PYROLYSIS-GAS CHROMATOGRAPHY/MASS SPECTROMETRY STUDY OF CHROMOPHORES IN DISSOLVING WOOD PULP

By

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ABSTRACT

Dissolving wood pulp (DWP) is bleached wood pulp that contains high cellulose content, typically >95%. The bleaching is done to remove remnants of lignin and hemicelluloses that are not necessary for the final DWP. The pulp is chemically processed to make high-grade products such as speciality papers, viscose fabrics, and microcrystalline cellulose used in applications such as textile fibres, fillers in pharmaceutical tablets, or as a thickener in food additives, and manufacture of paints. Frequently, the fully bleached DWP exhibits an unwanted yellowish haze. This phenomenon results in loss of brightness in the pulps and is referred to as brightness reversion. Remnants of polysaccharides on DWP are believed to give rise to chromophores responsible for the brightness reversion. Such reversion in brightness is viewed as an early sign of ageing or deterioration of the pulp.

The impact of chromophores on the quality of DWP is a pressing issue in the global pulp and paper industry. Thus, identification of chromophores in the pulps is an important aspect to solving this problem and efforts have been made to develop techniques for identification of the chromophores responsible for brightness reversion. For example, an elegant method, termed chromophore release and identification, has been developed. However, application of the methodology for analysis of chromophores in pulps is tedious and long. It takes, on average, seven days to generate results, and a large quantity of pulp is required for the analysis. Such a long processing time is not ideal for industrial applications where time is of the essence. Hence, in this study, a novel methodology that allows for rapid and accurate characterization of chromophores directly from pulp fibres has been developed. The method entails direct analysis of chromophores on pulps without pre-extraction of chromophores, and results are obtained in less than an hour. The methodology entails the use of analytical pyrolysis combined with gas chromatography/mass spectrometry (Py-GC/MS) for direct detection and identification of chromophores in DWP.

To develop the method, selected fully bleached DWP samples were induced for brightness reversion and then analysed by Py-GC/MS and any chromophores present were identified by mass spectrometry. Probable compounds that could have contributed to the brightness reversion were also induced for brightness reversion and analysed to ascertain any similarities with the pyrograms of the brightness reversed DWP samples as well as mass spectral identities of the compounds. The results showed that the pulps that were induced for brightness reversion contained relatively higher amounts of chromophores than the original pulps, with ketones and furan-type compounds (originating from degraded cellulose and remnants of the hemicelluloses) being the major chromophoric groups.

Analysis of data on pulps with varying brightness reversion values did not show correlation with the relative amounts of chromophores detected by Py-GC/MS. The results confirmed literature reports that brightness is not a good indicator of the concentration of chromophores in pulps.

The developed Py-GC/MS method was then used to identify chromophores in DWP samples produced from the industry and the laboratory. Considering that the industry-produced DWP was from a wood furnish comprised of a mixture of wood species, it was essential to understand how the different clones/species in the wood furnish influenced the formation of chromophores. the results showed that different wood species contained the same type of chromophores, with furan-type compounds and conjugated ketones being the major groups of compounds detected. Pulps were sampled from different unit operations in a mill to ascertain the profiles of chromophores along the mill process. Additionally to the industrial in-process pulps, a number of single clone acid bi-sulphite pulps were bleached in the laboratory to produce pulps (in-process) that were also analysed for chromophore content using Py-GC/MS. The main groups of chromophores identified in all the samples were still furans-type compounds and conjugated ketones. Wet chemical analysis of in-process pulps showed that the remnants of hemicelluloses and degraded cellulose in the pulps have a significant impact on the formation of the ketones and furan-type compounds.

Finally, the developed Py-GC/MS method was tested on other pulps (besides DWP) that contained higher amounts of lignin (viz., the newsprint and kraft pulp). This was done to ascertain if the method would apply to other pulps besides DWP. As expected, the results showed that newsprint contained very high amounts of chromophores due to lignin whereas kraft pulps exhibited smaller amounts of lignin-type pyrolysis products. Thus, lignin was the major cause of brightness reversion in pulps that contain lignin and residual amounts of lignin.

Overall, the major chromophoric compounds identified in DWP were conjugated ketones and furan-type compounds. These compounds originated from remnants of hemicelluloses and degraded cellulose in the pulps: this agrees with literature reports on the origin of chromophores in cellulosic materials. The Py-GC/MS is a novel tool for rapid and direct analysis of residual chromophores in fully bleached and in-process DWPs and can be utilised for rapidly identifying the presence and chemistry of residual chromophores in DWP. The technique is currently being used to monitor the quality of industrially-produced DWP from different pulp mills.

DECLARATION 1

PLAGIARISM

I, Vezekile Princess Dladla, 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 individuals.
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:
    a. Their words have been rewritten but the general information attributed to them has been referenced.
    b. Where their exact words have been used, then their writing has been placed in italics and inside quotation marks and referenced.
5. This thesis does not contain text, graphics or tables copied and pasted from the Internet, unless specifically acknowledged, and the source being detailed in the thesis and in the References sections.

Signed: ___________________(Vezekile Princess Dladla) Date: ____________

I hereby confirm that the above statement is true and correct.

Signed:___________________(Professor Bruce Sithole) Date: ____________
(Supervisor)

DECLARATION 2

PUBLICATIONS

The listed publications were written by the author of this thesis, whose main responsibilities were to design and conduct the laboratory experiments, data analysis and reporting of the results.

List of Publications:

Dladla, V. P., Sithole, B., Chunilall, V., Ramjugernath, D. Identification of chromophores in cellulosic materials: A review. Manuscript.

Dladla, V. P., Sithole, B., Chunilall, V., Ramjugernath, D. Development of Py-GC/MS method for identification of residual chromophores in cellulosic materials. Manuscript.

Dladla, V. P., Sithole, B., Chunilall, V., Ramjugernath, D. Identification of residual chromophores in wood pulps using Py-GC/MS. Manuscript.

Conference Presentations:

Dladla, V.P., Sithole, B., Chunilall, V., Ramjugernath, D. (2016): Identification of Chromophores in pre-hydrolysis kraft and acid bisulphite pulps. In: *UKZN College of Agriculture, Engineering and Science Research Day*. Durban. Oral presentation.

Zungu, V.P., Sithole, B., Chunilall, V., Ramjugernath, D. (2015): Identification and Characterization of Chromophores in Wood Pulp: A Review. In: *18th International Symposium on Wood, Fibre and Pulping Chemistry*. Vienna. Oral presentation.

Zungu, V.P., Sithole, B., Chunilall, V., Ramjugernath, D. (2015). Identification of Residual Chromophores in Dissolving Wood Pulp fibres using Py-GC/MS. In: *The South African Institute of Chemical Engineers Research Day*. Durban. Poster and Oral presentation.

Zungu, V.P., Sithole, B., Chunilall, V., Ramjugernath, D. (2015): The Role of Cellulose, hemicellulose and lignin in pulp yellowing. In: *Young Scientists' Conference*. Johannesburg. Poster presentation.

Zungu, V.P., Sithole, B., Chunilall, V., Ramjugernath, D. (2014). Identification of Chromophores in Wood Pulp. In: *The International Conference on Chemical Thermodynamics and the South African Institution of Chemical Engineers National Conference*. Durban. Poster presentation

Extended Abstract:

Zungu, V. P., Sithole, B., Ramjugernath, D., Chunilall, V. 2015. Isolation and Characterisation of Chromophores in Pulps: A Review. *18th International Symposium on Wood, Fibre and Pulping Chemistry*, 9-11 September 2015. Vienna, Austria, 266-268, ISBN: 978-3-900932-24-4.

Signed: ____________________(Vezekile Princess Dladla) Date: ____________

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It is not possible to mention all the names of the people who helped me during my PhD studies; I would like to thank everyone that contributed to my success.

James 1:12
Blessed is a man who perseveres under trial; for once he has been approved, he will receive the crown of life which the Lord has promised to those who love him.

DEDICATION

I dedicate this thesis to my late father, Mr D.W Zungu

08 August 1942 - 18 February 2015

Ji! Yadl'impisi

LIST OF ABBREVIATIONS

AQ	Anthraquinone
AS	Acid sulphite
CTMP	Chemi-thermomechanical pulp
DIP	De-inked pulp
DWP	Dissolving wood pulp
E	*Eucalyptus*
ECF	Elemental Chlorine Free
EGC	*Eucalyptus Grandis- camadulensis*
EGU W962	*Eucalyptus Grandis- urophylla* W962
FTIR	Fourier transform infrared spectrometer
G438	*Grandis* 438
GC	Gas chromatography
GWP	Ground wood pulp
H_2SO_4	Sulphuric acid
HMF	Hydroxymethylfurfural
HPLC	High performance liquid chromatography
ISO	International organization for standardization
MCC	Microcrystalline cellulose
Me	Methyl
MeO	Methoxy
MeOH	Methanol
Min	Minutes
NaOH	Sodium hydroxide
nm	Nano meter
NMR	Nuclear magnetic resonance
NSSC	Neutral sulphite semi-chemical
OH	Hydroxide

P1	Pulp sample 1
P1(MCC)	Microcrystalline cellulose derived from pulp sample 1
P2	Pulp sample 2
P2(MCC)	Microcrystalline cellulose derived from pulp sample 2
P3	Pulp sample 3
P3(MCC)	Microcrystalline cellulose derived from pulp sample 3
pH	Power of hydrogen
PHK	Prehydrolysis kraft
PPB	Parts per billion
PPM	Parts per million
Py-GC/MS	Pyrolysis-Gas Chromatography/ Mass Spectrometry
RMP	Refiner mechanical pulp
RT	Room temperature
S	Seconds
S_0	Ground state energy level
S_1	First excited state energy level
S10%	Total extractable hemicellulose content and degraded cellulose content
S18%	Total extractable hemicellulose content
S_2	Second excited state energy level
T1	Triplet state
TAPPI	Technical Association of the Pulp and Paper Industry
TLC	Thin layer chtomatography
TMP	Thermomechanical pulp
UV/Vis	Ultra violet/ visible

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CHAPTER 1

INTRODUCTION

1.1 Wood as a raw material

Wood is a pre-historic material that has always been essential to the life on earth. Over 10 000 years ago, wood was mainly used by humans for providing shelter, farming, construction, heat and for making furniture (Stalnaker and Harris, 1997). However, humans do not have control over the properties of wood, the properties vary depending on the species, moisture content and the specific gravity, the size and location of structural defects, all these factors affect the end products of wood (Stalnaker and Harris, 1997). Developments from different parts of the world have enabled the production of wood derived chemicals such as charcoal, tall oil for making adhesives and tar for covering road surfaces (Sjöström, 1993). 2200 years ago, wood was shown to be an excellent raw material to produce paper in China (Ek *et al.*, 2009).

Wood is classified into softwoods and hardwoods; Table 1.1 shows the chemical differences in the composition of softwoods and hardwoods. It shows that the percentage of cellulose and the extractives are the same in both wood types. However, softwoods contain a slightly higher percentage of the hemicelluloses and lignin compared to the hardwoods (Ek *et al.*, 2009).

Table 1.1: Chemical composition of softwoods and hardwoods. Adapted from Ek *et al*. (2009).

Wood type	Cellulose	Hemicellulose	Lignin	Extractives
Softwood	40-44%	20-32%	25-35%	2-5%
Hardwood	40-44%	15-35%	18-25%	2-5%

Softwoods and hardwoods are both used in the pulp and paper manufacture as a primary source of fibre: the choice of wood depends on the availability and the requirements of the product. Softwoods are non-seed-bearing plants belonging to a group of plants known as gymnosperms and produce pulp with long fibres. Hardwoods are seed bearing plants that belong to a group of angiosperms: their resulting pulps have short fibres (Stalnaker and Harris, 1997). Softwoods are mainly mechanically pulped and sometimes chemically pulped for the production of high strength papers whereas hardwoods are mostly used for chemical pulping (Ek *et al.*, 2009). More differences between softwoods and hardwoods are shown in Table 1.2. Most forests of the world such as the temperate mixed forests, forests of the tropical circle and tropical rainforests are dominated by the hardwoods (Ek *et al.*, 2009).

Table 1.2: Differences between softwoods and hardwoods. Adapted from Stalnaker (1997).

	Softwoods	**Hardwoods**
Plant group	Gymnosperm	Angiosperm
Tree density	Low tree density	High tree density
Leaves	Needle shape, loose leaves annually (deciduous trees)	Broad leaves, evergreen throughout the year
Uses	Pulp and paper making	Pulp and paper making and manufacture of solid wood materials.
Examples	Wattle, birch, oak, beech, aspen	*Eucalyptus*, spruce, willow, redwood, pine

Hardwoods are mainly used for pulping in countries that have a low density of softwoods, and thus, most hardwoods, especially the *Eucalyptus* species, are cultivated and harvested as plantations, usually located closer to the pulp and paper mill. Relative to the natural forests, plantations are harvested after five or seven years of growth compared to over 100 years of plant growth required for natural forests (Ek *et al.*, 2009). Large industrial plantations are found in China, United States, Brazil, Australia, India, Europe and South Africa. In South Africa, plantations cover more than 1.2 million hectares of arable land with over 80% located in the Mpumalanga, KwaZulu-Natal and the Eastern Cape provinces as shown in Figure 1.1 (safiri.co.za, 2011). The global pulp and paper industry is moving towards the use of plantations as an environmentally friendly strategy to conserve water and to restore damaged land (Ek *et al.*, 2009).

Figure 1.1: Forest distribution in South Africa, showing plantation regions. Adapted from safiri.co.za (2011).

1.2 The growth of wood in a tree

The microstructure of wood is illustrated in Figure 1.2 showing the tangential, transverse and radial sections of the pine stem (Ek *et al*., 2009). The growth rings develop annually around the pith in a circular arrangement and consist of the earlywood cells that develop early during the spring season also known as springwood. The earlywood cells are large and thin-walled thus allowing fast movement of water and nutrients. The latewood cells develop in summer during the slow growth season, hence, they become thick-walled thus making the latewood cells look darker than the earlywood cells (Ek *et al.*, 2009). The earlywood part of the annual ring contains less cellulose per unit area than the latewood part of the annual ring. The high cellulose content of the latewood cells make wood an important raw material for pulp and paper production (Stalnaker and Harris, 1997).

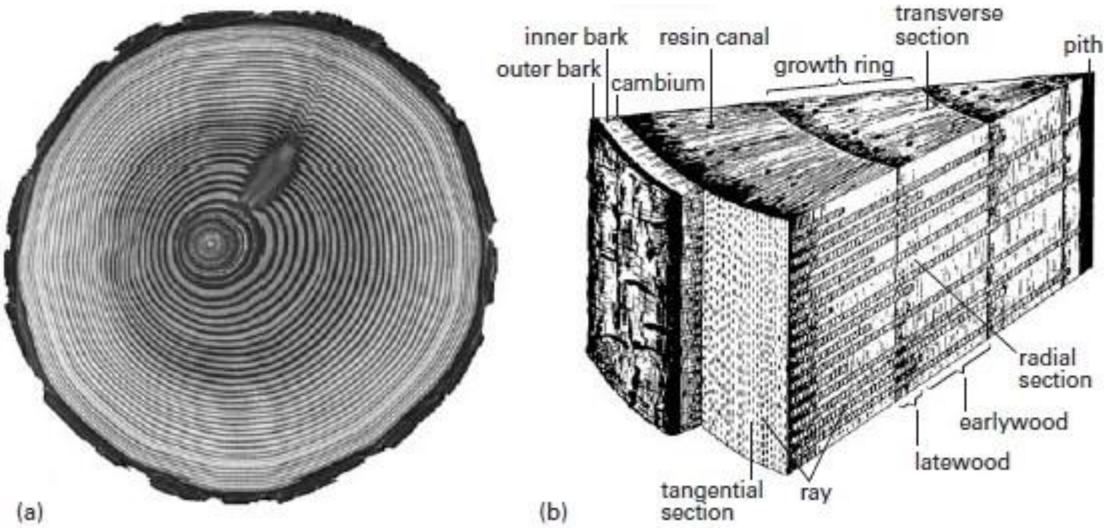


Figure 1.2: The microscopic structure of a pine stem showing: (a) a transverse section and (b) a detailed sectional view.
Adapted from Ek *et al.* (2009).

1.3 Wood in the pulp and paper industry

The primary raw materials used in the pulp and paper making are softwoods and hardwoods because they are naturally abundant, and they are easily harvested for transportation to the pulp mills. Ek et al. (2009) lists the following as vital properties of wood required for the pulping process: the colour (dark coloured wood requires intense bleaching), the homogeneity of wood cells (required for production of high quality pulps), the amount of extractives (causes pitch deposition during mechanical pulping) and the tree density (required for cost effective transportation and packing of the boilers) (Ek et al., 2009).

Other non-woody cellulosic raw materials used in the pulp and paper production include recycled paper and agricultural field residues (Ek *et al.*, 2009). Developing countries mainly use non-woody cellulosic materials for pulp and paper production such as bagasse, bamboo and straw reeds (Bajpai, 2010). In addition to wood and other non-woody materials, recycled paper is also one of the primary fibre sources following wood. (Ek et al., 2009). Figure 1.3 shows the annual consumption of the raw materials used in the pulp and papermaking, and it indicates that, following wood, the recycled pulp fibres also plays a significant role as a raw material (Ek et al., 2009).

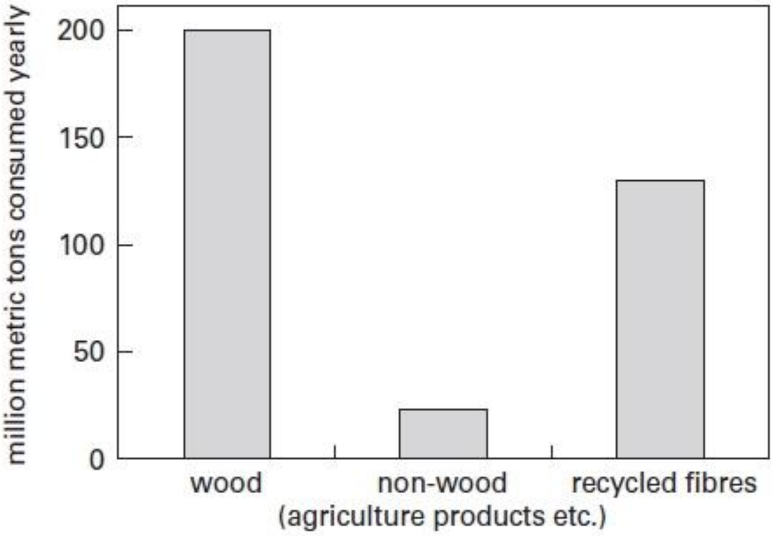


Figure 1.3: Raw materials for pulp and paper making.
Adapted from (Ek *et al.*, 2009).

The harvested cellulosic material is processed either mechanically or chemically to remove the lignin in a process known as delignification (for chemical pulps) and then bleached, depending on the requirements of the final pulp product. The main steps involved in pulp and paper making are the handling and preparation of the cellulosic raw material (debarking, chipping), followed by the pulping process (mechanical or chemical), pulp screening and washing, chemical recovery, bleaching and pulp drying or paper making as shown in Figure 1.4 (Bajpai, 2010).

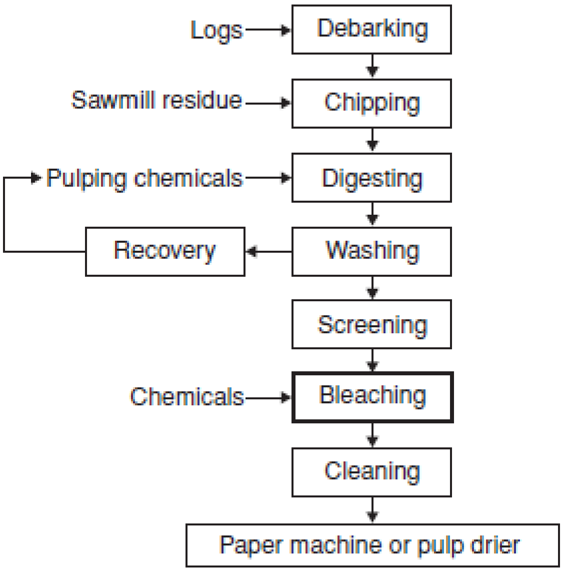


Figure 1.4: Overview of the pulp and paper making process.
Adapted from Bajpai (2010).

pulp and paper mills can exist independently or co-exist as an integrated operation. The pulp produced in an integrated mill (Figure 1.5) is packed for further downstream processing, and some of it is used for paper production. The main benefit of an integrated operation is the high-energy efficiency. The pulp and paper industry was ranked as the fourth industry with a high-energy consumption in 2006, consuming about 6% (6.7 EJ per annum) of the annual global industrial energy consumption. This was reduced to 2.1-2.4 EJ per annum through the improved efficiency brought by the integrated operations (iipnetwork.org, 2008).

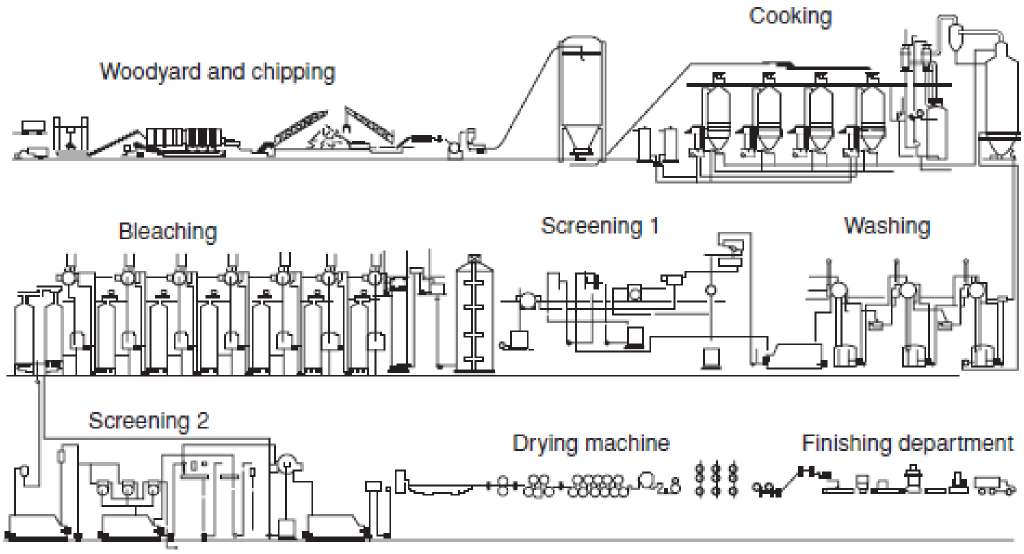


Figure 1.5: Schematic of an integrated pulp and paper mill.
Adapted from Bajpai (2010).

1.4 The pulping process

The pulping process utilises mechanical and chemical methods to produce pulp, hence, the pulps are classified into mechanical and chemical pulps. The following paragraphs will introduce the mechanical and chemical pulping methods.

1.4.1 Mechanical pulping

Mechanical pulping constitutes of three main pulping methods:

- Groundwood pulping (GWP)
- Refiner mechanical pulping (RMP)
- Chemi-mechanical pulping (CMP)

During GWP, the wood chips are refined at an elevated temperature to break the bonds between the fibres while weakening the lignin in the process. In GWP, hardwoods such as aspen are used to produce pulps of superior quality, which result in high brightness after bleaching. Figure 1.6 shows the main steps in GWP and RMP (Bajpai, 2010).

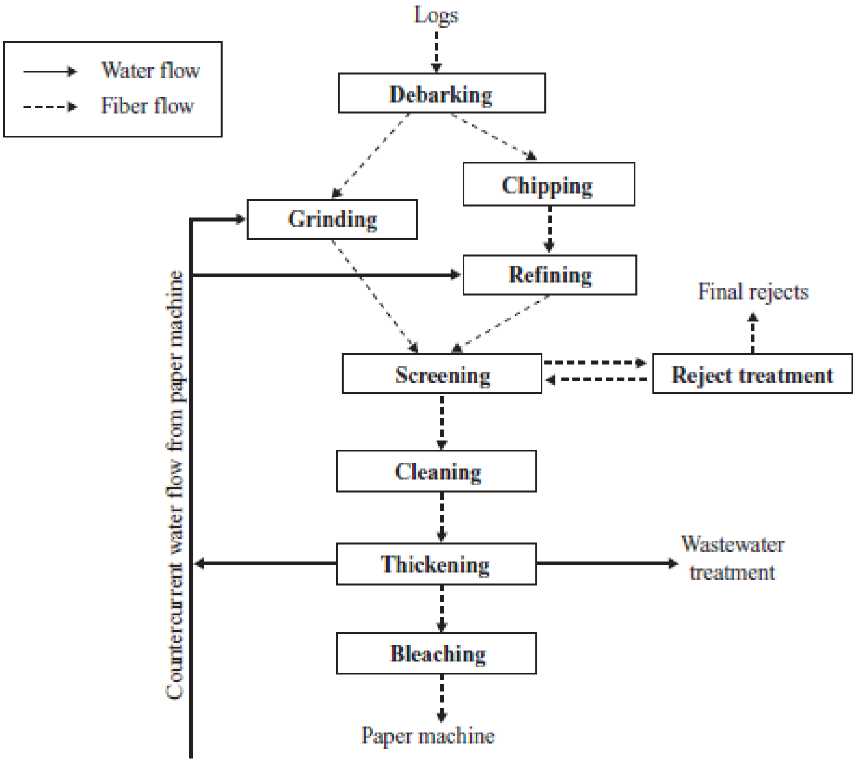


Figure 1.6: Schematic of the mechanical pulping process.
Adapted from Bajpai (2010).

The most commonly used RMP method in the pulp and paper industry is the thermomechanical pulping (TMP) and the common CMP method is the chemi-thermomechanical pulping (CTMP) (Bajpai, 2010).

In the TMP process, the wood chips are steamed before the mechanical refining stage. This breaks the bonds interconnecting the fibres and softens the lignin. It has been shown that the TMP pulps are better quality than the GWP and have been used as a cheaper material (relative to kraft pulps) for making newsprints, paperboard and tissue papers. Unlike GWP that uses hardwoods, the TMP process only produces good quality pulps from softwoods because the hardwoods do not give pulp with excellent strength properties when subjected to the TMP process (Bajpai, 2010).

In contrast to GWP and TMP, the CTMP produces good quality pulps from either softwoods or hardwoods because the wood chips are pretreated with hydrogen sulphite before the steaming and the refining stage. This causes the sulphonation of the lignin; the sulphonated lignin is then easily removed from the fibres during the refining stage.

The production cost of mechanical pulps is 50% cheaper than the production of chemical pulps. However, the quality of mechanical pulps is poorer compared to chemical pulps. The poor quality of mechanical pulps is due to the mixed sizes of fibres, fines and the high content of non-solubilized lignin (Ek, 2009, Bommarius and Riebel-Bommarius, 2004). Furthermore, in mechanical pulp production the energy consumed is very high, especially the TMP process even though GWP process has a lower energy demand compared to the TMP process, it is still energy demanding. Table 1.3 shows a comparative summary of the mechanical pulps and the chemical pulps.

Table 1.3: Basic properties of mechanical and chemical pulps. Adapted from Bajpai (2010).

Pulping Process	**Pulp colour**	**Yield (%)**	**Uses**
Thermomechanical	Brown	95	Paperboard, newsprints, paper bags
Chemi-thermomechanical	Light brown	85-95	Newsprint, speciality paper
Semi-chemical	Beige brown	60-80	Greaseproof papers, corrugating medium and bond papers
Kraft	Light brown	40-55	Newsprints, fine papers
Acid sulphite	Light brown	40-50	Speciality paper, viscose/ rayon
PHK	Light brown	40-50	Speciality paper, viscose/ rayon

1.4.2 Chemical pulping

Lignin is chemically dissolved during chemical pulping, while cellulose and some hemicelluloses remain. The yield of chemical pulps is comparatively lower than the yield of mechanical pulps. However, chemical pulps have excellent strength properties (Young, 1994). Traditionally, chemical pulps were manufactured using either the sulphate (kraft), the sulphite (Figure 1.7) or the soda process (Bohnet, 2003). Recently, chemical pulp manufacturers have introduced the pre-hydrolysis kraft (PHK) pulping process for the manufacture of DWP.

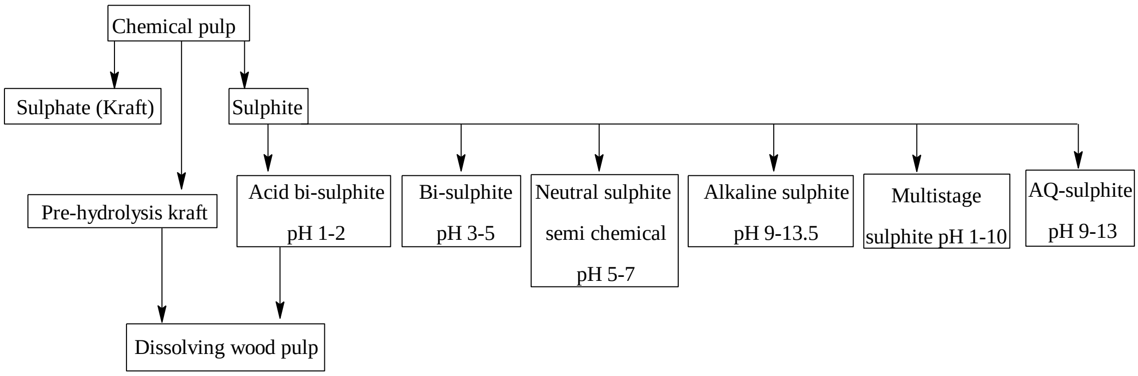


Figure 1.7: Types of chemical pulps.

Adapted from Bohnet (2003).

Kraft and PHK pulps follow a caustic chemical pulping process, whereas the sulphite process uses the entire pH range. During the kraft process, the wood chips are cooked in a solution of caustic soda and sodium sulphite, the resulting pulp is dark brown (brown stock) due to the high lignin content of the cooking liquor. The brown stock is washed with water to remove the black liquor and the pulp washings are collected as part of the chemical recovery process. Among the chemical pulping processes, the unbleached kraft pulp has a high yield (40-55%) and is mainly used to produce packaging paper products. The bleached grade of kraft pulp gives a lower yield than the unbleached kraft pulp, and the bleached grade is primarily utilized for the manufacture of white papers.

The kraft process has been continuously developed since the 1980s due to environmental concerns (Bajpai, 2010). The high volumes of the kraft mill effluents containing chlorinated compounds (from the chlorinated bleaching agents used) caused toxicity of water in receiving waters to aquatic biota and communities that are reliant on the waters. The kraft process dominates chemical pulp production, producing over 91% of chemical pulps due to its ability to generate high strength pulps while allowing chemical and energy recovery (Bajpai, 2010). Figure 1.8 represents a simplified schematic of the kraft process showing the chemical and energy recovery cycle.

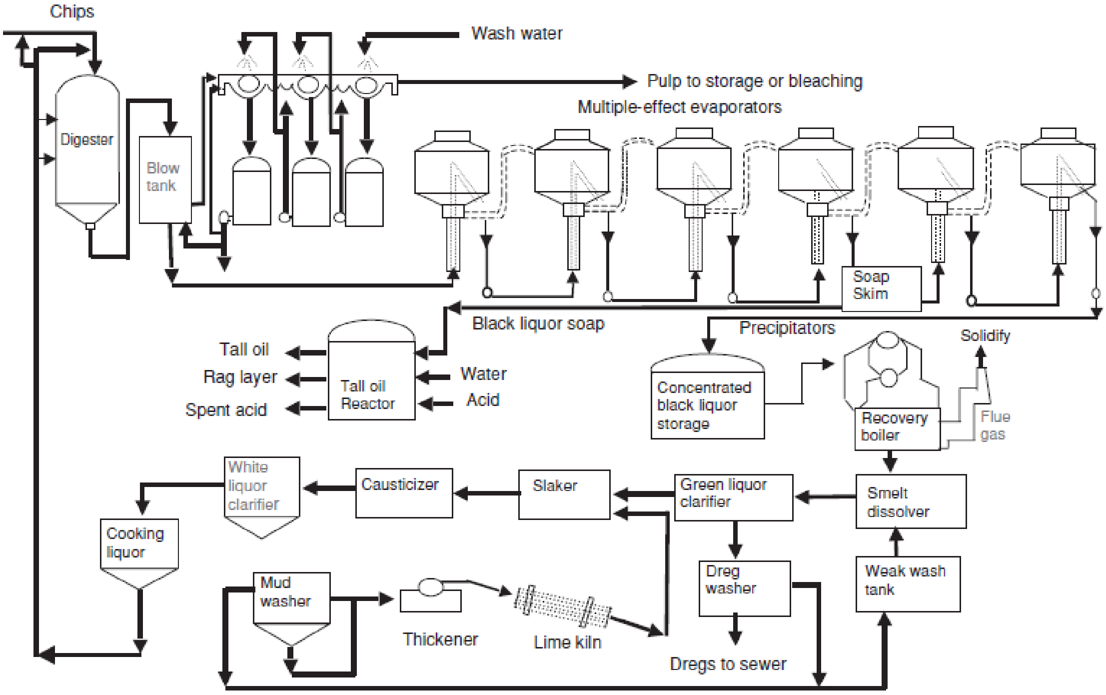


Figure 1.8: Schematic of the kraft process, showing cycles for chemical and energy recovery. Adapted from Bajpai (2010).

The term “sulphite process” was originally used for acid bisulphite pulping, but due to the flexibility of the process over a wide range of pH, several types of pulp are produced using the sulphite process. The pulp produced from each of the sulphite processes has different characteristics and therefore different industrial applications (Chunilall, 2009). The subdivisions of the sulphite process include the acid bi-sulphite, bi-sulphite, neutral sulphite semi-chemical (NSSC), alkaline sulphite, multistage sulphite and anthraquinone catalysed sulphite pulping (AQ-sulphite) as shown in Figure 1.7 (Bohnet, 2003). During sulphite pulping, various chemicals are used to solubilize and remove lignin to give brighter pulps (compared to kraft pulps) that are easily bleached to high brightness levels (Bajpai, 2010).

Semi-chemical pulping is one of the chemical pulping processes (Figure 1.9). The most commonly used semi-chemical pulping method is the NSSC contributing about 3.9% of the global production of the pulp. The process involves a moderate chemical treatment of wood chips before the mechanical refining stage. The hardwood chips are cooked in a buffered sodium sulphite solution, and then fibre separation is completed through mechanical refining. The NSSC operation is usually integrated to a kraft mill to allow effective chemical recovery; the sulphite spent liquor was processed with the kraft liquor to provide the required chemical makeup for the kraft process. However, modern kraft mills operate independently of the NSSC process for chemical recovery (Bajpai, 2010).

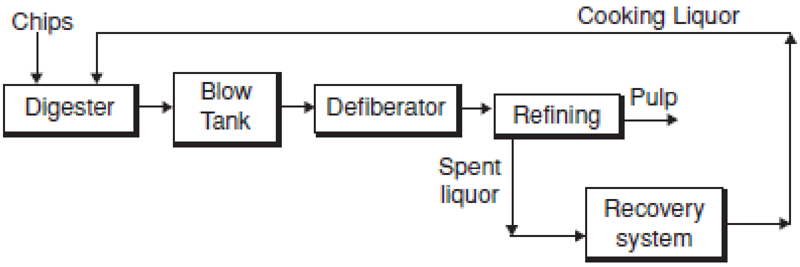


Figure 1.9: Schematic of the semi-chemical pulping process.
Adapted from Bajpai (2010).

In the acid sulphite (AS) process, the wood chips are cooked in a mixture of sulphur dioxide and a base. Calcium, sodium, magnesium or ammonium bases are usually used in the AS process (Figure 1.10). The choice of the base depends on the chemical and energy recovery requirements of the process. Bases of magnesium and sodium are mostly used in the AS process because they allow for chemical recovery. The average yield of unbleached AS pulps is between 40-50% and is reduced further during the bleaching process. The main by-product generated in the AS process are lignosulphonates that find applications as plasticisers during the manufacture of concrete or as binders for dust suppression in mining operations or untarred road (Chandra, 1996).

1.4.3 Dissolving wood pulp

Dissolving wood pulp (DWP) is the type of chemical pulp with a very high cellulose content and meager amounts of non-cellulosic contaminants (Sixta, 2006). The AS and PHK are two main processes used for producing DWP, whereas kraft pulp is mainly used for producing paper pulp. These processes were developed in the 1950s and are still used to produce DWP across the world (Bajpai, 2015, Bajpai, 2012, Sixta, 2006). Most of the residual lignin and hemicelluloses in the pulps are removed during the bleaching process to give pulp with a high cellulose content of 91-98% (Jahan *et al.*, 2008). DWP is also called dissolving cellulose pulp because it can be dissolved to increase reactivity and accessibility for the production of viscose/ rayon and other important cellulose derivatives (Woodings, 2001).

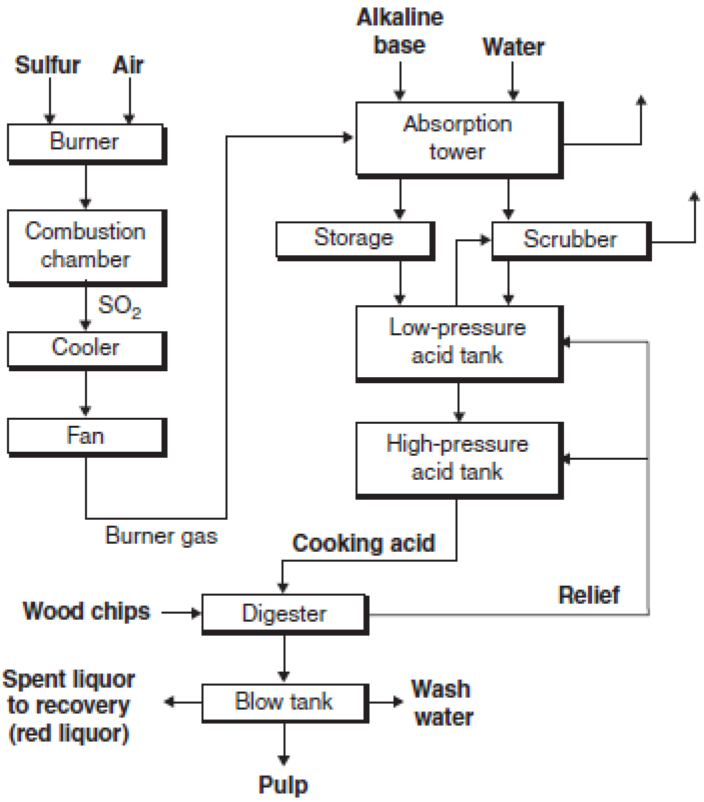


Figure 1.10: Schematic of the acid sulphite process.
Adapted from Bajpai (2010).

DWP is mainly produced in parts of the world that have rich forest resources, for example, South Africa, Brazil, China, North America and Canada (Pulp-paperworld.com, 2015). These countries produced over 6 million tonnes in 2012 that increased to 7.5 million tonnes in 2015 (risiinfo.com, 2016, Marketersmedia.com, 2016). The major companies producing DWP include Sappi, Aditya, Bracell, Fortress Paper, Neucel, Sateri, Lenzing, Rayonier and Sun paper (Marketersmedia.com, 2016).

DWP has excellent strength properties and high levels of brightness compared to a regular pulp, and the end use application depends on the purity of the cellulose (Sixta, 2006). The quality and purity of DWP rely on a combination of factors such as the origin of the wood material and the processing conditions employed during pulp manufacture, and these in turn, have an impact on brightness reversion (Jahan *et al.*, 2008). Above 75% of globally produced DWP is used for the manufacture of cellulose fibres, such as viscose/ rayon and filament yarn used for the production of fabrics in the textile industry (Bajpai, 2012, Kaur *et al.*, 2016). Other end products of DWP include pharmaceuticals, explosives, acetate film and rayon staple (Figure 1.11)

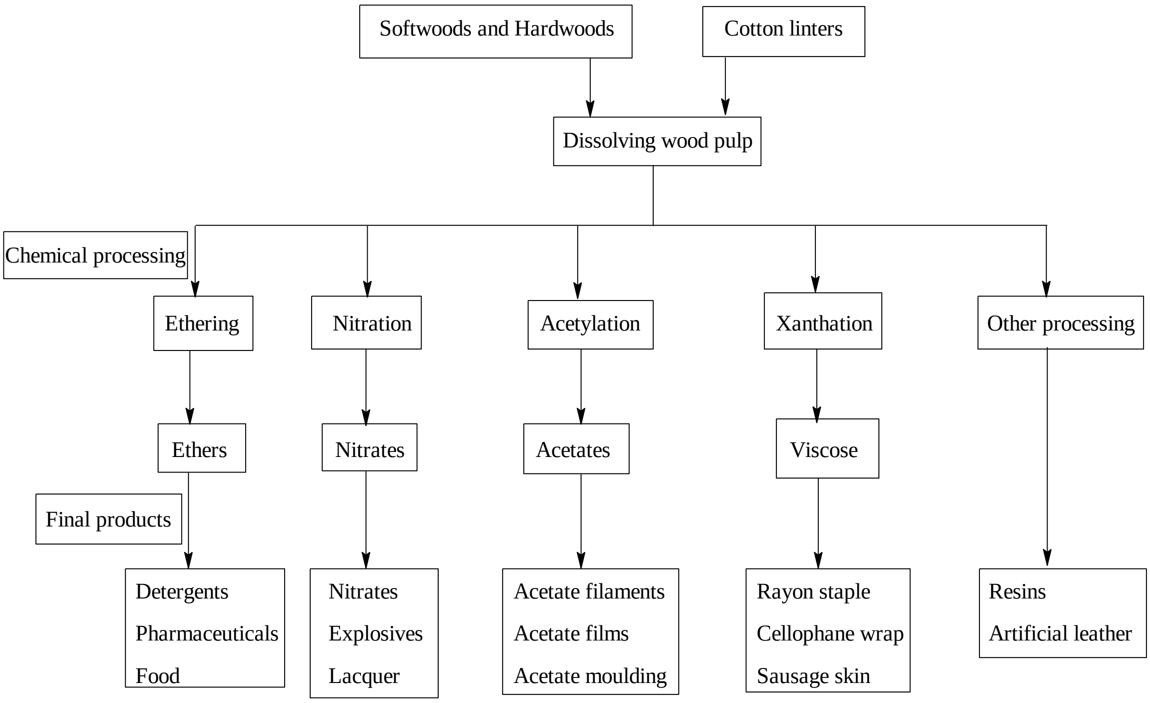


Figure 1.11: DWP: From raw material to finished products.
Adapted from Flickinger (2011).

The use of DWP for viscose fabric production started back in 1884 in south-eastern France (Echirolles) with viscose production based on a nitration process (Teräs and Jokinen, 2010). Developments in the early 1890s led to the use of the xanthation process for viscose production (Teräs and Jokinen, 2010) and the method is still used to date by leading manufacturers (Lenzing.com, 2015). Since the nitration process was environmentally unfriendly and costly, it was then terminated in 1940.

Forecasts show that global textile fibre consumption will increase by 61 million tonnes between 2010 and 2030, with an estimated average increase of 3.1% annually due to the increasing human population (Haemmerle, 2011, Sixta *et al.*, 2013). DWP is considered a good substitute for cotton since forestry does not require the use of expensive pesticides and is easier to grow. Moreover, the forecast shows that cotton production will slow down shortly due to the limited availability of the cotton farming land as the population increases (Haemmerle, 2011, Sixta *et al.*, 2013). The only feasible solution to this problem is to increase the production of high-quality DWP, meaning that the annual global DWP production should increase by 14.8 million tonnes (Shen and Patel, 2010) hence, this study will be focused on improving the quality of DWP.

DWP is bleached to very high brightness levels prior to the chemical processes mentioned in the preceding paragraphs to produce high brightness pulp for the manufacture of high-grade products. However, at times it has been observed that the brightness (whiteness) of the pulp decreases and imparts an undesirable yellowish haze on the final pulp, depending on the nature and conditions of storage of the pulp (Gamble, 2007). This undesirable phenomenon is termed brightness reversion or yellowing of DWP and is often viewed as an early sign of deterioration and ageing of the pulp: thus, pulp of lower brightness is perceived as low-quality pulp. Figure 1.12 shows fully bleached DWPs with high brightness and the pulp with low brightness due to brightness reversion.

Pulp brightness and yellowness are affected by factors such as the lignin and hemicellulose that remain after bleaching, bleaching chemicals, the presence of lipophilic extractives, transition metal complexes, the use of additives, environmental storage conditions and the amount of degraded cellulose (Bajpai, 2015). These factors result in the formation of chromophores, believed to be the main culprits in brightness reversion.

A chromophore is a structural feature of an organic compound that is responsible for the absorption of UV light. Chromophoric compounds contain a conjugated system of alternating, multiple, single and double bonds that absorb UV light and are, therefore, responsible for the colour of most organic compounds. Such compounds have high extinction coefficients and exhibit absorption and fluorescence in the UV-spectral region. Consequently, chromophores are easily noticed by the human eye due to their bright-yellow appearance (Rosenau *et al.*, 2004).

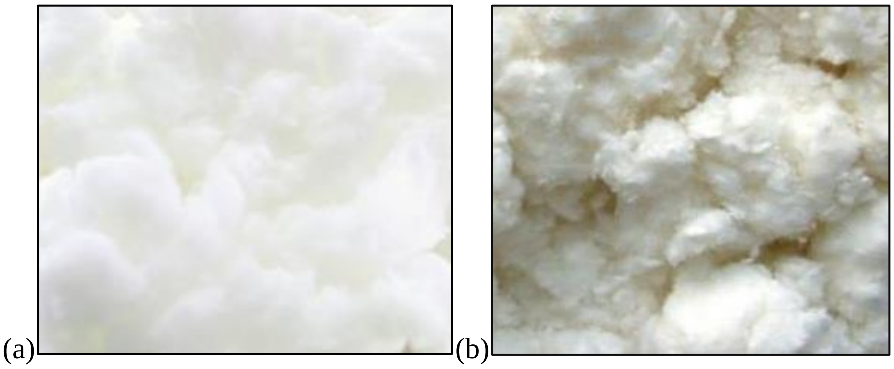


Figure 1.12: DWP with (a) high brightness and (b) low brightness.

The brightness reversion of fully bleached pulps has major economic implications for the world pulp markets in that such pulps are either rejected or sold at lower prices than normal pulps. As a result, the pulp and paper industry is looking for solutions to resolve this problem (Sappi.com, 2015). The problem is more severe in DWP markets since there is a growing demand of DWP in food, pharmaceutical, and textile industries. This suggests that research focussed on improving the quality of DWP is needed to meet the projected future demands.

1.5 Thesis statement

Brightness reversion in DWP is believed to be due to two factors, firstly, the hemicelluloses that survive the bleaching process and secondly, the residual lignin that is degraded to form chromophoric structures. In the DWP, these, in turn, give rise to chromophores with chemical structures that are dependent on the nature of the wood used as raw material, the mill processing conditions, and the pulp storage conditions.

1.6 Rationale and motivation

Although a number of studies have been undertaken to understand brightness reversion in fully bleached pulps, the causes and mechanisms of the reversion remain unclear in fully bleached DWP. Several laboratories have worked on this problem and have developed several approaches for the identification of chromophores in cellulosic materials, but no definite identification has been made, and no effective solutions to the problem have been proposed.

In this work, a rapid method was developed for identification of the residual chromophores present in DWP. Such identification was viewed as an essential first step that can lead to the development of effective procedures for removal or control of the chromophores. Novelty aspects of the project include:

- The use of Py-GC/MS for rapid identification of chromophores in DWP fibres, with no need for prior extraction from pulps. This is a novel and desirable technique that should significantly simplify the process for the analysis of chromophores in pulp fibres.
- The method developed in this study enables direct analysis of chromophores in DWP fibres – no studies have been reported on this.

1.7 Aim

The purpose of this study was to develop a novel and rapid methodology for identification of chromophores directly in DWP fibres. The method could then be used to identify unit operations that may be conducive to the formation of chromophores in DWP.

1.8 Objectives

- Develop a method for rapid chromophore identification on fibres using Py-GC/MS.
- Identify causes or probable sources of chromophores in DWP.
- Identify and compare chromophores from different commercial DWPs.
- Investigate the impact of processing conditions (cooking and bleaching) on DWP on the formation of chromophores.

1.9 Dissertation outline

This dissertation is organised into five chapters. Following this Chapter (1) is Chapter 2, which is a review of the types of chromophores in several types of pulps and previous studies that have been conducted to identify the chromophores in the pulps. Chapter 3 describes the development of the Py-GC/MS method for direct identification of chromophores on pulp fibres. Other supporting experimental procedures used are also described together with descriptions of the samples utilized in the study. The results are presented in Chapter 4, along with a discussion on their significance and reliability. The last Chapter (5) is a summary of the results and suggestions for future studies on the subject of chromophores in DWP.

1.10 References

Bajpai, P. 2010. Overview of Pulp and Papermaking Processes. *Environmentally Friendly Production of Pulp and Paper*. Hoboken, New Jersey: John Wiley & Sons.

Bajpai, P. 2012. Production of Dissolving-Grade Pulp. *Biotechnology for Pulp and Paper Processing*. Boston, MA: Springer US.

Bajpai, P. 2015. Pulp and Paper Chemicals. *Pulp and Paper Industry*. Amsterdam, Netherlands: Elsevier.

Bohnet, M. 2003. *Ullmann's Encyclopedia of Industrial Chemistry*. 6th, completely revised ed. Weinheim, Germany Wiley-VCH.

Bommarius, A. S. & Riebel-Bommarius, B. R. 2004. *Biocatalysis: Fundamentals and Applications,* Weinheim, Germany: John Wiley & Sons.

Chandra, S. 1996. *Waste Materials Used in concrete Manufacturing,* Westwood, New Jersey: Noyes Publications.

Chunilall, V. 2009. *Structure, Accessibility and 'Reactivity' of Cellulose I as Revealed by CP/MAS 13C-NMR Spectroscopy and Atomic Force Microscopy*. PhD, University of KwaZulu-Natal.

Ek, M. 2009. *Pulping Chemistry and Technology,* Berlin, Germany: Walter de Gruyter.

Ek, M., Gellerstedt, G. & Henriksson, G. 2009. *Wood Chemistry and Biotechnology,* Berlin, Germany: Walter de Gruyter.

Gamble, G. R. 2007. The Effect of Bale Ageing on Cotton Fiber Chemistry, Processing Perfomance, and Yarn Quality. *The Journal of Cotton Science,* 11**,** 98-103.

Haemmerle, F. M. 2011. The cellulose gap. *Lenzing Berichte,* 89**,** 12-21.

iipnetwork.org. 2008. Pulp and Paper. Available: http://ietd.iipnetwork.org/content/pulp-and-paper [Accessed 16 December 2016].

Jahan, M. S., Ahsan, L., Noori, A. & Quaiyyum, M. 2008. Process for the Production of Dissolving Pulp from Trema Orientalis (Nalita) By Prehydrolysis Kraft and Soda-Ethylenediamine (EDA) Process. *Bioresources,* 3**,** 816-828.

Kaur, P., Bhardwaj, N. K. & Sharma, J. 2016. Application of Microbial Enzymes in Dissolving Pulp Production. *In:* Shukla, P. (ed.) *Frontier Discoveries and Innovations in Interdisciplinary Microbiology*. New Delhi: Springer India.

Lenzing.com. 2015. *Ecological Responisbility-Viscose and Modal Fiber Production* [Online]. Lenzing. Available: http://www.lenzing.com/en/responsibility/ecological-responsibility/wood-based-cellulose-fibers/viscose-and-modal-production.html [Accessed 12 October 2016].

Marketersmedia.com. 2016. *Dissolving Pulp Industry Key Players* [Online]. Available: http://marketersmedia.com/dissolving-pulp-industry-key-players-sappi-aditya-birla-lenzing-sun-paper/116056 [Accessed 19 September 2016].

Pulp-paperworld.com. 2015. *Dissolving Pulp Industry Manufacturers Analysis & 2015 Forecast in New Market Research* [Online]. Available: http://www.pulp-paperworld.com/asian-news/item/3990-dissolving-pulp-industry-manufacturers-analysis-2015-forecast-in-new-market-research [Accessed 19 September 2016].

risiinfo.com. 2016. *World Dissolving Pulp Monitor: Keeping You Up-to-Date on Developments in Global Dissolving Pulp Markets!* [Online]. Available: http://www.risiinfo.com/product/world-dissolving-pulp-monitor/ [Accessed 19 September 2016].

Rosenau, T., Potthast, A., Milacher, W., Hofinger, A. & Kosma, P. 2004. Isolation and Identification of Residual Chromophores in Cellulosic Materials. *Polymer,* 45**,** 6437-6443.

safiri.co.za. 2011. Eastern Cape Freight Databank-Forestry. Available: http://www.safiri.co.za/ec/forestry.html [Accessed 15 December 2016].

Sappi.com. 2015. Chromophore Removal in Dissolving Pulps Available: https://ninesights.ninesigma.com/needs/-/needs-portlet/viewNeed/449 [Accessed 17 February 2015].

Shen, L. & Patel, M. K. 2010. Life Cycle Assessment of Man-Made Cellulose Fibres. *Lenzinger Berichte,* 88**,** 1-59.

Sixta, H. (ed.) 2006. *Pulp Properties and Applications,* New York: WILEY-VCH

Sixta, H., Iakovlev, M., Testova, L., Roselli, A., Hummel, M., Borrega, M., van Heiningen, A., Froschauer, C. & Schottenberger, H. 2013. Novel Concepts of Dissolving Pulp Production. *Cellulose,* 20**,** 1547-1561.

Sjöström, E. 1993. *Wood Chemistry: Fundamentals and Applications,* San Diego, California: Academic Press

Stalnaker, J. & Harris, E. 1997. *Structural Design in Wood,* Dordrecht, Netherland Springer Science & Business Media.

Teräs, T. & Jokinen, P. 2010. *Dissolving Pulp - The Great Come-back* [Online]. paperadvance.com. Available: http://www.paperadvance.com/sciences-a-innovations/sciences/176-dissolving-pulp-the-great-come-back.html [Accessed 12 October 2016].

Woodings, C. 2001. *Regenerated Cellulose Fibres,* Cambridge, England: Woodhead Publishing.

Young, R. 1994. Comparison of the Properties of Chemical Cellulose Pulps. *Cellulose,* 1**,** 107-130.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The main purpose of pulp bleaching is to improve the brightness of pulps by removing chromophores and any impurities that may interfere with pulp brightness. Suess (2010) described bleaching as the “destruction of chromophores” (Suess, 2010). The bleaching chemicals reduce the conjugation of the chromophoric compounds either by breaking the double bonds by strong oxidising agents or by reducing the double bonds using mild reducing agents. Good oxidising or reducing bleaching chemicals are characterised by their selectivity such that they avoid reacting with cellulose in the pulp. Examples of oxidising bleaching chemicals include oxygen, chlorine dioxide, hydrogen peroxide and ozone whereas those of reducing bleaching chemicals include sulphur dioxide, formamidine sulphinic acid and sodium dithionite (Suess, 2010).

Bleached chemical pulps undergo brightness reversion or yellowing over time, especially under acidic and humid conditions. Brightness reversion is the reduction of the brightness levels of bleached pulps that occur during storage or transportation, measured by calculating the difference between the values obtained before and after brightness reversion. An alternative method to measure the brightness reversion is the determination of the degree of yellowing, measured as the post colour (PC) number (Gullichsen, 1965). The PC number is calculated from the reflectance (k) and the light scattering coefficient (s) determined before and after brightness reversion (Suess, 2010). The values for k and s are calculated according to equation 1 and the PC number is calculated according to equation 2 below.

$$\frac{k}{s} = \frac{(1 - R_\infty)^2}{2R_\infty} \qquad (1)$$

$$PC = 100\left(\frac{k}{s}\, after\ aging - \frac{k}{s}\, before\ aging\right) \qquad (2)$$

Even though the cause of brightness reversion is not very clear; a good correlation has been shown between the PC number and the hexenuronic acid (Hex A) content in the kraft pulps as illustrated in Figure 2.1 (Ek, 2009). The PC number is useful when comparing small changes in the colour of the pulps; it is considered useful because it magnifies the small differences, low PC numbers are indicative of high colour stability (Suess, 2010). In addition to hexenuronic acid, other pulp components that are known for causing brightness reversion are residual lignin, chlorinated extractives and external factors such as the UV light, temperature, humidity, and time.

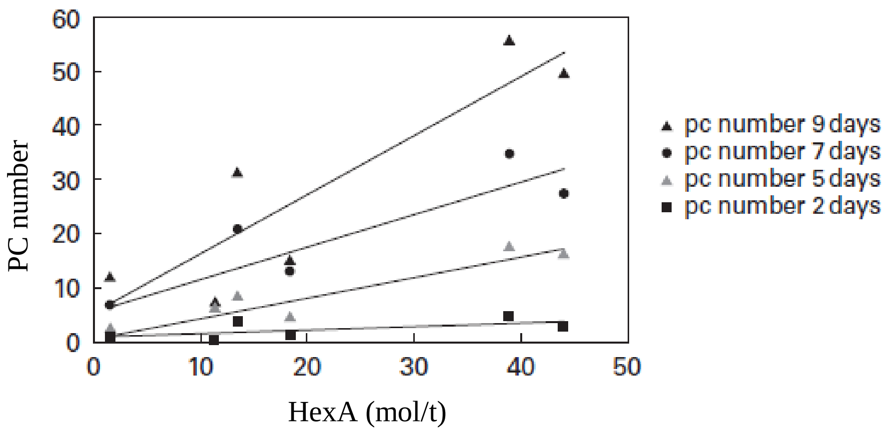


Figure 2.1: PC number of fully bleached kraft pulps measured over 9 days as a function of hexenuronic acid content.
Adapted from Ek (2009).

Yellowing pushes down the quality of the pulp and is an early sign of ageing and poor strength properties of pulps that negatively affects the downstream products. The manufacture of DWP of superior quality relies on the removal or control of the substances that are involved in pulp yellowing. Hence, accurate and detailed identification of the factors at play in brightness reversion, and finding solutions to this problem, are pressing issues that need resolution for the pulp and paper industry to maintain its share of world markets.

This review chapter includes identification of the causes of yellowing in cellulosic materials and the status of research and development on chromophores and their possible effect on brightness reversion. The chapter includes a detailed examination of the nature of chromophores in several types of pulp, methods that have been used for their identification and characterization, and methods used to improve the brightness of pulps.

2.2 Chromophores and absorption of UV light

It is important to understand the mechanism by which chromophores give colour in substances. The paragraphs below describe pathways that chromophores undergo to produce the observed yellowing effect in bleached pulps.

The mechanism of light absorption in chromophoric compounds is explained by the Jablonski energy level diagram (Figure 2.2), which demonstrates the physics of light absorption, fluorescence, and phosphorescence in conjugated systems. Absorption of light energy by molecules causes the electrons to move to a higher energy level, S_1 or S_2 excited states (Lakowicz, 2007). The light energy that was absorbed by the electrons in the ground state (S_0) is quickly (10^{-5} to 10^{-8} seconds) released from the excited state in the form of light at a longer wavelength, through a fluorescence mechanism that allows the colour to be visible to the human eye (Lakowicz, 2007).

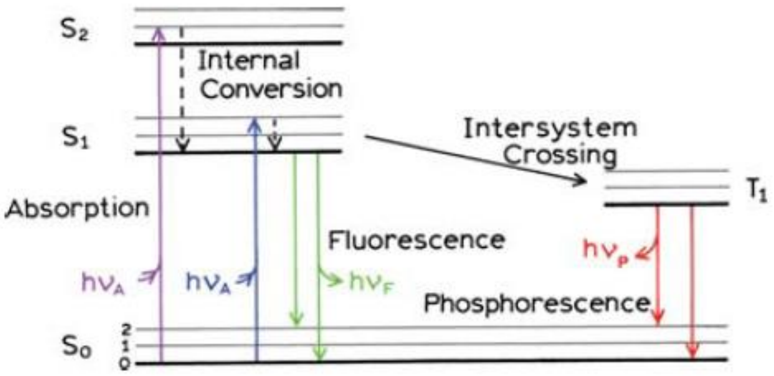


Figure 2.2: Jablonski energy level diagram.
Adapted from Lakowicz (2007).

The electrons in the excited state can also return to the ground state through emission of energy in a process called phosphorescence, a process that is slightly slower (10^{-4} seconds) than fluorescence. Conversion from S_1 to T_1 is called intersystem crossing (Lakowicz, 2007). This mechanism happens in a very short interval, converting light of one wavelength to another (Dyer, 2004, Valeur and Berberan-Santos, 2012). The singlet oxygen produced in the process has been shown to result in lignin degradation in wood pulps through oxidative reactions (Bonini *et al.*, 1998, Bonini *et al.*, 2002). The overall effect of this process in lignin containing pulps is brightness reversion. The effect of lignin degradation is observed by a decrease in brightness values of the pulp.

2.3 Measurement of brightness in pulps

In pulp and paper industries, brightness measurements are used to determine the amount of bleaching that the final pulp product has undergone, or they can be employed as an indication of how much bleaching is required to reach the set brightness target. Brightness measurement provides a means of comparison between bleached pulps.

Pulp brightness is defined as a measure of the reflection of blue light at 457 nm, expressed as a percentage in comparison with an ultimate reference brightness standard. This method provides an efficient means for pulp and paper industries to evaluate the changes in pulp grades during the production process (Johansson, 2000). However, there is no universal method for pulp brightness measurements thus making it difficult to compare pulps from mills across the world.

The methods for brightness measurement used by the American and European pulp and paper industries are directional and diffuse geometry respectively. These two approaches use different geometries and therefore give different brightness results because the brightness entirely depends on the optical properties of the instrument used as shown in Table 2.1 (RISI, 2006). Both methods are internationally accepted because they offer strong advantages and disadvantages for brightness measurements. Directional geometry uses the TAPPI standard T451, whereas diffuse geometry uses the ISO standard 2469 (Popson, Technical bulletin No. 101). General differences between the diffuse and directional brightness measurements are listed in Table 2.1.

Table 2.1: Differences between diffuse and directional geometry. Adapted from RISI (2006) and Popson (Technical Bulletin No. 101).

	Diffuse geometry	**Directional Geometry**
Traditional instrument	GE reflection metre	Zeiss Elrepho (TAPPI, 2016)
Year of the instrument	1930	1950
Angle of illumination	0°	45°- 0°
Effective wavelength	557 nm	572 nm
Industry standard	2469	T451

The technical bulletin by Popson (Technical Bulletin No. 101) describes the relative advantages of diffuse and directional geometry. It shows that diffuse geometry is more useful because it allows for light scattering, and therefore a larger surface area of the pulp is measured. It gives average brightness measurement results: hence, it avoids non-uniformity of the surface measured. However, neither method is ideal for determining the optical properties of pulps across the global pulp producing industries.

It is necessary to develop a universal instrument that combines the advantages and avoids the disadvantages of both methods. The common factor between the two brightness measurement methods is that they are only applicable to naturally coloured materials, such as near white pulp, bleached pulp, paper, and paperboard (TAPPI, 2016, ISO, 2009).

2.4 Chromophore formation in wood

Since wood is the raw material of interest here for pulp production, it is important to understand the possible effect of each of its primary components on the formation of chromophores. The main components of wood are cellulose (40-44%), hemicellulose (15-35%), lignin (18-35%) and extractives (2-5%) as shown in Table 1.1. (Ek *et al.*, 2009). Upon ageing of wood, oxidative reactions result in the formation of oxidised functional groups that act as new absorbing centres of UV light that enhance the yellowing effect (Carter, 1996, Mosca Conte *et al.*, 2012). These reactions in turn affect the primary components of wood. The following paragraphs discuss the contributions of the cellulose, hemicellulose, lignin and extractives in the formation of chromophores in DWP.

2.4.1 The role of cellulose in yellowing of pulps

The main component of DWP is cellulose, which is one of the most naturally abundant resources on earth. Studies have shown that pure cellulose does not absorb UV-light and therefore does not result in the yellowing of pulp (Mosca Conte *et al.*, 2012, Rosenau *et al.*, 2014). However, degraded cellulose has been found to be one of the contributors to the formation of chromophores, thus the formation of chromophores in DWP occurs because of cellulose oxidation that forms degraded cellulose. This results in loss of quality of cellulosic pulp and pulp derivatives. Oxidised functional groups, such as the carbonyl moiety of aldehyde groups and conjugated diketones, are known to be responsible for the yellowing of DWP (Mosca Conte *et al.*, 2012, Violante *et al.*, 2014). During the pulping process, cellulose is irreversibly oxidised by NaOH, in the cooking liquor to form water soluble and water insoluble derivatives that also contribute to the yellowing of the pulp (Sugano *et al.*, 2014).

The colour of cellulosic pulps is also induced by bleaching chemicals. Chlorinated bleaching chemicals cause yellowing by forming yellow chlorinated compounds (Burgess, 1982). Common oxidising bleaching chemicals such as chlorine, ozone and chlorine dioxide are used under acidic conditions that induce cellulose degradation into chromophores. Unlike the selective chlorine dioxide, chlorine and ozone are non-selective and result in cellulose degradation and reduction of pulp strength (Hon and Shiraishi, 2000, John Andelin *et al.*, 1989).

Cellulose oxidation can also take place under basic conditions by using bleaching agents such as hypochlorite, peroxide-alkali and oxygen-alkali systems. Oxidation with oxygen or a peroxide-alkali systems is selective because it occurs on the OH groups attached to C_2 or C_3 of the cellulose structure, unlike hypochlorite oxidation that is non-selective as it occurs on any hydroxyl group to form ketones that absorb UV-light thereby causing brightness reversion (Hon and Shiraishi, 2000, Knill and Kennedy, 2003).

2.4.2 The role of hemicellulose in yellowing of pulps

Brightness reversion due to hemicellulose content in the pulp has been investigated by Beyer et al. (2006). Findings from the study showed that the yellowing mechanism is a two-step process: the first step is the decay of unstable hemicellulose to form carbohydrate compounds followed by dehydration and condensation of the resulting compounds, to form coloured compounds that cause brightness reversion (Beyer *et al.*, 2006). It was also suggested that the brightness reversion in the wood pulp is associated with the amount of hydrolysable matter.

Beyer *et al*. (2006) used solvent extraction with methanol on a Soxhlet extractor to remove chromophores from pulps, and the structures of the isolated compounds were identified, along with their formation pathways, as shown in Figure 2.3 (Beyer *et al.*, 2006).

The mechanism (Figure 2.3) starts from decarboxylation and dehydration of glucose (**1**) to form the reductic acid (**2**). A condensation reaction of **2** and 5-hydroxymethyl-2 furan aldehyde (**7**) result in the formation of compound **3**. A series of reversible reactions lead to the formation of **9**, which further condenses with **7** to form **10**. A similar pathway was also proposed by Qiang *et al.* (2009) for the formation of low molecular weight furans during catalytic pyrolysis of wood biomass (Qiang *et al.,* 2009).

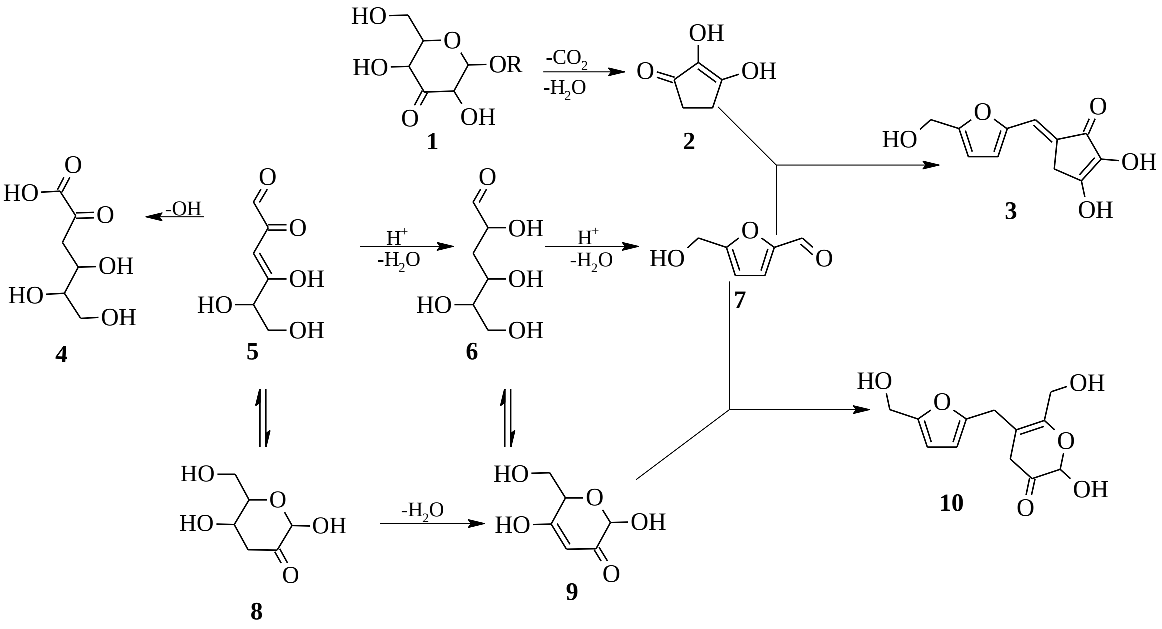


Figure 2.3: Chromophores generated from degradation of hemicelluloses.
Adapted from Beyer et al., (2006).

2.4.3 The role of lignin in yellowing of pulps

Lignin is a naturally occurring polymer found in the plant cell walls where it functions in the fibrous materials as a binding agent. There is evidence that lignin (in lignin containing pulps) inhibits auto-oxidative photodegradation by acting as an antioxidant that stops degradative reactions of the free radicals that are formed from cellulose (Schmidt *et al.*, 1995). It is believed that the phenolic groups in lignin prevent cellulose photodegradation by preventing oxidative and degradation reactions by absorbing UV-radiation (Barclay *et al.*, 1997, Albinsson *et al.*, 1999).

However, structural components of lignin such as phenolic, carboxyl, hydroxyl, methoxy and hydroxyl moieties, allow it to absorb metal cations such as Cu (II), Fe (II), Zn (II), Cd (II) (Guo *et al.*, 2008). During metal ion absorption, coloured metal complexes are formed via d-d transitions, charge transfer, or conjugations, between the ligand (lignin moiety) and the metal centre. To investigate the effects of transition metal complexes on the colour of pulp, Dyer (2004) studied several structures of a metal-ligand complex using a lignin model compound catechol (**12**) and an aqueous solution of copper (**11**), at different molar ratios as illustrated in Figure 2.4. In an aqueous solution, the water molecules in complex **11** were displaced by **12**. The reaction starts with the replacement of one water molecule by the catechol, to form **13**, but due to the instability of the catechol-metal complex formed, another water molecule is replaced by a catechol to form **14**. This reaction continues until the most stable catechol-metal (**16**) complex is formed. The resulting catechol-metal complex is chromophoric and absorbs UV light. This study revealed that the contribution of lignin to yellowing in wood materials could occur via metal complexation.

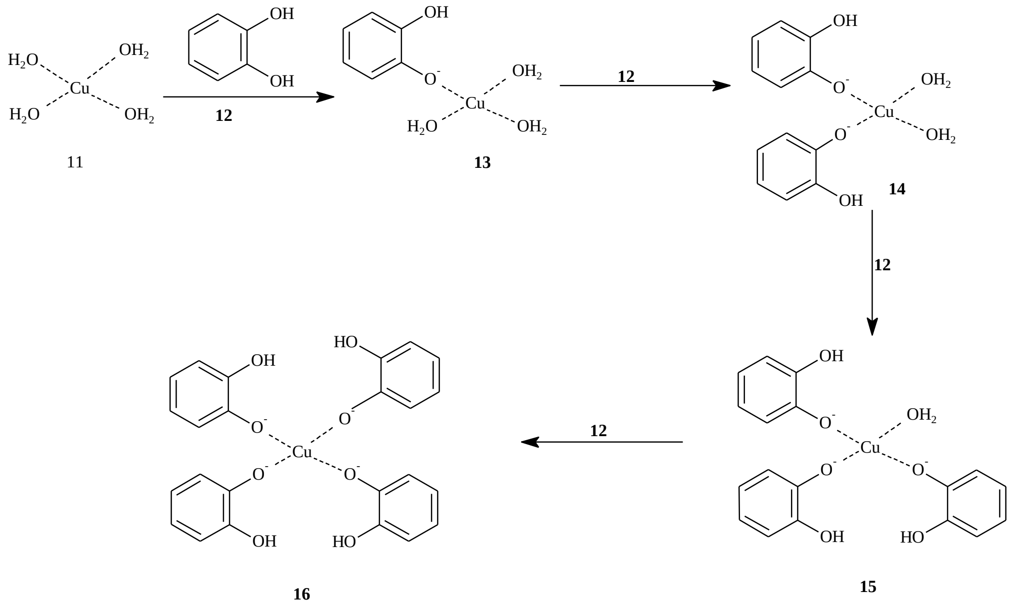


Figure 2.4: Catechol-Cu (II) complex.
Adapted from Dyer (2004).

2.4.4 The role of extractives in yellowing of pulps

In addition to cellulose, hemicellulose and lignin, wood also contains about 2-5% extractives (Feldman and Wegener, 1985). Extractives can be hydrophilic or hydrophobic depending on the extraction solvent used. In this case, the situation is related to hydrophobic extractives. Extractives are low-molecular-weight organic compounds found in the lumen and parenchyma cells of most tropical plants. Examples of extractives are fatty acids, fatty acid esters, sterols, sterol esters, terpineols and waxes that are soluble in water and common organic solvents (Back, 2000). They are essential for plant cell metabolism, and they protect plants against fungi and parasites. Pulp and paper researchers have extensively studied the roles played by extractives because they have been shown to negatively affect the pulp and paper manufacturing process and its products (Back, 2000). The effects of extractives have been observed mainly during the mechanical pulping process, where friction and compression forces are used to extract pulp fibres from wood (Zhang *et al.*, 2007). These forces release extractives from the lumen and resin canals, and this has a detrimental effect during manufacture of newsprint. The presence of extractives causes problems such as sticky deposition reduced physical and optical properties, and results in a reduced machine runnability (Zhang *et al.*, 2007).

The most common type of extractives are the fatty acids and their esters. During the pulp manufacturing process, some of the extractives react with the process chemicals producing mainly the ester derivatives of the fatty acids. Depending on the chemical structure of the reaction product, extractives get eliminated or survive the bleaching process (Kilulya, 2012). For example the mechanical and sulphite pulping are dominated by the glyceraldehydes, fatty acids and sterols, however, in the kraft pulping these extractives undergo saponification reaction to form soluble and insoluble soaps (Back, 2000). This shows that in chemical pulps, the sulphite pulps contain more extractives than the kraft pulps because the acidic conditions of the sulphite pulps cannot dissolve the wood resin (Sitholé *et al.,* 2009).

The impact of extractives in sulphite (dissolving) pulps causes a severe problem especially in the grades intended to produce rayon and pharmaceutical products. In rayon production, the extractives make the process more expensive because the costly spinneret (a metallic plate with filter nozzles) must frequently be changed and in pharmaceutical products, the extractives introduce unnecessary tastes and odours (Sitholé *et al.*, 2009).

Some of the extractives absorb in the UV spectral region at 457 nm and reflect a bright yellow colour, which contributes about 4% to the overall discolouration of the wood raw material (Johansson, 2000). Ona (2011) investigated the cause of brightness instability of chemi-thermomechanical pulps (CTMP) because the CTMP have excellent strength properties and are high yield pulps. Findings from the study by Ona (2011) showed a good correlation between the brightness of the CTMP and the amount of extractives as shown in Figure 2.5. Hence, it was suggested that during harvesting of the trees, the amount of extractives in wood should be considered as an important selection index (Ona, 2011)

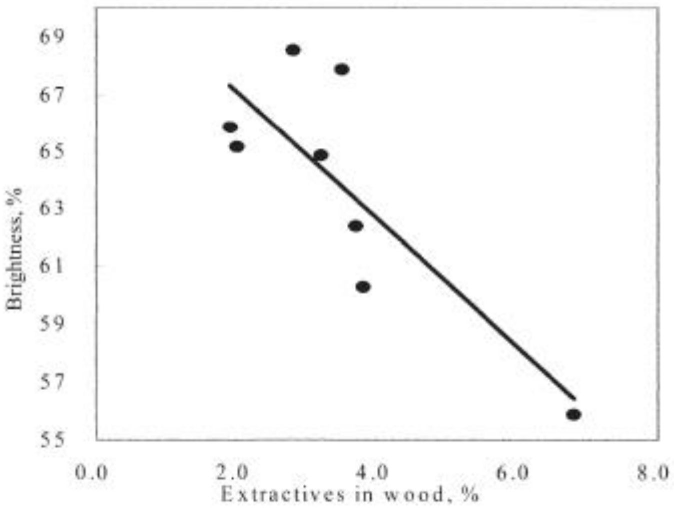


Figure 2.5: Relationship between wood extractives and CTMP brightness.
Adapted from Ona (2011).

Previous research has shown that each of the wood components contributes to the formation of chromophores. When the wood is converted to the pulp, some of the chromophores remains after the bleaching process, and some chromophores are formed during pulp ageing (Rosenau *et al.*, 2007b). The chromophores in DWP occur in ppb concentrations, even though chromophores absorb the UV light, there is no direct relationship between the brightness of the DWP because of their existence in minor concentrations and their orientation in the pulp fibres (Rosenau *et al.*, 2007b). However, due to their high extinction coefficient, they exhibit a bright yellow colour that is observed as discolouration in DWP (Rosenau *et al.,* 2004).

2.5 Causes of chromophore formation in different types of wood pulps

Various types of pulps undergo different processing conditions, and the cause of chromophores that are due to the processing conditions varies depending on the conditions employed during pulping. The following paragraphs discuss the causes of chromophores in mechanical pulps, chemical pulps and recycled pulps.

2.5.1 Causes of chromophore formation in mechanical pulps

During mechanical pulping, the cellulose fibres are mechanically separated and thus resulting in most of the lignin adhering to the cellulose fibres, which gives rise to a pulp of lower fibre strength (Kirwan, 2005). Mechanical pulps are high yield pulps ($>$95%) with low brightness, caused by photochemical reactions of lignin compounds that result in the formation of chromophores. These phytochemical reactions result in an undesirable yellowness and a short the life span of mechanical pulps (Schmidt and Heitner, 1993). Another challenge with mechanical pulps is alkaline darkening that occurs during peroxide bleaching; it negatively affects the bleaching efficiency. Alkaline darkening is caused by transition metals, oxygen, peroxide decomposition, the presence of quinoid structures and α,β-unsaturated carbonyl groups (Sain *et al.*, 1999, He *et al.*, 2005, Ragauskas, 1993). He *et al*. (2005) reported that the generation of peroxide resistant chromophores is caused by the harsh alkaline conditions, which can be avoided by reducing the alkaline treatment time. However, alkaline treatment is necessary for mechanical pulping since it enhances fibre strength properties (Pan, 2004), and catalyses the decomposition of hydrogen peroxide, as shown in equations 3 and 4 (Suss and Nimmerfroh, 1996).

$$H_2O_2 + OH^- \longrightarrow H_2O + HOO^- \qquad (3)$$

$$HOO^- + H_2O_2 \longrightarrow H_2O + O_2 + OH^- \qquad (4)$$

For the most part, brightness reversion in mechanical pulps is due to metal-lignin complexes, coloured metallic oxides, alkaline darkening and the chromophoric compounds. The following paragraphs review the causes of brightness reversion in the commonly used mechanical pulping methods namely: Groundwood pulping (GWP), thermomechanical pulping (TMP) and chemi-thermomechanical pulping (CTMP).

2.5.1.1 Groundwood pulp

In GWP, the wood material is directly ground into pulp at high temperatures, and there is no chemical pre-treatment of the pulp. As a result, this is the most cost-effective method for producing mechanical pulps, and this type of pulp is mainly used for making newsprints and other low-quality paper grades. Good quality groundwood pulps are produced when aspen is used as a starting material (Bajpai, 2010).

A study on exposure of GWP to UV light irradiation indicated that the yellowing of GWP was caused by chromophores absorbing at wavelengths below 330 nm (Heitner *et al.*, 2010). There is evidence that GWP loses colour at a faster rate in the presence of atmospheric oxygen and under humid conditions because of the high lignin content. Under these conditions, the compounds produced from the degradation of lignin (Figure 2.6) undergo radical reactions that result in the formation of chromophores that absorb the UV-light at shorter wavelengths and cause yellowing (Nolan *et al.*, 1945, Paulsson and Parkås, 2012).

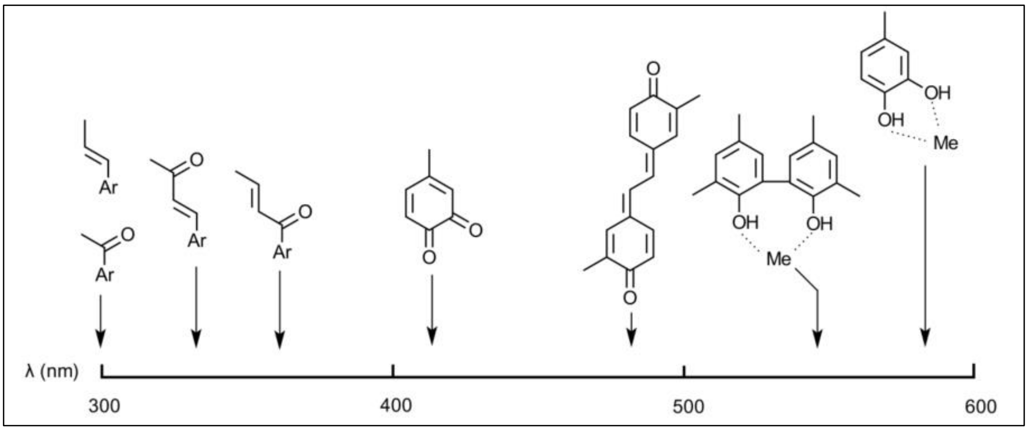


Figure 2.6: Absorption maxima of lignin-related compounds in mechanical pulps. Adapted from Paulsson and Parkås (2012).

2.5.1.2 Thermomechanical pulp

Thermomechanical pulp (TMP) is an improved type of mechanical pulp, which is preferable for newsprint manufacture (McDonald *et al.*, 2004). This kind of pulp is manufactured by heating wood chips with steam at temperatures above 100 °C, resulting in a mechanical separation of cellulose fibres. During thermal treatment, there are two processes that influence brightness reversion. The thermal decomposition of wood components described in section 2.4 that yields low molecular weight sugar monomers is followed by oxidative reactions in the cellulose surface, resulting in the overall yellowing of the TMP (Kocaefe *et al.*, 2008).

Free carboxylic acid groups that are formed during the decomposition of polysaccharide chains cause yellowing of the TMP. These free carboxylic acid groups further result in the formation of “Theander products” that are mainly caused by thermal treatment under acidic or basic conditions (Rosenau *et al.*, 2007a). (Johansson, 2000) investigated the stages of formation of the coloured compounds in TMP pulping. The findings revealed that the chromophores were formed in the first refining stage, this was indicated by an increase in UV-Vis absorption below 400 nm.

2.5.1.3 Chemi-thermomechanical pulp

During chemi-thermomechanical pulping (CTMP), the wood chips are pretreated with hydrogen sulphite prior to the steaming and the refining stage. The mixture is then heated to temperatures above 100 °C. The CTMP uses very mild conditions during chemical treatment, thus leaving most of the lignin adhering to the fibres (Prusas and Ohio, 1984). Studies show that the rate of brightness reversion upon irradiation of bleached CTMP is faster than that of bleached TMP (Schmidt and Heitner, 1993).

After mild chemical treatment, the remaining lignin undergoes degradation to yield ketyl and phenoxy radicals, which are important intermediates in the formation of lignin chromophores (Carter, 1996, Li and Ragauskas, 2000). Reaction pathways for the generation of lignin-based chromophores were described by Carter (1996), whereby the lignin molecules undergo photodegradation to yield pulp with low brightness (Figure 2.7).

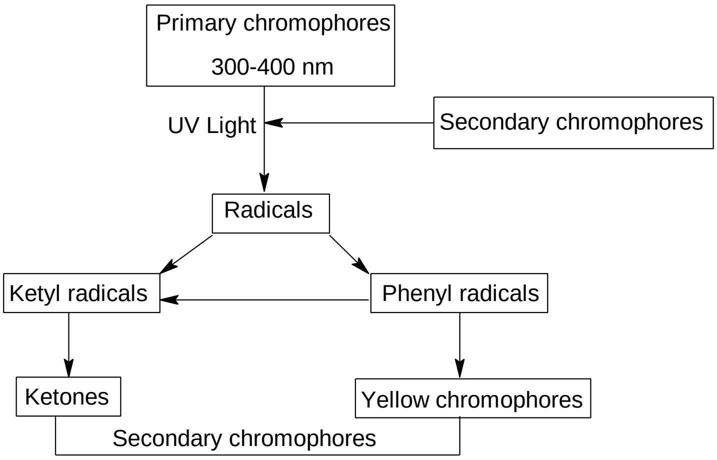


Figure 2.7: Lignin photodegradation and chromophore formation.
Adapted from Carter (1996).

Primary lignin chromophores absorb the UV light, which breaks down ether bonds to form free radicals from phenolic compounds and ketones (Carter, 1996). Secondary reaction results in the formation of unstable intermediates that rupture to form more phenoxy radicals and ketones, which act as secondary chromophores. In the process, oxidation of the phenoxy radicals in the presence of atmospheric oxygen occurs to form yellow compounds, which are referred to as secondary chromophores (Carter, 1996, Nemati *et al.*, 2013).

The preceding discussions indicate that the causes of chromophores in different types of mechanical pulps results from the pulping conditions such as the presence of the transition metal complexes, the effect of the bleaching process, and the components of the wood raw material. In these studies, the chromophores were generally associated with pulp yellowing because of their ability to absorb the UV-light resulting in pulp discolouration. In lignin containing pulps, it is known that an increased lignin content is interrelated to the low brightness levels of the pulp (Wilcox, 1975, John Andelin *et al.*, 1989).

2.5.2 Causes of chromophore formation in recycled pulp

Recycled or de-inked pulp (DIP) is manufactured using waste paper. The waste paper undergoes chemical processing to remove ink and other unwanted components (Borchardt, 1997). Since the raw material is waste paper, DIP may contain mechanical pulps, chemical pulps and semi-chemical pulps. Therefore, it is hard to determine a specific source of brightness reversion of the DIP.

Factors that cause the loss of brightness in DIP include the ink content, the particle size of the ink and size distribution, and the nature of the chromophores present (Bhardwaj and Nguyen, 2007). Bleaching of DIP with hydrogen peroxide has been shown to improve the brightness of DIP. Previous studies show that an increase in brightness by 10% was noted in one bleaching stage. However, a significant yield loss of the pulp was observed due to the alkaline soluble components of DIP (Bhardwaj and Nguyen, 2005, Bhardwaj and Nguyen, 2007).

2.5.3 Causes of chromophore formation in chemical pulps

In bleached chemical pulps, especially DWP, the lignin content is very low, hence its contribution to yellowness is minimal. As a result, studies have shown that there is no correlation between the pulp brightness and the content of the chromophores because they occur in minor quantities (Dyer, 2004, Rosenau *et al.*, 2007c). The following paragraphs review the formation of chromophores in chemical pulps.

2.5.3.1 Causes of chromophore formation in kraft pulps

Kraft pulping is the most popular chemical pulping method; it accounts for over 90% of the global production of chemical pulps (Sixta and Schild, 2009). During kraft pulping, the wood chips are cooked in caustic soda and sodium sulphite solution. The advantages of the kraft process, such as a shorter cooking time and good fibre strength, compared to other chemical cooking methods, make it cost effective and, therefore, preferred by most chemical pulp producing industries (Tran and Vakkilainnen, 2008). Furthermore, the kraft process allows for about 97% chemical recovery and accommodates both hardwoods and softwoods. In spite of these advantages, one of the shortcomings of kraft pulping is the dark colour or low brightness of the resulting pulp product (Dyer, 2004, Tran and Vakkilainnen, 2008).

Early research has shown that the dark colour of kraft pulps was due to the oxidative reactions and the presence of tannins (Holzer, 1934). However, it was assumed that most wood species contain tannins, of unknown chemical structures. Dyer (2004) reviewed the factors causing the low brightness of kraft pulps, and these factors include the nature of wood species, the presence of lignin, carbohydrate degradation products, transition metal complexes and absorption by aromatic structures. It was shown that the dark colour of kraft pulps involves, directly or indirectly, the chromophores, because all the factors participating in the yellowing of kraft pulps are light absorbing compounds (Dyer, 2004).

The role of hemicelluloses in the yellowing of bleached chemical pulps cannot be ignored. Beyer *et al*. (2006) studied the role of hemicelluloses in heat induced yellowing of totally chlorine free and elemental chlorine free kraft pulps. The findings showed that the yellowing mechanism occurs in a two-step reaction starting with the degradation of thermally unstable hemicelluloses to form low molecular weight carbohydrates that further undergo dehydration and condensation reactions to form chromophores. Partial degradation of cellulose was also reported as another contributing factor to the yellowing of the pulps. Chromophores identified from the study were compounds that were oligomers derived from furans such as reductic acid. It was further reported that the chromophore extraction method reported by Rosenau *et al*. (2004) did not allow for the detection of aromatic compounds, instead, the furans were detected. However, this was attributed to the differences in the heating conditions employed (Beyer *et al.*, 2006).

Organic-matter-bound chlorine has also been reported to cause a significant loss of pulp brightness in some of the bleached kraft pulps (Eiras *et al.*, 2009, Parthasarathy and Colodette, 2007). During bleaching of kraft pulps, oxidative bleaching chemicals such as chlorine dioxide, oxygen, ozone and hydrogen peroxide are employed to achieve high brightness levels of the pulp. In bleaching sequences ending with chlorine dioxide or hydrogen peroxide, the pulps showed less brightness reversion when the chlorine dioxide was used at higher temperatures than the standard chlorine dioxide bleached pulps (Eiras *et al.*, 2009). Even though the chlorine dioxide bleached pulps were brighter, their brightness stability was lower than the pulps bleached with the hydrogen peroxide in the final stage, meaning that the addition of H_2O_2 was necessary to provide brightness stability (Parthasarathy and Colodette, 2007). The chlorine dioxide selectively reacts with the lignin, however, in the process, the radicals of chlorine monoxide and chlorine are formed, and they further react with lignin to form quinones and also react with the C6 of cellulose to form the chromophoric hexenuronic acid (Parthasarathy and Colodette, 2007).

There is a good correlation between the amount of hexenuronic acid and the brightness reversion of kraft pulps (Ek, 2009, Silva *et al.*, 2011). High amounts of hexenuronic acid and xylan in kraft pulping are favoured by lower cooking temperatures (Colodette *et al.*, 2002). These studies indicate that the hemicelluloses are the part of the cause of yellowing in bleached kraft pulps. Other factors that contribute to yellowing include the degradation of cellulose due to oxidative bleaching chemicals (Rosenau *et al.*, 2004, Beyer *et al.*, 2006).

2.5.3.2 Causes of chromophore formation in acid bi-sulphite pulp

The acid bisulphite process is the major pulping method for the production of DWP, accounting for about 60% of global DWP production (Sixta, 2000). However, it is time and energy consuming and is being slowly replaced by the PHK pulping process in some pulp and paper industries (Sixta, 2006). The main cooking chemicals in the acid bisulphite process are sulphuric acid and bisulphite ions. The processes that take place in a stepwise manner during acid bisulphite pulping are the chemical penetration, pulping and chemical recovery.

The chemical penetration step takes about 3 hours, and the temperature can slowly increase to reach a maximum of 130 °C in the digester. The pulping process starts immediately after the penetration step and the temperature increases to about 135-145 °C, depending on the required degree of delignification. Finally, the pressure of the cooking vessel is reduced to below 100 kPa to allow for chemical recovery. Chemical recovery generally takes about 90 minutes. The overall acid bisulphite pulping process takes about 8,5 hours (Chunilall, 2009). The resulting pulp contains chemically modified lignin, organic compounds and metal ions inherited from the wood raw material. Hence, its colour is brown (Gadd, 2001). This raw pulp undergoes a stepwise bleaching process to produce different grades of dissolving pulp. The elevated temperatures and the bleaching chemicals employed in the acid bisulphite process induce the cellulose degradation thus leading to the formation of chromophores.

2.5.3.3 Causes of chromophore formation in pre-hydrolysis kraft pulp (PHK)

The PHK pulping process is one of the major processes for the production of DWP following the acid bisulphite process (Sixta, 2000). It produces fibres with excellent strength properties and requires a short cooking time than the acid bisulphite process. However, fully bleached PHK pulps have shown inferior pulp properties such as the darker colour (after bleaching) compared fully bleached acid bisulphite pulps (Duan *et al.*, 2015).

During the PHK pulping process, the wood chips are pre-hydrolysed to remove the hemicelluloses. The remaining hemicellulose-free wood chips undergo delignification in the digester that is heated to about 170 °C for 2 hours, depending on the required degree of delignification (Li *et al.*, 2010). This is an advanced type of kraft pulping since it requires a shorter cooking time and it is cost effective.

During the kraft process, some of the xylans dissolves into the cooking liquor and precipitates into the fibres, and some of it covalently bonds with lignin to form lignin-xylan (lignocarbohydrate) complexes (Garg *et al.*, 1998). These lignocarbohydrates adhere to the surface of the pulp fibres, where they prevent the penetration of bleaching agents, hence, the bleaching process becomes ineffective. Tunc *et al.*, (2010) explained that the chemical bonds in the lignocarbohydrates prevent the extraction of hemicelluloses, therefore, hemicellulose-type chromophores remain in the PHK pulp after bleaching.

Bio-bleaches, such as xylanases, have been used to achieve high brightness levels in PHK pulps. The rationale behind using bio-bleaches is that the xylanases hydrolyse the precipitated xylan and the lignocarbohydrate complexes, which therefore improves delignification (Roncero *et al.*, 2003, Garg *et al.*, 1998). Xylanase action allows bleaching chemicals to reach lignin surfaces, thus improves the bleaching efficiency and the brightness of PHK pulps (Thakur *et al.*, 2012). However, bio-bleaching does not remove all types of chromophores present in PHK pulps, such as the furfurals that are formed during cellulose degradation (Li *et al.*, 2010).

2.5.3.4 Causes of chromophore formation in dissolving wood pulp

The unbleached PHK or acid bi-sulphite pulps are the raw materials in the production of DWP. The raw pulp is bleached to very high brightness levels, measured as an effective reflectance, at 495 nm. The bleaching process aims to remove the lignin and hemicelluloses that remain after the pulping process, and therefore improves the brightness of pulp to produce high-quality dissolving pulp of different grades. Table 2.2 shows a list of bleaching chemicals and the purpose for their application. The purity of DWP depends on the bleaching sequence applied in the process. Some of the sequences commonly used by American and Canadian pulp mills are C-E-D-E-D, C-E-D-H, C-E-H-D-E-D, C-E-H and C-E-D (John Andelin *et al.*, 1989), the symbols are summarised in Table 2.2.

Table 2.2: Chemicals for bleaching chemical pulps. Adapted from Bohnet (2003).

Stage	**Abbreviation**	**Purpose**
Oxygen	O	Delignification and oxidation of lignin
Chlorine	C	Chlorination and oxidation of lignin
Chlorine dioxide	D	Improves brightness, oxidise and solubilize lignin
Extraction with NaOH	E	Extraction of hemicellulose and solubilisation of degraded lignin
Hypochlorite (Na/Ca)	H	Polymer chain scission controls viscosity oxidises and solubilizes residual lignin.
Hydrogen Peroxide	P	Improves brightness removes residual hemicellulose

Approximately 80% of globally produced DWP and fully bleached kraft pulps (Gehmayr and Sixta, 2011) are converted to viscose fibres. Other uses of DWP include the production of cellophane wraps and microcrystalline cellulose for applications such as fillers for pharmaceutical tablets, or as food additives such as thickeners in plain fat-free yoghurt (Sappi.com, 2014). DWP is mainly composed of cellulose, approximately 91- 96% of DWP is cellulose, and the remainder comprises hemicelluloses and residual lignin.

The global pulp producing industry is very concerned about brightness reversion in DWP because it is a raw material for the manufacture of many daily used products. There is a need for technologies that can permanently remove the chromophores in a cost-effective manner since they are suspected to be involved in the low brightness of the DWP. Thus the pulp and paper industry is searching for methods that do not damage the cellulose fibres and leave no trace of chemicals after the removal of chromophores (Sappi.com, 2015).

DWP contains small amounts of chromophores that are responsible for the off-white discolouration observed in cellulose derivatives. There is no known precise origin of chromophores in dissolving pulp; they could originate from the unbleached pulp, bleaching chemicals, or during further chemical derivatization of DWP (Rosenau *et al.*, 2004). The type of chromophores identified so far in DWPs are hydroxyl-1,4-benzoquinones, hydroxyl-1,4-naphthoquinones, and hydroxyacetophenones (Korntner *et al.*, 2015).

Furthermore, there is evidence that chemically pure cellulose (bacterial cellulose) does not initially contain chromophores. However, ageing treatment induces the formation of oxidised and degraded carbohydrates that result in the formation of chromophores. (Rosenau *et al.*, 2014). Further research is needed to investigate the effect of bleaching chemicals to ascertain how they induce the formation of chromophores in DWP.

2.6 Previous studies undertaken to understand brightness reversion in DWP

It has been demonstrated in the previous section, that different types of pulp may have various causes of chromophore formation. Research has been undertaken to understand the driving forces for chromophore formation, especially in DWP. Researchers have achieved this through pulp ageing studies using heat, pulp exposure to various light sources and, irradiation sources that induce brightness reversion.

2.6.1 Studies on the effect of pulp ageing using heat and UV light

Chemical pulps are subjected to various temperatures during processing. At higher temperatures above 100 °C, thermal decomposition of the polysaccharide chains in pulp fibres takes place. In order to study the effect of high temperatures in pulp ageing, the pulp is subjected to thermal reactions to cause yellowing, which has a negative result in the overall pulp production process (Beyer *et al.*, 2006).

Studies investigating thermal reactions during pulp production show that thermal decomposition and condensation reactions are necessary mechanisms that form chromophores in aged cellulosic materials. Thermal decomposition results in oxidised structures that further form chromophores upon ageing (Rosenau *et al.*, 2007c). The main compounds involved in brightness instability during heat exposure are oxidised compounds with functional groups such as the carbonyl, carboxy, ketones, furans and phenols (in lignin containing pulps) (Chirat and De La Chapelle, 1999).

Pulp ageing studies have also been undertaken by exposing pulp to UV light sources, such as sunlight, carbon arc, Xenon lamp, vapour lamp, and lasers, for accelerated ageing (Chirat and De La Chapelle, 1999). UV-light induces cellulose degradation by means of photolytic reactions at wavelengths below 340 nm. However, at wavelengths above 340 nm, photolysis reactions stop and the degradation proceeds by means of photosensitized reactions, that further result in pulp discolouration. The extent of pulp degradation depends on factors such as the thickness of pulp, impurities contained in the pulp sample, the intensity of the light source, and the energy distribution of the light source (Padfield, 1965).

Heat has been shown to causes a decrease in pulp viscosity and results in more brightness reversion than light exposure (Chirat and De La Chapelle, 1999). This suggests that different oxidative reactions occur during exposure to light and heat. It can also be deduced that more polymer chain scission takes place during heat exposure, thus forming more carbonyl compounds that cause yellowing. Heat and light ageing of pulps are used to simulate the properties of historical materials, but there is no evidence that the oxidative reactions that take place under natural conditions are similar to the reactions that occur at elevated temperatures and UV light.

The advantage of using heat is that it can introduce reactions that are unlikely to occur at room temperature, hence, it gives the opportunity to explore more reactions that can occur under adverse pulp storage conditions. UV light exposure has potential to cause ageing without significantly changing pulp properties. It is, therefore, better than heat ageing for imitating natural ageing conditions (Yatagai and Zeronian, 1994).

2.6.2 Studies on the effect of pulp irradiation

Irradiation of pulp using a source of energy, is usually used in studies aiming to improve the reactivity of dissolving pulp for downstream chemical processing, during the production of cellulose derivatives (Iller *et al.*, 2002). In effect, pulp irradiation results in two major reactions, the depolymerization and the oxidation of cellulose. Depolymerisation results in reduced cellulosic fibre strength due to the breaking of bonds and the formation of low molecular weight oxidised compounds. Cellulose oxidation results in colour reversion of the cellulose fibres

(Bouchard *et al.*, 2006). Both reactions that take place during irradiation of pulp lead to the formation of chromophores hence, brightness reversion.

The mechanism for cellulose oxidation occurs through a radical pathway, resulting in the formation of many oxidised compounds. In earlier studies, carbonyl compounds were believed to cause yellowing in pulps and then, later studies indicated that it was mainly ketones and furans that are formed during cellulose degradation, that result in the yellowing of cellulosic pulp (Beyer *et al.*, 2006, Shen and Gu, 2009, Mosca Conte *et al.*, 2012).

Chemical pulps are bleached extensively to reach high brightness levels. This means that the cellulose is not chemically pure, due to the presence of residual bleaching chemicals that can induce degradative reactions in the cellulose. There is evidence that chemically pure cellulose does not contain chromophores. However, the aged cellulose - either chemically induced ageing or natural ageing - results in the formation of chromophores (Rosenau *et al.*, 2014).

2.7 Methods to control chromophores

The dark colour of unbleached pulps is removed through bleaching. In the pulp and paper industry, the efficiency of the bleaching process is measured by the kappa number or the brightness levels of the final products (Barbosa *et al.*, 2013a). Beyond chemical bleaching of wood pulps, environmentally friendly techniques have been developed to improve the brightness of the pulp.

2.7.1 Chemical bleaching of pulps

Bleaching chemicals used in the pulp and paper industry are oxidising and reducing agents that achieve high brightness through solubilization, chlorination, decolonization and removal of the lignin (Bajpai, 2010). The lignin is the primary target during bleaching because it is the leading cause of the dark colour in unbleached pulps, (especially unbleached kraft pulps) due to its structural complexity, high molecular weight, and its hydrophobic nature (Heitner *et al.*, 2010).
In addition to the removal of lignin, the bleaching process also aims to remove impurities inherited from the digesters, hemicelluloses and extractives with the purpose of achieving high brightness pulp with a high cellulose content (Sixta *et al.*, 2006, Bajpai, 2010). In the manufacture of DWPs destined for making cellulose derivatives, it is important that the bleaching agents remove all the wood components other than cellulose.

Bleaching is carried out in a multi-stage sequence that alternates delignification and removal of dissolved material through alkaline extraction (Bajpai, 2010). The bleaching sequence is described using the following abbreviations: C (Chlorination), D (Chlorine dioxide), E (alkali, extraction with sodium hydroxide), H (Calcium or sodium hypochlorite), N (nitrogen dioxide), P (Hydrogen peroxide), O (Oxygen) and Z (ozone) as noted in Table 2.2 (Bohnet, 2003). For example, the five-stage bleaching sequence (CEDED) was popular in the 1950s for the bleaching of kraft pulps to achieve a high brightness pulps with good fibre strength (John Andelin *et al.*, 1989).

Due to environmental concerns and regulations regarding the release of toxic halogenated compounds, bleaching was achieved with or without chlorine-based chemicals (Bajpai, 2010). Elemental chlorine free (ECF) and totally chlorine free (TCF) procedures have been employed to comply with environmental regulations. The ECF uses chlorine dioxide within the set limits for the discharge of adsorbable halogenated organic compounds, and the TCF eliminates all the chlorine-based chemicals in the bleaching process (Suess, 2010).

Limitations: It has been shown that the use of bleaching chemicals can be harmful to the environment due to the release of toxic compounds. If the bleaching process is not done correctly, it can damage the pulp fibres and therefore resulting in reduced fibre strength. Furthermore, it has been shown that the bleaching chemicals induce cellulose degradation thus leading to the yellowing of the pulp through the formation of chromophoric compounds.

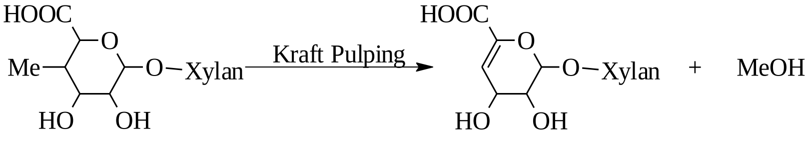
2.7.2 Microbial and enzymatic bleaching of pulps

To reduce environmental pollution resulting from chemical bleaching industries, microbial techniques have been used to treat the yellowing of wood pulps. These techniques have been developed over several years, and they seem to be successful in some of the pulping industries. Chuphal *et al*. (2005) studied the anaerobic treatment of pulp using six different types of bacterial colonies. Findings show that the aerobic treatment was more successful than anaerobic treatment. Aerobic treatment of the pulp resulted in a significant reduction of the yellow colour, the lignin and the total phenol content were significantly reduced (Chuphal *et al.*, 2005).

Pulp yellowing has also been reduced by introducing microbial enzymes during the bleaching process. This process is known as bio-bleaching, and it requires the control of parameters such as pH and temperature to prevent enzyme degradation. Kannan and Oblisami (1990) observed that the colour of the mill effluent was light brown due to the presence of lignin compounds resulting from blow-heat condensate washing (Kannan and Oblisami, 1990). To reduce the light brown colour, they used *Aspergillus niger* at various concentrations of glucose since earlier studies (Belsare and Prasad, 1988, Pellinen *et al.*, 1988, Yin *et al.*, 1989) had shown that the addition of a co-substrate like glucose improves the degradation of lignin and related compounds.

Subsequent studies of similar nature employed the xylanases for bleaching of kraft pulps. Xylanases are a class of enzymes responsible for the degradation of hemicellulose-based heteropolymers into useful sugars. It is well known for breaking the conjugated bonds of hexenuronic acid (**18**) that are formed from the dehydration of 4-methyl-glucuronic acid units (**17**) in xylan, Figure 2.8 (Kenealy and Jeffries, 2003, Petit-Breuilh *et al.*, 2004, McCarthy *et al.*, 1985).

Since some of the hemicelluloses are degraded during bleaching, the process of bleaching with the xylanases is simplified because the accessibility of the pulp is increased (Jeffries *et al.*, 1996). This pulp decolourization method has been widely used and has been shown to significantly improve the level of brightness in DWPs (Gangwar *et al.*, 2014, Nagar *et al.*, 2014).



17

18

Figure 2.8: Formation of chromophoric hexenuronic acid.
Adapted from Petit-Breuilh *et al.* (2004).

Limitations: Studies show that a few chromophoric compounds were identified during the microbial and enzymatic extraction. Most of them were eliminated by removing the yellow or light brown colour. It shows that this method does not determine the chemical structures (except for the hexenuronic) acid and the nature of chromophores. Thus, it cannot prevent the formation of chromophores, which is the ideal solution to brightness reversion.

2.8 Analysis of chromophores in wood pulps

The analysis of chromophores in pulps is difficult because of their existence in small quantities at ppm or ppb scales. A number of analytical methods that have been developed for the determination of chromophores are summarised below.

2.8.1 Chromophore release and identification method

The common challenge in the isolation and characterization of chromophores is their minute quantities in the pulps, and this is a typical problem in natural product isolation. However, this technique, of identifying and extracting the offending chromophores, remains relevant since it provides access to the discovery of new compounds that may be causing brightness reversion in wood pulps. Recently, compound isolation has been simplified by employing new technologies such as HPLC and NMR for the identification of novel compounds (Sasidharan *et al*., 2011).

The most efficient technique known thus for the analysis and identification of chromophores in cellulosic fibres was described by Rosenau *et al*. (2004). The technique, termed, chromophore release and identification (CRI) method was described as a three step process commencing with the pre-treatment of pulp fibres with boron trifluoride acetic acid complex (BF_3.2HOAc) and an antioxidant, followed by chromatographic purification of the resulting residue, and finally, identification of the structures of chromophores using mass and NMR spectroscopy techniques, in comparison to authentic compounds (Rosenau *et al.*, 2004, Rosenau *et al.*, 2005). A schematic of the method is illustrated in Figure 2.9.

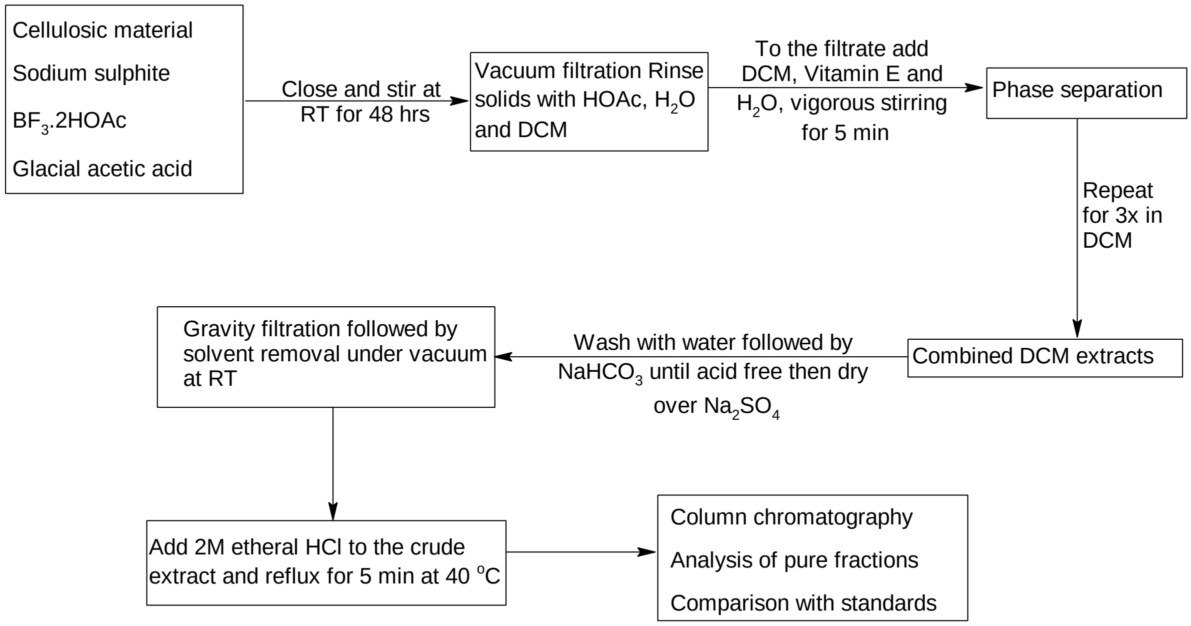


Figure 2.9: Chromophore release and identification procedure.
Adapted from Rosenau et al. (2004).

The CRI method enabled identification of two classes of chromophores that are believed to contribute to brightness reversion of chemical pulps; the primary and secondary chromophores (Rosenau *et al.*, 2004). Primary chromophores originate from wood pulp components such as cellulose, hemicellulose, lignin and extractive whereas secondary chromophores are formed by process chemicals used during pulping and bleaching, and contain functional groups inherited from the process chemicals (Rosenau *et al.*, 2007a).

The main compounds identified were substituted quinones and acetophenones arising from the oxidation and degradation reactions of the polysaccharides in pulp, belonging to the group of primary chromophores (Rosenau et al., 2014). The primary chromophores are structurally composed of carbon, hydrogen and oxygen, whereas the secondary chromophores contain compounds like sulphur, inherited during pulp processing (Korntner et al., 2015). Rosenau and co-workers isolated primary (**19-23**) and secondary chromophores (**24-28**) from lyocell fibres (**19-25**), cellulose triacetate (**26**) and viscose (rayon) fibres (**27-28**) (Rosenau *et al.*, 2004, Korntner *et al.*, 2015), as shown in Figure 2.10.

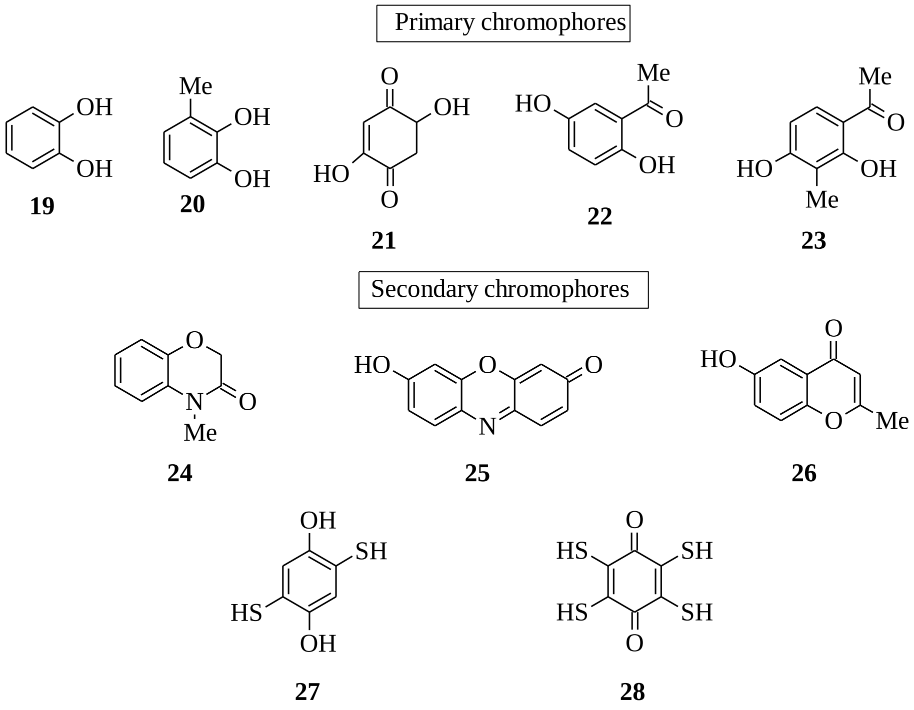


Figure 2.10: Primary and secondary chromophores isolated from lyocell fibres. Adapted from Rosenau et al. (2004) and Korntner et al. (2015).

Limitations: The chemical extraction of chromophores is only applicable to pulp materials containing very low amounts of lignin or lignin-free materials. Substantial quantities of lignin can overload the column and therefore lead to a poor separation and analysis of the compounds. The method is unable to provide quantitative data on the of amounts of individual chromophores due to their miniscule amounts of the purified extracts as well as the complexity of the technique (Korntner *et al.*, 2015). Furthermore, the CRI method is limited to the identification of quinoid and aromatic structures meaning that non-aromatic chromophores cannot be identified using this approach (Rosenau *et al.*, 2011). In general, the chemical extraction method uses expensive organic solvents, and the procedure is laborious in that it can takes about a week to generate results.

2.8.2 Spectroscopic methods

Several spectroscopic methods have been used for direct and indirect characterization of chromophores in wood pulps. These techniques include UV/Vis, FT-Raman, FTIR, NIR, NMR, mass spectrometry, and fluorescent spectroscopy (Schmidt and Heitner, 1993, Sikorska *et al.*, 2006, Wójciak *et al.*, 2014). Listed below are advantages and disadvantages of the techniques used to study chromophores in pulps.

Advantages

- Chromophores absorb UV light and are, therefore, easy to detect.
- Allows for quantitative analysis of chromophores.

- Can be used with solids and liquids.
- Usually fast and can detect a broad range of functional groups.

Disadvantages

- Spectra can overlap due to mixtures of molecules.
- Spectra are not highly specific to molecules.
- Light absorption can be dependent on sample conditions.

The spectroscopic techniques can yield accurate results if used in conjunction with other analytical techniques, such as chromatography, to compensate for the disadvantages, such as the overlap of the spectra.

2.8.3 Chromatographic methods

Chromatographic techniques, such as HPLC, TLC, column chromatography, gas chromatography, and size exclusion chromatography, have been commonly used for the study of chromophores in cellulosic materials (Gellerstedt and Dahlman, 2003, Rosenau *et al.*, 2004). Their pros and cons are listed below:

Advantages

- Can separate very complex mixtures.
- Individual components can be collected separately.
- Quick and accurate results are possible.
- Work well with most spectroscopic methods.

Disadvantages

- The sample must be able to dissolve in an organic solvent.
- May require the use of many expensive organic solvents.
- Can be laborious.
- Require the use of other analytical techniques for structural elucidation.

Since chromophores occur in very low concentrations in DWP, good separation of the compounds before structural elucidation is essential. However, achieving good separation of compounds that occur in small quantities can be tough to do. Since chromatographic techniques work well with most spectroscopic methods, it shows that chromatography in conjunction with spectroscopy can be a useful component in chromophore identification in DWP.

2.8.4 Analytical methods specific for carbonyl and carboxyl groups

Carbonyl and carboxyl functional groups found in pulps are originally present in wood as part of the 4-*o*-methyl glucuronic acid units of xylan and further generated during pulp bleaching. During pulp bleaching, the polysaccharides are oxidised, thus resulting in the formation of oxidised functional groups such as carbonyl, carboxyl, keto and aldehyde groups (Sjöström and Alén, 2013). These functional groups, especially the carbonyl groups have a significant contribution to reducing the strength of cellulose and most importantly, they result in the yellowing of bleached chemical pulps by forming chromophores (Lewin, 1997). Furthermore, the effect of the carbonyl groups is exacerbated by the presence carboxylic acid groups in the pulps (Barbosa *et al.*, 2013b).

Quantitative analysis of these functional groups is difficult due to their maniscule concentrations. As a result, these functional groups cannot be identified using conventional spectroscopic techniques such as UV, IR, NMR and Raman spectroscopy (Röhrling *et al.*, 2002). Determination of the carbonyl groups in pulp relies on their ability to form stable complexes with chelating agents such as phenylhydrazine through titration (Sjöström and Alén, 2013). Conventional methods for carbonyl determination such as copper number, oxime and cyanohydrin methods have largely been criticised for providing indirect determination by the copper number and low reproducibility provided by the oxime and cyanohydrin methods (Röhrling *et al.*, 2002).

The effect of carbonyl groups in cellulosic pulps has been widely investigated following the incompetence of the conventional methods. Innovative approaches for carbonyl analysis such as fluorescence spectroscopy have been introduced (Potthast *et al.*, 2003). The analysis of the carbonyl groups in cellulosic pulp was achieved through fluorescence spectroscopy because of its ability to identify oxidised functional groups at very low concentrations. Highly selective fluorescent labels such as carbazole-9-carboxylic acid [2-(2-aminooxyethoxy)ethoxy]amide and 9H-fluoren-2-yl-diazomethane have been used to selectively mark the carbonyl groups followed by analysis with gas permeation chromatography (Röhrling *et al.*, 2002, Potthast *et al.*, 2003, Bohrn *et al.*, 2006). A linear correlation between the post colour number and the carbonyl content was established in fully bleached kraft pulps with carbonyl groups that were introduced by the oxidising hypochlorous acid (Zhou *et al.*, 2011). The advantage of using the fluorescence markers is that they allow for the determination of the total carbonyl content, thus measuring the oxidising effect of the bleaching chemicals during bleaching that leads to pulp yellowing (Röhrling *et al.*, 2002).

It has been shown that the study of chromophores in the pulp is very challenging in terms of identification and characterization. It is evident that a lot of work still needs to be done about developing analytical techniques that can identify chromophores so that the occurrence of chromophores can be eliminated. To this end, a combination of spectroscopic and chromatographic techniques presents a promising means to be explored for chromophore identification in DWP.

2.9 Py-GC/MS as a novel and rapid analytical method for chromophore identification

In light of the disadvantages of the aforementioned methods, analytical techniques that allow for in-situ identification of chromophores in DWP are needed. Ideally, the techniques should be rapid, accurate, and applicable to pulps with minimal processing. Rapidity would allow for their use in monitoring industrial process samples where “time is money” and mills cannot afford to wait for results from procedures that take long times to process. Hence, in this study, a novel method was developed for direct analysis of chromophores in DWP.

Analytical pyrolysis, coupled with gas chromatography/mass spectrometry (Py-GC/MS), was used for direct analysis of chromophores in DWP. Unlike the previously reported methods for chromophore analysis, the Py-GC/MS analysis does not involve pre-extraction, and therefore, artefacts that may arise during extraction were avoided, hence, allowing the greater accuracy of results.

It is important to understand the primary aspects of analytical pyrolysis because it is the heart of this study.

2.10 Introduction to pyrolysis

Pyrolysis is defined as the breakdown of chemical bonds in an organic material at elevated temperatures and inert atmosphere. The two types of pyrolysis are applied pyrolysis and analytical pyrolysis (Sitholé, 2006). Applied pyrolysis involves the use of thermal reactions to produce useful chemicals, such as catalytic cracking used to produce hydrocarbons and hydrothermal treatments employed in the conversion of waste into valuable chemicals. Analytical pyrolysis is a technique that is used to study the molecular fragments released during pyrolysis in order to identify the nature and identity of the original substance (Sitholé, 2006, Wampler, 2006). The following paragraphs will focus on analytical pyrolysis and its application in the studies of biomass composition.

2.10.1 Analytical pyrolysis

The different types of analytical pyrolysis techniques include the isothermal furnace, inductively heated (curie point) filament, resistively heated filament and thermal extraction pyrolyzer. Sitholé (2006) reviewed the application of the different pyrolysis techniques, and the advantages and disadvantages of the techniques were outlined. Each of these pyrolysis techniques can use temperatures over 800 °C while providing reproducible results for pyrolysis of small samples. The choice of pyrolysis technique depends on factors such as the instrument availability, experimental requirements, the financial needs and personal preference. In this study, the isothermal furnace pyrolyzer was used due to its availability and its suitability for the experimental requirements.

The temperature of the isothermal furnace is constantly maintained at a specific temperature required for pyrolysis of the sample. The sample is introduced into the hot isothermal furnace for pyrolysis and then flushed into the GC column in order to prevent secondary reactions from taking place (Wampler, 2006). Traditional furnace pyrolyzers used to be large consisting of large pyrolysis tubes, hence, making the furnace to take longer to heat up to the set pyrolysis temperature (Figure 2.11). This type of pyrolysis used to require large sample sizes for analysis and required the use of a splitter for reducing the flow rate into the analytical flow rates before the analyte reaches the GC column (Sitholé, 2006). Modern isothermal furnace pyrolyzers are designed such that they fit directly into the inlet of the GC column and they are suitable for analysis of the small quantities of samples (Tsuge *et al.*, 2011).

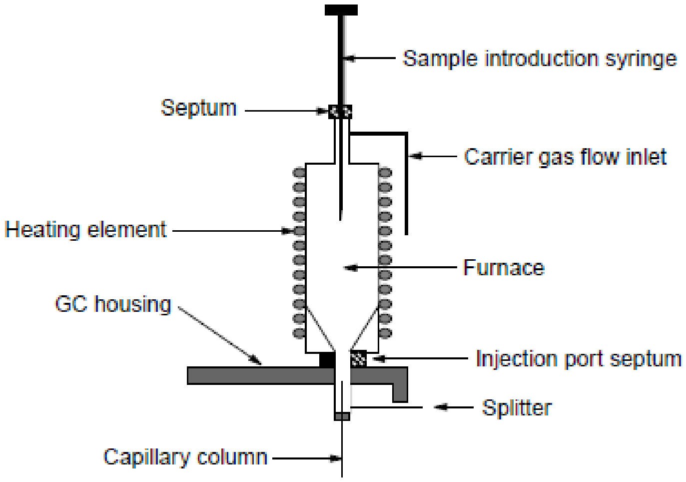


Figure 2.11: Schematic of a traditional furnace pyrolyzer.
Adapted from Sitholé (2006).

The sample can be introduced into the furnace pyrolyzer in the form of a liquid or a solid. Liquid samples are introduced by injection into the furnace where they are vaporised and pyrolyzed. Solid samples are also injected using a needle that is suitably designed for injection of solids (Sitholé, 2006). Soluble solid samples can be dissolved in a solvent and then injected in the form of a solution. However, insoluble solid samples were not suitable for this method. A modern method for introducing solid samples was developed by Emeritus Professor Shin Tsuge of Nagoya University in Japan. Tsuge's method uses a small stainless steel cup for containing the sample that free-falls into the ceramic heater of the micro-furnace (Frontier-Laboratories, 2013).

According to Tsuge's method, the stainless-steel cup (containing a sample) is attached to the pyrolyzer, and the sample drop button (Figure 2.12) is pressed when the instrument indicates that it is "ready for injection". This occurs when the temperature and pressure have stabilised. The stainless-steel cup containing the sample is then released into the ceramic heater where the pyrolysis of the sample takes place once the start button is clicked as indicated by the dialogue box on the computer. The pyrolysis products are flushed by the high-pressure carrier gas into the GC column for separation. The GC and MS analysis start immediately after the pyrolysis has been completed. Figure 2.12 shows a modern furnace pyrolyzer with the sample cup in a standby position and a dropped position where the pyrolysis occurs.

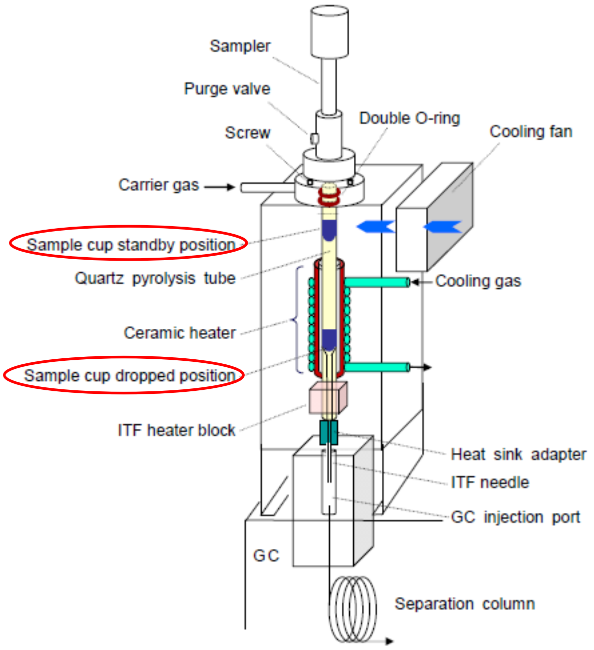


Figure 2.12: Schematic of a modern furnace pyrolyzer.
Adapted from Frontier-Laboratories (2013).

The fragments released during the pyrolysis are flushed into the GC column by the carrier gas shown in Figure 2.13. The main advantage of this method is that it allows for analysis of soluble and insoluble solid materials in minute quantities and has an improved reproducibility (Sitholé, 2006).

2.10.2 Pyrolysis temperature

The two processes involved during analytical pyrolysis are the thermal decomposition of the material followed by the detection of the pyrolysis products, with a suitable detector (Sitholé, 2006). The thermal decomposition of the sample is initiated by elevated pyrolysis temperatures. The isothermal furnace is heated by the heating element that is coiled around the furnace (Figure 2.11). The temperature of the pyrolyzer is monitored by a sensor that communicates to the controller where the temperature changes are made. The physical properties of the furnace (diameter, mass, length and thickness) can cause differences from the temperature experienced by the sample and the temperature inside the pyrolysis tube. Similarly, the physical properties of the sample such as the size and heat capacity can determine the heating rate and the temperature experienced by the sample (Wampler, 2006).

Pyrolysis of samples at a very low temperature does not cause fragmentation but can dry the sample and remove moisture and other volatile components that can cause interference in the analysis of the sample. Mild pyrolysis temperatures produce low amounts of pyrolysis products, and some polymers cannot be degraded at low temperatures. High pyrolysis temperatures result in high amounts of pyrolysis products that cannot be easily interpreted by a detector (Sitholé, 2006). To overcome this, the pyrolysis products can be flushed into the GC column by the carrier gas immediately after pyrolysis for chromatographic separation. Commonly used detectors in analytical pyrolysis are the mass spectrometer, FTIR spectrometer and flame ionisation detector (Sitholé, 2006, Wampler, 2006). In this study, the pyrolysis was coupled to the GC and the MS (Py-GC/MS) for effective identification of chromophores in DWP.

In Py-GC/MS, the pyrolysis products are flushed by the carrier gas into the GC where they are separated based on their volatility. The carrier gas is usually used at high flow rates, above 50 mL/min to prevent chromatographic co-elution and secondary pyrolysis reactions from taking place. An appropriate split ratio can be used to avoid column saturation. However, there is maximum sensitivity through the direct flow, without applying the split ratio. After adequate separation by the GC, the pyrolysis products are then detected by the MS. The complexity of the resulting chromatogram makes it difficult to identify individual peaks from the total ion chromatogram manually, and therefore the library attached to the instrument with thousands of compounds becomes a useful part of the instrument.

The ability of the Py-GC/MS to analyse insoluble materials, with complex structures at trace concentrations, makes it versatile and applicable for analysis of a wide range of samples. The combination of a multi-shot pyrolysis with a Py-GC/MS detector supersedes the performance of any other analytical techniques because it gives a complete analysis of a sample with minimal or no sample preparation. The multi-shot pyrolyzer labelled in Figure 2.13 allows for four analysis methods to be used, namely, single shot, double shot, evolved gas analysis and heart-cut EGA (Frontier-Laboratories, 2013). In this study, we used the single shot analysis using the stainless-steel cup as per method developed by Professor Tsuge.

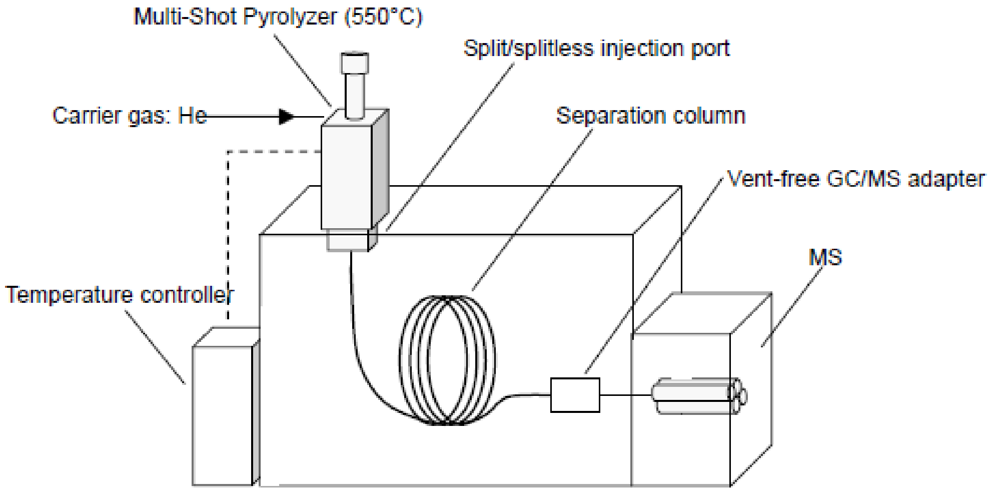


Figure 2.13: Schematic of the Py-GC/MS.
Adapted from Frontier-Laboratories (2013).

2.11 Previous studies on pyrolysis of biomass

To understand the pyrolysis of the lignocellulosic biomass, several studies have been undertaken with the focus on the three components of wood namely the cellulose, hemicellulose and lignin. The following paragraphs review the pyrolysis of these components with interest in the pyrolysis products.

2.11.1 Pyrolysis of cellulose

Cellulose is one of the most abundant polymers in the world accounting about 50% of the lignocellulosic biomass, and it is therefore used for understanding the changes that occur in biomass under various reaction conditions (Wang *et al.*, 2012). Cellulose is located in the secondary cell wall of the wood matrix where it is divided into three layers that are known as S1, S2 and S3 (Figure 2.14) (Behzad and Ahmadi, 2016). The structure of cellulose is composed of repeating units of β-D-glucopyranose linked through the 1,4-glycosidic bonds. The primary reaction during cellulose pyrolysis involves the breaking of the 1,4-glycosidic linkages; subsequent reactions include polymerization, dehydration and reforming reactions resulting in the formation of active cellulose (Demirbaş, 2000, Patwardhan *et al.*, 2011).

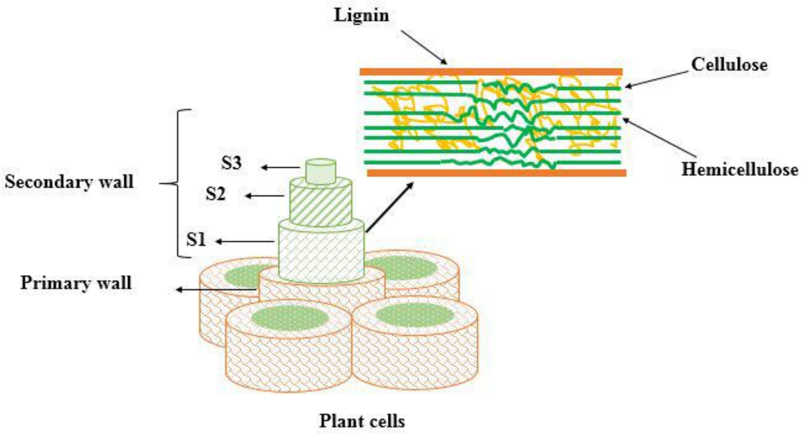


Figure 2.14: The location of cellulose in wood.

Adapted from Behzad and Ahmadi (2016).

The pyrolysis of cellulose starts at low temperatures (150 °C) however, low temperatures delays the first process that allows the formation of the active cellulose (Shen and Gu, 2009). At temperatures above 300 °C, cellulose pyrolysis occurs in two competitive reactions. Firstly, forming the char and gaseous products (carbon dioxide, carbon monoxide) followed by the formation of tars, mainly the levoglucosan (Kawamoto *et al.*, 2003). It has been shown that levoglucosan is the main pyrolysis product of cellulose among other anhydrosugars formed (Kawamoto *et al.*, 2003, Shen and Gu, 2009).

Wang et al. (2012) studied the mechanism of cellulose (microcrystalline cellulose) pyrolysis at 600 °C using the Py-GC/MS technique. From this study, it was shown that the main pyrolysis products of cellulose were the pyrans (such as levoglucosan and levoglucosenone) followed by the furans (such as furfural and 5-hydroxymethyl furfural) and other low molecular weight linear compounds as shown in Table 2.3. The area percentage of the furans was the highest in a range of temperatures between 450 °C and 700 °C (Wang *et al.*, 2012).

Table 2.3: Major pyrolysis products of MCC. Adapted from Wang et al. (2012).

Retention time (min)	**Compound**	**Area%**
1.45	Carbon dioxide	5.52
1.77	Acetaldehyde	4.19
2.22	Furan	0.57
3.44	2,3-Butanedione	2.35
8.20	1-Hydroxy-2-propanone	3.60
9.14	2-Cyclopenten-one	0.47
10.55	Acetic acid	2.12
10.84	Furfural	15.91
10.93	2(5H)-Furanone	1.80
11.46	Ethanone,1-(2-furanyl)-	2.84
11.93	Propanoic acid	1.39

12.51	5-Methyl furfural	1.64
13.75	Furan methanol	1.28
15.37	1,2-Cyclopentanedione	2.86
16.15	2-Hydroxy-3-methyl-2-cyclopenten-1-one	1.09
16.46	Dihydro-4-hydroxy-2(2H)-furanone	2.53
18.00	Maltol	0.84
18.40	Levoglucosenone	8.71
21.71	3,5-Dihydroxy-2-methyl-4H-pyranone	3.52
23.17	1,4:3,6-Dianhydro-α—D-glucopyranose	2.53
24.23	5-Hydroxymethyl furfural	6.41
42.91	Levoglucosan	4.52

A similar study of microcrystalline cellulose pyrolysis was performed at temperatures ranging from 300 – 700 °C and over 5 s, 10 s and 30 s (Lu *et al.*, 2011). Figure 2.15 shows the results obtained at 600 °C over 5 s and 30 s. The names of the numbered peaks (1-13) are given in Table 2.4. Lu *et al.* (2011) indicated that the anhydrosugars (peak 11 and peak12) were the main cellulose pyrolysis products in both 5 s and 30 s pyrolysis times. Figure 2.15 shows that at 5 s, the major pyrolysis products were the compounds represented by peaks 1 and 11 (hydroxyacetaldehyde and 1,5-anhydro-4-deoxy-D-glycerohex-1-en-3-ulose) followed by peak 12 (levoglucosan). However, when the pyrolysis time was increased to 30 s, the levoglucosan peak (12) was most dominant peak. This indicates that longer pyrolysis time and higher temperature favour the formation of levoglucosan.

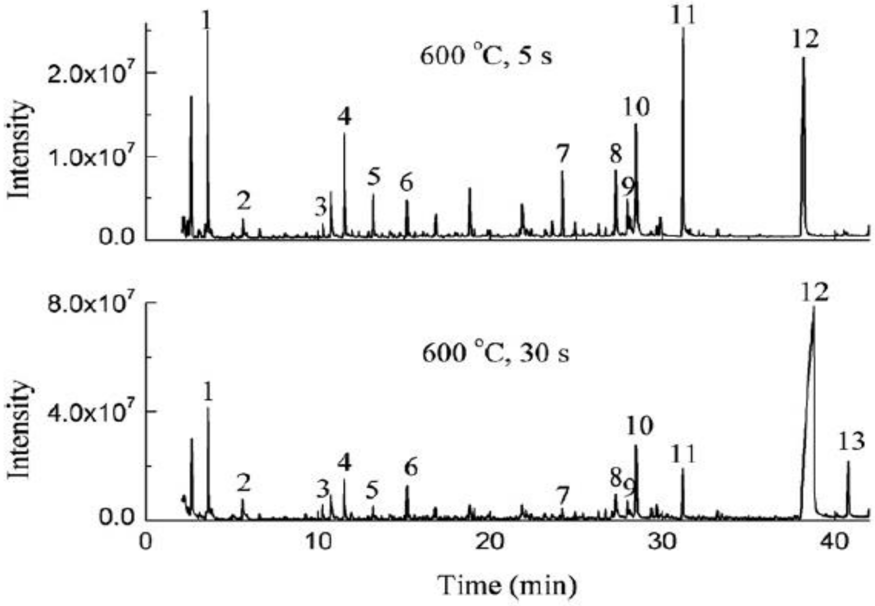


Figure 2.15: Chromatograms from Py-GC/MS analysis of MCC at 600 °C over 5 s and 30 s. Adapted from Lu *et al.* (2011).

Table 2.4: Peak identification for MCC at 600 °C. Adapted from Lu *et al*. (2011).

Compound No.	Compound
1	Hydroxyacetaldehyde
2	1-hydroxy-2-propanone
3	Methyl pyruvate
4	Furfural
5	4-hydroxydihydro-2(3H)-furanone
6	1,2-Cyclopentanedione
7	Levoglucosenone
8	1-Hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one
9	1,4:3,6-Dianhydro-α-D-glucopyranose
10	5-Hydroxymethyl-furfural
11	1,5-Anhydro-4-deoxy-D-glycerohex-1-en-3-ulose
12	Levoglucosan
13	1,6-anhydro-β-D-glucofuranose

Table 2.5 shows that some of the anhydrosugars are favoured by low temperatures and longer pyrolysis time. However, some of the anhydrosugars and derivatives are similar to levoglucosan, they can survive higher pyrolysis temperatures and longer pyrolysis time.

Table 2.5: Peak area percentage of anhydrosugars and derivatives at different pyrolysis conditions. Adapted from Lu et al. (2011).

Temperature (°C)	Time (Seconds)	Peak Area (%)
400	30	83.7
450	5	77.3
	10	58.3
	30	63.8
500	5	54.8
	10	50.2
	30	72.1
550	5	41.5
	10	43.2
	30	69.8
600	5	39.3
	10	44.8
	30	69.8
700	5	44.3
	10	52.1
	30	64.0

2.11.2 Pyrolysis of hemicellulose

Hemicellulose forms part of the primary cell wall of wood; it is the second most abundant component of wood. Relative to the crystalline and strong structure of cellulose, the structure of hemicellulose is random and amorphous with lower strength, organised around the cellulose matrix (Guo *et al.*, 2011), Figure 2.14. Sugars such as xylose, mannose, rhamnose and fructose, are the saccharides contained in hemicellulose. The composition of hemicelluloses differs in hardwoods and softwoods, the hardwoods are dominated by *o*-acetyl-(4-*o*-methylglucorono)xylan, and the softwoods are dominated by galactoglucomannan and a small amount of arabino-(4-*o*-methylglucorono)xylan (Ek *et al.*, 2009). Xylan is the most abundant hemicellulose, and therefore it is commonly used as a model compound for studies involving reactions of hemicellulose. In contrast to studies of cellulose and lignin pyrolysis, there has not been much interest in pyrolysis studies of the hemicelluloses.

Pyrolysis of xylan at low temperatures between 220 – 315 °C resulted in a rapid weight loss producing mainly gaseous products such as methane, carbon monoxide and carbon dioxide (Yang *et al.*, 2007). Xylan pyrolysis at high temperatures above 800 °C produced gases, tar, water and char with the furans being the most abundant constituents of the tar residue (Khezami *et al.*, 2005). Heating of xylan at temperatures between 450 – 700 °C over 10 seconds showed that a short retention time resulted in a high conversion of xylan with a rapid weight loss by 4.7% and longer retention times resulted in severe decomposition of xylan (Wang *et al.*, 2013). The main pyrolysis products identified were the carboxylic acids such as acetic acid and propanoic acids, the aldehydes, furans and ketones. The chromatogram obtained from fast pyrolysis of xylan is shown in Figure 2.16, and the major compounds are listed in Table 2.6 (Wang *et al.*, 2013).

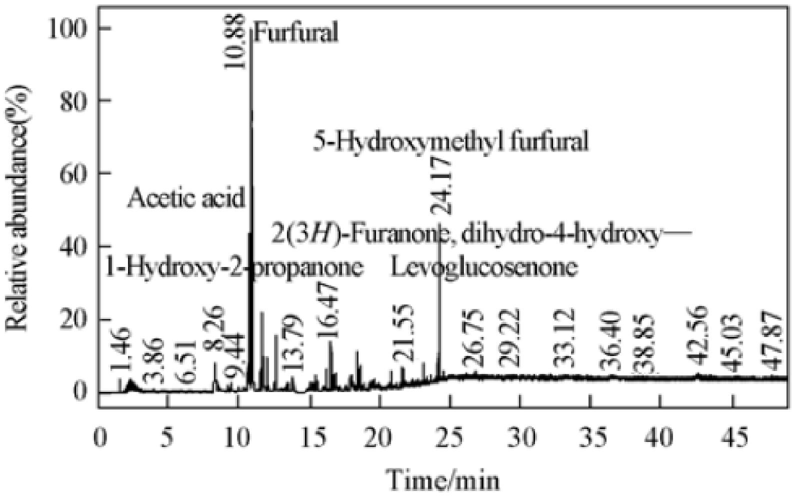


Figure 2.16: Chromatograms from Py-GC/MS analysis of xylan showing the main pyrolysis products.

Adapted from Wang *et al*. (2013).

Table 2.6: Pyrolysis degradation products of xylan. Adapted from Wang *et al*. (2013).

Retention time (min)	**Compound**	**Area (%)**
8.26	1-Hydroxy-2-propanone	3.31
8.54	Glycolic aldehyde	0.68
9.15	2-Cyclopenten-1-one	0.65
10.64	Acetic acid	20.11
10.88	Furfural	20.24

11.60	Formic acid	7.60
11.99	Propanoic acid	2.16
12.57	5-Methyl furfural	3.37
15.40	1,2-Cyclopentanedione	0.86
16.47	2(3H)-Furanone, dihydro-4-hydroxy	3.56
18.39	Levoglucosenone	2.12
23.13	1,4:3,6-Dianhydro-α-d-glucopyranose	1.23
24.17	5-Hydroxymethyl furfural	6.39
42.56	Levoglucosan	1.07

2.11.3 Pyrolysis of lignin

Lignin is one of the primary components of the middle lamella of the plant cell wall and therefore forms an important part of the lignocellulosic biomass. Similar to hemicellulose, the composition of lignin is different between softwoods and hardwoods. Softwoods contain about 28%, and hardwoods contain about 20% of lignin (Heitner *et al.*, 2010). The complex structure of lignin is composed of three alcohol monomers known as *p*-coumaryl (**29**), coniferyl (**30**) and syringyl alcohol (**31**) as shown in Figure 2.17. Further degradation of the lignin monomers results in the formation of low molecular weight aromatic compounds such as compounds **32** – **35**. The aromatic rings of the lignin monomers are named based on the number of methoxy (OMe) groups attached to the aromatic ring.

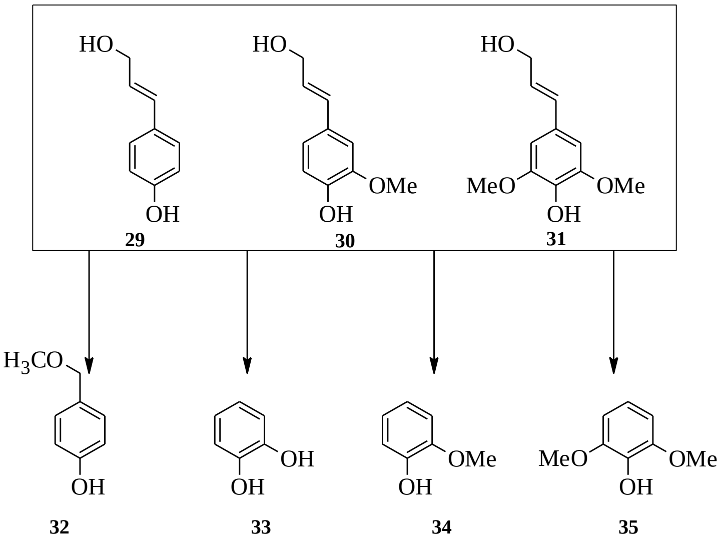


Figure 2.17: Examples of lignin monomers and their degradation products. Adapted from Heitner et al. (2010).

The aromatic ring without the OMe group is known as the *p*-hydroxyphenyl monomer, derived from the *p*-coumaryl alcohol, the ring with one OMe group is known as the guaiacyl monomer, derived from the coniferyl alcohol and the ring with two OMe groups is known as the syringyl alcohol. Softwood lignin is mainly composed of the coniferyl alcohol, and the hardwood lignin mainly consists of the coniferyl and sinapyl alcohol (Heitner *et al.*, 2010, Kutscha and Gray, 1970). This shows that the coniferyl alcohol is the main component of lignin in both softwoods and hardwoods.

Due to the complexity of the lignin structure, the pyrolysis of lignin is usually carried out at higher temperatures above 550 °C. The pyrolysis of unbleached softwood kraft lignin was conducted at 580 °C for 2 seconds (Figure 2.18), findings showed that the main degradation products of lignin were the hydroxyphenyl compounds originating from the polysaccharides formed during kraft pulping (Ohra-aho *et al.*, 2005). The main compounds identified were the guaiacyl type compounds, and a few *p*-hydroxyphenyl compounds were identified (Table 2.7). A portion of the softwood lignin structure is presented in Figure 2.19. Units A and C indicate branches from the main chain (B), with the numbers 1-10 showing the linkages of the coniferyl alcohol unit (Heitner *et al.*, 2010).

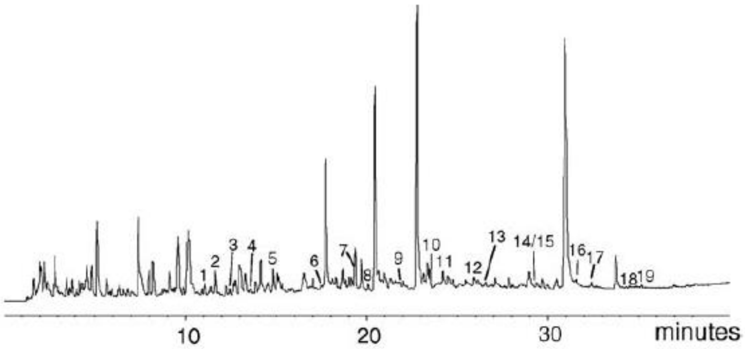


Figure 2.18: Chromatogram of unbleached kraft pulp showing peaks of main pyrolysis products.
Adapted from Ohra-aho et al. (2005).

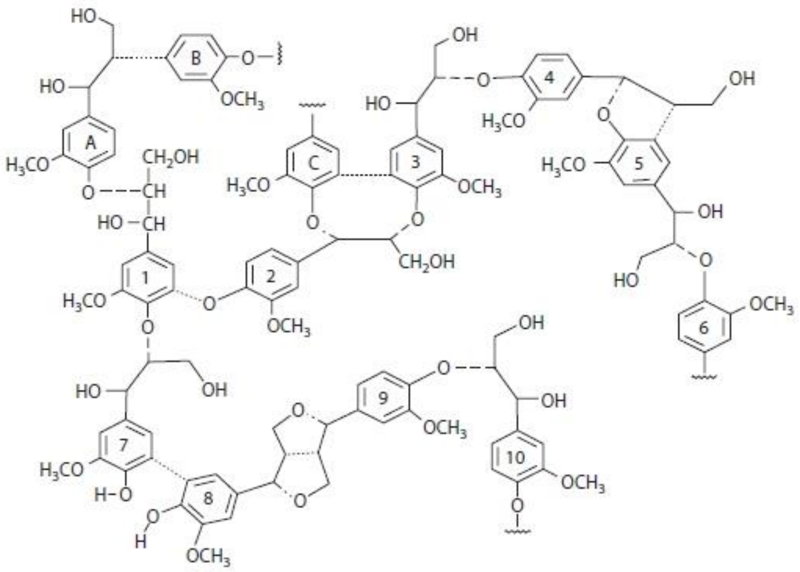


Figure 2.19: Schematic of softwood lignin.

Adapted from Heitner *et al*. (2010).

The brown colour of kraft lignin is usually associated with the presence of lignin, hence, it was interesting to compare the pyrolysis products of the kraft pulp to those of lignin. The Py-GC/MS analysis of unbleached kraft pulps resulted in a very low amount of lignin degradation products such as guaiacol and syrinyl compounds indicating that there were significant changes that occurred in the structure of the lignin during kraft pulping (del Río *et al.*, 2001).

Table 2.7: Aromatic pyrolysis products of unbleached kraft pulp. Adapted from Ohra-aho *et al*. (2005).

Peak number	**Compound**	**Structure**
1	Phenol	H
2	Guaiacol	G
3	2-Methylphenol	H
4	4-Methylphenol	H
5	4-Methylguaiacol	G
6	4-Ethylguaiacol	G
7	4-Vinylguaiacol	G
8	Eugenol	G
9	*cis*-Isoeugenol	G
10	*trans*-Isoeugenol	G
11	Vanillin	G
12	Homovanillin	G
13	Acetoguaiacone	G
14	4-(Oxy-allyl)guaiacol	G
15	4-(Hydroxy-prop-2-enyl)guaiacol	G
16	Dihydroconiferyl alcohol	G
17	*cic*-Coniferyl alcohol	G
18	*trans*-Coniferyl alcohol	G
19	Coniferaldehyde	G
H: Hydroxyphenyl-type; **G**: Guaiacyl-type		

2.11.4 Summary on pyrolysis of biomass

The reviewed studies on pyrolysis of the main components of the wood show that the cellulose, hemicellulose and lignin consist of some common pyrolysis products. Besides the gaseous pyrolysis products (CO_2 and CO), compounds such as levoglucosan, levoglucosenone, furfural and 5-hydroxymethylfurfural were common pyrolysis in both cellulose and xylan (Wang *et al.*, 2012, Wang *et al.*, 2013). Lignin pyrolysis products were distinct from cellulose and xylan pyrolysis products, they were mainly aromatic compounds. Furthermore, it was shown that there were minor quantities of lignin-type compounds in kraft pulp (unbleached and bleached) due to the structural changes that occur in lignin during pulping (del Río *et al.*, 2001).

2.12 Conclusion

This chapter has covered the background on chromophores and their formation in diverse types of wood pulps with the focus on DWP. Previous methods of identification of chromophores were reviewed with their advantages and disadvantages. A review of the previously used methods intimated that PY-GC/MS could be used as a viable method for rapid analysis of chromophores directly on pulps fibres without pre-extraction of the compounds from the pulp fibres. Thus, a novel, rapid, and efficient technique (Py-GC/MS) for identification of chromophores in DWP was introduced, and the method will be outlined in Chapter 3.

2.13 References

Albinsson, B., Li, S., Lundquist, K. & Stomberg, R. 1999. The Origin of Lignin Fluorescence. *Journal of Molecular Structure,* 508**,** 19-27.

Back, E. 2000. *Resin in Suspensions and Mechanisms of its Deposition,* Atlanta, USA: TAPPI Press.

Bajpai, P. 2010. *Environmentally Friendly Production of Pulp and Paper,* Hoboken, New Jersey: John Wiley & Sons.

Barbosa, B. M., Gomes, F., Colodette, J., Carvalho, D. & Manfredi, M. 2013a. Effect of Optical Brightening Agent (OBA) on Bleaching Process on Paper of Eucalyptus Kraft Pulp. *Natural Resources,* 4**,** 378-382.

Barbosa, L. C., Maltha, C. R., Demuner, A. J., Cazal, C. M., Reis, E. L. & Colodette, J. L. 2013b. A Rapid Method for Quantification of Carboxyl Groups in Cellulose Pulp. *Bioresources,* 8**,** 1043-1054.

Barclay, L. R. C., Xi, F. & Norris, J. Q. 1997. Antioxidant Properties of Phenolic Lignin Model Compounds. *Journal of Wood Chemistry and Technology,* 17**,** 73-90.

Behzad, T. & Ahmadi, M. 2016. Nanofibers. *In:* Rahman, M. M. & Asiri, A. M. (Eds.) *Nanofiber Research - Reaching New Heights.* Rijeka, Croatia: Intech.

Belsare, D. & Prasad, D. 1988. Decolorization of Effluent from the Bagasse-Based Pulp Mills By White-Rot Fungus, Schizophyllum Commune. *Applied Microbiology and Biotechnology,* 28**,** 301-304.

Beyer, M., Koch, H. & Fischer, K. 2006. Role of Hemicelluloses in the Formation of Chromophores During Heat Treatment of Bleached Chemical Pulps. *Macromolecular Symposia,* 232**,** 98-106.

Bhardwaj, N. K. & Nguyen, K. L. 2005. Charge Aspects of Hydrogen Peroxide Bleached De-Inked Pulps. *Colloids And Surfaces A: Physicochemical and Engineering Aspects,* 262**,** 232-237.

Bhardwaj, N. K. & Nguyen, K. L. 2007. Photoacoustic Fourier Transform Infrared Spectroscopic Study of Hydrogen Peroxide Bleached De-Inked Pulps. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 301**,** 323-328.

Bohnet, M. 2003. *Ullmann's Encyclopedia of Industrial Chemistry.* 6th, completely revised ed. Weinheim, Germany Wiley-VCH.

Bohrn, R., Potthast, A., Schiehser, S., Rosenau, T., Sixta, H. & Kosma, P. 2006. The FDAM Method: Determination of Carboxyl Profiles in Cellulosic Materials by Combining Group-Selective Fluorescence Labeling with GPC. *Biomacromolecules,* 7**,** 1743-1750.

Bonini, C., Carbone, A. & D'Auria, M. 2002. Singlet Oxygen Mediated Degradation of Lignin - A Kinetic Study. *Photochemical & Photobiological Sciences,* 1**,** 407-411.

Bonini, C., D'Auria, M., D'Alessio, L., Mauriello, G., Tofani, D., Viggiano, D. & Zimbardi, F. 1998. Singlet Oxygen Degradation of Lignin. *Journal of Photochemistry and Photobiology A: Chemistry,* 113**,** 119-124.

Borchardt, J. K. 1997. The Use of Surfactants in De-Inking Paper for Paper Recycling. *Current Opinion in Colloid & Interface Science,* 2**,** 402-408.

Bouchard, J., Methot, M. & Jordan, B. 2006. The Effects of Ionizing Radiation on the Cellulose of Woodfree Paper. *Cellulose,* 13**,** 601-610.

Burgess, H. D. 1982. Relationships Between Colour Production in Cellulose and the Chemical Changes Brought About by Bleaching. *AIC Annual Meeting.* Milwaukee, Wisconsin: The American Institute for Conservation.

Carter, H. A. 1996. The Chemistry of Paper Preservation: Part 2. The Yellowing of Paper and Conservation Bleaching. *Journal of Chemical Education,* 73**,** 1068-1073.

Chirat, C. & De La Chapelle, V. 1999. Heat-and Light-Induced Brightness Reversion of Bleached Chemical Pulps. *Journal of Pulp and Paper Science,* 25**,** 201-205.

Chunilall, V. 2009. *Structure, Accessibility and 'Reactivity' of Cellulose I as Revealed by CP/MAS 13C-NMR Spectroscopy and Atomic Force Microscopy.* PhD, University of KwaZulu-Natal.

Chuphal, Y., Kumar, V. & Thakur, I. S. 2005. Biodegradation and Decolorization of Pulp and Paper Mill Effluent by Anaerobic and Aerobic Microorganisms in a Sequential Bioreactor. *World Journal of Microbiology and Biotechnology,* 21**,** 1439-1445.

Colodette, J. L., Gomide, J. L., Girard, R., Jääskeläinen, A.-S. & Argyropoulos, D. S. 2002. Influence of Pulping Conditions on Eucalyptus Kraft Pulp Yield, Quality, and Bleachability. *Tappi Journal,* 1**,** 14-20.

del Río, J. C., Gutiérrez, A., Romero, J., Martínez, M. J. & Martínez, A. T. 2001. Identification of Residual Lignin Markers in Eucalypt Kraft Pulps by Py–GC/MS. *Journal of Analytical and Applied Pyrolysis,* 58–59**,** 425-439.

Demirbaş, A. 2000. Mechanisms of Liquefaction and Pyrolysis Reactions of Biomass. *Energy Conversion and Management,* 41**,** 633-646.

Duan, C., Li, J., Ma, X., Chen, C., Liu, Y., Stavik, J. & Ni, Y. 2015. Comparison of Acid Sulfite (AS)-and Prehydrolysis Kraft (PHK)-Based Dissolving Pulps. *Cellulose,* 22**,** 4017-4026.

Dyer, T. J. 2004. *Elucidating the Formation and Chemistry of Chromophores During Kraft Pulping.* PhD, University of Wisconsin-Stevens Point.

Eiras, K. M. M., Colodette, J. L. & Silva, V. L. 2009. The Role of Bound Chlorine in the Brightness Reversion of Bleached Hardwood Kraft Pulp. *Química Nova,* 32**,** 51-55.

Ek, M. 2009. *Pulping Chemistry and Technology,* Berlin, Germany: Walter de Gruyter.

Ek, M., Gellerstedt, G. & Henriksson, G. 2009. *Wood Chemistry and Biotechnology,* Berlin, Germany: Walter de Gruyter.

Feldman, D. & Wegener, G. 1985. *Wood: Chemistry, Ultrastructure, Reactions,* Berlin and New York: Walter de Gruyter.

Frontier-Laboratories. 2013. Multi-Shot Pyrolyzer EGA/PY-3030D Operation Manual. Available: http://www.frontier-lab.com/catalog/en/PY-3030D_E.pdf [Accessed 08 August 2016].

Gadd, G. M. (ed.) 2001. *Fungi in Bioremediation,* Cambridge, United Kingdom: Cambridge University Press.

Gangwar, A. K., Prakash, N. T. & Prakash, R. 2014. Applicability of Microbial Xylanases in Paper Pulp Bbleaching: A Review. *BioResources,* 9**,** 3733-3754.

Garg, A., Roberts, J. & McCarthy, A. 1998. Bleach Boosting Effect of Cellulase-Free Xylanase of *Streptomyces Thermoviolaceus* and its Comparison with Two Commercial Enzyme Preparations on Birchwood Kraft Pulp. *Enzyme and Microbial Technology,* 22**,** 594-598.

Gehmayr, V. & Sixta, H. 2011. Dissolving Pulps from Enzyme Treated Kraft Pulps for Viscose Application. *Lenzinger Berichte,* 89**,** 152-160.

Gellerstedt, G. & Dahlman, O. Recent Hypothesis for Brightness Reversion of Hardwood Pulps. Proc. International Colloquium on Eucalyptus Kraft Pulp, 2003.

Gullichsen, J. 1965. Influence of Temperature and Humidity on Colour Reversion of Pulp. *Paper Ja Puu-Papper Och Tra,* 47**,** 215f.

Guo, X., Wang, S., Zhou, Y. & Luo, Z. 2011. Catalytic Pyrolysis of Xylan-Based Hemicellulose Over Zeolites. *International Journal of Energy and Environment,* 5**,** 137-142.

Guo, X., Zhang, S. & Shan, X.-q. 2008. Adsorption of Metal Ions on lignin. *Journal of Hazardous Materials,* 151**,** 134-142.

He, Z., Ni, Y. & Zhang, E. 2005. Alkaline Darkening and its Relationship to Peroxide Bleaching of Mechanical Pulp. *Journal of Wood Chemistry and Technology,* 24**,** 1-12.

Heitner, C., Dimmel, D. & Schmidt, J. 2010. *Lignin and Lignans: Advances in Chemistry,* Boca Raton, Florida: CRC press.

Holzer, W. F. 1934. *A study of the Coloring Matter in Pine Kraft Pulps.* PhD, Georgia Institute of Technology.

Hon, D. N.-S., & Shiraishi, N. 2000. *Wood and Cellulosic Chemistry, Second Edition, Revised, and Expanded*: CRC Press.

Iller, E., Kukiełka, A., Stupińska, H. & Mikołajczyk, W. 2002. Electron-Beam Stimulation of the Reactivity of Cellulose Pulps for Production of Derivatives. *Radiation Physics and Chemistry,* 63**,** 253-257.

ISO. 2009. Paper, Board and Pulps - Measurement of Diffuse Blue Reflectance Factor - Part 1: Indoor Daylight Conditions (ISO brightness). Available: https://www.iso.org/obp/ui/#iso:std:iso:2470:-1:ed-1:v1:en [Accessed 13 April 2016].

Jeffries, T. W., Grabski, A. C., Patel, R. N., Elegir, G. & Szakacs, G. 1996. Method of Removing Color from Wood Pulp Using Xylanase from Streptomyces Roseiscleroticus NRRL B-11019. United States Of America: Google Patents.

Johansson, M. 2000. *Formation of Chromophores and Leucochromophores During Manufacturing of Mechanical Pulp.* PhD, Royal Institute of Technology.

John Andelin, Robert W. Niblock & Curlin, J. W. 1989. Pulp Bleaching Technology. *Technologies for Reducing Dioxin in the Manufacture of Bleached Wood Pulp.* Washington, USA: U.S Government Printing Office.

Kannan, K. & Oblisami, G. 1990. Decolorization of Pulp and Paper Mill Effluent by Growth of Aspergillus niger. *World Journal of Microbiology and Biotechnology,* 6**,** 114-116.

Kawamoto, H., Murayama, M. & Saka, S. 2003. Pyrolysis Behavior of Levoglucosan as an Intermediate in Cellulose Pyrolysis: Polymerization into Polysaccharide as a Key Reaction to carbonized Product Formation. *Journal of Wood Science,* 49**,** 469-473.

Kenealy, W., R. & Jeffries, T., W. 2003. Enzyme Processes for Pulp and Paper: A Review of Recent Developments. *Wood Deterioration and Preservation.* Washington, D.C., United States: American Chemical Society.

Khezami, L., Chetouani, A., Taouk, B. & Capart, R. 2005. Production and Characterisation of Activated Carbon from Wood Components in Powder: Cellulose, Lignin, Xylan. *Powder Technology,* 157**,** 48-56.

Kilulya, K. F. 2012. *Profiling of Organic Extractives in Wood and Dissolving Pulping Process by Chromatographic and Spectroscopic Methods.* PhD, University of Johannesburg.

Kirwan, M. J. (ed.) 2005. *Paper and Paperboard Packaging Technology,* Oxford, United Kingdom: Blackwell.

Knill, C. J. & Kennedy, J. F. 2003. Degradation of Cellulose Under Alkaline Conditions. *Carbohydrate Polymers,* 51**,** 281-300.

Kocaefe, D., Poncsak, S. & Boluk, Y. 2008. Effect of Thermal Treatment on the Chemical Composition and Mechanical Properties of Birch and Aspen. *BioResources,* 3**,** 517-537.

Korntner, P., Hosoya, T., Dietz, T., Eibinger, K., Reiter, H., Spitzbart, M., Röder, T., Borgards, A., Kreiner, W., Mahler, A., Winter, H., Groiss, Y., French, A., Henniges, U., Potthast, A. & Rosenau, T. 2015. Chromophores in Lignin-Free Cellulosic Materials Belong to Three Compound Classes. Chromophores in Cellulosics, XII. *Cellulose,* 22**,** 1053-1062.

Kutscha, N. P. & Gray, J. R. 1970. *The Potential of Lignin Research. Technical Bulletin 41.* MSc, University of Maine.

Lakowicz, J. R. 2007. *Principles of Fluorescence Spectroscopy,* Baltimore, Maryland, USA: Springer.

Lewin, M. 1997. Oxidation and Aging of Cellulose. *Macromolecular Symposia,* 118**,** 715-724.

Li, C. & Ragauskas, A. J. 2000. Brightness Reversion of Mechanical Pulps. Part XVII: Diffuse Reflectance Study on Brightness Stabilization by Additives Under Various Atmospheres. *Cellulose,* 7**,** 369-385.

Li, H., Saeed, A., Jahan, M. S., Ni, Y. & van Heiningen, A. 2010. Hemicellulose Removal From Hardwood Chips in the Pre-Hydrolysis Step of the Kraft-Based Dissolving Pulp Production Process. *Journal of Wood Chemistry and Technology,* 30**,** 48-60.

Lu, Q., Yang, X.-c., Dong, C.-q., Zhang, Z.-f., Zhang, X.-m. & Zhu, X.-f. 2011. Influence of Pyrolysis Temperature and Time on the Cellulose Fast Pyrolysis Products: Analytical Py-GC/MS Study. *Journal of Analytical and Applied Pyrolysis,* 92**,** 430-438.

McCarthy, A., Peace, E. & Broda, P. 1985. Studies on the Extracellular Xylanase Activity of Some Thermophilic Actinomycetes. *Applied Microbiology and Biotechnology,* 21**,** 238-244.

McDonald, D., Miles, K. & Amiri, R. 2004. The Nature of the Mechanical Pulping Process. *Pulp Paper Canada,* 105**,** 27-32.

Mosca Conte, A., Pulci, O., Knapik, A., Bagniuk, J., Del Sole, R., Lojewska, J. & Missori, M. 2012. Role of Cellulose Oxidation in the Yellowing of Ancient Paper. *Physical Review Letters,* 108**,** 158301.

Nagar, S., Mittal, A. & Gupta, V. K. 2014. Two Way Strategy for Utilizing Agricultural Waste ‘Wheat Bran’for Production and Immobilization of Xylanase. *Journal of Innovative Biology* 1**,** 035-044.

Nemati, M., Hemmasi, A. H., Talaeipour, M. & Samariha, A. 2013. Studying the effect of photo-yellowing on the brightness property of chemi-mechanical pulping paper. *Cellulose Chemistry and Technology,* 47**,** 103-109.

Nolan, P., Van den Akker, J. A. & Wink, W. A. 1945. The Fading of Groundwood by Light. II. Physical Mechanism of Fading. *Paper Trade Journal,* 121**,** 101-105.

Ohra-aho, T., Tenkanen, M. & Tamminen, T. 2005. Direct Analysis of Lignin and Lignin-Like Components from Softwood Kraft Pulp by Py-GC/MS Techniques. *Journal of Analytical and Applied Pyrolysis,* 74**,** 123-128.

Ona, T. (ed.) 2011. *Improvement of Forest Resources for Recyclable Forest Products*, Tokyo, Japan: Springer Science & Business Media.

Padfield, T. 1965. The deterioration of Cellulose: A Literature Review. *Problems of Conservation in Museums.* Paris, France: Eyrolles.

Pan, G. X. 2004. Relationship Between Dissolution of Fiber Materials and Development of Pulp Strength in Alkaline Peroxide Bleaching of Mechanical Pulp. *Holzforschung,* 58**,** 369-375.

Parthasarathy, V. & Colodette, J. 2007. Influence of Final Bleaching Stage on ECF Brightness Development, Refineability and Pulp Properties. *3rd International Colloquium on Eucalyptus Pulp.* Belo Horizonte, Brazil.

Patwardhan, P. R., Dalluge, D. L., Shanks, B. H. & Brown, R. C. 2011. Distinguishing Primary and Secondary Reactions of Cellulose Pyrolysis. *Bioresource Technology,* 102**,** 5265-5269.

Paulsson, M. & Parkås, J. 2012. Review: Light-Induced Yellowing of Lignocellulosic Pulps - Mechanisms and Preventive Methods. *BioResources,* 7**,** 5995-6040.

Pellinen, J., Yin, C.-F., Joyce, T. & Chang, H.-M. 1988. Treatment of Chlorine Bleaching Effluent Using a White-rot Fungus. *Journal of Biotechnology,* 8**,** 67-75.

Petit-Breuilh, X., Zaror, C. & Melo, R. 2004. Hexenuronic Acid Removal from Unbleached Kraft Eucalyptus Pulp by Peroxymonosulfuric Acid. *Journal of the Chilean Chemical Society,* 49**,** 355-360.

Popson, S. J. Technical bulletin No. 101. Diffuse vs. Directional Brightness Measurement. Available: http://www.idminstruments.com.au/sites/default/files/Micro%20S-5%20Brightmeter%20(Diffuse%20vs.Directional%20Brightness).pdf [Accessed 31 July 2015].

Potthast, A., Röhrling, J., Rosenau, T., Borgards, A., Sixta, H. & Kosma, P. 2003. A Novel Method for the Determination of Carbonyl Groups in Cellulosics by Fluorescence Labeling. 3. Monitoring Oxidative Processes. *Biomacromolecules,* 4**,** 743-749.

Prusas, Z. C. & Ohio, C. 1984. *Chemithermomechanical Pulping Process Employing Separate Alkali and Sulfite Treatments*. United States of America Patent Application 551,392.

Qiang, L., Wen-zhi, L., Dong, Z. & Xi-feng, Z. 2009. Analytical Pyrolysis–Gas Chromatography/Mass Spectrometry (Py–GC/MS) of Sawdust with Al/SBA-15 Catalysts. *Journal of Analytical and Applied Pyrolysis,* 84**,** 131-138.

Ragauskas, A. J. 1993. Photoreactivity of Ligninlike Quinoid Structures. *Photochemistry of Lignocellulosic Materials.* Altlanta, GA: American Chemical Society.

RISI. 2006. Pulp & Paper Magazine: Brighter, Whiter Freesheet Trend Offers Opportunity with Tradeoffs. [Accessed 12 April 2016].

Röhrling, J., Potthast, A., Rosenau, T., Sixta, H. & Kosma, P. 2002. Determination of Carbonyl Functions in Cellulosic Substrates. *Lenzinger Berichte,* 81**,** 89-97.

Roncero, M. B., Torres, A. L., Colom, J. F. & Vidal, T. 2003. Effect of Xylanase on Ozone Bleaching Kinetics and Properties of Eucalyptus Kraft Pulp. *Journal of Chemical Technology & Biotechnology,* 78**,** 1023-1031.

Rosenau, T., Potthast, A., Kosma, P., Suess, H. U. & Nimmerfroh, N. 2007a. Chromophores in Aged Hardwood Pulp-Their Structure and Degradation Potential. *TAPPSA Journal,* 61**,** 656-661.

Rosenau, T., Potthast, A., Kosma, P., Suess, H. U. & Nimmerfroh, N. 2007b. Chromophores in Aged Hardwood Pulp-Their Structure and Degradation Potential. *International Symposium of Wood, Fibre and Pulping Chemistry* Durban: TAPPSA Journal.

Rosenau, T., Potthast, A., Kosma, P., Suess, H. U. & Nimmerfroh, N. 2007c. Isolation and Identification of Residual Chromophores from Aged Bleached Pulp Samples. *Holzforschung,* 61**,** 656-661.

Rosenau, T., Potthast, A., Krainz, K., Hettegger, H., Henniges, U., Yoneda, Y., Rohrer, C. & French, A. D. 2014. Chromophores in Cellulosics, XI: Isolation and Identification of Residual Chromophores from Bacterial Cellulose. *Cellulose,* 21**,** 2271-2283.

Rosenau, T., Potthast, A., Krainz, K., Yoneda, Y., Dietz, T., Shields, Z. P.-I. & French, A. D. 2011. Chromophores in Cellulosics, VI. First Isolation and Identification of Residual Chromophores from Aged Cotton Linters. *Cellulose,* 18**,** 1623-1633.

Rosenau, T., Potthast, A., Milacher, W., Adorjan, I., Hofinger, A. & Kosma, P. 2005. Discoloration of Cellulose Solutions in N-Methylmorpholine-N-Oxide (Lyocell). Part 2: Isolation and Identification of Chromophores. *Cellulose,* 12**,** 197-208.

Rosenau, T., Potthast, A., Milacher, W., Hofinger, A. & Kosma, P. 2004. Isolation and Identification of Residual Chromophores in Cellulosic Materials. *Polymer,* 45**,** 6437-6443.

Sain, M., Daneault, C. & Parentaeu, M. 1999. Elimination of Chromophores from Secondary Fiber of Wood Mechanical Pulp. I. Effect of Zeolite on Hydrogen Peroxide Brightening. *Journal of Wood Chemistry and Technology,* 19**,** 79-98.

Sappi.com. 2014. *Dissolving wood pulp* [Online]. Available: http://www.sappi.com/group/Sustainability/FAQs/Sappi-FAQs-Dissolving-wood-pulp.pdf [Accessed 05 March 2015].

Sappi.com. 2015. Chromophore Removal in Dissolving Pulps Available: https://ninesights.ninesigma.com/needs/-/needs-portlet/viewNeed/449 [Accessed 17 February 2015].

Schmidt, J. A. & Heitner, C. 1993. Use of UV-Visible Diffuse Reflectance Spectroscopy for Chromophore Research on Wood Fibers: a Review. *Tappi Journal* 76**,** 14.

Schmidt, J. A., Rye, C. S. & Gurnagul, N. 1995. Lignin Inhibits Autoxidative Degradation of Cellulose. *Polymer Degradation and Stability,* 49**,** 291-297.

Shen, D. K. & Gu, S. 2009. The Mechanism for Thermal Decomposition of Cellulose and its Main Products. *Bioresource Technology,* 100**,** 6496-6504.

Sikorska, E., Khmelinskii, I. V., Krawczyk, A., Oliveira, A. S., Ferreira, L. F. V., Wójciak, A. & Sikorski, M. 2006. Spectral and Photophysical Properties of Thermomechanical Pulps Bleached with the use of Acidified and Alkaline Hydrogen Peroxide. *Journal of Photochemistry and Photobiology A: Chemistry,* 184**,** 66-72.

Silva, V. L., Lino, A. G., Ribeiro, R. A., Colodette, J. L., Forsström, A. & Wackerberg, E. 2011. Factors Affecting Brightness Reversion of Hardwood Kraft Pulps. *BioResources,* 6**,** 4801-4814.

Sitholé, B., Shirin, S., Zhang, X., Lapierre, L., Pimentel, J. & Paice, M. 2009. Deresination Options in Sulphite Pulping. *BioResources,* 5**,** 187-205.

Sitholé, B. B. 2006. Pyrolysis in the Pulp and Paper Industry. *In:* Meyers, R. A. (ed.) *Encyclopedia of Analytical Chemistry.* Chichester, England: John Wiley & Sons.

Sixta, H. 2000. Comparative Evaluation of TCF Bleached Hardwood Dissolving Pulps. *Lenzing Ber,* 79**,** 119-128.

Sixta, H. (ed.) 2006. *Pulp Properties and Applications,* New York: WILEY-VCH

Sixta, H. & Schild, G. 2009. A New Generation Kraft Process. *Lenzinger Berichte,* 87**,** 26-37.

Sixta, H., Süss, H. U., Potthast, A., Schwanninger, M. & Krotscheck, A. W. 2006. Pulp Bleaching: Sections 7.1–7.3.5. *Handbook of Pulp.* Weinheim, Germany: Wiley-VCH.

Sjöström, E. & Alén, R. 2013. *Analytical Methods in Wood Chemistry, Pulping, and Papermaking,* Heidelberg: Springer Science & Business Media.

Suess, H. U. 2010. *Pulp Bleaching Today,* Berlin, New York: Walter de Gruyter.

Sugano, Y., Latonen, R.-M., Akieh-Pirkanniemi, M., Bobacka, J. & Ivaska, A. 2014. Electrocatalytic Oxidation of Cellulose at a Gold Electrode. *ChemSusChem,* 7**,** 2240–2247.

Suss, H. & Nimmerfroh, N. Hydrogen Peroxide in Chemical Pulp Bleaching. ABTCP Meeting on Pulp Bleaching at Vitoria, Espirito Santo, Brazil, 1996.

TAPPI. 2016. Brightness of Pulp, Paper, and Paperboard (Directional Reflectance at 457 nm), Test Method T 452 om-08. Available: http://imisrise.tappi.org/TAPPI/Products/01/T/0104T452.aspx [Accessed 13 April 2016].

Thakur, V. V., Jain, R. K. & Mathur, R. M. 2012. Studies on Xylanase and Laccase Enzymatic Prebleaching to Reduce Chlorine-Based Chemicals During CEH and ECF Bleaching. *BioResources,* 7**,** 2220-2235.

Tran, H. & Vakkilainnen, E. K. 2008. The Kraft Chemcial Recovery Process. Available: http://www.tappi.org/content/events/08kros/manuscripts/1-1.pdf [Accessed 21 August 2015].

Tsuge, S., Ohtani, H. & Watanabe, C. 2011. *Pyrolysis-GC/MS Data Book of Synthetic Polymers: Pyrograms, Thermograms and MS of Pyrolyzates,* Amsterdam: Elsevier.

Valeur, B. & Berberan-Santos, M. N. 2012. *Molecular Fluorescence: Principles and Applications, Second Edition,* Weinheim, Germany: Wiley-VCH.

Violante, C., Teodonio, L., Mosca Conte, A., Pulci, O., Kupchak, I. & Missori, M. 2014. An Ab-initio Approach to Cultural Heritage: The Case of Ancient Paper Degradation. *Phys. Status Solidi B,* 252**,** 112–117.

Wampler, T. P. 2006. Analytical Pyrolysis: An Overview. *In:* Wampler, T. P. (ed.) *Applied Pyrolysis Handbook.* Boca Raton, Florida CRC Press.

Wang, S.-r., Liang, T., Ru, B. & Guo, X.-j. 2013. Mechanism of Xylan Pyrolysis by Py-GC/MS. *Chemical Research in Chinese Universities,* 29**,** 782-787.

Wang, S., Guo, X., Liang, T., Zhou, Y. & Luo, Z. 2012. Mechanism Research on Cpyrolysis by Py-GC/MS and Subsequent Density Functional Theory Studies. *Bioresource Technology,* 104**,** 722-728.

Wilcox, M. D. 1975. Measuring the brightness, Light Absorption Coefficient, and Light Scattering Coefficient of Wood. *Svensk Papperstidning,* 78**,** 22-26.

Wójciak, A., Kasprzyk, H., Sikorska, E., Krawczyk, A., Sikorski, M. & Wesełucha-Birczyńska, A. 2014. FT-Raman, FT-Infrared and NIR Spectroscopic Characterization of Oxygen-Delignified Kraft Pulp Treated with Hydrogen Peroxide Under Acidic and Alkaline Conditions. *Vibrational Spectroscopy,* 71**,** 62-69.

Yang, H., Yan, R., Chen, H., Lee, D. H. & Zheng, C. 2007. Characteristics of Hemicellulose, Cellulose and Lignin Pyrolysis. *Fuel,* 86**,** 1781-1788.

Yatagai, M. & Zeronian, S. H. 1994. Effect of Ultraviolet Light and Heat on the Properties of Cotton Cellulose. *Cellulose,* 1**,** 205-214.

Yin, C. F., Joyce, T. W. & Chang, H. M. 1989. Role of Glucose in Fungal Decolorization of Wood Pulp Bleaching Effluents. *Journal of Biotechnology,* 10**,** 77-83.

Zhang, X., Nguyen, D., Paice, M. G., Tsang, A. & Renaud, S. 2007. Degradation of Wood Extractives in Thermo-Mechanical Pulp by Soybean Lipoxygenase. *Enzyme and Microbial Technology,* 40**,** 866-873.

Zhou, Z., Jääskeläinen, A.-S., Adorjan, I., Potthast, A., Kosma, P. & Vuorinen, T. 2011. Brightness Reversion of Eucalyptus Kraft Pulp: Effect of Carbonyl Groups Generated by Hypochlorous Acid Oxidation. *Holzforschung,* 65**,** 289-294.

CHAPTER 3

MATERIALS AND METHODS

3.1 Summary of experimental design

Analytical pyrolysis coupled with gas chromatography/mass spectrometry (Py-GC/MS) has been widely used for the analysis of diverse components of biomass (Sithole, 2000; Wampler, 2000). In this study, the Py-GC/MS was specifically employed for identification of chromophores in dissolving wood pulp (DWP). To achieve this, a method for chromophore analysis needed to be developed. The development of the method entailed analysis of fully bleached DWPs with high brightness and the pulps that exhibited brightness reversion; other cellulosic materials that were unlikely to contain impurities were also analysed to ascertain if there are any differences in pyrograms of these samples. This was followed by analyses of probable compounds that could have induced brightness reversion to ascertain any similarities with the pyrograms of the brightness reversed samples. These were xylan, sugar monomers and several types of lignin. Following the successful development of the method, it was then tested for reproducibility through replicate analysis of selected DWP samples. Finally, the method was applied for analysis of industry and laboratory produced pulps.

The developed method was first used for chromophore analysis in a fully bleached industrial DWP, of known brightness. With fully bleached DWP, it was important to evaluate all possible factors that influence both the chromophore content and the brightness and to understand how these relate to the effect of heat ageing and the effect of pulping and bleaching.

DWP undergoes several process stages before reaching the fully bleached stage. The fully bleached pulp is prone to ageing (brightness reversion), depending on the conditions of storage. Thus, the industry produced fully bleached pulps were induced for brightness reversion as described in section 3.4.3, with brightness and yellowness measurements recorded before and after brightness reversion. Both sets of samples were then analysed for chromophore content using Py-GC/MS.

During the industrial production of microcrystalline cellulose (MCC) at one mill, it was observed that the brightness of the MCC was lower than the brightness of the corresponding DWP samples used to produce the MCC: the cause needed to be investigated. Hence, the brightness and yellowness of fully bleached DWPs with their corresponding MCC samples were determined and compared. The chromophore content of these samples was determined using the developed Py-GC/MS method.

Since the industrial pulp is manufactured from of a mixture of wood species, the effect of cooking and bleaching processes needed to be identified. Thus, acid bisulphite and PHK pulps were collected from the different stages of cooking and bleaching (in-process pulps) unit operations. The samples were air dried and then analysed using the Py-GC/MS. Furthermore, the laboratory prepared fully bleached DWP samples were prepared from several *Eucalyptus* tree species (*E. dunnii*, *E. Grandis* and *E. Smithii*) (Figure 3.1). In both laboratory and industrial samples, pulps were collected after each unit operation to ascertain the effects of the unit operations on the formation of chromophores in pulps.

The wet chemical properties of the pulps, viz., solubility (total hemicellulose content and degraded cellulose/ short chain glucan) and lignin content were analysed to determine the relationship, if any, between the properties and the amounts of chromophores determined in the pulps as measured by Py-GC/MS. Finally, the Py-GC/MS method was applied to other pulps to ascertain if it would be applicable to other pulps besides DWP. The experimental design is summarised in Figure 3.1.

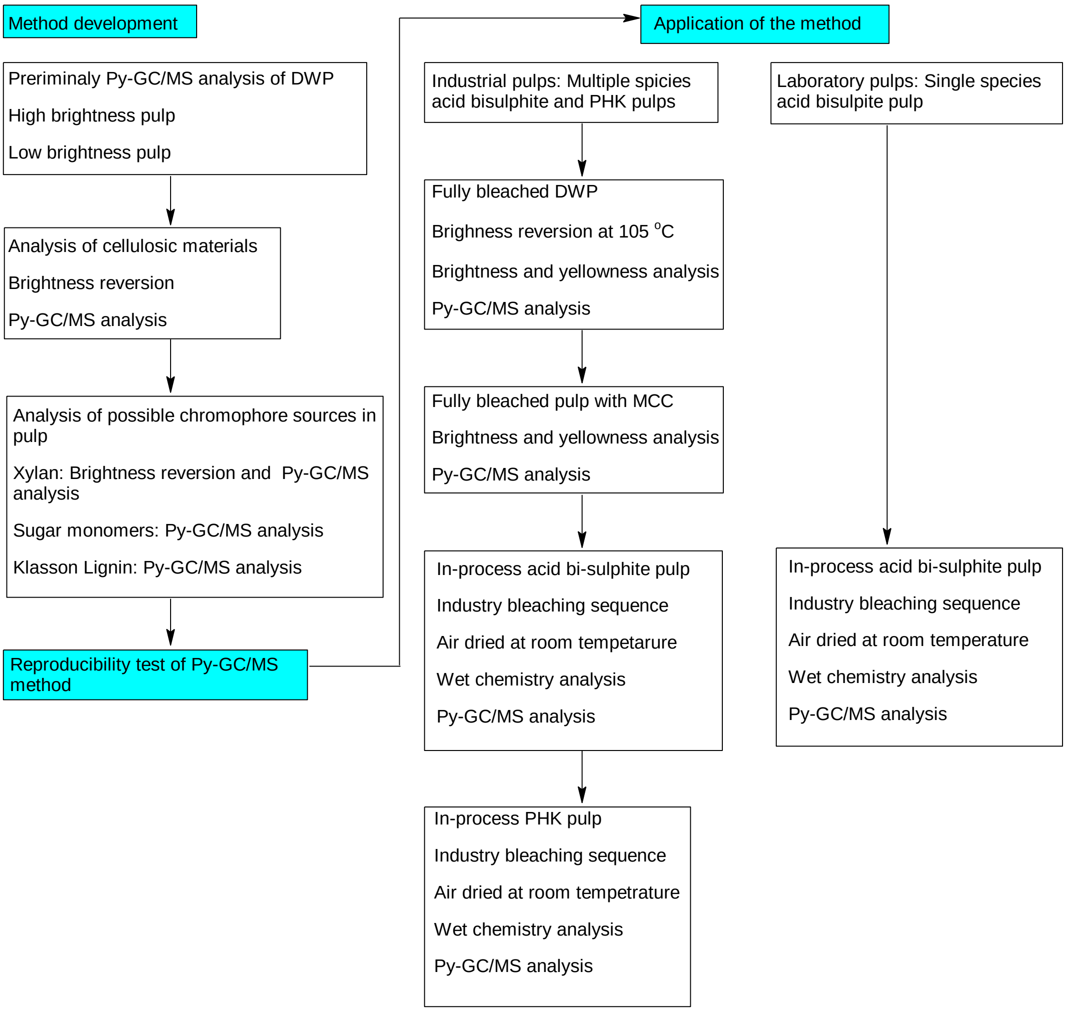


Figure 3.1: Schematic of experimental design.

3.2 Experimental samples

3.2.1 Fully bleached pulps

Fully bleached pulps were obtained from local and international DWP mills. The samples included acid bisulphite and pre-hydrolysis (PHK) pulps.

3.2.2 Cellulosic materials

Cellulose-rich materials such as the laboratory filter paper and cotton linters were analysed for chromophore content using Py-GC/MS. Cotton linters were obtained from a local pulp mill, and the filter papers were purchased from Sigma-Aldrich.

3.2.3 Microcrystalline cellulose

Microcrystalline cellulose (MCC) is a partially depolymerised, pure cellulose that was discovered in 1955 (Thoorens *et al.*, 2014). It is a major product of DWP, conventionally generated in the presence of mineral acids at elevated temperatures (Trache *et al.*, 2016). MCC is a renewable, biodegradable, non-toxic material with excellent strength properties. These properties make MCC a versatile product that finds a broad range of applications such as binders in pharmaceutical formulations and food processing, agricultural formulations, house care products, such as detergents and personal care products, such as cosmetics (Kopesky and Ruszkay, 2003).

Since MCC is a derivative of DWP, it was interesting and informative to investigate whether DWP and MCC contain the same type of chromophores that contribute to brightness reversion. To investigate this, samples of MCC with their corresponding (original) pulp samples were collected from a local pulp mill for analysis and used without any chemical modification.

3.2.4 In-process pulps

Pulps collected from different stages of cooking and bleaching (in-process) in the industry and in our research laboratory were subjected to wet chemistry analysis according to the method described in section 3.4.7 and analysed for chromophore content using Py-GC/MS.

3.2.5 Potential sources of chromophores in pulps

According to studies cited in the literature, it appears that chromophore formation in fully bleached pulps is caused by cellulose degradation, and the presence of hemicelluloses and remnants of lignin (Carter, 1996, Beyer *et al.*, 2006, Loureiro *et al.*, 2010). Accordingly, representative components of hemicellulose and lignin were isolated and examined to study the formation of chromophores.

3.2.5.1 Xylan

Xylan from beechwood was purchased from Aldrich and used without any chemical treatment. It was subjected to brightness reversion according to the method described in section 3.4.3, and the samples were analysed for chromophore content by Py-GC/MS before and after brightness reversion.

3.2.5.2 Sugar monomers

The sugar monomers: glucose, arabinose, xylose, galactose, rhamnose and mannose, were purchased from and used without further purification. The sugar monomers were analysed for chromophore content using Py-GC/MS according to the temperature program shown in Method 1 (Figure 3.2).

3.2.5.3 Klason lignin

The Klason lignin samples were obtained through extraction from the sawdust and precipitation from kraft black liquor. The methods employed for obtaining the lignin from the sawdust and the kraft liquor are described in sections 3.4.4 and 3.4.5 respectively.

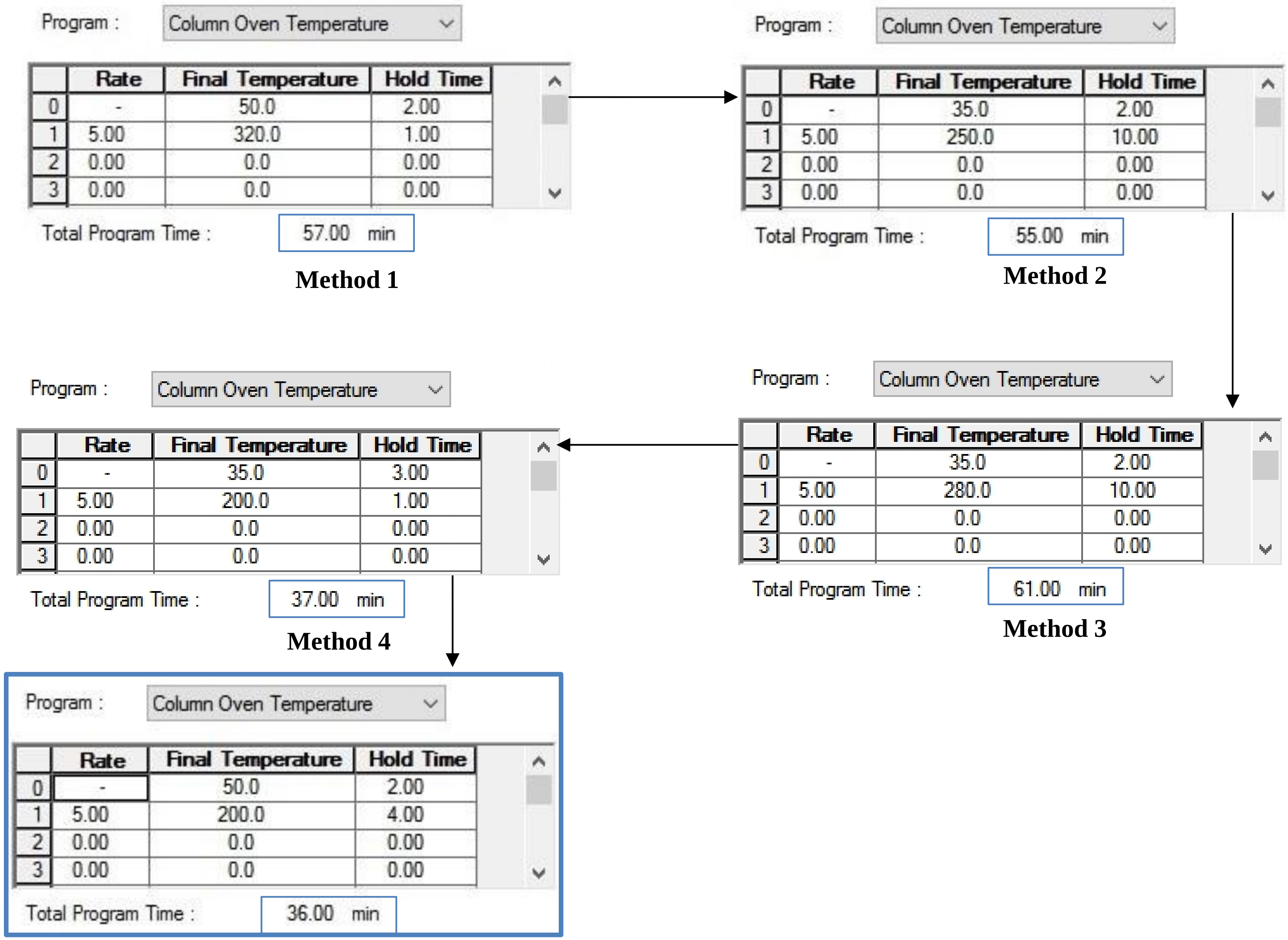
3.2.6 Lignin-containing materials

3.2.6.1 Newsprints

Blank newsprints were obtained from a local paper producing mill to understand the effect of chromophores in fresh and aged newsprints. Brightness reversion of the blank newsprints was carried out using the method described in section 3.4.3. The Py-GC/MS analysis of the newsprints was performed before and after brightness reversion.

3.2.6.2 Kraft pulps

Unbleached and fully bleached kraft pulps obtained from a local kraft mill were analysed for chromophore content using Py-GC/MS. The chromophores identified in the unbleached kraft pulp were compared to the chromophores identified in fully bleached kraft pulp. The type of chromophores identified in the kraft pulps was also compared to the chromophores identified in the acid sulphite and PHK pulp.



Program : Column Oven Temperature

	Rate	Final Temperature	Hold Time
0	-	50.0	2.00
1	5.00	320.0	1.00
2	0.00	0.0	0.00
3	0.00	0.0	0.00

Total Program Time : 57.00 min

Method 1

Program : Column Oven Temperature

	Rate	Final Temperature	Hold Time
0	-	35.0	2.00
1	5.00	250.0	10.00
2	0.00	0.0	0.00
3	0.00	0.0	0.00

Total Program Time : 55.00 min

Method 2

Program : Column Oven Temperature

	Rate	Final Temperature	Hold Time
0	-	35.0	2.00
1	5.00	280.0	10.00
2	0.00	0.0	0.00
3	0.00	0.0	0.00

Total Program Time : 61.00 min

Method 3

Program : Column Oven Temperature

	Rate	Final Temperature	Hold Time
0	-	35.0	3.00
1	5.00	200.0	1.00
2	0.00	0.0	0.00
3	0.00	0.0	0.00

Total Program Time : 37.00 min

Method 4

Program : Column Oven Temperature

	Rate	Final Temperature	Hold Time
0	-	50.0	2.00
1	5.00	200.0	4.00
2	0.00	0.0	0.00
3	0.00	0.0	0.00

Total Program Time : 36.00 min

Method 5

Figure 3.2: Column oven temperature program for the Py-GC/MS method development.

3.3 Development of the Py-GC/MS method

As described in section 2.8, current methods for analysis of chromophores in pulp samples are long and tedious and can take up to a week to generate results. This is not ideal for troubleshooting industrial production where time is money, and rapid analytical procedures are a major requirement. The desire was to develop a rapid test that could be used to troubleshoot production problems, e.g., ascertain what unit operations or pulp storage conditions are conducive to the formation of chromophoric compounds. Analytical pyrolysis was selected as an ideal technique because:

- It is a rapid method that can generate results in about an hour.
- Very little sample preparation is required.
- Very little sample is required.
- It is a very sensitive technique that can detect compounds at ppb levels.
- Very good library databases are available that facilitate identification of the pyrolysis products.
- In-house libraries can be created for compounds that are not available in commercial library databases.

3.3.1 Py-GC/MS experimental details

A multi-shot pyrolyzer, EGA/PY-3030 D (Frontier Lab, Japan), attached to an ultra-alloy capillary column (30 m x 0.25 mm, 0.25 µm), was used for analysis. An autosampler (AS-1020E/ET) was attached to the pyrolyzer to allow for automatic and continuous analysis of up to 48 samples (Figure 3.3). The mass of each sample, ranging between 100 – 500 µg, was determined by means of an AND microbalance (AD-1672). The samples were pyrolyzed at 550 °C for 20 seconds, and the interface temperature was set at 350 °C.

The chromatographic separation of the volatile components released by pyrolysis was performed using an ultra-alloy column. The injection temperature was set to 280 °C, and the flow rate of the GC column was set at 1.0 mL per minute, with helium used as a carrier gas. The ion source and the interface temperatures of the mass spectrometer were set to 200 °C, and 300 °C respectively. The scan range used for the mass selective detector was m/z 40-650. Initially, the column oven temperature was programmed as follows (Method 1, Figure 3.2):

(i) 50 °C for 2 minutes
(ii) 320 °C for 1 minutes
(iii) Rate 5 °C per minute

The total program time for Method 1 was 57 minutes. Following this, the initial temperature was adjusted to 35 °C with a hold time of 2 minutes and the final temperature was reduced to 250 °C with a hold time of 10 minutes (Method 2, Figure 3.2), this resulted in a decrease in the total program time from 57 minutes to 55 minutes. However, the results obtained were not satisfactory, hence the column oven temperature was further modified as shown in methods 3-5 (Figure 3.2) until satisfactory results were obtained.

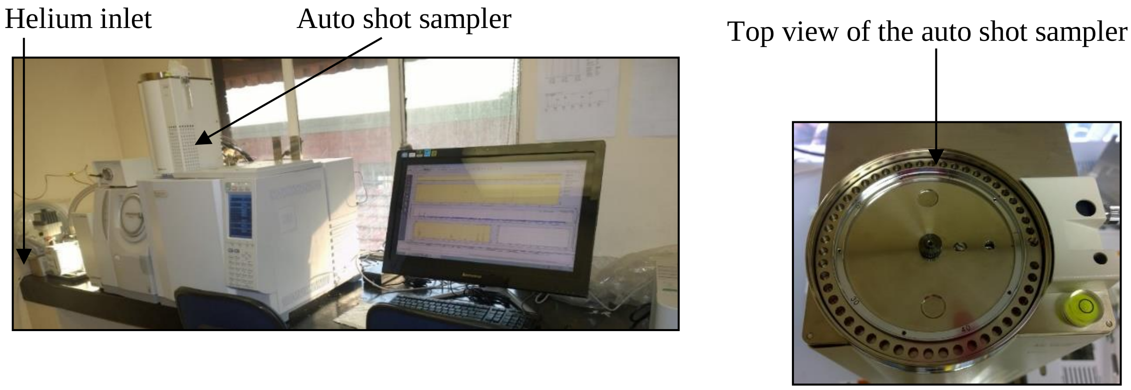


Figure 3.3: Photograph of the autosampler Py-GC/MS.

The column oven temperature of the successfully used method (Method 5) was programmed as follows:

(i) 50 °C for 2 minutes
(ii) 200 °C for 4 minutes
(iii) Rate 5 °C per minute

The advantage of this temperature program was that it allowed the identification of all the compounds within a period of 36 minutes. This shows that this method is efficient and can be used for rapid identification of chromophores in pulps.

3.3.2 Identification of chromophores using Py-GC/MS

Data analysis was carried out using the Shimadzu Postrun analysis software. The area percentage of the individual peaks in the chromatogram was measured using a peak integration function. The peak areas of all the compounds identified per sample added up to 100 %.

The pyrolysis products were identified using the NIST library search function that shows the name and structure of compounds. This option allows one to see the structure of a compound, and then to classify it as a chromophore if it contains a conjugated bond system or other UV absorbing functional groups. Peak fittings >90% were considered acceptable in the identification of compounds.

The pyrolysis products were identified by comparing their mass spectra with the mass spectrum NIST library attached to the instrument. The relative amounts of chromophores of the individual compounds that were quantitatively determined by the chromatogram were further classified by the NIST library. Based on their structure, these chromophoric compounds were classified into compound groups, such as furan-type compounds, ketones, arenes and other low molecular weight chromophores.

3.3.3 Optimisation of the Py-GC/MS method

It was observed that there were no chromophores identified after 35 minutes, thus, the conditions were optimised as shown in Method 5 (Figure 3.2). Method 5 showed promising results, hence, the remainder of the samples were analysed using the method.

3.3.4 Validation of the Py-GC/MS method

Five replicates of selected DWP samples were analysed using the same approach and the same experimental conditions to validate the methodology. The results obtained were within the same range per sample. A small shift in the results was attributed to the lack of homogeneity of the pulp samples.

3.3.5 Application of the Py-GC/MS method

Chromophores in industrial and laboratory-produced pulps were identified using the developed Py-GC/MS method. The fully bleached pulps were subjected to brightness reversion using the method described in section 3.4.3. The pulp and paper industry uses the brightness scale to determine the quality of the fully bleached pulps because it is an efficient method to identify variations in the pulp quality during production (Johansson, 2000). The brightness and yellowness were, therefore, measured before and after brightness reversion, and compared to chromophore content as determined by the Py-GC/MS. The second set of samples were fully bleached DWP and their corresponding MCC samples. These pulp samples were not induced for brightness reversion. However, their chromophore content, brightness and yellowness levels of the original pulp and MCC samples were compared. The methods used for measuring brightness and yellowness of the industrially produced fully bleached pulps are described in sections 3.4.1 and 3.4.2, respectively.

The pulps collected from different unit operations of cooking and bleaching processes (in-process pulps) were analysed for wet chemical properties, and their chromophore contents were determined using the Py-GC/MS method. The wet chemistry data was compared to the chromophore content to investigate any relationship between the wet chemical properties and the chromophores. Pulp bleaching and wet chemistry analysis procedures for the laboratory produced in-process pulps are described Sections 3.4.6 and 3.4.7.

3.4 Other experimental methods

3.4.1 Brightness measurements

The brightness of the pulp is described as the absorption at a wavelength of 457 nm expressed on a scale of 0-100%. The brightness was measured using a reflectometer according to the ISO 2470-1:2009 method.

3.4.2 Yellowness measurement

Yellowing, or discolouration of pulps, was determined using the DIN 6167 test method. The degree of yellowing was expressed as a yellowing number (REF description of yellowness of near-white or near-colourless materials. DIN 6167 1979-12).

3.4.3 Brightness reversion

Previous studies have shown that accelerated heat exposure resulted in the formation of chromophores (Rosenau *et al.*, 2007, Fischer and Beyer, 2000); hence, similar brightness reversion inducements were done on samples used in this study. Heat-induced brightness reversion was carried out in an oven at 105±2 °C overnight. The chromophore content was measured before and after brightness reversion using Py-GC/MS analysis to evaluate the effect of heat induced brightness reversion on the formation of chromophores. Samples that were induced for brightness reversion were the cellulosic materials, xylan, fully bleached acid bisulphite pulp, PHK pulp, newsprints and fully bleached kraft pulps.

3.4.4 Extraction of lignin from sawdust

Accurately weighed (0.70 g), fine single clone *Eucalyptus* sawdust samples were dissolved in sulphuric acid (72%, 3 mL), in test tubes (12 x 15 mL). The contents of the test tubes were heated in a constant temperature water bath (30 ± 3 °C) for 1 hour, with occasional stirring, using a glass rod. The resulting mixture was washed into Schott bottles (250 mL) with deionized water (85 mL), and placed in an autoclave (103 ± 7 kPa, 120 °C) for 1 hour. Afterwards, the samples were cooled to room temperature and filtered under vacuum using Büchner filtration apparatus with a pre-weighed nylon filter paper (0.45 µm). After drying at room temperature for two days, the mass of the acid insoluble lignin and the filter papers were accurately recorded to four decimal places, using an analytical balance. The air-dried lignin was analysed for chromophore content using Py-GC/MS.

3.4.5 Precipitation of lignin from kraft black liquor

Softwood (SW) and hardwood (HW) kraft liquor were obtained from a South African kraft pulp mill. Each solution was stirred at room temperature for 1 hour. The SW and HW kraft lignin were extracted according to the following procedure: A portion (50 mL) of the stirred kraft liquor was sampled into a conical flask (100 mL) and allowed to stir at room temperature for 15 minutes. To the stirring liquor, H_2SO_4 (6M) was slowly added until pH 9 was reached. The mixture of the black liquor and the H_2SO_4 (6M) was stirred at room temperature for 1 hour before further addition of H_2SO_4 (6M) to pH 4. When pH 4 was reached, the mixture formed a highly viscous liquid that was filtered using a Büchner funnel. The filtrate was washed successively with H_2SO_4, starting from 6M, reducing to 3M and finally, 1M H_2SO_4 was added until the filtrate was clear. The lignin was further washed several times with deionized water until the pH of the filtrate was 5. The obtained lignin was dried at room temperature for two days before it was ground, using a mortar and pestle, to be made ready for analysis (Namane *et al.*, 2015, Zhu and Theliander, 2015).

3.4.6 Laboratory pulp bleaching

Single species/clone, acid bisulphite pulp samples of *E. dunnii, E. Grandis and E. Smithii* were prepared in the laboratory after which they were subjected to oxygen delignification at a constant temperature and pressure. The pulps were then bleached, using a 5-stage sequence that mimicked industrial bleaching sequence for an acid bi-sulphite pulp (Chunilall, 2009). The purpose of each bleaching stage is shown in Table 3.1.

Table 3.1: Laboratory pulp bleaching stages.

Bleaching Stages	**Purpose**
Stage 1	Oxidation and solubilization of the lignin remaining after pulping
Stage 2	Lignin oxidation and solubilization to improve pulp brightness
Stage 3	Hydrolysis of lignin and removal of hemicelluloses and degraded carbohydrates
Stage 4	Lignin oxidation and solubilization to improve pulp brightness
Stage 5	Lignin oxidation and solubilization to improve pulp brightness

3.4.7 Wet chemistry analysis

Pulp samples from each of the bleaching stages were allowed to dry at room temperature for 24 hours. The wet mass of the pulp samples was determined using a measuring balance (Ohaus, Pioneer^{TM}), and the dry mass of the pulp samples was determined using a moisture analyser (Ohaus, MB_{45}), before wet chemistry analysis. The wet chemical properties, total lignin content (Klason lignin and acid soluble lignin) and solubility (S10/S18), were determined as described in the following paragraphs.

3.4.7.1 Determination of acid insoluble lignin

Acid-insoluble lignin (Klason lignin) is defined as the insoluble remnants of the pulp in 72% H_2SO_4 solution. The 72% H_2SO_4 solution solubilizes most of the carbohydrates in the pulp, and the Klason lignin remains. Analysis of the acid-insoluble lignin was determined using the TAPPI test method T 222 om-88 (TAPPI, 1996a), described as follows: Pulp samples collected from the different stages of bleaching were hand torn and shredded using a coffee blender until fine pulp was obtained. The moisture content of the pulp was determined using the moisture analyser at 180 °C. The pulp samples were accurately weighed to about 0.2 g using an analytical balance. The weighed samples were transferred into test tubes (15 mL) using a glass rod. The weighed samples in the test tubes were treated with sulphuric acid (72%, 3 mL), and heated at a constant temperature in a water bath (30 ± 3 °C) for 1 hour with occasional stirring, using a glass rod.

The resulting mixture was washed into Schott bottles (250 mL) using deionized water (85 mL), and placed in an autoclave (103 ± 7 kPa, 120 °C) for 1 hour. Afterwards, the samples were cooled to room temperature and filtered under vacuum through pre-weighed nylon filter paper (0.45 µm). The filter papers were allowed to dry at room temperature, and the final mass of the filter papers, containing the lignin, were measured to obtain the amount of the acid insoluble lignin. The filtrates were used as described in the following section.

3.4.7.2 Determination of acid soluble lignin

Analysis of the acid-insoluble lignin was determined using the TAPPI test method UM 250 (TAPPI, 1996a), described as follows: The filtrates (from section 3.4.7.1) were transferred into separate volumetric flasks (200 mL), and the volume was made up to 200 mL using deionized water. The diluted samples were kept in gas-tight vials (50 mL) in a refrigerator, ready for UV/Vis analysis. The refrigerated samples, with volumes ranging between 1-5 mL, were pipetted into separate volumetric flasks (10 mL). The volume was made up to 10 mL, using a sulphuric acid solution (3%) as a blank. The blank was prepared by diluting H_2SO_4 (15mL, 72%) in a volumetric flask (1000 mL). The volume of the blank was made up to 1000 mL using deionized water.

The UV/Vis absorption was measured using a Varian spectrophotometer (Cary, 50 Conc), and an absorbance ranging between 0.2 and 0.7 at 205 nm was recorded. If the absorbance was not within the range of 0.2 to 0.7, the solution was diluted further, until the correct absorbance was obtained.

The determination of acid insoluble lignin (section 3.8.3.1) and acid-soluble lignin (section 3.8.3.2) in the pulp allows for the identification of the total lignin content in the pulp that is calculated according to equations 5-9 shown below. The Symbols used in equations 5-9 are described in Table 3.2.

$$Lignin\ (g/L) = \frac{A}{b\ x\ a} \tag{5}$$

$$Lignin\ (g/L), B = \frac{A}{110}\ (in\ undiluted\ filtrate) \tag{6}$$

$$Lignin\ (g/L), B = \frac{A}{110}\ x\ D\ (in\ undiluted\ filtrate) \tag{7}$$

$$D = \frac{V_D}{V_o} \tag{8}$$

$$Lignin\ \% = \frac{B\ x\ V\ x\ 100}{1000\ x\ W} \tag{9}$$

Table 3.2: Description of symbols

Symbol	Units	Description
A	-	Absorbance
a	$1g^{-1}cm^{-1}$	Absorptivity (110) in $1g^{-1}cm^{-1}$
B	g/L	Undiluted filtrate
b	cm	Light path length
V	mL	Total volume of the filtrate
W	g	Oven dry weight of the pulp
V_O	mL	Volume of original filtrate
V_D	mL	Volume of diluted filtrate
D	-	Dilution factor

3.4.7.3 Alkali solubility (S10 and S18)

Pulp samples from each of the bleaching stages were torn by hand and shredded using a coffee blender until fine pulp was obtained. The fine pulp was analysed for moisture content using a moisture analyser at 180 °C. The alkali solubility of the pulp was determined using TAPPI classical method T235 cm-85 (TAPPI, 1996b), described as follows: The pulp samples were accurately weighed to about 1.6 g using an analytical balance. The pulps were stirred into a NaOH (100 mL, 18%) solution for S18 determination (for S10, 10% NaOH was used), for 3 minutes in a stoppered glass bottle (250 mL). The mixture was allowed to stir for 1 hour at 20±0.2 °C and filtered under vacuum using a dry G3 filter crucible. The initial filtrate of about 10 to 15 mL was discarded, and the remainder was collected into a conical flask and used for titration as described in the following paragraph:

The filtrate (10 mL) was pipetted into a conical flask (1L), followed by the addition of potassium dichromate (10 mL, 0.4M), and fast addition of concentrated H_2SO_4 (30 mL) to increase the temperature of the solution to about 120-130 °C. Deionized water (500 mL) was added 10 minutes later to decrease the temperature of the solution to about 15 °C. A solution of potassium iodide (20 mL) was pipetted into the conical flask and stirred for 5 minutes before titrating with a solution of sodium thiosulphate (10 N). The solution was stirred continuously while titrating. The end point was observed when the colour changed from brown to yellow-green. When the colour changed to yellow-green, a starch indicator was added, and the solution changed to a dark-blue colour, and later turned to light blue, when the end point was reached. The volume at the end point was recorded.

A blank titration was carried out by pipetting NaOH (10 mL, 18%) into a 1L conical flask instead of using the filtrate and the rest of the procedure was similar. The alkali solubility was calculated using equations 10 and 11 shown below with the factor 0.685% representing the amount of cellulose and other dissolved carbohydrates. Description and units for the symbols used in equations 10 and 11 are presented in Table 3.3.

$$G = \frac{Weight\ of\ pulp\ x\ (100 - \%\ moisture)}{100} \tag{10}$$

$$\%\ Alkali\ solubility\ (S_{10}\ or\ S_{18}) = \frac{(B - A)\ x\ 0.685\%}{G} \tag{11}$$

Table 3.3: Description of symbols

Symbol	**Units**	**Description**
A	mL	Volume used for titrating the pulp
B	mL	Volume used for blank titration
G	g	Oven dried mass of the pulp

3.5 References

Beyer, M., Koch, H. & Fischer, K. 2006. Role of Hemicelluloses in the Formation of Chromophores During Heat Treatment of Bleached Chemical Pulps. *Macromolecular Symposia,* 232**,** 98-106.

Carter, H. A. 1996. The Chemistry of Paper Preservation: Part 2. The Yellowing of Paper and Conservation Bleaching. *Journal of Chemical Education,* 73**,** 1068-1073.

Chunilall, V. 2009. *Structure, Accessibility and 'Reactivity' of Cellulose I as Revealed by CP/MAS 13C-NMR Spectroscopy and Atomic Force Microscopy.* PhD, University of KwaZulu-Natal.

Fischer, K. & Beyer, M. 2000. Comparison of Light-Induced and Heat-Induced Yellowing of Pulp. *Lenzinger Berichte,* 79**,** 25-31.

Johansson, M. 2000. *Formation of Chromophores and Leucochromophores During Manufacturing of Mechanical Pulp.* PhD, Royal Institute of Technology.

Kopesky, R. & Ruszkay, T. 2003. Production of Microcrystalline Cellulose. Google Patents.

Loureiro, P. E., Fernandes, A. J., Furtado, F. P. & Carvalho, D. V. 2010. New Insights Into Chromophore Chemistry of Eucalypt Pulps Assessed by UV-Resonance Raman Micro-Spectroscopy. *XXI TECNICELPA Conference and Exhibition VI Iberoamerican Congress on Pulp and Paper Research.* Lisbon.

Namane, M., Sithole, B. B. & Ramjugernath, D. 2015. Centrifugal Washing and Recovery as an Improved Method for Obtaining Lignin Precipitated from South African Kraft Mill Black Liquor. *Journal of Scientific & Industrial Research,* 74**,** 571-576.

Rosenau, T., Potthast, A., Kosma, P., Suess, H. U. & Nimmerfroh, N. 2007. Chromophores in Aged Hardwood Pulp-Their Structure and Degradation Potential. *TAPPSA Journal,* 61**,** 656-661.

TAPPI 1996a. TAPPI test methods 1996-1997. *Acid-insoluble lignin in wood and pulp. T 222 om-88.* Atlanta, GA: TAPPI Press.

TAPPI 1996b. TAPPI test methods 1996-1997. *Alkali solubility of pulp at 25 °C. T 235 cm-85.* Atlanta, GA: TAPPI Press.

Thoorens, G., Krier, F., Leclercq, B., Carlin, B. & Evrard, B. 2014. Microcrystalline Cellulose, a Direct Compression Binder in a Quality by Design Environment—A review. *International Journal of Pharmaceutics,* 473**,** 64-72.

Trache, D., Hussin, M. H., Chuin, C. T. H., Sabar, S., Fazita, M. N., Taiwo, O. F., Hassan, T. & Haafiz, M. M. 2016. Microcrystalline Cellulose: Isolation, Characterization and Bio-Composites Application—A Review. *International Journal of Biological Macromolecules,* 93**,** 789-804.

Zhu, W. & Theliander, H. 2015. Precipitation of Lignin from Softwood Black Liquor: an Investigation of the Equilibrium and Molecular Properties of Lignin. *BioResources,* 10**,** 1696-1714.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Introduction

The results obtained during the development of the Py-GC/MS method for identification of chromophores in the experimental samples are presented and discussed in this chapter. The method was developed using a variety of samples as described in Chapter 3. After successful development of the method, it was then used for the analysis of industrially and laboratory produced pulps. It has already been determined that identification of chromophores in dissolving wood pulp (DWP) is complex due to the low amount (ppb range) of chromophores. As explained in section 2.8.1, the most efficient method used, known thus far, is time-consuming and is limited to the identification of quinoid and aromatic structures.

To overcome this challenge, the use of analytical pyrolysis gas chromatography-mass spectrometry (Py-GC/MS) for chromophore identification was undertaken, as a new alternative means to analyse residual chromophores in DWP. In addition to Py-GC/MS analysis, brightness and yellowness measurements were performed for fully bleached industrial pulps so that any relationship between chromophores and the brightness, or the yellowness, could be established. Furthermore, wet chemistry analysis was performed to understand the impact of degraded cellulose, hemicellulose and lignin on the formation of chromophores in industrial and laboratory prepared pulps, collected from various stages of bleaching. Afterwards, the pulps were analysed for chromophore content using the developed Py-GC/MS method. Finally, other pulp samples such as newsprints and kraft pulps were also analysed for chromophore content using Py-GC/MS.

4.2 Development of the Py-GC/MS method

Trial analyses for the detection of chromophores were performed using DWPs that exhibited high and low brightness levels. In addition to DWPs, other cellulose-rich materials were also analysed for chromophore content using Py-GC/MS. Afterwards, a variety of samples that are possible sources of chromophores in pulps were also analysed for chromophore content. The samples included xylan, hemicellulose compounds, and several types of lignin. Selected samples were induced for brightness reversion (as described in section 3.4.3) to observe the changes in the chromophore content after heat-induced brightness reversion. Following this, the method was modified based on the experimental observations. Subsequently, selected DWP samples were analysed in replicates using the developed method to evaluate its reproducibility.

4.2.1 Preliminary study on chromophore identification

Fully bleached DWP samples with different brightness levels, ranging from 89.4% to 93.3%, were analysed for chromophore content using Py-GC/MS. Results obtained during the analysis of the high and low brightness pulps are outlined below.

4.2.1.1 Analysis of high brightness DWPs

The pyrogram of the high brightness (93.3%) DWP sample T1 exhibited chromophores that totalled 20.9%. The pyrogram of T1 is shown in Figure 4.1 and the chromophoric compounds detected are listed in Table 4.1. The chromophores eluted between 2 and 20 minutes, these compounds have been previously identified by other researchers (Shen and Gu, 2009, Lu *et al.*, 2011).

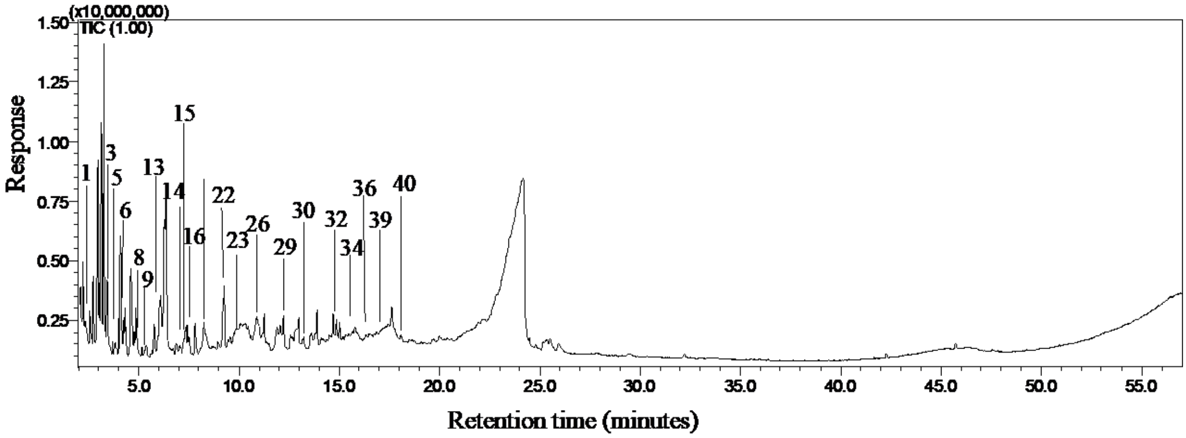


Figure 4.1: Pyrogram of pulp T1.

Figure 4.2 shows a summary of the chromophoric compounds identified during the trial analysis of pulp samples T1, T2, T3 and T4. The pulp samples were arranged in the order of decreasing brightness (Table 4.2), with T1 having the highest brightness (93.3%), and T4 had the lowest brightness (89.4%) in this set of samples. Findings indicated that there was no relationship between the measured brightness of the pulps and the amounts of chromophoric compounds detected.

Table 4.1: Peak identification for pulp T1.

Peak number	Retention time (min)	Area %	Compound
1	2.35	0.7	4-Methyl-5H-furan-2-one
2	2.58	0.6	Vinyl crotonate
3	2.73	0.7	2(5H)-Furanone
4	3.05	0.5	2(5H)-Furanone
5	3.70	0.2	3-Furaldehyde
6	3.83	0.2	4-Methyl-5H-furan-2-one

7	4.01	0.3	Furan-2-carbonyl chloride, tetrahydro-
8	4.09	1.0	Furfural
9	4.27	0.4	Vinyl crotonate
10	4.87	0.6	4-Hexen-2-one
11	5.16	0.2	4-Cyclopentene-1,3-dione
12	5.29	0.1	Cyclopent-4-ene-1,3-dione
13	5.94	0.2	Ethanone, 1-(2-furanyl)-
14	6.09	1.2	2(5H)-Furanone
15	6.29	1.5	1,2-Cyclopentanedione
16	6.37	1.7	1,2-Cyclopentanedione
17	6.72	0.2	2(5H)-Furanone, 5-methyl-
18	6.86	0.3	2,5-Furandione, 3-methyl-
19	7.51	0.3	2(3H)-Furanone, 5-acetyldihydro-
20	7.68	0.1	2-Cyclopenten-1-one, 3,4,4-trimethyl-
21	9.27	1.0	1,2-Cyclopentanedione, 3-methyl-
22	9.53	0.4	2-Cyclopenten-1-one, 2,3-dimethyl-
23	10.05	0.6	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-
24	10.15	0.3	Phenol, 2-methyl-
25	10.61	0.4	4H-1,3-Benzodioxin-4-one, hexahydro-4a,5-dimethyl-, [4as-(4a.alpha.,5.beta.,8a.beta.)]-
26	11.91	0.9	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-
27	12.22	0.6	2,4(3H,5H)-Furandione, 3-methyl-
28	12.59	0.5	2-Cyclohexen-1-one, 3,4-dimethyl-
29	13.24	0.8	2,5-Dihydroxybenzaldehyde
30	14.12	0.4	4H-Pyran-4-one, 3,5-dihydroxy-2-methyl-
31	15.17	0.4	2-Coumaranone
32	15.66	0.6	5-Hydroxymethylfurfural
33	16.47	0.3	1H-Inden-1-one, 2,3-dihydro-
34	16.53	0.5	2,6,6-Trimethyl-2-cyclohexene-1,4-dione
35	16.74	0.3	2,6,6-Trimethyl-2-cyclohexene-1,4-dione
36	18.36	0.4	7-Methylindan-1-one
37	18.50	0.4	4-Hydroxy-1-indanone
38	19.09	0.3	1-(4-Methoxyphenyl)-1,5-pentanediol
39	19.24	0.5	2-Carbamyl-9-[.beta.-d-ribofuranosyl]hypoxanthine
40	19.48	0.4	7-Methylindan-1-one
Total chromophore area %		**20.9**	

Furthermore, the data in Figure 4.2 indicates that compounds containing furan and ketone moieties were major classes of chromophores in DWPs.

Table 4.2: Brightness of trial DWP pulp samples.

Pulp name	**Description**	**Brightness (%)**
T1	High brightness pulp	93.3

T2	High brightness pulp	92.1
T3	Low brightness pulp	90.2
T4	Low brightness pulp	89.4

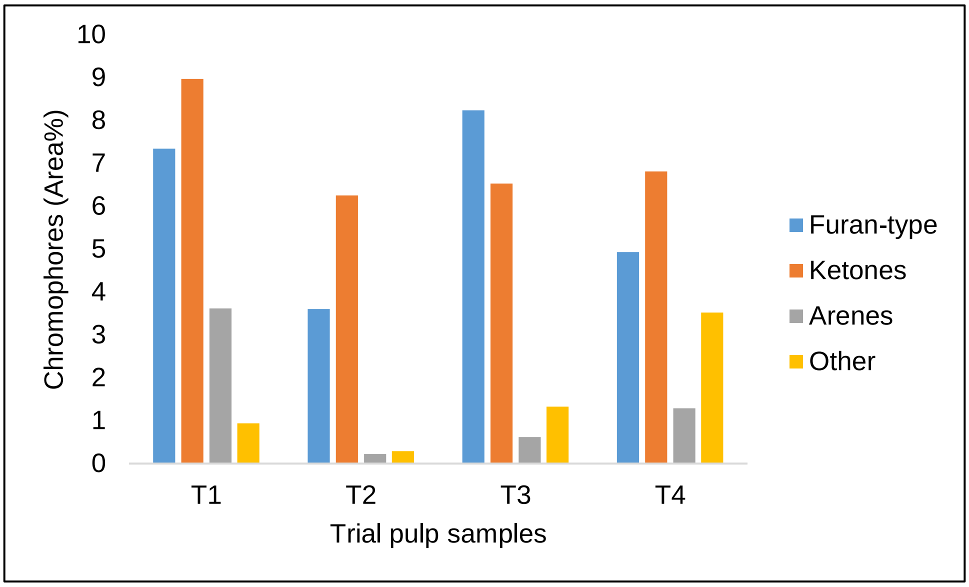


Figure 4.2: Summary of chromophores identified in the trial analysis of DWPs.

Analysis of the second sample, T2 (pulp brightness 92.1%) revealed the presence of similar compounds but with a lower total chromophoric content of 10.5%. The pyrogram of sample T2 and the identified chromophores are shown in Figure 4.3 and Table 4.3, respectively. The chromophores eluted between 2 and 18 minutes (Figure 4.3).

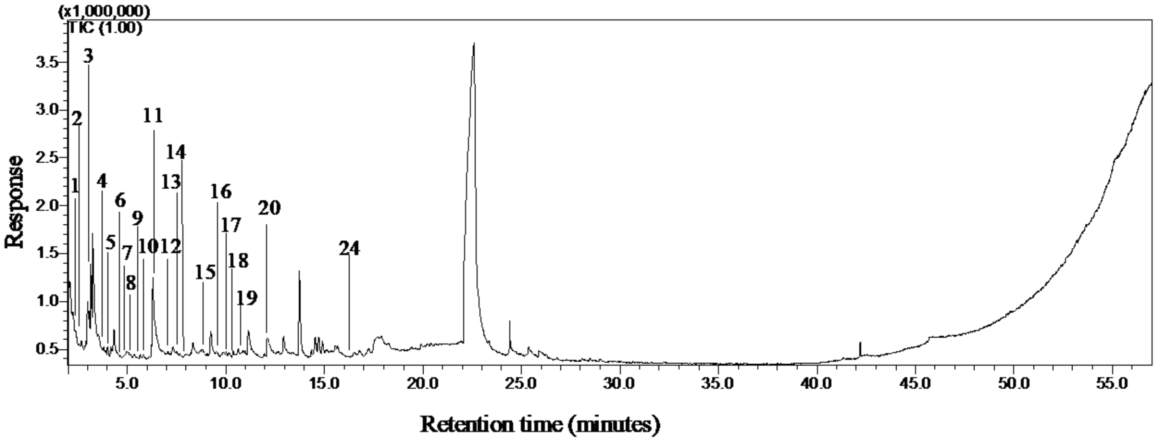


Figure 4.3: Pyrogram of pulp T2

Classification of the chromophores into different compound groups shown in Figure 4.2 revealed that the ketones were the most dominant compounds in pulp T2 followed by the furan-type compounds.

Table 4.3: Peak identification for pulp T2.

Peak number	**Retention time (min)**	**Area %**	**Compound**
1	2.21	0.4	Furan, 2,5-dimethyl-
2	2.36	0.4	4-Methyl-5H-furan-2-one
3	3.06	0.9	2(5H)-Furanone
4	3.60	0.3	4-Methyl-5H-furan-2-one
5	4.01	0.2	Furan-2-carbonyl chloride
6	4.16	0.3	2-Cyclopenten-1-one
7	4.50	0.1	1,2-Hydrazinedicarboxamide
8	5.18	0.1	2H-Pyran-3(4H)-one, dihydro-
9	5.74	0.0	6,7-Dihydropyrido(2,3-d)pyridazine-5,8-dione
10	5.81	0.2	2-Cyclopenten-1-one, 2-methyl-
11	6.30	4.0	1,2-Cyclopentanedione
12	7.27	0.1	3-Methylcyclopentane-1,2-dione
13	8.19	0.0	1-(1H-Imidazol-2-yl)-ethanone
14	8.24	0.1	1,2-Cyclohexanedione
15	9.23	1.1	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-
16	9.51	0.2	2-Cyclopenten-1-one, 2,3-dimethyl-
17	9.61	0.1	1,3-Benzodioxol-2-amine, hexahydro-N,N-dimethyl-
18	10.03	0.1	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-
19	10.86	0.1	Furaneol
20	10.97	0.1	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-
21	11.94	0.1	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-
22	11.98	0.0	o-Fluorothiophenol
23	12.11	1.3	2,4(3H,5H)-Furandione, 3-methyl-
24	17.23	0.1	Phenol, 2-(1,1-dimethylethyl)-4-(1-methyl-1-phenylethyl)-
Total chromophore area %		**10.3**	

The loss of brightness in fully bleached pulps is usually associated with the presence of chromophores. However, analysis of the high brightness pulps T1 and T2 did not show any relationship between pulp brightness and the chromophores identified by Py-GC/MS.

4.2.1.2 Analysis of low brightness DWPs

In pulp T3 (brightness 90.2%) the corresponding chromophore compounds totalled 16.7% and eluted between 2 and 17 minutes (Figure 4.4). Similar to samples T1 and T2, the major chromophoric compounds detected were furans and ketones as illustrated in the pyrogram in Figure 4.4 and the data shown in Table 4.4.

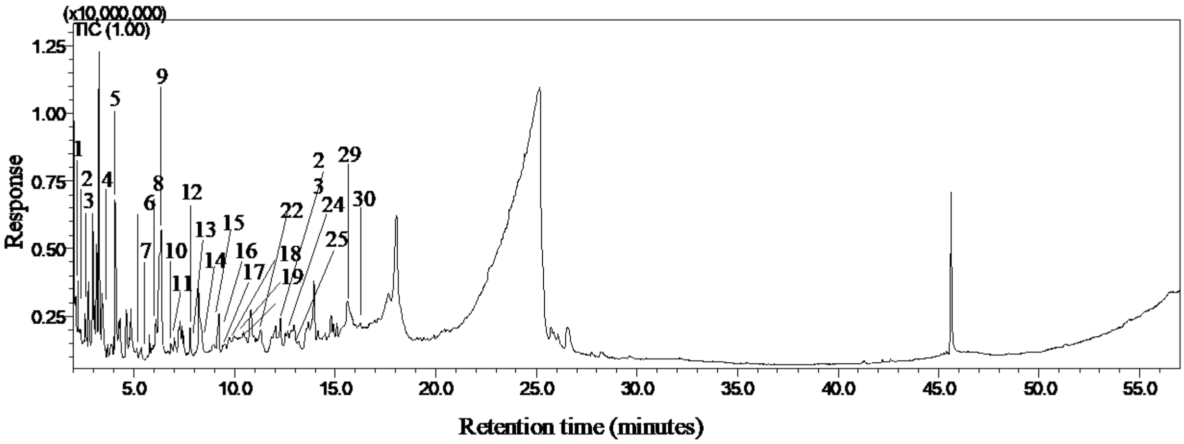


Figure 4.4: Pyrogram of pulp T3.

Figure 4.2 shows that the major group of compounds in pulp T3 were the furan-type compounds with a total area percentage of 8.2% followed by the ketones at 6.5%. Arenes and other low molecular weight chromophores had total area percentages of 0.6% and 1.3%, respectively.

Table 4.4: Peak identification for pulp T3.

Peak number	**Retention time (min)**	**Area %**	**Compound**
1	2.585	0.4	Vinyl crotonate
2	2.734	0.6	1-Penten-3-one
3	3.044	0.3	2(5H)-Furanone
4	3.696	0.1	3-Furaldehyde
5	4.076	0.9	3-Furaldehyde
6	5.356	0.3	2-Furanmethanol
7	5.897	0.1	Ethanone, 1-(2-furanyl)-
8	6.088	0.5	2(5H)-Furanone
9	6.35	2.1	1,2-Cyclopentanedione
10	6.695	0.2	2(5H)-Furanone, 5-methyl-
11	6.833	0.3	2,5-Furandione, 3-methyl-
12	7.485	0.3	2(3H)-Furanone, 5-acetyldihydro-
13	8.575	0.1	N-(2-Furoyl)glycine, 2,2,3,3,3-pentafluoropropyl ester
14	8.769	0.2	2-Cyclohexen-1-one, 4,4-dimethyl-
15	8.966	0.3	2-Cyclopenten-1-one,3-hydroxy-2-methyl-
16	9.218	0.6	1,2-Cyclopentanedione, 3-methyl-
17	9.479	0.4	2-Cyclopenten-1-one, 2,3-dimethyl-
18	9.756	0.5	4-Methyl-5H-furan-2-one
19	9.995	0.4	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-
20	10.095	0.2	Phenol, 2-methyl-
21	10.175	0.2	3-Furoic acid, anhydride with acetic acid
22	10.821	1.1	2,5-Dimethylfuran-3,4(2H,5H)-dione
23	11.841	0.5	Maltol
24	12.285	0.6	2,4(3H,5H)-Furandione, 3-methyl-

25	12.539	0.4	2-Cyclohexen-1-one, 3,4-dimethyl-
26	12.641	0.3	But-1-ene-3-yne, 1-ethoxy-
27	12.851	0.5	4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl-
28	13.201	0.4	2,5-Dihydroxybenzaldehyde
29	15.634	3.1	5-Hydroxymethylfurfural
30	16.415	0.4	1H-Inden-1-one, 2,3-dihydro-
Total chromophore Area %		**16.1**	

As can be seen in Figure 4.5 and Table 4.5, pulp T4 with the least brightness level (89.4%), also exhibited the same types of chromophores as in the other pulp samples, but the total chromophore amount was 17.0%. The major chromophore identified was peak 14 (Figure 4.5) representing 1,2-cyclopentanedione (4.1%) as shown in Table 4.5. Grouping of the compounds in Table 4.5 showed that the ketones (6.8%) were the major group of compounds in pulp T4, followed by the furan-type compounds (4.9%), (Figure 4.2). The arenes were the smallest group of chromophores with a total area percentage of 1.3%, and the other low molecular weight chromophores totalled 3.5%.

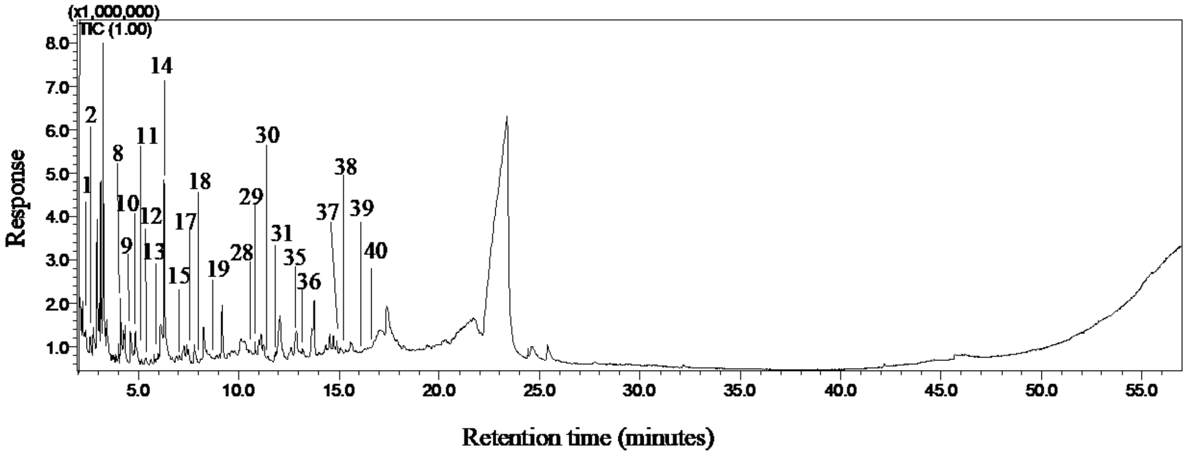


Figure 4.5: Pyrogram of pulp T4.

Table 4.5: Peak identification for pulp T4.

Peak number	**Retention time (min)**	**Area %**	**Compound**
1	2.36	0.9	4-Methyl-5H-furan-2-one
2	2.60	0.7	Vinyl crotonate
3	2.76	0.7	1,4-Pentadien-3-one
4	3.05	0.7	2(5H)-Furanone
5	3.60	0.2	4-Methyl-5H-furan-2-one
6	3.71	0.1	3-Furaldehyde
7	4.11	1.0	3,5-Dimethylpyrazole-1-methanol
8	4.27	0.4	Vinyl crotonate
9	4.87	0.7	4-Hexen-2-one

10	5.38	0.2	2-Furanmethanol
11	5.78	0.2	2-Cyclopenten-1-one, 2-methyl-
12	5.92	0.1	Ethanone, 1-(2-furanyl)-
13	6.29	4.1	1,2-Cyclopentanedione
14	6.69	0.0	2(5H)-Furanone, 5-methyl-
15	6.90	0.1	2,5-Furandione, 3-methyl-
16	7.40	0.3	2-Cyclopenten-1-one, 3-methyl-
17	8.09	0.0	Phenol
18	8.15	0.1	4,4-Dimethyl-2-cyclopenten-1-one
19	8.39	0.3	2-Furanone, 2,5-dihydro-3,5-dimethyl
20	8.72	0.1	Benzyl alcohol
21	9.18	0.9	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-
22	9.48	0.2	2-Cyclopenten-1-one, 2,3-dimethyl-
23	9.52	0.1	6-Phenyl-5-hexyn-3-ol
24	9.79	0.4	4-Methyl-5H-furan-2-one
25	10.00	0.2	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-
26	10.12	0.6	dl-Leucine, N-[(phenylmethoxy)carbonyl]-
27	10.29	0.3	1H-Cyclopenta[c]furan-1,4(3H)-dione, tetrahydro-
28	10.34	0.3	Imidazole-4-acetic acid
29	10.81	0.4	2,5-Dimethylfuran-3,4(2H,5H)-dione
30	11.78	0.1	Maltol
31	11.85	0.1	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-
32	12.06	1.1	2,4(3H,5H)-Furandione, 3-methyl-
33	13.20	0.3	2,5-Dihydroxybenzaldehyde
34	13.49	0.0	Benzenemethanol, 4-methyl-
35	14.00	0.2	4H-Pyran-4-one, 3,5-dihydroxy-2-methyl-
36	14.21	0.1	1,3-Cyclohexanediol, 5-(1,1-dimethylethyl)-, (1.alpha.,3.beta.,5.alpha.)-
37	16.06	0.1	5-(Furan-3-yl)-2-methylpent-1-en-3-ol
38	16.32	0.1	Ethanone, 1-(2,5-dihydroxyphenyl)-
39	16.44	0.1	1H-Inden-1-one, 2,3-dihydro-
40	16.58	0.1	(1-Methylenebut-2-enyl)benzene
Total chromophore area%		**16.1**	

A comparative analysis of the data can be summarised as follows:

- A few lignin pyrolysis products were detected, this confirms that the pulps were fully bleached and contained very low amounts of lignin residuals.
- The major pyrolysis products were levoglucosan, ketones and the furans-type compounds.
- Since levoglucosan is a major pyrolysis product of cellulose and low amounts of lignin compounds were detected in the pyrolysis products, it can be deduced that the presence of ketones and furan-type compounds is indicative of the presence of chromophoric compounds emanating from cellulose degradation. This is in accordance with literature

reports (Chapter 2) that implicate ketones and furans as causatives of brightness reversion in pulps. For example, these compounds are known to form complexes with the ferrous salts and cause pulp yellowing (Loureiro *et al.*, 2012).

- With respect to the pulps analysed, there appears to be no correlation between pulp brightness and the amounts of chromophores detected in the pulps.

The non-correlation between brightness reversion and amount of chromophore content was investigated further to understand this observation better. Cellulose-rich materials and compounds that are potential sources of chromophores in pulps were analysed. The cellulose-rich samples used were the cotton linters and a laboratory filter paper. Compounds considered as possible sources of chromophores included hemicelluloses (represented by xylan in this study), sugar monomers, and Klason lignin.

4.2.2 Analysis of cellulosic materials

Cellulose-rich materials, viz., a laboratory filter paper (98% cellulose content) and cotton linters (99% cellulose content) were analysed for chromophore content using Py-GC/MS. These materials were induced for brightness reversion and then analysed for chromophore content before and after brightness reversion. The results are discussed below.

4.2.2.1 Analysis of the laboratory filter paper

The pyrogram obtained from the analysis of a laboratory filter paper is presented in Figure 4.6. The numbered compounds in the pyrograms indicate chromophoric compounds. Small amounts of chromophores were detected as shown in Table 4.6. The chromophores detected were 1,2-cyclopentanedione (0.2%), furazane, 3-amino-4-iodo- (0.1%), 6,7-dihydropyrido(2,3-d)pyridazine-5,8-dione (0.1%), and 2,5-dimethyl-4-hydroxy-3(2H)-furanone (0.1%) as listed in Table 4.6. The presence of these compounds in a cellulose rich sample indicates that part of the cellulose was degraded during storage and transportation of the filter papers.

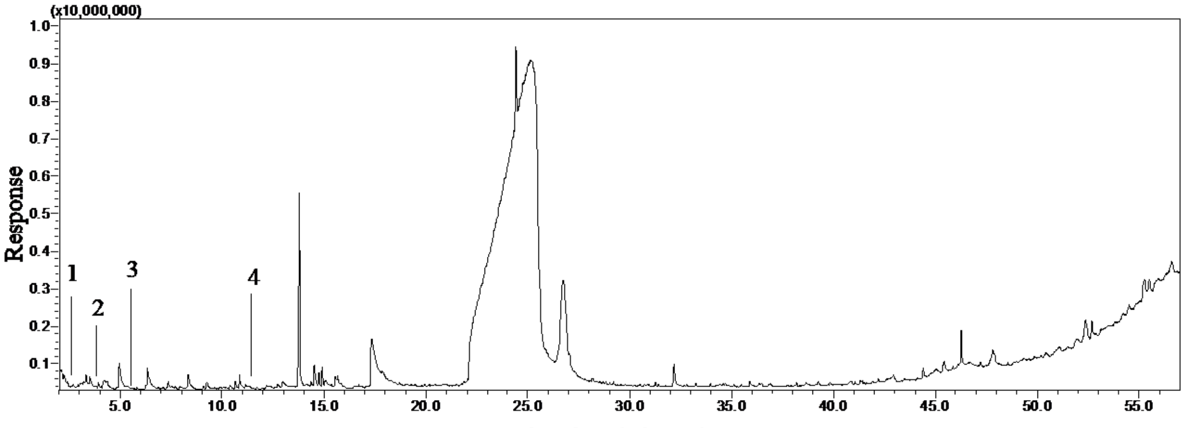


Figure 4.6: Pyrogram of the laboratory filter paper.

Table 4.6: Peak identification for the laboratory filter paper.

Peak number	**Retention time (min)**	**Area%**	**Compound**
1	3.49	0.1	Furazane, 3-amino-4-iodo-
2	3.93	0.1	6,7-Dihydropyrido(2,3-d)pyridazine-5,8-dione
3	6.33	0.2	1,2-Cyclopentanedione
4	10.85	0.1	2,5-Dimethyl-4-hydroxy-3(2H)-furanone
Total chromophore area %		**0.5**	

Analysis of the filter paper after brightness reversion showed that the total chromophore content increased by 2.2%. The heat induced brightness reversion resulted in the formation of new chromophores that were not present before brightness reversion. They included compounds such as 2(5H)-furanone (0.1%), furfural (0.6%) and 2,4(3H,5H)-furandione, 3-methyl- (0.2%). The amounts of some of the chromophores that were detected in the original sample increased after brightness reversion. These included 1,2-cyclopentanedione and 2,5-dimethyl-4-hydroxy-3(2H)-furanone. The pyrograms of the filter paper samples, with and without brightness reversion, are compared in Figure 4.7.

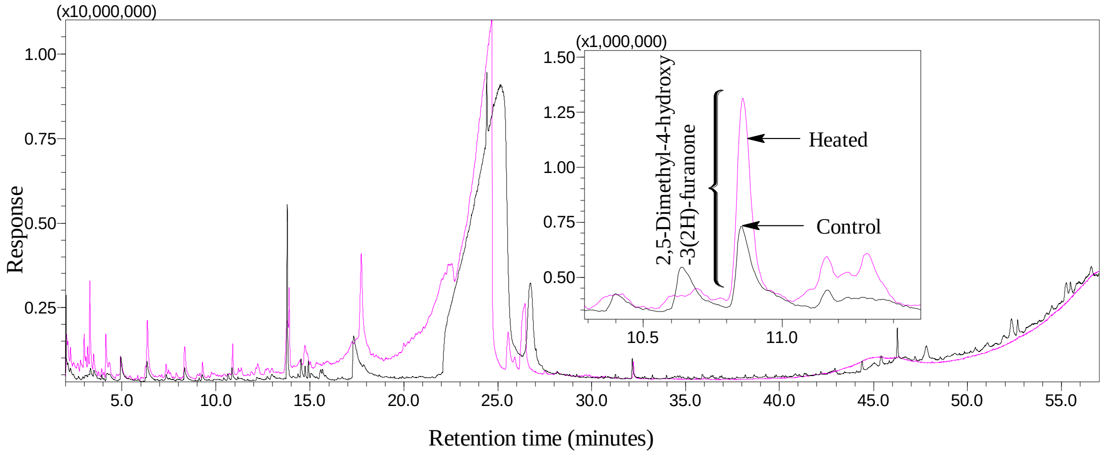


Figure 4.7: Pyrogram of the laboratory filter paper before (Control) and after (Heated) brightness reversion.

4.2.2.2 Analysis of the cotton linters

The cotton linters are regarded as the purest form of natural cellulose/ pulp. Analysis of the pyrolysis products of the cotton linters showed that four chromophoric compounds were present in the sample. The chromophores are labelled in Figure 4.8, and listed in Table 4.7. The major chromophores identified were furfural (2.8%) followed by 5-hydroxymethylfurfural (1.9%). The total area percentage of the chromophores identified was 7.6%. Since the cotton linters are regarded as the purest form of cellulose, the chromophores identified in the samples can be associated with ageing of cellulose that occurred due to storage conditions or transportation that resulted in the degradation of cellulose (Rosenau *et al.*, 2011).

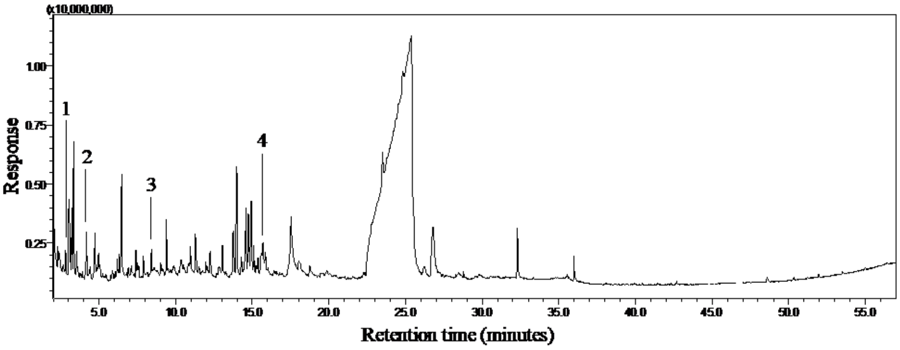


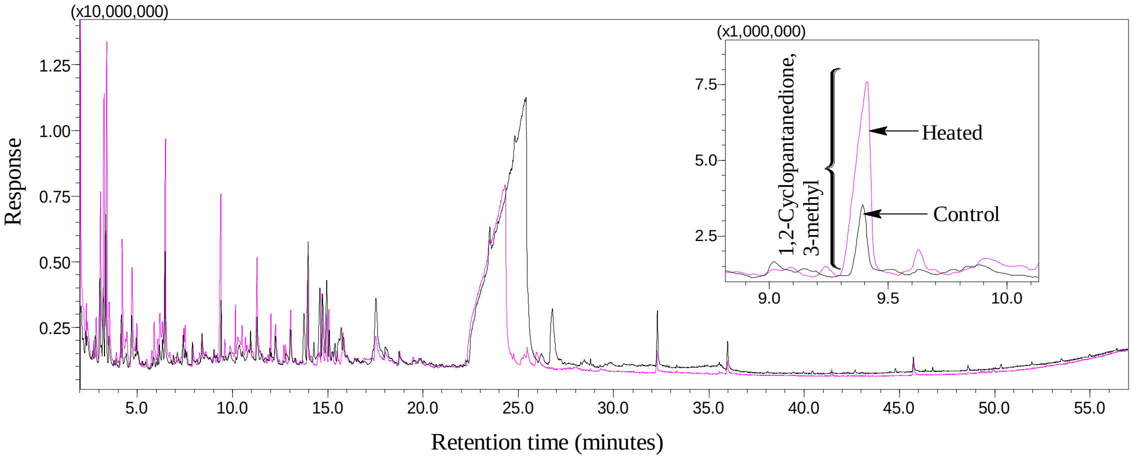
Figure 4.8: Pyrogram of cotton linters.

Table 4.7: Peak identification for cotton linters.

Peak number	**Retention time (min)**	**Area%**	**Compound**
1	2.81	1.1	1-Penten-3-one
2	4.16	2.8	Furfural
3	9.39	1.8	1,2-Cyclopentanedione, 3-methyl-
4	15.53	1.9	5-Hydroxymethylfurfural
Total chromophore area %		**7.6**	

Figure 4.9 compares pyrograms of the cotton linters before and after brightness reversion. From the pyrograms, it is evident that the amount of some of the compounds increased after brightness reversion. For example, 1,2-cyclopentanedione, 3-methyl- was identified before and after brightness reversion, the percentage increased by 0.9%. The total chromophore area percentage increased from 7.6% to 8.4% due to the heat accelerated ageing. Similar to the laboratory filter paper, the chromophores increased as a result of cellulose degradation that was induced by the heating process.

Figure 4.9: Pyrograms of the cotton linters before (Control) and after (Heated) brightness reversion.



The analysis of the cellulosic materials showed that the cotton linters contained more chromophores (7.6%) than the laboratory filter paper (0.5%). As expected, the major pyrolysis product in both samples was levoglucosan that eluted between 24 and 26 minutes. In both samples, the area percentage of the levoglucosan decreased after brightness reversion. Levoglucosan is the primary degradation product of cellulose. The reduction of the levoglucosan percentage due to brightness reversion indicates that some of the cellulose was degraded during the ageing process and contributing to the formation of chromophores. Furthermore, it was observed that it was mainly furan-type compounds that dominate when the cellulose is degraded. This concurs with studies that employ degradation of cellulose for conversion into furans (Barbosa *et al.*, 2014, Mascal and Nikitin, 2008). The chromophores identified in both samples, the filter paper, and the cotton linters were non-aromatic structures; they are different from the compounds that were identified from old cotton linters in the study by (Rosenau *et al.*, 2011). This difference may be a function of the brightness reversion mode in action.

4.2.3 Analysis of possible chromophore sources in pulp

It is reported in the literature that the most likely sources of chromophores in fully bleached pulps are the hemicelluloses that survive the bleaching process and residual lignin (Kato and Cameron, 1999, Li *et al.*, 2012, Beyer *et al.*, 2006). Therefore, studies to determine the contributions of these compounds to the formation of chromophores in DWP were conducted. This was done by pyrolyzing the most likely sources of chromophores such as hemicelluloses and lignin. The pyrolysis products of these samples were analysed for the presence of chromophoric compounds. The following paragraphs present the results obtained from the analysis of these samples.

4.2.3.1 Analysis of xylan

Xylan was used as a model compound to study the pyrolysis products of the hemicellulose because it is the most abundant polymer of the hemicelluloses (Bendahou *et al.*, 2007, Wang *et al.*, 2006). Using the method described in Chapter 3, xylan was induced for brightness reversion to observe the chemical changes that occur as a result of brightness reversion. The pyrogram of a control sample (before brightness reversion) of xylan is shown in Figure 4.10 with the numbering indicating the peaks of the chromophoric compounds that were identified. A detailed listing of the chromophores is provided in Table 4.8.

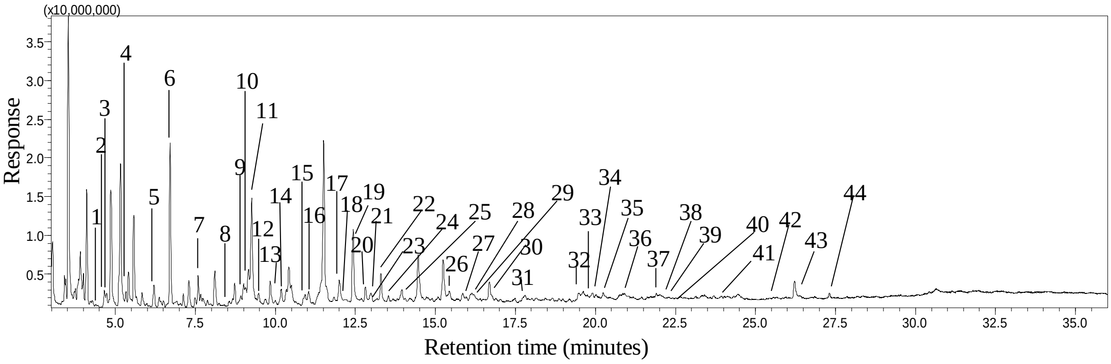


Figure 4.10: Pyrogram of xylan.

The total area percentage of the chromophores identified in the control xylan sample was 35.6% as shown in (Table 4.8). The major chromophoric compounds identified were furfural (4.8%), 1,2-cyclopentanedione (4.9%) and 1,2-cyclopentanedione, 3-methyl- (3.3%). The identified chromophores were grouped into furan-type compounds, ketones, arenes and other low molecular weight chromophores as summarised in Figure 4.11. The total area percentage of the furan type compounds was 8.7%, the ketones added up to 14.0%, the arenes were 10.4%, and the other low molecular weight chromophores were added up to 2.8%.

Table 4.8: Peak identification for xylan.

Peak number	Retention time (min)	Area %	Compound
1	3.75	0.3	2(3H)-Furanone, 5-methyl-
2	3.90	2.8	2,3-Pentanedione
3	4.66	0.5	3-Penten-2-one, (E)-
4	5.33	0.5	2(5H)-Furanone
5	6.37	0.3	3-Furanmethanol
6	6.71	4.8	Furfural
7	7.66	0.4	2(3H)-Furanone, 5-methyl-
8	7.88	0.2	4-Cyclopentene-1,3-dione
9	8.73	0.8	2-Cyclopenten-1-one, 2-methyl-
10	9.01	0.8	2(5H)-Furanone

11	9.26	4.9	1,2-Cyclopentanedione
12	9.48	0.6	2(5H)-Furanone, 3-methyl-
13	9.83	1.0	2,5-Furandione, 3-methyl-
14	10.50	0.8	2-Cyclopenten-1-one, 3-methyl-
15	10.93	0.4	2(5H)-Furanone, 3-methyl-
16	11.04	0.7	Phenol
17	12.00	1.5	5-Pyrimidinecarboxaldehyde, 1,2,3,4-tetrahydro-2,4-dioxo-
18	12.22	0.9	4-Methyl-2-oxo-(1H)-pyrimidine
19	12.43	3.3	1,2-Cyclopentanedione, 3-methyl-
20	12.81	0.8	2-Cyclopenten-1-one, 2,3-dimethyl-
21	12.98	0.7	Glutaric acid, 3-methylbut-2-en-1-yl 2-nitrophenyl ester
22	13.67	0.3	6-Methoxy-2-phenacyloxy-3(2H)-pyridazinone
23	13.95	1.1	Phenol, 3-methyl-
24	14.06	0.2	Indolizine, octahydro-
25	14.90	0.2	Phenol, 2,6-dimethyl-
26	15.09	0.4	Maltol
27	15.97	0.2	2,3,4,4a,8,8a-Hexahydro-pyrano[3,2-b]pyran
28	16.14	0.6	2,4-Imidazolidinedione, 5,5-dimethyl-
29	16.48	0.3	2,3-Methylenedioxyphenol
30	16.69	1.1	2,3-Dihydroxybenzaldehyde
31	17.49	0.2	2(1H)-Naphthalenone, 4a,5,6,7,8,8a-hexahydro-4a-methyl-, trans-
32	19.49	0.5	1,2-Benzenediol, 4-methyl-
33	19.62	0.6	Guanosine
34	19.92	0.4	Resorcinol, 2-acetyl-
35	20.03	0.2	1H-Inden-1-one, 2,3-dihydro-
36	20.76	0.3	Benzaldehyde, 3-hydroxy-
37	20.92	0.5	2-Methoxy-4-vinylphenol
38	21.19	0.2	Ethanone, 1-(6-methyl-3-pyridinyl)-
39	21.71	0.2	2-Nitrophenethyl alcohol, pentafluoropropionate
40	21.90	0.2	Phenol, 2,6-dimethoxy-
41	24.46	0.4	2-Hydroxy-5-methylisophthalaldehyde
42	25.67	0.2	Benzoic acid, 3-formyl-4,6-dihydroxy-2,5-dimethyl-, methyl ester
43	26.22	0.9	2H-1-Benzopyran-2-one, 3,4-dihydro-6-hydroxy-
44	27.31	0.2	4-Methyl-2,5-dimethoxybenzaldehyde
Total chromophore area%		**35.6**	

Heat induced brightness reversion in xylan resulted in 4.9% increase in the total area percentage of the chromophores. A comparison of the pyrograms of the control and the brightness reversed xylan shown in Figure 4.12, indicates that there was an increase in peak areas of chromophores after brightness reversion, e.g., the growth in peak area of 1,2-cyclopentanedione is highlighted. The furan-type compounds and ketones each increased by 2.1% (Figure 4.11).

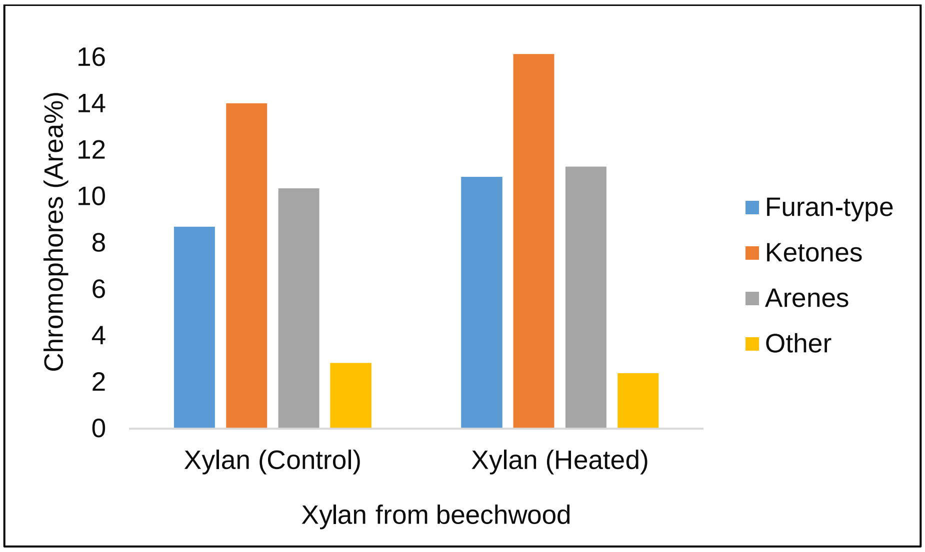


Figure 4.11: Summary of chromophores identified in xylan (control and heated).

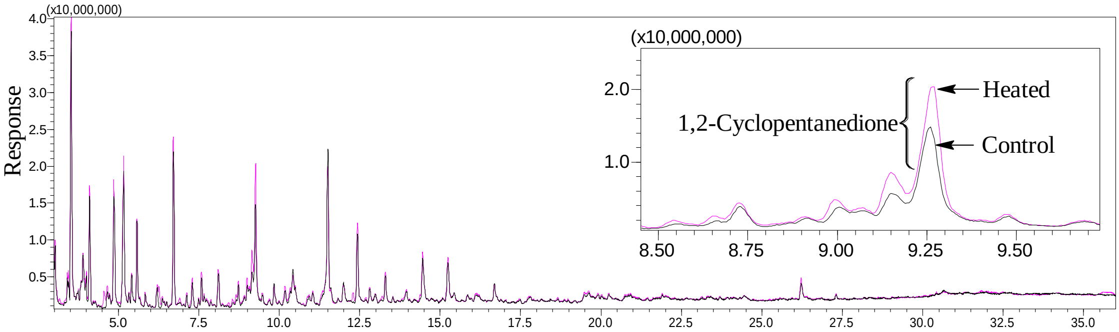


Figure 4.12: Pyrograms of xylan before (control) and after (heated) brightness reversion.

4.2.3.2 Analysis of sugar monomers

Sugar monomers, viz., glucose, arabinose, xylose, galactose, rhamnose, and mannose were analysed for chromophore content using Py-GC/MS and the results are illustrated in Figures 4.13-4.15 and Tables 4.9-4.11.

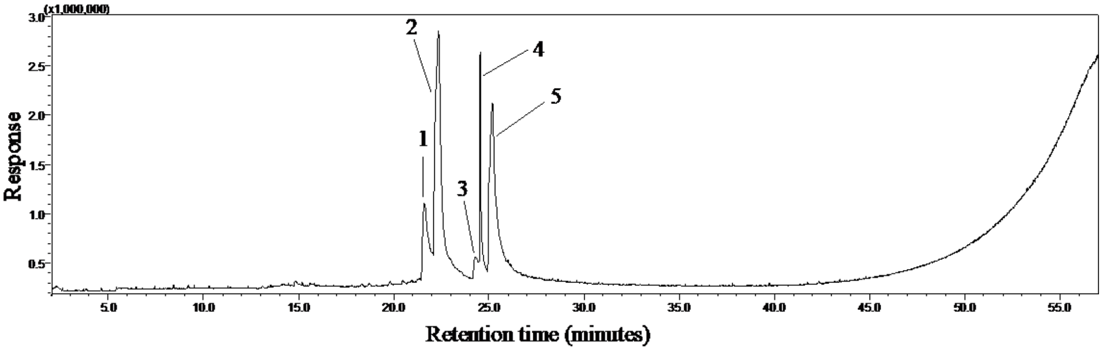


Figure 4.13: Pyrogram of glucose.

Table 4.9: Peak identification for glucose.

Peak number	**Retention time**	**Area%**	**Compound**
1	21.60	14.6	Sucrose
2	22.34	39.2	β-D-Glucopyranose
3	24.30	2.9	α-D-Glucopyranose
4	24.53	7.4	Heptadecane
5	25.18	36.0	Glucose

Py-GC/MS analysis of glucose (Figure 4.13) produced mainly β-D-glucopyranose (levoglucosan) with an area percentage of 39.2% followed by glucose (36.0%) and sucrose (14.6%). Only five compounds were produced during the pyrolysis of glucose, and no chromophores were identified (Table 4.9). These findings indicate that glucose is not a potential source of chromophores in pulps.

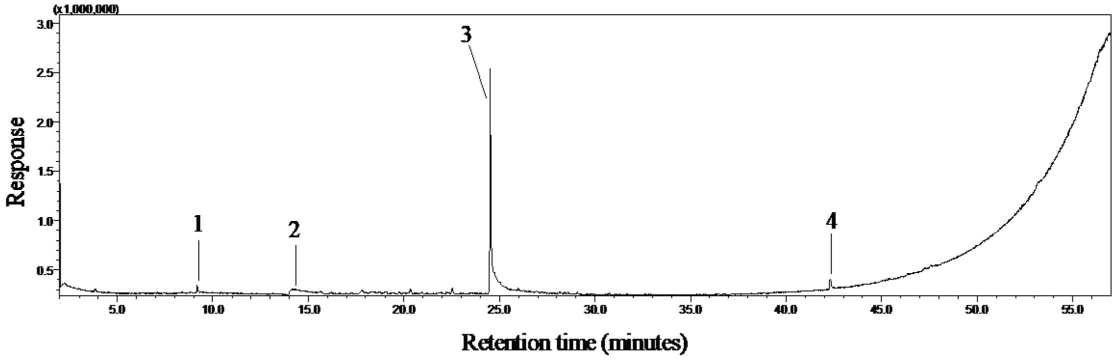


Figure 4.14: Pyrogram of arabinose.

Table 4.10: Peak identification for arabinose.

Peak number	**Retention time (min)**	**Area%**	**Compound**
1	9.16	1.8	D-Limonene
2	14.20	8.8	1,3-Propanediol, 2-(hydroxymethyl)-2-nitro-
3	24.51	84.9	Heptadecane
4	42.32	3.5	Diisooctyl phthalate

The analysis of the pyrolysis products of arabinose also showed no evidence for the presence of chromophores (Figure 4.14). The diisooctyl phthalate (Peak number 4, Table 4.10) is an aromatic hydrocarbon. However, it was regarded as a contaminant since the phthalates are well-known contaminants in pulp and paper production (Xue *et al.*, 2010). The primary pyrolysis product of arabinose was heptadecane with an area percentage of 84.9%. These results confirm that the arabinose sugar is not a potential source of chromophores in pulps.

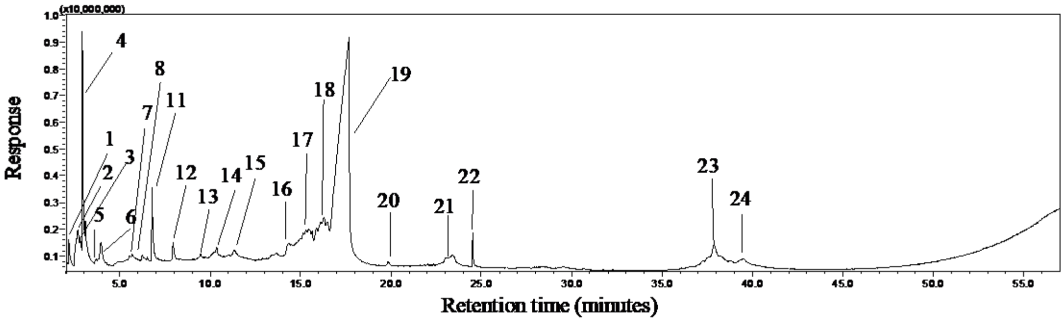


Figure 4.15: Pyrogram of xylose.

Table 4.11: Peak identification for xylose, highlighting the chromophoric compounds.

Peak number	**Retention time (min)**	**Area%**	**Compound**
1	2.17	1.1	2-Pyrrolidinone
2	2.69	3.1	Glyceraldehyde
3	2.79	0.2	Glyceraldehyde
4	2.93	5.4	3-Furaldehyde
5	3.68	0.2	2-Furanmethanol
6	3.95	1.3	2(3H)-Furanone
7	5.54	0.3	2-Cyclohexen-1-ol
8	5.68	0.1	6-Methoxypiperidin-2-one
9	6.23	0.3	Piperazine, 1,4-dimethyl-
10	6.53	0.1	N-Methylvaleramide
11	6.79	2.7	Butanedioic acid, cyclic hydrazide
12	7.95	0.8	Oxazolidine, 2,2-diethyl-3-methyl-
13	9.47	0.2	N-Methoxymethyl-N-methylacetamide
14	10.35	0.6	6-Oxa-bicyclo[3.1.0]hexan-3-ol
15	11.32	0.6	.alpha.-D-Glucose
16	14.72	2.6	1-(.beta.-d-Arabinofuranosyl)-4-O-difluoromethyluracil
17	15.46	2.1	1,3-Propanediol
18	16.28	3.9	1,3-Propanediol
19	17.68	62.9	1,3-Propanediol
20	19.84	0.3	2-(5-[1,3]Dioxolan-2-yl-pentyl)-3-methylaziridine
21	23.43	2.7	L-Lyxose
22	24.52	1.1	Heptadecane
23	37.88	5.9	.beta.-d-Lyxofuranoside
24	39.48	1.6	.alpha.-D-Glucopyranose

The major pyrolysis product of xylose was 1,3-propanediol with an area % of 68.9% (Table 4.11, Peak number 17-19). Xylose was different from the other sugars because it produced conjugated compounds such as 3-furfural (5.4%) and 2(3H)-furanone (1.3%) as listed in Table 4.11. This indicates that that the presence of trace amounts of xylose in pulps can result in the formation of chromophores. Xylose and xylan have also been used as starting materials in the production of furfural (Bunzel and Ralph, 2006). Furthermore, the furans and their derivatives are formed as reaction products of the aldol condensation and have been identified as chromophores that cause yellowing of fully bleached chemical pulps (Beyer *et al.*, 2006).

The analysis of the sugar monomers indicated that only xylose degrades to chromophores. The chromophores identified in xylose degradation were similar to the pyrolysis products of xylan. It was expected that the xylose would produce chromophoric compounds during pyrolysis since it is a monomer of xylan.

4.2.3.3 Analysis of lignin samples

To understand the type of chromophores released during lignin pyrolysis, Klason lignin samples were analysed. The compounds identified by Py-GC/MS analysis of the lignin samples were mainly aromatic compounds.

Figure 4.16 shows the pyrogram of the lignin that was isolated from *E.Dunnii* sawdust using the acid hydrolysis procedure described in Chapter 3. Most of the pyrolysis products of the *E. Dunni* lignin were chromophoric compounds that accounted for 96.1% of the peaks that were detected. The major chromophores identified are listed in Table 4.12. It is evident that the primary pyrolysis products of lignin were substituted aromatic chromophores such as 1,2-benzenediol, 3-methoxy- (6.1%), 1,2,4-trimethoxybenzene (9.5%), phenol, 2,6-dimethoxy- (12.7%) and ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)- (4.5%).

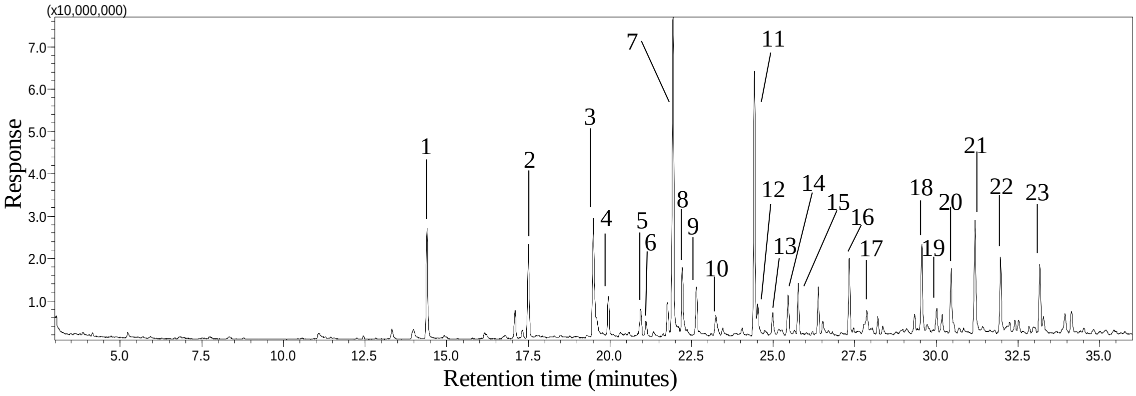


Figure 4.16: Pyrogram of *E.Dunnii* lignin.

Table 4.12: Peak identification for *E.Dunnii* lignin.

Peak number	**Retention time (min)**	**Area%**	**Compound**
1	14.39	3.8	Phenol, 2-methoxy-
2	17.50	3.2	Creosol
3	19.49	6.1	1,2-Benzenediol, 3-methoxy-

4	19.95	1.6	Phenol, 4-ethyl-2-methoxy-
5	20.94	1.2	4-Hydroxy-3-methylacetophenone
6	21.76	1.2	Phenol, 2,6-dimethoxy-
7	21.93	12.7	Phenol, 2,6-dimethoxy-
8	22.22	2.8	Phenol, 3,4-dimethoxy-
9	22.65	1.7	1,2,3-Trimethoxybenzene
10	23.24	1.1	Benzaldehyde, 3-hydroxy-4-methoxy-
11	24.43	9.5	1,2,4-Trimethoxybenzene
12	24.53	1.5	3-Allyl-6-methoxyphenol
13	24.99	1.0	1,2,4-Trimethoxybenzene
14	25.77	1.8	Benzene, 1,2,3-trimethoxy
15	26.38	1.7	Benzene, 1,2,3-trimethoxy-5-methyl-
16	27.33	2.7	3',5'-Dimethoxyacetophenone
17	27.87	1.2	Butyrovanillone
18	29.55	3.5	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-
19	30.01	1.0	3-(2-Methoxy-5-methylphenyl)acrylic acid
20	30.45	2.3	(E)-2,6-Dimethoxy-4-(prop-1-en-1-yl)phenol
21	31.18	4.5	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-
22	31.96	2.9	3,5-Dimethoxy-4-hydroxyphenylacetic acid
23	33.16	2.6	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-
Total chromophore area %		**96.1**	

Analysis of lignin samples from other *Eucalyptus* species yielded virtually the same type of compounds as illustrated in Figure 4.17.

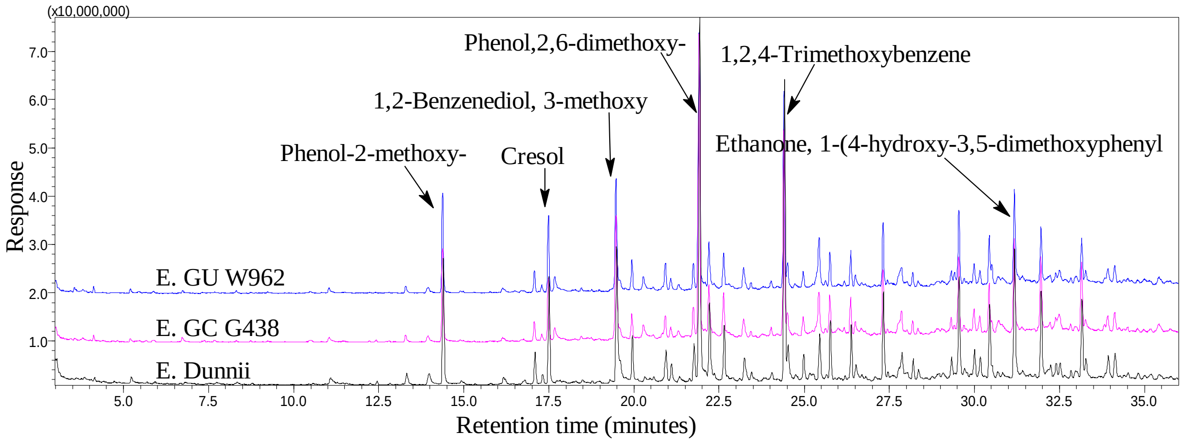


Figure 4.17: Pyrograms of *Eucalyptus* lignin.

The pyrolysis products were grouped into furans, ketones, arenes and catch all group termed “others”. The total area percentage of the chromophores identified in E. GC G438 and E. GU W962 were 92.3% and 96.1% respectively. Compounds such as furans, ketones and other low molecular weight chromophores were found at percentages below 0.4%. However, the area percentages of the arenes were above 90% in all the samples, hence, Figure 4.18 was split into parts (a) and (b), with part (a) showing all the chromophores identified and part (b) showing the chromophores that were below 0.4%.

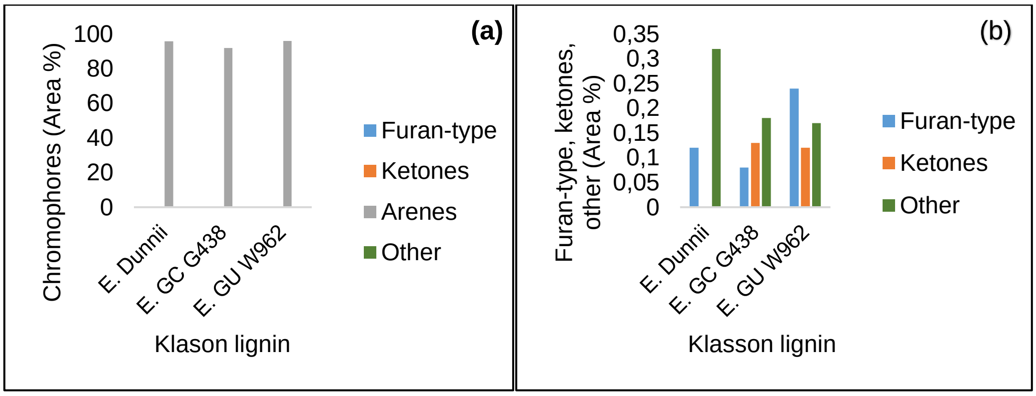


Figure 4.18: Py-GC/MS analysis of acid insoluble *Eucalyptus* sawdust lignin; (a) shows all the group of chromophores and (b) shows the chromophore groups that were present in small amounts.

Further analysis of the arenes identified in the *Eucalyptus* lignin samples revealed that the main constituents were the phenolic, syringyl, guaiacol and other aromatic compounds such as aromatic hydrocarbons and methoxybenzenes (Figure 4.19). These chromophores are well-known lignin degradation products that have been identified in previous studies on lignin pyrolysis (Ohra-aho *et al.*, 2005, Ibarra *et al.*, 2005). The quantities of the identified aromatic compounds agree with the results reported in the literature (Alves *et al.*, 2006, del Río *et al.*, 2001, Gu *et al.*, 2013).

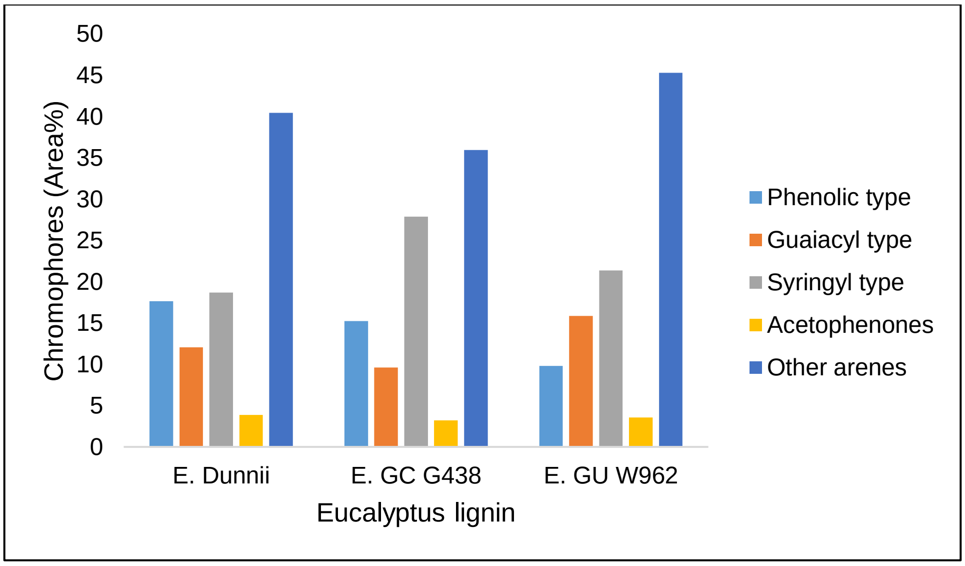


Figure 4.19: Distribution of aromatic compounds from pyrolysis of *Eucalyptus* lignin.

Further analysis of the aromatic pyrolysis products showed that the different *Eucalyptus* lignin samples contained different amounts of the grouped aromatic compounds (Figure 4.19). Studies have shown that the constituent compounds of lignin vary depending on the method used for lignin extraction, the origin of the plant material, the type of wood species and the age of the wood material (Brebu and Vasile, 2010, Rencoret *et al.*, 2007, Ház *et al.*, 2013). In this study, the three lignin samples were obtained using the same method, hence, the similarity in chromophores identified can be attributed to the method employed. However, the relative area percentages of the common compounds differ – this may possibly be reflective of the different growing sites of the trees.

Figure 4.20 only shows the major chromophoric compounds identified after pyrolysis of a hardwood kraft lignin. A total of 138 chromophoric compounds were identified with a total area percentage of 91.6%. The retention times, area percentages and names of the major peaks in Figure 4.20 are shown in Table 4.13. The major chromophores identified in the hardwood kraft lignin were furfural (6.8%), 1,2-benzenediol, 3-methoxy- (8.2%), phenol, 2,6-dimethoxy- (11.1%) and 3,5-dimethoxy-4-hydroxytoluene (7.3%), Table 4.13.

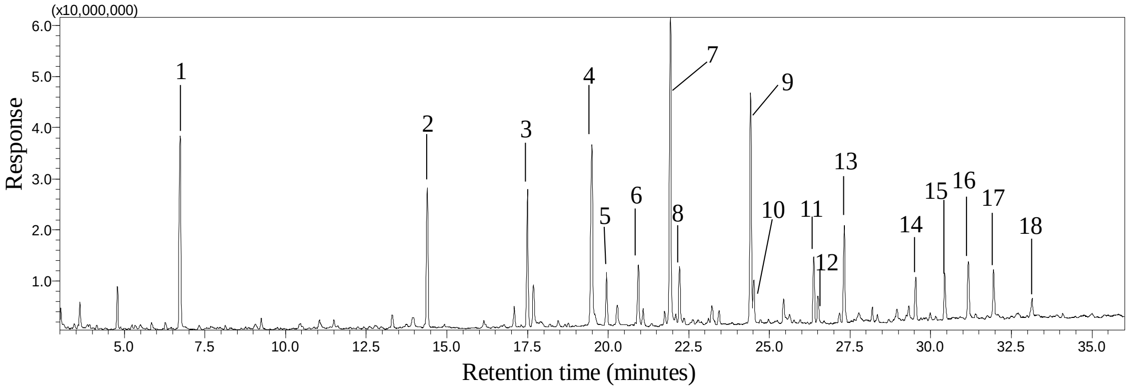


Figure 4.20: Pyrogram of hardwood kraft lignin.

Table 4.13: Peak identification for hardwood kraft lignin.

Peak number	**Retention time (min)**	**Area %**	**Compound**
1	6.73	6.8	Furfural
2	14.39	4.4	Phenol, 2-methoxy-
3	17.69	1.8	Catechol
4	19.50	8.2	1,2-Benzenediol, 3-methoxy-
5	20.28	1.1	1,2-Benzenediol, 4-methyl-
6	20.94	2.2	2-Methoxy-4-vinylphenol
7	21.93	11.1	Phenol, 2,6-dimethoxy-
8	22.21	2.1	Phenol, 3,4-dimethoxy-
9	24.42	7.3	3,5-Dimethoxy-4-hydroxytoluene
10	24.52	1.5	Phenol, 2-methoxy-4-(1-propenyl)-, (Z)-

11	26.38	2.0	Benzene, 1,2,3-trimethoxy-5-methyl-
12	26.51	1.0	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-
13	27.32	3.1	3',5'-Dimethoxyacetophenone
14	29.54	1.6	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-
15	30.44	1.6	(E)-2,6-Dimethoxy-4-(prop-1-en-1-yl)phenol
16	31.17	2.2	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-
17	31.95	2.0	3,5-Dimethoxy-4-hydroxyphenylacetic acid
18	33.15	1.0	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-
Total chromophore area %		**91.6**	

A comparison of softwood and hardwood kraft lignin pyrograms shows that most of the chromophores present in the lignin samples are similar; however, their relative area percentages are different (Figure 4.21). For example, the area percentage of furfural in softwood lignin was 0.6%, whereas, in the hardwood lignin, it was 6.8%. Overall, the chromophore content was 92% in hardwood lignin and 95% in softwood lignin.

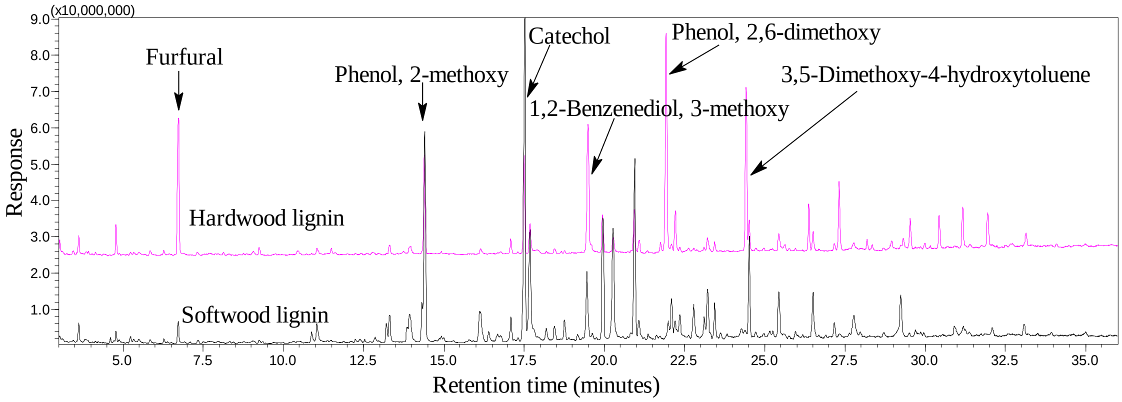


Figure 4.21: Pyrograms of softwood and hardwood kraft lignin.

Similarly, in the *Eucalyptus* lignin, the dominant pyrolysis products in both softwood and hardwood kraft lignin were aromatic compounds. The softwood lignin contained 93.3% of aromatic (arenes) compounds, whereas the hardwood lignin contained 82.5% of aromatic compounds (Figure 4.22). The hardwood lignin contained more furan-type compounds (8.2%) than the softwood lignin that only contained 1.2% of the furan-type compounds. The ketones were less than 1% in both kraft lignin samples. In contrast to the lignin samples that were extracted from the sawdust, the kraft lignin contained more furan-type compounds and ketones. These compounds are a good indication of the presence of hemicelluloses and degraded carbohydrates remaining after the kraft pulping process (Lin *et al.*, 2015).

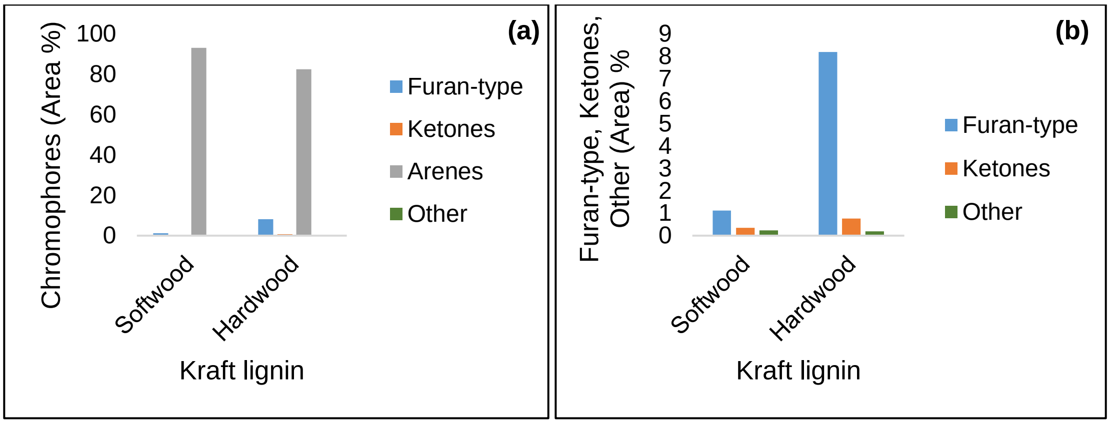


Figure 4.22: Chromophores identified in softwood and hardwood kraft lignin; (a) shows the total chromophore content and (b) shows the chromophore groups that were present in small amounts.

In kraft lignin, the major aromatic compounds were phenolics (Figure 4.23), and softwood lignin contained 11.6% more phenols than the hardwood lignin. The guaiacol type compounds were also found at a higher percentage (24.3%) in the softwood lignin, compared to 11.5 % found in the hardwood lignin. In contrast to hardwood lignin, the syringyl type compounds were found in minor amounts in the softwood lignin (0.4%) compared to 14.5% found in the hardwood lignin. This shows that in the softwood lignin, more demethoxylation reactions occurred, thus converting most of the syringyl type compounds to form more guaiacol type compounds. However, in the hardwood lignin, there was less demethoxylation even though the pyrolysis temperature used was the same. These findings are in agreement with the results obtained in previous studies on the thermal degradation of hardwood and softwood lignin (Zhao *et al.*, 2014).

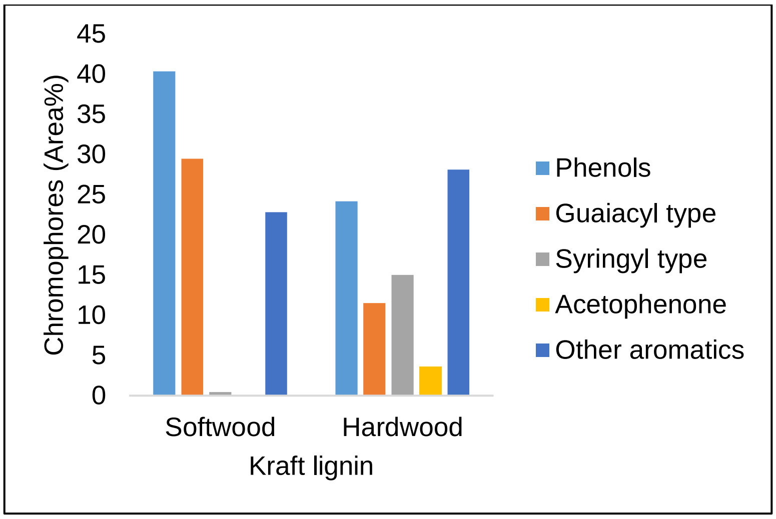


Figure 4.23: Distribution of aromatic compounds identified after pyrolysis of kraft lignin.

The findings obtained from the analysis of the trial samples of DWP, cellulosic materials and the potential sources of chromophores in pulps, show that most of the chromophores eluted within 30 minutes with the developed Py-GC/MS method.

4.2.4 Reproducibility of the Py-GC/MS method

The reproducibility of the Py-GC/MS method was tested using two acid bisulphite pulps, a high brightness pulp (Pulp A) and a low brightness pulp (Pulp B) as shown in Figure 4.24 and Figure 4.25. Replicate analyses of the pulp samples showed excellent reproducibilities in the pyrograms obtained and in the peak areas of the identified chromophoric compounds. Chromophores such as 1,2-cyclopentadione, 4H-pyran-4-one, 3,5-dihydroxy-2-methyl and 2-furancarboxaldehyde-5-hydroxymethyl were common in both pulp samples as shown in Figure 4.24 and Figure 4.25.

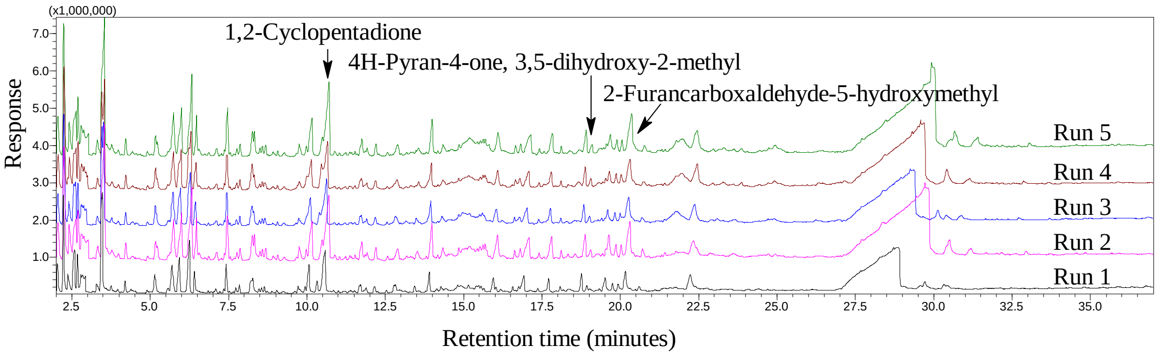


Figure 4.24: Pyrograms from replicate analyses of a high brightness DWP (Pulp A).

Figure 4.24 shows five replicate analyses of pulp A. The retention times, and the area percentages of the three labelled chromophores are shown in Table 4.14.

Table 4.14: Peak identification for pulp A.

1,2-Cyclopentadione			**4H-Pyran-4-one**		**2-Furancarboxaldehyde-5-hydroxymethyl**	
Run	**Retention time (min)**	**Area %**	**Retention time (min)**	**Area %**	**Retention time (min)**	**Area %**
1	10.58	4.0	18.94	0.3	20.16	1.4
2	10.70	3.7	19.06	0.3	20.31	1.8
3	10.63	3.6	19.02	0.3	20.27	2.5
4	10.66	3.1	19.06	0.3	20.32	1.4
5	10.71	3.5	19.10	0.3	20.36	2.1
Mean ± SD	10.62±0.05	3.6±0.3	19.04±0.06	0.3±0.0	20.28±0.08	1.9±0.5

The chromophores identified in pulp A were grouped into furans-type, ketones, arenes and other low molecular weight compounds (Table 4.15). The average area percentage and standard deviation of the different chromophore groups also presented in Table 4.15. In pulp A. the highest amounts of chromophore groups were the furans-type compounds (7.3±1.4%) followed by ketones

(5.5±1.6%). The arenes and other low molecular weight chromophores were minimal or not present in pulp A. This shows that the main contributors to yellowness of pulp A were furan and ketones type compounds.

Table 4.15: Chromophores identified in pulp A.

Run	**Furans (Area %)**	**Ketones (Area %)**	**Arenes (Area %)**	**Other (Area %)**
1	5.6	5.7	0.4	0.0
2	7.9	7.5	0.0	0.7
3	8.5	6.5	0.0	0.0
4	8.2	4.7	0.0	0.0
5	6.0	3.3	0.0	0.0
Mean±SD	7.3±1.4	5.5±1.6	0.1±0.2	0.1±0.3

Replicate analyses of pulp B also produced similar pyrograms for the five runs (Figure 4.25). The reproducibility of the retention times and the area percentages of the selected chromophores are shown in Tables 4.16 and 4.17.

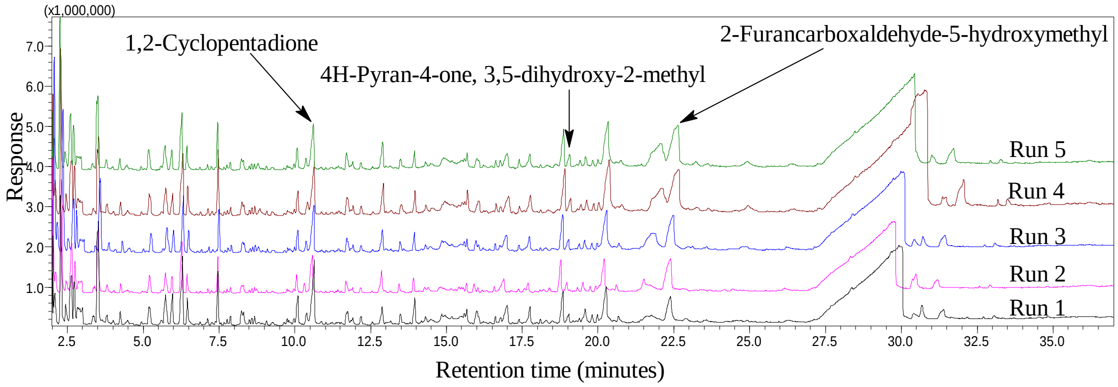


Figure 4.25: Pyrograms from replicate analyses of a low brightness DWP (pulp B).

The retention times of the selected chromophores in pulp A and pulp B were similar: for example, 1,2-cyclopentadione was identified at 10.62±0.05 minutes in pulp A and identified at 10.61±0.03 minutes in pulp B (as shown in Table 4.14 and Table 4.16, respectively). The average retention times for 4H-pyran-4-one and 2-furancarboxaldehyde-5-hydroxymethyl were also very similar in both samples. This demonstrates the reproducibility of the method regarding identifying similar compounds at the same retention times.

Table 4.16: Peak identification for pulp B.

	1,2-Cyclopentadione		**4H-Pyran-4-one**		**2-Furancarboxaldehyde-5-hydroxymethyl**	
Run	**Retention time (min)**	**Area %**	**Retention time (min)**	**Area %**	**Retention time (min)**	**Area %**
1	10.64	2.9	19.03	0.2	20.27	1.5

2	10.58	2.1	18.97	0.4	20.20	1.6
3	10.63	2.0	19.01	0.3	20.28	2.3
4	10.65	1.8	19.10	0.4	20.37	2.9
5	10.61	1.6	19.07	0.3	20.33	2.6
Mean ± SD	10.61±0.03	2.1±0.5	19.04±0.05	0.3±0.1	20.29±0.06	2.2±0.6

Similarly, to pulp A, the chromophores identified in pulp B were grouped into furans, ketones, arenes, and other low molecular weight compounds. The average area percentages were highest for furans at 5.4±0.8% and ketones at 4.1±1.1% (Table 4.17). Arenes and other low molecular weight chromophores were identified at deficient amounts. The furans and ketones were also the dominant chromophores in pulp B. However; their average area percentages were lower than in Pulp A, i.e., the amount of chromophores detected did not correlate with pulp brightness since pulp A was of higher brightness than pulp B.

Table 4.17: Chromophores identified in pulp B.

Run	**Furans (Area%)**	**Ketones (Area%)**	**Arenes (Area%)**	**Other (Area%)**
1	5.7	5.2	0.0	0.0
2	4.4	5.4	0.0	0.5
3	5.5	3.6	0.0	0.0
4	6.5	3.0	0.4	0.3
5	4.8	3.3	0.0	0.3
Mean±SD	5.4±0.8	4.1±1.1	0.1±0.2	0.2±0.2

Thus far it has been observed that the analysed DWPs contain deficient amounts of lignin-type chromophores (arenes) and there is no relationship between chromophores and brightness or yellowness. The data and results from the preceding paragraphs confirm the development of a novel and rapid method for analysis and identification of chromophoric compounds in pulp and paper matrices.

4.3 Application of the Py-GC/MS method

The developed method was used for analysis and identification of chromophores in various pulps. These were:

- Fully bleached industrial dissolving pulps
- In-process industrial pulps collected from various unit operations
- In-process laboratory pulps collected from various unit operations

4.3.1 Analysis of fully bleached industrial pulps

As mentioned in Chapter 3, fully bleached, acid bisulphite and PHK pulps, obtained from different mills across the world, were induced for brightness reversion by conditioning in an oven at 105 °C overnight. Brightness, yellowness measurements, and chromophore content were recorded before and after brightness reversion to observe the effect of brightness reversion on the formation of chromophores. The second set of fully bleached pulps were DWPs with their corresponding microcrystalline cellulose (MCC). The brightness, yellowness and chromophore content of the DWPs were compared to those of the MCC.

4.3.1.1 Analysis of fully bleached acid bisulphite pulp

Table 4.18 shows the effect of brightness reversion on the brightness and yellowness of fully bleached acid bi-sulphite pulps. It was observed that the brightness values on average, decreased by 1.8% and the degree of yellowness increased by 1.7% after the samples were induced for brightness reversion (Table 4.18). To understand the role of chromophores in the loss of brightness and the increase in the yellowness, further analysis was performed using Py-GC/MS. Pulp number 2 showed the highest brightness (93.4%) and lowest yellowness (3.4%) before brightness reversion. Pulp number 3 was the opposite, with a brightness of 89.3% and the yellowness of 6.4% hence, it was of interest to take a closer look at the type of chromophores present in these two samples.

Table 4.18: Brightness and yellowness of fully bleached acid bisulphite pulps.

	Before brightness reversion (A)		**After brightness reversion (B)**	
Pulp number	**Brightness (%)**	**Yellowness (%)**	**Brightness (%)**	**Yellowness (%)**
1	90.5	5.0	89.0	6.4
2	93.4	3.4	90.9	5.8
3	89.3	6.4	87.2	8.2
4	90.8	4.6	88.4	6.8
5	90.6	5.1	89.4	6.2
6	90.4	6.2	89.3	7.3

Figure 4.26 shows the pyrogram of pulp number 2 with the numbered peaks indicating the chromophoric compounds. Similar to the laboratory filter paper and the cotton linters, the main peak in the pyrogram of pulp number 2 was the to levoglucosan peak since it is the main pyrolysis product of cellulosic materials.

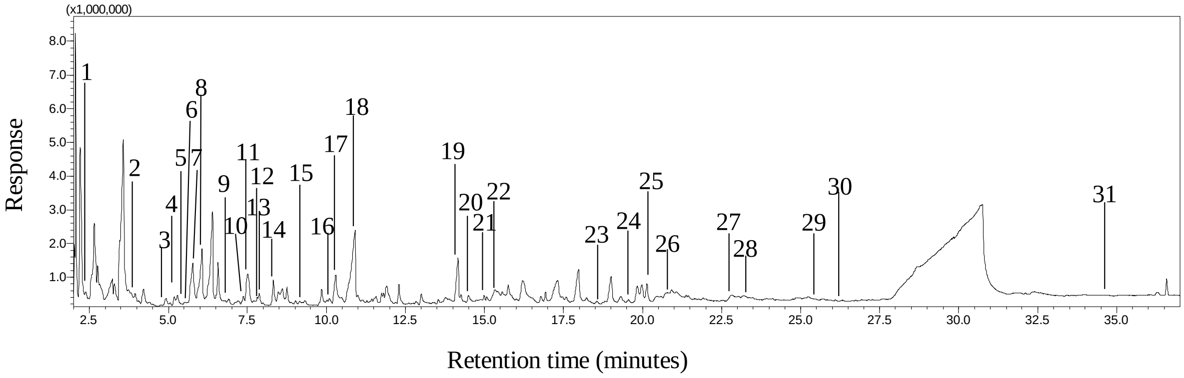


Figure 4.26: Pyrogram of a fully bleached acid bisulphite pulp number 2.

In comparison to the laboratory filter paper and the cotton linters, pulp number 2 had a higher total chromophore content with 31 chromophoric compounds with a total area percentage of 15.7% (Table 4.19). The major chromophores identified in the pulp was 2-cyclopenten-1-one, 2-hydroxy- (peak number 18) with an area percentage of 3.7%. The identified compounds were grouped into furans, ketones, arenes and other low molecular weight chromophores and changes in the compound groups before and after brightness reversion for the acid bisulphite pulps were summarised in Figure 4.27.

Table 4.19: Peak identification for pulp number 2.

Peak number	**Retention time (min)**	**Area%**	**Compound**
1	2.38	0.1	1,3-Cyclopentadiene
2	3.95	0.1	2,3-Pentanedione
3	4.75	0.1	Furan, 3-methyl-
4	4.93	0.2	3-Penten-2-one, (E)-
5	5.06	0.3	2,5-Furandione, 3,4-dimethyl-
6	5.19	0.2	Furan, 2-methyl-
7	5.29	0.3	1-Penten-3-one
8	6.57	0.9	(S)-5-Hydroxymethyl-2[5H]-furanone
9	6.91	0.2	3-Furaldehyde
10	7.37	0.2	Furan-2-carbonyl chloride, tetrahydro-
11	7.51	1.1	1H-Pyrazole, 3,5-dimethyl-
12	8.11	0.1	Furan, 2-(2-propenyl)-
13	8.47	0.3	2-Furanmethanol
14	8.61	0.5	2(3H)-Furanone, 5-methyl-
15	9.15	0.9	2-Cyclopentene-1,4-dione
16	10.02	0.1	Ethanone, 1-(2-furanyl)-
17	10.30	1.2	2(5H)-Furanone
18	10.90	3.7	2-Cyclopenten-1-one, 2-hydroxy-
19	14.17	1.5	1,2-Cyclopentanedione, 3-methyl-
20	14.50	0.3	4-Methyl-5H-furan-2-one
21	15.00	0.7	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-
22	16.94	0.5	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-
23	18.57	0.1	2(1H)-Naphthalenone, 4a,5,6,7,8,8a-hexahydro-8a-methyl-, trans-
24	19.32	0.3	4H-Pyran-4-one, 3,5-dihydroxy-2-methyl-
25	20.93	1.9	2-Furancarboxaldehyde, 5-(hydroxymethyl)-
26	21.39	0.4	Ethanone, 1-(2,5-dihydroxyphenyl)-
27	24.13	0.1	Ethyl Vanillin
28	24.48	0.2	7-Methylindan-1-one
29	26.33	0.1	2H-1-Benzopyran-2-one, 3,4-dihydro-6-hydroxy-
30	26.95	0.1	Naphthalene, 1,4-dimethoxy-
31	34.58	0.2	Benzene, 1,2,4-trimethoxy-5-(1-propenyl)-, (Z)-

Total chromophore area %	**15.7**

Py-GC/MS analysis showed that the effect of brightness reversion resulted in an increase in the groups of chromophores in the individual samples as illustrated in Figure 4.27. This means that the amount of chromophores increases when the pulp was induced for brightness reversion. However, Figure 4.27 shows that with samples 4 and 5, not all the chromophore groups increased as a result of brightness reversion and this was attributed to the slight differences that may have occurred in the mill unit operations such as slight changes and in temperature. The ketones and furan-type compounds were at a higher amount than the low molecular weight chromophores. The average increase of the amount of ketones in the acid bisulphite pulps after brightness reversion was 0.5% and the amount of furan-type compounds increased by 0.7%. Other low molecular weight chromophores were less than 3% in all the fully bleached acid bisulphite pulps, and the arenes were less than 2.5%. However, sample 6 was different because it contained over 4% of other low molecular weight chromophores, this can also be attributed to slight differences that may have occurred in the mill unit operations.

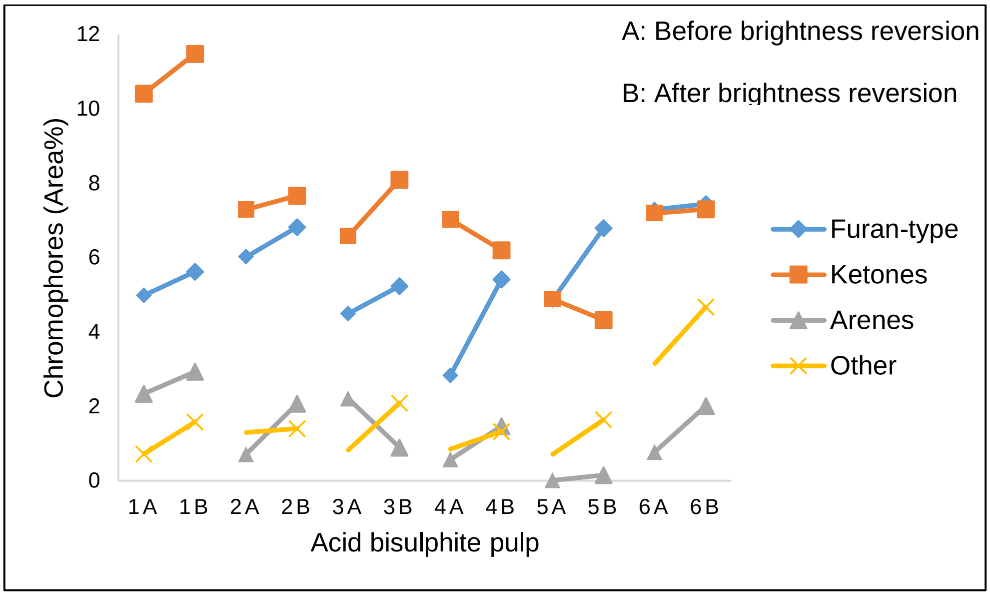


Figure 4.27: Chromophores identified in fully bleached acid bisulphite pulp before (A) and after (B) brightness reversion.

Before brightness reversion, pulp number 2 showed a higher brightness and a lower yellowness than pulp number 3 (Table 4.15). The pyrogram of pulp number 3 before brightness reversion is shown in Figure 4.28 with the labelled peaks showing the chromophoric compounds. The retention times, area percentages and the names of the identified chromophores are shown in Table 4.20. The total area percentage of the chromophores identified in pulp number 3 was 14% (Table 4.20), a value that was 1.7% lower than the total chromophore area percentage of pulp number 2. This further confirms that there is no relationship between the brightness/ yellowness parameters of the pulps and their chromophore content.

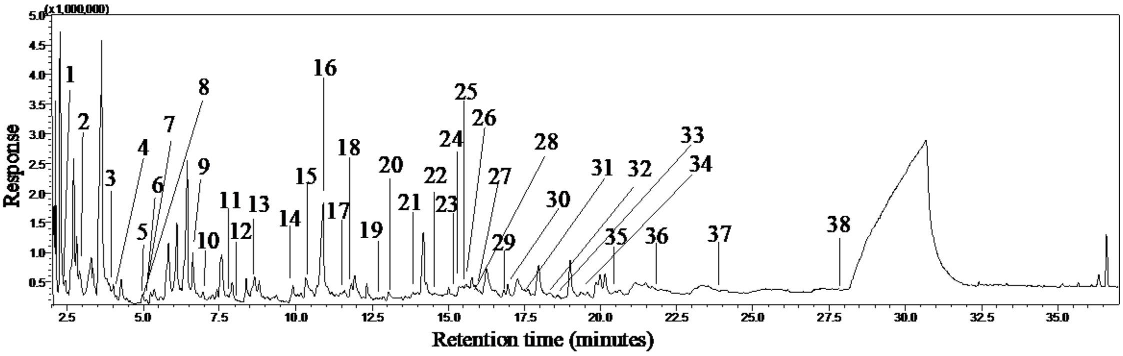


Figure 4.28: Pyrogram of pulp number 3.

Similarly, the summary of the Py-GC/MS data in Figure 4.27 shows that pulp number 2 (93.4% brightness) had a higher total chromophore content (15.2%) than pulp number 4 (11.3%) with 90.8% brightness, before brightness reversion. This data also confirms that the chromophore content is not related to brightness or yellowness of the sample. This indicates that high brightness or low yellowness of fully bleached acid bisulphite pulp does not necessarily imply lower chromophore content in the pulp. These findings confirm the results from previous studies on chromophores in pulps (Dyer, 2004, Rosenau *et al.*, 2007). However, it must be noted that the total chromophore content on individual samples the chromophores increase as a result of brightness reversion.

Table 4.20: Chromophore peak identification for pulp number 3

Peak number	Retention time (min)	Area %	Compound
1	2.43	0.1	1,3-Cyclopentadiene
2	2.81	0.6	2-Butanone, 1-(2-furanyl)-
3	3.80	0.02	2(3H)-Furanone, 5-methyl-
4	4.01	0.1	2,3-Pentanedione
5	4.98	0.2	3-Penten-2-one, (E)-
6	5.11	0.1	2,5-Furandione, 3,4-dimethyl-
7	5.24	0.1	Furan, 2-methyl-
8	5.35	0.3	1-Penten-3-one
9	6.62	1.0	(S)-5-Hydroxymethyl-2[5H]-furanone
10	6.96	0.3	Furfural
11	7.75	0.1	Carbamic acid, phenyl ester
12	8.15	0.03	Furan, 2-(2-propenyl)-
13	8.65	0.7	3-Furanmethanol
14	9.90	0.3	2-Cyclopenten-1-one, 2-methyl-
15	10.33	0.9	2(5H)-Furanone
16	10.90	2.8	2-Cyclopenten-1-one, 2-hydroxy-

17	11.47	0.2	2(3H)-Furanone, 5-methyl-
18	11.61	0.3	6-(Hydroxy-phenyl-methyl)-2,2-dimethyl-cyclohexanone
19	12.76	0.1	Benzofuran
20	12.86	0.1	1,2-Cyclohexanedione
21	14.18	1.5	1.2-Cyclopentanedione. 3-methyl-
22	14.77	0.1	2-Cyclohexen-1-one, 2-methyl-
23	15.02	0.2	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-
24	15.13	0.1	Phenol. 2-methyl-
25	15.37	0.3	Imidazole-4-acetic acid
26	15.47	0.3	2-Cyclopenten-1-one. 3-ethyl-
27	15.78	0.4	2.5-Dimethyl-4-hydroxy-3(2H)-furanone
28	15.89	0.3	2-Cyclohexen-1-one. 3-(hydroxymethyl)-6-(1-methylethyl)-
29	16.82	0.2	Maltol
30	16.95	0.3	2-Cyclopenten-1-one. 3-ethyl-2-hydroxy-
31	17.62	0.2	4-Cyclopentene-1.3-dione. 4-propyl-
32	18.32	0.2	2.3-Dihydroxybenzaldehyde
33	18.60	0.1	2(1H)-Naphthalenone. 4a.5.6.7.8.8a-hexahydro-8a-methyl-. trans-
34	19.36	0.2	4H-Pyran-4-one. 3.5-dihydroxy-2-methyl-
35	21.48	0.9	1H-Inden-1-one. 2.3-dihydro-
36	22.43	0.3	Benzofuran-4(5H)-one. 6.7-dihydro-. oxime
37	24.33	0.2	Cyclopenta[c]pyran-4-carboxylic acid
38	27.61	0.2	Phenol. 2.6-bis(1.1-dimethylethyl)-
Total chromophore area %		**14.0**	

In the study by Dyer (2004), the total visible absorption (integral of the absorption coefficient throughout the visible region) and the chromophore index (integral of the Kubelka-Munk remission function throughout the visible region) of kraft pulp were measured. The results showed a linear correlation between the total visible absorption and the chromophore index. However, there was no relationship between the brightness of the pulp, the total visible absorption and the chromophore index (Dyer, 2004).

Rosenau and co-workers (2007) isolated a number of different chromophoric structures using the chromophore release and identification procedure described in Chapter 2. Findings from this study showed that there was no correlation between the number and the overall concentration of the chromophores: a small number of chromophores does not imply that the concentration of the chromophores was lower because there may be a few compounds occurring in high amounts. It was also mentioned that the concentration of the chromophores was not related to the brightness of the pulp (Rosenau *et al.*, 2007).

These observations show that chromophores in pulps absorb the UV light but do not directly affect the pulp brightness since the ISO brightness depends on two factors, the light absorption coefficient and the light scattering coefficient. The value of the light absorption coefficient varies according to the chemical composition of the pulp, and the value of the light scattering properties depends on the physical composition of the pulp (Johansson, 2000). This means that the brightness of the pulp is affected by the changes in both the chemical and physical properties occurring in the pulp. However, the chromophores do not represent the overall chemical structures or chemical information (the chromophores were present amongst other compounds that are not chromophores) of the pulp and are not related to the physical properties of the pulp.

4.3.1.2 Analysis of fully bleached PHK pulps

Table 4.21 shows the effect of brightness reversion on brightness and yellowness of the PHK pulps. Similar to the fully bleached acid bi-sulphite pulps, the brightness decreased with an increase in yellowness after the samples were induced for brightness reversion. The average decrease in brightness was 2.6% and the average increase in the yellowness was 2.4%. Further analysis of the chromophores in fully bleached PHK pulps was carried out using the Py-GC/MS.

Table 4.21: The effect of brightness reversion on fully bleached PHK pulps.

	Before brightness reversion (A)		**After brightness reversion (B)**	
Pulp number	**Brightness (%)**	**Yellowness (%)**	**Brightness (%)**	**Yellowness (%)**
7	93.3	4.4	88.9	7.4
8	90.0	4.7	88.7	7.6
9	89.7	5.6	86.7	7.9
10	92.0	5.0	87.5	7.7
11	91.0	5.2	89.1	6.7
12	88.4	5.1	88.1	6.8

Pulp number 7 contained 42 chromophores as shown in the pyrogram in Figure 4.29 and in the list in Table 4.22. The total area percentage of the identified chromophores was 11.6% with major compounds being 2,3-butanedione (1.5%) and 2-cyclopenten-1-one, 2-hydroxy-3-methyl- (1.3%).

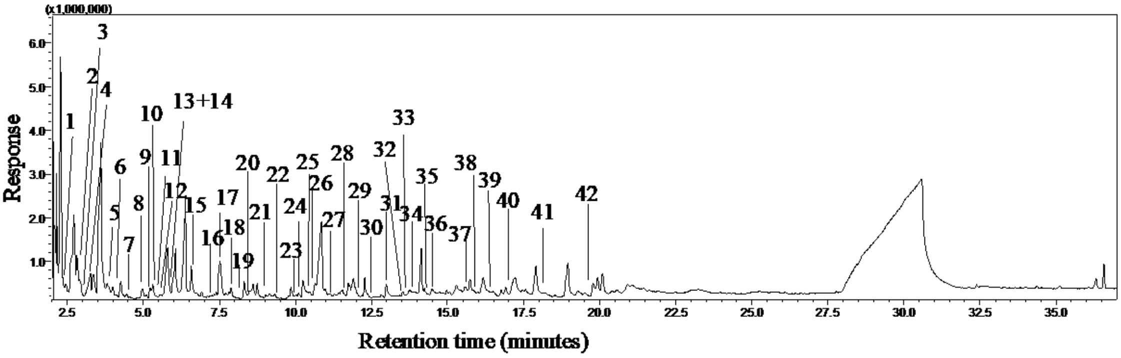


Figure 4.29: Pyrogram of pulp number 7.

Table 4.22: Peak identification for pulp number 7.

Peak number	Retention time (min)	Area %	Compound
1	2.39	0.2	1,3-Cyclopentadiene
2	2.65	1.5	2,3-Butanedione
3	3.12	0.1	1,3-Cyclohexadiene
4	3.52	0.1	3-Buten-2-one, 3-methyl-
5	3.79	0.1	2-Propenoic acid, 2-methyl-, ethenyl ester
6	3.84	0.1	2,3-Pentanedione
7	4.28	0.1	4-Methyl-5H-furan-2-one
8	4.70	0.3	3-Penten-2-one, (E)-
9	4.81	0.1	1,3-Butadiene
10	4.99	0.5	2H-Pyran, 3,4-dihydro-
11	5.43	0.3	2(5H)-Furanone
12	6.41	0.1	Furfural
13	6.53	0.2	Pyrrolidine
14	6.62	0.1	4-Methyl-5H-furan-2-one
15	7.01	0.5	Furfural
16	7.12	0.1	1H-Imidazole, 2,4-dimethyl-
17	7.75	0.5	2-Furanmethanol
18	7.92	0.2	2(3H)-Furanone, 5-methyl-
19	8.09	0.1	2-Cyclopenten-1-one, 2-methyl-
20	8.22	0.1	4-Cyclopentene-1,3-dione
21	9.09	0.3	2-Cyclopenten-1-one, 2-methyl-
22	9.33	0.8	2(5H)-Furanone
23	10.08	0.3	2(5H)-Furanone, 5-methyl-
24	10.31	0.1	2,5-Furandione, 3-methyl-
25	10.79	0.1	1-Penten-3-one, 2,4-dimethyl-
26	10.90	0.3	2H-Pyran-2-one, 4,6-dimethyl-
27	11.61	0.1	Phenol
28	12.31	0.2	2-Furanmethanol
29	12.47	0.1	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-
30	12.57	0.1	4(1H)-Pyrimidinone, 6-methyl-

31	12.94	1.3	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-
32	13.21	0.1	2-Cyclopenten-1-one, 2,3-dimethyl-
33	13.84	0.2	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-
34	14.16	0.2	Furan, 3-methyl-
35	14.54	0.1	1,4-Benzenediol, 2-methyl-
36	14.60	0.1	Methyl 2-furoate
37	15.61	0.1	Maltol
38	15.66	0.2	2,4(3H,5H)-Furandione, 3-methyl-
39	15.79	0.3	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-
40	16.41	0.1	2-Cyclopenten-1-one, 3-methyl-
41	17.80	0.1	2(3H)-Furanone, dihydro-5-propyl-
42	19.09	0.9	5-Hydroxymethylfurfural
Total chromophore area %		**11.6**	

The chromophores in the PHK pulps were also grouped as done for the previous samples. As shown in Figure 4.30 ketones and furan-type compounds were found at higher amounts than in fully bleached acid bisulphite pulps. After brightness reversion, the ketones increased by an average of 2.2% whereas the furans increased by an average of 0.8%. Arenes were detected at low amounts, below 0.8% and other low molecular weight chromophores were found at amounts below 3%. Pulp samples 11 and 12 showed a decrease in the percentage of furans than the other PHK pulps after brightness reversion. The amounts of ketones in sample 12 also decreased after brightness reversion. These differences in the behaviour of the same type of fully bleached pulp, when induced for brightness reversion under controlled conditions, was probably a result of the slight differences that may have occurred in the mill unit operations.

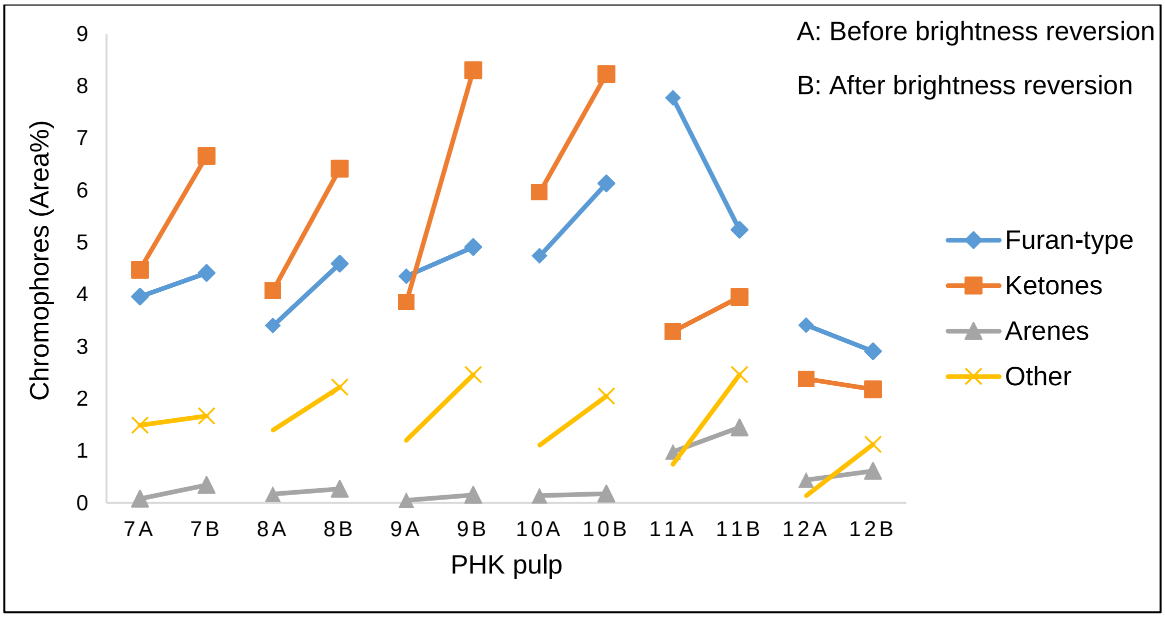


Figure 4.30: Chromophores identified in fully bleached PHK pulp before (A) and after (B) brightness reversion.

In the case of fully bleached PHK pulps, sample 12 had the lowest amount of chromophores and displayed the lowest brightness as shown in Figure 4.30. The pyrogram of sample 12 and the identified chromophores are shown in Figure 4.31 and Table 4.23, respectively. Pulp samples 7 and 10 exhibited very high brightness levels and lower yellowness values, however, their total amount of chromophore was also very high. Thus, there is no correlation between the brightness or yellowness and the total chromophore content of the fully bleached PHK pulps in the samples analysed.

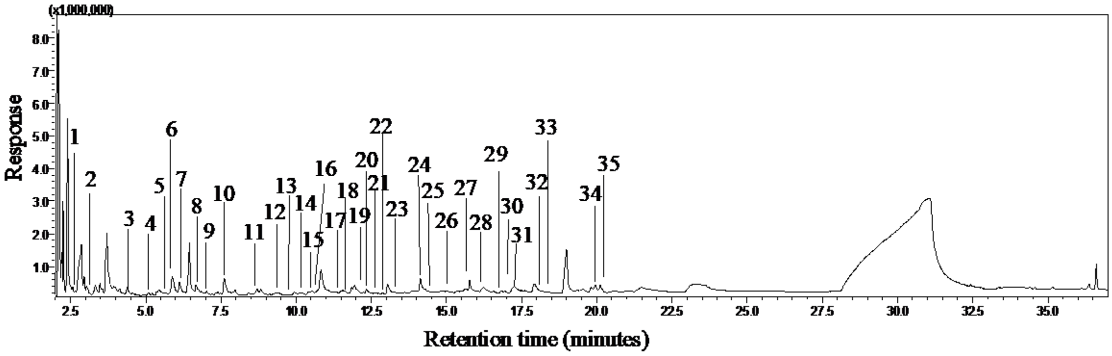


Figure 4.31: Pyrogram of pulp number 12.

The brightness decreased with increase in yellowness for both the acid bisulphite and PHK pulps, and this shows that there is a correlation between pulp brightness and yellowness: the brightness is inversely proportional to the yellowness of the pulp (Rosenau *et al.*, 2007). The brightness value of both the acid bisulphite and PHK pulps were similar, ranging from 88.4 - 93.3% and the yellowness ranged from 3.4 to 6.4% for the acid bisulphite pulp and 4.4 to 5.6% for the PHK pulp prior to brightness reversion (Table 4.21). Brightness reversion resulted in an increase of the chromophore content in both samples. However, intra-sample comparison of the chromophore content and the brightness did not show any correlation. Thus, the brightness of the pulp samples were not indicative of the amount of chromophores identified in the pulp samples: indeed, in some cases, pulps with high brightness levels also contained high chromophore content (e.g., samples 1, 2 and 12).

Table 4.23: Peak identification for pulp number 12.

Peak number	**Retention time (min)**	**Area%**	**Compound**
1	2.58	0.1	1,3-Cyclopentadiene
2	3.93	0.2	2(3H)-Furanone, 5-methyl-
3	4.14	0.2	2,3-Pentanedione
4	5.10	0.1	3-Penten-2-one, (E)-
5	5.36	0.1	Furan, 2-methyl-
6	5.44	0.3	1-Penten-3-one
7	6.85	0.1	4-Methyl-5H-furan-2-one

8	7.03	0.1	Furfural
9	7.35	0.1	3-Furanmethanol
10	7.62	0.6	Furfural
11	8.71	0.2	2(3H)-Furanone, 5-methyl-
12	9.41	0.1	2-Furanmethanol
13	9.93	0.1	2-Cyclopenten-1-one, 2-methyl-
14	10.03	0.3	1-Penten-3-one, 2,4-dimethyl-
15	10.20	0.1	Imidazole, 1,4,5-trimethyl-
16	10.44	0.1	2(5H)-Furanone
17	10.71	0.1	2-Furanmethanol
18	11.05	0.1	2(5H)-Furanone, 5-methyl-
19	11.21	0.1	2,5-Furandione, 3-methyl-
20	11.48	0.2	2(3H)-Furanone, 5-methyl-
21	12.34	0.1	2,4-Diaminopyrimidine
22	12.87	0.1	1,2-Cyclohexanedione
23	12.93	0.1	2-Cyclopenten-1-one, 2,3-dimethyl-
24	14.14	0.4	1,2-Cyclopentanedione, 3-methyl-
25	14.29	0.1	2-Cyclopenten-1-one, 2,3-dimethyl-
26	15.00	0.1	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-
27	15.78	0.3	2,5-Dimethyl-4-hydroxy-3(2H)-furanone
28	16.56	0.1	2-Furanmethanol
29	16.83	0.1	Maltol
30	16.94	0.1	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-
31	17.27	0.6	2,4(3H,5H)-Furandione, 3-methyl-
32	18.39	0.1	2,3-Dihydroxybenzaldehyde
33	19.34	0.2	4H-Pyran-4-one, 5-hydroxy-2-(hydroxymethyl)-
34	21.50	0.3	5-Hydroxymethylfurfural
35	21.57	0.1	5-Hydroxymethylfurfural
Total chromophore area %		**6.1**	

Ketones were the largest group of chromophores, followed by the furans; low molecular weight compounds and arenes were at lower amounts. The amount of chromophore groups in both pulp types were similar, since the acid bisulphite and PHK processes give rise to the same type of chromophores. This indicates that the mechanism of chromophore formation is similar, irrespective of the pulp processing conditions.

4.3.1.3 Analysis of DWP and its corresponding microcrystalline cellulose

To understand the effect of pulp derivatization during the MCC production, on the formation of chromophores, fully bleached DWP samples with their corresponding MCC samples were analysed for chromophore content using the Py-GC/MS. The pyrogram of pulp sample P1 is shown in Figure 4.32 and details of the chromophores are shown in Table 4.24. The total area percentage of the chromophores added up to 19.4%. The major chromophores were 2,3-

butanedione (1.3%), 2(5H)-furanone (1.9%), 1,2-cyclopentanedione (5.7%), and 2-cyclopenten-1-one, 2-hydroxy-3-methyl- (1.5%) as shown in Table 4.24.

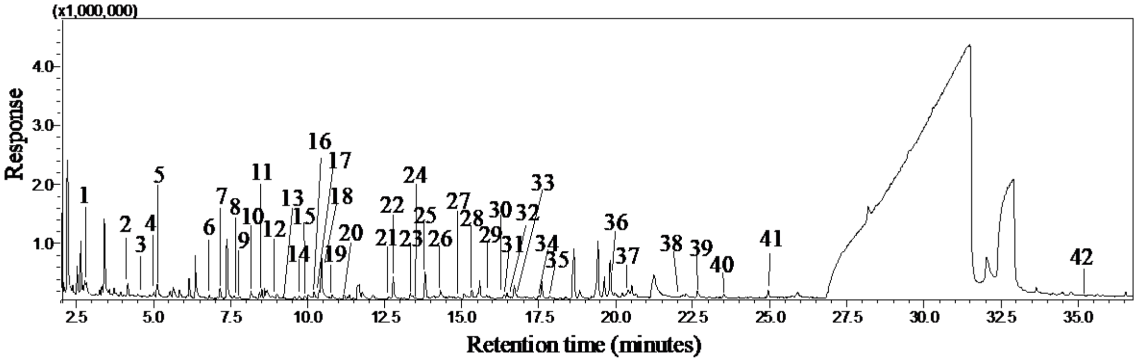


Figure 4.32: Pyrogram of pulp sample P1.

Table 4.24: Peak identification for pulp sample P1.

Peak number	**Retention time (min)**	**Area%**	**Compound**
1	2.71	1.3	2,3-Butanedione
2	3.99	0.1	2,3-Pentanedione
3	4.48	0.1	1-Penten-3-one, 2-methyl-
4	4.93	0.1	3-Penten-2-one, (E)-
5	5.18	1.0	1-Penten-3-one
6	6.86	0.1	Furfural
7	7.11	0.2	3-Furanmethanol
8	7.53	0.1	Vinyl crotonate
9	7.65	0.1	2-Cyclopentene-1,4-dione
10	8.27	0.8	2-Furanmethanol
11	8.56	0.2	2(3H)-Furanone, 5-methyl-
12	8.88	0.1	2-Cyclopentene-1,4-dione
13	9.05	0.1	2-Cyclopentene-1,4-dione
14	9.72	0.2	Vinyl crotonate
15	9.77	0.2	2-Cyclopenten-1-one, 2-methyl-
16	10.03	1.9	2(5H)-Furanone
17	10.15	0.1	2-Cyclohexen-1-one, 2-methyl-
18	10.57	5.7	1,2-Cyclopentanedione
19	10.84	0.1	2(5H)-Furanone, 5-methyl-
20	11.51	0.1	2-Benzoyl-3-isobutylidene-hexahydro-pyrrolo[1,2-a]pyrazin-1,4-dione
21	12.55	0.1	Phenol
22	13.42	0.4	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-
23	13.55	0.1	2,5-Furandione, dihydro-3-methyl-
24	13.78	0.1	2-Cyclohexene-1,4-dione
25	13.92	1.5	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-

26	14.14	0.1	2-Cyclopenten-1-one, 2,3-dimethyl-
27	14.25	0.2	4-Methyl-5H-furan-2-one
28	15.53	0.4	3-Furancarboxylic acid, methyl ester
29	16.02	0.2	Benzenamine, 3-methoxy-4-[3-(1-piperidinyl)propoxy]-
30	16.17	0.1	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-
31	16.56	0.2	Maltol
32	16.90	0.1	2(3H)-Furanone, 5-acetyldihydro-
33	16.98	0.1	1H-Imidazole, 2-ethyl-
34	17.37	0.3	2-Cyclohexen-1-one, 3,4-dimethyl-
35	18.07	0.2	2,3-Dihydroxybenzaldehyde
36	20.08	0.9	2-Furancarboxaldehyde, 5-(hydroxymethyl)-
37	21.38	0.1	1H-Inden-1-one, 2,3-dihydro-
38	22.40	0.2	Benzaldehyde, 3-hydroxy-
39	23.18	0.1	1,3-Bis(trimethylsiloxy)benzene
40	24.70	0.1	4-Hydroxy-2-methylbenzaldehyde
41	25.08	0.6	Phenol, 4,4'-methylenebis[2,6-dimethyl-
42	35.80	0.7	1,2-Benzenedicarboxylic acid, diisooctyl ester
Total chromophore Area %		**19.4**	

The brightness and yellowness of fully bleached DWP and with corresponding MCC samples were analysed and compared to determine if there was any relationship between chromophores and brightness of these samples. The brightness of the pulp samples was higher than the brightness of the MCC produced from each pulp sample. For example, the brightness of pulp sample P1 pulp was 6% greater than the brightness of P1(MCC), as shown in Figure 4.33. The average reduction in brightness when the pulps were converted to MCC was about 8%. Pulp sample P1 showed the highest brightness (93.2%) and the lowest yellowness (3.7%), Figure 4.33.

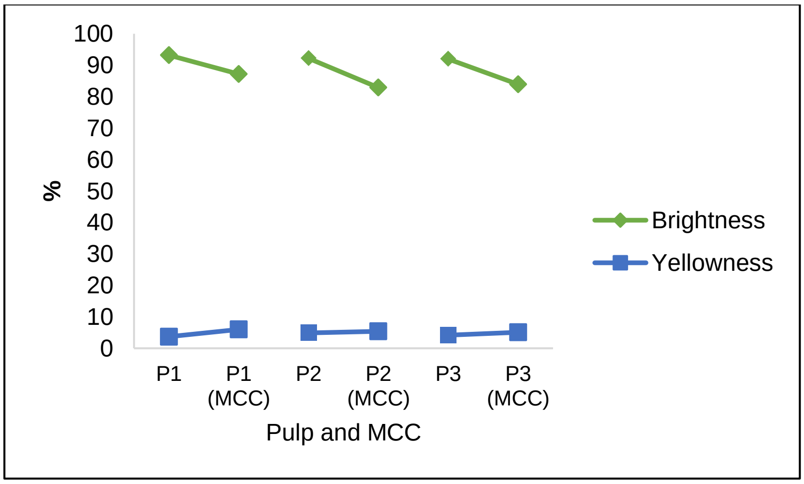


Figure 4.33: Brightness of the pulp vs. MCC.

The pyrogram of P1(MCC) is shown in Figure 4.34, with the labelled peaks indicating the chromophores. The retention times, area percentage and the names of the chromophores identified are listed in Table 4.25.

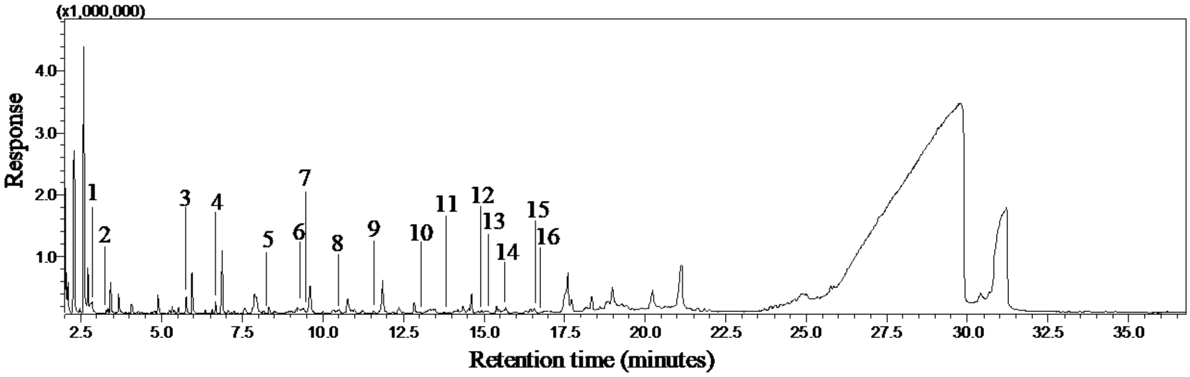


Figure 4.34: Pyrogram of P1(MCC).

Table 4.25: Peak identification for P1(MCC).

Peak number	**Retention time (min)**	**Area %**	**Compound**
1	2.71	0.3	Methyl vinyl ketone
2	2.84	0.1	Furan, 2-methyl-
3	6.87	0.4	Furfural
4	7.89	0.2	2(3H)-Furanone, 5-methyl-
5	8.33	0.1	4-Cyclopentene-1,3-dione
6	9.17	0.1	Ethanone, 1-(2-furanyl)-
7	9.23	0.1	2(5H)-Furanone
8	10.31	0.1	3(2H)-Pyridazinone
9	12.37	0.1	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-
10	12.84	0.1	1,2-Cyclopentanedione, 3-methyl-
11	13.28	0.1	4-Methyl-5H-furan-2-one
12	14.53	0.1	Methyl 2-furoate
13	14.61	0.1	2,5-Dimethyl-4-hydroxy-3(2H)-furanone
14	15.39	0.1	2-Furanmethanol
15	15.68	0.1	2,4(3H,5H)-Furandione, 3-methyl-
16	16.56	0.1	2(3H)-Furanone, dihydro-4-methyl-
Total chromophore area %		**1.8**	

In sample P1(MCC), a total of 38 chromophores were identified (Table 4.25 only shows the major chromophores). However, the total area percentage of the identified chromophores added up to 1.8% that is much lower than the total area percentage of the chromophores identified in the original pulp sample P1. This proves the fact that the number of chromophores is not representative of their amount nor the brightness levels of the cellulosic material (Rosenau *et al.*, 2007).

Pulp samples P2 and P3 had similar brightness levels of 92.2% and 92.0%, respectively, with a yellowness of 4.9% for P2 and 4.2% for P3 (Figure 4.33). The brightness decreased, and the yellowness was observed to increase after the pulps were converted to MCC. The average increase of the yellowness as a result of pulp derivatisation to MCC was 1.2%. The decrease in brightness levels and the increase in yellowness observed when the pulp was converted to MCC can be attributed to the degradative reactions that occur during cellulose hydrolysis.

The results showed that the pulp samples contain a higher amount of the chromophores compared to the corresponding MCC samples (Figure 4.35). The average difference in the chromophore amount between the pulp and the corresponding MCC samples was 12.4%. The main chromophore groups identified in the pulp samples were the furan-type compounds followed by ketones. Pulp sample P1 had the highest amount of chromophores, and sample P3 had the lowest amount of chromophores. The difference in the chromophore amount in these pulp samples can be attributed to the slight variations in the mill unit operations. The concentration of the arenes in P1 was 2.3% and was significantly higher than 0.6 and 0.7%, detected in P2 and P3 samples respectively.

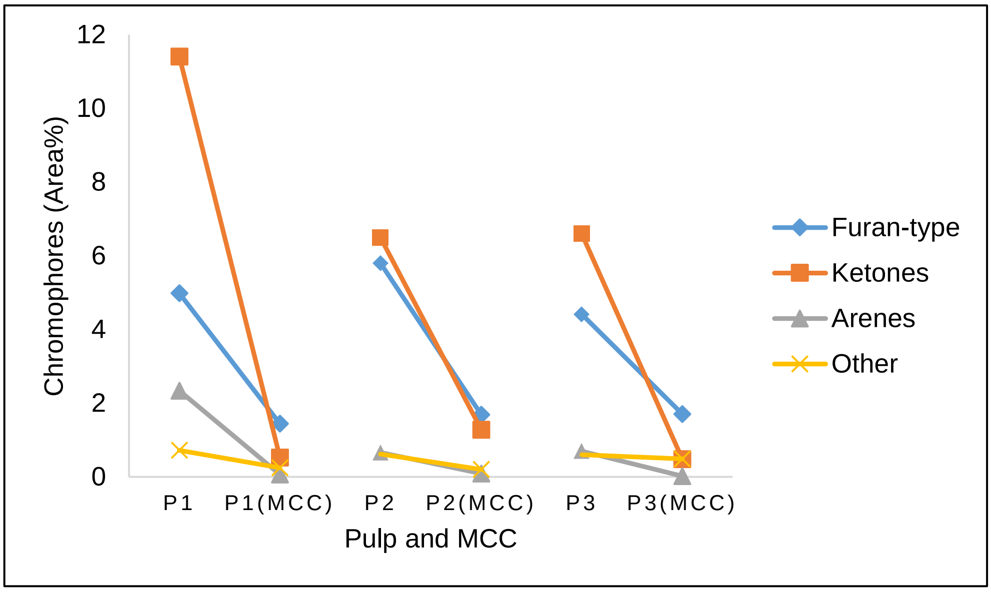


Figure 4.35: Comparison of chromophores identified in DWP and MCC.

P2 (MCC) showed the highest total chromophore content followed by P3 (MCC) and then P1 (MCC) (Figure 4.35). The total chromophore content in P2 (MCC) was 3.2% with the furan-type compounds contributing 1.7% and the ketones contributing 1.3% to the total chromophore content. This shows that the chromophore content of the MCC is independent of the chromophore content of the pulp sample from which the MCC was produced. If the total chromophore content was dependent on the amount of chromophores in the pulp sample, P1 (MCC) would have had the highest chromophore content, and P3 (MCC) would contain the lowest chromophore content.

It was expected that the MCC samples would exhibit a higher brightness than the original pulp samples because it is considered as a high purity material that is used to produce high-grade products. However, the brightness of the MCC was lower than the brightness of the pulp. These results further confirm that there is no relationship between the brightness and the total chromophore content. Figure 4.32 and Figure 4.33 show that sample P1 had a very high brightness and a high chromophore content. However, the corresponding MCC, P1(MCC) had the highest brightness (93.2%) and the lowest chromophore content.

The MCC is produced from DWP under harsh acidic conditions and elevated temperatures, furthermore, the amount of chromophores in the MCC has been observed to be about 3% on average, compared to the average of 15% found in DWP. This can be attributed to the degradation of hydroxymethylfurfural (HMF) to the non-chromophoric levulinic acid (**38**) and formic acid (**39**) under acidic conditions (Figure 4.36), HMF (**7**) is one of the pre-cursors for chromophore formation in cellulosic materials (Shen and Gu, 2009).

As explained in Chapter 2, the main component of DWP is cellulose, described as a polymer consisting repeating glucose monomers that are connected through 1,4-β-glucosidic covalent bonds (Ben, 2014). When cellulose is converted to MCC under harsh acidic conditions using H_2SO_4 (Eartrakulpaiboon and Tonanon, 2015) and elevated temperatures, reactions of glucose such as reversion, condensation, isomerization and dehydration reactions take place (Van Dam *et al.*, 1986). However, the main reaction that occurs is the dehydration reaction.

During the dehydration reaction, the 1,4-β-glucosidic bonds in the cellulose (**36**) are cleaved to release glucose monomers (**37**), Figure 4.36 (Kupiainen *et al.*, 2012). Under acidic conditions, the glucose decomposes to form **7** that further reacts with the acid to form levulinic acid (**38**) and formic acid (**39**) (Kupiainen, 2012, Van Dam *et al.*, 1986). The conversion of HMF to these acids (does not occur in pulp) eliminates the formation of many chromophoric structures such as furfuraldehyde, cyclopentadiene and 5-methyl-furfural, hence, the MCC ends up having a lower amount of chromophores than the original pulp sample.

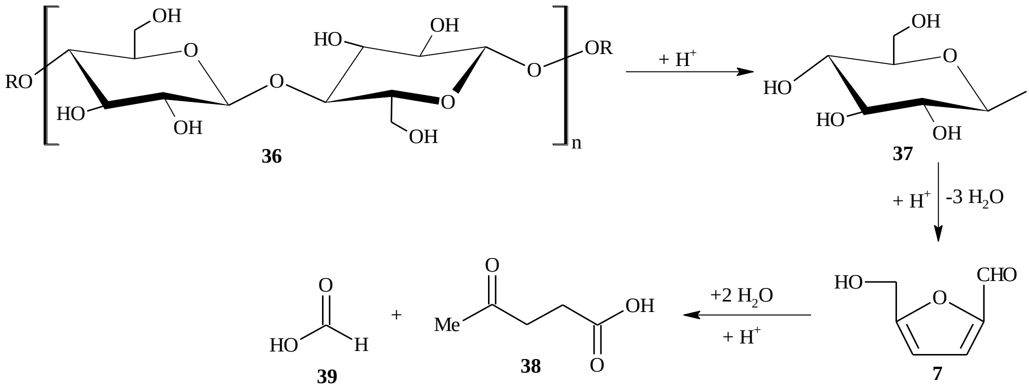


Figure 4.36: Acid-catalyzed hydrolysis of cellulose (Kupiainen, 2012).

The observation that brightness of the MCC was significantly lower than the brightness of the pulps from which it was produced does not imply that the MCC has higher chromophore content than the pulp as shown by the experimental results. This indicates that the amount of chromophores in the pulp or MCC was not related to the levels of brightness or yellowness of the material. Part of the cellulose was degraded during derivatization, however, a minimum amount of chromophores were formed, this indicates that the degraded cellulose only contributes a small percentage of the chromophores in the pulp.

4.3.2 Analysis of in-process industrial pulps

To understand the changes in brightness and the chromophore content (as determined by the Py-GC/MS) of the fully bleached industrial pulps, wet chemical properties of in-process industrial pulp (acid bisulphite and PHK pulp) from different stages of bleaching were determined.

4.3.2.1 Analysis of in-process acid bisulphite pulps

In-process pulp samples were collected from the acid bisulphite pulp mill at each stage of the unit operation to understand the effect of bleaching unit operations on chromophore formation. Table 4.26 presents the wet chemical properties of the industry produced in-process acid bi-sulphite pulp processed using 92α bleaching conditions. Table 4.26 shows the changes in the total lignin content and the changes in the S10, S18, S10-S18 were further summarised in Figure 4.37.

Terminology

S10 (%): Degraded cellulose and hemicellulose (total extractable material)
S18 (%): Hemicellulose
S10-S18 (%): Degraded cellulose

It is evident that there was a significant reduction in the total lignin content from the raw stage (8.2%) to the O_2 stage (3.0%), Table 4.26. Afterwards, the total lignin content decreased slowly and finally reached 1.2% in the hypo stage. The difference in the total lignin content between the raw stage and the hypo stage was 6.9%, and this shows that it is only a fraction of lignin that remains after bleaching that can be a potential source of chromophores in the final pulp.

Table 4.26: Wet chemical properties of the in-process acid bisulphite pulp.

	Unbleached	**Bleaching Stages**				
Acid bi-sulphite pulp	**Raw**	**O_2**	**D_1**	**E**	**D_2**	**Hypo**
Lignin (%)	8.2	3.0	1.8	1.5	1.3	1.2
S10 (%)	7.9	7.4	7.8	7.2	6.8	7.5
S18 (%)	6.2	6.2	6.4	5.9	4.7	4.7
S10-S18 (%)	1.7	1.3	1.4	1.2	2.1	2.8

The effect of bleaching on the S10 (%), the S18 (%) and the S10-S18 (%), through the bleaching process, was summarised in Figure 4.37. The S10 (%) and the S18 (%) decreased by 0.5% and 0.3%, respectively, from the raw pulp to the O_2 bleaching stage. This shows that the increase of the chromophore content (Figure 4.38) from the raw pulp to the O_2 stage was not because of the total extractable material.

However, the oxygen that was used at this stage is a strong oxidising agent, hence, the increase in the chromophore content at this stage (Figure 4.38) can be attributed to the oxidising ability of the oxygen, i.e., the oxidation of the carbohydrate structures resulted in the formation of chromophores. The oxygen allows for the use of low temperatures and, therefore, thermal degradation reactions are unlikely to occur at this bleaching stage (Suchy and Argyropoulos, 2002). The effect of oxygen delignification was also shown by the significant reduction of lignin from the raw stage to the O_2 stage, as shown in Table 4.26. The lignin further decreased throughout the stages of bleaching, hence, the increase in chromophore content at in the O_2 stage cannot be fully associated with lignin (Figure 4.38). The S18 (%) increased from 6.2% (raw stage) to 6.4% in the D_1 stage (Figure 4.37). As a result, the total chromophore content was observed to increase (Figure 4.38).

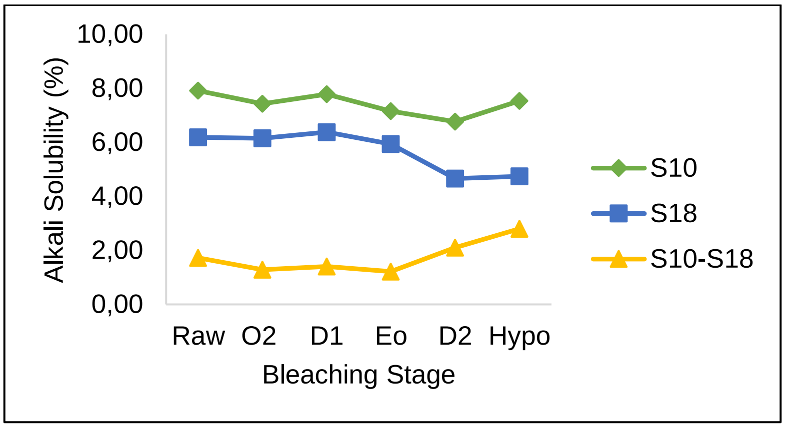


Figure 4.37: Alkali solubility of industrial acid bi-sulphite pulp.

The second bleaching stage (D_2) involved the use of chlorine dioxide that is a strong oxidising agent. A significant increase in the amount of the furan-type compounds and ketones was noted in the D_2 bleaching stage. Figure 4.38 shows that the total chromophore content increased from 8.7% (O_2 bleaching stage) to 15.4% in the D_1 bleaching stage, with the furan-type compounds at 9.1% and the ketones at 5.2%. The formation of oxygen-rich compounds along with furan-type compounds and conjugated ketones can be associated with chlorine bleaches and oxidation of hemicelluloses and cellulose fibres. Furthermore, chlorinated bleaches are associated with the formation of yellow chlorinated pulp fibres (Burgess, 1982).

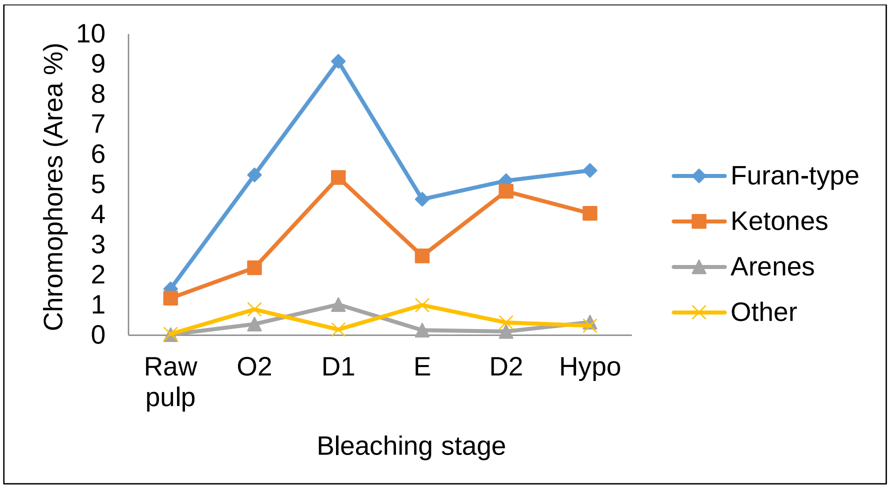


Figure 4.38: Chromophores identified at different stages of bleaching the acid bi-sulphite pulp.

Figure 4.37 shows a decrease in the S10 (%) by 0.4% from the D_1 stage to the E Stage, and this corresponds to the reduction in the total chromophore content by 7.1% (Figure 4.38). A significant reduction of furan-type compounds from 9.1% in the D_1 stage to 4.5% in the E stage followed by a decline of ketones from 5.24% in the D_1 stage to 2.6% in the E stage was observed. This reduction was a result of the removal of oxidised structures and degraded carbohydrates in the E stage. This result demonstrates the effectiveness of pulp washing using sodium hydroxide.

The second chlorine dioxide treatment (D_2 stage) opposed the effect of the E stage, the total concentration of chromophores increased by 2.2% from the E stage to the D_2 stage (Figure 4.38) due to the strong oxidising ability of the chlorine dioxide. At this stage, there was a slight increase in the amount of S10-S18 (%), Figure 4.37. This shows that the chlorine dioxide induced depolymerization in the cellulose. As a result, the degraded cellulose, probably increased the concentration of chromophores.

A further increase of the furan-type compounds upon treatment with the sodium hypochlorite (Hypo stage) was noted, the concentration of ketones decreased, thus making the total chromophore area percentage to be slightly lower in the Hypo stage (10.3%) compared to the D_2 stage (10.5%). The sodium hypochlorite causes chain scission of the polymers and the formation of short chains compounds. Due to the strong oxidising ability of hypochlorites under acidic or basic conditions (Chirat and De La Chapelle, 1999), most compounds were oxidised to corresponding chromophores as a result, there was no significant decrease in the total chromophore content in the Hypo stage. The effect of the hypochlorite bleach also had a pronounced effect on the increase of the S10 (%) by 0.8% that resulted in a slight increase of chromophores.

Figure 4.39 shows a decrease in the peak area of levoglucosan from the raw stage (80.7%) to the hypo stage (24.6%). This decrease is indicative of the reduction of degraded cellulose during the bleaching process. This shows that towards the final stages of bleaching, there is a low percentage of degraded cellulose that could be responsible for chromophore formation, hence, the increase in the chromophore content towards the hypo stage observed in figure 4.38 cannot be solely attributed to the degraded cellulose.

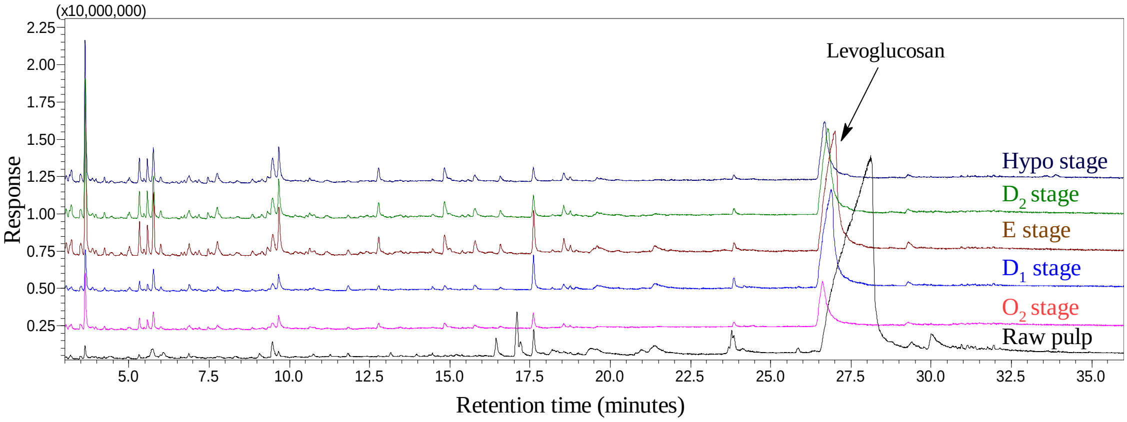


Figure 4.39: Pyrograms of the acid bisulphite pulp.

The wet chemical properties and the total lignin content of the industrial in-process PHK pulps are listed in Table 4.27, the alkali solubility data was summarised in Figure 4.40. Similar to the in-process acid bisulphite pulp, the lignin decreased significantly from the raw pulp to the Ex O$_2$ bleaching stage. The percentage of the total lignin further decreased by 0.4% from the Ex Do stage to the final pulp (Table 4.27).

4.3.2.2 Analysis of in-process PHK pulps

Table 4.27: Wet chemical properties of the in-process PHK pulp.

	Unbleached	**Bleaching Stages**					
PHK pulp	**Raw**	**Ex O$_2$**	**Ex Do**	**Ex Z**	**Ex Eop**	**Ex D$_1$**	**Final**
Lignin (%)	8.3	2.7	1.6	1.3	1.3	1.2	1.2
S10 (%)	9.0	8.1	7.0	9.1	9.2	10.8	9.6
S18 (%)	6.9	5.2	6.1	8.8	8.5	5.4	7.4
S10-S18 (%)	2.1	2.9	0.92	0.3	0.6	5.4	2.2

Figure 4.40 shows that the S10 (%) and S18 (%) decreased from the raw stage to the Ex O$_2$ stage while the S10-S18 (%) increased. In effect, the total chromophore content (Figure 4.41) increased as the ketones sharply increased by 3.5% from the raw pulp to the Ex O$_2$ stage while the furan-type compounds, arenes and other low molecular weight chromophores decreased. The increase of the total chromophore content towards the O2 stage was attributed to the increase of the degraded cellulose. The total chromophore content decreased towards the final stage of bleaching,

responding to the decrease of the S10 (%) and the S10-S18 (%), meaning that both the hemicellulose and degraded cellulose were involved in chromophore formation.

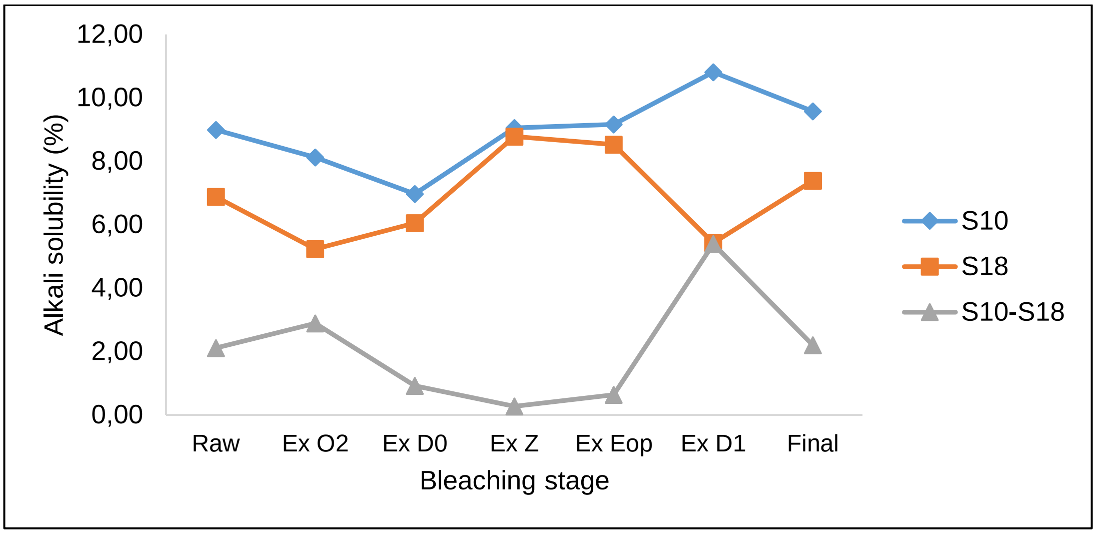


Figure 4.40: Alkali solubility of industrial PHK pulp.

In this case, it shows that both the S10-S18 (%) and the S18 (%) are responsible for generating the furan-type compounds and the ketones during pyrolysis of the pulp. However, the S18 (%) seem to have a major effect on the formation of these chromophores. In the final stages of bleaching, there is less degraded cellulose, and there are some bleach resistant hemicelluloses that may have survived the bleaching process and gave rise to the chromophores.

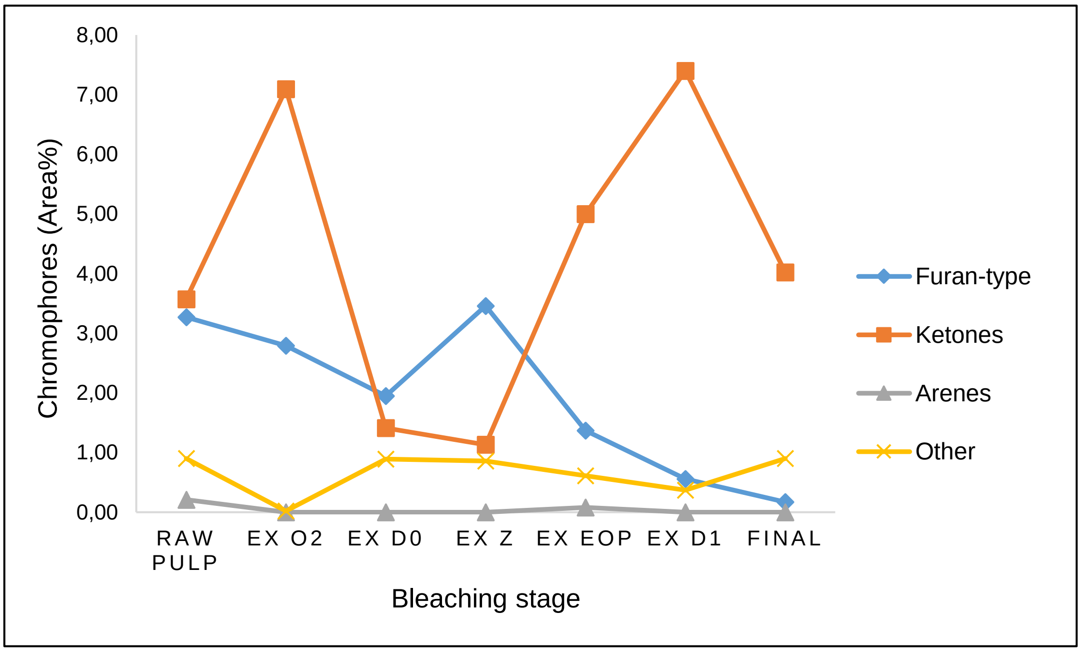


Figure 4.41: Chromophores identified at various stages of bleaching the PHK pulp.

The analysis of fully bleached DWP showed that the brightness and yellowness levels of the acid bisulphite and PHK pulps were similar. Py-GC/MS analysis also showed that the type of chromophores identified in the acid bisulphite and PHK pulps were the same type of compounds. The comparison of the brightness/yellowness, when the samples were induced for brightness reversion, and Py-GC/MS results showed that there was a decrease in brightness (increase in yellowness) with the increase in the chromophore content in each of the DWP samples analysed. However, the inter-sample comparison did not show any relationship between the brightness and the chromophore content. This was verified through the analysis of the MCC with the corresponding pulps which had a lower brightness and very low chromophore content than the original pulp samples. These findings were also useful because they showed that pulp derivatisation reduces the chromophores that are present in the fully bleached pulp. Further analysis through wet chemistry analysis of the in-process industrial pulps revealed that the degraded cellulose and the hemicellulose were responsible for the chromophore formation in the industrial pulps.

4.3.3 Analysis of laboratory produced in-process pulps

Single clone laboratory produced pulps, collected from each of the acid bisulphite bleaching stages were analysed for wet chemical properties to understand the relationship between the components of the pulp and the chromophores identified by Py-GC/MS. The O_2 delignified acid bisulphite pulps were bleached using the 92α bleaching conditions. The raw pulp was bleached using the bleaching chemicals in the following order: chlorine dioxide (D_1)-sodium chloride (E)- chlorine dioxide (D_2)-hypochlorite (H).

Figure 4.42 shows the changes in the total lignin content in raw pulp and through four stages of bleaching of the *E. Dunnii*, *E. Grandis* and *E. Smithii* species. A sharp decrease of the total lignin content was observed as the raw pulp was bleached with the oxygen (O_2 stage) during oxygen delignification. This shows the effectiveness of oxygen delignification in removing the lignin that remained after the acid bisulphite pulping. The lignin percentage decreased continuously through the bleaching process, but a minimal decrease was observed from the E stage to the hypo stage, thus indicating that the remaining lignin was recalcitrant to the bleaching chemicals. The residual lignin from the O_2 stage to the fully bleached pulp in the hypo stage resulted in a low percentage of arenes, observed during the analysis of the fully bleached pulps and the in-process pulps.

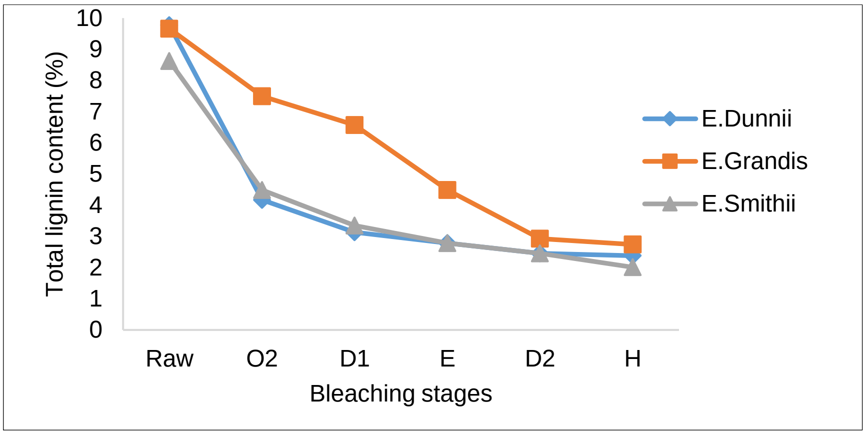


Figure 4.42: Comparison of total lignin content in *E. Dunnii*, *E. Grandi* and *E. Smithii*.

Figure 4.43 shows a decrease in the S10 (%) and the S18 (%) from the raw pulp to the D_1 bleaching stage while the S10-S18 (%) increased. The S10 (%) decreased from 10.7% in the raw stage to 9.6% in the O_2 stage but decreased by 0.9% to the D_1 stage. The S18 (%) also showed a decrease by 1.3% from the raw stage to the D_1 stage. Towards the hypo stage, the S10(%), S18 (%) and S10-S18 (%) showed a slight increase, indicating that the bleaching conditions favoured the formation of hemicellulose type compounds and also encouraged cellulose degradation.

4.3.3.1 Analysis of *E. Dunnii* in-process pulps

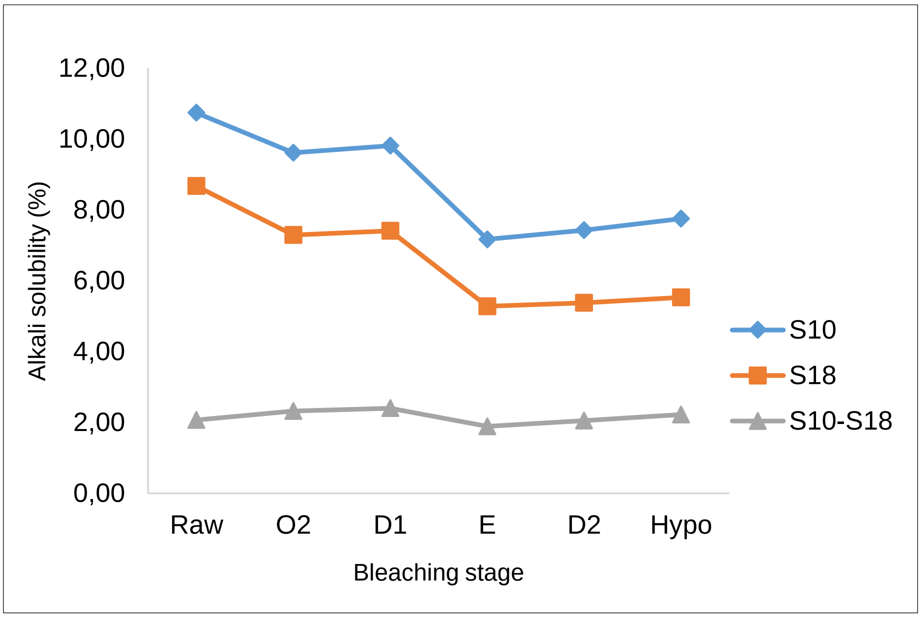


Figure 4.43: Comparison of the S10 (%), S18 (%) and the S10-S18 (%) of the *E. Dunnii*.

In the *E. dunnii* in-process pulps, the furan-type compounds were found at the highest concentration followed by the ketones. The arenes and the other low molecular weight chromophores were observed at the lowest concentration throughout the stages of bleaching (Figure 4.44). The increase of the furan-type compounds and ketones from the raw stage to the D_1

stage was attributed to the slight increase of the S10-S18 (%). A similar increase of the S10-S18 (%) was observed towards the D_2 stage, as a result, the total chromophore content also showed an increase (Figure 4.44). This was evidenced by the increase of the furan-type compounds, ketones and other low molecular weight chromophores. The pyrograms of the E.Dunnii pulps through the bleaching stages are shown in Figure 4.45.

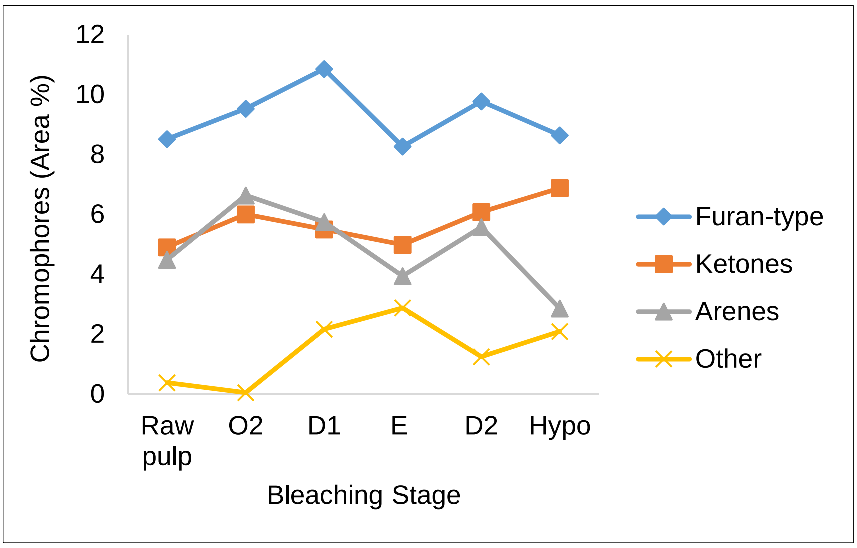


Figure 4.44: Chromophores identified in the *E. Dunnii* in-process pulp.

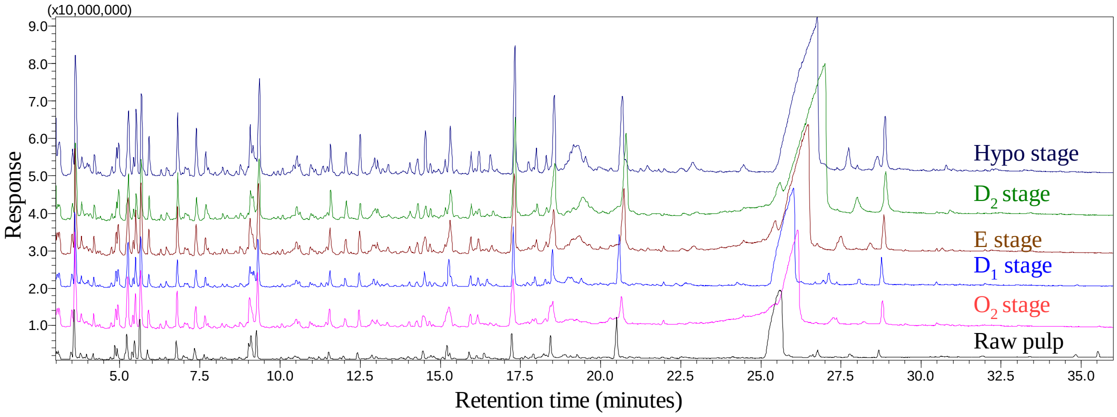


Figure 4.45: Pyrograms of *E.Dunnii* in-process pulps.

It is evident that the hemicellulose and degraded cellulose contribute to the formation of chromophores in the pulp. Therefore, it is important to understand the behaviour of these substances during pyrolysis. The following paragraphs explain the thermal degradation pathway of hemicellulose and cellulose during pyrolysis.

Hemicelluloses constitute about 6.5% of fully bleached pulps, and cellulose (**36**) is the main component of DWP (over 90%) (Beyer *et al.*, 2006). Xylan (**40**) is the most abundant hemicellulose and is, therefore, typically used as a model compound to study the reactions of hemicelluloses (Figure 4.46). During thermal degradation of **40**, (2*E*)-3-(4-hydroxy-3-methoxyphenyl) prop-2-enoic acid (**41**) and hydroxymethylfurfural (**7**) are formed as primary degradation products. The chemical structure of **41** resembles the structure of coniferyl alcohol, a degradation product of lignin. Further degradation of **41** results in fragments that are similar to the degradation products of coniferyl alcohol. This moiety brings a challenge when trying to differentiate between xylan and some of the lignin degradation products because it resembles the structure of the guaiacol moiety of lignin.

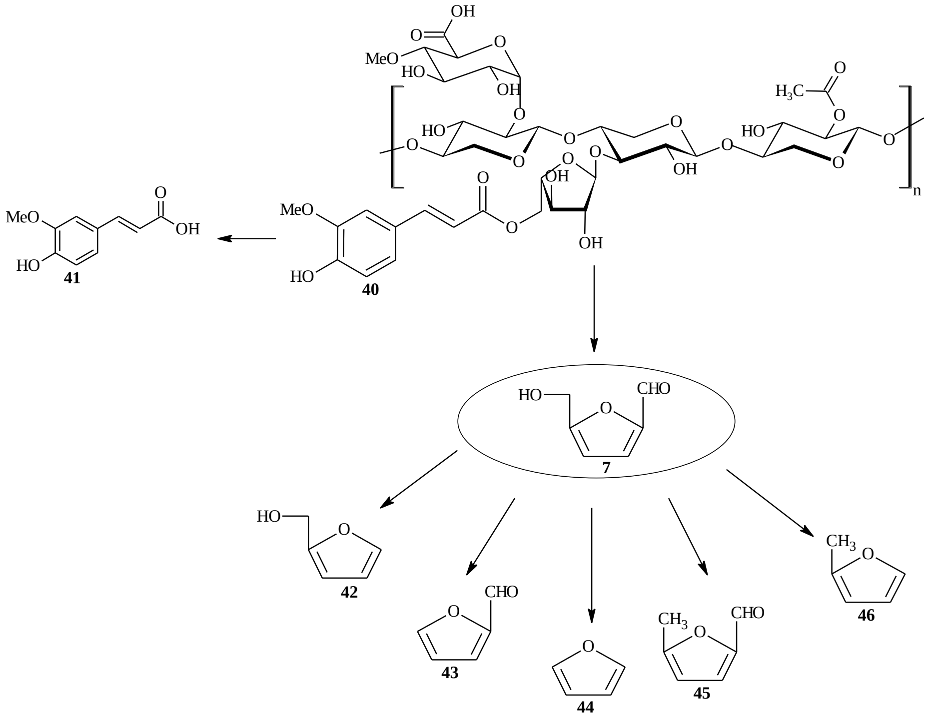


Figure 4.46: Degradation pathway of xylan (**40**).

Depolymerization of cellulose results in the formation of levoglucosan (**48**) which is considered as the main degradation product of cellulose (Qiang *et al.*, 2009). (4*Z*)-2,3,5,6-tetrahydroxyhex-4-enal (**49**) is also formed during cellulose depolymerization followed by the ring opening reactions (Figure 4.47). Condensation of **49** results in the formation of (2*Z*,4*Z*)-2,5,6-trihydroxyhexa-2,4-dienal (**50**) which further forms **7** through dehydration and cyclisation reactions. During thermal degradation of cellulose, **48** and **50** are the main producers of **7** that result in the formation of furans and other low molecular weight chromophores (**42-46**).

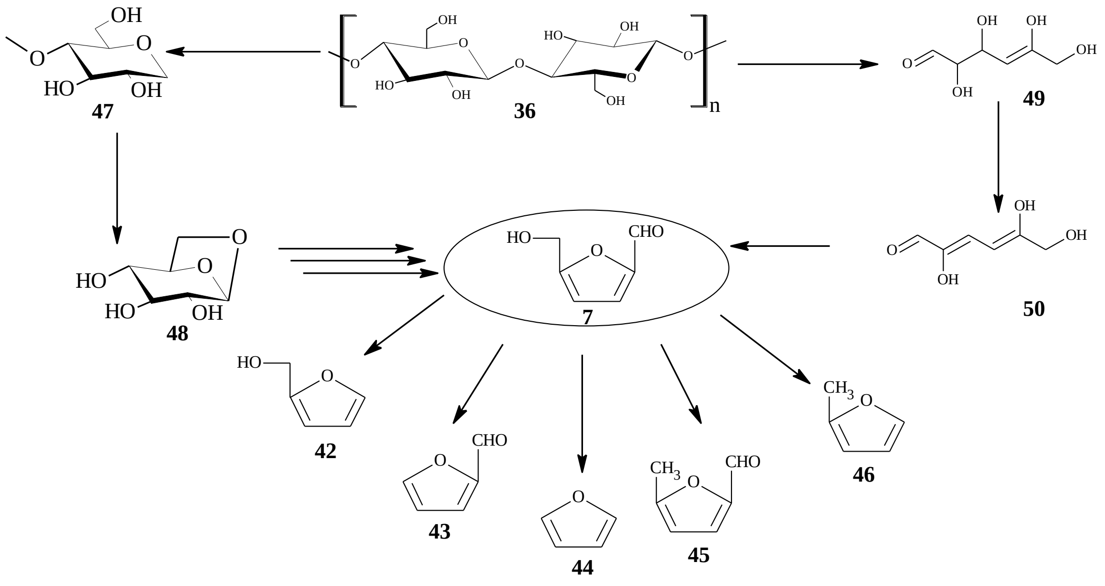


Figure 4.47: Degradation pathway of cellulose (**36**).

Secondary reactions, such as ring opening and cyclisation reactions of the pyran ring of **40** are the main producers of chromophores. During pyrolysis of **40** and **36**, the secondary reactions result in the formation of 5-hydroxymethyl furaldehyde (**7**), which is further degraded to light furan-type compounds (**42-46**) (Shen and Gu, 2009, Shen *et al.*, 2013). The carbohydrate chains of **40** and **36** are very similar, hence, they produce similar thermal degradation products during pyrolysis (Qiang *et al.*, 2009) and this makes it difficult to differentiate between degradation products of **40** and **36**. Furthermore, furan-type compounds are known to be the main contributors to the yellowness of chemical pulps (Loureiro *et al.*, 2010).

4.3.3.2 Analysis of *E. Grandis* in-process pulps

Figure 4.48 shows that the raw pulp contained a high S10% and S18%, 10.7%, and 8.7% respectively. Towards the O_2 stage, the S10 (%) decreased by 1.1%. The Py-GC/MS results (Figure 4.49) indicated that there was a high percentage of the total chromophore content (25.3%) in the raw pulp that decreased to 22.2% after the O_2 bleaching stage. The main contributing compound group to the high chromophore content observed at this stage were the other low molecular weight chromophores (Figure 4.49).

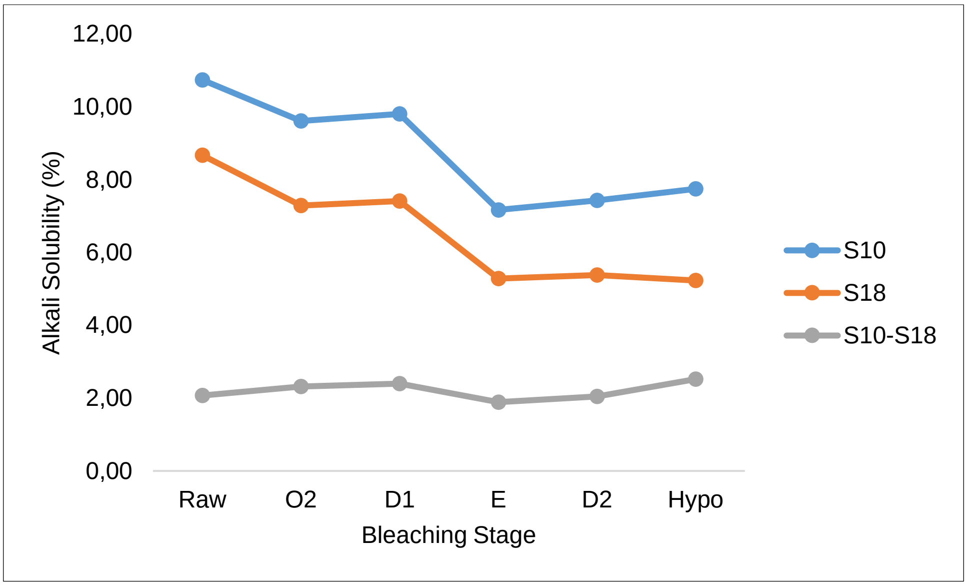


Figure 4.48: Comparison of the S10 (%), S18 (%) and S10-S18 (%) of the *E. Grandis*.

During the O_2 stage, the furans, arenes and other low molecular weight chromophores decreased while the ketones increased by 2.6% (Figure 4.49). The increase of the ketones was atributed to the slight increase (0.3%) of the S10-S18 as shown in figure 4.48. Bleaching with the chlorine dioxide at the D_1 stage resulted to an increase of S10%, S18%, and S10-S18%; and thus, the total chromophore content increased by 2.1% (Figure 4.48). The S10 (%) decreased after the alkaline extraction in the E stage, and the chromophore content declined by 4.2%. From the E stage to the Hypo stage, the total chromophore content increased by 2.4% following the increase of the S10 by 0.58%. Pyograms of the E-grandis pulps through the stages of bleaching are shown in Figure 4.50.

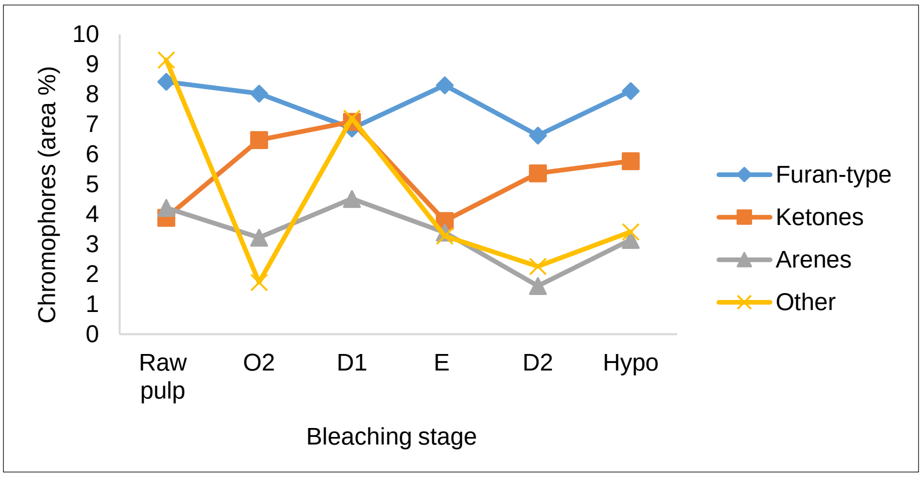


Figure 4.49: Chromophores identified during Py-GC/MS analysis of *E. Grandis*.

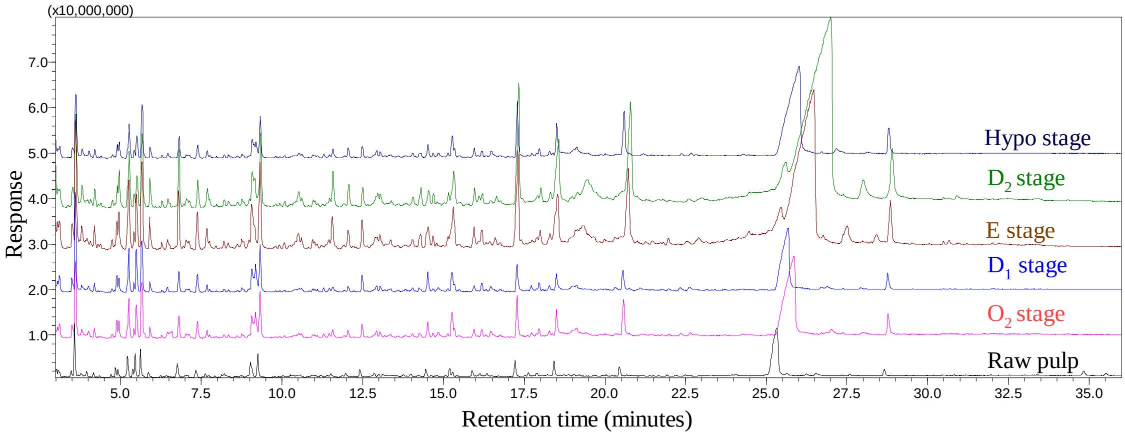


Figure 4.50: Pyrograms of *E.Grandis* in-process pulps.

4.3.3.4 Analysis of *E. Smithii* in-process pulps

In the analysis of *E. Smithii*, the S10 decreased from the raw stage to the O_2 stage (Figure 4.51). The pyrograms of the *E.Smithii* pulps through the bleaching stages are shown in Figure 4.52. Py-GC/MS results in Figure 4.53 shows that the arenes decreased by 1.8%, showing that at this stage, a significant amount of lignin was removed, causing a reduction in the aromatic chromophores. However, the total chromophore content increased by 2.9% due to the increase of the furans, ketones and other low molecular weight chromophores. This increase can be attributed to the oxidation reactions induced by the oxygen used in the O_2 bleaching stage. In comparison to the *E. Grandis*, these two species reacted differently towards the O_2 bleaching.

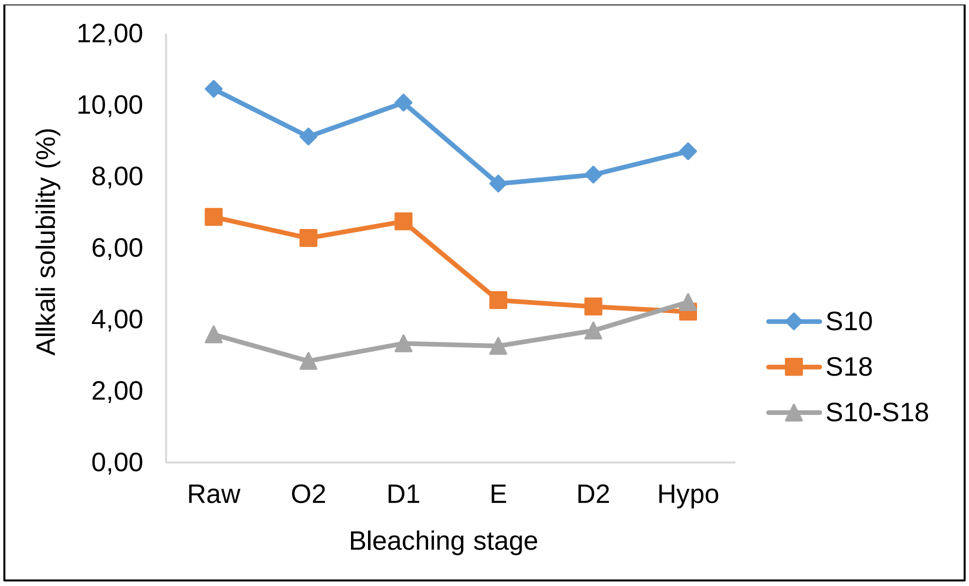


Figure 4.51: Solubility analysis of *E. Smithii*

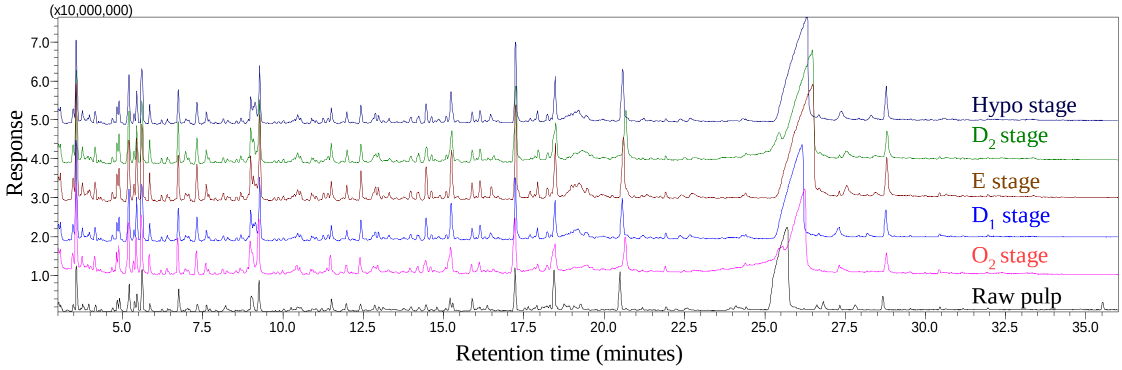


Figure 4.52: Pyrograms of the *E.Smithii* in-process pulps.

Chlorine dioxide bleaching (D_1) resulted in an increase of the S10 (%). In effect, a further increase of the total chromophore content was observed. However, the alkaline extraction (E stage) reduced the S10 (%) by 2.3% hence resulted in the overall decrease of the total chromophore content by 7.9% (Figure 4.53).

The second chlorine dioxide bleaching stage (D_2) resulted in an increase in the S10 (%), and as a result, the chromophores increased by 0.9%. In the hypo stage, there was a slight increase of the S10 (%) and the degraded cellulose while the S18 (%) showed a slight decrease. At this stage, the total chromophore content increased due to the increase in the percentage of the furan-type compounds, indicating that the slight increase of the degraded cellulose resulted in a pronounced effect on the chromophore formation.

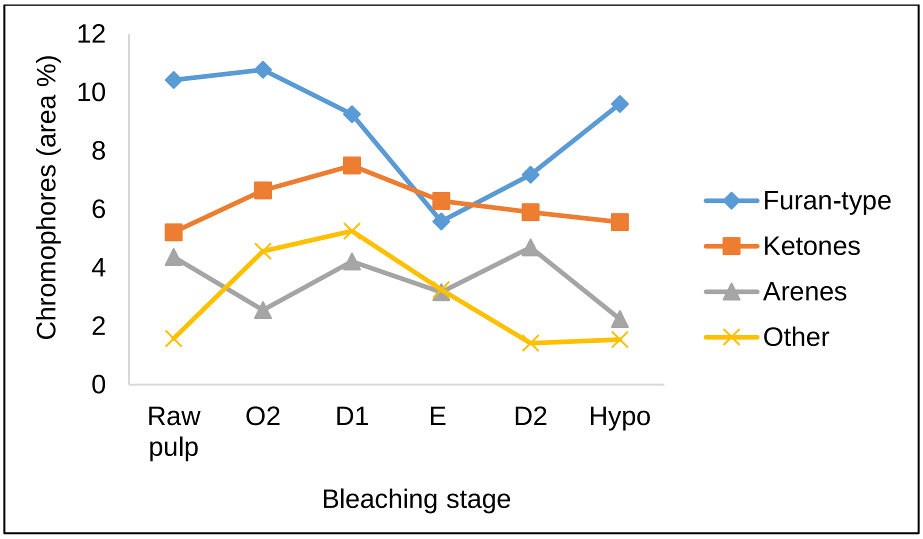


Figure 4.53: Py-GC/MS analysis of *E.Smithii*.

The analysis of single clones of *E.Dunnii*, *E.Smithii*, and *E.Grandis* have shown that different species react differently to pulping and bleaching conditions. Even though the bleaching conditions were controlled, different results were obtained for each of the species analysed. The wet chemical properties differ for all species and the chromophore content determined at each bleaching stage differs from species to species. However, the E stage has shown to reduce the chromophores present in the pulp. It can, therefore, be deduced that the amount of chromophores differs with wood species. This means that, in addition to the cooking and bleaching conditions, the chromophores identified in industrial pulps originate from the mixture of wood species used.

4.3.4 Py-GC/MS analysis of newsprint and kraft pulp

Additional samples were analysed to further investigate the effect of lignin and heat induced brightness reversion. Unprinted newsprint and fully bleached kraft pulp samples were analysed for chromophore content using Py-GC/MS before and after brightness reversion. The results obtained were summarized below.

A lignin-rich material, blank (unprinted) newsprints were analysed for chromophore content using Py-GC/MS. The newsprints were heated at 105 °C overnight to induce brightness reversion in order to investigate the changes of the chromophore content in the newsprints before and after brightness reversion. The identified chromophores were grouped into furan-type compounds, ketones, arenes and other low molecular weight chromophores. Figure 4.54 shows that the arenes were the most abundant compounds in all the three samples of newsprints both before and after heating, contributing about 30-40% to the total chromophore content per sample. Similar to fully bleached pulps, the amount of all chromophore groups in the newsprints increased after brightness reversion.

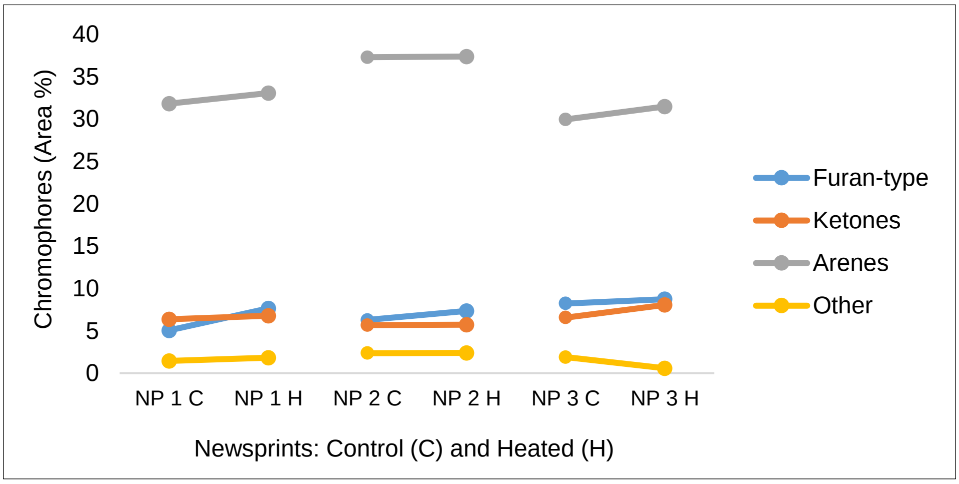


Figure 4.54: Py-GC/MS analysis of newsprint before (C) and after brightness reversion (H).

The comparison of the chromatograms of the control and heated newsprints (NP1) revealed that some of the compounds increased in area percentage because of heating. Thus, the chromophore concentration increased after brightness reversion (Figure 4.55).

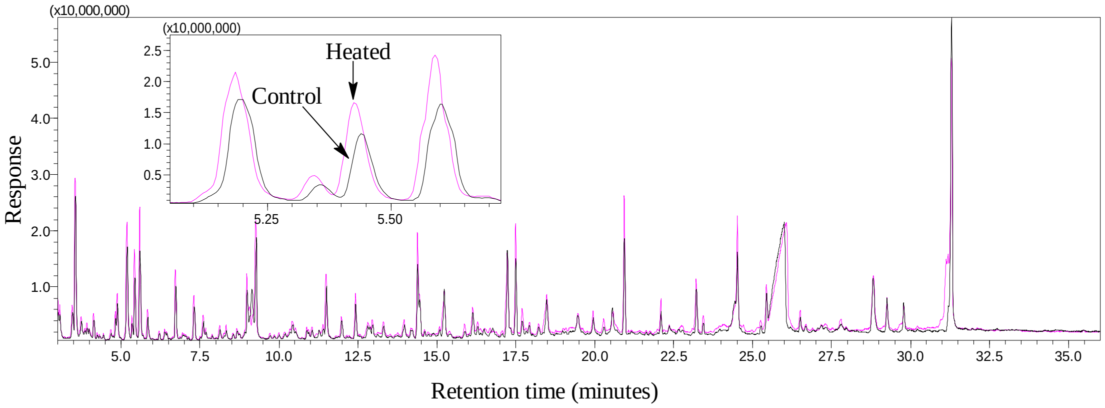


Figure 4.55: Pyrogram of NP1 before (control) and after (heated) brightness reversion.

Peaks of the chromophores identified in the control sample of NP1 are shown in Figure 4.56, the area percentages and the names of the identified compounds are shown in Table 4.28. The total area percentage of the chromophores identified in control NP1 was 44.6%, and the heated NP1 sample contained a total area percentage of 49.3%, with the arenes being the dominant compound group.

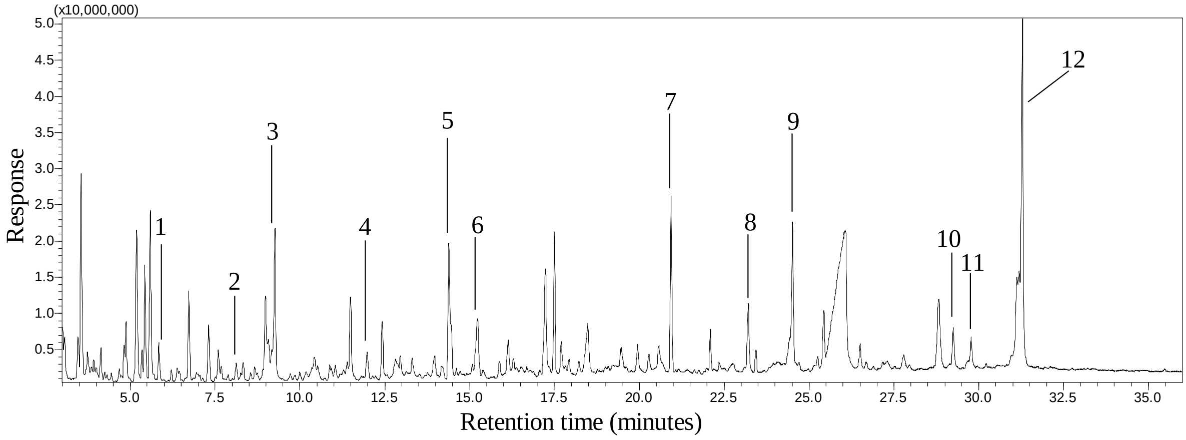


Figure 4.56: Pyrogram of NP1 before brightness reversion.

Table 4.28: Peak identification for control newsprints (NP1).

Peak number	**Retention time (min)**	**Area %**	**Compound**
1	6.72	1.2	Furfural
2	8.98	1.2	2(5H)-Furanone
3	9.26	2.2	1,2-Cyclopentanedione
4	12.42	1.0	1,2-Cyclopentanedione, 3-methyl-
5	14.39	2.7	Phenol, 2-methoxy-
6	15.23	1.4	2,4(3H,5H)-Furandione, 3-methyl-
7	20.94	2.4	2-Methoxy-4-vinylphenol
8	23.21	1.4	Vanillin

9	24.51	3.5	trans-Isoeugenol
10	29.26	1.1	Benzenepropanol, 4-hydroxy-3-methoxy-
11	29.79	1.2	(E)-4-(3-Hydroxyprop-1-en-1-yl)-2-methoxyphenol
12	31.29	10.0	(E)-4-(3-Hydroxyprop-1-en-1-yl)-2-methoxyphenol
Total chromophore area %		**44.6**	

Fully bleached kraft pulps were analysed for chromophore content before and after brightness reversion. Heat-induced brightness reversion of the fully bleached kraft pulp resulted in the increase of the total chromophore content of the pulp. As shown in Figure 4.57, some of the compounds resulted in a higher area percentage after heating. The total chromophore content before brightness reversion was 20.1% (Table 4.29) and increased to 22.2 % after brightness reversion. The main contributing compound groups before brightness reversion were the furan-type compounds (4.9%) followed by the ketones (1.9%). The arenes and other low molecular weight chromophores were found at a lower concentration, 1.9% and 0.8% respectively. After brightness reversion, the furan-type compounds and the ketones increased by 6.4% and 3.9% respectively.

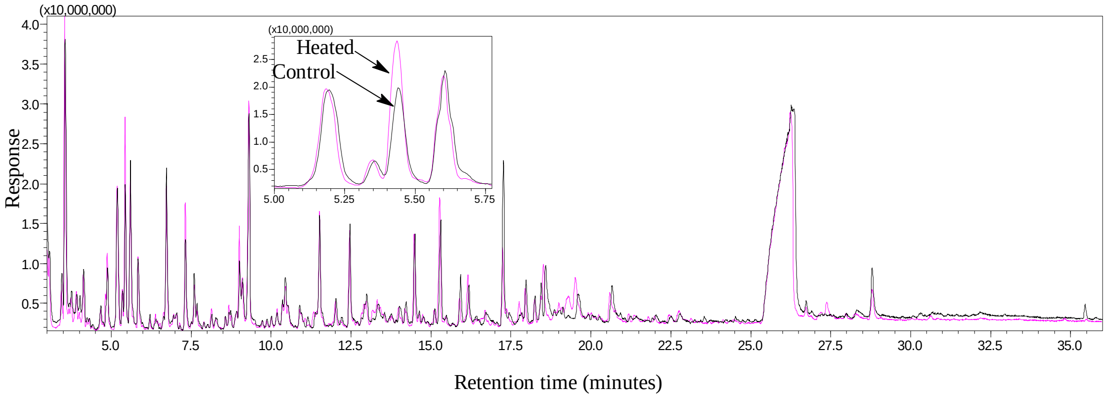


Figure 4.57: Pyrogram of fully bleached kraft pulp before (control) and after (heated) brightness reversion.

The major chromophores (with an area percentages above 1 percent) identified in the kraft pulp before heating were labelled with numbers in Figure 4.58. The compound names of the numbered peaks are shown in Table 4.29. These results indicate that the type of chromophores identified in kraft pulps are similar to the type of chromophores identified in DWP samples. This implies that the source of chromophores in the chemical pulps is similar in nature, thus confirming that the mechanism for the formation of chromophores in chemical pulps is similar.

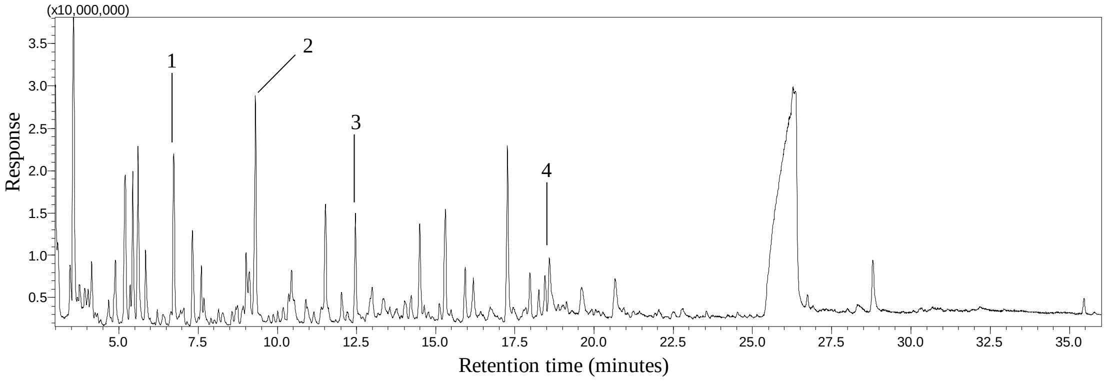


Figure 4.58: Pyrogram of fully bleached kraft pulp before brightness reversion.

In comparison to the DWPs, the kraft pulp resulted in a higher percentage of the arenes after brightness reversion. However, the percentage of the arenes in the kraft pulp was much lower compared to the arenes identified in the newsprint samples. This confirms that there are structural changes that occur in the lignin during chemical pulping (del Rıo *et al.*, 2001).

Table 4.29: Peak identification for kraft pulp before brightness reversion.

Peak number	**Retention time (min)**	**Area%**	**Compound**
1	6.73	2.3	3,5-Dimethylpyrazole-1-methanol
2	9.32	3.5	2-Cyclopenten-1-one, 2-hydroxy-
3	12.47	1.7	1,2-Cyclopentanedione, 3-methyl-
4	18.59	1.7	5-Hydroxymethylfurfural
Total chromophore area %		**20.1**	

4.4 Summary of main results

Analysis of chromophores in xylan and lignin using Py-GC/MS showed that the sources of chromophores in DWP are the oxidation and degradation products of carbohydrates. The aromatic compounds were found at the lowest concentration in the majority of pulp samples analysed, confirming that lignin is not the primary source of chromophores in fully bleached DWP. The major pyrolysis product of all the pulps samples analysed in this study was the levoglucosan, the main degradation product of cellulose. Identified chromophores were grouped into furan-type compounds, ketones, arenes and other low molecular weight chromophores.The newsprints contained a very low percentage of the levoglucosan and a high percentage of lignin-related chromophores. This confirms that in the pulp samples or in the cellulose rich materials, cellulose degradation is the primary cause of chromophore formation whereas, in the materials with a low cellulose content, cellulose-type chromophores were minimal. In addition to cellulose degradation, it has also been demonstrated that the hemicelluloses have a significant contribution towards chromophore formation. However, it is known that DWP contain minute amounts of hemicellulose and therefore, it can be concluded that most of the chromophores originate from cellulose degradation.

4.5 References

Alves, A., Schwanninger, M., Pereira, H. & Rodrigues, J. 2006. Analytical Pyrolysis as a Direct Method to Determine the Lignin Ccontent in Wood: Part 1: Comparison of Pyrolysis Lignin with Klason Lignin. *Journal of Analytical and Applied Pyrolysis,* 76**,** 209-213.

Barbosa, B. M., Colodette, J. L., Longue Júnior, D., Gomes, F. J. B. & Martino, D. C. 2014. Preliminary studies on furfural production from lignocellulosics. *Journal of Wood Chemistry and Technology,* 34**,** 178-190.

Ben, H. 2014. Pyrolysis of Biomass to Bio-Oils. *Materials for Biofuels.* Toh Tuck Link, Singapore: World Scientific.

Bendahou, A., Dufresne, A., Kaddami, H. & Habibi, Y. 2007. Isolation and structural characterization of hemicelluloses from palm of Phoenix dactylifera L. *Carbohydrate Polymers,* 68**,** 601-608.

Beyer, M., Koch, H. & Fischer, K. 2006. Role of hemicelluloses in the formation of chromophores during heat treatment of bleached chemical pulps. *Macromolecular Symposia,* 232**,** 98-106.

Brebu, M. & Vasile, C. 2010. Thermal degradation of lignin - a review. *Cellulose Chemistry & Technology,* 44**,** 353-363.

Bunzel, M. & Ralph, J. 2006. NMR characterization of lignins isolated from fruit and vegetable insoluble dietary fiber. *Journal of Agricultural and Food Chemistry,* 54**,** 8352-8361.

Burgess, H. D. 1982. Relationships between colour production in cellulose and the chemical changes brought about by bleaching. *AIC Annual Meeting.* Milwaukee, Wisconsin: The American Institute for Conservation.

Chirat, C. & De La Chapelle, V. 1999. Heat-and light-induced brightness reversion of bleached chemical pulps. *Journal of pulp and paper science,* 25**,** 201-205.

del Rıo, J., Gutiérrez, A., Romero, J., Martınez, M. & Martınez, A. 2001. Identification of residual lignin markers in eucalypt kraft pulps by Py–GC/MS. *Journal of Analytical and Applied Pyrolysis,* 58**,** 425-439.

del Río, J. C., Gutiérrez, A., Romero, J., Martínez, M. J. & Martínez, A. T. 2001. Identification of residual lignin markers in eucalypt kraft pulps by Py–GC/MS. *Journal of Analytical and Applied Pyrolysis,* 58–59**,** 425-439.

Dyer, T. J. 2004. *Elucidating the formation and chemistry of chromophores during kraft pulping.* PhD, University of Wisconsin-Stevens Point.

Eartrakulpaiboon, S. & Tonanon, N. 2015. Preparation of microcrystalline cellulose from dissolving cellulose by cryo-crushing and acid hydrolysis. *International Conference on Science and Technology.* Pathum Thani, Thailand: IEEE.

Gu, X., Ma, X., Li, L., Liu, C., Cheng, K. & Li, Z. 2013. Pyrolysis of poplar wood sawdust by TG-FTIR and Py–GC/MS. *Journal of Analytical and Applied Pyrolysis,* 102**,** 16-23.

Ház, A., Jablonský, M., Orságová, A. & Šurina, I. 2013. Characterization of lignins by py-GC/MS. *4th International Scientific Conference, Renewable Energy Sources.* Tatranské Matliare, Slovakia.

Ibarra, D., del Río, J. C., Gutiérrez, A., Rodríguez, I. M., Romero, J., Martínez, M. J. & Martínez, Á. T. 2005. Chemical characterization of residual lignins from eucalypt paper pulps. *Journal of Analytical and Applied Pyrolysis,* 74**,** 116-122.

Johansson, M. 2000. *Formation of chromophores and leucochromophores during manufacturing of mechanical pulp.* PhD, Royal Institute of Technology.

Kato, K. & Cameron, R. 1999. A review of the relationship between thermally-accelerated ageing of paper and hornification. *Cellulose,* 6**,** 23-40.

Kupiainen, L. 2012. *Dilute acid catalyzed hydrolysis of cellulose-extension to formic acid.* PhD, University of Oulu.

Kupiainen, L., Ahola, J. & Tanskanen, J. 2012. Distinct Effect of Formic and Sulfuric Acids on Cellulose Hydrolysis at High Temperature. *Industrial & Engineering Chemistry Research,* 51**,** 3295-3300.

Li, D., Ibarra, D., Köpcke, V. & Ek, M. 2012. Production of Dissolving Grade Pulps from Wood and Non-Wood Paper-Grade Pulps by Enzymatic and Chemical Pretreatments. *Functional Materials from Renewable Sources.* American Chemical Society.

Lin, X., Sui, S., Tan, S., Pittman, C. U., Sun, J. & Zhang, Z. 2015. Fast pyrolysis of four lignins from different isolation processes using Py-GC/MS. *Energies,* 8**,** 5107-5121.

Loureiro, P. E., Domingues, M. R. M., Fernandes, A. J., Carvalho, M. & Evtuguin, D. V. 2012. Discriminating the brightness stability of cellulosic pulp in relation to the final bleaching stage. *Carbohydrate Polymers,* 88**,** 726-733.

Loureiro, P. E., Fernandes, A. J., Furtado, F. P. & Carvalho, D. V. 2010. New insights into chromophore chemistry of eucalypt pulps assessed by uv-resonance raman micro-spectroscopy. *XXI TECNICELPA Conference and Exhibition VI Iberoamerican Congress on Pulp and Paper Research.* Lisbon.

Lu, Q., Yang, X.-c., Dong, C.-q., Zhang, Z.-f., Zhang, X.-m. & Zhu, X.-f. 2011. Influence of pyrolysis temperature and time on the cellulose fast pyrolysis products: Analytical Py-GC/MS study. *Journal of Analytical and Applied Pyrolysis,* 92**,** 430-438.

Mascal, M. & Nikitin, E. B. 2008. Direct, High-yield conversion of cellulose into biofuel. *Angewandte Chemie,* 120**,** 8042-8044.

Ohra-aho, T., Tenkanen, M. & Tamminen, T. 2005. Direct analysis of lignin and lignin-like components from softwood kraft pulp by Py-GC/MS techniques. *Journal of Analytical and Applied Pyrolysis,* 74**,** 123-128.

Qiang, L., Wen-zhi, L., Dong, Z. & Xi-feng, Z. 2009. Analytical pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS) of sawdust with Al/SBA-15 catalysts. *Journal of Analytical and Applied Pyrolysis,* 84**,** 131-138.

Rencoret, J., Gutierrez, A. & del Rio, J. C. 2007. Lipid and lignin composition of woods from different eucalypt species. *Holzforschung,* 61**,** 165-174.

Rosenau, T., Potthast, A., Kosma, P., Suess, H. U. & Nimmerfroh, N. 2007. Chromophores in aged hardwood pulp-their structure and degradation potential. *International symposium of wood, fibre and pulping chemistry* Durban: TAPPSA Journal.

Rosenau, T., Potthast, A., Krainz, K., Yoneda, Y., Dietz, T., Shields, Z. P.-I. & French, A. D. 2011. Chromophores in Cellulosics, VI. First Isolation and Identification of Residual Chromophores from Aged Cotton Linters. *Cellulose,* 18**,** 1623-1633.

Shen, D., Xiao, R., Gu, S. & Zhang, H. 2013. The Overview of Thermal Decomposition of Cellulose in Lignocellulosic Biomass. *In:* Van De Ven, T. & Kadla, J. (eds.) *Cellulose - Biomass Conversion.* China: INTECH.

Shen, D. K. & Gu, S. 2009. The Mechanism for Thermal Decomposition of Cellulose and its Main Products. *Bioresource Technology,* 100**,** 6496-6504.

Suchy, M. & Argyropoulos, D. S. 2002. Catalysis and Activation of Oxygen and Peroxide Delignification of Chemical Pulps: A Review. *Tappi Journal,* 1**,** 1-18.

Van Dam, H., Kieboom, A. & Van Bekkum, H. 1986. The Conversion of Fructose and Glucose in Acidic Media: Formation of Hydroxymethylfurfural. *Starch-Stärke,* 38**,** 95-101.

Wang, S.-r., Tan, H., Luo, Z.-y., Wang, L. & Cen, K.-f. 2006. Experimental Research on Rapid Pyrolysis of Xylan. *Journal-Zhejiang University Engineering Science,* 40**,** 419.

Xue, M.-G., Wang, S.-F., Huang, C.-X. & Xia, N.-N. The Analysis of Organic Contaminants in Printing Paper Food Packaging Materials. Proceedings of the 17th IAPRI World Conference on Packaging, 2010. 360-363.

Zhao, J., Xiuwen, W., Hu, J., Liu, Q., Shen, D. & Xiao, R. 2014. Thermal Degradation of Softwood Lignin and Hardwood Lignin by TG-FTIR and Py-GC/MS. *Polymer Degradation and Stability,* 108**,** 133-138.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

The original motivation for this study was to identify a link between the presence of chromophores and brightness reversion in dissolving wood pulps (DWPs), proceeding from the belief that chromophores were the cause of brightness reversion. Surprisingly, not long into the study, it became evident that no direct link could be identified between chromophores and brightness or brightness reversion. To determine and analyse the role of chromophores in causing brightness reversion, it was first necessary to develop a tool to perform this investigation, since the current methods have some significant limitations as described in chapter 2. Pyrolysis-gas chromatography-mass/spectrometry (Py-GC/MS) was chosen as the means to undertake this study, and it has been successfully used as a novel tool for chromophore identification in DWPs.

Since no accounts could be found in the use of Py-GC/MS for the identification of chromophores in DWPs, a method was developed using several types of samples such as DWP with and without signs of brightness reversion, cellulose-rich materials and samples of materials that could be potential sources of chromophores in the pulp such as the xylan, sugar monomers and lignin.

As part of method development, the cellulose-rich materials and the xylan were induced for brightness reversion, and the chromophore content was analysed before and after brightness reversion. Results showed an increase of chromophores after brightness reversion. It was observed that some of the chromophores that were identified before brightness reversion had an increased area percentage after brightness reversion and new chromophores were identified, meaning that more cellulose was degraded in the ageing process and thus forming more chromophores.

The xylan contained ketones, the furan-type and aromatic compounds. Upon brightness reversion of xylan, the identified chromophores' percentage increased showing that the chromophores produced by xylan are promoted by heat ageing. This also implies that some of the chromophores in DWP that originate from the residual xylan (hemicellulose) increase when the heating conditions are employed during pulp processing and contribute to pulp discolouration.

Among the six sugar monomers analysed, the xylose was the only sugar that contained chromophoric compounds, the furan-type compounds were identified in xylose. The cellulose-rich materials contained the ketones and the furan-type chromophores; no aromatic compounds were identified in these samples, indicating the absence of lignin.

The chromophore analysis of lignin was undertaken through Py-GC/MS analysis of Klason lignin samples, obtained by acid hydrolysis of sawdust, and through precipitation from kraft liquor.

Although the sources of the Klason lignin were different, both sets of lignin contained over 80% of arenes. The furans, ketones and other low molecular weight chromophores were detected in minor amounts. Further analysis of the arenes showed that the main constituents of the lignin were the phenolic, guaiacol and syringyl type compounds, and other groups of aromatic compounds such as alkylated and methoxylated aromatic rings. It was observed that the kraft lignin contained a slightly higher amount furans and ketones, compared to the lignin that was isolated from the sawdust. The presence of the furans and ketones was associated with hemicelluloses and degraded carbohydrates resulting from the kraft pulping process.

Once the method was developed and tested for reproducibility using selected DWP samples, the Py-GC/MS was employed as an effective tool to examine chromophores. Specific sets of samples (industry and laboratory produced pulps) were used to achieve the aim of the study that was to develop a novel and rapid methodology for efficient identification of chromophores directly in DWP fibres.

Firstly, using the Py-GC/MS, residual chromophores were analysed in a set of industrially produced fully bleached DWPs, with known brightness and yellowness, collected from various pulp producing mills across the world. The effect of heat induced brightness reversion was observed by a decrease in brightness, an increase in yellowness and finally, an increase of the chromophore content in all the fully bleached DWP samples analysed. In each of the fully bleached DWP samples, the chromophores increased after brightness reversion. However, the inter-sample comparison showed that the changes of the chromophore content of the pulps were not consistent with the changes in brightness and yellowness, and this was attributed to the differences in the processing conditions. It was established that the major classes of chromophores found in fully bleached were the conjugated ketones and furan-type chromophores. Arenes and other low molecular weight chromophores were found in low amounts.

Further analysis of fully bleached pulps was undertaken by investigating the effect of derivatization on the formation of chromophores. Fully bleached DWP with corresponding microcrystalline cellulose (MCCs) were analysed for chromophore content. It was evident that some of the chromophores were diminished during derivatization since the MCC samples had a lower chromophore content than the parent pulp samples. However, the brightness of the MCC samples was lower than the brightness of the original DPWs, hence, it was expected that the chromophore content of the MCC would be higher. Findings from this part of the study confirmed that there was no relationship between the pulp brightness and the chromophore content.

Secondly, the effect of each of the process steps in the formation of chromophores, during the production of DWP, was investigated through the analysis of pulps collected at various processing stages (in-process pulp). Industrially produced in-process DWPs and laboratory produced in-process DWPs were subjected to wet chemistry analysis to understand the effect of the processing steps in the pulp components and the formation of chromophores. Even though the composition of the industrial and laboratory pulps was different, the results showed that the hemicelluloses and the degraded cellulose/short chain glucan were the chief contributing factors in the formation of chromophores in the in-process and fully bleached pulps.

Newsprints samples were analysed before and after brightness reversion, findings showed that they mainly contained lignin because the analysed samples contained at least 35% of the aromatic compounds, the furans and ketones were found in amounts less than 10%. The effect of heat induced brightness reversion of the newsprints was also accompanied by an increase of the chromophores identified before brightness reversion. Unlike DWP, it is known that newsprints contain more lignin than cellulose. Hence, this component of the study revealed the ability of the PY-GC/MS technique to distinguish between cellulose rich materials and lignin-rich materials.

Unbleached and bleached kraft pulps were also analysed for chromophore content. The fully bleached kraft pulps were subjected to brightness reversion. Like fully bleached DWP, the unbleached and bleached kraft pulps contained a deficient percentage of the aromatic compounds. The heat induced brightness reversion also resulted in an increased total chromophore content of the fully bleached kraft pulps.

The use of Py-GC/MS to identify chromophores in DWP has shown the following advantages:

- It allows for identification of a wide range of chromophore classes even at minor amounts. Chromophores identified were grouped into furans, ketones, arenes and other low molecular weight chromophores.
- It is the most efficient method for chromophore identification in DWP reported thus far.
- It does not involve pre-extraction and laborious sample preparation.

From this study, it can be deduced that the Py-GC/MS has enabled the identification of residual chromophores and it is evident that the amount of chromophores is affected by ageing and the bleaching chemicals. Further studies through wet chemical analysis showed that the chromophore content was also affected by the hemicelluloses and the degraded carbohydrates. It was evident that there was no correlation between the brightness or yellowness and chromophores in the pulp when a range of similar samples was compared. However, within individual samples, the brightness decreased with an increase in the chromophore content. This was attributed to the differences in the processing conditions and the lack of homogeneity within a given set of samples.

Results from this study will allow researchers to focus specifically on the control of the furans, ketones, arenes and other low molecular weight chromophores. Since it was shown that the main contributors to the formation of chromophores in DWP were the hemicelluloses and degraded cellulose, future studies should focus on the removal of the recalcitrant hemicellulose and the stabilisation of cellulose to avoid degradative reactions to reduce chromophore formation from these substances. Py-GC/MS analysis of chemically pure cellulose, i.e. bacterial cellulose, will be beneficial regarding understanding the pyrolysis products of the cellulose without any interference from the bleaching chemicals.