage for the thermal ECF sequence which is considerably excessive.

The thermal ECF control and photochemical TCF sequences appeared to fall onto two different curves for a plot of brightness versus kappa number (Figure 4.83). This suggests that the two sequences employed different reaction mechanism during their respective bleaching processes, with one being thermally driven while the other was photochemically driven. Thus, the thermal ECF control sequence, using thermal energy, would have given a broad general activation of all chemical processes (i.e. Boltzmann energy distribution) in its bleaching activities, while the photochemical TCF sequence would have given a more selective specific activation of the bleaching activities based on the selective

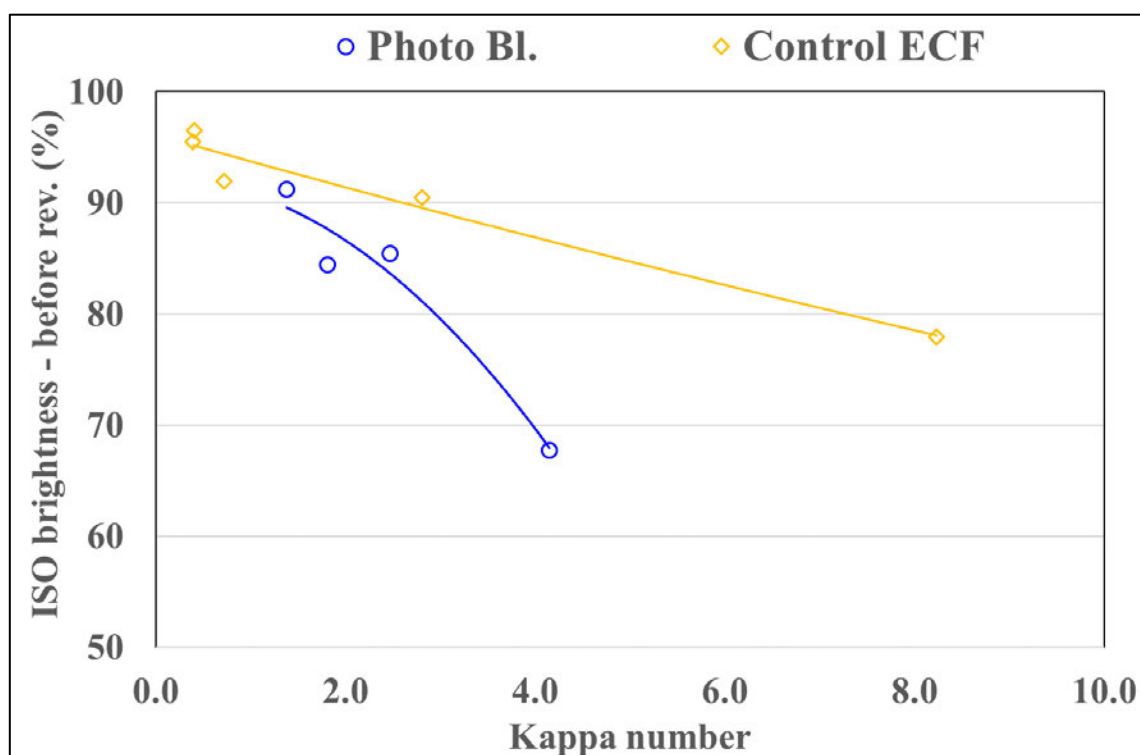


Figure 4.83: Brightness versus kappa number for the present thermal ECF control and the photochemical TCF based sequences.

Conditions:

- Photo Bl. Charges (kg t⁻¹): 18.0 NaOH + 2.0 Mg²⁺ + 400 kPa O₂ (bubbling), 18.0 NaOH + 80.0 H₂O₂, .0 NaOH + 350 kPa O₂, 18.0 NaOH + 55.0 H₂O₂; temperature (°C): 65*, 65*, 100 (thermal stage), 65* (* starting temperature of photobleaching stage); time (minutes): 90, 90, 20, 60; consistency (%): 0.5, 0.5, 9.0, 0.5; Pulp mass (g): 180.0, 140.0, 120.0, 100.0.
- Thermal ECF. Charges (kg t⁻¹): 23.0 NaOH + 680 kPa O₂, 8.0 ClO₂, 34.0 NaOH + 350 kPa O₂, 7.0 ClO₂, 2.0; NaOH + 5.0 NaClO; temperature (°C): 90, 60, 100, 65, 60; time (minutes): 60, 60, 120, 180, 120; consistency (%): 10.0, 10.0, 10.0, 10.0, 10.0; Pulp mass (g): 310.0, 200.0, 160.0, 40.0, 80.

photochemical absorption of ultraviolet light in a given narrow distribution of wavelengths (i.e. energy quantization –Sections 2.3.2 and 2.3.3). This photochemical approach would have hypothetically reduced or negated any unwanted side reactions. However, in reality, other energy transfer processes such as molecular thermal, rotational and vibrational deactivation of the photochemical excited states would also reduce the selectivity of photochemical reactions to a small extent. Overall, this greater selectivity is a known advantage and characteristic of photochemically driven reaction processes and appeared to generate few chromophores and quinonics, while also selectively destroying more of these chromophores and quinonics that were generated, than the thermal bleaching. This is very similar to what was observed for the thermophotochemical bleaching of paper grade pulps.

Both the control ECF (556 ml g⁻¹) and photochemical TCF (535 ml g⁻¹) sequences gave final viscosity results within the targeted range of 500 to 560 ml g⁻¹ for typical dissolving viscose grade pulps (Figure 4.84). The exact quantity of hydrogen peroxide added for the photochemical P_{1uv} stage (photochemical

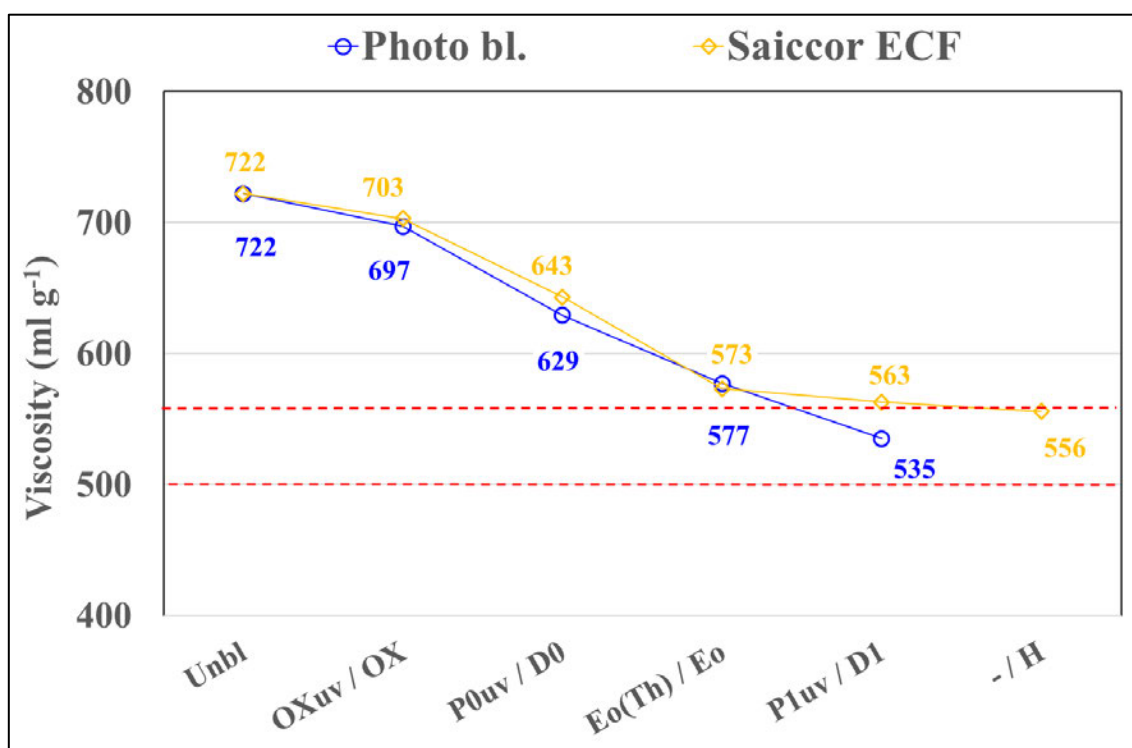


Figure 4.84: Viscosity for the present thermal ECF control and the photochemical TCF based sequences.

Conditions:

- Photo Bl. Charges (kg t⁻¹): 18.0 NaOH + 2.0 Mg²⁺ + 400 kPa O₂ (bubbling), 18.0 NaOH + 80.0 H₂O₂, .0 NaOH + 350 kPa O₂, 18.0 NaOH + 55.0 H₂O₂; temperature (°C): 65*, 65*, 100 (thermal stage), 65* (* starting temperature of photobleaching stage); time (minutes): 90, 90, 20, 60; consistency (%): 0.5, 0.5, 9.0, 0.5; Pulp mass (g): 180.0, 140.0, 120.0, 100.0.
- Thermal ECF. Charges (kg t⁻¹): 23.0 NaOH + 680 kPa O₂, 8.0 ClO₂, 34.0 NaOH + 350 kPa O₂, 7.0 ClO₂, 2.0; NaOH + 5.0 NaClO; temperature (°C): 90, 60, 100, 65, 60; time (minutes): 60, 60, 120, 180, 120; consistency (%): 10.0, 10.0, 10.0, 10.0, 10.0; Pulp mass (g): 310.0, 200.0, 160.0, 40.0, 80.

sequence) and hypochlorite added for the H stage (thermal ECF sequence) is determined by the final targeted viscosity of the pulp with these two stages being employed for viscosity control of their related bleaching sequence. As the reactivity is related to viscosity and is a key process control parameter, both pulps would be expected to have met the viscosity specifications to be able to demonstrate acceptable viscose reactivity rates.

Besides similar pulp yields across the oxygen stages for the control ECF and photochemical TCF sequences (93.8% and 94.5%, respectively), the control ECF sequence generally gave higher pulp yields for each bleaching stage than the photochemical TCF sequence (Figure 4.85). Overall, the control ECF sequence total yield was significantly larger than the photochemical TCF sequence (86.9% and 81.1%, respectively). This was likely due to the minimal yield losses expected from the two chlorine dioxide stages as opposed to the alkali extraction and peroxide stages of the photochemical TCF sequence, where a higher level of cellulose dissolution was expected in both.

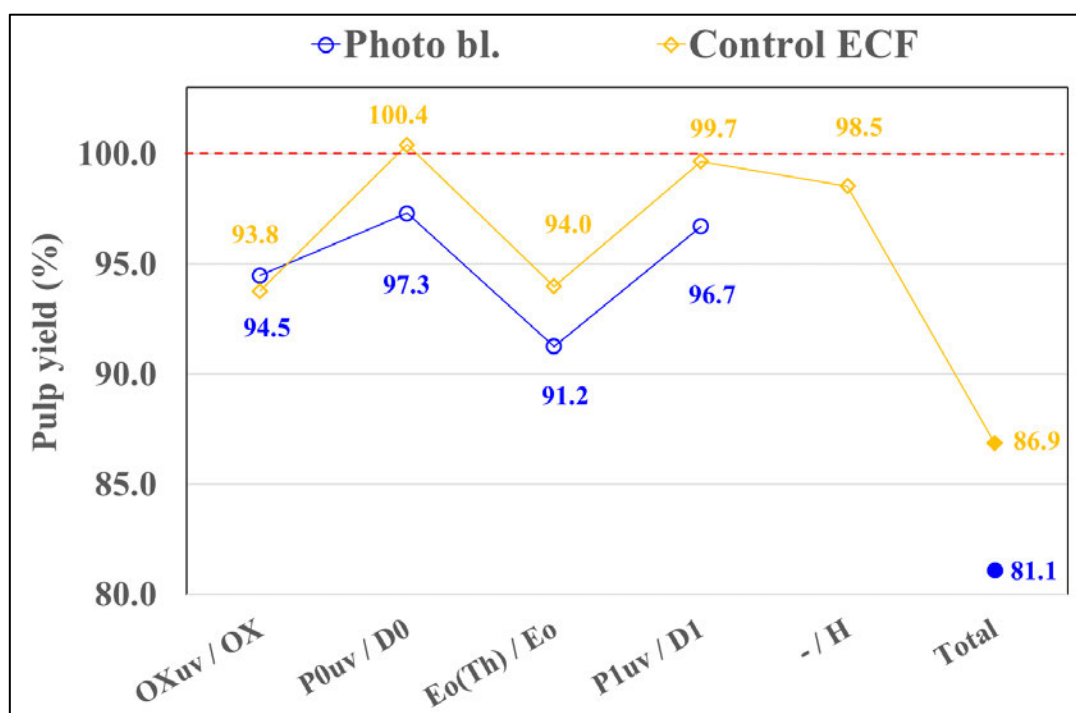


Figure 4.85: Pulp Yield for the present thermal ECF control and the photochemical TCF based sequences.

Conditions:

- Photo Bl. Charges (kg t^{-1}): 18.0 NaOH + 2.0 Mg^{2+} + 400 kPa O_2 (bubbling), 18.0 NaOH + 80.0 H_2O_2 , .0 NaOH + 350 kPa O_2 , 18.0 NaOH + 55.0 H_2O_2 ; temperature ($^{\circ}\text{C}$): 65*, 65*, 100 (thermal stage), 65* (* starting temperature of photobleaching stage); time (minutes): 90, 90, 20, 60; consistency (%): 0.5, 0.5, 9.0, 0.5; Pulp mass (g): 180.0, 140.0, 120.0, 100.0.
- Thermal ECF. Charges (kg t^{-1}): 23.0 NaOH + 680 kPa O_2 , 8.0 ClO_2 , 34.0 NaOH + 350 kPa O_2 , 7.0 ClO_2 , 2.0; NaOH + 5.0 NaClO; temperature ($^{\circ}\text{C}$): 90, 60, 100, 65, 60; time (minutes): 60, 60, 120, 180, 120; consistency (%): 10.0, 10.0, 10.0, 10.0, 10.0; Pulp mass (g): 310.0, 200.0, 160.0, 40.0, 80.

No chemical residuals were given for the oxygen and the caustic soda charged to the oxygen stages and the alkaline extraction stages of both the photochemical and the thermal ECF sequences, as both the oxygen and caustic soda were deliberately used in excess for the bleaching stages undertaken and could not be accurately measured or estimated (Table 4.38). The first peroxide stage of the photochemical TCF sequence (i.e. P_{0UV}) gave a considerably elevated chemical residual (78.5% peroxide residual) which was due to the hydrogen peroxide used in considerable excess with its charge being based on much of the earlier photochemical bleaching with alkali peroxide suspensions. For the second peroxide stage of the photochemical sequence (i.e. P_{1UV}) and all three relevant stages of the thermal ECF sequence (i.e. D_0 , D_1 and H), the measured chemical residuals were nil or much smaller than originally charged with total or near complete consumption measured. In all these cases, the bleaching reagents were not employed in excess. Lastly, the photochemical pulp suspensions appeared to become more transparent to the ultraviolet light from the UV LED array as their brightness increased. This was supported by the much lower residual peroxide in the final P_{1UV} stage as compared to the earlier P_{0UV} stage, despite the significant difference in peroxide charge between the two peroxide stages (i.e. 8.0 kg t^{-1} versus 5.5 kg t^{-1} respectively). Future work for the photochemical bleaching sequence should employ better optimization of chemical charges.

Table 4.38: Residual chemical charge for the present thermal ECF control and the photochemical TCF based sequences.

PHOTBLEACHING SEQUENCE					
Stage	O_{XUV}	P_{0UV}	$E_o(Th)$	P_{1UV}	N / A
Prop. Res. Bleach reagent (%)	-	78.5	-	7.9	N / A
THERMAL ECF SEQUENCE					
Stage	OX	D_0	E_o	D_1	H
Prop. Res. Bleach reagent (%)	-	9.5	-	15.7	0.0

The photochemical TCF and control ECF sequences gave similar carbohydrate profiles as the pulp from Saiccor mill's commercial operations for viscose grade pulps (Figure 4.86). This is expected given that both sequences used an unbleached acid sulfite dissolving viscose grade pulp from Sappi Saiccor mill as a starting pulp. These results suggested that no undesirable anomalous side reactions or process deviations took place, and that the pulps were subjected to adequate chemical refining in both bleaching

sequences. It also suggested that both pulps were of acceptable chemical purity (xylose content less than 3.0%, preferably less than 2.5%) as compared to the Saiccor commercially produced viscose pulp.

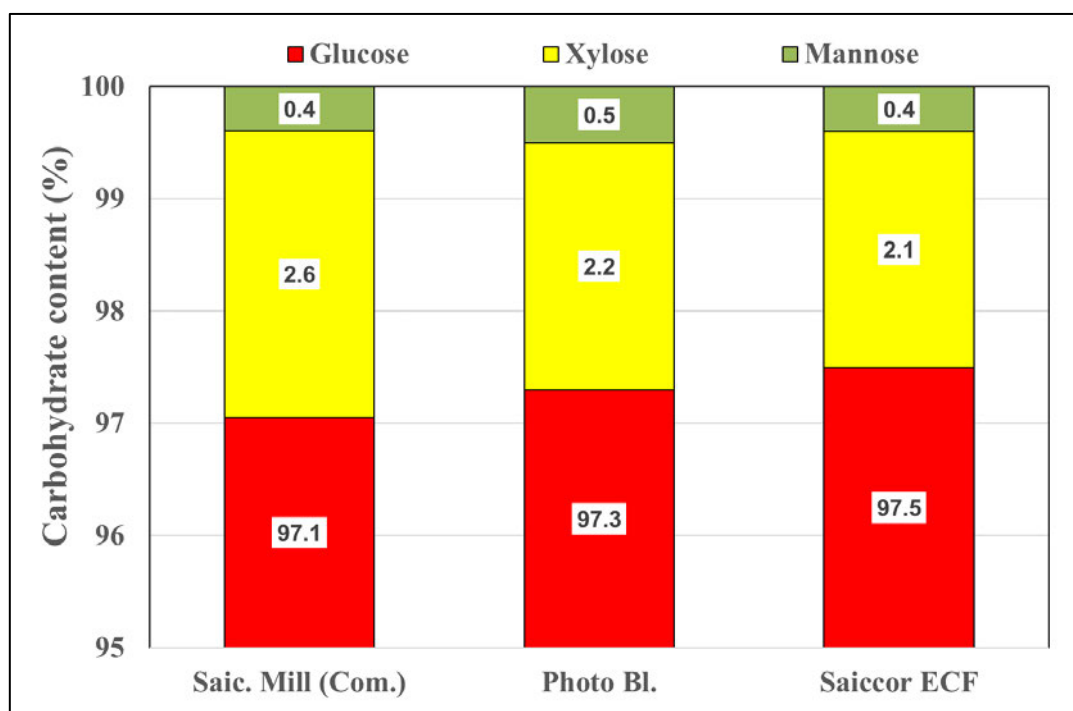


Figure 4.86: Comparison of the carbohydrate content for the thermal ECF control and the photochemical TCF based sequences, with a Saiccor mill commercial viscose pulp.

Conditions:

- Photo Bl. Charges (kg t^{-1}): 18.0 NaOH + 2.0 Mg^{2+} + 400 kPa O_2 (bubbling), 18.0 NaOH + 80.0 H_2O_2 , .0 NaOH + 350 kPa O_2 , 18.0 NaOH + 55.0 H_2O_2 ; temperature ($^{\circ}\text{C}$): 65*, 65*, 100 (thermal stage), 65* (* starting temperature of photobleaching stage); time (minutes): 90, 90, 20, 60; consistency (%): 0.5, 0.5, 9.0, 0.5; Pulp mass (g): 180.0, 140.0, 120.0, 100.0.
- Thermal ECF. Charges (kg t^{-1}): 23.0 NaOH + 680 kPa O_2 , 8.0 ClO_2 , 34.0 NaOH + 350 kPa O_2 , 7.0 ClO_2 , 2.0; NaOH + 5.0 NaClO; temperature ($^{\circ}\text{C}$): 90, 60, 100, 65, 60; time (minutes): 60, 60, 120, 180, 120; consistency (%): 10.0, 10.0, 10.0, 10.0, 10.0; Pulp mass (g): 310.0, 200.0, 160.0, 40.0, 80.

The photochemical TCF and control ECF sequences gave alkali solubilities (S_{10} / S_{18} of 8.1% / 2.7% and 7.2 % / 4.0%, respectively) that were within the historic average obtained by Saiccor mill at 10.1% / 5.2% (Table 4.39). The estimated degraded cellulose content can be calculated by the difference between the S_{10} value and S_{18} value. Based on this, the control ECF laboratory pulp (3.2%) showed less cellulose degradation than the Saiccor historic mill data (4.9%), while the photochemical TCF sequence showed about 10% more than that typically obtained at the mill (5.4%). Thus, despite the slightly elevated results for the photochemical TCF sequence, neither the photochemical TCF nor the

Table 4.39: Alkali solubility and Sappi quick reactivity index for the thermal ECF control and the photochemical TCF-based sequences.

Sample	Alkali solubility / S₁₀ : S₁₈ (% / %)	Estimated degraded cellulose / S₁₀ - S₁₈ (%)	Sappi quick reactivity index (undissolved fibres)
Saiccor historical average	10.1 / 5.2 *	4.9	5.00 to 9.50
Saiccor good reacting control	-	-	3.26
Thermal ECF Control	7.2 / 4.0	3.2	7.89 / 7.89
Photochemical TCF	8.1 / 2.7	5.4	9.23 / 9.39

NOTE: * Approximate mill average for year of 2020 for S₁₀ and S₁₈ were 9.96 and 4.90 respectively

The control ECF pulps had been subjected to excessively large damage during their respective bleaching processes. In addition, both the photochemical TCF and control ECF sequences gave reasonably similar Sappi quick reactivity indices (9.23 / 9.39 and 7.89 / 7.89 respectively) that were within the acceptable limits (5.00 to 9.50), but with both pulps being near the upper limits (Table 4.39). The photochemical TCF sequence gave a higher index score than the control ECF sequence, suggesting that it contained more unreacted fibre material and degraded cellulose fractions than the ECF control. This was not unexpected, given the overall milder conditions of the photochemical TCF sequence which resulted in less chemical refining in the oxygen stage. The application of a harsher oxygen or a different alkali extraction stage (e.g. cold caustic extraction with caustic soda charges of 750 – 1200 kg t⁻¹) would likely have given a better chemical refinement of the pulp.

Both the photochemical TCF and thermal ECF control sequences showed a clear shift in fibre distribution to shorter fibre lengths (Figure 4.87). This was due the chemical refining process occurring during chemical bleaching operations, particularly around the E_O stage in both sequences. However, a greater shift in fibre length to shorter fibres was observed for the thermal ECF control sequence as compared to the photochemical TCF sequence due to the harsher bleaching conditions employed in the thermal ECF control sequence, particularly during the oxygen stage.

The shift to shorter fibre lengths for the photochemical TCF and thermal ECF control sequences noted earlier was further illustrated in the significant reduction in mean fibre length for both pulps as

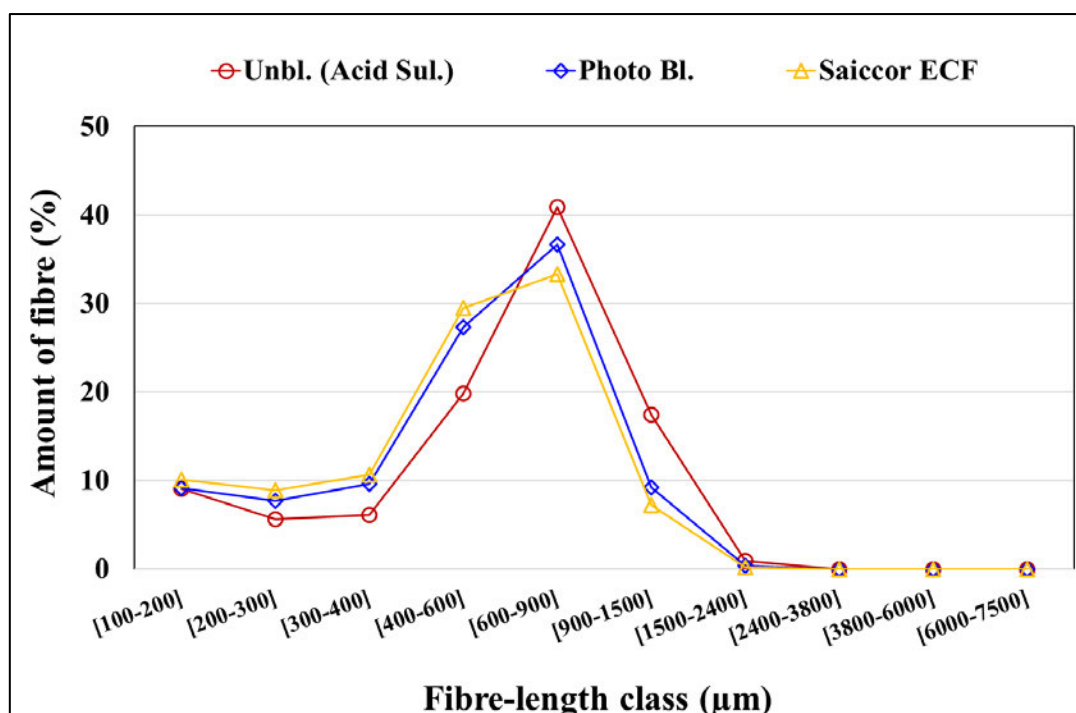


Figure 4.87: Lorentzen and Wettre Fiber Tester Plus fibre morphology for the present thermal ECF control and the photochemical TCF based sequences.

Conditions:

- Photo Bl. Charges (kg t⁻¹): 18.0 NaOH + 2.0 Mg²⁺ + 400 kPa O₂ (bubbling), 18.0 NaOH + 80.0 H₂O₂, .0 NaOH + 350 kPa O₂, 18.0 NaOH + 55.0 H₂O₂; temperature (°C): 65*, 65*, 100 (thermal stage), 65* (* starting temperature of photobleaching stage); time (minutes): 90, 90, 20, 60; consistency (%): 0.5, 0.5, 9.0, 0.5; Pulp mass (g): 180.0, 140.0, 120.0, 100.0.
- Thermal ECF. Charges (kg t⁻¹): 23.0 NaOH + 680 kPa O₂, 8.0 ClO₂, 34.0 NaOH + 350 kPa O₂, 7.0 ClO₂, 2.0; NaOH + 5.0 NaClO; temperature (°C): 90, 60, 100, 65, 60; time (minutes): 60, 60, 120, 180, 120; consistency (%): 10.0, 10.0, 10.0, 10.0, 10.0; Pulp mass (g): 310.0, 200.0, 160.0, 40.0, 80.

compared to their starting pulp; but there is little change in the fibre width of both pulps (Table 4.40). However, both fully bleached fibres showed a similar extent of swelling of the fibre cell wall with an increased fibre wall thickness. This was likely due to delamination and opening up of the fibre cell wall upon chemical refining. Both fully bleached pulps showed a reduction in the fibre curl latency due to bleaching, but a large increase in the level of kinked fibre fractions due to chemical damage to the fibres. The proportion of fibrillation of the control ECF sequence pulp was significantly larger than the starting pulp, but there was only a small increase for the photochemical TCF sequence. Similarly, the control ECF sequence showed an increase in fines while the photochemical TCF sequence did not. This was due to the harsher bleaching conditions in the control ECF sequence. Lastly, both bleached pulps were coarser than the starting pulp.

Table 4.40: Fibre characteristics for the thermal ECF control and the photochemical TCF-based sequences.

Fibre characteristics	Unbl. Acid Sul.	Photo Bl.	Thermal ECF
Mean length weighted fibre length (μm)	653	575	544
Mean fibre width (μm)	18.8	18.5	18.9
Fiber wall thickness (μm)	1.433	1.900	1.800
Shape factor [Curl] (%)	89.3	80.6	78.1
Mean kink index (%)	2.171	5.665	6.434
Fibrillation index (area based) %	1.100	1.233	1.433
Fibrillation index (perimeter based) %	2.933	3.100	3.567
Primary (coarse) fines (%)	10.533	9.433	10.067
Secondary (fine) fines (%)	14.667	14.833	19.067
Mean fines content %	25.200	24.233	29.133
Coarseness (mg m^{-1})	0.047	0.059	0.058

In summary, both the thermal ECF control and photochemical TCF sequences achieved above the target brightness (91.0%). and met targets for all key control parameters around viscosity (500 to 550 ml g⁻¹), carbohydrate content (xylose < 3.0%; mannose < 1.0%), alkali solubility (S₁₀ / S₁₈: 10.1% / 5.2%) and Sappi quick reactivity index (5.00 to 9.50). Both the control ECF and photochemical TCF sequences showed a shift to shorter fibre lengths in their fibre distributions from their starting pulps due to bleaching activities with the control ECF sequence giving the largest shift due to its harsher bleaching conditions at temperature. Both pulps showed an increase in the level of kink fibre fractions, but only the control ECF control pulp showed a significant increase in the extent of fibrillation of the fibre as well as the generation of fines. A review of the plot of brightness versus kappa number indicated that the control ECF and photochemical TCF sequences were bleaching pulp via different reaction mechanisms. The control ECF sequence was driven by a general thermal mechanism, while the photochemical TCF sequence was driven by selective photochemical activation via a photochemical mechanism. Overall, the generation of viscose grade quality pulp using a photochemical TCF sequence as opposed to the thermal ECF sequence appears to be a possible option. However, the low consistency of the photochemical bleaching stages (i.e. 0.5%) are not practical for commercial applications and achieving similar photochemical bleaching performances at higher consistencies (i.e. 5.0 to 10%) would be necessary. In addition, the photochemical TCF would likely require harsher chemical refining in the E₀ stage than presently employed at the mill to improve the photochemical TCF sequence's viscose quality by the removal or activation of the residual unreacted fibre material and degraded cellulose fractions in the pulp. As with the thermophotochemical bleaching sequences of paper grade pulp, the

thermophotochemical bleaching of dissolving pulp, was also supported by the work of Castellan et al. and Machado et al., who achieving significantly brighter pulps using multi stage photochemical bleaching sequences [220, 225].

4.3.14 Reaction kinetics study for the pure caustic soda, alkaline peroxide and alkaline oxygen options utilizing the UV LED array reactor design

The aim in the combined analysis of these collective results was to perform a brief kinetics-based study of the three photochemical bleaching oxidants and their reaction mechanisms compared with each other (i.e. hydrogen peroxide, pure caustic soda, and oxygen) [316 - 318, 321]. A description of the experimental work is given in Sections 3.6.1, 3.6.2, and 3.6.5. Based on the reagents involved, the rate law for each option could be defined as $v = k'[\text{caustic soda}]^a[\text{oxidant}]^b[\text{pulp lignin}]^c$ for this study [337]. However, as both the caustic soda and the oxidant (where relevant) were employed in excess, both can be regarded as constant for the purpose of this study to give the pseudo rate law: $v = k[\text{pulp lignin}]^c$. The shape of the resulting curves and the reaction rate constants would provide an indication as to the type of reactions, their rates and their reaction orders. A review of the four bleaching options (i.e. control – alkaline/no UV, alkaline peroxide with UV LED, pure caustic soda with UV LED, and alkaline oxygen with UV LED) showed that a plot of the reciprocal of the calculated pulp suspension lignin concentration versus time gave “pseudo” second order reaction kinetic relationships for all four options (Figure 4.88). This was based on all four options giving straight line curves for the reciprocal concentration plots, which clearly indicated second order reaction kinetics [337]. The reaction rate constant (k value) as determined from the slope of each of these reciprocal concentration curves gave four differing values for each of the four options, despite all three oxidants using the same bleaching species, namely the hydroxyl radical (Table 4.41). This would suggest that all four employed reaction mechanisms that were different from each other. The literature reviewed (Chapter 2) indicated that the likely bleaching species for the three oxidants is the hydroxyl radical, with the only difference between the three oxidants being how the hydroxyl radical is generated, at what quantities, and how quickly. For the control (no UV), the likely mechanism is not based on bleaching via the hydroxyl radical, but rather the extraction of residual degraded lignin from the pulp resulting in minimal reduction in the kappa number (Figure 4.35). This is consistent with the k value obtain for the control, which was the smallest k value of the four (i.e. $0.732 \text{ M}^{-1} \text{ s}^{-1}$). The control was followed by the pure caustic soda under UV irradiation, which gave the next largest k value (i.e. $3.13 \text{ M}^{-1} \text{ s}^{-1}$), with the likely reaction mechanism being the generation of hydroxyl radicals by the direct photolysis of water or hydroxide ions by hydrogen abstraction. This is not a favoured photochemical process resulting in a low rate of hydroxyl radical generation, which was consistent with the slower bleaching process for the pure caustic soda. The alkaline oxygen process follows the caustic soda, being the second fastest process (i.e. $3.61 \text{ M}^{-1} \text{ s}^{-1}$), with hydrogen peroxide formed from the dissolved oxygen via the generation of peroxy radical, which then generated hydroxyl radicals by the chemolysis of the peroxide. The fastest process

was the hydrogen peroxide which had the largest k value (i.e. $5.37 \text{ M}^{-1} \text{ s}^{-1}$). The hydroxyl radicals for the peroxide were generated by the direct photolysis of hydrogen peroxide.

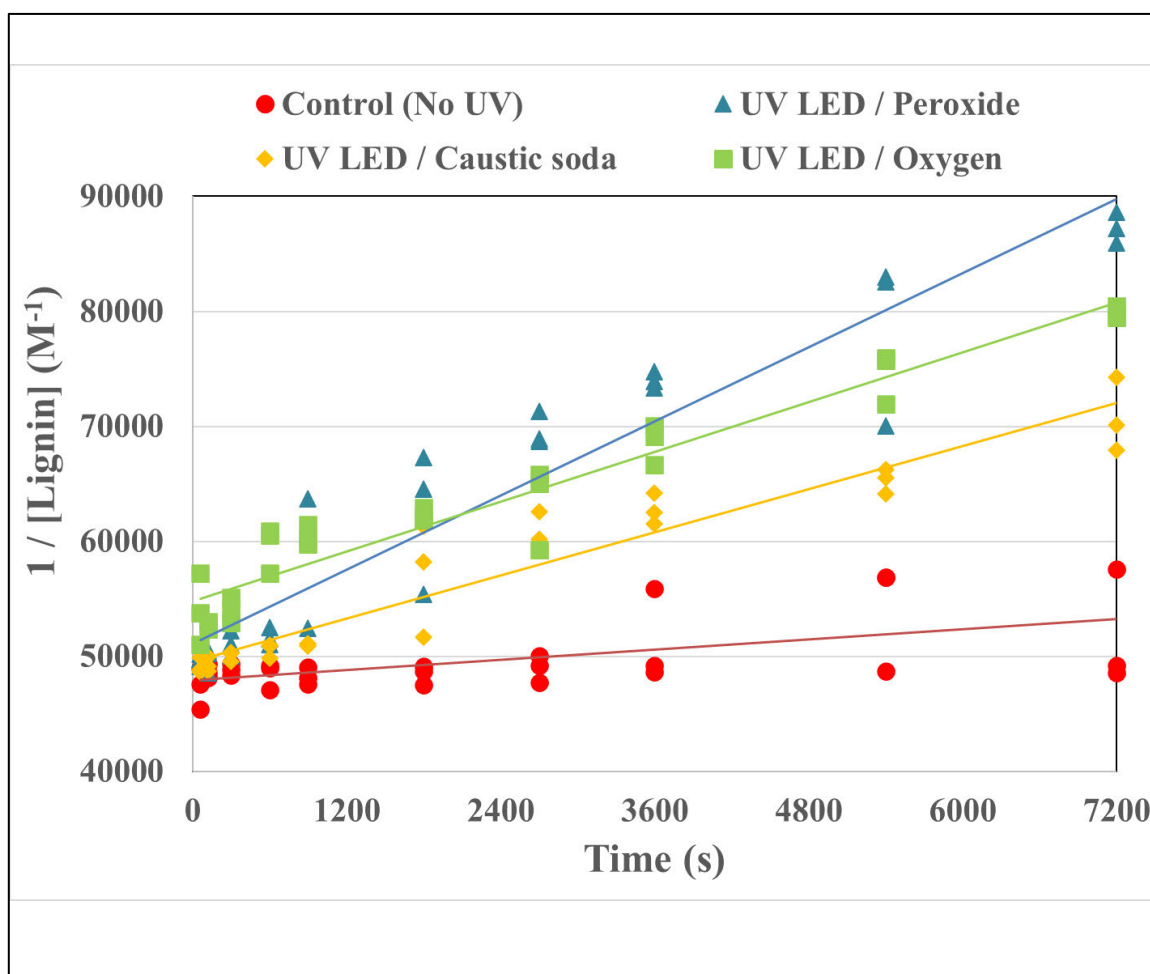


Figure 4.88: Second order plot for the photobleaching of Cloquet Aspen paper grade pulp with a UV LED array reactor in the presence of caustic soda and different oxidants.

Conditions:

- Control (No UV): $18.0 \text{ kg t}^{-1} \text{ NaOH}$, $80.0 \text{ kg t}^{-1} \text{ H}_2\text{O}_2$; 20.0 g pulp ; $25.0 \text{ }^\circ\text{C}$ (Room temperature); 0.5% consistency; UV LED array (unpowered – no light source).
- UV LED / Peroxide: $18.0 \text{ kg t}^{-1} \text{ NaOH}$, $80.0 \text{ kg t}^{-1} \text{ H}_2\text{O}_2$; 20.0 g pulp ; $25.0 \text{ }^\circ\text{C}$ (Room temperature); 0.5% consistency; UV LED array (full power).
- UV LED / Caustic soda. $18.0 \text{ kg t}^{-1} \text{ NaOH}$; 20.0 g pulp ; $25.0 \text{ }^\circ\text{C}$ (Room temperature); 0.5% consistency; UV LED array (full power).
- UV LED / Oxygen: $18.0 \text{ kg t}^{-1} \text{ NaOH}$, $80.0 \text{ kg t}^{-1} \text{ H}_2\text{O}_2$ where relevant; oxygen bubbled into suspension through needle valve, cylinder 400 kPa where relevant; 20.0 g pulp ; $25.0 \text{ }^\circ\text{C}$ (Room temperature); 0.5% consistency; UV LED array (full power).

Table 4.41: Reaction rate constants for the photobleaching of Cloquet Aspen paper grade pulp with the UV LED array reactor in the presence of caustic soda and different oxidants.

BLEACHING PROCESS	Slope / k ($\text{M}^{-1} \text{s}^{-1}$)
Control (No UV)	0.732
UV LED / Peroxide	5.37
UV LED / Caustic soda	3.13
UV LED / Oxygen	3.61

A similar review of the reciprocal of the pulp viscosity versus time for the four bleaching options (i.e. control – alkaline/no UV, alkaline peroxide with UV LED, pure caustic soda with UV LED, and alkaline oxygen with UV LED) gave “pseudo” second order reaction kinetics relationships for the three oxidants used, while the control without UV irradiation appeared unaffected by the irradiation – i.e. zero order reaction kinetics (Figure 4.89). A review of the reaction rate constants for the four options showed similar, but, extremely small constants for the three oxidants, suggesting minimal impact on the viscosity over time; while the control showed a small negative reaction rate constant suggesting a minimal increase in the viscosity of the control over time (Table 4.42). This would be consistent with dissolution of small chain cellulose out of the pulp by alkaline extraction over time. These findings were consistent with the viscosity curves of these four options which demonstrated minor viscosity losses over time (Figures 4.25 and 4.36).

The calculated reaction rate constants were consistent with the rate/extent of pulp delignification, and viscosity losses observed for all three oxidants. These “pseudo” second order reaction kinetics obtained in this study are in contrast to Marcoccia who observed “pseudo” first order reaction rate kinetics for both pulp delignification and viscosity degradation when the start kappa of the pulp was discounted [232 - 233]. The exact cause of this discrepancy is likely due to the difference in conditions, apparatus, and concentrations employed in this study as opposed to Marcoccia’s investigation.

The three oxidants investigated in this study gave “pseudo” second order reaction kinetics for a plot of the reciprocal of the brightness (before reversion) versus time, but, as inverse linear curves – i.e. lines with negative slopes (Figure 4.90). Of the three oxidants, the most significant bleaching effect occurred

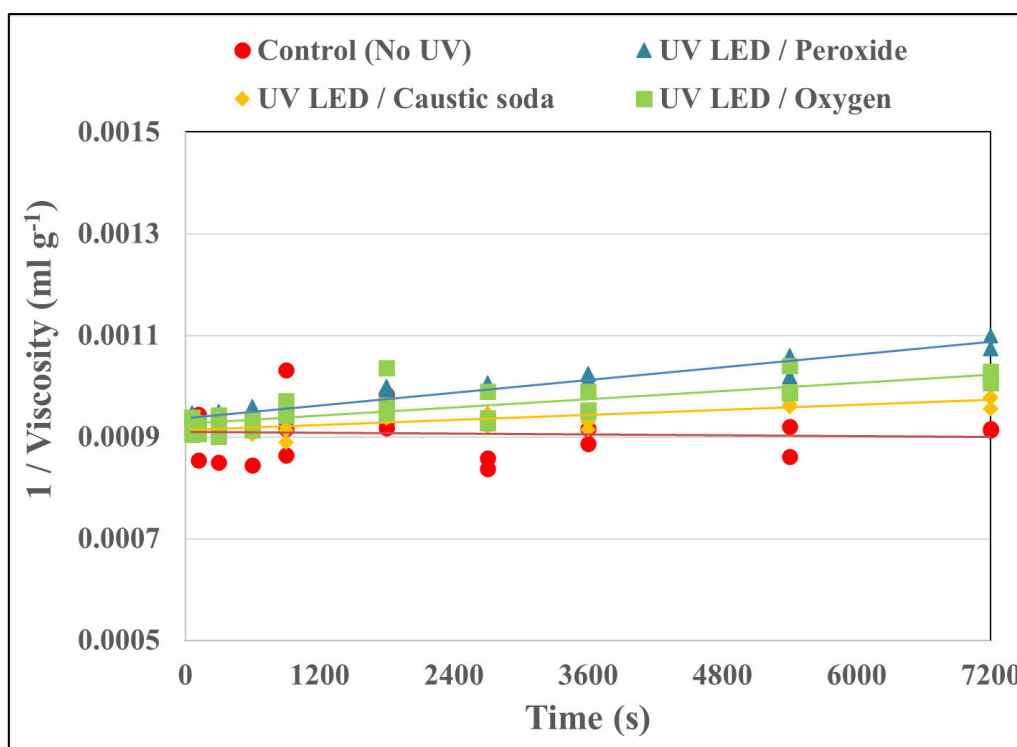


Figure 4.89: Effects of pulp viscosity on the kinetics of photobleaching of Cloquet Aspen paper grade pulp with the UV LED array reactor in the presence of caustic soda and different oxidants.

Conditions:

- Control (No UV): 18.0 kg t⁻¹ NaOH, 80.0 kg t⁻¹ H₂O₂; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency; UV LED array (unpowered – no light source).
- UV LED / Peroxide: 18.0 kg t⁻¹ NaOH, 80.0 kg t⁻¹ H₂O₂; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency; UV LED array (full power).
- UV LED / Caustic soda. 18.0 kg t⁻¹ NaOH; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency; UV LED array (full power).
- UV LED / Oxygen: 18.0 kg t⁻¹ NaOH, 80.0 kg t⁻¹ H₂O₂ where relevant; oxygen bubbled into suspension through needle valve, cylinder 400 kPa where relevant; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency; UV LED array (full power).

Table 4.42: Reaction rate constants for the effect of pulp viscosity on the photobleaching of Cloquet Aspen paper grade pulp with the UV LED array reactor in the presence of caustic soda and different oxidants.

BLEACHING PROCESS	Slope / k (g ml ⁻¹ s ⁻¹)
Control (No UV)	-1×10^{-9}
UV LED / Peroxide	2×10^{-8}
UV LED / Caustic soda	8×10^{-9}
UV LED / Oxygen	1×10^{-8}

for the alkaline peroxide, and the least effect with the pure caustic soda, with the alkaline oxygen being in between these two extremes. The observed inverse linear relation of the three oxidants in the aforementioned reciprocal brightness plot corresponded well with the (negative k values taken from the fitted line functions) slopes of the three inverse linear curves (Table 4.43). The values of the slopes follow the trend of the reciprocal brightness plot with the alkaline peroxide and the alkaline oxygen both giving the largest slopes (i.e. $-1 \times 10^{-6} \%^{-1} \text{ s}^{-1}$ for both), and the pure caustic soda, the smallest i.e. $-6 \times 10^{-7} \%^{-1} \text{ s}^{-1}$). This corresponded well with the similar pattern observed for the reciprocal lignin content curves of the three oxidants used in this study.

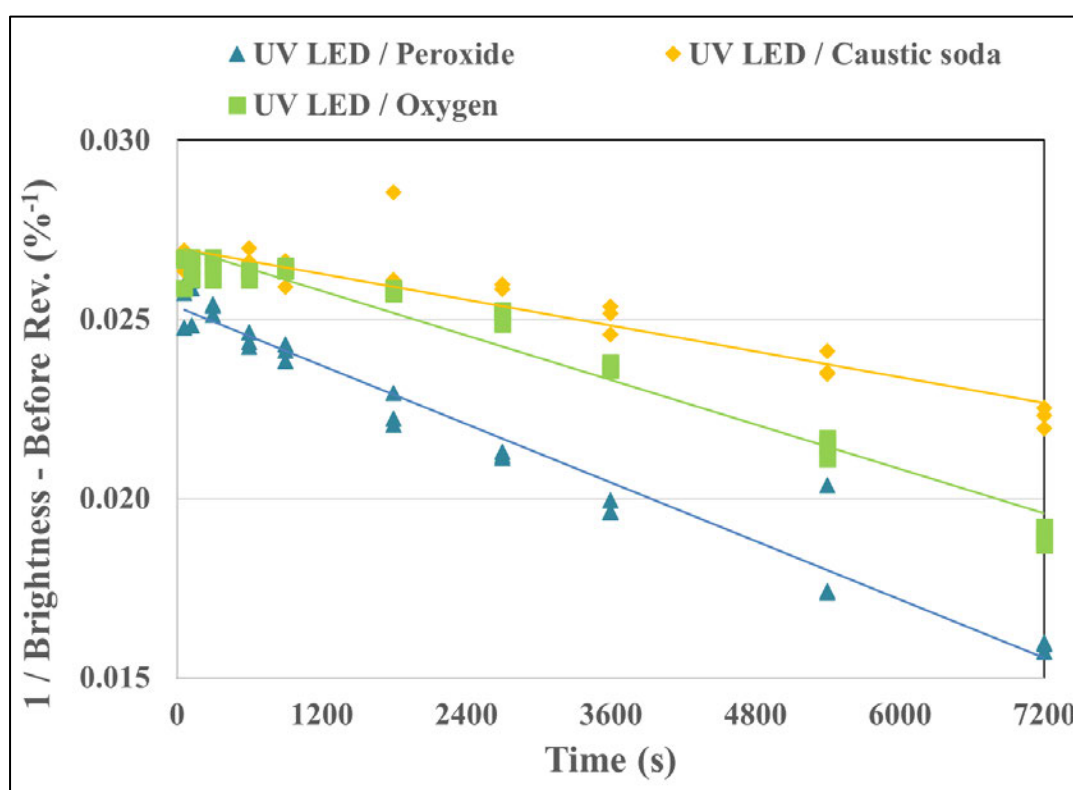


Figure 4.90: Plot of reciprocal brightness before reversion versus time for the photobleaching of Cloquet Aspen paper grade pulp with a UV LED array reactor in the presence of caustic soda and different oxidants.

Conditions:

- Control (No UV): 18.0 kg t⁻¹ NaOH, 80.0 kg t⁻¹ H₂O₂; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency; UV LED array (unpowered – no light source).
- UV LED / Peroxide: 18.0 kg t⁻¹ NaOH, 80.0 kg t⁻¹ H₂O₂; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency; UV LED array (full power).
- UV LED / Caustic soda. 18.0 kg t⁻¹ NaOH; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency; UV LED array (full power).
- UV LED / Oxygen: 18.0 kg t⁻¹ NaOH, 80.0 kg t⁻¹ H₂O₂ where relevant; oxygen bubbled into suspension through needle valve, cylinder 400 kPa where relevant; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency; UV LED array (full power).

Table 4.43: Pulp brightness (before reversion) reaction rate slopes for the photobleaching of Cloquet Aspen paper grade pulp with a UV LED array reactor in the presence of caustic soda and different oxidants.

BLEACHING PROCESS	Slope (% ⁻¹ s ⁻¹)
UV LED / Peroxide	-1×10^{-6}
UV LED / Caustic soda	-6×10^{-7}
UV LED / Oxygen	-1×10^{-6}

A plot of the normalized reciprocal lignin content versus the normalized reciprocal brightness value (before reversion) showed three distinction linear relationships that were moderately closely related (Figure 4.91). The normalization of the reciprocal lignin contents and reciprocal brightness values were achieved by dividing the respective parameters by the averages of their reciprocal values at the 1 minute time period. The observed pattern corroborated well with the similar negative linear slope values for these three curves (Table 4.44). The alkaline peroxide and pure caustic soda gave similar slope values, with the alkaline peroxide being the largest of the two, while the alkaline oxygen gave a lower slope value than the other two. Collectively, these observations support the findings made prior around the three oxidants photochemical bleaching reaction mechanisms, namely that all three employ hydroxyl radicals for their photochemical bleaching, however, the three oxidants differed in their reaction mechanism to how those radicals are generated, to what quantity, and how quickly.

In summary, the three oxidants (i.e. pure caustic soda, alkaline peroxide, and alkaline oxygen) demonstrated “pseudo” second order rate kinetics when under UV LED irradiation. The rate constants (i.e. k value) of the three gave values that matched the extent/rate of delignification, and viscosity degradation, with the pure caustic soda having the smallest rate constant and the alkaline peroxide having the largest. All three rate constants matched the hydroxyl radical generation method and favourability given in the literature, with all three employing hydroxyl radicals for bleaching, but, utilizing three different reaction mechanisms to generate the bleaching radical and at different rates. The reaction mechanism for the control without UV irradiation, which was significantly slower than all three oxidants, was due to simple alkaline extraction of already the degraded lignin residual and short chain cellulose rather than hydroxyl radical generation for bleaching. The three oxidants also followed “pseudo” second order rate kinetics for their brightness development, matching the pattern observed for the extent/rate of delignification. The discrepancy between Marccocia’s “pseudo” first order reaction mechanism and the “pseudo” second order reactions mechanisms of all three oxidants in this study was due to the difference in conditions, apparatus, and concentrations employed.

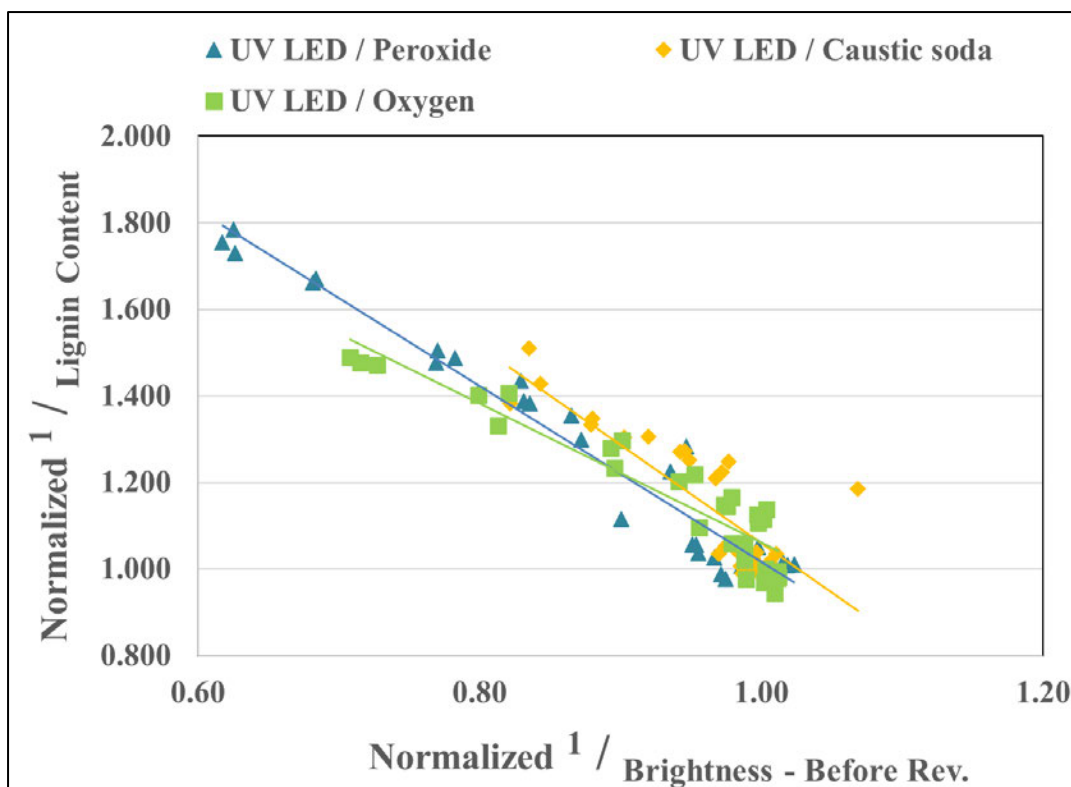


Figure 4.91: Plot of normalized reciprocal lignin content versus normalized reciprocal brightness (before reversion) for the photobleaching of Cloquet Aspen paper grade pulp with a UV LED array reactor in the presence of caustic soda and different oxidants.

Conditions:

- Control (No UV): 18.0 kg t⁻¹ NaOH, 80.0 kg t⁻¹ H₂O₂; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency; UV LED array (unpowered – no light source).
- UV LED / Peroxide: 18.0 kg t⁻¹ NaOH, 80.0 kg t⁻¹ H₂O₂; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency; UV LED array (full power).
- UV LED / Caustic soda. 18.0 kg t⁻¹ NaOH; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency; UV LED array (full power).
- UV LED / Oxygen: 18.0 kg t⁻¹ NaOH, 80.0 kg t⁻¹ H₂O₂ where relevant; oxygen bubbled into suspension through needle valve, cylinder 400 kPa where relevant; 20.0 g pulp; 25.0 °C (Room temperature); 0.5% consistency; UV LED array (full power).

Table 4.44: Slope values for normalized reciprocal lignin content versus normalized reciprocal brightness (before reversion) plots for the photobleaching of Cloquet Aspen paper grade pulp with a UV LED array reactor in the presence of caustic soda and different oxidants.

BLEACHING PROCESS	Slope (no units)
UV LED / Peroxide	-2.03
UV LED / Caustic soda	-2.28
UV LED / Oxygen	-1.61

4.3.15 Overall discussion of results obtained in present study

As a final discussion of all results obtained in this study, three potential light sources for the photochemical bleaching of pulps were evaluated. These three light sources were: solar radiation, MDELs and UV LED arrays. Of these three evaluated, only solar radiation (i.e. sunlight) and the UV LED array illuminants were shown to perform photochemical bleaching, with the UV LED array alone being both viable and practical.

During the photochemical bleaching of Cloquet mill pulp (i.e. post-oxygen stage Aspen) utilizing solar radiation, the application of pure caustic soda and alkali peroxide gave an approximately 0.5 to 0.7 unit drop in the kappa number for both when subjected to solar irradiation as opposed to their respective controls without. However, the use of alkali peroxide also gave an increased kappa reduction for both its solar experiment and control, as compared to that achieved with caustic soda alone for both of its experiment and control. Thus, the use of peroxide to improve the delignification of pulp was successful, regardless whether the pulp was irradiated with sunlight or not. However, solar irradiation of the pulp further improved on the bleaching process by peroxide. The addition of photocatalysts and other additives (i.e. TiO_2 , Al_2O_3 , CaCO_3 , MgO) all gave reduced photochemical bleaching effects due to the increased opaqueness of the pulp suspension in conjunction with the low light intensity of the sunlight illuminating the pulp. However, pulp viscosity with the additives as opposed without was elevated, suggesting pulp protecting effects with many of these materials. This effect is also observed and expected in the thermal bleaching of pulps. The total bleaching effect was slow requiring a full five days of exposure to give the brightness increase and kappa reduction achieved. In addition, the pulp was only subjected to illumination for less than half that time due to sunset and sunrise separating the 24 h period into two halves. In conclusion, while the solar bleaching of pulp was achieved, it was impractically long to be truly useful.

A commercial Primarc MDEL showed irregular and random ignition and burn/non-burn intervals within the microwave oven chamber of a Roto SYNTH microwave reactor up to power levels of 1200 W. This irregular ignition and burn pattern were due to neither the Primarc MDEL and the microwave chamber of the Roto SYNTH microwave reactor having been adequately tuned or optimized as regards the standing microwave pattern within the microwave chamber. However, overall, the MDEL still showed a rough increased ignition and burn pattern as the Roto SYNTH microwave reactor power levels were increased from 1000 W to 1200 W. Four different MDEL reactor designs were evaluated, which consisted of the flat round bottom flask combination reactor, immersed sleeve reactor, MDEL core tubular coil combination reactor, and suspended MDEL and “bucket” combination reactor. Of these four reactor designs, the suspended MDEL and “bucket” combination reactor design showed the most promise. However, during photochemical bleaching of pulp within the suspended MDEL and “bucket” combination reactor placed within the microwave chamber of the ROTO SYNTH microwave oven, no

significant difference was observed between the irradiated experiments and their controls, without irradiation, based on the analysis of variances (ANOVA). There was no notable difference for kappa number and viscosity across time, although the impact of thermal bleaching during microwave heating was clearly evident as the kappa number for both decreased similarly.

The photochemical bleaching of pulp (as measured by kappa number and brightness) utilizing the UV LED array at the experimental conditions of: (i) pure caustic soda, (ii) alkaline peroxide, and (iii) alkaline oxygen showed significant bleaching/delignification for all three options, with the alkaline peroxide and alkaline oxygen giving the best results as compared to their controls, while the pure caustic soda option performed more poorly, but still significantly well as compared to its controls without irradiation. These differences were statistically significantly as given by the Student comparative T-test. Interestingly, despite delignifying to similar kappa numbers, the brightness development for the photobleaching alkaline peroxide was significantly better than that for the photobleaching alkaline oxygen. In all three cases pulp strength, as given by pulp viscosity, was mostly maintained, while pulp yield losses were minimal. The main active bleaching agent in all three cases was likely the hydroxyl radical as indicated by the reports reviewed in Section 2.4. In the alkaline peroxide experiments, these radicals were generated by the direct photolysis of the hydrogen peroxide added as the main source of hydroxyl radicals, and the hydrogen/electron abstraction of a hydrogen atom from a water or a hydroxide ion as a secondary source. In the alkaline oxygen experiments, the dissolved oxygen served as a source for generating hydrogen peroxide via the peroxy radical which then generated hydroxyl radicals while under UV LED array illumination. A minor source of hydroxyl radicals in the presence of oxygen was also the direct generation of hydroxyl radicals from oxygen. Consequently, the alkaline peroxide and alkaline oxygen performed similarly in bleaching efficiency giving similar bleaching effects. For the pure caustic soda experiments, the only source of hydroxyl radicals was from the direct photolysis of water or hydroxide ions by hydrogen abstraction. As this direct photolysis of water/hydroxide ions is less favoured than the other processes mentioned above, the pure caustic soda option consequently performed more poorly than the alkaline peroxide and oxygen options. The thermal contribution to the total bleaching effect was minimal given the low initial and final temperature for all three bleaching options.

An evaluation of the impact of the starting pH of the pulp suspension, UV LED array power levels, pulp suspension temperature, and pulp suspension consistency, as well as the impact of various photocatalysts, was performed using the alkaline peroxide photochemical bleaching option. In addition, the evaluation of the impact of various photosensitizers on the alkaline oxygen photochemical bleaching option was undertaken.

Photochemical bleaching occurred across the entire pH range, with bleaching performance being at its poorest in the acidic and neutral pH range (i.e. 2.5 to 8.0) where it plateaued, but increased as the pH became more alkaline above pH 8.0 given a maximal effect at about pH 10.5. The pulp strength, as given by the pulp viscosity, was mostly maintained with only minor losses at the neutral to acidic pH range. This observation of “reduced” delignification at acidic pH ranges was consistent with the findings of Maroccia who found that an acidic photo-enhanced oxygen delignification process required a subsequent thermal alkali extraction stage to achieve the full delignification potential of the acidic photobleaching process [232].

As regards the impact of power levels, the extent of photochemical bleaching of pulp was found to increase linearly with rising power levels of the UV LED array, which is directly associated to the intensity of the UV illumination, from a power setting of 10% up to the full 100%. Although pulp strength was mostly maintained, it decreased slightly in small increments as the power level rose.

For the impact of temperature, higher temperatures gave a larger bleaching effect for pulp photochemically bleached with alkaline peroxide. Generally, bleaching improved as the temperature rose from room temperature (i.e. 25 °C) up to about 43 °C, but showed no statistical difference between 43 °C and 75 °C based on a Student comparative T-test and an ANOVA analysis. A plot of the brightness versus kappa number for the different temperatures showed that both the room temperature (25 °C) and elevated temperatures (50 to 80 °C aimed/43 to 75 °C actual) were not statistically different from each other, which suggested no change to the reaction mechanisms involved at higher temperatures, but rather only an acceleration of the existing mechanism. Pulp strength (i.e. pulp viscosity) showed a small to moderate drop as the temperature rose.

As regards pulp suspension consistency, the extent of delignification by photochemical bleaching dropped from about 57 to 48% as the consistency rose from 0.5 to 1.5%, whereafter it plateaued as the consistency was increased up to 3.0%. This reduced photobleaching efficiency was due to the increasing opaqueness of the pulp suspension with increased pulp consistency. As the consistency was increased, a point was reached where the suspension was sufficiently thick, such that the light did not penetrate beyond the top layer of the suspension. This created the observed brightness/kappa number plateauing effect. Thereafter, adequate continuous mixing of the whole pulp suspension became impossible with the present reactor set-up used, not allowing any further proper analysis above the maximum tested consistency of 3.0%. Pulp viscosity and pulp yield were mostly maintained across the entire consistency range.

A number of photocatalysts were subjected to initial testing (i.e. the photodegradation of hydrogen peroxide in solution). The list of photocatalysts so tested included titanium dioxide, cerium dioxide,

bismuth trioxide, tungsten trioxide, and zinc oxide. Of these, only titanium dioxide and cerium dioxide proved to be potentially viable photocatalysts for the photochemical bleaching of pulp based on a Student comparative T-test and an ANOVA analysis. In subsequent experiments with pulp, both the titanium dioxide and cerium dioxide showed improved alkaline peroxide photochemical bleaching at the longer times of 90 to 120 minutes, using the optimum charge levels of 5.0 and 20.0 kg t⁻¹ respectively. The apparent lack of photocatalytic activity for both titanium dioxide and cerium dioxide at shorter periods (i.e. 45 to 60 minutes) was likely due to the increased opacity of the pulp suspension at the given optimal charges. There were some additional losses in pulp viscosity for titanium dioxide over time, whereas no such loss was observed for cerium dioxide. Last, neither photocatalyst experienced darkening discolouration upon photocatalytic activity making them more desirable as photocatalysts for pulps, particularly titanium dioxide that retained its white colour.

The experimental results for the alkaline oxygen photochemical bleaching of pulp with the photosensitizers methylene blue and rose bengal suggested some small improvement at short time-scales of 15 to 45 minutes based on the Student comparative T-test and the ANOVA analysis. However, control solvent washing experiments (i.e. no irradiation) showed these improvements to be solely an effect of the organic solvent washing process used to remove most of the residual photosensitizers that remained attached to the pulp fibre after, the pulp had been washed with excess water at the end of the alkaline oxygen experiments with photosensitizers.

Generally, the alkaline peroxide photochemical bleaching of various starting pulps gave positive results for delignification. However, the actual outcome varied from pulp to pulp depending on the type and the starting kappa number, which were determined by the fibre source and type of pulping process employed. The starting pulps gave reductions in kappa number from 11.0 to 6.0 for the Cloquet kraft unbleached pulp, from 6.6 to 3.5 for the Ngodwana PHK unbleached pulp, from 14.1 to 8.1 for the Stanger unbleached pulp, from 5.5 to 3.0 for the Saiccor acid sulphite unbleached pulp, from 23.2 to 17.4 for the Gratkorn magnifite unbleached pulp, and from 16.2 to 12.0 for the Somerset continuous kraft unbleached pulp. This represented about a 45% delignification for Cloquet, Ngodwana, Stanger and Saiccor, and about a 28% for Gratkorn and Somerset. Thus, the higher extent of delignification was associated with pulps of lower starting kappa numbers and mostly kraft/soda based pulping processes, while the smaller extent of delignification was associated with pulps with higher starting kappa numbers (including the Gratkorn magnifite pulp which retains more of its lignin content and relies on brightening the lignin rich pulp rather than bleaching it). Pulp strength, as given by pulp viscosity, was mostly maintained, except for the two kraft pulps for Cloquet and Somerset, where small but significant losses were observed.

Comparison of the thermal ECF and TCF bleaching sequences, as opposed to the thermophotochemical TCF bleaching sequence, showed that all three performed adequately, with the thermal ECF and thermophotochemical TCF sequences giving brightness results above the target of 89%, and the thermal TCF underperforming slightly with a final brightness a little below the target (i.e. 85%). The thermal ECF and thermophotochemical TCF sequences gave adequate viscosity results, while the thermal TCF sequence gave a much lower final viscosity result. Pulp yields for all three sequences were as expected. The thermal TCF bleaching sequence gave the poorest overall hand sheet strength properties, followed by better results for the thermal ECF sequence, with the thermophotochemical TCF sequence giving the best hand sheet strength properties. For fibre morphology, the thermophotochemical TCF sequence retained fibre length and had the least generation of fibrillation and fines, while reductions in fibre length were observed for both thermal bleaching sequences together with more fines and fibre fibrillation. The one disadvantage for the thermophotochemical TCF sequence was a retention of pulp curl latency. Thus, the thermophotochemical TCF sequence was shown to be a viable alternative to the thermal ECF and TCF bleaching sequences save for its low operational consistency (i.e. 0.5 versus about 10%).

As regards dissolving pulps, the thermal control ECF bleaching sequence and the thermophotochemical TCF sequence both gave brightness results at or above the target value of 91%, with final viscosity results for both within the specified range of 500 to 560 ml g⁻¹. The kappa numbers for the thermal control sequence were within the expected values at all bleaching stages, although the kappa number of the final thermophotochemical TCF stage was notably higher than the control suggesting the retention of excessive and unwanted lignin content, despite the good brightness development. This excessive lignin content in the thermophotochemical TCF sequence may require a harsher chemical refining stage in future work. Pulp yields for the thermal ECF sequence were within the expected range, but the thermophotochemical TCF sequence gave a final pulp yield lower than the thermal ECF control. Both sequences gave acceptable results for carbohydrate sugar content, alkali solubility and the quick reactivity index. Both sequences showed a notable shift to shorter fibres as expected due to chemical refining of the pulp within the bleaching process.

Evaluation of the kinetic studies undertaken on the three oxidants (alkaline peroxide, pure caustic soda, and alkaline oxygen), employed in this study, indicated that all three oxidants operated via “pseudo” second order reaction kinetics with respect to the extent / rate of delignification, the pulp viscosity, and the pulp brightness when irradiated with the UV LED array at 365 nm. Of these analytical parameters, the extent/rate of delignification and brightness demonstrated the strongest relationships for the three oxidant’s kinetic reaction rates as seen in the significant reductions in kappa number and brightness improvements observed, while the relationship between the pulp viscosity and the kinetic parameters was poor as illustrated by the minimal viscosity reductions observed. In regards the performance of

each oxidant with regards their reaction kinetics, the best reaction kinetics for the extent/rate of lignification and brightness were achieved by alkaline peroxide, followed by alkaline oxygen, with pure caustic soda performing the worst among the three oxidants. Overall, the kinetics studies support findings made from the earlier experimental data and review of the literature, namely, that although all three oxidants employ the hydroxyl radical species for photochemical bleaching, they generated that hydroxyl radical via three different reaction mechanisms. Pure caustic soda employed direct photolysis and hydrogen abstraction of water molecules or hydroxide anions to generate hydroxyl radicals. However, this process is not a favourable chemical process and occurred slowly and at poor quantum yields giving the slowest reaction kinetics. Alkaline oxygen generated the hydroxyl radical via first generation of peroxides from photo-excited oxygen via the peroxy radical, followed by the chemical lysis of those generated peroxides into hydroxyl radicals. This is a significantly more favoured photochemical process than the direct photolysis and hydrogen abstraction of water and hydroxide anions, and gave better reaction kinetics and quicker photochemical bleaching. The alkaline peroxide employed primarily the direct photolysis of hydrogen peroxide into the hydroxyl radicals and was the most photochemically favoured process resulting in the fastest reaction kinetics observed. During Marcoccia's investigation of the photochemical bleaching of pulp via oxygen, Marcoccia noted "pseudo" first order reaction kinetics as opposed to the "pseudo" second order reaction kinetics in this study. The difference in the conditions, apparatus, and charges employed, account for the discrepancies between the two investigations. Lastly, a review of the relationship between the kinetics of the extent / rate of delignification and those for the brightness kinetics supported the above indicated reaction mechanisms.

As discussed in Chapter 2, the molecular structure of lignin is highly complex involving a large variety of different functional groups, chemical bonds, and molecular arrangements. As a result, the number of possible photochemical reactions available to lignin (based on this large variety) is large, and most of these reaction pathways would be followed given that the energy requirements for each are not vastly different from each other. Consequently, it would be impossible to reduce the entire photochemical bleaching process of pulp to one or two specific photochemical reactions with a specific discussion and formulation of the exact reactions' kinetic models of these photochemical reactions. Thus, a proper discussion of the topic on the photochemical bleaching of pulp would involve more generalised discussions around commonly employed and generated photobleaching agents (e.g. hydroxyl radicals, peroxy radicals, etc.) via generalised common pathways (e.g. phenolic pathway, phenacyl pathway, ketyl pathway, etc.) involving all the various functional groups, chemical bonds, and molecular arrangements (e.g. α -carbonyls, α -hydroxy β -ether-4's, α -ether-4's, etc.) rather than narrowing it down to one or two specific reactions.

In conclusion, the overall results from this study showed that the photochemical bleaching of pulp, using an ultraviolet light emitting diode array at 365 nm, is as a viable alternative to thermally-driven bleaching. However, this is conditional on resolving certain technical issues which include increasing the operational consistency from low consistency (i.e. 0.5%) to medium and high consistency (i.e. about 10% and more), and ensuring that the comparative energy efficiency of thermal- versus photo-bleaching favours the use of ultraviolet light over heat (i.e. steam) as an energy source.

CONCLUSION AND RECOMMENDATIONS FOR FUTURE WORK

Of the three light sources evaluated for the photochemical bleaching of pulps (i.e.: solar radiation, MDELs, and UV LED arrays), only the solar radiation (i.e. sunlight) and the UV LED array were viable, while the UV LED array alone proved practical.

The solar bleaching of Cloquet mill pulp (i.e. post-oxygen stage Aspen) gave moderate kappa number reductions for both pure caustic soda and alkaline peroxide, with alkaline peroxide performing better. The application of photocatalysts and other additives (i.e. TiO_2 , Al_2O_3 , CaCO_3 , MgO) gave reduced solar bleaching effects due to the increased opaqueness of the suspension, but, also the improved pulp viscosity, suggesting a pulp protecting effect these materials. Solar bleaching progressed slowly requiring five days of exposure to achieve kappa reductions of 0.5 and 1.0 for pure caustic soda and alkaline peroxide respectively. Overall, while solar bleaching was viable, it was impractically long to be useful.

Due to the lack of appropriate tuning of the microwave cavity between the commercial Primarc MDEL and the Roto SYNTH microwave reactor in which it was placed, an irregular and random ignition pattern was observed up to power levels of 1200 W. Of the four different MDEL reactor designs evaluated (i.e. the flat round-bottom flask combination reactor, immersed sleeve reactor, MDEL core tubular coil combination reactor, and suspended MDEL and “bucket” combination reactor), the suspended MDEL and “bucket” combination reactor design was the most promising. However, during photochemical bleaching of pulp with the suspended MDEL and “bucket” combination reactor design, analysis of variance (ANOVA) of the kappa number and brightness results showed no significant difference between the irradiated experiments and their controls, without irradiation. The kappa number and viscosity showed no notable difference across time, despite the impact of thermal bleaching during microwave heating being clearly evident.

Utilization of the UV LED array in combination with: the oxidants (i) pure caustic soda, (ii) alkaline peroxide, and (iii) alkaline oxygen, was successful in the photochemical bleaching of pulp giving significant bleaching/delignification for all three options. The alkaline peroxide and alkaline oxygen gave the best bleaching performances, with the pure caustic soda option performing more poorly. A student comparative T-test showed that these differences were statistically significant between the three.

In addition, alkaline peroxide gave better brightness development than alkaline oxygen despite delignifying to similar kappa numbers. In all three cases, pulp strength, as indicated by pulp viscosity, was mostly maintained and pulp yield losses were minimal. As suggested by previous reports (Section 2.4), the hydroxyl radical is the main bleaching agent in all three cases, however, the mechanisms for generating it vary according to the three oxidants employed with hydrogen peroxide being the most efficient generator of the hydroxyl radical and pure caustic soda being the least efficient generator, while oxygen is in between the two mechanisms. The thermal contribution to the total bleaching effect was minimal as indicated the low initial and final temperature for all three bleaching options.

For the photochemical bleaching by alkali peroxide, reductions in the pulp lignin content were observed across the entire pH range tested (i.e. acidic to alkaline), with significantly better photochemical bleaching occurring at increasingly alkaline pH values. This is consistent with similar observations made by Marcoccia for photochemical oxygen bleaching [232]. The impact of variable pH on pulp viscosity and yield were minimal. The extent of photochemical bleaching via alkaline peroxide increased linearly with rising UV LED power levels, while pulp strength (as given by pulp viscosity) was mostly maintained. For the impact of temperature, better photochemical alkaline peroxide bleaching at higher temperatures was observed as the temperature increased from room temperature (i.e. 25 °C) to about 43 °C, but showed no statistical difference between 43 °C and 75 °C based on student comparative T-test and ANOVA analyses. In addition, the relationship between brightness and kappa number for the different temperatures showed that the photochemical bleaching reaction mechanism remained the same, regardless of temperature, but, only accelerated the reaction rate of that existing mechanism. Pulp strength showed a moderate reduction as the temperature rose. As the consistency increased from 0.5 to 1.5%, the extent of delignification by photochemical alkaline peroxide bleaching dropped from about 57 to 48% over the same time frame (i.e. 60 minutes), whereafter it plateaued as the consistency was increased to 3.0%. This reduced photobleaching efficiency occurred as a result of an increase in the opaqueness of the pulp suspension at higher consistencies. The pulp viscosity and yield were mostly unchanged across the entire consistency range. Of the various photocatalysts tested for alkaline peroxide bleaching (i.e. titanium dioxide, cerium dioxide, bismuth trioxide, tungsten trioxide, and zinc oxide), only titanium dioxide and cerium dioxide showed a viable potential based on a student comparative T-test and an ANOVA analysis. In later experimental work, both titanium dioxide and cerium dioxide gave improved photochemical bleaching at longer times (90 to 120 minutes) using the optimum charge levels of 5.0 and 20.0 kg t⁻¹ respectively. Viscosity losses were larger for titanium dioxide and cerium dioxide. For the photochemical bleaching of alkali oxygen, neither photosensitizers: methylene blue and rose bengal, showed any significant improvement due to photosensitization processes, with the improvements that were observed being due to organic solvent washing effects on the pulp.

In general, various starting pulps were successfully delignified by the alkaline peroxide photochemical bleaching process, with the final outcome being dependent on the type and the starting kappa number of the pulp. The photochemical bleaching process gave about a 45% delignification for Cloquet, Ngodwana, Stanger, and Saiccor pulps, and about 28% for Gratkorn and Somerset pulps; with the higher extent of delignification associated with the pulps of lower starting kappa numbers and mostly kraft/soda-based pulping processes, and smaller extents of delignification associated with pulps with higher starting kappa numbers. The pulp viscosity, indicating pulp strength, was mostly maintained, except for Cloquet and Somerset pulps, where small but significant losses were observed.

A comparison of the thermal ECF, thermal TCF and thermophotochemical TCF bleaching sequences, gave good brightness development for all three, with the thermal ECF and thermophotochemical TCF sequences being above the target of 89%, and the thermal TCF being below the target (i.e. 85%). Final viscosities for the thermal ECF and thermophotochemical TCF sequences were acceptable, while the thermal TCF sequence gave a much lower final viscosity result. The thermophotochemical TCF sequence giving the best hand sheet strength properties, followed by the thermal ECF sequence, and lastly the thermal TCF bleaching sequence. For fibre morphology, the thermophotochemical TCF sequence retained fibre length and had the lowest levels of fibrillation and fines, while drops in fibre length were observed for both thermal bleaching sequences together with more fines and fibre fibrillation. However, the thermophotochemical TCF sequence did retain higher levels of pulp curl latency. Thus, the thermophotochemical TCF sequence was shown to be a viable alternative to the thermal ECF and TCF bleaching sequences save for its low operational consistency (i.e. 0.5 versus about 10%).

For dissolving pulp bleaching, the thermal control ECF and the thermophotochemical TCF sequences both gave acceptable brightness results (above target: 91%), and final viscosity results within the specified range of 500 to 560 ml g⁻¹. However, the kappa number of the final thermophotochemical TCF stage was notably higher than the control suggesting the retention of excessive and unwanted lignin content, which may require a harsher chemical refining stage in future work. Pulp yields for the thermal ECF sequence were within acceptable ranges, with the thermophotochemical TCF sequence being slightly lower. Both sequences gave acceptable carbohydrate sugar content, alkali solubility and the quick reactivity index results. A notable shift to shorter fibres was observed for both pulps due to chemical refining of the pulp within the bleaching process.

Kinetic studies of the three oxidants (alkaline peroxide, pure caustic soda, and alkaline oxygen) employed in this study utilizing the UV LED array reactor, showed “pseudo” second order reaction kinetics for the extent/rate of delignification, viscosity, and brightness parameters. The extent/rate of delignification and the brightness demonstrated the strongest relationship with regards to the three

oxidants, while that of viscosity was notably less significant. All results illustrated the proposed photochemical mechanism for bleaching involved the use of generated hydroxyl radicals in all three cases, but, the three oxidants generated the hydroxyl radicals via three different mechanisms. These three mechanisms were primarily the direct photolysis of hydrogen peroxide, the photolysis and hydrogen abstraction of water or hydroxide ions, and the generation of peroxide from oxygen via the peroxy radical intermediate followed by the chemolysis of the generated peroxide, for the alkaline peroxide, pure caustic soda, and alkaline oxygen oxidants respectively. The discrepancy between the observed “pseudo” second order reaction kinetics in this study and the “pseudo” first order reaction kinetics in Marcoccia’s investigation were due to differences in the conditions, apparatus, and charges employed in both.

Based on the large number of photochemical reactions possible due to the highly complex molecular structure of lignin (see Chapter 2), and similarly sized energetics of these reactions, the photochemical bleaching of pulp becomes a complex mix of numerous simultaneous reactions resulting in a large number of photochemical products. Consequently, it would be impossible to narrow any photochemical bleaching study of pulp down to a single or two specific photochemical reactions allowing for a very selective and focussed discussion and formulation of the exact reactions’ kinetics models involved. Thus, a proper discussion of the photochemical bleaching of pulp must always involve more generalised discussions around commonly employed and generated photobleaching agents (e.g. hydroxyl radicals, peroxy radicals, etc.) employing generalised common pathways (e.g. phenolic pathway, phenacyl pathway, ketyl pathway, etc.) which involves all the various functional groups, chemical bonds, and molecular arrangements (e.g. α -carbonyls, α -hydroxy β -ether-4’s, α -ether-4’s, etc.).

As indicated in earlier discussion, the overall results from this study showed that the photochemical bleaching of pulp, using an ultraviolet light emitting diode array at 365 nm, is as a technically viable alternative to thermally-driven bleaching. However, for this to be a commercially practical solution certain technical issues must be addressed including increasing the operational consistency from low (i.e. 0.5%) to medium and high consistency (i.e. about 10% and more), while also ensuring that the comparative energy efficiency of thermal- versus photo-bleaching favours the use of ultraviolet light over heat (i.e. steam) as an energy source.

With a view to potential future work the following recommendations are suggested covering the immediate, the short- to medium-term, and long-term futures. The immediate term could be done using existing equipment, the short- to medium-term would require some changes or additions to the existing equipment, while the long-term is completely new research requiring completely new equipment. With regards the immediate future, the following is proposed:

- The UV LED array experiments with alkaline peroxide employed an excessive peroxide charge (i.e. 8.0 kg t^{-1}) to ensure that there would be no shortfall in peroxide charge for any of the experiments undertaken. One of the tasks for future work should be to optimize the hydrogen peroxide charge employed to minimize any waste. Also, the possible impact of poorer photochemical bleaching performance at lower charges must be explored as an excessive peroxide charge may provide a thermodynamic- or concentration-based drive to better bleaching performance.
- Future work must involve a more extensive and in-depth evaluation of various photocatalysts (both those tested and others not tested). Among these must be included photocatalysts that have been doped with various halides, alkali and alkaline earth metals, and other elemental additives to allow for photocatalysis with visible light wavelengths. Each photocatalyst must be tested and optimized for its operational conditions and its application.
- Future work must include an adequately designed and more extensive evaluation of the present (i.e. methylene blue and rose bengal) and other possible photosensitizers. A variety of conditions and applications must be tested and optimized for. A more extensive evaluation of photosensitizers to activate selected photocatalysts using visible rather than ultraviolet light must be investigated.
- The thermophotochemical bleaching TCF sequence for dissolving pulp showed an excessive/elevated lignin content. This excessive lignin is likely to cause problems in the AlkCell generating process, and a means of removing this lignin must be found. In other words, a more intense chemical refining of the dissolving pulp must be undertaken. One such possibility is the cold caustic extraction process (i.e. about 1000 kg for every ton of pulp at about 10% consistency). Future work must evaluate the impact of a cold caustic extraction (CCE) stage for the thermophotochemical TCF sequence.

With regards to the short- to medium-term future, the following is proposed:

- A linear relationship between the radiant intensity and the photochemical bleaching performance was observed in the experimental work undertaken. Future work must examine the impact of significantly higher radiant intensity levels (i.e. UV LED arrays with significantly higher power levels than 8.0 W cm^{-2}). This is required to address the three questions raised during the evaluation of UV LED array intensity/power levels:
 - Question 1: How much can the photobleaching be sped up with a more intense ultraviolet light source (i.e. a UV LED of greater power output than 8.0 W cm^{-2})?
 - Question 2: At what irradiation intensity level would the linear relationship between the power level and the rate of photobleaching effect break-down due to saturation of the process with photonic events?

Question 3: At the point of saturation, would the fundamental photochemical mechanism significantly change?

- Future work must test and quantify the impact over a broader range of consistencies (particularly high consistencies). An operational consistency of 0.5% is not practical for bleaching during commercial operations on any industrial scale. A means of operating easily at consistencies of 5.0 to 10.0% and even higher must be found.
- The present UV LED array employed radiation at a wavelength of 365 nm. Longer and shorter wavelengths may significantly alter the extent of photochemical bleaching. This must be investigated in future work by evaluating the photochemical bleaching effect at different wavelengths over a wide range (i.e. from UVC to blue/violet to green wavelengths).

With regards to the long-term future, the following is proposed:

- Future work must include a proper evaluation of continuous flow thin film reactors at higher consistencies as a method of addressing the increasing opaqueness of pulp suspensions as consistency rises [338].
- The experimental work around the photochemical bleaching of pulp via MDELs (i.e. the Primarc MDEL) was not successful in part due to the microwave irradiation chamber of the Roto SYNTH microwave reactor not being properly calibrated and tuned for the used Primarc MDEL. Future work must evaluate the use of a properly tuned MDEL in a properly designed microwave irradiation chamber for the photochemical bleaching of pulp. The use of microwave focusing metal cones is strongly suggested. The synergistic effects of UV light together with microwave radiation (as noted in Section 2.5.4) must be thoroughly evaluated in this proposed MDEL future work.
- Discharge electrodeless lamps (DELs) can be ignited/induced and kept “burning” by electromagnetic radiation wavelengths other than microwaves (e.g. radio wavelengths). Future work should evaluate such alternatively induced and sustained DELs in the photochemical bleaching of pulp.

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Appendix A

SAPPI SPECIFIC LABORATORY METHODS

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Manual	VISCOSE LABORATORY MANUAL		
Title	DETERMINATION OF VISCOSE REACTIVITY INDEX (BRT Method)		
Document #	VISC TEST 025	Page	1 of 7
Compiled by	TECHNOLOGIST	Rev Date	02/11/2022
Approved by	SCIENTIST II	Rev No.	3

1. Purpose

The purpose of this work instruction is to detail how to determine the reactivity of dissolving pulp based on a gravimetric test method adopted from **BRT**. A high percentage of recovered fibres from the prepared viscose dope indicates a high reactivity index which is representative of a poor performing dissolving pulp and vice versa.

2. Scope

These instructions are applicable to viscose dope generated from all types of dissolving pulps.

3. Reference

LAB TEST 018 – Solubility test method

4. Abbreviations and Definitions

N/A

5. Responsibility and Authority

The Analyst I/II or Technologist is responsible for carrying out the instructions contained in this document. Any deviations from these procedures must be authorised by the Scientist II/ Lead Scientist.

6. PPE Requirements

Heat resistant gloves, acid resistant overalls, safety glasses, nitrile gloves, full/ half ABEK mask and safety shoes.

7. SHEQ Hazard, Risk and Consequence Table

No.	HAZARD	RISK	CONSEQUENCE	Consequence
1.	CS ₂ liquid	Eye contact	Eye irritation	May cause severe eye irritation
		Skin contact	Causes skin irritation.	May be absorbed through the skin in harmful amounts. Prolonged and/or repeated contact may cause defatting of the skin and dermatitis. Dermatitis and vesiculation may result from skin contact with the vapour or liquid.
		Ingestion	May cause digestive tract disturbances.	May cause effects similar to those for inhalation exposure. Aspiration of material into the lungs may cause chemical pneumonitis, which may be fatal. Can cause nervous system damage. Ingestion may cause convulsions, seizures and possible coma.
		Inhalation	May cause respiration disturbances.	Intoxication can involve all parts of the central and peripheral nervous systems including damage to the nerves with paresthesia, muscle weakness, unsteady gait, and tremors. Exposure may accelerate the development or worsen, coronary heart disease.
		Chronic	Chronic exposure may cause coronary heart disease.	Prolonged or repeated exposure can cause psychic abnormalities such as anxiety, depression and excitability. May cause reproductive and fetal effects. Chronic exposure may cause visual disturbances. Repeated exposure may cause central and peripheral nervous system damage and digestive tract disturbances.

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2.	NaOH	Inhalation	Dry/sore throat. Coughing.	Irritation of the respiratory tract. Irritation of the nasal mucous membranes. Possible oedema of the upper respiratory tract. Possible laryngeal spasm/oedema. Risk of lung oedema.
		Skin Contact	Blisters. Caustic burns/corrosion of the skin.	Slow-healing wounds.
		Eye contact	Corrosion of the eye tissue.	Permanent eye damage.
		Ingestion	Dry/sore throat. Nausea. Abdominal pain. Blood in vomit.	Difficulty in swallowing. Possible esophageal perforation. Burns to the gastric/intestinal mucosa. Bleeding of the gastrointestinal tract. Shock.
		Chronic	REPEATED EXPOSURE/CONTACT: Dry skin.	Skin rash/inflammation. Possible inflammation of the respiratory tract. Gastrointestinal complaints.
3.	Acetic acid	Inhalation	Irritation of the respiratory tract.	Irritation of the nasal mucous membranes. Coughing. EXPOSURE TO HIGH CONCENTRATIONS: Corrosion of the upper respiratory tract. FOLLOWING SYMPTOMS MAY APPEAR LATER: Respiratory difficulties. Possible inflammation of the respiratory tract. Risk of pneumonia. Risk of lung oedema.
		Skin contact	Blisters/burns.	Corrosion of the skin.
		Eye contact	Corrosion of the eye tissue.	Permanent eye damage.
		Ingestion	Risk of aspiration pneumonia	Burns to the gastric/intestinal mucosa. Possible esophageal perforation. Blood in vomit. Diarrhoea. Shock. Change in the blood composition. Change in urine composition. Decreased renal function.
		Chronic	Red skin	May stain the skin. Slight irritation. Inflammation/damage of the eye tissue. Dry/sore throat. Possible inflammation of the respiratory tract. Affection/discolouration of the teeth. Gastrointestinal complaints.

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8. Activity

8.1 Reagents / Apparatus

500 mL measuring cylinder
250 mL wide neck Erlenmeyer flask
250 mL beaker
100 mL beaker
25 mL burette
100 mL quick-fit Erlenmeyer flask with stopper
Büchner filtration set up (funnel and flask)
Nylon cloth
Centrifuge – 6000 rpm
Pore 3 sintered crucibles
Vortex
Micropipette with a tip
3 x 50 mL centrifuge tubes
18% NaOH solution
14% NaOH solution
10% acetic acid
1 M NaOH solution
Carbon disulphide (CS₂)
Shaker
Parafilm
Glass stirring rod
Temperature controlled heating magnetic stirrer
50 mL glass beaker

8.2 Analytical Procedure

- 8.2.1 Heat up the temperature controlled magnetic stirrer to 25°C in a fumehood.
- 8.2.2 In a 50 mL glass beaker, place 20 mL of 18% NaOH on the heating magnetic stirrer for about 30 minutes or until the caustic solution reaches 25°C. Verify the temperature of the solution using a thermometer. Cover the beaker with parafilm to prevent the dust particles falling into the solution.
- 8.2.3 The test must be done in duplicate to minimise sources of errors.
- 8.2.4 Tear dissolving pulp into approximately 0.5 x 0.5 mm pieces.

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- 8.2.5 Before weighing the sample on the analytical balance, please make sure the daily verifications have been done and it is thoroughly cleaned before use.
- 8.2.6 Weigh approximately 1.0000 g of dissolving pulp based on equations 1 and 2.

$$A = 100 - \left(\frac{S_{10} + S_{18}}{2} \right) \quad \text{Equation 1}$$

Where: A = alpha cellulose

$$m = \frac{1.647 \times 100 \times 100}{A \times (100 - MC)} \quad \text{Equation 2}$$

m = pulp mass

MC = pulp moisture content

1.647 = constant

- 8.2.7 **Add the torn pulp into the solution and stir with a glass rod every 15 min for an hour.**
- 8.2.8 **Filter the pulp slurry using the Büchner setup with a nylon cloth to drain the steeping caustic.**
- 8.2.9 **Press out the remaining caustic from the alkcell cake with a hand sheet press to obtain a mass of 5.8 – 6.2 g.**
- 8.2.10 **Crumble the pulp cake and carefully place it into the 100 mL Erlenmeyer flask.**
- 8.2.11 **Add with a micropipette 1.5 mL of distilled water and 70 mL of 14% NaOH solution.**
- 8.2.12 **Dosing the pulp slurry with CS₂ should always be done in front of the extraction system with all the required PPE as per below. Record the temperature of the CS₂ room.**
- 8.2.12.1 **Wipe the burette tip using a clean paper towel.**
- 8.2.12.2 **Carefully fill the burette with CS₂ to the 0 mL mark.**
- 8.2.12.3 **Insert the burette tip inside the conical flask containing the sample.**
- 8.2.12.4 **Ensure the burette tip is sufficiently submerged in the pulp slurry and 5 mm above the base of the conical flask at a 45° angle.**
- 8.2.12.5 **Dose the pulp slurry with 0.6 mL of CS₂. This stage should be performed in front of the extractor.**
- 8.2.12.6 **Close the conical flask immediately with a stopper after completing the CS₂ dose. Be careful that the stopper does not pop off. Tighten the stopper with parafilm.**
- 8.2.12.7 **Wipe the burette tip using a clean paper towel.**

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- 8.2.13 Please note that stage from 8.2.14 to 8.2.24 should be performed inside the fume hood with the sash pulled down to the recommended height.
- 8.2.14 Dissolve the pulp solution with continuous shaking on a shaker for 3 hours at 250 rpm. Record the temperature of the fume hood.
- 8.2.15 Transfer the viscose dope into a 250 mL wide neck Erlenmeyer flask and wash the flask with 70 mL deionised water, which is then transferred into the 250 mL Erlenmeyer flask.
- 8.2.16 Place a magnetic stirrer in the flask and stir the solution for 5 minutes to obtain a homogeneous mixture.
- 8.2.17 Transfer 50 mL of the diluted viscose dope into three separate centrifuge tubes.
- 8.2.18 Precipitate the undissolved fibers by centrifuging the tubes for 15 minutes at 6000 rpm.
- 8.2.19 Decant the supernatant into a beaker and add 10 mL of 1M NaOH to each tube and vortex the solution for about 3 minutes.
- 8.2.20 Place the vortexed solution into the centrifuge and precipitate the fibres by centrifuging the solution at 6000 rpm for 15 minutes.
- 8.2.21 Repeat stages 6.3.16 – 6.3.17 until a clear supernatant is obtained.
- 8.2.22 Decant the clear NaOH and add 25 mL of 10% acetic acid in each tube and vortex until a homogeneous solution is obtained.
- 8.2.23 Transfer the solution into a 250 mL beaker and add 3 drops of phenolphthalein indicator and cover with a watch glass.
- 8.2.24 Allow the solution to stand at room temperature for 1 hour.
- 8.2.25 Transfer the solution into a weighed crucible and filter.
- 8.2.26 Wash the fibers in the crucible with 750 mL hot water and filter under vacuum.
- 8.2.27 Place the crucible into an oven set at 70°C and dry the fibres overnight.
- 8.2.28 Weigh out the cooled crucible to determine the reactivity index of the pulp using Equation 3.
- 8.2.29 After all the work has been completed, all the glassware must be washed in the sink that has a fumehood.

$$RI = \frac{UP \times 100 \times 100}{ms \times (100 - MC)} \quad \text{Equation 3}$$

Where: *UP* = weight of undissolved pulp

ms = mass of the sample

MC = moisture content of the pulp

- 8.2.30 Discard the viscose dope according to the waste viscose dope regeneration ISO document (VISC 021).

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9. Records

The log sheet should be signed by the person performing the task. The Technologist/ Project Manager or Scientist I or II needs to sign off to verify the results.

The log sheet must be kept in the respective project file.

10. Attachments

N/A

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Responsibility	Name	Designation	Signature	Date
Originator	Z. Khatshane	Scientist		17.02.2021
Approver	R. Fischer	Fibre Processing Manager		17.02.2021

1. SCOPE

This document describes the procedures to be used for the operation and maintenance of the Lorentzen & Wettre (L&W) FT Plus (FT+) fibre tester (Version 4.2). The L&W FT+ tester is used to determine morphological characteristics of cellulose fibres and fine elements through size criteria. L&W FT+ (Code 912+) has different optics and uses a camera with higher resolution than the L&W 912HW fibre tester (Version 4.01). These features allow for better measurement of small particles present in the pulp, fines or macro fibrils. Up to six beakers containing disintegrated pulp samples can be placed on the sample-changer carousel (Figure 1). After a test is started with the software, the sample is drawn into the tester and diluted to the right concentration for testing. The fibre suspension is pumped through a measuring cell, where it is photographed. The photos are then processed in an image-analysis program for further analysis. For more information see the L&W FT Plus User Guide.

2. SAFETY

- While the operation of the L&W FT+ fibre tester is not considered a high-risk activity, safety shoes, safety glasses and a laboratory coat are required when preparing and analysing samples.

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Responsibility	Name	Designation	Signature	Date
Originator	Z. Khatshane	Scientist		17.02.2021
Approver	R. Fischer	Fibre Processing Manager		17.02.2021

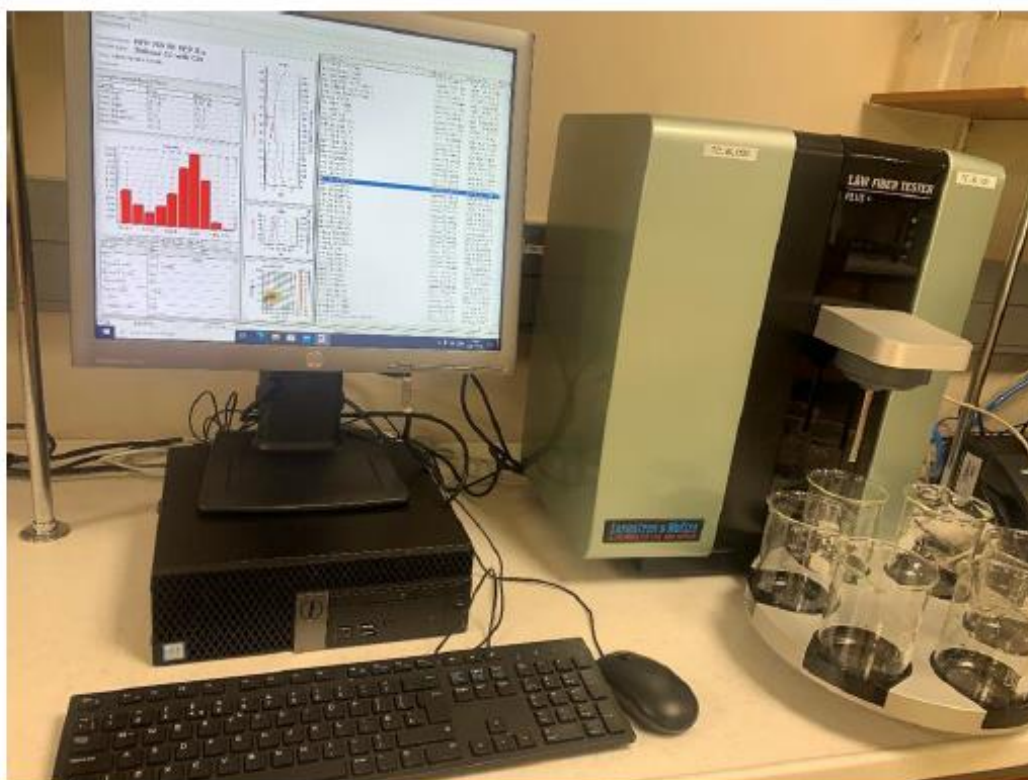


Figure 1: L&W FT+ instrument showing the sample-changer carousel and PC

3. WASTE DISPOSAL

- There is no waste generated.

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4. ENVIRONMENTAL CONTROL

- NEVER move the L&W FT+ fibre tester unit from its current location. Movement will disturb the focus settings of the camera, which in turn will interfere with the calibration settings of the equipment.
- Ensure a clean water supply to the L&W FT+ fibre tester (free from particles greater than 5 µm).
- The water temperature should be controlled between 30 and 40°C.
- Compressed air to the L&W FT+ fibre tester should be clean, dry and free from oil. The compressed air pressure should be 0.5 to 1.0 MPa.

5. INTERFERENCES

The plastic beaker, measuring cylinders and 500 ml glass beakers should be clean and dry. Make sure that the blades of the hand-held blender are not contaminated with a previous pulp sample.

6. EQUIPMENT

For the description of equipment components, see the L&W FT Plus User Guide.

7. CALIBRATION

- Calibration is conducted annually by the supplier.

8. VERIFICATION

Run a test using approximately 0.1 g of any of the reference fibres supplied by Lorentzen & Wettre. Compare the readings with the specified values (Table 1) and contact Lorentzen & Wettre (see Section 8) if two subsequent tests give values outside the specified tolerances.

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Table 1: Reference fibres' specification limits

Reference fibre type	Fibre length (µm)	Fibre width (µm)
Rayon fibre 1mm	1004 ± 20	32.5 ± 0.5
Short fibre	910 ± 30	21.5 ± 0.6
Long fibre	2140 ± 60	28.5 ± 0.5

9. OPERATION

9.1 Classification limits

- A fibre is classified as an object where its shape (percentage projected length / absolute length) is greater than 50.
- Default value (ISO) categorises all particles with a length below 0.2 mm as a fine. Fines are reported as a percentage, based on the proportion of fines to the number of fibres and fines. Fines are also categorised in P-fines (coarser class of fines, primary fines) and S-fines (finer class of fines, secondary fines).
- The shape of a fibre is defined as the projected length divided by the actual length and is expressed as a percentage.
- The kink index is an indication of fibre deformation along the length of a fibre and is expressed in percentage.
- Coarseness is the fibre weight per unit length and is expressed as µg/m. To obtain the coarseness, the actual dry weight of the sample must be known.

9.2 Sample preparation

To analyse a pulp sample using the L&W FT+ fibre tester, add the equivalent to 1 g of oven-dry pulp to 1 L of water, taking into account the consistency of the sample (LQM/PULP/M009). For example, if the consistency is measured to be 91.50%, then 1.09 g of pulp is required:

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$$\text{Wet weight required (g)} = \frac{1 \text{ g} \times 100}{91.50\%} = 1.09 \text{ g}$$

Accurately weigh off the calculated amount of pulp on a balance (to at least two decimal numbers) and transfer the pulp to a 1 L beaker. Add approximately 300 ml water to the sample and briefly use a handheld blender, if necessary, to break up and mix the pulp. Transfer the pulp suspension to a 1 L measuring cylinder, then add approximately 700 ml water to the 1 L mark. Transfer back to the 1 L beaker and weigh off three 100 g samples in 500 ml glass beakers, to obtain three repeats containing 0.1 g of oven-dry pulp each.

9.3 Sample analysis

Switch on the L&W FT+ PC and start the L&W FT+ software on the desktop of the PC. Make sure the water valves are open and compressed air is switched on as shown in Figure 2. Place approximately 110 ml of water in a glass beaker on the sample-changer carousel in the desired position (1 to 6) and the three 0.1 g pulp suspensions on the sample-changer carousel in the desired positions (1 to 6). Enter the sample names in the various carousel positions (1 to 6) in the sample-changer window (red circle in Figure 3), and choose the correct sample type from the drop-down list for each sample (‘Pulp with Crill method’ for fibre and fines analysis or ‘Pulp with shives’ method where shives are required). **Please do not use any special characters e.g. /, “, @ or \$, when entering sample names, leave a space instead.** Click on the edit button for each test to enter the sample weight as 0.1 g (Figure 4). This parameter must be filled in to calculate the coarseness of the samples. Do not tick the boxes asking for ‘save images’ and ‘save vessel images’ as this will take up a large amount of memory and slow the test down. Click on the green arrow to start the test for each individual sample.

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Figure 2 : Main water valve (1), compressed air gage (2) and L&W FT+ water valve (3).

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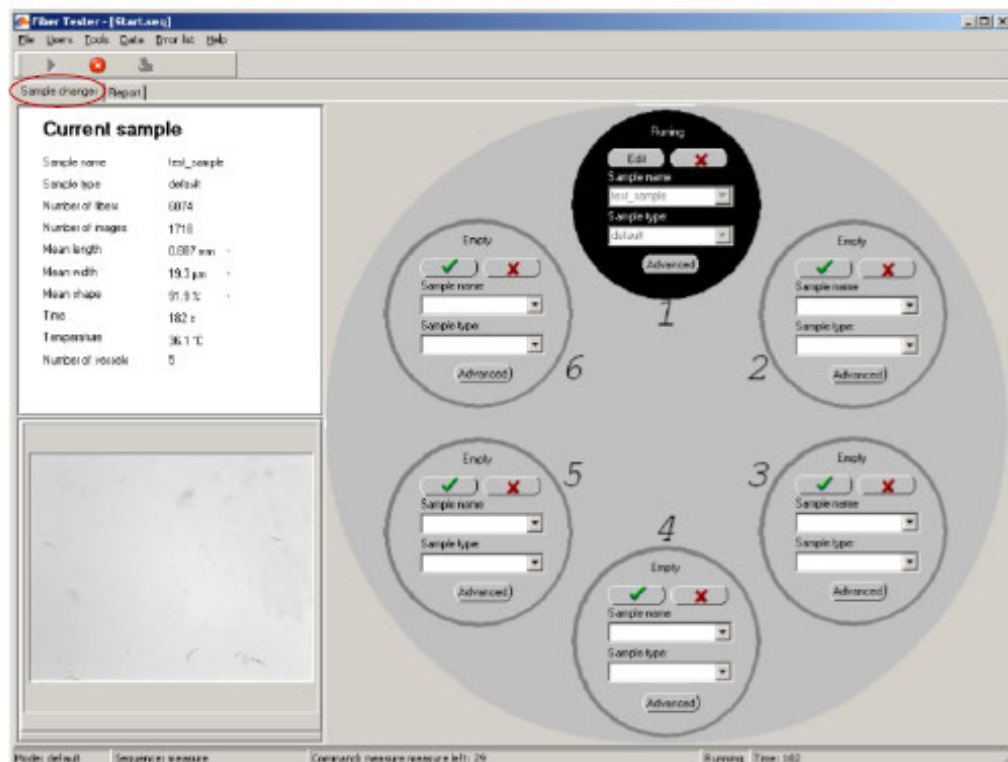


Figure 3: Screenshot indicating the sample-changer window (red circle) with inputs required to run a test.

The test will start automatically, and the sample will be drawn out of the beaker which is automatically flushed a few times to ensure that the entire fibre sample is included in the test. Next, the tester dilutes the sample to the required concentration, the air in the sample is purged by the vacuum pump, and the sample is pumped through a measuring cell.

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The real-time display on the left of the sample-changer window shows the sample ID, the number of fibres detected, the number of images taken and the mean values of the measured properties. The camera images can also be seen. The test is terminated when either the maximum running time has been reached or the minimum number of fibres has been analysed. A complete test cycle, including dilution and flushing, for shives analysis takes about sixteen minutes for a measuring time of approximately 972 seconds.

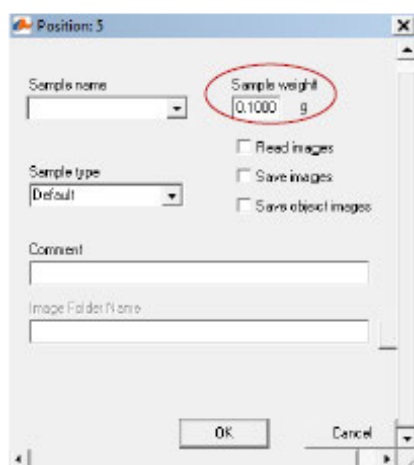


Figure 4: Screenshot indicating the *Advanced* window, requiring sample weight (red circle)

After all the samples are analysed, run a test with 100 ml clean water using the same test conditions as the samples. If less than 100 fibres are detected during the test, the system is considered clean.

9.4 Data export and report

The test readings are saved in a database that is accessible from the *Standard Report* list (right-hand pane on Report tab) for three months (Figure 5). Thereafter, the files will be transferred to an archive database.

Subject: Operation and maintenance of the Lorentzen & Wettre Fiber Tester Plus (L&W FT+)

Sappi Southern Africa
Technology Centre

Reference no	LQM/BIOTECH/P037			
Effective date	26 November 2020	Revision no: 0	Page 9 of 12	
Responsibility	Name	Designation	Signature	Date
Originator	Z. Khatshane	Scientist		17.02.2021
Approver	R. Fischer	Fibre Processing Manager		17.02.2021

Test readings are exported into a single tab-separated text file by selecting all the tests required (press Ctrl then left-click on individual test readings) and then right-clicking on all the readings and selecting *save to file*. The default folder to which the text file will be saved is C:\LorentzenWettre\Fibretester\FT_data. This text file can be saved onto a Sappi controlled USB memory stick for data processing on another computer.

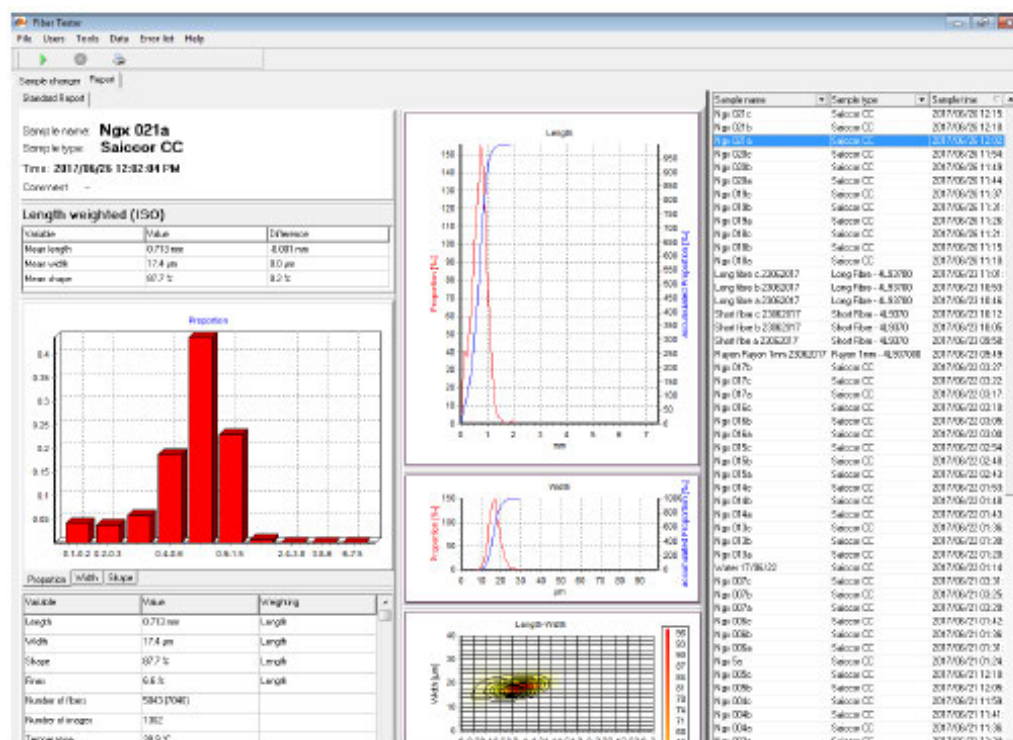


Figure 5: Screenshot indicating Standard Report window.

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Responsibility	Name	Designation	Signature	Date
Originator	Z. Khatshane	Scientist		17.02.2021
Approver	R. Fischer	Fibre Processing Manager		17.02.2021

10. MAINTENANCE

3.1. Cleaning

The system is automatically flushed out between tests to prevent residual fibres and fibre particles from clogging or fouling the circuit. During the flushing process, the gap between the measuring cell discs is increased for maximum effect. The system can be washed with a low-foaming, liquid dishwasher detergent once a day. Place a beaker containing a mixture of 100 to 200 ml of water and 20 ml of a low-foaming, liquid dishwasher detergent onto the carousel, and then run a test as per normal procedure.

Cleaning of the measuring cell should only be conducted by suitably qualified personnel. Meticulous care must be taken during cleaning, as any tiny particles left inside or on top of the measuring cell are likely to cause errors in the readings recorded. Contact the L&W service technician (See Troubleshooting) for assistance.

11. GENERAL INFORMATION

11.1 Trouble shooting

Refer to 'Table B Error Codes' on page 40 of the L&W fibre tester manual when encountering any error on the equipment. Alternatively contact Mattias Lindgren (ABB AB / Lorentzen & Wettre, Sweden) for any other maintenance or trouble shooting required on the L&W fibre analyser software or hardware:

email: [REDACTED]

office: +[REDACTED]

cell: [REDACTED]

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Responsibility	Name	Designation	Signature	Date
Originator	Z. Khatshane	Scientist		17.02.2021
Approver	R. Fischer	Fibre Processing Manager		17.02.2021

For any work done on either the hardware or the software of the L&W FT+ fibre tester, complete the Instrument Maintenance log BIOTECH/W002, located in lab F25.

12. MAINTENANCE

3.2. Cleaning

The system is automatically flushed out between tests to prevent residual fibres and fibre particles from clogging or fouling the circuit. During the flushing process, the gap between the measuring cell discs is increased for maximum effect. The system can be washed with a low-foaming, liquid dishwasher detergent once a day. Place a beaker containing a mixture of 100 to 200 ml of water and 20 ml of a low-foaming, liquid dishwasher detergent onto the carousel, and then run a test as per normal procedure.

Cleaning of the measuring cell should only be conducted by suitably qualified personnel. Meticulous care must be taken during cleaning, as any tiny particles left inside or on top of the measuring cell are likely to cause errors in the readings recorded. Contact the L&W service technician (See Troubleshooting) for assistance.

13. REFERENCES

L&W Fibre Tester User Guide Code 912 ed 4.2 e.

**LABORATORY PROCEDURE****Subject: Operation and maintenance of the Lorentzen & Wettre Fiber Tester Plus (L&W FT+)****Sappi Southern Africa
Technology Centre**

Reference no	LQM/BIOTECH/P037			
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Responsibility	Name	Designation	Signature	Date
Originator	Z. Khatshane	Scientist		17.02.2021
Approver	R. Fischer	Fibre Processing Manager		17.02.2021

REVISION CONTROL SHEET

Page number and section affected	Statement as in previous revision	Statement as in current revision or new additions

Appendix B

RAW DATA

4.1 Solar bleaching of pulps

Table B1: Raw data for control and solar bleaching of pulp with and without photocatalysts and additives.

LABEL		Start	CONTROL										PHOTO. BL.									
		Start 321-322																				
H ₂ O ₂ Charge (Start) kg/ton	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	
NaOH Charge (Start) kg/ton	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	
Retention Time (days)	0.0	0.0	0.25	0.43	1.00	1.42	2.00	3.00	4.00	5.00	5.00	0.25	0.43	1.00	1.42	2.00	3.00	4.00	5.00	5.00	5.00	
Residual H ₂ O ₂																						
Residual H ₂ O ₂ Charge kg/ton	58.1	58.3	48.1	54.9	27.6	43.9	32.6	28.3	0.7	0.7	38.9	46.7	48.9	50.3	43.2	33.3	30.4	0.3	0.7	38.5	38.5	
Residual H ₂ O ₂ (%)	100.0	100.0	82.9	94.5	47.6	75.6	56.1	48.8	1.2	1.2	67.0	80.5	84.1	86.6	74.4	57.3	52.4	0.6	1.2	66.4	66.4	
H ₂ O ₂ Consum. (%)	0.0	0.0	17.1	5.5	52.4	24.4	43.9	51.2	98.8	98.8	33.3	19.5	15.9	13.4	25.6	42.7	47.6	99.4	98.8	33.9	33.9	
End-of-Stage pH value	10.14		10.08	10.16	10.33	10.24	10.24	10.23	10.72	5.29	10.57	9.87	10.21	10.22	9.82	10.01	10.17	10.85	6.34	10.38	10.38	
Kappa Number	8.015	N / A	7.383	7.557	7.308	7.289	7.013	6.867	6.786	6.809	6.943	7.223	7.229	7.079	6.873	6.604	6.223	6.137	6.389	6.149	6.149	
Visc. (CED)	997.2		942	978	972	947	942	902	860	855	938	968	980	961	959	945	887	839	837	955	955	
ADDITIVE / TiO ₂																						
ADDITIVE / Al ₂ O ₃																						
H ₂ O ₂ Charge (Start) kg/ton	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	
NaOH Charge (Start) kg/ton	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	
Retention Time (days)	0.25	0.43	1.00	1.29	2.00	3.00	4.00	5.00	0.25	0.43	1.00	1.29	2.00	3.00	4.00	5.00	5.00	5.00	5.00	5.00	5.00	
Residual H ₂ O ₂																						
Residual H ₂ O ₂ Charge kg/ton	47.5	36.1	41.0	37.5	37.5	35.1	25.0	22.2	49.3	35.4	45.1	38.2	39.6	34.7	29.2	32.3	32.3	32.3	32.3	32.3	32.3	
Residual H ₂ O ₂ (%)	81.9	62.2	70.5	64.6	64.6	60.4	43.0	38.3	84.9	61.0	77.7	65.8	68.1	59.8	50.2	55.6	55.6	55.6	55.6	55.6	55.6	
H ₂ O ₂ Consum. (%)	18.1	37.8	29.5	35.4	35.4	39.6	57.0	61.7	15.1	39.0	22.3	34.2	31.9	40.2	49.8	44.4	44.4	44.4	44.4	44.4	44.4	
End-of-Stage pH value	10.98	10.29	10.92	10.76	10.56	10.10	10.70	10.68	10.87	10.15	10.82	10.75	10.49	9.82	10.63	10.70	10.70	10.70	10.70	10.70	10.70	
Kappa Number	7.470	6.780	7.395	6.846	6.771	6.579	6.344	6.456	7.305	6.821	7.263	6.841	6.755	6.568	6.375	6.236	6.236	6.236	6.236	6.236	6.236	
Visc. (CED)	1001	964	998	997	1003	988	938	955	1002	973	975	1008	989	973	943	929	929	929	929	929	929	

Table B1 cont.: Raw data for control and solar bleaching of pulp with and without photocatalysts and additives.

LABEL	ADDITIVE / CaCO ₃										ADDITIVE / MgO									
	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0
H ₂ O ₂ Charge (Start) kg/ton	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0
NaOH Charge (Start) kg/ton	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0
Retention Time (days)	0.25	0.39	1.00	1.38	2.00	3.00	4.00	5.00	0.25	0.39	1.00	1.38	2.00	3.00	4.00	5.00				
Residual H ₂ O ₂																				
Residual H ₂ O ₂ Charge kg/ton	44.6	46.7	39.0	35.6	38.2	16.0	32.6		43.2	41.8	27.2	46.7	43.0	36.1	41.6	45.1				
Residual H ₂ O ₂ (%)	76.9	80.5	67.2	61.2	65.8	27.5	56.2		74.5	72.1	46.8	80.5	74.1	62.2	71.7	77.7				
H ₂ O ₂ Consum. (%)	23.1	19.5	32.8	38.8	34.2	72.5	43.8		25.5	27.9	53.2	19.5	25.9	37.8	28.3	22.3				
End-of-Stage pH value	11.39	11.32	11.36	11.26	10.84	9.86	10.87		11.36	11.36	11.47	11.34	11.02	10.61	11.06	10.76				
Kappa Number	6.982	7.026	6.690	6.520	6.792	6.205	6.146	6.326	6.865	7.002	6.797	6.615	6.894	6.369	6.615	6.438				
Visc. (CED)	1020	984	977	981	1009	913	957	974	1014	1000	889	994	1001	980	1014	988				

4.2 Microwave Discharge Electrodeless Lamps (MDEL) / Evaluation of various reactor designs

4.2.1. Primarc commercial UV curing lamp: General performance and operational testing of unattached and unshielded (“naked”) MDEL

Table B2: Raw data for general performance and operational testing of unattached/unshielded microwave discharge electrodeless lamp.

	Power (W)	Ig. Time (s)	Power (W)	Ig. Time (s)
Triplicate 1	100	70	700	45
Triplicate 2	100	70	700	40
Triplicate 3	100	70	700	33
Triplicate 1	200	70	800	10
Triplicate 2	200	13	800	5
Triplicate 3	200	70	800	10
Triplicate 1	300	47	900	36
Triplicate 2	300	36	900	17
Triplicate 3	300	6	900	39
Triplicate 1	400	70	1000	4
Triplicate 2	400	70	1000	8
Triplicate 3	400	24	1000	53
Triplicate 1	500	50	1100	18
Triplicate 2	500	70	1100	33
Triplicate 3	500	24	1100	9
Triplicate 1	600	70	1200	46
Triplicate 2	600	17	1200	4
Triplicate 3	600	8	1200	19

Table B3: Raw data for ignition/burn profile of MDEL over time in Roto SYNTH microwave reactor at 1200 W power level.

Time (s)		0	1	2	3	4	5	6	7	8	9	10
Ignition (1 no / 2 yes)	Rotated MDEL Repeat 1	1	2	2	2	2	2	2	2	2	2	2
	Rotated MDEL Repeat 2	1	2	2	2	2	2	2	2	2	2	2
	Rotated MDEL Repeat 3	1	1	1	2	2	2	2	2	2	2	2
	Un-rotated MDEL	1	1	1	1	1	1	2	2	2	2	2
Time (s)		11	12	13	14	15	16	17	18	19	20	
Ignition (1 no / 2 yes)	Rotated MDEL Repeat 1	2	2	2	2	1	1	2	2	1	2	
	Rotated MDEL Repeat 2	2	2	2	1	1	2	2	2	2	1	
	Rotated MDEL Repeat 3	2	2	2	2	2	1	2	2	1	1	
	Un-rotated MDEL	2	2	2	2	2	2	2	2	2	2	
Time (s)		21	22	23	24	25	26	27	28	29	30	
Ignition (1 no / 2 yes)	Rotated MDEL Repeat 1	1	2	1	2	2	2	1	1	1	2	
	Rotated MDEL Repeat 2	1	2	2	2	2	1	1	1	1	1	
	Rotated MDEL Repeat 3	1	1	1	1	1	1	2	2	2	2	
	Un-rotated MDEL	1	1	2	2	2	1	1	2	2	1	
Time (s)		31	32	33	34	35	36	37	38	39	40	
Ignition (1 no / 2 yes)	Rotated MDEL Repeat 1	2	2	2	2	1	1	2	2	1	1	
	Rotated MDEL Repeat 2	2	2	2	1	2	1	2	2	1	1	
	Rotated MDEL Repeat 3	2	2	2	1	1	2	1	2	1	1	
	Un-rotated MDEL	1	2	2	2	2	2	1	1	1	1	
Time (s)		41	42	43	44	45	46	47	48	49	50	
Ignition (1 no / 2 yes)	Rotated MDEL Repeat 1	1	1	2	2	2	1	2	2	1	1	
	Rotated MDEL Repeat 2	2	1	1	1	1	2	2	2	2	1	
	Rotated MDEL Repeat 3	1	2	2	2	1	1	2	2	2	2	
	Un-rotated MDEL	1	1	1	2	2	2	2	1	1	1	
Time (s)		51	52	53	54	55	56	57	58	59	60	
Ignition (1 no / 2 yes)	Rotated MDEL Repeat 1	2	2	2	1	1	2	1	2	1	1	
	Rotated MDEL Repeat 2	1	1	1	1	2	2	2	2	1	1	
	Rotated MDEL Repeat 3	1	2	2	2	2	2	1	1	1	1	
	Un-rotated MDEL	1	1	2	2	2	2	2	1	1	1	
Time (s)		61	62	63	64	65	66	67	68	69	70	
Ignition (1 no / 2 yes)	Rotated MDEL Repeat 1	1	2	2	2	2	1	1	1	2	1	
	Rotated MDEL Repeat 2	1	1	2	2	2	2	2	1	2	1	
	Rotated MDEL Repeat 3	1	2	2	2	1	1	1	1	1	1	
	Un-rotated MDEL	2	2	2	1	1	1	1	1	2	1	

4.2.2. Reactor designs: Roto SYNTH, MDEL, round flat-bottomed flask combination as well as immersed sleeve designs

Table B4: Raw data for ignition time for Roto SYNTH, MDEL, round flat-bottomed flask combination at variable water content levels.

Water level/cond.	Ignition Time (AVE)		
	Triplicate 1	Triplicate 2	Triplicate 3
No Water	8	8	10
1000ml (1/4 covered)	15	12	16
1200ml	>70	>70	>70
1500ml (45% covered)	32	24	38
1900ml (full)	>70	>70	>70

4.2.3. Reactor design: Immersed sleeve

Table B5: Raw data for ignition Roto SYNTH, MDEL, immersed sleeve reactors at variable water content levels.

Water level/cond.	Ignition Time (AVE)		
	Triplicate 1	Triplicate 2	Triplicate 3
Inner (MDEL) / Outer (thick water sheath)	>70	>70	>70
Inner (MDEL) / Outer (thin water sheath)	>70	>70	>70

4.2.4. Reactor design: MDEL core, tubular coil combination

Table B6: Raw data for ignition time of MDEL core, tubular coil combination reactor at variable coil rotations.

Replicates	Number of coils	Ignition Time (s)	Replicates	Number of coils	Ignition Time (s)
Triplicate 1	0	19	Triplicate 1	6	25
Triplicate 2	0	4	Triplicate 2	6	18
Triplicate 3	0	12	Triplicate 3	6	26
Triplicate 1	2	18	Triplicate 1	8	21
Triplicate 2	2	8	Triplicate 2	8	27
Triplicate 3	2	45	Triplicate 3	8	43
Triplicate 1	4	15	Triplicate 1	10	15
Triplicate 2	4	4	Triplicate 2	10	10
Triplicate 3	4	6	Triplicate 3	10	10

Table B7: Raw data for ignition times at 1100 W and 1200 W of MDEL core/tubular coil combination reactor.

	Power (W)	Ig. Time (s)
Triplicate 1	1100	64
Triplicate 2	1100	-
Triplicate 3	1100	-
Triplicate 1	1200	15
Triplicate 2	1200	10
Triplicate 3	1200	10

4.2.5. Reactor design: *Suspended MDEL, “bucket” combination*

Table B8: Raw data for ignition times of suspended MDEL “bucket” combination at variable water content levels.

	Height	Ig. Time (s)
Triplicate 1	Above (~2cm)	20
Triplicate 2		41
Triplicate 3		13
Triplicate 1	Above (Contact)	50
Triplicate 2		52
Triplicate 3		67
Triplicate 1	Semi Submerged ($\frac{1}{2}$ way)	71
Triplicate 2		77
Triplicate 3		74
Triplicate 1	Fully Submerged (just below surface)	73
Triplicate 2		72
Triplicate 3		71
Triplicate 1	Submerged (1 cm)	72
Triplicate 2		84
Triplicate 3		73
Triplicate 1	Submerged (2 cm)	73
Triplicate 2		76
Triplicate 3		73

4.2.6. Photobleaching of pulp utilizing the suspended MDEL, “bucket” combination

Table B9: Raw data for photobleaching of Cloquet unbleached HW control at variable times in the combination Roto SYNTH, MDEL “bucket” reactor (no irradiation/UV LED array nil power).

Bleach sequence	P _Δ	P _Δ	P _Δ	P _Δ	P _Δ	P _Δ	P _Δ	P _Δ	P _Δ	P _Δ
Mass pulp _{OD} (g)	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0
Consistency	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70
Total Weight	2000.0	2000.0	2000.0	2000.0	2000.0	2000.0	2000.0	2000.0	2000.0	2000.0
Mass pulp _{Wet} (g)	39.8	39.8	39.8	39.8	39.8	39.8	39.8	39.8	39.8	39.8
Chemical charge (%):										
NaOH	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80
H ₂ O ₂	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Lamp / Light Source	None	None	None	None	None	None	None	None	None	None
Temperature (°C)	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
Time (Minutes)	1	2	5	10	15	30	45	60	90	120
Triplicate 1										
Final pH	9.82	9.21	9.17	9.56	9.84	10.17	9.40	9.23	9.35	8.87
Initial pH		9.38	9.87	9.77	10.49	10.66	9.67	10.01	10.25	10.08
% Res. on charge (%)	97.5	97.0	100.3	83.2	67.2	30.1	10.3	3.8	1.0	0.3
Kappa Number (ml)	10.77	10.59	10.41	9.71	9.33	8.54	8.91	8.32	8.11	8.69
Viscosity / CED (ml.g ⁻¹)	1070	1113	1101	1040	992	905	847	829	825	839
Temp. (RotoSYNTH) / °C			65	99	109	109	113	113	113	113
Temp. (Actual) / °C	-1.5	-1.5	54.8	84.3	92.9	92.9	96.4	96.4	96.4	96.4
Triplicate 2										
Final pH	9.38	9.67	9.17	9.72	9.88	9.71	9.29	9.71	9.88	9.80
Initial pH	10.14	9.13	9.48	9.92	10.47	9.83	10.28	10.83	10.50	8.87
% Res. on charge (%)	100.8	97.8	95.0	81.0	59.9	25.1	6.5	1.5	0.0	2.4
Kappa Number (ml)	11.00	11.11	10.86	10.30	9.73	8.80	8.57	8.28	8.34	7.64
Viscosity / CED (ml.g ⁻¹)	1129	1127	1111	1062	993	925	868	843	837	879
Temp. (RotoSYNTH) / °C	37	47	75	105	109	111	113	112	112	109
Temp. (Actual) / °C	30.6	39.2	63.5	89.4	92.9	94.6	96.4	95.5	95.5	92.9
Triplicate 3										
Final pH	9.77	9.35	9.69	9.64	9.77	9.73	9.59	9.60	9.4	9.58
Initial pH		9.58	9.45	10.14	10.69	10.71	10.49	9.95	8.9	8.89
% Res. on charge (%)	100.5	97.5	96.8	71.5	45.0	11.2	3.2	2.4	0.7	1.0
Kappa Number (ml)	11.10	10.86	10.81	9.89	9.37	8.72	8.60	8.50	8.11	8.29
Viscosity / CED (ml.g ⁻¹)	1114	1103	1101	1027	990	927	919	896	889	895
Temp. (RotoSYNTH) / °C	36	45	78	105	110	110	110	110	114	115
Temp. (Actual) / °C	29.7	37.5	66.1	89.4	93.8	93.8	93.8	93.8	97.2	98.1

Table B10: Raw data for photobleaching of Cloquet unbleached HW pulp at variable times in the combination Roto SYNTH, MDEL “bucket” reactor (under irradiation/UV LED array 100% power).

Bleach sequence	P _Δ	P _Δ	P _Δ	P _Δ	P _Δ	P _Δ	P _Δ	P _Δ	P _Δ	P _Δ
Mass pulp _{OD} (g)	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0
Consistency	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70
Total Weight	2000.0	2000.0	2000.0	2000.0	2000.0	2000.0	2000.0	2000.0	2000.0	2000.0
Mass pulp _{Wet} (g)	39.8	39.8	39.8	39.8	39.8	39.8	39.8	39.8	39.8	39.8
Chemical charge (%):										
NaOH	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80
H ₂ O ₂	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Lamp / Light Source	Primarc.	Primarc.	Primarc.	Primarc.	Primarc.	Primarc.	Primarc.	Primarc.	Primarc.	Primarc.
Temperature (°C)	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
Time (Minutes)	1	2	5	10	15	30	45	60	90	120
Triplicate 1										
Final pH	9.20	9.24	9.55	9.58	9.69	9.66	9.44	9.93	9.37	9.41
Initial pH	9.73	9.52	9.48	10.13	10.63	10.30	10.17	9.97	10.07	10.17
% Res. on charge (%)	99.7	94.8	95.5	77.3	61.5	24.6	16.5	11.4	0.2	0.0
Kappa Number (ml)	11.10	10.54	9.96	10.10	9.48	8.92	8.43	8.18	8.05	7.89
Viscosity / CED (ml.g ⁻¹)	1102	1116	1080	1066	993	926	884	873	860	888
Temp. (RotoSYNTH) / °C	35	44	76	105	110	115	113	112	115	113
Temp. (Actual) / °C	28.8	36.6	64.3	89.4	93.8	98.1	96.4	95.5	98.1	96.4
Triplicate 2										
Final pH	10.22	10.07	9.73	9.89	9.90	10.23	10.29	9.68	9.73	9.16
Initial pH	10.43	10.52	10.30	10.32	10.38	10.68	10.76	10.41	10.44	10.08
% Res. on charge (%)	97.2	98.0	94.3	84.1	63.9	16.5	5.3	1.9	0.5	0.5
Kappa Number (ml)	11.02	11.05	10.58	9.95	9.59	8.74	8.20	8.26	7.99	8.05
Viscosity / CED (ml.g ⁻¹)	1114	1136	1121	1048	1004	921	863	864	860	838
Temp. (RotoSYNTH) / °C	35	45	75	105	110	110	110	112	114	114
Temp. (Actual) / °C	28.8	37.5	63.5	89.4	93.8	93.8	93.8	95.5	97.2	97.2
Triplicate 3										
Final pH	10.59	9.23	10.18	9.82	9.94	9.37	9.30	9.43	9.35	9.31
Initial pH	10.72	9.53	10.74	10.72	10.74	10.00	10.07	9.98	10.09	10.06
% Res. on charge (%)	96.8	98.0	98.2	78.0	60.8	25.0	9.2	4.4	3.9	2.2
Kappa Number (ml)	10.64	10.79	10.49	9.82	9.26	8.48	8.39	8.33	8.19	6.26
Viscosity / CED (ml.g ⁻¹)	1121	1082	1086	1053	1011	880	865	857	838	844
Temp. (RotoSYNTH) / °C	37	45	75	109	110	115	113	115	113	114
Temp. (Actual) / °C	30.6	37.5	63.5	92.9	93.8	98.1	96.4	98.1	96.4	97.2

4.3 UVet UV led array

4.3.1. Photochemical pulp bleaching with UV LED array: Establishing control blanks for pulp and alkali peroxide solution

Table B11: Raw data for photobleaching of control blanks of Cloquet unbleached HW pulp at variable times in UV LED array reactor (nil irradiation/UV LED array nil power).

Bleach sequence	P _{TEST}	P _{TEST}	P _{TEST}	P _{TEST}	P _{TEST}	P _{TEST}	P _{TEST}	P _{TEST}	P _{TEST}	P _{TEST}
Mass pulp _{OD} (g)	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
Consistency	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Total Weight	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0
Mass pulp _{wet} (g)	56.8	56.8	56.8	56.8	56.8	56.8	56.8	56.8	56.8	56.8
Chemical charge (%):										
NaOH	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80
H ₂ O ₂	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Lamp / Light Source	None	None	None	None	None	None	None	None	None	None
Temperature (°C)	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
Time (Minutes)	1	2	5	10	15	30	45	60	90	120
Triplicate 1										
Final pH	10.76	10.77	10.71	10.81	10.85	10.76	10.89	10.82	10.98	10.93
Initial pH	10.75	10.69	10.61	10.92	10.90	10.62	10.92	10.93	11.23	10.91
Yield %	97.9	97.7	102.2	96.9	95.6	95.8	103.7	97.0	98.9	97.7
% Res. on charge (%)	97.7	101.8	98.1	96.9	96.2	95.4	106.3	96.9	93.9	94.7
Kappa Number (ml)	10.94	10.54	10.76	11.05	10.93	10.96	10.39	9.31	9.15	9.04
Viscosity / CED (ml.g ⁻¹)	1065	1059	1104	1081	969	1075	1165	1127	1161	1092
Triplicate 2										
Final pH	11.06	10.93	11.12	11.10	11.10	10.93	11.14	11.11	11.05	10.92
Initial pH	11.14	11.20	10.97	11.16	11.14	11.17	11.16	11.12	11.05	11.12
Yield %	99.8	99.5	98.9	98.5	96.9	99.6	94.9	98.7	105.2	99.2
% Res. on charge (%)	95.1	101.4	99.2	95.8	95.4	96.6	96.6	95.4	93.6	98.8
Kappa Number (ml)	10.63	10.72	10.55	10.62	10.81	10.69	10.58	10.58	9.15	10.58
Viscosity / CED (ml.g ⁻¹)	1088	1080	1085	1170	1176	1185	1158	1016	1194	1091
Triplicate 3										
Final pH	11.06	10.95	11.00	10.83	11.04	11.24	11.12	11.05	11.04	11.24
Initial pH	11.15	11.14	11.14	11.20	10.83	11.30	11.20	11.15	11.17	11.35
Yield %	104.9	98.0	99.3	95.4	99.1	100.4	100.3	97.9	102.7	101.7
% Res. on charge (%)	93.6	96.2	92.1	96.6	100.3	94.7	96.2	97.3	97.7	96.6
Kappa Number (ml)	11.47	10.81	10.65	10.58	10.60	10.59	10.90	10.70	10.69	10.71
Viscosity / CED (ml.g ⁻¹)	1087	1095	1058	1107	1100	1098	1104	1097	1092	1089

Table B12: Raw data for photobleaching of control blanks on peroxide solution at variable times in UV LED array reactor (nil irradiation/UV LED array nil power).

Bleach sequence	P _{WATER}	P _{WATER}	P _{WATER}	P _{WATER}	P _{WATER}	P _{WATER}	P _{WATER}	P _{WATER}	P _{WATER}	P _{WATER}
Mass pulp _{OD} (g)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Consistency	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Total Weight	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0
Mass pulp _{Wet} (g)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Chemical charge (%):										
NaOH (as per 20 g pulp)	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80
H ₂ O ₂ (as per 20 g pulp)	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Lamp / Light Source	None	None	None	None	None	None	None	None	None	None
Temperature (°C)	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
Time (Minutes)	1	2	5	10	15	30	45	60	90	120
TriPLICATE 1										
Final pH	11.15	11.13	11.19	11.12	11.13	11.13	11.10	10.88	10.97	10.67
Initial pH	11.14	11.11	11.20	11.19	11.19	11.13	11.17	11.14	11.17	11.12
% Resid. on charge (%)	98.9	91.4	98.2	94.8	92.2	92.2	92.2	90.3	93.7	86.1
TriPLICATE 2										
Final pH	10.95	10.91	11.05	10.95	11.05	11.08	10.87	10.58	10.68	10.75
Initial pH	10.20	11.03	11.08	11.06	10.93	11.03	10.98	10.93	10.78	11.05
% Resid. on charge (%)	98.8	98.5	97.8	96.4	94.1	96.1	91.7	97.1	90.3	94.4
TriPLICATE 3										
Final pH	11.04	11.12	11.03	11.08	11.00	10.95	10.85	10.90	10.85	10.69
Initial pH	10.98	11.08	10.91	10.99	10.94	10.96	10.97	10.99	11.02	10.95
% Resid. on charge (%)	99.5	98.1	100.8	98.1	98.5	97.8	95.8	98.5	95.8	92.7

Table B13: Raw data for photobleaching of peroxide solution at variable times in UV LED array reactor (under irradiation/UV LED array 100% power).

BLEACHING	1.20	1.21	1.22		1.02	1.03	1.04	1.05	1.06	1.07	1.08	1.09	1.10	1.11	1.12
Bleach Number	ZERO-1	ZERO-2	ZERO-3	BBS-1	BBS-2	BBS-3	BBS-4	BBS-5	BBS-6	BBS-7	BBS-8	BBS-9	BBS-10	BBS-11	BBS-12
Bleach sequence	P _{WATER}	P _{WATER}	P _{WATER}	P _{WATER}	P _{WATER}	P _{WATER}	P _{WATER}	P _{WATER}	P _{WATER}	P _{WATER}	P _{WATER}	P _{WATER}	P _{WATER}	P _{WATER}	P _{WATER}
Mass pulp _{OD} (g)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Consistency	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Total Weight	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0
Mass pulp _{Wet} (g)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Chemical charge (%):															
NaOH	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80
H ₂ O ₂	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Lamp / Light Source	None	None	None	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED
Temperature (°C)	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
Time (Minutes)	0	0	0	15	30	45	60	15	30	45	60	15	30	45	60
Final pH	10.28	10.28	10.29	10.26	10.18	10.22	10.28	10.19	10.26	10.18	10.37	10.31	10.32	10.30	10.25
Initial pH	10.28	10.28	10.29	10.24	10.20	10.31	10.49	10.31	10.30	10.29	10.51	10.31	10.32	10.33	10.40
Initial Temp. (°C)	26.4	25.9	25.9	24.0	24.4	25.0	25.1	25.5	24.2	25.2	24.3	24.9	22.5	25.6	24.8
Final Temp. (°C)	26.4	25.9	25.9	26.0	29.9	31.0	33.0	27.1	29.3	30.9	31.6	26.9	28.9	31.8	32.1
% Res. on charge (%)	92.1	96.1	94.8	85.9	66.6	43.5	11.2	86.3	68.6	46.9	17.3	86.6	69.6	39.4	10.9

4.3.2. Photochemical bleaching of pulp with UV LED array: Photobleaching effect on pulp in the presence and absence of hydrogen peroxide

Table B14: Raw data for photobleaching of pulp with UV LED array with alkali hydrogen peroxide.

Bleach sequence	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}
Mass pulp _{OD} (g)	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
Consistency	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Total Weight	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0
Mass pulp _{Wet} (g)	56.8	56.8	56.8	56.8	56.8	56.8	56.8	56.8	56.8	56.8
Chemical charge (%):										
NaOH	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80
H ₂ O ₂	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Lamp / Light Source	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED
UV Power level (%)	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%
Temperature (°C)	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
Time (Minutes)	1	2	5	10	15	30	45	60	90	120
Triplicate 1										
Final pH	10.47	10.34	10.34	10.27	10.20	10.26	10.21	10.07	10.05	9.95
Initial pH	10.51	10.41	10.30	10.37	10.33	10.52	10.49	10.42	10.41	10.42
Final Temp (°C)	23.7	23.6	24.5	25.4	26.7	28.2	30.2	33.1	33.9	38.1
Initial Temp (°C)	24.0	23.2	23.7	23.8	24.0	23.7	22.9	24.4	23.0	25.0
Yield %	104.0	97.6	102.2	87.8	101.8	100.7	98.5	103.3	95.7	105.5
% Res.on charge (%)	101.7	99.7	100.4	92.3	100.4	99.7	99.0	95.7	88.9	96.0
Kappa Number (ml)	10.60	10.72	10.40	10.20	8.55	8.07	7.55	7.09	7.43	6.05
Viscosity / CED (ml.g ⁻¹)	1056	1088	1053	1053	1046	1011	1012	987	981	931
Brightness (R457)	40.38	40.25	39.79	40.58	41.94	44.98	47.17	51.00	49.07	62.60
Shade / L*-value	80.95	80.85	80.62	81.07	81.69	83.19	84.16	85.86	84.98	90.03
Shade / a*-value	1.24	1.24	1.16	1.11	1.02	0.79	0.57	0.27	0.46	-0.33
Shade / b*-value	19.90	19.87	20.05	19.83	19.25	18.28	17.50	16.31	16.85	12.10
Triplicate 2										
Final pH	10.01	10.07	10.11	10.07	10.12	10.01	9.95	9.91	9.80	9.66
Initial pH	10.04	10.02	10.18	10.17	10.22	10.18	10.23	10.20	10.29	10.35
Final Temp (°C)	25.8	25.0	25.1	26.6	26.5	29.1	30.9	32.9	35.4	38.5
Initial Temp (°C)	24.0	24.7	24.4	25.1	24.5	24.4	23.2	23.4	23.1	24.3
Yield %	98.7	97.2	102.0	95.2	103.2	104.3	98.9	98.5	98.3	103.0
% Res.on charge (%)	102.8	98.7	101.7	101.1	99.0	100.0	101.4	101.7	96.0	96.7
Kappa Number (ml)	10.45	10.32	10.20	9.92	8.17	7.73	7.30	6.96	6.27	5.87
Viscosity / CED (ml.g ⁻¹)	1063	1079	1058	1056	1048	1003	994	976	943	910
Brightness (R457)	38.84	38.64	39.38	41.25	41.43	45.33	47.31	50.93	57.38	62.72
Shade / L*-value	80.24	80.13	80.49	81.31	81.35	83.21	84.15	85.74	88.19	90.02
Shade / a*-value	1.16	1.16	1.11	1.10	1.03	0.84	0.62	0.36	-0.10	-0.39
Shade / b*-value	20.61	20.65	20.35	19.44	19.28	17.93	17.33	16.16	13.87	11.97
Triplicate 2										
Final pH	10.62	10.60	10.61	10.57	10.56	10.43	10.36	10.31	9.91	9.80
Initial pH	10.63	10.65	10.63	10.61	10.62	10.59	10.60	10.62	10.30	10.35
Final Temp (°C)	23.4	25.0	25.1	25.8	26.6	29.1	31.3	32.9	36.9	38.0
Initial Temp (°C)	24.3	23.5	24.5	23.9	23.8	24.1	24.1	23.5	24.3	24.9
Yield %	97.6	101.6	100.3	101.1	102.5	100.7	104.9	98.9	98.0	103.1
% Res.on charge (%)	100.4	107.1	100.7	99.0	100.7	103.1	101.1	98.7	97.0	96.3
Kappa Number (ml)	10.38	10.36	9.96	10.1	9.92	9.39	7.57	7.04	6.30	5.97
Viscosity / CED (ml.g ⁻¹)	1082	1097	1064	1041	1067	1001	998	978	957	931
Brightness (R457)	38.50	38.33	39.32	41.05	41.13	43.56	46.95	50.11	57.54	63.54
Shade / L*-value	79.97	79.95	80.43	81.25	81.39	82.49	84.07	85.45	88.36	90.35
Shade / a*-value	1.12	1.11	1.10	1.12	0.98	0.82	0.61	0.35	-0.11	-0.45
Shade / b*-value	20.56	20.74	20.30	19.59	19.73	18.74	17.59	16.53	14.01	11.80

Table B15: Raw data for photobleaching of pulp with UV LED array with caustic soda only.

Bleach sequence	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}
Mass pulp _{OD} (g)	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
Consistency	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Total Weight	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0
Mass pulp _{Wet} (g)	56.6	56.6	56.6	56.6	56.6	56.6	56.6	56.6	56.6	56.6
Chemical charge (%):										
NaOH	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80
Lamp / Light Source	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED
UV Power level (%)	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%
Temperature (°C)	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
Time (Minutes)	1	2	5	10	15	30	45	60	90	120
TriPLICATE 1										
Final pH	11.16	11.08	11.01	10.98	10.95	10.93	10.86	10.82	10.70	10.57
Initial pH	11.14	11.09	11.08	11.04	11.07	11.11	11.14	11.15	11.16	11.09
Final Temp (°C)	23.8	24.5	26.3	27.2	28.3	29.9	31.6	33.0	36.2	38.4
Initial Temp (°C)	23.7	26.2	25.5	26.2	25.6	25.0	23.9	24.2	24.0	24.4
Yield %	101.4	102.6	100.2	104.4	101.0	101.7	101.2	104.0	102.5	94.2
Kappa Number (ml)	10.70	10.60	10.51	10.44	10.23	8.94	8.65	8.46	8.12	7.66
Viscosity / CED (ml.g ⁻¹)	1101	1094	1076	1084	1074	1053	1075	1093	1016	1047
Brightness (R457)	37.94	37.41	37.99	37.57	38.60	35.02	38.51	39.44	41.47	45.55
Shade / L*-value	79.59	79.38	79.58	79.36	79.77	76.93	79.69	80.15	81.15	83.04
Shade / a*-value	1.29	1.30	1.39	1.41	1.52	1.50	1.46	1.38	1.28	1.05
Shade / b*-value	20.61	20.92	20.53	20.67	20.04	20.08	20.00	19.63	18.86	17.39
TriPLICATE 2										
Final pH	11.09	11.09	10.91	10.88	10.85	10.71	10.85	10.79	10.64	10.52
Initial pH	11.09	11.12	10.93	10.90	10.93	10.92	11.19	11.16	11.11	11.07
Final Temp (°C)	23.1	24.4	26.4	26.8	27.8	30.1	31.3	33.0	34.5	37.9
Initial Temp (°C)	22.9	24.1	25.5	25.2	25.5	25.3	24.1	23.6	24.1	24.5
Yield %	104.2	101.0	102.7	99.4	104.2	101.2	101.1	104.5	101.3	104.9
Kappa Number (ml)	10.66	10.42	10.35	10.23	10.20	10.07	8.32	8.11	7.94	7.01
Viscosity / CED (ml.g ⁻¹)	1109	1106	1091	1084	1124	1066	1057	1052	1037	1024
Brightness (R457)	37.13	37.83	37.66	37.04	37.55	38.41	39.58	40.68	42.57	44.82
Shade / L*-value	79.21	79.61	79.49	79.09	79.31	79.65	80.28	80.81	81.71	82.75
Shade / a*-value	1.22	1.22	1.24	1.34	1.40	1.44	1.40	1.36	1.22	1.05
Shade / b*-value	21.00	20.79	20.77	20.90	20.60	20.09	19.69	19.24	18.52	17.69
TriPLICATE 3										
Final pH	10.94	10.95	10.82	10.73	10.66	10.50	10.50	10.30	10.56	10.49
Initial pH	10.92	10.82	10.89	10.78	10.83	10.64	10.74	10.64	11.08	11.08
Final Temp (°C)	25.0	26.6	23.6	24.9	24.3	28.7	31.0	31.6	36.4	37.4
Initial Temp (°C)	24.9	26.3	21.8	23.6	21.8	23.8	23.3	23.3	24.6	24.3
Yield %	98.9	101.1	101.4	99.5	102.4	100.4	100.1	100.2	100.7	105.9
Kappa Number (ml)	10.42	10.68	10.36	10.22	10.19	8.49	8.76	8.33	7.85	7.42
Viscosity / CED (ml.g ⁻¹)	1082	1090	1077	1105	1094	1047	1086	1075	1042	1022
Brightness (R457)	37.21	37.65	37.87	37.85	38.04	38.32	38.68	39.71	42.52	44.39
Shade / L*-value	79.26	79.60	79.41	79.39	79.41	79.47	79.61	80.11	81.67	82.53
Shade / a*-value	1.22	1.12	1.44	1.47	1.49	1.57	1.54	1.48	1.23	1.01
Shade / b*-value	20.98	20.99	20.35	20.34	20.12	19.85	19.65	19.22	18.49	17.80

4.3.3. Photochemical pulp bleaching with UV LED array: Impact of pH on the photobleaching of pulp

Table B16: Raw data for photobleaching of pulp with UV LED array/Impact of pH.

Bleach sequence	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}
Mass pulp _{OD} (g)	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
Consistency	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Total Weight	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0
Mass pulp _{Wet} (g)	56.6	56.6	56.6	56.6	56.6	56.6	56.6	56.6	56.6	56.6
Chemical charge (%):										
NaOH						0.50	1.00	1.80	2.00	3.00
H ₂ O ₂	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
H ₂ SO ₄	3.00	2.00	1.00	0.50						
Lamp / Light Source	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED
UV Power level (%)	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%
Temperature (°C)	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
Time (Minutes)	120	120	120	120	120	120	120	120	120	120
TriPLICATE 1										
Final pH	2.94	3.25	4.57	6.22	6.79	8.63	9.56	9.99	10.00	10.28
Initial pH	2.85	3.06	3.54	3.99	6.21	9.66	10.22	10.53	10.57	10.86
Final Temp (°C)	35.7	35.6	36.4	35.1	36.2	36.1	35.1	35.4	36.1	35.1
Initial Temp (°C)	23.4	23.4	23.4	20.7	23.0	23.1	23.5	22.9	23.2	20.6
Yield %	99.5	99.3	100.7	105.0	101.5	102.6	100.9	98.1	98.5	102.0
% Res. on charge (%)	98.1	97.7	99.4	98.7	101.1	99.1	96.8	95.8	100.7	93.8
Kappa Number (ml)	8.32	8.25	8.28	7.404	7.513	6.63	7.55	6.45	5.88	5.49
Viscosity / CED (ml.g ⁻¹)	902	907	831	840	886	937	929	931	935	931
Brightness (R457)	43.05	43.23	43.81	43.83	45.33	55.44	59.51	62.04	62.83	63.08
Shade / L*-value	81.24	81.37	81.58	82.14	82.93	87.37	88.51	89.41	89.72	89.83
Shade / a*-value	3.24	3.17	3.03	1.11	0.95	0.18	1.30	1.02	0.97	0.91
Shade / b*-value	17.69	17.69	17.35	17.77	17.41	14.35	12.76	11.91	11.72	11.68
TriPLICATE 2										
Final pH	2.93	2.88	4.45	6.40	7.18	9.23	9.65	10.02	10.08	10.25
Initial pH	2.82	2.80	3.45	4.31	8.21	10.06	10.29	10.57	10.65	10.83
Final Temp (°C)	35.2	35.6	34.4	35.1	36.2	34.2	33.9	34.4	33.8	36.2
Initial Temp (°C)	21.6	22.7	19.9	20.7	22.2	18.8	20.8	22.0	20.1	21.9
Yield %	99.1	98.6	101.5	101.1	101.2	100.6	99.8	100.7	101.6	100.3
% Res. on charge (%)	101.1	100.4	106.0	105.4	107.7	100.4	97.1	98.4	95.8	94.8
Kappa Number (ml)	8.232	8.527	8.01	8.68	8.09	6.66	6.10	5.64	5.67	5.53
Viscosity / CED (ml.g ⁻¹)	917	913	892	915	958	965	950	950	935	955
Brightness (R457)	43.78	43.28	43.58	44.50	49.91	56.43	59.99	61.11	62.30	63.01
Shade / L*-value	81.71	81.56	81.64	81.96	84.62	87.78	89.16	89.53	89.91	90.25
Shade / a*-value	3.16	3.24	3.05	2.83	2.35	0.12	-0.22	-0.31	-0.31	-0.42
Shade / b*-value	17.64	17.95	17.73	17.22	15.74	14.08	13.04	12.60	12.15	12.09
TriPLICATE 3										
Final pH	2.88	3.20	4.54	6.46	7.30	9.12	9.63	10.07	10.16	10.36
Initial pH	2.79	2.98	3.41	4.09	8.36	9.91	10.03	10.69	10.72	10.88
Final Temp (°C)	33.5	33.7	35.1	36.3	33.9	34.2	35.5	32.9	35.6	35.8
Initial Temp (°C)	19.5	20.2	20.9	22.2	19.8	20.7	21.9	18.2	20.7	22.5
Yield %	93.5	100.7	101.1	98.4	102.4	98.8	100.2	100.8	100.0	102.8
% Res. on charge (%)	98.4	103.4	104.4	106.0	105.4	103.4	100.1	97.4	100.4	93.4
Kappa Number (ml)	7.04	7.25	7.29	7.37	8.27	7.33	6.93	6.78	6.79	6.49
Viscosity / CED (ml.g ⁻¹)	935	931	889	912	975	964	949	945	944	946
Brightness (R457)	43.24	42.99	43.68	44.33	51.03	57.53	60.14	60.44	61.00	62.69
Shade / L*-value	81.57	81.32	81.67	81.92	85.03	87.79	88.74	88.85	89.08	89.70
Shade / a*-value	3.23	3.18	3.01	2.85	2.24	1.51	1.27	1.15	1.10	1.00
Shade / b*-value	18.02	17.90	17.68	17.35	15.28	13.44	12.56	12.45	12.32	11.80

4.3.4. Photochemical pulp bleaching with UV LED array: Impact of UV LED array power levels on the photochemical bleaching of pulp

Table B17: Raw data for photobleaching of pulp with UV LED array/Impact of power level.

Bleach sequence	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}
Mass pulp _{OD} (g)	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
Consistency	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Total Weight	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0
Mass pulp _{wet} (g)	56.6	56.6	56.6	56.6	56.6	56.6	56.6	56.6	56.6	56.6
Chemical charge (%): NaOH	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80
H ₂ O ₂	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Lamp / Light Source	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED
UV Power level (%)	10%	20%	30%	40%	50%	60%	70%	80%	90%	100%
Temperature (°C)	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
Time (Minutes)	120	120	120	120	120	120	120	120	120	120
TriPLICATE 1										
Final pH	10.12	10.06	10.07	10.04	10.06	9.93	9.93	9.83	9.92	9.78
Initial pH	10.22	10.35	10.44	10.31	10.28	10.41	10.47	10.22	10.47	10.29
Final Temp (°C)	23.7	23.9	26.4	27.6	29.4	31.3	32.7	34.0	33.3	35.7
Initial Temp (°C)	21.4	20.5	20.9	21.3	21.9	22.6	22.5	23.4	19.9	22.1
Yield %	100.5	102.2	103.4	101.0	101.2	101.1	103.9	100.4	99.1	100.8
% Res. on charge (%)	102.2	100.0	100.4	105.6	98.9	102.6	100.0	103.4	100.0	101.1
Kappa Number (ml)	7.96	7.55	7.63	7.15	6.92	6.70	6.28	6.09	6.26	6.21
Viscosity / CED (ml.g ⁻¹)	1012	996	933	960	961	902	924	1068	916	912
Brightness (R457)	45.24	47.28	49.54	49.88	51.08	53.08	57.83	59.33	58.94	61.84
Shade / L*-value	83.25	83.66	85.14	85.28	85.85	86.69	88.39	89.00	88.87	89.89
Shade / a*-value	0.77	2.41	0.46	0.44	0.32	0.16	-0.13	-0.24	-0.25	-0.45
Shade / b*-value	18.10	17.03	16.61	16.49	16.20	15.57	13.77	13.38	13.63	12.57
TriPLICATE 2										
Final pH	10.18	10.12	10.06	10.12	10.07	9.98	10.04	9.98	9.70	9.65
Initial pH	10.38	10.45	10.46	10.42	10.43	10.38	10.46	10.37	10.50	10.22
Final Temp (°C)	24.1	26.5	27.7	27.7	27.6	30.0	31.4	33.4	32.7	35.5
Initial Temp (°C)	21.0	21.8	22.4	21.7	21.7	21.1	21.1	21.9	20.3	20.4
Yield %	102.2	100.8	97.6	97.5	102.9	103.4	102.7	102.2	99.8	99.2
% Res. on charge (%)	104.1	104.5	104.1	101.9	101.9	100.7	95.9	100.4	96.6	100.0
Kappa Number (ml)	8.00	7.78	7.44	7.28	6.97	6.78	6.63	6.32	6.22	6.15
Viscosity / CED (ml.g ⁻¹)	945	979	993	943	1001	922	918	990	917	912
Brightness (R457)	44.93	46.72	49.13	52.02	53.50	55.67	58.30	59.67	60.32	62.10
Shade / L*-value	83.21	84.00	85.17	86.35	86.88	87.69	88.55	89.08	89.31	89.89
Shade / a*-value	0.73	0.61	0.36	0.20	0.11	-0.05	-0.14	-0.22	-0.29	-0.36
Shade / b*-value	18.40	17.72	17.10	16.09	15.48	14.69	13.61	13.19	12.99	12.32
TriPLICATE 3										
Final pH	10.22	10.08	10.16	10.03	10.04	10.04	10.06	10.07	9.96	10.63
Initial pH	10.19	10.39	10.41	10.33	10.35	10.40	10.56	10.59	10.38	10.44
Final Temp (°C)	25.7	24.1	26.2	26.4	28.0	30.1	30.1	32.1	33.4	34.5
Initial Temp (°C)	23.1	20.6	20.3	18.9	19.7	20.0	19.8	20.9	21.4	21.5
Yield %	100.6	101.2	98.8	100.3	101.4	102.3	100.8	98.4	97.5	98.1
% Res. on charge (%)	103.4	107.1	107.9	106.4	102.2	97.7	99.6	95.9	96.2	96.2
Kappa Number (ml)	8.13	7.70	7.45	6.971	6.77	6.56	6.42	6.23	6.12	5.95
Viscosity / CED (ml.g ⁻¹)	994	958	963	903	981	961	970	940	969	972
Brightness (R457)	45.03	46.84	48.45	54.14	55.60	57.81	58.98	60.21	61.54	62.72
Shade / L*-value	83.31	84.06	84.77	87.04	87.68	88.49	88.88	89.28	89.77	90.11
Shade / a*-value	0.72	0.60	0.49	0.18	0.06	-0.10	-0.13	-0.20	-0.28	-0.31
Shade / b*-value	18.43	17.69	17.14	15.10	14.73	13.97	13.50	13.02	12.62	12.12

4.3.5. Photochemical pulp bleaching with UV LED array using molecular oxygen gas as oxidant (O₂)

Table B18: Raw data for photobleaching of pulp with UV LED array with alkali oxygen.

Bleach sequence	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}
Mass pulp _{OD} (g)	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
Consistency	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Total Weight	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0
Mass pulp _{Wet} (g)	56.6	56.6	56.6	56.6	56.6	56.6	56.6	56.6	56.6	56.6
Chemical charge (%): NaOH	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80
Lamp / Light Source	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED
UV Power level (%)	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%
Temperature (°C)	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
Time (Minutes)	1	2	5	10	15	30	45	60	90	120
Oxygen Pres. (kPa)	400	400	400	400	400	400	400	400	400	400
Triplicate 1										
Final pH	10.77	10.86	10.65	10.75	10.96	10.88	10.79	10.84	10.70	10.74
Initial pH	11.12	10.82	10.94	10.98	11.09	11.11	11.35	11.10	11.24	11.34
Final Temp (°C)	24.1	24.8	27.2	26.8	26.8	29.1	29.4	33.5	37.6	36.9
Initial Temp (°C)	24.0	24.4	26.7	24.3	24.3	24.5	22.9	24.9	25.9	23.3
Yield %	104.3	101.9	101.5	102.4	97.0	95.2	100.4	101.0	100.8	97.6
Kappa Number (ml)	9.67	9.94	9.44	8.55	8.71	8.41	7.90	7.80	7.23	6.47
Viscosity / CED (ml.g ⁻¹)	1065	1078	1111	1084	1060	1038	1078	1049	1012	981
Brightness (R457)	37.41	37.78	38.32	37.96	37.93	38.80	39.73	42.25	46.55	53.45
Shade / L*-value	79.51	79.56	79.67	79.57	79.47	79.89	80.40	81.65	83.68	86.49
Shade / a*-value	1.18	1.32	1.44	1.39	1.50	1.49	1.39	1.21	0.85	0.32
Shade / b*-value	21.17	20.76	20.24	20.52	20.40	19.99	19.70	18.79	17.34	14.83
Triplicate 2										
Final pH	10.87	11.05	10.69	10.79	10.86	10.84	10.56	10.90	10.85	10.71
Initial pH	10.96	10.94	10.73	10.73	10.97	10.95	11.30	11.31	11.30	11.24
Final Temp (°C)	26.5	26.5	27.4	27.4	27.3	29.2	31.0	34.0	35.0	37.0
Initial Temp (°C)	26.6	26.1	26.7	25.5	25.3	24.5	23.7	25.3	24.4	25.2
Yield %	99.0	101.9	103.4	101.8	101.3	99.5	102.4	98.6	99.5	97.4
Kappa Number (ml)	9.09	9.81	9.63	8.60	8.64	8.27	8.79	7.43	6.87	6.52
Viscosity / CED (ml.g ⁻¹)	1105	1103	1091	1094	1059	1059	1010	1053	962	972
Brightness (R457)	38.66	37.39	37.73	37.90	37.79	38.66	39.59	42.01	47.35	52.89
Shade / L*-value	79.92	79.47	79.49	79.63	79.43	79.80	80.31	81.65	84.02	86.30
Shade / a*-value	1.28	1.27	1.48	1.39	1.52	1.54	1.44	1.18	0.80	0.41
Shade / b*-value	20.27	21.11	20.68	20.71	20.49	20.02	19.71	19.09	17.03	15.09
Triplicate 3										
Final pH	10.83	10.64	10.58	10.97	11.10	10.93	10.89	10.56	10.80	10.71
Initial pH	10.93	10.80	10.76	11.06	11.13	10.98	11.31	11.35	11.30	11.24
Final Temp (°C)	26.4	26.5	28.1	26.1	27.2	30.8	30.2	32.9	35.6	37.5
Initial Temp (°C)	26.9	26.5	27.6	24.7	24.5	25.3	23.8	23.1	24.7	25.8
Yield %	99.2	103.8	99.8	104.0	100.8	101.9	99.1	102.2	101.3	97.6
Kappa Number (ml)	10.20	9.85	9.83	9.09	8.47	8.39	8.00	7.53	6.85	6.55
Viscosity / CED (ml.g ⁻¹)	1068	1080	1060	1068	1030	965	1067	1011	1013	993
Brightness (R457)	37.50	38.27	37.41	38.31	37.72	38.88	40.20	42.39	46.11	52.03
Shade / L*-value	79.60	79.80	79.43	79.74	79.39	79.94	80.64	81.88	83.59	86.05
Shade / a*-value	1.23	1.28	1.36	1.43	1.51	1.47	1.37	1.16	0.82	0.41
Shade / b*-value	21.20	20.54	21.00	20.36	20.51	19.97	19.52	19.04	17.69	15.54

4.3.6 Photochemical pulp bleaching with UV LED array: Impact of temperature on the photochemical bleaching of pulp

Table B19: Raw data for photobleaching of pulp with UV LED array/Impact of variable time at temperature of 70 °C.

Bleach sequence	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}
Mass pulp _{OD} (g)	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
Consistency	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Total Weight	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0
Mass pulp _{Wet} (g)	55.3	55.3	55.3	55.3	55.3	55.3	55.3	55.3	55.3	55.3
Chemical charge (%):										
NaOH	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80
H ₂ O ₂	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Lamp / Light Source	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED
UV Power level (%)	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%
Temperature (°C)	70.0	70.0	70.0	70.0	70.0	70.0	70.0	70.0	70.0	70.0
Time (Minutes)	1	2	5	10	15	30	45	60	90	120
TriPLICATE 1										
Final pH	9.99	9.99	10.00	9.97	10.11	9.92	9.86	9.77	9.83	
Initial pH	9.72	9.95	9.90	9.87	9.88	9.90	9.92	9.98	10.00	9.95
Final Temp (°C)	54.9	54.9	54.6	53.2	55.0	49.0	46.7	60.7	44.4	
Initial Temp (°C)	56.6	58.3	58.0	64.8	62.7	57.4	57.4	60.7	60.9	62.5
Yield %	101.9	97.8	99.9	100.0	101.5	102.0	98.0	98.3	100.5	98.4
% Res. on charge (%)	93.6	89.6	97.0	94.0	89.9	99.1	93.7	88.6	88.6	81.9
Kappa Number (ml)	9.29	9.30	9.01	8.59	8.32	7.99	7.29	6.80	6.41	5.69
Viscosity / CED (ml.g ⁻¹)	1088	1092	1076	1045	1033	1023	1002	958	933	896
Brightness (R457)	39.65	39.27	40.25	43.38	44.66	47.31	50.39	55.41	62.50	68.58
Shade / L*-value	#DIV/0!	80.89	81.35	82.99	83.56	84.66	85.86	87.76	90.20	91.82
Shade / a*-value	#DIV/0!	0.92	0.92	0.65	0.58	0.46	0.32	0.03	-0.30	-0.56
Shade / b*-value	#DIV/0!	21.20	20.77	19.86	19.36	18.22	16.96	15.08	12.48	9.83
TriPLICATE 2										
Final pH	9.96	9.78	10.01	9.88	9.90	9.84	9.68	9.48	9.56	9.97
Initial pH	9.92	9.85	9.94	9.74	9.84	9.72	9.74	9.65	9.66	9.89
Final Temp (°C)	59.2	61.6	57.1	53.8	58.3	48.8	43.7	46.3	45.0	41.6
Initial Temp (°C)	63.1	62.2	61.3	58.8	57.8	59.8	52.4	62.2	60.9	63.5
Yield %	98.4	99.9	100.9	101.4	97.8	101.3	101.4	97.6	101.6	101.8
% Res. on charge (%)	99.8	85.4	85.0	93.4	92.1	25.6	93.4	60.7	56.9	78.0
Kappa Number (ml)	9.33	9.16	9.04	8.65	8.42	7.32	7.72	6.34	5.74	5.44
Viscosity / CED (ml.g ⁻¹)	1080	933	1046	1064	1020	881	997	912	875	863
Brightness (R457)	38.29	38.49	40.06	42.72	44.24	49.90	49.88	59.89	68.17	70.46
Shade / L*-value	80.29	80.39	81.27	82.62	83.34	85.61	85.74	89.21	91.73	92.47
Shade / a*-value	1.02	1.11	0.93	0.72	0.61	0.18	0.27	-0.26	-0.44	-0.51
Shade / b*-value	21.41	21.31	20.86	19.98	19.43	17.07	17.29	13.21	10.03	9.33
TriPLICATE 3										
Final pH	9.87	9.9	9.93	10.01	10	10.05	10.03	10.1	9.95	9.24
Initial pH	9.50	9.85	9.89	9.74	9.49	9.87	9.92	9.92	9.79	9.64
Final Temp (°C)	58.0	57.8	55.3	58.4	51.6	49.3	46.8	46.1	44.1	42.0
Initial Temp (°C)	58.8	59.8	58.6	64.1	64.4	62.0	62.2	62.2	62.0	59.3
Yield %	99.1	100.2	101.1	98.8	100.6	102.2	99.7	102.8	105.5	101.1
Percentage Residual on c	71.0	85.4	64.3	28.1	73.5	78.3	62.3	32.3	51.8	78.0
Kappa Number (ml)	8.99	8.99	8.51	8.01	7.99	7.67	6.66	6.09	5.53	5.57
Viscosity / CED (ml.g ⁻¹)	1012	1052	N / A	949	965	959	920	863	870	850
Brightness (R457)	40.16	39.60	41.67	43.49	46.59	50.72	56.94	61.70	68.55	69.26
Shade / L*-value	81.43	81.07	82.20	83.01	84.39	86.08	88.38	89.96	91.98	92.00
Shade / a*-value	0.64	0.85	0.62	0.59	0.46	0.26	-0.09	-0.30	-0.45	-0.52
Shade / b*-value	21.06	21.10	20.52	19.74	18.59	17.00	14.63	12.81	10.15	9.55

Table B20: Raw data for photobleaching of pulp with UV LED array/Impact of variable temperature at 60 minutes.

Bleach sequence	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}
Mass pulp _{OD} (g)	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
Consistency	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Total Weight	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0
Mass pulp _{Wet} (g)	56.8	56.8	56.8	55.3	55.3	55.3	55.3	55.3	55.3	55.3	55.3	55.3	55.3	55.3	55.3
Chemical charge (%):															
NaOH	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80
H ₂ O ₂	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Lamp / Light Source	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED
UV Power level (%)	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%
Temperature (°C)	25.0	25.0	25.0	50.0	50.0	50.0	60.0	60.0	60.0	70.0	70.0	70.0	80.0	80.0	80.0
Time (Minutes)	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60
Final pH	10.07	9.91	10.31	10.05	10.15	10.17	9.95	10.08	10.11	9.77	9.48	10.10	9.80	9.93	9.79
Initial pH	10.42	10.20	10.62	10.25	10.19	10.19	10.02	10.18	10.09	9.98	9.65	9.92	9.81	9.84	9.80
Final Temp (°C)	33.1	32.9	32.9	38.0	37.3	37.0	41.0	43.3	42.9	60.7	46.3	46.1	47.0	48.0	48.0
Initial Temp (°C)	24.4	23.4	23.5	42.0	42.0	41.3	54.1	53.4	52.7	60.7	62.2	62.2	69.0	74.0	76.0
Yield %	103.3	98.5	98.9	99.8	100.7	101.2	99.9	102.1	102.8	98.3	97.6	102.8	102.5	99.7	104.4
% Res.on charge (%)	90.5	101.7	98.7	87.6	92.1	84.1	61.4	72.3	73.5	88.6	60.7	32.3	64.6	35.5	65.9
Kappa Number (ml)	7.09	9.07	7.04	7.00	6.92	6.94	6.39	6.24	6.34	6.80	6.34	6.09	5.95	6.04	6.09
Viscosity / CED (ml.g ⁻¹)	987	976	978	948	932	932	824	900	898	958	912	863	882	849	896
Brightness (R457)	51.00	50.93	50.11	54.66	54.58	53.34	59.14	58.86	58.33	55.41	59.89	61.70	62.79	60.41	62.19
Shade / L*-value	85.86	85.74	85.45	-	87.35	86.77	88.89	88.87	88.68	87.76	89.21	89.96	90.31	89.43	90.08
Shade / a*-value	0.27	0.36	0.35	-	0.13	0.00	-0.44	-0.17	-0.21	0.03	-0.26	-0.30	-0.26	-0.20	-0.28
Shade / b*-value	16.31	16.16	16.53	-	15.19	15.44	13.37	13.61	13.79	15.08	13.21	12.81	12.40	13.09	12.56

4.3.7 . Photochemical pulp bleaching with UV LED array: Initial calibration and optimization of photocatalysts and photosensitisers

Table B21: Raw data for photodegradation of peroxide solution with and without UV LED array/Initial calibration and optimization – blanks and controls.

Bleach sequence	P _{WATER}	P _{WATER}	P _{WATER}	P _{WATER}	P _{WATER}	P _{WATER}	P _{WATER}
Mass pulp _{OD} (g)	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Consistency	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Total Weight	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0
Mass pulp _{Wet} (g)	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Chemical charge (%):							
NaOH	1.80	1.80	1.80	1.80	1.80	1.80	1.80
H ₂ O ₂	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Catalyst Name	None	None	None	None	None	TiO1	TiO2
Catatyst Charge						0.00	0.00
Lamp / Light Source	None	None	None	None	None	UV LED	UV LED
Temperature (°C)	25.0	25.0	25.0	25.0	25.0	25.0	25.0
Time (Minutes)	0	0	0	30	30	30	30
Final pH	10.75	10.89	10.81	10.68	10.79	10.80	10.64
Initial pH				10.77	10.75	10.67	11.02
Final Temp. (°C)	20.1	19.3	19.6	19.2	19.0	22.5	22.6
Initial Temp. (°C)				19.2	19.0	19.1	18.9
% Res. on charge (%)	100.9	96.4	98.3	99.6	98.0	85.2	90.0

Table B22: Raw data for photodegradation of peroxide solution with UV LED array/Initial calibration and optimization – various photocatalysts.

Bleach sequence	P _{WATER}	P _{WATER}	P _{WATER}	P _{WATER}	P _{WATER}	P _{WATER}	P _{WATER}
Mass pulp _{OD} (g)	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Consistency	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Total Weight	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0
Mass pulp _{Wet} (g)	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Chemical charge (%):							
NaOH	1.80	1.80	1.80	1.80	1.80	1.80	1.80
H ₂ O ₂	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Catatyst Charge	0.10	0.25	0.50	1.00	2.00	4.00	6.00
Lamp / Light Source	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED
Temperature (°C)	25.0	25.0	25.0	25.0	25.0	25.0	25.0
Time (Minutes)	30	30	30	30	30	30	30
Titanium dioxide							
Final pH	10.67	10.79	10.88	10.94	10.97	10.97	10.93
Initial pH	10.79	10.77	10.83	10.76	10.80	10.69	10.83
Final Temp. (°C)	23.0	22.9	23.3	23.7	22.1	21.7	22.4
Initial Temp. (°C)	20.1	19.9	19.1	20.1	18.6	17.8	18.7
% Res. on charge (%)	80.3	65.9	51.4	36.6	42.4	37.0	37.9
Aluimina							
Final pH	10.11	10.01	10.11	10.16	10.37	10.16	10.10
Initial pH	10.38	10.18	10.24	10.21	10.37	10.18	10.20
Final Temp. (°C)	21.9	22.1	22.0	21.9	21.9	20.1	20.4
Initial Temp. (°C)	18.4	18.6	18.4	19.1	18.8	17.9	18.0
% Res. on charge (%)	92.0	81.1	77.3	87.8	84.5	95.0	90.1
Bismuth trioxide							
Final pH	10.14	10.24	10.24	10.23	10.41	9.99	10.06
Initial pH	10.31	10.36	10.42	10.41	10.37	10.04	10.08
Final Temp. (°C)	21.6	22.3	22.1	22.8	22.9	24.2	24.6
Initial Temp. (°C)	18.1	18.2	18.6	18.6	18.8	19.9	19.7
% Res. on charge (%)	87.8	88.2	84.8	51.4	53.7	52.6	43.9
Tungsten trioxide							
Final pH	9.90	9.85	10.02	10.04	10.01	9.91	9.98
Initial pH	9.98	9.88	10.34	10.22	10.14	10.15	10.22
Final Temp. (°C)	24.5	24.3	20.9	21.7	22.4	22.5	23.0
Initial Temp. (°C)	19.5	19.7	17.1	17.0	17.6	17.8	18.3
% Res. on charge (%)	91.2	89.0	102.5	92.0	97.6	98.4	91.6
Zinc Oixde							
Final pH	10.01	10.10	10.19	10.16	9.99	9.90	9.72
Initial pH	10.14	10.24	10.21	10.19	10.19	10.04	9.87
Final Temp. (°C)	23.5	24.2	24.2	24.8	25.4	22.2	22.8
Initial Temp. (°C)	18.7	19.7	20.1	19.9	20.3	17.5	17.8
% Res. on charge (%)	93.1	93.1	89.3	82.6	74.3	73.6	73.2
Cesium dioxide							
Final pH	10.73	10.74	10.68	10.26	10.77	10.71	10.70
Initial pH	10.79	10.78	10.81	10.78	10.74	10.74	10.75
Final Temp. (°C)	24.0	25.2	26.8	26.0	27.0	24.9	25.0
Initial Temp. (°C)	20.7	21.2	22.6	22.5	21.9	20.6	20.0
% Res. on charge (%)	93.1	91.6	89.3	85.2	78.8	71.0	69.4

Table B23: Raw data for photobleaching of pulp with UV LED array/Initial calibration and optimization of photocatalysts and photosensitisers – selected photocatalysts.

Bleach sequence	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}
Mass pulp _{OD} (g)	20.0	20.0	20.0	20.0	20.0	20.0
Consistency	0.50	0.50	0.50	0.50	0.50	0.50
Total Weight	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0
Mass pulp _{Wet} (g)	54.8	54.8	54.8	54.8	54.8	54.8
Chemical charge (%):						
NaOH	1.80	1.80	1.80	1.80	1.80	1.80
H ₂ O ₂	8.00	8.00	8.00	8.00	8.00	8.00
Catatyst Charge	0.25	0.50	1.00	2.00	4.00	6.00
Lamp / Light Source	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED
Temperature (°C)	25.0	25.0	25.0	25.0	25.0	25.0
Time (Minutes)	30	30	30	30	30	30
Titanium dioxide						
Final pH	10.62	10.71	10.63	10.69	10.90	10.94
Initial pH	10.86	10.66	10.83	10.83	10.85	10.86
Final Temp. (°C)	22.4	23.5	22.7	23.0	23.6	23.9
Initial Temp. (°C)	18.1	18.5	18.6	20.0	19.7	19.9
Yield %	96.8	99.0	91.2	96.5	96.2	89.4
% Res. on charge (%)	93.0	88.2	95.2	67.2	55.7	54.2
Kappa Number (ml)	8.11	7.98	8.00	8.05	8.31	8.42
Viscosity / CED (ml.g ⁻¹)	975	968	967	965	1000	1038
Brightness (R457)	44.19	44.53	45.10	44.42	43.02	42.64
Shade / L*-value	82.69	82.83	83.14	82.78	82.15	82.00
Shade / a*-value	0.93	0.89	0.82	0.89	1.01	1.04
Shade / b*-value	18.32	18.18	18.05	18.21	18.77	18.95
Cesium dioixde						
Final pH	10.69	10.75	10.69	10.55	10.63	10.65
Initial pH	10.84	10.85	10.80	10.74	10.81	10.74
Final Temp. (°C)	25.4	27.0	26.9	26.0	26.3	26.6
Initial Temp. (°C)	20.8	21.5	21.9	22.4	21.5	21.7
Yield %	98.3	103.4	99.9	102.4	97.3	99.3
% Res. on charge (%)	99.0	97.1	98.6	91.5	89.6	90.8
Kappa Number (ml)	8.27	8.41	8.31	8.18	8.21	8.19
Viscosity / CED (ml.g ⁻¹)	995	1017	1022	996	1001	1012
Brightness (R457)	43.94	43.77	44.21	45.02	44.84	44.68
Shade / L*-value	82.80	82.75	82.98	83.30	83.29	83.23
Shade / a*-value	0.81	0.80	0.75	0.73	0.66	0.68
Shade / b*-value	18.83	18.95	18.82	18.45	18.64	18.71

Table B24: Raw data for photobleaching of pulp with UV LED array/Initial calibration and optimization of photocatalysts and photosensitisers – selected photosensitizers.

Bleach sequence	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}
Mass pulp _{OD} (g)	20.0	20.0	20.0	20.0	20.0	20.0
Consistency	0.50	0.50	0.50	0.50	0.50	0.50
Total Weight	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0
Mass pulp _{Wet} (g)	57.2	57.2	57.2	57.2	57.2	57.2
Chemical charge (%):						
NaOH	1.80	1.80	1.80	1.80	1.80	1.80
Sensitizers Charge	0.025	0.05	0.125	0.25	0.50	1.00
Lamp / Light Source	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED
Temperature (°C)	25.0	25.0	25.0	25.0	25.0	25.0
Time (Minutes)	30	30	30	30	30	30
Oxygen Pressure (kPa)	400	400	400	400	400	400
Methylene Blue						
Final pH	10.98	11.02	10.90	11.08	10.93	10.96
Initial pH	11.18	10.95	10.97	11.10	11.08	11.07
Final Temp. (°C)	26.9	27.1	25.8	24.4	25.7	26.2
Initial Temp. (°C)	21.9	22.4	21.0	22.3	21.3	21.3
Yield %	98.8	104.5	98.7	105.5	98.1	99.1
Kappa Number (ml)	8.31	8.62	8.96	8.57	8.59	8.44
Viscosity / CED (ml.g ⁻¹)	1067	1094	1050	1038	1019	1054
Brightness (R457)	41.28	41.23	41.02	41.71	40.50	38.16
Shade / L*-value	80.42	79.33	78.73	78.33	76.62	73.34
Shade / a*-value	-1.52	-3.83	-4.85	-6.12	-7.83	-10.53
Shade / b*-value	17.86	16.04	15.26	13.74	12.26	9.52
Rose Bengal						
Final pH	10.41	10.38	10.38	10.19	10.37	10.38
Initial pH	10/91	10.99	10.77	10.53	10.80	10.86
Final Temp. (°C)	29.8	29.8	31.4	28.7	30.1	29.6
Initial Temp. (°C)	25.1	25.2	27.2	23.0	26.2	25.1
Yield %	95.7	101.0	102.2	115.4	99.2	100.7
Kappa Number (ml)	10.01	10.04	10.07	10.02	9.95	10.05
Viscosity / CED (ml.g ⁻¹)	1054	1009	1009	970	940	974
Brightness (R457)	37.09	37.12	36.95	36.73	37.06	37.09
Shade / L*-value	78.31	78.37	78.18	77.68	78.19	78.22
Shade / a*-value	1.93	1.86	1.90	2.05	2.00	2.01
Shade / b*-value	19.40	19.48	19.37	18.79	19.23	19.25

4.3.8. Photochemical pulp bleaching with UV LED array: Application of photocatalysts in the photochemical bleaching of pulp

Table B25: Raw data for photobleaching of pulp with UV LED array/Application of titanium dioxide photocatalyst in the photochemical bleaching of pulp.

Bleach sequence	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}
Mass pulp _{OD} (g)	20.0	20.0	20.0	20.0	20.0	20.0
Consistency	0.50	0.50	0.50	0.50	0.50	0.50
Total Weight	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0
Mass pulp _{Wet} (g)	54.8	54.8	54.8	54.8	54.8	54.8
Chemical charge (%):						
NaOH	1.80	1.80	1.80	1.80	1.80	1.80
H ₂ O ₂	8.00	8.00	8.00	8.00	8.00	8.00
Catalyst Name	TiO ₂	TiO ₂	TiO ₂	TiO ₂	TiO ₂	TiO ₂
Catalyst Charge	0.50	0.50	0.50	0.50	0.50	0.50
Lamp / Light Source	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED
Temperature (°C)	25.0	25.0	25.0	25.0	25.0	25.0
Time (Minutes)	15	30	45	60	90	120
TriPLICATE 1						
Final pH	10.83	10.67	10.59	10.43	10.47	10.08
Initial pH	10.87	10.80	10.81	10.70	10.16	10.63
Final Temp. (°C)	23.1	25.6	24.8	26.0	30.9	31.5
Initial Temp. (°C)	20.5	21.0	18.4	18.0	18.6	18.8
Yield %	96.8	99.0	96.9	98.6	100.9	100.5
% Res. on charge (%)	93.0	80.7	80.3	62.8	37.4	8.6
Kappa Number (ml)	8.56	7.96	7.45	6.87	5.95	5.53
Viscosity / CED (ml.g ⁻¹)	1082	1060	1016	966	860	903
Brightness (R457)	41.28	44.64	48.97	53.15	63.25	67.59
Shade / L*-value	81.21	82.85	84.73	86.55	90.25	91.59
Shade / a*-value	1.11	0.86	0.55	0.22	-0.34	-0.53
Shade / b*-value	19.23	18.10	16.50	15.25	11.86	10.30
TriPLICATE 2						
Final pH	10.78	10.72	10.56	10.52	10.41	10.33
Initial pH	10.88	10.85	10.87	10.85	10.81	10.86
Final Temp. (°C)	22.9	25.5	29.6	30.7	23.1	34.4
Initial Temp. (°C)	20.7	21.4	21.4	21.7	20.5	20.7
Yield %	98.3	97.6	95.7	97.6	96.7	94.2
% Res. on charge (%)	93.0	93.4	85.9	82.2	73.6	47.1
Kappa Number (ml)	8.79	8.14	7.51	6.89	6.41	5.65
Viscosity / CED (ml.g ⁻¹)	1055	967	971	965	926	892
Brightness (R457)	41.67	44.22	48.65	51.92	61.19	66.28
Shade / L*-value	81.64	82.84	84.81	86.22	89.68	91.30
Shade / a*-value	1.00	0.81	0.49	0.22	-0.28	-0.67
Shade / b*-value	19.51	18.55	16.97	15.95	12.81	10.97
TriPLICATE 3						
Final pH	11.17	10.67	10.60	10.54	10.42	10.45
Initial pH	11.19	10.79	10.73	10.79	10.85	10.86
Final Temp. (°C)	23.1	25.7	28.0	28.7	30.9	34.1
Initial Temp. (°C)	20.5	20.8	20.9	20.9	19.9	21.1
Yield %	97.1	96.8	96.1	98.3	99.3	94.4
% Res. on charge (%)	100.9	94.5	91.5	84.4	85.9	67.6
Kappa Number (ml)	8.72	8.12	7.67	7.14	6.51	5.80
Viscosity / CED (ml.g ⁻¹)	1018	980	967	930	939	900
Brightness (R457)	41.47	44.51	48.46	52.72	59.38	66.49
Shade / L*-value	81.70	83.09	84.79	86.58	89.08	91.37
Shade / a*-value	0.87	0.73	0.44	0.21	-0.11	-0.44
Shade / b*-value	19.87	18.66	17.17	15.75	13.48	10.91

Table B26: Raw data for photobleaching of pulp with UV LED array/Application of cerium dioxide photocatalyst in the photochemical bleaching of pulp.

Bleach sequence	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}
Mass pulp _{OD} (g)	20.0	20.0	20.0	20.0	20.0	20.0
Consistency	0.50	0.50	0.50	0.50	0.50	0.50
Total Weight	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0
Mass pulp _{Wet} (g)	57.2	57.2	57.2	57.2	57.2	57.2
Chemical charge (%):						
NaOH	1.80	1.80	1.80	1.80	1.80	1.80
H ₂ O ₂	8.00	8.00	8.00	8.00	8.00	8.00
Catalyst Name	CeO ₂	CeO ₂	CeO ₂	CeO ₂	CeO ₂	CeO ₂
Catatyst Charge	2.00	2.00	2.00	2.00	2.00	2.00
Lamp / Light Source	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED
Temperature (°C)	25.0	25.0	25.0	25.0	25.0	25.0
Time (Minutes)	15	30	45	60	90	120
TriPLICATE 1						
Final pH	10.68	10.62	10.57	10.16	10.47	10.50
Initial pH	10.95	10.81	10.42	11.00	10.84	10.57
Final Temp. (°C)	23.2	25.9	28.1	31.9	33.7	35.3
Initial Temp. (°C)	21.0	21.3	21.0	23.1	21.7	21.0
Yield %	92.6	95.0	86.5	93.6	95.0	96.9
% Res. on charge (%)	85.9	79.2	74.0	69.8	46.3	28.0
Kappa Number (ml)	8.99	8.71	7.70	7.66	6.81	6.05
Viscosity / CED (ml.g ⁻¹)	1083	1064	1005	986	945	906
Brightness (R457)	37.54	39.49	41.82	44.24	50.93	58.23
Shade / L*-value	78.49	79.76	80.96	82.26	85.44	88.30
Shade / a*-value	1.44	1.23	0.98	0.87	0.28	-0.12
Shade / b*-value	19.15	18.89	18.09	17.50	15.63	13.21
TriPLICATE 2						
Final pH	10.09	10.65	10.06	10.60	10.61	10.46
Initial pH	10.24	10.85	10.34	10.64	10.86	11.08
Final Temp. (°C)	23.2	28.6	28.1	31.5	34.7	35.7
Initial Temp. (°C)	20.8	23.3	20.9	23.5	22.5	22.0
Yield %	96.8	97.8	98.2	95.1	93.1	94.9
% Res. on charge (%)	93.4	82.2	71.3	65.4	44.1	33.2
Kappa Number (ml)	9.18	8.71	8.20	7.67	6.72	6.03
Viscosity / CED (ml.g ⁻¹)	1046	1023	990	990	952	882
Brightness (R457)	36.33	38.97	40.37	44.56	50.78	57.79
Shade / L*-value	77.79	79.46	80.23	82.47	85.37	88.14
Shade / a*-value	1.59	1.29	1.16	0.81	0.34	-0.18
Shade / b*-value	19.51	19.00	18.60	17.49	15.67	13.36
TriPLICATE 3						
Final pH	10.40	10.82	10.65	10.42	10.36	10.48
Initial pH	10.49	10.74	10.32	10.71	10.41	10.83
Final Temp. (°C)	24.1	26.2	28.9	31.2	33.4	34.9
Initial Temp. (°C)	21.9	21.8	21.4	22.3	21.9	21.0
Yield %	95.9	94.8	97.1	95.7	97.1	96.5
% Res. on charge (%)	91.5	83.3	77.3	67.2	45.6	30.6
Kappa Number (ml)	9.22	8.53	8.25	8.27	6.90	6.10
Viscosity / CED (ml.g ⁻¹)	1040	1005	989	988	940	909
Brightness (R457)	36.23	38.64	41.06	43.99	51.41	58.16
Shade / L*-value	77.81	79.18	80.66	82.19	85.59	88.31
Shade / a*-value	1.59	1.36	1.06	0.88	0.33	-0.13
Shade / b*-value	19.68	18.95	18.51	17.67	15.39	13.30

4.3.9. Photochemical pulp bleaching with UV LED array: Application of photosensitizers in the photochemical bleaching of pulp

Table B27: Raw data for photobleaching of pulp with UV LED array/Application of methylene blue photosensitizer in the photochemical bleaching of pulp.

Bleach sequence	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}
Mass pulp _{OD} (g)	20.0	20.0	20.0	20.0	20.0	20.0
Consistency	0.50	0.50	0.50	0.50	0.50	0.50
Total Weight	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0
Mass pulp _{Wet} (g)	57.2	57.2	57.2	57.2	57.2	57.2
Chemical charge (%): NaOH	1.80	1.80	1.80	1.80	1.80	1.80
Sensitizers Name	Meth. Blue	Meth. Blue	Meth. Blue	Meth. Blue	Meth. Blue	Meth. Blue
Sensitizers Charge	0.20	0.20	0.20	0.20	0.20	0.20
Lamp / Light Source	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED
Temperature (°C)	25.0	25.0	25.0	25.0	25.0	25.0
Time (Minutes)	15	30	45	60	90	120
Oxygen Pres. (kPa)	400	400	400	400	400	400
TriPLICATE 1						
Final pH	10.50	10.53	10.18	10.00	10.18	10.16
Initial pH	10.94	10.87	10.67	10.53	10.82	10.81
Final Temp. (°C)	24.9	27.6	27.4	31.4	34.8	36.1
Initial Temp. (°C)	22.8	23.1	22.8	23.4	24.0	23.7
Yield %	96.7	96.6	98.9	102.1	96.4	99.7
Kappa Number (ml)	10.70	10.30	8.54	8.21	7.64	7.22
Viscosity / CED (ml.g ⁻¹)	1047	1062	1027	1015	978	934
Brightness (R457)	36.51	35.70	36.72	37.59	41.08	43.07
Shade / L*-value	74.48	72.61	73.34	73.27	75.60	74.88
Shade / a*-value	-6.57	-9.65	-9.09	-9.75	-8.66	-10.79
Shade / b*-value	13.57	11.38	11.31	10.05	9.71	6.08
TriPLICATE 2						
Final pH	10.52	10.48	10.10	9.87	10.11	10.06
Initial pH	10.80	10.85	10.51	10.60	10.44	10.97
Final Temp. (°C)	25.0	28.2	30.1	31.8	34.9	37.1
Initial Temp. (°C)	22.6	24.0	23.2	23.4	23.2	22.7
Yield %	99.0	98.6	97.7	96.5	99.4	98.4
Kappa Number (ml)	10.60	10.10	8.46	8.21	7.75	7.31
Viscosity / CED (ml.g ⁻¹)	998	1001	1003	964	917	934
Brightness (R457)	35.98	36.12	36.64	37.59	39.87	42.83
Shade / L*-value	74.05	73.61	73.35	73.06	73.70	74.72
Shade / a*-value	-7.15	-8.10	-9.09	-10.17	-10.71	-10.65
Shade / b*-value	13.50	12.56	11.42	9.67	7.90	6.06
TriPLICATE 3						
Final pH	10.61	10.33	10.07	10.25	10.40	10.76
Initial pH	10.37	10.69	10.50	11.00	10.62	10.38
Final Temp. (°C)	25.3	27.7	29.7	31.7	35.0	37.3
Initial Temp. (°C)	22.8	23.0	23.3	23.3	23.0	23.2
Yield %	97.8	99.4	99.3	100.4	99.8	98.6
Kappa Number (ml)	10.50	10.10	8.51	8.26	7.78	7.11
Viscosity / CED (ml.g ⁻¹)	1025	1006	995	986	898	972
Brightness (R457)	35.76	35.76	36.53	37.37	39.92	43.48
Shade / L*-value	73.02	73.14	72.87	73.13	73.16	75.06
Shade / a*-value	-9.36	-8.66	-9.84	-9.88	-11.57	-10.70
Shade / b*-value	12.02	12.23	10.73	10.08	6.90	5.91

Table B28: Raw data for photobleaching of pulp with UV LED array/Application of rose bengal photosensitizer in the photochemical bleaching of pulp.

Bleach sequence	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}
Mass pulp _{OD} (g)	20.0	20.0	20.0	20.0	20.0	20.0
Consistency	0.50	0.50	0.50	0.50	0.50	0.50
Total Weight	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0
Mass pulp _{Wet} (g)	57.2	57.2	57.2	57.2	57.2	57.2
Chemical charge (%): NaOH	1.80	1.80	1.80	1.80	1.80	1.80
Sensitizers Name	Rose Beng.	Rose Beng.	Rose Beng.	Rose Beng.	Rose Beng.	Rose Beng.
Sensitizers Charge	0.72	0.72	0.72	0.72	0.72	0.72
Lamp / Light Source	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED
Temperature (°C)	25.0	25.0	25.0	25.0	25.0	25.0
Time (Minutes)	15	30	45	60	90	120
Oxygen Pres. (kPa)	400	400	400	400	400	400
TriPLICATE 1						
Final pH	10.26	10.15	11.09	11.01	10.88	10.36
Initial pH	11.14	10.97	11.15	11.04	11.28	11.13
Final Temp. (°C)	26.0	27.7	29.6	32.1	34.3	34.5
Initial Temp. (°C)	23.3	23.9	22.8	23.3	23.5	23.5
Yield %	102.6	95.5	97.7	97.3	97.2	99.6
Kappa Number (ml)	10.20	9.40	8.71	8.34	7.99	7.08
Viscosity / CED (ml.g ⁻¹)	1077	1061	1027	1015	986	868
Brightness (R457)	35.95	36.70	37.17	37.90	40.58	44.80
Shade / L*-value	77.42	78.01	78.23	78.81	80.09	82.25
Shade / a*-value	1.57	1.98	1.97	1.76	1.73	1.21
Shade / b*-value	19.39	19.41	19.17	19.24	18.09	16.84
TriPLICATE 2						
Final pH	10.74	10.53	11.12	11.14	10.91	10.26
Initial pH	10.75	10.54	11.53	11.50	11.44	10.64
Final Temp. (°C)	24.6	28.0	30.2	32.1	33.4	35.7
Initial Temp. (°C)	23.6	23.5	23.0	23.2	23.3	23.6
Yield %	96.0	98.3	102.2	97.7	101.9	96.8
Kappa Number (ml)	10.10	8.92	8.75	8.54	7.86	7.13
Viscosity / CED (ml.g ⁻¹)	1012	1011	960	987	939	932
Brightness (R457)	36.19	36.98	36.87	37.95	40.46	44.24
Shade / L*-value	77.66	78.22	78.12	78.75	80.16	81.96
Shade / a*-value	1.83	1.96	1.96	1.87	1.68	1.33
Shade / b*-value	19.48	19.40	19.37	19.07	18.37	16.98
TriPLICATE 3						
Final pH	10.65	10.80	11.14	11.10	10.94	10.37
Initial pH	10.85	10.24	11.52	11.43	11.49	10.71
Final Temp. (°C)	27.0	27.0	30.3	31.3	33.5	35.5
Initial Temp. (°C)	24.1	23.0	23.2	23.8	23.0	23.4
Yield %	97.4	95.8	102.6	95.8	98.3	94.5
Kappa Number (ml)	10.10	8.92	8.66	8.39	7.85	7.18
Viscosity / CED (ml.g ⁻¹)	1034	1006	1005	977	957	938
Brightness (R457)	36.30	36.76	37.18	38.39	40.64	44.15
Shade / L*-value	77.68	78.07	78.34	79.01	80.23	81.92
Shade / a*-value	1.67	2.00	1.90	1.83	1.74	1.33
Shade / b*-value	19.37	19.43	19.36	18.95	18.25	17.01

4.3.10. Photochemical pulp bleaching with UV LED array: Impact of variable consistency on the photochemical bleaching of pulp

Table B29: Raw data for photobleaching of pulp with UV LED array/Impact of variable pulp consistency.

Bleach sequence	P _{UV} Cont 1	P _{UV} Cont 2	P _{UV} PULP	P _{UV} PULP	P _{UV} PULP	P _{UV} PULP	P _{UV} PULP	P _{UV} PULP	P _{UV} PULP	P _{UV} PULP
Mass pulp _{OD} (g)	20.0	100.0	30.0	40.0	50.0	60.0	80.0	140.0	120.0	160.0
Consistency	0.50	2.50	0.75	1.00	1.25	1.50	2.00	2.50	3.00	4.00
Total Weight	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0	5600.0	4000.0	4000.0
Mass pulp _{Wet} (g)	57.2	286.1	85.8	114.4	143.1	171.7	228.9	400.6	343.3	457.8
Chemical charge (%):										
NaOH	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80
H ₂ O ₂	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Lamp / Light Source	None	None	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED
UV Power level (%)	0%	0%	100%	100%	100%	100%	100%	100%	100%	100%
Temperature (°C)	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
Time (Minutes)	90	90	90	90	90	90	90	90	90	90
Final pH	9.90	10.18	9.86	9.89	9.96	9.87	9.95	9.90	9.88	9.88
Initial pH	10.21	10.01	10.57	10.49	10.18	10.35	10.18	10.12	10.70	10.19
Final Temp (°C)	23.5	26.7	35.5	35.6	34.4	35.6	33.6	33.0	32.5	33.2
Initial Temp (°C)	24.7	23.9	25.3	23.8	23.1	24.8	24.6	24.0	24.8	25.3
Yield %	97.9	99.4	97.7	101.8	97.7	92.5	98.8	99.4	96.3	99.0
% Res. on charge (%)	101.0	94.0	90.8	92.9	91.8	91.4	86.3	92.4	88.9	89.1
Kappa Number (ml)	8.96	8.76	6.68	6.82	6.94	7.23	7.38	7.28	7.31	6.19
Viscosity / CED (ml.g ⁻¹)	1057	1065	944	964	977	965	973	1035	998	796
Brightness (R457)	38.83	40.90	53.58	52.47	51.92	49.70	49.24	48.07	49.10	56.85
Shade / L*-value	79.50	81.00	86.37	86.04	85.90	85.02	84.94	84.63	84.97	87.46
Shade / a*-value	1.29	0.90	0.18	0.46	0.45	0.57	0.57	0.48	0.57	-0.72
Shade / b*-value	19.29	19.34	14.46	15.02	15.35	16.19	16.55	17.32	16.75	13.11

4.3.11. Photochemical pulp bleaching with UV LED array of various Sappi mill pulps

Table B30: Raw data for photobleaching of various research and mill Sappi pulps with UV LED array.

Bleach sequence	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}	P _{UV PULP}
Pulp	Cloquet paper kraft	Ngodwana PHK pulp	Stanger bagasse pulp	Saic. Dis. viscose pulp	Gratkorn paper pulp	Somerset paper pulp
Mass pulp _{OD} (g)	20.0	20.0	20.0	20.0	20.0	20.0
Consistency	0.50	0.50	0.50	0.50	0.50	0.50
Total Weight	4000.0	4000.0	4000.0	4000.0	4000.0	4000.0
Mass pulp _{Wet} (g)	56.8	74.1	72.5	63.8	58.0	56.9
Chemical charge (%):						
NaOH	1.80	1.80	1.80	1.80	1.80	1.80
H ₂ O ₂	8.00	8.00	8.00	8.00	8.00	8.00
Lamp / Light Source	UV LED	UV LED	UV LED	UV LED	UV LED	UV LED
UV Power level (%)	100%	100%	100%	100%	100%	100%
Temperature (°C)	25.0	25.0	25.0	25.0	25.0	25.0
Time (Minutes)	120	120	120	120	120	120
Final pH	9.80	10.11	10.08	10.07	9.97	10.04
Initial pH	10.37	10.63	10.62	10.62	10.58	10.60
Final Temp (°C)	38.2	33.2	34.5	34.0	35.2	32.4
Initial Temp (°C)	24.7	19.6	20.2	21.4	21.8	18.4
Yield %	103.9	102.0	94.0	103.6	99.8	98.7
% Res. on charge (%)	96.3	86.8	89.8	97.4	90.8	80.5
UNBLEACHED						
Kappa Number (ml)	10.98	6.634	14.072	5.469	23.201	16.187
Viscosity / CED (ml.g ⁻¹)	1089	900	710	694	987	1078
Brightness (R457)	38.96	34.17	22.65	57.59	49.45	27.55
PHOTO-BLEACHED						
Kappa Number (ml)	5.96	3.49	8.06	2.99	17.37	11.21
Delig. Extent (%)	45.7	47.4	42.7	45.3	25.1	30.8
Viscosity / CED (ml.g ⁻¹)	924	855	696	669	934	946
Brightness (R457)	62.95	53.80	33.54	73.55	52.51	42.54

4.3.12. Evaluation of various combined thermophotochemical and thermal bleaching sequences for paper grade pulp

Table B31: Raw data of total chlorine free (TCF) thermo-photochemical bleaching sequence for paper grade pulp/Evaluation of various combined thermo-photochemical and thermal bleaching sequences.

Bleach sequence	Ox _{UV PULP}	P _{UV PULP (0)}	E _{PΔ}	P _{UV PULP (1)}	P _{UV PULP (2)}
Mass pulp _{OD} (g)	20.0 x 18	20.0 x 16	93.3 x 3	20.0 x 12	20.0 x 10
Consistency	0.50	0.50	10.00	0.50	0.50
Total Weight	4000 x 18	4000.0	933.3	4000.0	4000.0
Mass pulp _{Wet} (g)	57.2 x 18	61.9	285.4	63.3	65.0
Chemical charge (%):					
NaOH	1.80	1.80	1.50	1.80	1.80
H ₂ O ₂		8.00	0.90	8.00	4.50
Catalyst Name		TiO ₂			
Catatyst Charge		0.50			
Mg ²⁺	0.20				
Lamp / Light Source	UV LED	UV LED	None	UV LED	UV LED
Temperature (°C)	65.0	65.0	85.0	65.0	65.0
Time (Minutes)	120	90	45	120	60
Oxygen Pres. (kPa)	400				
Final pH	10.31	10.15	11.30	10.85	10.81
Initial pH	10.12	9.97	11.91	10.18	10.21
pH Adjustment Target	>10	>9	>10	>9	>9
Final Temp. (°C)	42.7	42.7	67.4	36.8	43.3
Initial Temp. (°C)	57.4	57.7	42.8	58.4	59.3
Yield %	97.0	96.1	99.9	99.1	97.3
Total Yield (%)	89.7				
% Res. on charge (%)	N / A	54.4	0.0	0.1	0.5
Kappa Number (ml)	7.37	4.39	3.98	3.66	3.75
Viscosity / CED (ml.g ⁻¹)	1003	791	671	598	546
Brightness (R457)	44.85	78.1	81.26	85.11	88.13
ISO Bri. / Before Rev.	45.56	79.67	83.35	89.05	90.64
ISO Bri. / After Rev.	45.09	76.85	80.96	85.82	87.87
Shade / L*-value	-	-	-	-	82.91
Shade / a*-value	-	-	-	-	1.04
Shade / b*-value	-	-	-	-	17.12
Unbl. Kappa	12.013	Unbl. ISO Bri / Before Rev.			34.37
Unbl. Visc./CED (ml.g ⁻¹)	1102	Unbl. ISO Bri / After Rev.			34.42
Unbl. Bri (R457)	34.26	Unbl. Shade / L*-value (R457)			76.35
Time (nil)	0	Unbl. Shade / a*-value (R457)			1.73
		Unbl. Shade / b*-value (R457)			19.8

Table B32: Raw data of elemental chlorine free (ECF) thermal bleaching sequence for paper grade pulp/Evaluation of various combined thermo-photochemical and thermal bleaching sequences.

Bleach sequence	MOX	Z (MC)	D ₀	E _{OP}	D ₁
Mass pulp _{OD} (g)	2000.0	1500.0	120.0 x 3	160.0 x 2	110.0 x 2
Consistency	10.00	12.00	11.0	11.5	11.5
Total Weight	20000.0	12500.0	1090.9 x 3	1391.3 x 2	956.5 x 2
Mass pulp _{Wet} (g)	5722.5	4728.9	401.2 x 3	496.6 x 2	356.4 x 2
Chemical charge (%):					
ClO ₂			1.10		0.35
NaOH	3.30			1.70	
H ₂ O ₂				0.45	
Ozone (%)		0.38			
H ₂ SO ₄		0.65			0.120
Temperature (°C)	85 / 95	<25.0	70.0	77.0	80.0
Time (Minutes)	20 / 50	±10.0	60	120	240
Oxygen Pres. (kPa)	760 / 275			380	
Final pH	12.27	4.66	2.17	10.85	1.36
Start pH	-	-	3.03	-	1.96
pH Adjustment Target	-	-	2.0-2.5	-	3.3 - 3.8
Yield %	98.3	96.8	97.1	100.4	97.5
Total Yield / %	90.6				
% Res. on charge (%)	N / A		N / A	0.0	0.0
Kappa Number (ml)	6.63	5.08	2.80	1.91	0.37
Viscosity / CED (ml.g ⁻¹)	827	798	826	682	577
Brightness (R457)	46.27	52.04	66.31	82.57	86.13
ISO Bri. / Before Rev.	47.71	54.73	72.82	85.78	90.60
ISO Bri. / After Rev.	46.80	53.35	68.43	84.10	88.18
Shade / L*-value	-	-	-	-	82.91
Shade / a*-value	-	-	-	-	1.04
Shade / b*-value	-	-	-	-	17.12
Unbl. Kappa	12.01	Unbl. ISO Bri / Before Rev.			34.37
Unbl. Visc./CED (ml.g ⁻¹)	1102	Unbl. ISO Bri / After Rev.			34.42
Unbl. Bri (R457)	34.26	Unbl. Shade / L*-value (R457)			76.35
Time (nil)	0	Unbl. Shade / a*-value (R457)			1.73
		Unbl. Shade / b*-value (R457)			19.8

Table B33: Raw data of total chlorine free (TCF) thermal bleaching sequence for paper grade pulp/Evaluation of various combined thermo-photochemical and thermal bleaching sequences.

Bleach sequence	MOX	Z (MC)	A	P ₀	E _{OP}	P ₁	P ₂
Mass pulp _{OD} (g)	2000.0	1500.0	135.0 x3	120.0 x 3	160.0 x 2	120.0 x 2	100.0 x 2
Consistency	10.00	12.00	11.0	11.0	11.5	11.5	11.5
Total Weight	20000.0	12500.0	1227.3 x 3	1090.9 x 3	1391.3 x 2	1043.5 x2	869.6 x 2
Mass pulp _{Wet} (g)	5722.5	4728.9	451.4 x 3	359.6 x 3	515.8 x 2	347.5 x 2	357.0 x 2
Chemical charge (%):							
NaOH	3.30			1.50	1.75	1.20	1.50
H ₂ O ₂				1.00	0.50	1.40	2.00
Ozone (%)		0.38					
H ₂ SO ₄		0.65	0.60				
Temperature (°C)	85 / 95	<25.0	65.0	85.0	70.0	80.0	85.0
Time (Minutes)	20 / 50	±10.0	30	60	120	210	210
Oxygen Pres. (kPa)	760 / 275				380		
Final pH	12.27	4.66	2.39	11.94	12.64	11.70	11.65
Start pH	-	-	2.64	11.34	-	10.86	10.99
pH Adjustment Target	-	-	<3.0	>9.0	>10.5	>9.0	>9.0
Yield %	98.3	96.8	99.3	98.8	98.9	97.2	98.2
Total Yield / %	88.1						
% Res. on charge (%)	N / A	N / A		0.5	0.9	0.0	0.2
Kappa Number (ml)	6.63	5.08	4.96	4.09	3.73	3.15	2.79
Viscosity / CED (ml.g ⁻¹)	827	798	826	454	522	388	303
Brightness (R457)	46.27	52.04	52.28	63.06	68.95	-	81.63
ISO Bri. / Before Rev.	47.71	54.73	58.02	69.20	73.19	77.89	85.02
ISO Bri. / After Rev.	46.80	53.35	56.52	67.99	70.33	80.11	81.80
Shade / L*-value	-	-	-	-	94.39	95.45	96.68
Shade / a*-value	-	-	-	-	-0.80	-1.34	-0.75
Shade / b*-value	-	-	-	-	10.46	8.54	5.02
Unbl. Kappa	12.01	Unbl. ISO Bri / Before Rev.					34.37
Unbl. Visc./CED (ml.g ⁻¹)	1102	Unbl. ISO Bri / After Rev.					34.42
Unbl. Bri (R457)	34.26	Unbl. Shade / L*-value (R457)					76.35
Time (nil)	0	Unbl. Shade / a*-value (R457)					1.73
		Unbl. Shade / b*-value (R457)					19.8

Table B34: Raw data of hand sheet properties/Evaluation of various combined thermo-photochemical and thermal bleaching sequences.

Label	PFI Beatings	Freeness	Grammage (Cond)	Grammage (B.D)	Thickness	Bulk specific $\text{cm}^3 \cdot \text{g}^{-1}$	Moisture	Stretch	Breaking Length	Brt. 680	Brt. R457	Burst Index $\text{kPa} \cdot \text{m}^2 \cdot \text{g}^{-1}$	Tear Index $\text{mN} \cdot \text{m}^2 \cdot \text{g}^{-1}$	T.E.A	Porosity $\text{ml} \cdot \text{min}^{-1}$	Opacity
Unbl. Aspen	Revs	ml	gsm	gsm	μm	$\text{cm}^3 \cdot \text{g}^{-1}$	%	%	m	%	%	$\text{kPa} \cdot \text{m}^2 \cdot \text{g}^{-1}$	$\text{mN} \cdot \text{m}^2 \cdot \text{g}^{-1}$	$\text{J} \cdot \text{m}^{-2}$	$\text{ml} \cdot \text{min}^{-1}$	%
	0	640	59.11	55.06	0.14	2.37	6.86	0.96	1953	71.0	40.8	0.81	2.54	6.86	5000	96.6
	2000	500	62.11	57.80	0.11	1.85	6.93	1.67	4223	69.1	38.8	2.38	6.78	29.13	2723	95.7
	4000	380	61.47	57.18	0.12	1.96	6.97	2.42	5800	69.1	38.5	3.09	6.85	57.76	1833	94.5
Photo BL	6000	360	61.40	57.09	0.10	1.66	7.01	2.15	5453	68.8	37.9	3.46	7.44	48.89	867	94.2
	0	620	60.16	56.17	0.13	2.22	6.63	1.59	2533	93.3	87.6	1.15	4.17	16.93	5000	77.5
	2000	520	62.30	58.16	0.11	1.79	6.65	2.50	4994	93.0	87.1	2.62	7.25	54.60	2948	74.1
	4000	440	59.81	55.78	0.11	1.76	6.72	2.99	6054	92.9	86.4	3.51	7.17	75.77	1433	73.1
Thermal ECF	6000	340	62.78	58.57	0.10	1.64	6.72	3.02	6345	92.7	85.6	4.02	7.42	83.35	739	72.1
	0	530	61.98	58.00	0.14	2.18	6.43	1.98	1996	94.1	85.7	1.07	3.83	17.87	5000	78.6
	2000	460	60.67	56.76	0.11	1.87	6.45	2.96	3658	93.7	84.7	2.21	6.29	48.77	3565	75.5
	4000	400	61.20	57.22	0.11	1.79	6.51	2.99	4590	93.6	84.9	2.66	7.07	60.39	2051	74.1
Thermal TCF	6000	340	60.53	56.62	0.11	1.75	6.47	3.42	4938	93.4	85.0	3.12	7.46	74.25	1205	74.0
	0	480	62.98	58.90	0.12	1.98	6.47	2.53	2656	93.2	83.0	1.46	4.55	31.73	5000	77.6
	2000	330	62.66	58.58	0.11	1.77	6.50	2.92	4012	92.9	81.7	2.70	5.43	54.38	1832	75.5
	4000	230	62.76	58.60	0.10	1.67	6.63	2.87	4693	92.9	81.2	3.30	5.39	61.76	673	74.4
	6000	160	60.28	56.30	0.10	1.67	6.61	3.32	5387	93.1	81.6	3.75	5.20	79.38	319	72.8

Table B35: Raw data of Lorentzen and Wettre fibre tester , and Lorentzen and Wettre fibre morphology for paper grade pulp/Evaluation of various combined thermo-photochemical and thermal bleaching sequences.

Sample description	Thermal TCF (Paper)			Thermal ECF (Paper)			Photo-Bl. (Paper)			Unbl. Aspen Cloquet		
	c	b	a	ave.	c	b	a	ave.	c	b	a	ave.
Mean length mm	0.749	0.746	0.747	747.33	0.743	0.743	0.748	744.67	0.779	0.779	0.777	778.33
Mean width µm	21.7	21.8	21.6	21.7	21.7	21.6	21.8	21.7	22.2	22.2	22.1	22.167
Mean shape %	86.6	86.7	86.6	86.633	87.3	87.2	87.3	87.267	89.2	89.1	89.2	89.167
Mean fibril area %	1.4	1.5	1.4	1.4333	1.6	1.6	1.5	1.5667	1.3	1.3	1.3	1.3
Mean fibril perimeter %	3.4	3.6	3.5	3.5	3.6	3.5	3.4	3.5	3	3	3.2	3.0667
FinesP Length	6.4	6.6	6.4	6.4667	6.6	6.6	6.6	6.6	4.9	4.8	4.8	4.8333
FinesS Length	14	14.9	14.6	14.5	17.8	15.1	14.7	15.867	8.7	8.7	11	9.4667
Mean fines %	20.5	21.5	21	21	24.4	21.7	21.3	22.467	13.6	13.5	15.9	14.333
Coarseness	58.3	60	58	0.0588	77.9	69.9	68.1	0.072	91.4	85.4	86.1	0.0876
No. fibers in sample	1980746	1910673	1977596	19.56	1437869	1647709	1679123	15.88	1334831	1419282	1383788	13.79
Fiber Wall Thickness	1.5	1.6	1.5	1.5333	2.1	1.9	1.8	1.9333	2.5	2.3	2.3	2.3667
Mean kink index	2.992	2.986	2.955	2.9777	2.772	2.847	2.792	2.8037	2.227	2.261	2.204	2.2307
Crill Quota UV/IR	0.93	0.928	0.921	0.9263	0.921	0.921	0.915	0.919	0.872	0.857	0.866	0.865
Weighting	Length			Length			Length			Length		
[100-200]	0.054	0.057	0.055	5.5333	0.058	0.056	0.056	5.6667	0.04	0.04	0.04	4
[200-300]	0.038	0.04	0.04	3.9333	0.04	0.04	0.039	3.9667	0.034	0.033	0.035	3.4
[300-400]	0.058	0.056	0.057	5.7	0.059	0.06	0.056	5.8333	0.052	0.056	0.052	5.3333
[400-600]	0.185	0.185	0.189	18.633	0.184	0.186	0.181	18.367	0.173	0.171	0.178	17.4
[600-900]	0.347	0.351	0.349	34.9	0.346	0.35	0.354	35	0.356	0.351	0.352	35.3
[900-1500]	0.3	0.292	0.294	29.533	0.297	0.293	0.298	29.6	0.325	0.33	0.325	32.667
[1500-2400]	0.017	0.018	0.016	1.7	0.015	0.016	0.015	1.5333	0.019	0.019	0.017	1.8333
[2400-3800]	0.001	0.001	0.001	0.1	0	0	0.001	0.0333	0.001	0.001	0.001	0.1
[3800-6000]	0	0	0	0	0	0	0	0	0	0	0	0
[6000-7500]	0	0	0	0	0	0	0	0	0	0	0	0

4.3.13. Evaluation of various combined thermo-photochemical and thermal bleaching sequences for dissolving/chemical grade pulp

Table B36: Raw data of total chlorine free (TCF) thermo-photochemical bleaching sequence for dissolving viscose grade pulp/Evaluation of various combined thermo-photochemical and thermal bleaching sequences.

Bleach sequence	Ox _{UV PULP}	P _{UV PULP (0)}	E _{O Δ}	P _{UV PULP (1)}
Mass pulp _{OD} (g)	20.0 x 9	20.0 x 7	120.0	20.0 x 5
Consistency	0.50	0.50	9.00	0.50
Total Weight	4000 x 9	4000 x 7	1333.3	4000 x 5
Mass pulp _{Wet} (g)	66.8 x 9	81.0 x 7	473.4	81.0 x 5
Chemical charge (%):				
NaOH	1.80	1.80	3.40	1.80
H ₂ O ₂		8.00		5.50
Mg ²⁺	0.20			
Lamp / Light Source	UV LED	UV LED	None	UV LED
Temperature (°C)	65.0	65.0	100.0	65.0
Time (Minutes)	90	90	120	60
Oxygen Pres. (kPa)	400		350	
Final pH	10.65	10.38	8.59	10.80
Initial pH	10.46	10.21	N / A	N / A
pH Adjustment Target	>10	>9	>10	>9
Final Temp. (°C)	42.5	43.0	N / A	45.3
Initial Temp. (°C)	57.4	56.0	N / A	N / A
Yield %	94.5	97.3	91.2	96.7
Total Yield (%)	81.1			
% Res. on charge (%)	N / A	78.5	N / A	7.9
Kappa Number (ml)	4.15	2.47	1.81	1.38
Viscosity / CED (ml.g ⁻¹)	697	629	577	535
Brightness (R457)	64.09	-	-	-
ISO Bri. / Before Rev.	67.76	85.42	84.43	91.22
ISO Bri. / After Rev.	68.07	84.01	83.27	90.24
Shade / L*-value	-	-	-	90.96
Shade / a*-value	-	-	-	0.77
Shade / b*-value	-	-	-	9.05
Unbl. Kappa	8.235	Unbl. ISO Bri / Before Rev.		63.4
Unbl. Visc./CED (ml.g ⁻¹)	722	Unbl. ISO Bri / After Rev.		63.59
Unbl. Bri (R457)	-	Glucose Bl. (%)		97.3
Time (nil)	0	Mannose Bl. (%)		2.2
		Xylose Bl. (%)		0.5

Table B37: Raw data of elemental chlorine free (ECF) thermal bleaching sequence for dissolving viscose grade pulp/Evaluation of various combined thermo-photochemical and thermal bleaching sequences.

Bleach sequence	MOX	D ₀	E _O	D ₁	H
Mass pulp _{OD} (g)	160.0	100.0 x 2	160.0	70.0 x 2	80.0
Consistency	10.50	10.0	10.0	10.0	10.0
Total Weight	1523.8	1000 x 2	1600.0	700 x 2	800.0
Mass pulp _{Wet} (g)	493.2	308.3 x 2	503.6	277.9 x 2	300.0
Chemical charge (%):					
ClO ₂		0.80		0.70	
NaOH	2.35		3.40		0.20
NaClO					0.50
H ₂ SO ₄				0.120	
Temperature (°C)	90	60.0	100.0	65.0	60.0
Time (Minutes)	60	60	120	180	120
Oxygen Pres. (kPa)	680		350		
Final pH	10.08	1.27	9.26	1.63	10.75
Start pH	-	1.32	-	1.42	10.98
pH Adjustment Target	>10	2.0-2.5	>10.0	3.3 - 3.8	>9.0
Yield %	93.8	100.4	94.0	99.7	98.5
Total Yield / %	86.9				
% Res. on charge (%)	N / A	9.5	N / A	15.7	0.0
Kappa Number (ml)	2.81	0.72	0.39	0.41	0.22
Viscosity / CED (ml.g ⁻¹)	703	643	573	563	556
Brightness (R457)	-	-	-	-	-
ISO Bri. / Before Rev.	77.89	90.49	91.97	95.52	96.50
ISO Bri. / After Rev.	76.16	85.31	91.48	94.44	95.59
Shade / L*-value	-	-	-	-	90.96
Shade / a*-value	-	-	-	-	0.77
Shade / b*-value	-	-	-	-	9.05
Unbl. Kappa	8.24	Unbl. ISO Bri / Before Rev.			63.4
Unbl. Visc./CED (ml.g ⁻¹)	722	Unbl. ISO Bri / After Rev.			63.59
Unbl. Bri (R457)	-	Glucose Bl. (%)			97.5
Time (nil)	0	Mannose Bl. (%)			2.1
		Xylose Bl. (%)			0.4

Table B38: Raw data of HPLC carbohydrate content, alkali solubility and Sappi quick reactivity for dissolving viscose grade pulp/Evaluation of various combined thermo-photochemical and thermal bleaching sequences.

Sample ID	Sugars (% of pulp)			Alkali solubility / $S_{10} : S_{18}$ (% / %)	Estimated degraded cellulose / $S_{10}-S_{18}$ (%)	Sappi quick reactivity index
	Glucose	Xylose	Mannose			
Saic Std mill pulp	97.1	2.6	0.4	10.1 / 5.2	4.9	5.00 to 9.50
Thermo-photo TCF pulp	97.3	2.2	0.5	7.2 / 4.0	3.2	7.89 / 7.89
Thermal ECF pulp	97.5	2.1	0.4	8.1 / 2.7	5.4	9.23 / 9.39

Table B39: Raw data of Lorentzen and Wettre fibre tester, and Lorentzen and Wettre fibre morphology for dissolving viscose grade pulp/Evaluation of various combined thermo-photochemical and thermal bleaching sequences.

Sample description	Thermal ECF (Viscose)			Phot-BL (Viscose)			Unbl. (Acid Sul)			Satc. Std pulp 09 03 21		
	c	b	a	ave.	c	b	a	ave.	c	b	a	ave.
Mean length mm	0.543	0.544	0.546	544.33	0.571	0.578	0.575	574.67	0.658	0.643	0.659	653.33
Mean width µm	18.9	18.9	18.9	18.9	18.5	18.5	18.5	18.5	18.9	18.8	18.8	18.833
Mean shape %	78.2	78.1	78	78.1	80.7	80.6	80.6	80.633	89.3	89.4	89.2	89.3
Mean fibril area %	1.5	1.4	1.4	1.4333	1.3	1.2	1.2	1.2333	1.1	1.1	1.1	1.1
Mean fibril perimeter %	3.7	3.5	3.5	3.5667	3.2	3	3.1	3.1	2.9	2.9	3	2.9333
FinesP Length	10	10.3	9.9	10.067	9.4	9.4	9.5	9.4333	10.5	10.8	10.3	10.533
FinesS Length	20.2	18.6	18.4	19.067	16.5	14.1	13.9	14.833	14	15.5	14.5	14.667
Mean fines %	30.2	28.9	28.3	29.133	25.8	23.5	23.4	24.233	24.5	26.3	24.8	25.2
Coarseness	64	55.7	54.1	0.0579	66	55.5	55.5	0.059	41.7	55.9	42.4	0.0467
No. fibers in sample	2141816	2488515	2578861	24.031	2099379	2531977	2552164	23.945	2831129	2144996	2783740	25.866
Fiber Wall Thickness	2	1.7	1.7	1.8	2.1	1.8	1.8	1.9	1.3	1.7	1.3	1.4333
Mean kink index	6.439	6.402	6.462	6.4343	5.636	5.686	5.672	5.6647	2.151	2.167	2.194	2.1707
Crill Quota UV/IR	0.849	0.844	0.84	0.8443	0.824	0.829	0.826	0.8263	0.827	0.829	0.827	0.8277
Weighting	Length			Length			Length			Length		
[100-200]	0.102	0.103	0.099	10.133	0.092	0.091	0.091	9.1333	0.09	0.093	0.089	9.0667
[200-300]	0.09	0.09	0.088	8.9333	0.079	0.075	0.078	7.7333	0.056	0.057	0.056	5.6333
[300-400]	0.108	0.105	0.107	10.667	0.095	0.096	0.098	9.6333	0.058	0.063	0.062	6.1
[400-600]	0.294	0.297	0.293	29.467	0.279	0.269	0.272	27.333	0.198	0.203	0.194	19.833
[600-900]	0.332	0.329	0.338	33.3	0.363	0.371	0.365	36.633	0.408	0.41	0.41	40.933
[900-1500]	0.072	0.074	0.072	7.2667	0.09	0.094	0.093	9.2333	0.179	0.165	0.179	17.433
[1500-2400]	0.001	0.002	0.003	0.2	0.003	0.005	0.004	0.4	0.01	0.007	0.011	0.9333
[2400-3800]	0	0	0	0	0	0	0	0	0	0	0	0
[3800-6000]	0	0	0	0	0	0	0	0	0	0	0	0
[6000-7500]	0	0	0	0	0	0	0	0	0	0	0	0

Appendix C

PERSONAL COMMUNICATION - JIM BORSUK

“...Craig,

Just to reiterate the point, we couple the RF in a tuned cavity. The coupling is what energizes (heats the gases) in the bulb which creates the Plasma that emits UV radiation.

You have to find a way to couple the bulb with enough energy to accomplish this. Coupling can be done with tuned slots in a cavity to which other companies may do or by some other way which transfers the energy. In order to emit the UV radiation the Mercury must evaporate into the plasma. This plasma creates heat to which you will require cooling. Air will need to be used to keep the quartz from melting, thus failing the bulb.

Placing the bulb in a large cavity(oven) does not concentrate the energy. It may have a slight reaction to which you see an intermittent light but this is not coupling enough energy.

Even with your design, I am not sure if I can help you in determining if correct or not.

I am sorry that this is all the information I can share. If you are looking for expert help, there are universities that have programs using magnetron energy and coupling which may be able to help you . University of Michigan is one.

Regards,

Jim Borsuk

Sr. Application Engineer

Nordson Ultraviolet Curing Systems

ICS Division ...”

Appendix D

SPECTRA OF METHYLENE BLUE AND ROSE BENGAL

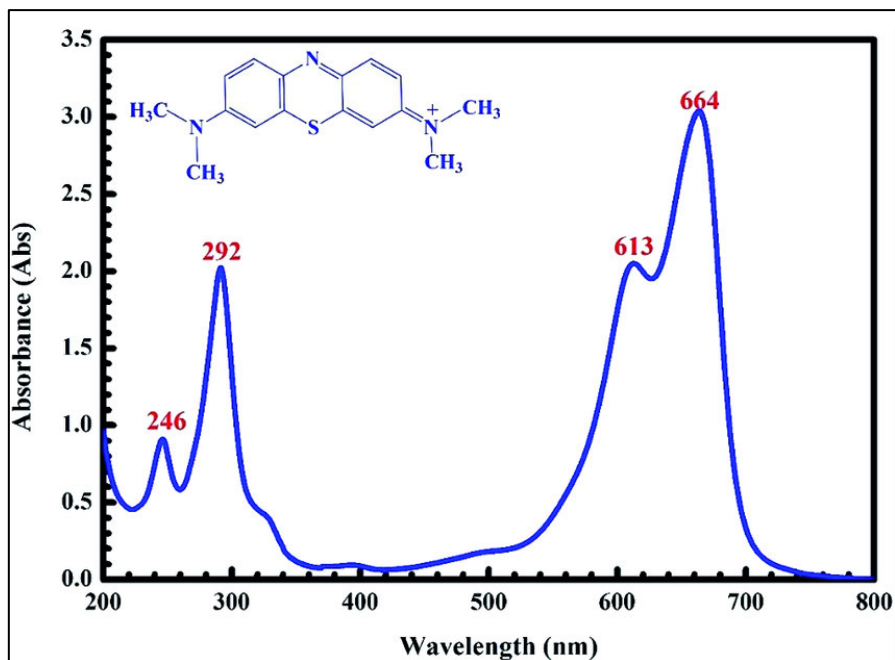


Figure D1: Absorption spectrum of methylene blue between the wavelengths of 200 – 800 nm [335].

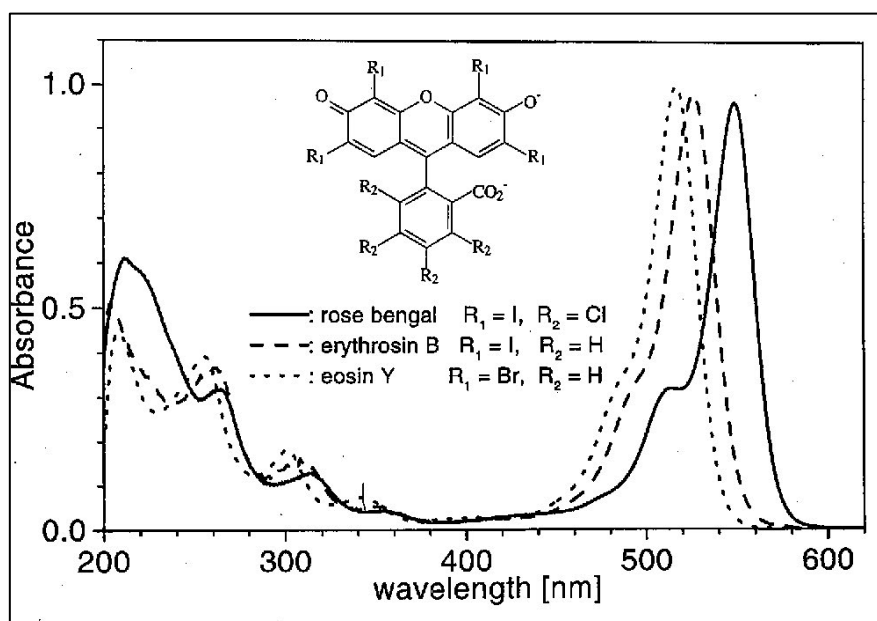


Figure D2: Absorption spectrum of rose bengal, erythrosine, and eosin between the wavelengths of 200 – 650 nm [336].