FLUIDISED BED GASIFICATION OF SPENT SODA AND SULPHITE LIQUORS FROM THE PAPER INDUSTRY

By

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A dissertation submitted at the School of Chemical Engineering
University of Natal
Durban

In fulfillment of the requirements for the degree
Master of Science in Engineering (Chemical)

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April 2004

Declaration

This project was undertaken at the University of Natal in the School of Chemical Engineering under the supervision of Prof. D.R. Arnold.

All work that is presented in this dissertation is my own, except as otherwise specifically acknowledged in the text. This work has not been submitted in part, or in whole to any other University.

Pravesh Sewnath

Date

Declaration by supervisor

I, Prof. D. R. Arnold, acknowledge that I have read and understood all the work presented in this dissertation by P. Sewnath. I therefore approve this thesis for submission.

Prof. D.R. Arnold	Date

ACKNOWLEDGEMENTS

- To my supervisor, Prof. D. Arnold, thank you.
  This project would not have been completed if it were not for you. I take away from this project all that you have shown and taught me.

- To my parents and my sister.
  By your love and support, I have successfully completed another chapter in my life. The patience and love that you have shown me, goes beyond all boundaries.

- To my beautiful Thirusha.
  Words cannot express my gratitude and appreciation for all the support, help and love that you have given me. Thank you. You believed in me and made me who I am. Thank you for your patience and your faith in me.

- To Kelly Robertson, Les Henderson and Ken Jack. I am honoured to be associated with people of such great talent, who have helped me time and time again.

- To Bheki Dlamini. I am forever indebted to you. Thank you for all the work that you have done for me. It is greatly appreciated.

- To the late Fiona Graham.
  May you find peace and happiness where ever you are. Your kindness and generosity knew no boundaries. You will surely be missed!

- To Sappi, thank you for your generous financial support and assistance.

ABSTRACT

The pulp and paper industry uses pulping chemicals for the treatment of bagasse, straw and wood chips. Spent liquor or effluent liquor, with high carbon content is produced and sent to chemical recovery to recover pulping chemicals. In addition, energy from the spent liquor is recovered and utilised to generate steam for electricity supply, thereby reducing fossil fuel power consumption.

Spent liquor is destroyed using conventional incineration technology, in a recovery furnace or recovery boiler, which is the heart of chemical recovery. These units have over the past few decades been prone to numerous problems and are a major concern to the pulp and paper industry. They pose a threat to the environment, are expensive to maintain and constitute a safety hazard. Thus the pulp and paper industry is now looking at a replacement technology; an alternative that will effectively regenerate pulping chemicals and recover energy for generating electricity, ultimately to make the plant energy self-sufficient.

Gasification technology may be the chosen technology but is yet to be applied to the pulp and paper sector. However, this technology is not new. It has been integrated and used successfully in the petroleum industry for decades, with applications in coal mining and the mineral industry.

The overall objective of this study is to develop a better understanding of gasification using a pilot-scale fluidised bed reactor which was designed and developed at the University of Natal. The reactor, "the Gasifier", is operated at temperatures below the smelt limits of inorganic salts (<750°C) in the spent liquor. In this investigation, spent liquor is injected directly into an inert bed of aluminium oxide grit, which is fluidised by superheated steam. The atomized liquor immediately dries when it contacts the grit in the bed, pyrolyses and the organic carbon is gasified by steam. Pyrolysis and steam gasification reactions are endothermic and require heat. Oxidised sulphur species are partially reduced by reaction with gasifier products, which principally consist of carbon monoxide, carbon dioxide and hydrogen. The reduced sulphur is said to be unstable in the gasifier environment, and reacts with steam and carbon dioxide to form solid sodium carbonate and gaseous hydrogen sulphide. (Rockvam, 2001)

The focus of this study will be to determine the Gasifier's ability to gasify spent liquor, from soda and sulphite pulping of bagasse, at different operating conditions. In addition, the fate of process and non-process elements will be investigated.

The product gas generated in the gasification of spent soda and sulphite liquors consisted of hydrogen, carbon dioxide, carbon monoxide and methane. In the gasification of spent sulphite liquor, hydrogen sulphide was also produced. The water-gas shift reaction, which was the main reaction, was found to be temperature dependent. In addition, organic carbon conversion increased with temperature. Furthermore, most of the sulphur in the bed predominated in the form of hydrogen sulphide with very little sulphur in the form of sulphate. This indicated that gasification would reduce sulphate levels, which are responsible for dead load in a chemical recovery cycle. Finally, an important result was that the aluminium oxide grit was successfully coated. It was previously speculated that this would not be possible.

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NOMENCLATURE

ΔP	Pressure drop across bed
A	Area of cross section
H_{mf}	Height of bed at minimum fluidisation
ρ_s	Density of particle
ρ_g	Density of gas
g	Gravity
$\overline{dp}$	Mean diameter
ρ	Density of fluid
$N_{\mathrm{Re},mf}$	Reynolds Number at minimum fluidisation
ϕ_s	Sphericity
ε_{mf}	Void fraction of the bed at minimum fluidisation
D_p	Diameter of particle
ρ_p	Density of particle
μ	Viscosity
v_{mf}	Minimum fluidisation velocity
x	Mass fraction
A_r	Archimedes Number
v_1	Velocity at position 1
v_2	Velocity at position 2
p_1	Pressure at position 1
p_2	Pressure at position 2
C_v	Discharge coefficient
D_1	Diameter at position 1
D_2	Diameter at position 2
Y	Expansion correction factor
m	Mass flowrate
ΔG^o	Standard Gibbs Energy change
K_i	Equilibrium constant of specie i
Y_i	Vapour fraction
R	Gas Law Constant

T	Temperature
v_{fs}'	Minimum velocity for which the bed weight is fully supported by the fluid

CHAPTER 1:
INTRODUCTION

Waste material is currently destroyed using incineration technology based on a combustion process. Applications of this technology extend widely from municipal waste destruction to the destruction of chlorinated hydrocarbons. The worrisome factor is that research (Orr et al., 2000) has now shown that incineration technology causes more harm to the environment than it prevents.

In the pulp and paper industry, incineration technology is used in the recovery of pulping chemicals from alkaline pulping of wood and non-wood material. Spent liquor is produced in the pulping stage of the papermaking process and the pulping chemicals are re-generated from the spent liquor using incineration technology in a recovery boiler. Since spent liquor has a high energy content, it is currently used to generate steam; and this together with pulping chemical recovery, are the main products of the recovery boiler.

The only conventional recovery system at present is the Tomlinson recovery boiler which is used solely in the Kraft pulping process. This process utilises sodium hydroxide and sodium sulphide as pulping chemicals. Other pulping processes such as the soda pulping of bagasse do not have a recovery system. Instead a combustor, a fluidised bed reactor, is employed to incinerate the spent liquor, which produces an ash by-product that is sold.

Incineration technology is an increasing threat to the environment with the production of NO_x and SO_x gases. Increasing stringent environmental regulations have put limitations on recovery boiler operations with the requirement of expensive pollution control equipment to be installed into new and older units.

Apart from being expensive to construct and renovate, recovery boilers are dangerous to operate. This stigma has been attached to these units because of the high risk of explosions, which has plagued it since commercialisation. Furthermore, the recovery boiler is inflexible to changing pulping chemistry demands and thus limits its future use in the pulp and paper industry. Due to these restraints, recovery boilers are now perceived as the "bottle neck" of operations in the pulp and paper industry (Dickenson, 1998).
The future for the pulp and paper industry therefore lies not in incineration technology but rather in an alternative that can cater for the industry's fast changing needs.

The paper industry strongly believes that energy self sufficiency is the key to its future. This stems from oil price shocks in the 1970's which left the paper and allied industries vulnerable to outside influence. It is envisaged that gasification based systems in paper mills will provide enough energy for the plant to function and at the same time be a net exporter of

energy (Tucker, 2002). It is proposed that gasification technology with combined cycle power generation in the form of gas turbines may be able to accomplish this great feat of a self sufficient plant.

In addition, the increasing demand for paper and paper board has left paper mills with limited options to expand production. The expansion of mills is a costly venture and therefore a last resort. Added pressure of a higher yield pulp and better quality product has made this industry very competitive.

Gasification technology is based on the principle of partial oxidation of carbon containing materials with the formation of a valuable synthesis gas of high energy content. It provides a cleaner way of operating with the ability to generate electricity and valuable by-products from low value waste material. A gasifier in conjunction with a gas turbine can be used to generate steam for steam turbines which in turn can be used to generate electricity.

Other advantages include the separation of sulphur from sodium, little or no dependence on fossil fuel energy, greater flexibility to change in pulping chemistry and the production of quality products from low value fuels or waste streams. It is therefore no wonder that many companies believe that spent liquor gasification will eventually replace the Tomlinson recovery boiler as the preferred chemical recovery technology (Finchem, 1995).

There are two categories of gasification processes, namely, high temperature and low temperature gasification. The working definition of these categories is based on the operating temperature of these processes with respect to the melting point of inorganic salts present in spent liquor. Another definition is based on the state of the material leaving the reactor. Inorganic salts are reported to melt at a temperature of over 750°C (Backman et al., 1993). The high temperature process results in the formation of molten material, due to the melting of the inorganic salts present in the material. Low temperature processes result in the prevention of inorganic salts from melting and the product leaves the reactor in a solid form. In the low temperature gasification process fluidised bed reactors are used.

Fluidised bed reactors offer the advantage of isothermal conditions, with simple and reliable control in operation. This type of reactor offers excellent gas-solid contacting with no hot spots even with highly exothermic reactions; good gas-to-particle heat transfer and the ease of solids handling which is important when working with catalysts (Werther et al, 2003).

In low temperature spent liquor gasification, spent liquor is injected into an inert bed of aluminium oxide grit in a fluidised bed reactor. As the hot liquor makes contact with the bed grit, the liquor undergoes drying, pyrolysis and char gasification process. Endothermic reactions produce a product gas which consists of hydrogen, carbon monoxide, carbon dioxide and methane. If sulphur is present in the liquor, hydrogen sulphide is produced in the product gas. It is believed that sulphur is separated from the sodium which is present as

inorganic salts. This is believed to occur due to the reaction of sodium sulphate with steam and carbon dioxide to produce sodium sulphide and solid sodium carbonate. Since sodium sulphide is unstable, it is converted to hydrogen sulphide. Hydrogen sulphide is a notorious pollutant, which can negatively impact the environment. It can, however, be removed with a downstream wet scrubber at high sulphur removal rates. (Rockvam, 2001)

In this study, low temperature fluidised bed gasification of spent liquor is investigated. The spent liquors used in this study are from soda and semi-alkaline sulphite pulping. These spent liquors are generated from the pulping of sugar cane bagasse from Sappi-Stanger Mill. Sappi-Stanger Mill has no chemical recovery of pulping chemicals from soda pulping and the spent liquor generated as a by-product or waste is incinerated in a combustor (fluidised bed). The by-product soda ash produced is a valuable commodity which is then sold for use in other industries. Currently, Sappi is looking at increasing their pulping yields and they hope to achieve this with a semi-alkaline sulphite pulping chemistry with anthraquinone catalyst (SASAQ). However, no suitable chemical recovery process for spent SASAQ liquor exists.

Sappi's motivation towards this project is three-fold. Firstly, a semi-alkaline sulphite pulping chemistry with anthraquinone catalyst (SASAQ) increases yield by 25% as compared to soda pulping with anthraquinone catalyst. Secondly, gasification technology offers them the possibility to separate sodium from sulphur. Thirdly, gasification technology provides a suitable recovery process for spent SASAQ liquor. However, the only work that has been done for them thus far was by an outside company situated in the U.S. Therefore, it is an iniative by Sappi to develop this technology in South Africa at a prominent institution. This task was undertaken by the University of Natal, School of Chemical Engineering in the form of a research project towards an MScEng degree.

The overall objective of this project was to develop a better understanding of fluidised bed gasification of spent liquor below 750°C on a pilot scale. The following primary objectives were proposed for this study:

- Evaluate the capability of the pilot unit in its original state.
- Modifications and additions to existing gasification system.
- To determine the effect of the following process variables with the objective of providing a safe operating window. Spent soda and sulphite liquor were used in this investigation, with sulphite (SASAQ) liquor limited to temperature and time. The process variables investigated are:
    - Temperature
    - Spent liquor to steam ratio
    - Spent liquor solids content
    - Time
- An investigation into carbon conversion.

- The fate of non-process elements in the system such as chlorides, potassium and silica. Non-process elements are elements brought into the process by water, raw materials etc., which ultimately hinder the process.
- Perform mass balances on the system with respect to sodium, sulphur, chlorides and potassium.
- Determine the factors affecting the water-gas shift reaction theoretical versus those observed experimentally with respect to the process variables.

The project followed a two-tiered approach, which was based on the current status of the system at the start of this MSc. Since the project was designed and constructed by a previous student who did not hand over design information, the first tier was to apply a reverse engineering approach. In this manner, the modifications and the additions required to develop the existing gasification system were evaluated. This had to be done by running the gasifier and finding out how well it worked, its limitations and its necessities for good systems operation, experimentation, sampling and analysis.

The next tier was experimentation and data collection. The approach used to investigate the effect of the process variables was to sample the product gas and determine the effect that the process variable had on the product gas compositions. Gas chromatography was employed for this purpose. Thereafter, the approach used to determine the carbon conversion, the effect of non-process elements and mass balances was obtained from analysis of the bed material by X-ray fluorescence. Lastly, comments were made with respect to the water-gas shift reaction from theory and from experimental work done based on the process variables.

In retrospect, this project is a preliminary study to develop a better understanding of fluidised bed gasification of spent liquor. This technology may indeed find eventual commercial application in the paper industry, in the not too distant future.

CHAPTER 2:

LITERATURE SURVEY

The first section focuses on chemical recovery, spent liquor produced; pulping chemistry and the problems associated with non-wood spent pulping liquor. Thereafter, current technology is reviewed with a look at modern incineration systems and the recovery boiler in particular. In addition, the fundamentals of spent liquor conversion are discussed. Following this, gasification is introduced and defined. The motivation for this technology, its benefits and its applications are then discussed. Further on, the gasification process is classified and a brief history of gasification in the coal industry is reviewed. Thereafter, research on spent liquor gasification and the chemistry of it are elaborated upon. The mechanisms of alkali catalysts are described in the following section. Commercial spent liquor gasification processes are then described with results shown. A brief section on biomass gasification follows this. The next section elaborates on combined cycle power generation and its association with gasification technology. This chapter concludes with the significance of this study discussed.

2.1 Background

2.1.1 Chemical Recovery

Chemical recovery (Figure 2-1) is an indispensable part of the pulping process in which pulping chemicals and process energy is recovered. The recovered pulping chemicals are then re-used in pulping with the recovered process energy used to generate steam for electricity supply. Plant mills can contribute up to 55% towards their basic energy requirements (Larson et al. 1997).

In chemical recovery, pulping chemicals are recovered from the by-product spent liquor produced in the pulping stage. Pulping refers to a process in which fibres are freed by pulping chemicals, at high temperatures and pressures, from wood or other fibrous raw materials to form a pulp.

From the literature reviewed, most of the conventional chemical recovery processes for recovering pulping chemicals are similar. Therefore, the Kraft recovery process will be used to describe chemical recovery in a paper mill.

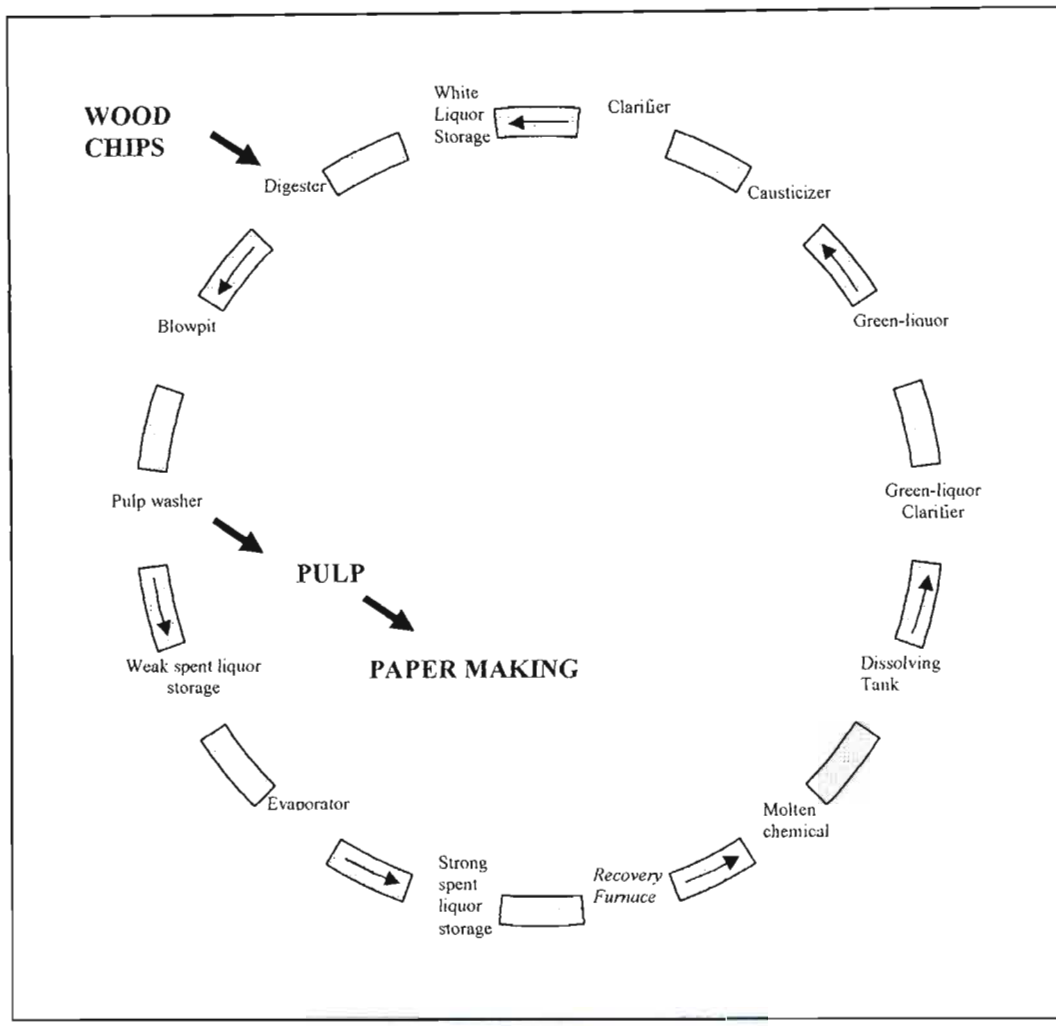


Figure 2 - 1: Kraft Chemical Recovery (Kocurek, 1989)

The Kraft process is widely used throughout the world in wood pulping processes. It is the only standard industrial pulping process where the pulping chemicals can be recovered and reused in the pulping process. All other processes can at best recover the inorganic material in the dry form and another chemical compound by incineration.

In Kraft pulping, wood chips after initial wood handling operations, are fed into a reactor called a digester. Here wood chips are cooked at high temperatures and pressures in a solution of pulping chemicals composed of sodium hydroxide and sodium sulphide, in order to free wood fibres (Macek, 1999).Organic acids present in the chemical matrix of the wood are neutralised and the lignin dissolves into the aqueous solution called "white liquor" (maybe referred to as pulping liquor or cooking liquor), which is used in the pulping process (Marklund, 2002). Pulping liquor leaves the digester as a by-product or effluent spent liquor. The fibrous mass or pulp is then removed from the digester and washed. After washing, the pulp is then sent to bleaching and papermaking.

Weak spent liquor is concentrated to strong spent liquor in a train of evaporators. A high solids content of the spent liquor is required for incineration in the next stage. The weak spent liquor has a solids content of less than 20% and is then concentrated to approximately 65% solids (Kocurek, 1989).

The strong spent liquor is then incinerated in a *recovery unit* called the chemical recovery furnace/boiler, where the energy in spent liquor is converted by the oxidation of the organics. This unit is the heart of chemical recovery. In this full combustion mode, a smelt of inorganic salts is produced with product gases evolved such as carbon dioxide and water vapour.

The smelt is then slaked i.e. dissolved in water, to form green liquor. This green liquor is then causticised i.e. green liquor reacts with lime to form "white liquor". This liquor is then fed back to the digester in the pulping stage.

2.1.2 Spent liquor

Spent liquor is produced during pulping and the type of spent liquor produced depends on the pulping chemistry used. Pulping chemistry refers to the makeup of the pulping liquor used in freeing fibres from the raw material during pulping. For example, soda pulping chemistry, which utilises sodium hydroxide only in its pulping liquor, is commonly employed for the pulping of non-wood raw materials such as bagasse.

Another characteristic of spent liquor is the colour which it gains and again is dependent on the pulping chemistry used. An example of this is the semi-alkaline sulphite pulping chemistry with anthraquinone catalyst used in non-wood pulping, which produces spent liquor of a distinctive red colour and is accordingly referred to as "red liquor". This pulping chemistry utilises sodium sulphite and sodium hydroxide (or sodium carbonate) at high pH. In addition, spent liquor from Soda and Kraft pulping is referred to as "black liquor" based on its distinctive dark brown to black colour.

Spent liquor has high organic carbon content and is the reason why process energy recovery is possible. Larger mills have the capability and financial resources to recover pulping chemicals and process energy from spent liquor however, smaller mills tend to dispose of it, finding it cumbersome and costly (Bhattacharya, 1986).

A typical elemental analysis of spent soda and sulphite (SASAQ) liquor is given below.

Analysis of liquor	Soda Liquor / % (w/w)	Sulphite Liquor / % (w/w)
Sodium	17.28	15.90
Carbon	40.50	30.00
Nitrogen	0.28	0.31
Hydrogen	3.53	3.10
Sulphur	0.03	9.60
Oxygen	35.76	38.03
Potassium	0.17	1.50
Chlorine	0.49	0.26
Silica as SiO_2	1.95	1.30
Total	100.00	100.00

Table 2 - 1: Liquor Analysis for Spent Soda and Sulphite Liquors

2.1.3 Pulping Chemistry

As mentioned in the previous section, pulping chemistry refers to the chemical make-up of the aqueous solution of the pulping liquor used to pulp the raw material in the pulping stage of the papermaking process. The pulping liquor used is responsible for the freeing of fibres used for papermaking.

An interest in a semi-alkaline-sulphite pulping chemistry with anthraquinone catalyst (SASAQ) is growing for pulping of non-wood raw material. Together with the addition of an anthraquinone catalyst, a more effective pulping chemistry is achieved. The following benefits (Dimmel et al, 1999) of SASAQ are:

- Increased pulping rates.
- Higher yields.
- Stronger pulps.
- Improvement in the chemical recovery system with regards to capacity.

However, a suitable chemical recovery process has not been established.

2.1.4 Problems with Recovery of Chemicals from Non-wood Spent Pulping Liquor

The spent liquor used in this study is obtained from soda and SASAQ pulping of bagasse. Spent soda liquor has a lower sulphur content compared to spent Kraft liquor and is reported to smelt with a much higher melting temperature (Tucker, 2002). The only source of sulphur in the spent soda liquor comes from bagasse. Therefore, spent soda liquor has very low sulphur content compared to SASAQ liquor (Table 2-1).

In addition, soda liquor has a high chloride, potassium, and silica content, commonly referred to as non-process elements. Non-process elements (NPE's) are elements brought into the process, for example; by purchased chemicals, the raw material itself or by water. They pose problems and may hinder the process. Chlorides and potassium in particular, are reported to affect the eutectics of sodium salts by reducing their melting points. (Backman et al, 1993)

The main difficulty in recovering chemicals and energy from spent liquor from non-wood pulping is the high silica content. It is especially problematic in recovery of pulping chemicals from spent soda liquor. An increase in the hydroxide ion concentration increases pH levels and at a high pH in the range of 12-14, the following reaction occurs.

$$NaOH + SiO_2 \rightarrow NaSiO_{3\,(ppt)} \qquad (2\text{-}1)$$

The silicate is responsible for fouling and scaling of heat transfer surfaces and possibly the very high viscosity of spent liquor after concentration. In a NLK-Celpap report, it was stated that in recovery boilers, high viscosity silicate glass is formed which scales boiler walls. In addition, silicate causes plugging of tube banks leading to difficulties in combustion. This results in frequent boiler shutdowns and overhauls. In addition increased viscosity in the smelt occurs.

2.2 Current Technology

Incineration technology is currently used to recover pulping chemicals and process energy from spent liquor. Recovery boiler technology has been the dominant design used in the Kraft process for many decades. Finchem (1995), reports that the issue of installing new recovery boiler capacity or increasing their existing capacity in the years to come is growing and this is due to the changes in fibrelines and the age of these boilers.

Cantrell (2001) and others estimate that some recovery boilers are approaching their 35 to 45+ year life span and will be in need of a major rebuild at some point in the near future. In addition, environmental regulations such as the Environmental Protection Agency's (EPA's) Maximum Achievable Technology (MACT) regulation, for pulp and paper combustion sources, may make rebuilding an economic consideration. This is likely to be the case as any future rebuild will require sophisticated pollution control equipment. Total rebuild costs are likely to be equivalent to the costs of building a new unit especially when down time costs are taken into account. (Cantrell, 2001)

2.2.1 Modern Incineration Systems

There are four major types of combustion chamber designs (Orr et al., 2002):

- liquid injection
- fluidised bed
- rotary kiln and fixed hearth

These designs are subject to the physical form and ash content of the waste being combusted. However, the general method of combustion is the same. Large volumes of air are used to create an oxidizing environment, which ensures that hydrocarbon waste destruction efficiencies are maximized. Orr et al. (2000) describes these systems.

2.2.1.1 Liquid Injection:

The liquid injection combustion chamber design is applied to waste material that can be pumped easily and injected into the combustion chamber in the form of an atomized spray using a spray nozzle design. It is important that the liquid waste feed is atomized to achieve maximum destruction efficiencies. An example of liquid injection combustion chamber design is the Tomlinson Recovery Boiler.

2.2.1.1. a The Recovery Boiler

The recovery boiler (Figure 2-2) used in chemical recovery of Kraft pulping chemicals, acts as both a high pressure steam boiler and a chemical reactor with reductive and oxidative zones (Marklund, 2002). The functions (Kocurek, 1989) of the recovery boiler are as follows:

- Recovery of inorganic pulping chemicals namely, sodium sulphide and sodium hydroxide from spent liquor.
- Generate steam by utilizing the chemical energy of spent liquor.
- Reduces the threat to the environment by destroying organic wastes.

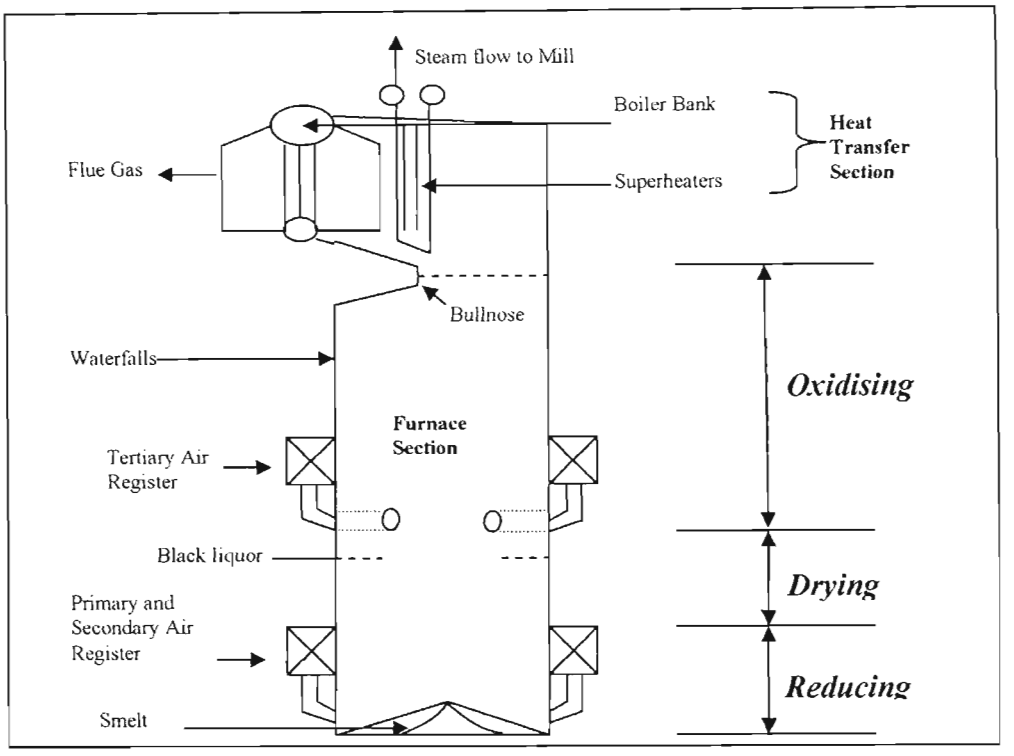


Figure 2 - 2: Sketch of the Recovery Boiler (Kocurek, 1989)

2.2.1.1. b Features of Recovery boiler

The boiler is made up of the furnace section - responsible for mixing and combustion; and the heat transfer section - responsible for generating steam to the boiler water.

Spent liquor is injected or fired into the furnace section / combustion chamber, via a series of liquor spray nozzles or liquor guns which are located near the bottom of the boiler. The atomized spent liquor is combusted in the presence of excess air which is delivered to the furnace section via three air ports or air registers namely, the primary, secondary and tertiary (Figure 2-2). In the presence of air, the atomized spent liquor droplets undergo drying, pyrolysis, char conversion and smelt formation.

Smelt consists of inorganic metal salts and is removed from the boiler via smelt spouts, located below the primary air registers at the bottom of the boiler. Vertical tubes with water flowing in them, referred to as "waterfalls", make up the walls of the furnace section and are 6.7 -7.6cm in diameter. The heat transfer section comprises of a superheater, boiler bank and economizer, in which steam is generated in bundles of tubes. These tubes are 6.4cm in diameter and spaced roughly 12 cm apart for cleaning purposes. (Kocurek, 1989)

The bullnose featured protects the superheater from direct radiation from the furnace section. Combustion gases move around the bullnose to ensure that a uniform flow for heat transfer is produced (Marklund, 2002).

2.2.1.1. c Operation of the Recovery Boiler

Concentrated spent liquor at ~120°C is fired into the furnace section via liquor spray nozzles. The boiler is operated at 900°C (Marklund, 2002). The liquor droplets undergo rapid drying and pyrolysis as it moves towards the bottom of the boiler and lands on a char bed where complete char conversion takes place releasing inorganic salts from the char (Kocurek, 1989). The inorganic salts melt at these operating temperatures and form a smelt which is removed via smelt spouts.

Air from the primary air register controls the position and shape of the char bed, and facilitates char combustion. The secondary air register provides air that controls the position at the top of the bed and also burns pyrolysis gases and carbon monoxide from the bed. Complete combustion and mixing of the combustion gases occurs with air provided from the tertiary air register located above the liquor spray nozzles. (Kocurek, 1989)

As the combustible gases are burned by the air from the different heat registers, steam is generated in the waterfalls, superheaters, economizer and boiler bank. In a typical mill, this steam would then be used to run a steam turbine to produce electricity or utilised in other mill processes (Marklund, 2002).

2.2.1.2 Fluidised Bed Incinerators

Fluidised bed incinerators such as the Copeland reactor or combustor (Figure 2-3), is the most widely used in South Africa. These combustors are used in processes where the inorganic material is recovered in a dry form and no pulping chemical recovery exists. It operates at 760°C-871°C and is used to incinerate sludge or shredded material in a bubbling bed or circulating bed design. Inert particles such as silica or sand etc. are used as bed material. Combustion air is used as the fluidising medium and enters at the bottom of the vessel. For in-situ acid gas neutralization applications, lime or limestone can be added to the fluidised bed. (Orr et al, 2000)

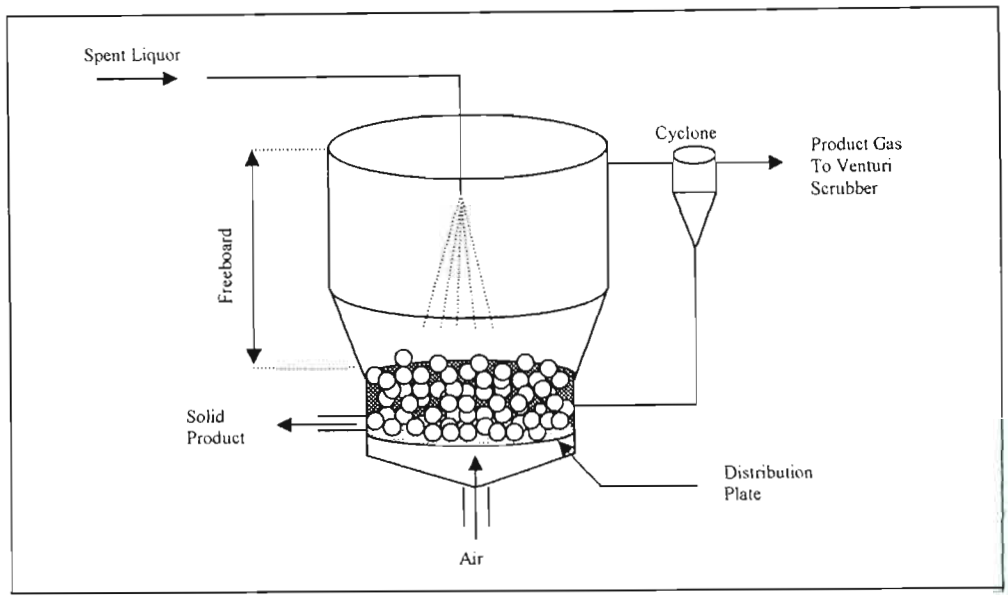


Figure 2 - 3: Sketch of a Fluidised Bed Combustor (Hanway, 1970)

2.2.1.2. a Combustor

Most non-wood pulping processes use sodium hydroxide or caustic soda in the pulping chemistry. Due to the size of most mills and the presence of silica in the raw material; the use of a lime kiln to re-burn lime, after converting sodium carbonate back to sodium hydroxide, is uneconomic. Hence mills burn the liquor in a fluidised bed but recover no energy or pulping chemicals. The by-product bed material sodium carbonate (soda ash) is sold.

The use of fluidization technology in the recovery of pulping chemicals in the pulp and paper industry is relatively new (Hanway, 1970). Commercial scale combustor units have found applications in the recovering of pulping chemicals from soda liquor.

Spent liquor is injected into the freeboard region of the combustor unit. This unit is operated at temperatures close to the fusion point of the bed therefore this process is known as a freeboard-feed agglomerative process. The controlling mechanism is the chemical reaction and the kinetics are not limited by heat and mass transfer effects. (Hanway, 1970)

2.2.1.2. b Operation of Combustors

Spent liquor is concentrated to 35% total solids in an evaporator train in order for the organics to sustain the autogeneneous oxidation during incineration. The concentrated liquor is then fed into the combustor unit and injected into the freeboard region. Water present in this concentrated liquor is evaporated with the formation of carbon dioxide and water vapour by the oxidation of the organics in the liquor.

Sodium sulphite, sodium sulphate and sodium carbonate are also present in the spent liquor. Sodium sulphite present in the spent liquor is converted to sodium sulphate. The residual inorganics in the form of sodium sulphate and sodium carbonate is deposited on the bed particles. Continuous depositing on the bed particles causes the bed particles to grow and this solid product is removed to maintain a constant bed inventory. Product gases from the combustor unit are directed to a cyclone and then to a venturi scrubber. The solid sodium sulphate and sodium carbonate product is spherical in shape and is a valuable by-product. (Hanway, 1970)

2.2.1.3 Rotary Kiln Incinerators and Fixed Hearth Incinerators

Rotary Kiln and Fixed Hearth incinerators are two stage combustion processes. The rotary kilns are cylindrical units positioned at an incline and operate at very high temperatures. They are used to dispose of a wide variety of waste feeds such as solid wastes, slurries and liquids. The two stages are the rotary kiln and the afterburner stage. Rotation of kiln ensures that the waste material is mixed. In the combustion chamber wastes are converted to gases through a series of volatilisation, destructive distillation, and partial combustion reactions. Combustion of gas species is then completed in the afterburner.

In a fixed heart incinerator, the first stage at 649-982°C, ensures that the waste material is burned in the absence of air/oxygen i.e. under pyrolysis conditions. Thereafter, pyrolysis products and smoke enter the second stage where excess air is used to complete the combustion process.

2.3 Fundamentals of Spent Liquor Conversion in a Recovery Boiler

2.3.1 Introduction

Most spent liquor combustion studies reviewed use the term "black liquor" to describe spent liquor. Therefore, it should be mentioned that the spent liquors used in these studies differ with respect to their chemical composition. As pointed out earlier, the chemical composition is dependent on the pulping chemistry.

Spent liquor combustion research began as early as 1963 with work done by Monaghan and co-workers. Using a single drop combustion technique and calcium-sulphite liquor droplets, Monaghen established that combustion occurred in separate stages.

However, work done by Hupa et al. (1987), using a similar experimental technique, identified and labelled these stages. Kraft and soda-based liquor were used in this investigation. Four stages were identified, namely; drying, pyrolysis, char burning and

inorganic reactions stage with the first three stages forming the burning stages (Whitty et al., 1997). In addition, they also evaluated the combustion behaviours of these liquors.

Most literature after 1987 use the term devolatilisation to refer to pyrolysis; and inorganic reactions stage as smelt reactions or smelt formation stage. Macek (1999) reports spent liquor combustion to consist of the following stages: heat up to the boiling point, drying, devolatilisation, combustion of volatiles, combustion of char and smelt coalescence. Other researchers such as Grace et al. (1986) refer to pyrolysis as the volatiles burning stage. Marklund (2002), on the other hand, refers to the char burning stage as the char conversion stage. However, from all the literature reviewed, the general idea of spent liquor combustion is the same

Further work followed and researchers Frederick et al. (1994) examined the effect of recovery furnace variables namely; temperature and gas composition, on the swelling of spent liquor droplets during devolatilisation. They developed a relationship for this.

A more comprehensive study was carried out by Whitty et al. (1997) using various kraft, soda and sulphite liquors with the aim of measuring the specific burning properties of these liquors. Four different reactors were used and measurements where made over a wide range of temperatures and pressures. A single-droplet muffle furnace, a tube reactor, a pressurized grid heater and a pressurized thermogravimetric reactor was used in their investigations.

Fundamentals of spent liquor combustion have been well accepted by the research community, throughout the world. Since the fundamentals of spent liquor combustion are well established, modelling studies based on single drop combustion have recently begun to gain momentum. Most of the literature, today, is based on the development and improvement of existing models. Details of the modelling studies will not be of interest to this study, however the details of spent liquor combustion are.

2.3.2. Spent Liquor Combustion Stages

The importance of this section is to give the reader some insight into spent liquor combustion since the ***conversion of spent liquor droplets in a gasifier is similar*** (Marklund, 2002). The only distinguishing characteristic of spent liquor conversion in gasification is that after the initial drying and devolatilisation stages, the char that is formed is gasified and depending on the temperature, smelt formation may or may not occur. In combustion processes, the char that is formed is combusted with the oxygen from air in the char burning stage (Whitty et al., 1997).

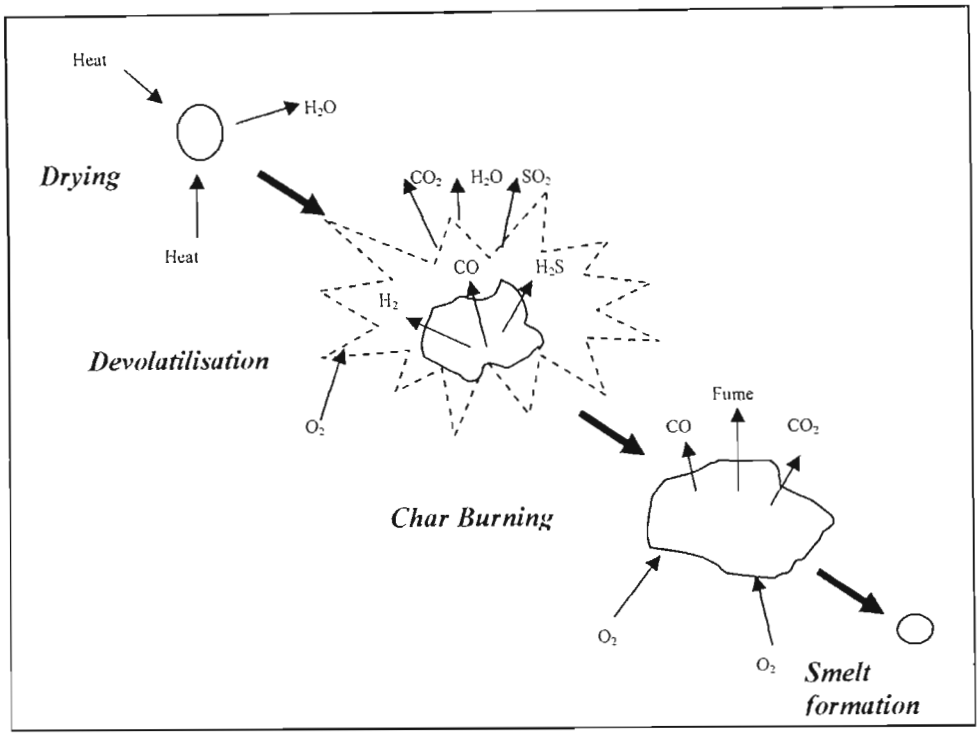


Figure 2 - 4: Spent Liquor Conversion (Grace et al., 1986)

It is apparent from the literature reviewed, that the general concept of spent liquor combustion is the same. When spent liquor is sprayed into the recovery boiler, it is exposed to hot gases. As a result, these finely dispersed droplets undergo drying, devolatilisation, char burning and smelt formation (Figure 2-4).

In drying, water from a spent liquor droplet is removed and becomes a major heat sink. The rate at which the droplet dries is controlled by heat transfer. In this stage, the droplet begins to expand.

Devolatilisation of the spent liquor droplet then takes place. During this stage, the organic matter in the liquor degrades, forming various combustible gaseous compounds from volatile substances (Marklund, 2002). Grace, as cited by Marklund (2002), states that the gases that form are hydrogen, carbon monoxide, methane, total reduced sulphur (TRS) gases, carbon dioxide, water and heavier carbonates. These gases burn when they contact air. Grace et al. (1986) reports, that the devolatilisation rate is temperature dependent and is a relatively fast process. They also suggest that this stage is the source of the sulphur gases namely, hydrogen sulphide and sulphur dioxide. The spent liquor droplet undergoes morphological changes and is transformed into a swollen, porous char particle with a considerable part of it made up of inorganic salts namely, sodium carbonate, sodium sulphide, sodium sulphate, and corresponding potassium salts.

The last stage is char burning. In this stage there is no visible flame with burning occurring on the particle. Any residual carbon is burnt out with the inorganics present in a molten state. It is important to note that sulphur reduction occurs with sulphur reduced to sulphide. Temperature and air supply govern the rate of the char burning stage. Unlike the devolatilisation stage, char burning is a relatively slow process and maybe the source of volatile inorganics. (Grace et al., 1986)

Grace, as cited by Marklund (2002), reports that in this stage, mainly gas phase species react with the organics in the char to produce gases. The following reactions that take place in the conversion of carbon in char:

$$C + \tfrac{1}{2} O_2 \rightarrow CO \quad (2\text{-}2)$$

$$C + O_2 \rightarrow CO_2 \quad (2\text{-}3)$$

$$C + CO_2 \rightarrow 2CO \quad (2\text{-}4)$$

$$C + H_2O_{(g)} \rightarrow CO \quad (2\text{-}5)$$

$$C + \tfrac{1}{2} Na_2SO_4 \rightarrow CO_2 + \tfrac{1}{2} Na_2S \quad (2\text{-}6)$$

$$C + \tfrac{1}{4} Na_2SO_4 \rightarrow CO + \tfrac{1}{2} Na_2S \quad (2\text{-}7)$$

Reactions 2-4 and 2-5 are gasification reactions and char combustion will be dependent on these reactions when the oxygen concentration is low, as the oxygen available will be consumed by the combustion of gases surrounding the particle. (Marklund, 2002)

Finally, after the residual carbon is burnt off, the char particle collapses into a small droplet of smelt hence smelt formation. It consists of inorganic salts namely; sodium sulphide, sodium carbonate, and to a lesser degree sodium sulphite and sodium chloride.

2.3.3 The Sulphate-Sulphide cycle

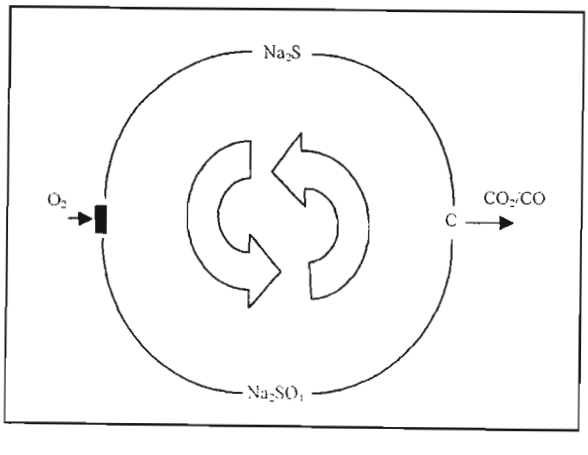


Figure 2 - 5: The sulphate-sulphide cycle (Grace et al., 1986)

The sulphate-sulphide cycle (Figure 2-5) permits two contradictory processes, namely; carbon burn-up and sulphate reduction, to take place simultaneously. (Grace et al., 1986)

The main aspect of this cycle is that the direct oxidation of carbon during char combustion does not take place; instead oxygen reacts with sodium sulphide in an oxidation reaction to from sodium sulphate (Macek, 1999). Carbon reacts with the oxygen associated with sodium sulphate and reduces sodium sulphate to reform sodium sulphide. Carbon dioxide and carbon monoxide are also formed. Sodium sulphide then reacts with oxygen and the cycle continues (Grace, 1986).

Grace et al. (1986) report that the relative rates of sulphide oxidation and sulphate reduction determines the reduction efficiency. For example, if the rate limiting step is the oxidation of sulphide by air, carbon will react with sulphate as soon as it is formed and keeps the sulphate concentration low thus resulting in high reduction efficiency.

Macek (1999) points out that the desired products of char reactions for a recovery boiler is the formation of sodium sulphide and sodium carbonate. Sodium sulphate is also formed but is undesirable from a chemical recovery point of view as it leads to increased dead-load in the chemical recovery system. However, formation of sodium sulphate in an oxygen environment is inevitable due to the sulphate-sulphide cycle.

2.4. Concerns with Chemical Recovery Boilers

Some recovery boilers are reaching the end of their service lifespan. The pulp and paper industry are aware of this and are faced with the decision of either renovating the old unit or building a new one.

The thought of having to build a new one is based on the EPA's MACT (maximum achievable control technology) regulation, which requires more stringent and sophisticated pollution prevention equipment to be installed.

Consequently, such equipment is expensive but must be installed in older units in order to comply with environmental regulations. As a result costs escalate to such an extent that these costs are comparable to building a new recovery boiler, especially when downtime is considered.

In addition, the recovery boiler constitutes a safety hazard. This is due to the catastrophic explosions that plague recovery boilers. These explosions are generally caused by cracked water tubes in the unit. As a result, smelt contact with water causes a rapid generation of steam and ultimately an explosion.

2.5 Gasification

2.5.1 Introduction

From a technological point of view, gasification has the ability to revolutionise the chemical processing industry with a cleaner way of operating. At a time where environmental pollution is prevalent, gasification may provide the answer.

One of the major advantages of gasification is the ability to produce synthesis gas, which can be used to generate electricity, making industries less reliant on fossil fuel power. In addition, the ability to process a variety of potential feedstocks, such as sewage sludge and hazardous waste, makes it a very attractive and versatile option (Figure 2-6). Furthermore, the financial aspects of constructing and operating a gasification process, is many times cheaper than constructing and operating an incineration process, making gasification an appealing alternative. Also, the great promise of the gasification process is that it may be able to provide a commercially viable recovery process for the various types of sulphite pulping processes.

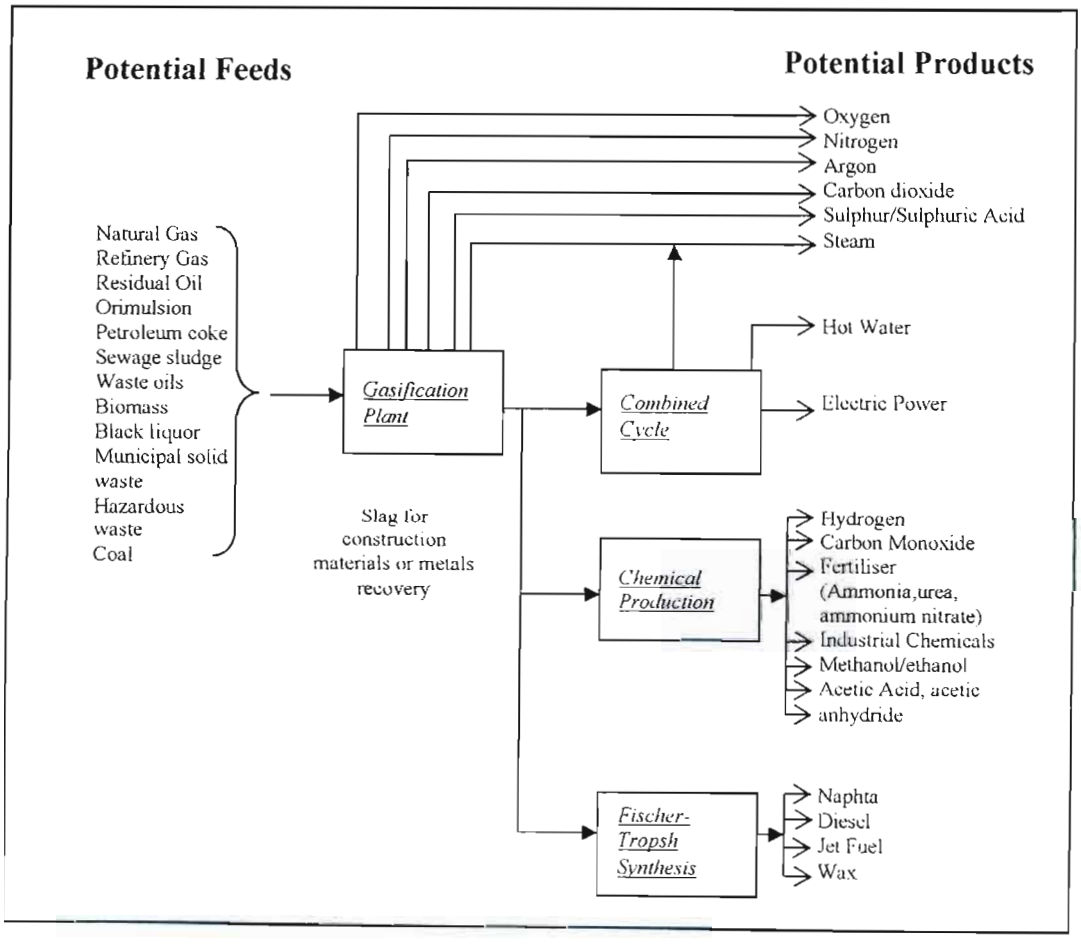


Figure 2 - 6: Potential Feeds and Products (Phillips, 2002)

2.5.2 Definition of Gasification

The Gasification Technologies Council (GTC) has proposed the following definition of gasification which was reported by Orr et al. (2000).

- "A process technology that is designed and operated for the purpose of producing synthesis gas (a commodity which can be used to produce fuels, chemicals intermediated products, or power) through the chemical conversion of carbonaceous materials.
- A process that converts carbonaceous materials through a process involving partial oxidation of the feedstock in a reducing atmosphere in the presence of steam at temperatures sufficient to convert the feedstock to synthesis gas, to convert inorganic matter in the feedstock (when the feedstock is a solid or semi-solid) to a glassy solid material known as vitreous frit or slag, and to convert halogens into the corresponding acid halides.
- A process that incorporates a modern, high-temperature pressurised gasifier (which produces a raw synthesis gas) with auxiliary gas and water treatment systems to produce a refined product synthesis gas, which when combusted produces emissions in full compliance with the Clean Air Act."

2.5.3 Motivation for Gasification Technology

In 1970's, the papermaking industry had to bare the unprecedented increases in oil prices. This devastated not only the papermaking industry but all industries that were dependent on fossil fuel power. Many governing bodies decided that a need for alternative energy source was required so that a crisis like this could be averted in the future.

Many technological options were proposed but one with greatest promise was the use of gasification technology. Gasification is able to produce a synthesis gas that can be used to generate electricity for the plant via gas turbine technology, making the plant self sufficient. This meant that;

- the energy/power requirements of the plant are satisfied "in-house".
- reduced dependence on fossil fuel energy for meeting power requirements.

An integrated combined cycle gasification system (IGCC) or gasifier combined cycle (GCC) cogeneration systems was born with the benefit of environmental friendly technology combining to produce electricity. The idea behind IGCC and GCC technology is the same.

2.5.4 Benefits of Gasification

- The technology is environmentally sound – "*green technology*"
  - Reduced SO_x and NO_x emissions.
  - Reduced greenhouse gas emissions.

- Able to ***process a wide-variety of feedstock*** such as low value materials, wastes or refinery discards, viz:
  - Sewage sludge
  - Biomass
  - Municipal solid wastes
  - Refinery gas

- Electricity generator
  - Key to "***self-sufficiency***" using gas turbine technology.
  - Reduced fossil fuel energy dependence.
  - Defence against oil price hikes.

- The synthesis gas of ***great value*** (Phillips, 2002)
  - Provides a fuel source.
  - Can be used as feedstock for the manufacture of a range of petrochemicals or transportation fuels of high quality from low value feedstock.

- Operations – a ***technological advancement*** (Rockvam,2001)
  - Lower maintenance and operating costs.
  - Offers more stability and better to operate.
  - Better reliability.
  - Recover more energy.
  - Process liquors of different chemistries.

2.5.5 Applications of Gasification Technology (Phillips, 2002)

There is a great demand for petroleum products in today's market which may have put some strain on the petroleum industry. Gasification can be used to meet these demands with the added advantage of producing high quality petroleum products from low value feedstock (Phillips, 2002).

Underground coal gasification (UCG) is the process in which the gasification of coal takes place in situ with the resulting syngas used after extraction from production wells. This technology is used by coal producing countries like India, Australia and China. The Soviet Union was the first to commercialise this technology in 1952. Due to greater environmental benefits with UCG, there has been a renewed interest in this method of coal recovery.

In the mineral industry, direct reduced iron is a raw material for making steel. It is made by the reduction of iron ore with carbon monoxide and/or hydrogen gas. Currently, countries in the Middle East and some American countries use the carbon monoxide/hydrogen reducing

gas prepared from available natural gases. Phillips (2002) believes that the reducing gas could be made equally well from low value refinery residues using gasification technology.

2.5.6 Classification of Gasification Processes

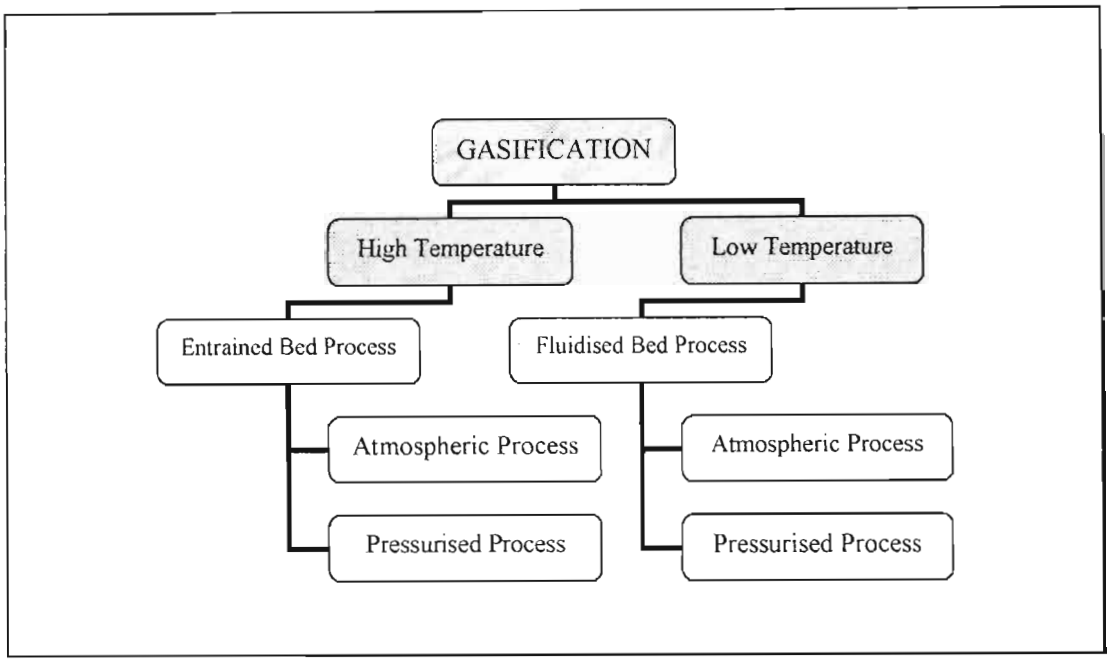


Figure 2 - 7: Classification of Gasification Process

Gasification processes can be divided into two categories as shown in Figure 2-7: low temperature and high temperature. This classification is made on the basis of the physical state of the inorganic salts which remain after gasification.

These categories are further sub-divided into atmospheric or pressurised processes. Pressurised processes offer the following benefits:

- Reduced size of process equipment.
- In conjunction with combined cycle power generation, plants would be able to double the electrical energy production from spent liquor.(Kelleher, 1985)

2.5.6.1 Low Temperature Gasification (Zeng et al., 2000)

Low temperature gasifiers operate at temperatures below the melting point of the inorganic metal salts. This ensures that these salts leave the gasifier as dry solids. Fluidised bed reactors are used for low temperature gasification.

The advantages are:

- There are no smelt-water explosions (no molten phase).
- A higher power-steam ratio is attainable.

The disadvantages are:

- Slow carbon gasification.
- Low sulphate reduction rates.

2.5.6.2 High Temperature Gasification (Zeng et al., 2000)

High temperature gasifiers operate at temperatures above the melting point of inorganic metal salts. Consequently, the inorganic metal salts leave the gasifier as a molten smelt. Examples of these gasifiers are entrained bed process reactors which are typically oxygen or air-blown reactor.

The advantages are:

- There are no kinetic limitations.

The disadvantages are:

- The formation of smelt – maintenance problems.
- Sodium emission rates are high – alkali aerosols (fume) cause gas turbine blade corrosion. (Dickenson et al., 1998)

2.6 Coal Gasification

2.6.1 History of Coal Gasification

In the 1930's, gasification processes employed stationary or slowly moving fixed-beds; fluidised beds and entrained bed processes. These processes were commonly referred to as the Lurgi, Winkler and Krupp-Koppers processes respectively.

Early coal gasification processes where used to generate electricity with the synthesis gas later used to manufacture petrochemical products. However, many of these processes were not very efficient and resulted in the formation of coke and tar. This led to development of higher carbon conversion, more efficient processes, which reduced the formation of these unwanted by-products and ensured a greater utilisation of the chemical energy stored in coal.

Hotchkiss (2003) reported that fixed bed systems were more stable to variations in fuel, air or steam flow. In addition, internal heat exchange offered greater chemical energy recovery in the product gas, in relation to the sensible heat. The major problem faced by this system was the large extent of tar generation. Fluidised bed systems were reported to use finer coal sizes than fixed beds and was capable of gasifying certain variety of coals. Entrained systems were found to use finely ground coal but their low fuel inventories made them very sensitive to control of the oxidant to fuel ratio. However, improved carbon burn-up was achieved at elevated reaction temperatures.

2.6.2 Background

2.6.2.1 Fixed Bed Gasification Technology

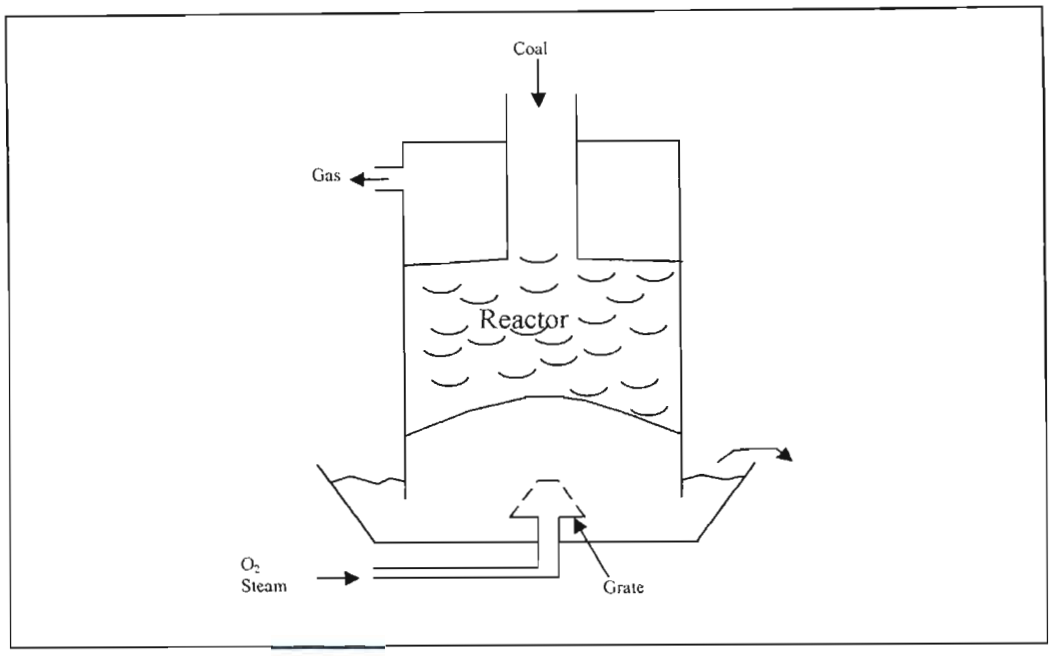


Figure 2 - 8: Simple sketch of a Fixed Bed Reactor [Lurgi Process] (Cornills, 1987)

Fixed bed process such as the Lurgi process (Figure 2-8), uses conventional lump coal as feed. An oxygen/steam mixture is fed in at the bottom of the gasifier and fresh coal enters from the top. Both of which enter at relatively low temperatures. This counter current movement of the coal and gas, ensures that the heat is well utilised. However, disadvantages include coal carbonization and by-products formation such as tars, phenols, methane and oils. In the Lurgi processs, coal of 10-50mm size range is fed intermittently into the Gasifier at operating conditions of 20-30 bar and temperatures as high as 650°C.

2.6.2.2 Fluidised Bed Gasification Technology

The behaviour of the fluidised beds makes it possible for a continuous through-put of the coal. This can be attributed to the *constant temperature distribution and good heat conversion* with the reduction in the formation of impurities such as methane and tars in the synthesis gas. However, back-mixing of fresh coal with reacted coal is a problem because unreacted carbon is removed. Since the application of fluidised bed technology involves operating under dry conditions, the melting point of the feed is an important factor. Therefore, a fluidised bed gasifier must operate at a temperature below the melting point of the feed, in this case below the ash melting point of coal.

In the Winkler process (Figure 2-9), finely grained coal, with a diameter of no greater than 6mm is fed continuously to the bottom section of the fluidised bed gasifier. The fluidised bed

gasifier operates at atmospheric pressure and at a temperature of 900°C. Oxygen and steam are used to fluidise the bed.

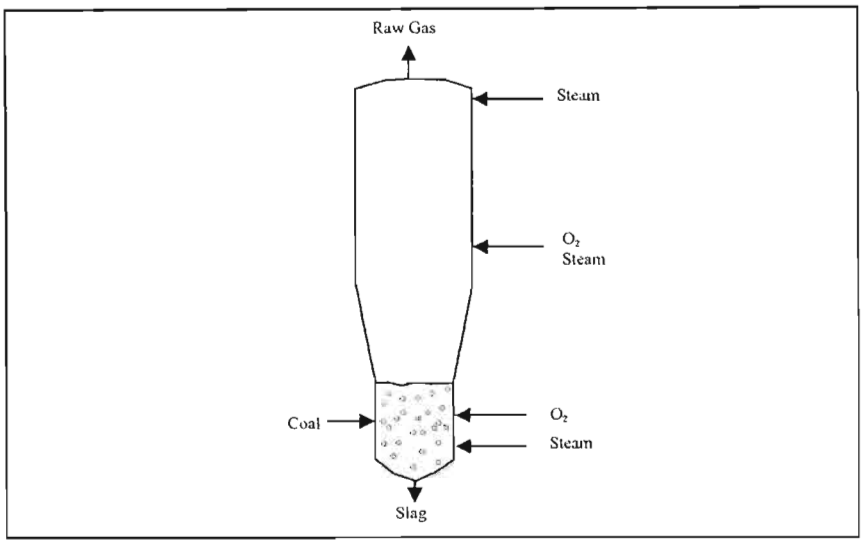


Figure 2 - 9: Simple Sketch of Fluidised Bed Reactor [Winkler Process] (Cornills, 1987)

2.6.2.3 Entrained Bed Gasification Technology

The Krupp-Koppers/Koppis-Totzek process (Figure 2-10) is based on entrained-bed technology. Fine grained coal (less then 0.7mm) is gasified co-currently with steam and oxygen at temperatures above the melting point of ash and at atmospheric pressure. At this temperature, agglomeration is favoured, with the formation of molten material or slag. Coal dust from coal mining can also be processed using this technology.

Entrained bed technology is renowned for producing a product gas that has no by-products such as tars, phenols or oils. In addition, high conversion efficiencies can be attained due to the high operating temperatures.

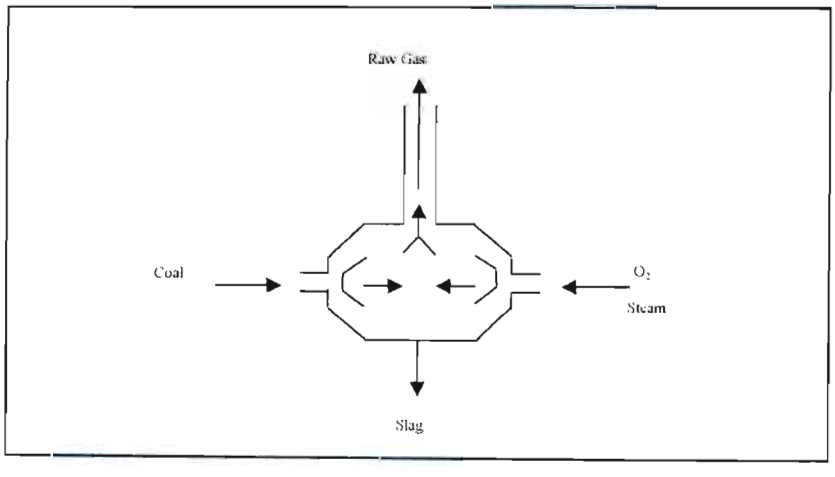


Figure 2 - 10: Simple Sketch of Entrained Bed Reactor (Cornills, 1987)

2.7 Spent Liquor Gasification

2.7.1 Introduction

Research into spent liquor gasification began as early as 1960 with a pyrolysis study by Gauvin and co-workers, using the atomised suspension technique (AST). In the AST process, concentrated spent liquor is sprayed into a tubular reactor. Thereafter, the atomised liquor undergoes evaporation and thermal decomposition in the absence of air. Further work on a pilot-scale AST reactor was conducted, at wall temperatures of 750°C-850°C and at pressures of 2 atm using neutral sodium-base liquor (Gauvin et al., 1960).

Prahacs (1967) later carried out tests on the above pilot plant AST reactor, using neutral sodium-based liquor at 800°C with air and noted that at this temperature there was significant hydrogen sulphide production. However, there was no notable reduction of sulphate to sulphide except in the absence of air.

Around this time, a two-stage experimental unit was designed, constructed and operated to pyrolyse and completely gasify the organics in concentrated pulping liquors. The concentrated pulping liquors used in this study were kraft and neutral sulphite semi-chemical (NSSC) pulping liquors. The unit was called the pyrolysis–gasification-combustion (PGC) reactor. The first stage was used for pyrolysis and gasification reactions at a maximum temperature of 700°C. The first stage was similar to the AST design by Gauvin et al. (1960). The second stage ensured that complete combustion of pyrolysis products occurred, with air or air/oxygen mixture. The temperature in this stage was controlled by the gas mixture. The maximum permissible temperature in the second stage was 1100°C. However, no results were given. (Brink et al., 1975)

In 1978, Rockwell International in an experimental study evaluated the possibility of converting spent liquor into a valuable product gas so that it could be used as a fuel. This study was conducted in a lab-scale molten salt pool gasifier with dried spent liquor injected with air into the melt. Although this study proved that spent liquor could be converted into a valuable product gas, a major problem was encountered. The pre-dried spent liquor made it difficult for it to be injected. (Kohl, 1986)

In 1982, a follow up study by Rockwell, with the support of the U.S. Department of Energy (DOE), aimed at investigating the feasibility of Kraft spent liquor gasification and composition of the product gas. Tests were carried out on a bench-scale molten salt gasifier with a sodium carbonate melt, operating at a 1000°C. Air/oxygen was added with the spent liquor. This study was not very successful with the product gas from air blown gasification not able to produce a product gas with a sufficiently high heating value which was required for direct firing in a combustor gas turbine. Consequently, major turbine development and redesign would be necessary to accommodate the low heating value product gas. However,

with air-oxygen blown gasification, the required heating value product gas was achieved. In addition, poor reduction of sulphur compounds to sulphide was noted. Rockwell explained that the poor performance was due to the high concentration of water in the spent liquor. (Kelleher, 1984)

Further work, by Rockwell led to an improved system, which later led to the development of the spent liquor gasification process which was based on the concept of a two-zone gasification system. (Figure 2-11)

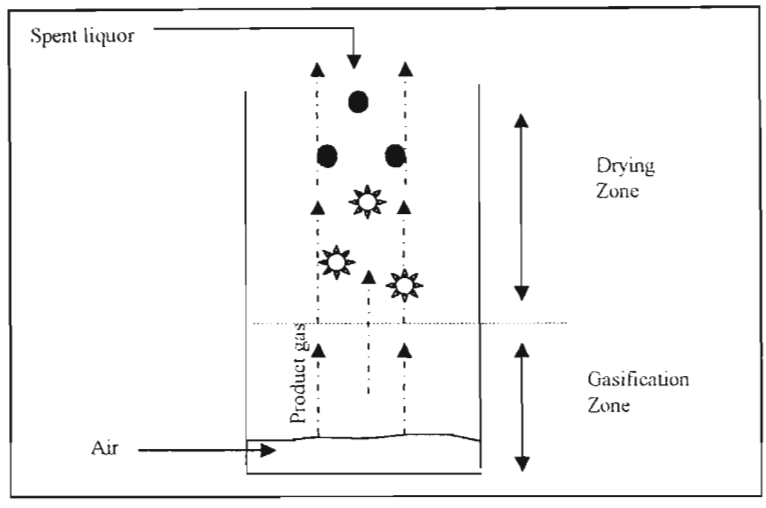


Figure 2 - 11: Simple Sketch of the Two-Zone Molten Gasifier

This was a great feat of engineering. The idea was to avoid pre-drying of spent liquor. In this two-zone gasifier, spent liquor was first dried by the counter-current contact with hot product gas in the drying zone. The product gas loses heat to the spent liquor and is therefore cooled. In the gasification zone, the lower zone, gasification of spent liquor occurs with air, at a temperature of 870^0C to 1040^0C.

Two important results for satisfactory reduction were noted. Firstly, the bottom of the gasifier should be free from water and secondly, the conditions in the melt should be strongly reducing. In addition, the gas heating value is a convenient indicator of the reducing conditions since the combustible gases (syngas) represent key reducing agents. (Kohl, 1986)

A few years later, the kinetics of spent liquor gasification from Kraft pulping liquor was studied thermogravimetrically by Li et al. (1989). Carbon dioxide was used to gasify the spent liquor char at temperatures as high as 775°C. From their results, they found that spent liquor char was significantly more reactive than sodium carbonate catalysed coal char. It was believed to be due to a large number of carbon free sites, formed during pyrolysis from the highly dispersed sodium salts in the spent liquor char. Further evidence of the unique gasification properties of spent liquor char was obtained by them using a scanning electron

microscope and energy dispersive spectroscopy (SEM-EDS) mapping and line scan techniques (Li et al, 1990a).

A further study by Li et al. (1990b) investigated sodium emission during pyrolysis and gasification of spent liquor char by the same method. These experiments where carried out at temperatures below 800°C with pyrolysis occurring in a helium atmosphere prior to gasification with carbon dioxide. Results from this study showed that sodium emission increases at higher temperatures (675°C – 800°C) and is a function of the final pyrolysis temperature with negligible emission of sodium during gasification.

Pressurised gasification studies were reported by Frederick et al. (1991, 1993). This study was also conducted in a thermogravimetric unit at temperatures in the range of 600-800°C and pressures of 1-30bar. Gasification of spent liquor char was carried out with carbon dioxide. An important result from this study was that increasing the total pressure slowed down the gasification rate. A decrease in gasification rate by a factor of 4-6 was reported as pressure increased from 1-30bar. In addition, gasification rate was found to be strongly temperature dependent even at higher pressures i.e. gasification rate increased with temperature.

Other researchers involved in pressurised gasification studies of spent liquor char were Whitty et al. (1995). Steam gasification of spent liquor char was investigated using thermogravimetric analysis. The results from these studies indicate that steam gasification reactions are temperature sensitive and that the gasification rate decreases with increasing pressure. However, Whitty reports that the rate of gasification with steam is far higher than with carbon dioxide (approximately 4 times higher).

One of the most important kinetic studies of spent liquor gasification was conducted by Li et al. (1991b). Steam was used to gasify spent liquor char in a thermogravimetric unit at a maximum temperature of 700°C and at atmospheric pressure. Reactions proposed by them are given in the next section. Also investigated in a later study by Li (1994) was the rate process of hydrogen sulphide emission during steam gasification of spent liquor char. A similar experimental system was used at temperatures of 600-700°C and atmospheric pressure. Important result from this work was that the hydrogen sulphide emission rate increases with increasing temperature and verifies Prahacs (1967) observations. In addition, hydrogen sulphide emission reaches a maximum at 700°C but stopped when all the carbon was gasified.

Pyrolysis and steam gasification processes of spent liquor were conducted by Demirbas (2002). A tubular reactor was used and placed in an electric heater at pyrolysis and gasification temperature ranges of 500-800K and 275-1350 respectively.

The following conclusions from the above studies were arrived at:

- It has been shown that reduced water concentration in spent liquor would ensure better performance.
- Spent liquor char is more reactive than coal due to the highly dispersed sodium salts in the liquor
- The sodium emission increases with increasing temperature.
- Increasing the total pressure reduces the gasification rate considerably.
- Hydrogen sulphide emission rate increases at higher temperatures and reaches a maximum at 700°C.

2.7.2 Chemistry of Gasification

Li and van Heiningen (1991b) proposed that the following reactions take place in steam gasification of spent liquor:

$$C + H_2O \leftrightarrow CO + H_2 \quad (2\text{-}8)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (2\text{-}9)$$

$$C + 2H_2 \leftrightarrow CH_4 \quad (2\text{-}10)$$

$$Na_2S + H_2O + CO_2 \leftrightarrow H_2S + Na_2CO_3 \quad (2\text{-}11)$$

Reaction (2-8) is the gasification reaction and (2-9) is the water-gas shift reaction. Taylor et al. (1921) points out that reaction 2-8 maybe faster than reaction 2-9 in the absence of a catalyst.

In their investigations, Taylor et al. (1921) found that the potassium and sodium carbonates where the best and only efficient catalysts for catalysing the carbon-steam reaction (2-8) with potassium catalyst being the most reactive of the two. Carbon dioxide–carbon interactions where also accelerated by these catalysts. They reported that other alkalies and alkaline earths have only a slight effect.

In spent liquor gasification, it is possible to separate sodium and sulphur. This is important because in current recovery furnaces oxidized sulphur forms, add to the dead load chemicals as seen in the Table 2-2 below. Dead load chemicals reduce the digester yields. Spent liquor gasification with steam, such as the ThermoChem process (Rockvam, 2001), has shown that in this low temperature gasification process separation of solid sodium carbonate is possible. Furthermore, this process eliminates the oxidized form of the sulphur thereby reducing dead load chemicals.

One of the major problems facing spent liquor gasification research is the production of hydrogen sulphide in the synthesis gas. Sadowski et al (1999), suggest producing a separate stream of hydrogen sulphide from the synthesis gas and then removing the sulphur; thereby, making it possible to apply polysulphide generation to the digesters. The point is that the

clean synthesis gas (i.e., no sulphur) can then be used in new gas turbines, and existing boilers and kilns. Unclean synthesis gas will cause physical damage like corrosion to equipment.

	Spent liquor	White Liquor
NaOH	6-7	53
Na_2S	19	21
Na_2CO_3	36	15 (partially dead load)
Na_2SO_3	9	3 (dead load)
Na_2SO_4	13	5 (dead load)
$Na_2S_2O_3$	16	3 (dead load)

Table 2 - 2: Typical Liquor Consumption, by percent of weight (Sadowski et al., 1999)

2.7.3 Mechanism of Alkali Catalysts

Numerous mechanisms for alkali metal catalysed gasification of char have been reported in the literature (Wood et al., 1984; Mckee, 1983; Chen et al., 1993).These mechanisms can be classed according to the following: oxygen transfer, electrochemical or electron transfer, and a third group consisting of intermediates such as charge transfer complexes, electron donor acceptor complexes, and intercalate or lamellar compounds (Sams et al., 1986).

The oxygen transfer mechanism seems to be the most popular of mechanisms. Sams et al. (1986) describes this mechansim as having an oxidation/reduction cycle in which the catalyst continuously cycles between the oxidised and reduced form. The reduced form is said to be a highly reactive compound that acts as an oxygen carrier. It is believed to split the gaseous reactant and transfer the oxygen atom to the carbon surface where it reacts with the carbon substrate to form carbon monoxide. Consequently, the carbon monoxide reduces the catalyst compound and the cycle is said to be complete.

The McKee et al. (1975) mechanism was a further development. In this mechanism, they believed that the alkali metal carbonate is reduced by carbon to the metal form. Thereafter, the gaseous species namely, steam or carbon dioxide oxidises the metal form into a metal hydroxide and metal oxide for steam and carbon dioxide gasification respectively. The reactive intermediates is said to be the free alkali metals and metal hydroxide and the active intermediates is said to be the free alkali metals and metal oxides (Sams et al., 1986).

In a more detailed mechanism for carbon dioxide gasification is given by Sams et al. (1986), the initial step is the reduction of the alkali metal (M) carbonate

$$M_2CO_3 \leftarrow C \rightarrow (-CO_2M) + (-COM) \qquad (2\text{-}12)$$

The subsequent step is the oxidation/reduction cycle

$$(-CO_2M) + C \leftrightarrow (-COM) + CO \qquad (2\text{-}13)$$

$$(-COM) + CO_2 \leftrightarrow (-CO_2M) + CO \qquad (2\text{-}14)$$

Sams et al. (1986) report that the ($-CO_2M$) and (-COM) are carboxylic and phenolic groups which are formed by the decomposition of carbonate on carbon sites. These are surface oxides.

In 1991, Li et al. (1991b) proposed a redox mechanism for steam gasification involving the transformation of alkali-metal surface oxide complexes. The initial step involves the reduction of the alkali metal carbonate by carbon.

$$M_2CO_3 \leftarrow C \rightarrow (-C\ (=O)-OM) + (-C-OM) \qquad (2\text{-}15)$$

This is based on the assumption that all the alkali metal surface complexes are formed by the reduction of carbonate by carbon. They believed that the carboxylic and phenolic surface oxides represented the oxidised and reduced forms in the redox mechanism. Two routes considered by them for the formation of carbon dioxide and carbon monoxide are:

Route 1:

$$(-C-OM) + H_2O \leftrightarrow (-C\ (=O)-OM) + H_2 \qquad (2\text{-}16)$$

$$(-C\ (=O)-OM) + C \rightarrow (-C-OM) + CO \qquad (2\text{-}17)$$

Route 2:

$$(-C-OM) + H_2O \leftrightarrow (-C\ (=O)-OM) + H_2 \qquad (2\text{-}18)$$

$$(-C\ (=O)-OM) + H_2O + C \rightarrow (-C-OM) + CO_2 + H_2 \qquad (2\text{-}19)$$

From route 1 reactions, the phenolic group is oxidised with the formation of the carboxylic group. This is then followed by the reduction of the carboxylic group to carbon monoxide and a phenolic group on the surface of carbon.

$$C + H_2O \leftrightarrow CO + H_2 \qquad (2\text{-}20)$$

The above gasification reaction is the overall result of route 1 reactions. Route2 reactions follow the similar idea.

Chen et al. (1993) showed that on an alkali-catalysed C-H_2O reaction, surface phenolate groups (-C-O-M) are not as active as clusters of M_2O (or M_xO_y). This demonstrated that M_2O clusters take an active part in H_2O dissociation to form O atoms. The carbon substrate contribution to H_2O dissociation activity is such that carbon serves as a scavenger or trap for O atoms and it reduces the oxidation state of M in the clusters.

2.7.4 Tar Formation

The following definitions of tars were reported by Sricharoenchaikul et al. (2002b).

- In biomass gasification, tars are defined as the organic matter that condenses downstream of the gasifier under normal process conditions.
- Tars are organic compounds with boiling points higher then a specified temperature.
- Any organic compound that condenses at or below the temperature of the tar-trapping system employed.

The above definitions of tars differ considerably and a proper definition of tars has not been established.

Tars (condensable organic matter) are the primary volatile product that is released during devolatilisation. In devolatilisation light gases and char is also produced. In addition, tars form semi-volatile compounds. Furthermore, secondary reactions transform tar compounds to lighter gases, lighter tar species and soot. (Sricharoenchaikul et al, 2002a)

In pyrolysis or gasification of biomass, tar occurs as follows (as stated by Evans and Milne and cited by Sricharoenchaikul (2002b)). It is dependent on process parameters such as residence time and reactor temperature.

1. Primary products: cellulose-, hemicellulose-, and lignin-derived products such levoglucosan, hydroxyl-acetaldehyde, furfurals, and methoxyphenol.
2. Secondary products: phenolics and olefins.
3. Alkyl tertiary products: methyl derivatives of aromatics such as methylacenaphthylene, methylnaphthalene, and toluene.
4. Condensed tertiary products: aromatic hydrocarbons without substituents such as benzene, naphthalene, acenapthylene, and pyrene.

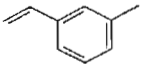
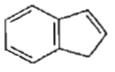
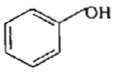
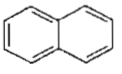
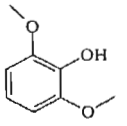
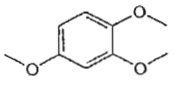
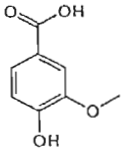
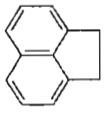
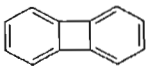
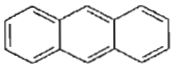
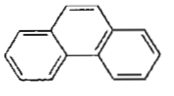
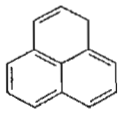
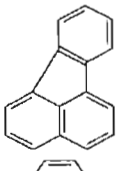
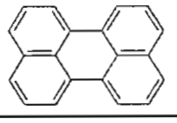
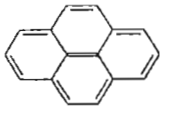
Compound	Structure	BP (°C)	Compound	Structure	BP (°C)
Benzene		80	Toluene		111
o-, m-, p-Xylene		139-145	Methylstyrene		170
Indene		181	Phenol		182
Naphthalene		218	2,6-Dimethoxy-phenol		234
Trimethoxy-benzene		247	Hydroxy-methoxy-benzoic acid		250
Acenaphthene		279	Biphenylene		(m.p. 109°C)
Anthracene		340	Phenanthrene		336
Phenalene		292	Fluoranthene		375
Perylene		350-400	Pyrene		404

Figure 2 - 12: Possible Tar Compounds from Spent Liquor (Sricharoenchaikul, 2002b)

2.7.5 Autocausticisation

Tucker (2002), reports that in autocausticisation, a portion of the sodium in the solid phase is combined with an autocauticising agent. As a result the formation of say sodium carbonate is prevented. Examples of autocausticising agents are titanium dioxide or sodium borate.

Autocausticisation has a number of advantages (Zeng et al., 2000):

- When sodium carbonate in spent liquor reacts with titanium dioxide, high melting (>/= 960°C) sodium titanates are formed thereby preventing smelt formation.
- Sodium emission is minimised.
- It is reported that due to the amphoteric character of titanium dioxide, hydrolysis of some of the sodium titanates into sodium hydroxide and a titanium dioxide-

containing solid phase occurs. This solid phase can then be recycled, so that the fossil fuel consumption in lime causticisation may be eliminated.

- Autocausiticising agents expand the operating window for higher temperatures operations and increased conversion of organic carbon in fluidised bed gasifiers.

2.8 Commercial Scale Applications (Finchem, 1995)

2.8.1 The ABB-CE Gasification process

2.8.1.1 Description

A circulating fluidized bed (CFB) is used in this gasification process. It operates at a temperature of 700^0C where spent liquor is partially combusted with air. A cyclone is used to remove particles present in the product gas. The bed material consisting of sodium carbonate and sodium sulphide particles is removed at the bottom of the reactor. Preheated air is used as the fluidizing medium. The bed material is dissolved in a dissolving tank to form green liquor which is made up of the dissolved sodium carbonate and sodium sulphide. The green liquor is causticised (green liquor is reacted with lime) to produce white liquor (sodium hydroxide and sodium sulphide). The product gas is passed through the cyclone and into a wet scrubber where the hydrogen sulphide is removed. The clean gas consisting of methane, carbon dioxide, carbon monoxide and hydrogen is then passed back into a gas heater located within the cyclone exit. The clean gas is sent to a power boiler. A superheater and evaporator located in the exit of the cyclone takes in the heat from the unclean product gas to produce steam.

2.8.1.2 Results

- The amount of hydrogen sulphide produced in the product gas varied inversely with temperature.
- The sodium carbonate was separated from sodium sulphide naturally in this process.
- There was no tar formation.
- Good carbon conversion efficiency was achieved.
- This has been claimed to be the most energy efficient process.

2.8.3 The Ahlstrom Kamyr Gasification Technology

2.8.3.1 Description:

This technology, utilizes a downflow pressurized reactor operating at temperatures above the melting point of the inorganics present in spent liquor.

2.8.3.2 Results:

- High Carbon conversion efficiencies were reported.
- Pilot system demonstrated no improved energy efficiency over traditional recovery boilers.

2.8.4 Babcock and Wilcock Process:

This process is a low temperature process i.e. operates at temperatures below the melting point of the inorganics in spent liquor. The reactor operates in a bubbling fluidized mode. The Babcock and Wilcock process is similar to the ABB-CE process. Steam and sub-stoichiometric amounts of pre-heated air is used to fluidise the bed. The particulate material present in the product gas is removed via a cyclone.

2.8.5 Kvaerner Pulping Process:

Kvaerner Pulping is a company widely known for their Chemrec Process which was the first spent liquor gasification system in commercial operation (Finchem, 1995). This commercial scale operation is located in Sweden and has been operating since August 1991.

2.8.5.1 Description

An entrained flow reactor, operating at 950°C and atmospheric pressure, is used to gasify spent liquor. An added feature in this process is that it utilises an integrated quench dissolver which is used to separate the entrained smelt and product fuel gas. Green liquor is thus formed and is then re-causticised in the caustic plant located in the mill. A venturi scrubber is used to wash the product gas followed by a hydrogen sulphide scrubber. The product gas is then suitable for burning in a power boiler.

2.8.5.2 Results:

- Product gas contained 10% moisture after leaving scubbers.
- Product fuel gas was about 75 to 95 Btu/scf but was dependent on spent liquor composition and stoichiometry.
- 95% reduction efficiencies were reported.
- >99% carbon conversions were reported.

2.8.6 The NSP Project

NSP is the Swedish abbreviation for New Kraft Recovery Process. This technology also uses gasification except this is accomplished in a series of units (Figure 2-13). Since there is a need for better process control, reduction in emissions, better energy efficiency, and a safer way of operating (non-explosion hazard); this process was developed.

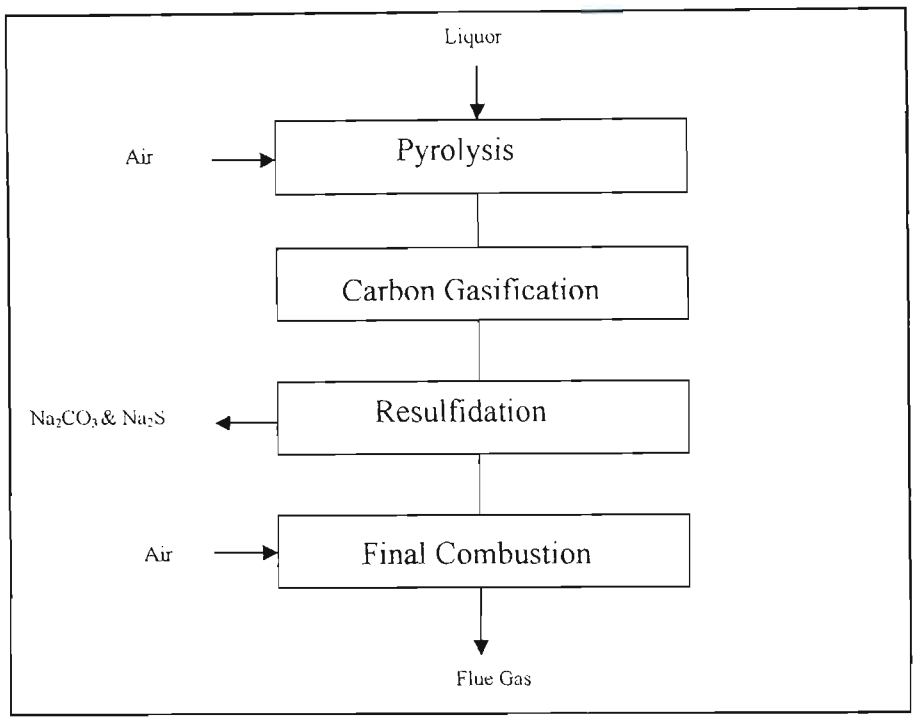


Figure 2 - 13: The NSP Project

2.8.7 The MTCI Steam Reformer (Rockvam, 2001)

Manufacturing and Technology Conversion International (MTCI), a company in the U.S, has developed a steam reformer for the gasification of spent liquor and biomass. The steam reformer is currently marketed by ThermChem Recovery International (TRI). It is available for use in spent liquor recovery and biomass applications (Rockvam, 2001).

In the reformer, steam reacts with spent liquor that is injected directly into a fluidized bed of sodium carbonate particles. The spent liquor droplets coat these particles uniformly, ensuring high rates of heating, pyrolysis and steam reforming (steam gasification).

The reformer operates at bed temperatures below the melting point of inorganic salts, thus preventing smelt formation altogether. In the reformer environment with no oxygen present, steam reacts with spent liquor endothermically to produce a hydrogen rich gas with a medium heating value. Rockvam (2001), reports that sulphur present in spent liquor is temporarily reduced to sodium sulphide. However, sodium sulphide is unstable in this environment and forms gaseous hydrogen sulphide and solid sodium carbonate.

2.8.7.1 Description of Steam Reformer

The steam reformer is operated at atmospheric pressure and at temperatures of 582°C to 620°C. Low pressure superheated steam is used to fluidise the bed at a low superficial velocity of 0.5m/s in a bubbling bed mode. Rockvam (2001), reports that the residence time

for the vapor/gas is 13-20 seconds and the carbon fluid-bed solids residence time is over 50-60 hours.

The walls of the reformer are lined with refractory material, and heat exchangers, with pulsed enhanced resonance tubes, are located within the bed. These heat exchangers provide heat for maintaining operating conditions and endothermic gasification reactions. Therefore, in order to sustain the life of the refractory and resonance tubes, these operating conditions are maintained. The resonance tubes have a heat transfer coefficient of five times greater then conventional fire-tube heaters. As a result, heat exchangers are reduced in size and cost.

In the steam reformer system, a part of the product gas is burned in the pulsed heater resonance tubes providing superheat for the fluidising steam and for gasification reactions. Rockvam (2001), claims that with such a feature, the steam reformer is self sufficient on its own fuel.

Gases leaving the pulsed heater resonance tubes are sent to a heat recovery steam generator. Particulate material from the product gas is removed and the particulate-free product gas is then sent to a second heat recovery steam generator. The cooled product gas is then quenched and scrubbed.

A high quality product gas is produced in this process which can be combusted to produce fuel for boilers and gas turbines with reduced emissions to the environment, reduced scrubbing costs and reduced pressure drop constraints.

Product gas at 590°C exits the reformer and is sent to a bank of high efficiency cyclones for removal of entrained solids. It is then sent to a heat recovery steam generator for gas cooling. A wet venturi scrubber is used to remove fine particulates that escaped the cyclones and condenses hydrocarbons present in the product gas.

2.8.7.2 Results

- The product gas from the reformer typically consisted of hydrogen, carbon dioxide, carbon monoxide, methane and other higher hydrocarbons with volumetric concentrations of 73%, 14%, 5%, 5% and 3% respectively (after H_2S removal).
- A heating value of 13.3 MJ/m^3 was reported for the product gas.
- Carbon conversions as high as 98% was possible.
- Sulphur reduction of 95% was also possible.

(Rockvam, 2001)

2.9 Biomass Gasification

In Europe, there are many commercially available air-blown biomass gasifiers in operation. These gasifiers operate at atmospheric pressure. Their functions include providing fuel to pulp mill lime kilns. (Larson et al, 1997)

"Biomass gasifiers can be classified according to how heat is provided to drive the gasification reactions" (Larson et al, 1997). These are partial oxidation and indirectly heated designs. Bubbling or circulating fluidized bed (CFB) reactors are used in the partial oxidation design. In this type of design, some of the biomass in the feed is burned. This is essential in order to maintain operating temperatures of 850 - 1000°C.In an indirect heated gasifier, the feedstock is heated by a heat-exchange mechanism. The operating temperatures for such a gasifier are in the region of 700 – 900°C.

2.9.1 Partial Oxidation Gasifiers

A Swedish company known as TPS, is a leading developer of this type of gasifier. Their design is based on a circulating fluidized bed reactor which operates at atmospheric pressure. Other companies are Foster-Wheeler, Carbona and Lurgi/HTW. Foster –Wheeler, Carbona and Lurgi/HTW, all have pressurized CFB designs. (Larson et al, 1997)

2.9.2 Indirectly Heated Gasifiers

Battelle-FERCO offers an atmospheric-pressure twin-CFB design. In this design, heat is provided by hot sand. MTCI offer a design which Larson et al. (1997) claims is similar to their spent liquor gasifier design.

2.10 Integrated Gasification Combined Cycle (IGCC) Power Generation

IGCC stems from the coal industry where coal combustors (pressurized fluidised bed) with steam turbines are used. These steam turbines are used to generate electricity. A gasifier and gas turbine provides a replacement to the conventional coal combustor. In such an arrangement the exhaust heat from the gas turbine is able to produce steam for the steam turbine. The gas turbine and steam turbine is said to operate in combined cycle and when integrated with the gasifier is referred to as the Integrated Gasification Combined Cycle system (IGCC). (Orr et al, 2000)

Researchers such as McKeuogh (1993), state that IGCC plants have the ability to produce more power than conventional processes with lower investment costs. Furthermore, the high efficiencies of gas turbine cycles compared to those of steam turbines increase electricity generation (Raymond, 1996). McDonald (1999) claims that combined cycle systems generate two to three times the electrical power of the conventional recovery steam cycle.

This would thus save on fossil fuel energy, thus reducing electricity costs of plants, making the papermaking industry self-sufficient. Self-sufficiency can be achieved by commercializing spent liquor and biomass gasification with IGCC. Tucker (2002) claims, that without commercialising this technology, the pulp and paper industry will be subject to supply and pricing variability of fossil fuel-based power generation. However, with this technology the industry will be an important supplier of "green" power which would create crosscutting impacts from energy to pulping yield (Tucker, 2002). However, this can only be achieved if the gasification process can produce a synthesis gas that is of suitable content with regards to composition and a gas with a high heating value (HHV).

2.11 Significance of this work

Spent liquor gasification has come along way since the bench-scale experiments of Rockwell in 1987. However, with an emerging technology such as this, "gaps" in this technology can be expected.

Tucker (2002), reports that these gaps are present in both spent liquor and biomass gasification. Although Tucker refers to Kraft liquors, these gaps can be identified in spent liquor as a whole. Since this study is based on low temperature spent liquor gasification (LT-BLG), our focus is on the gaps pertaining to this process.

The major gap reported by Tucker is that carbon conversion of greater than 97% was not achieved in the pilot scale testing which may influence its commercialisation. He believes it is a key technical challenge since the melting temperature creates an upper limit on the operating temperature. This is thought to be a major obstacle and may decide whether low temperature gasification (LT-BLG) will be a realized process breakthrough or not.

With this in mind he suggests that to fill this gap i.e. confirm that LT-BLG can be effectively applied to spent liquors and to determine the window of operation; lab and pilot-scale experiments need to be conducted. He proposes that lab and pilot plant experiments are required and should aim to fill the following gaps

1. Evaluation of carbon conversion, sulphur reduction and bed stability.
2. Evaluate the fate of sulphur and chloride in LT-BLG.
3. Characterisation and the quantification of tars
4. Understand how the sulphur partitions (gas vs. solid phase) and in what form.
5. Understand the sulphate-to-sulphide ratio – sulphate represents dead load.
6. How chlorides affect agglomeration temperature and how it partitions is also needed.

Thus far the approach outlined by Tucker to developing a fundamental understanding of LT-BLG is similar to the work that is being done in this study. The only difference being the use of soda and SASAQ liquor as opposed to Kraft liquor.

The other proposed recommendations of study by Tucker are the following:

7. Characterise refractory (the unburned) carbon.

8. Another gap in the technology is that with LT-BLG there is a higher re-causticising load as compared to conventional technology. This is due to the partitioning of sodium into the solid phase as sodium carbonate. Tucker proposes that autocausticisation may be the answer to filling this gap

CHAPTER 3:
CONCEPTS AND THEORY

In this chapter, the concepts and theory of subject matter relevant to this study are focussed on. This is to enlighten the reader and provide background information that may be referred to when reading the results and discussion chapter.
The main part of this chapter deals with fluidisation. The last section is brief, with the focus on Le Chatelier's Principle.

3.1 Fluidisation

3.1.1 Introduction

Consider a fluid flowing upwards through a packed bed of solids in a cylinder. As the fluid flows through the solids, the solids experience a drag force which is exerted by the fluid. The movement of fluid through the solids creates a pressure drop (ΔP) across the bed. A further increase (Figure 3-1) in the fluids velocity results in an increase in the pressure drop. The fluids velocity based on the cross section area of the cylinder, is referred to as the superficial velocity. (Geankoplis, 1993)

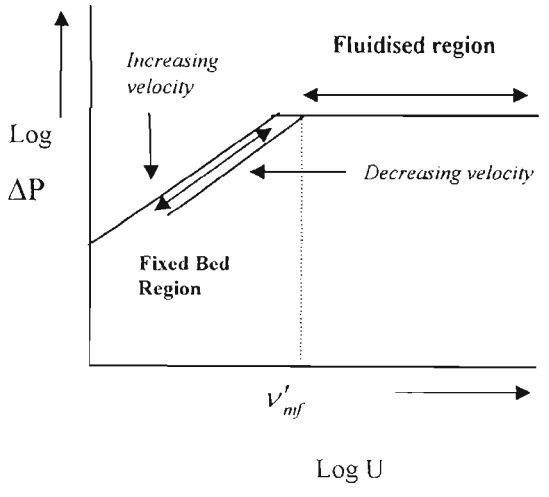


Figure 3 - 1: Ideal pressure drop-velocity curve (Richardson, 1971)

Initially, the solids in the bed appear stationary. Thereafter, a further increase in the superficial velocity causes the bed to reach a point where the drag force exerted on the solids

by the upward moving gas is sufficient to sustain the weight of the solids in the bed. More specifically, "the force obtained from the pressure drop times the cross-sectional area must equal the gravitational force exerted by the mass of the solids minus the buoyant force of the displaced fluid" (Equation 3-1; Geankoplis, 1993). As the particles just begin to move, this is regarded as the onset of incipient or minimum fluidisation (v'_{mf}).

$$\Delta P A = H_{mf} A(1-\varepsilon_{mf})(\rho_s - \rho_g)g \qquad (3\text{-}1)$$

ΔP - Pressure drop across bed

A - Area of cross section

H_{mf} - Height of bed at minimum fluidisation

ε_{mf} - Void fraction of the bed at minimum fluidisation

ρ_s - Density of particle

ρ_g - Density of gas

g - Gravity

As the bed begins to expand, the solids in the bed offers less resistance to the movement of the fluid. Any subsequent increase in the superficial velocity results in a constant pressure drop across the bed (Figure 3- 1).

In reality ideal behaviour is impossible to achieve. Deviations from ideal behaviour are the result of intra-particle forces and to maldistribution of the fluid in the bed. Therefore, a better representation of pressure drop versus velocity curves are given by the deviations from ideal behaviour as stated by Richardson (1971). These deviations are characterised by the following;

1. In some instances, a small characteristic "hump" is apparent on pressure drop versus velocity curves. This is caused when particles tend to interlock with each other with the result that partial bridging occurs. This is a common problem in fluidised beds of small diameter where frictional forces are significant and are exerted by the walls onto the bed. Therefore, pressure drops in excess of the theoretical value is possible. The curve will pass through a point of maximum pressure drop and may exhibit a small characteristic hump. Kunii et al. (1991), states that this behaviour is common to "not-too-small uniformly sized particles".(Figure 3-2)

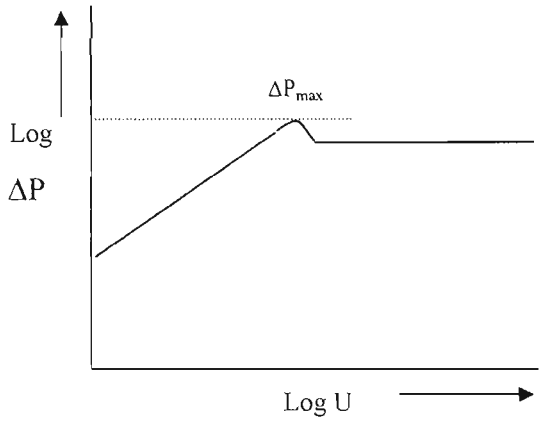


Figure 3 - 2:"Hump" displayed on pressure drop versus velocity curve due to particles interlocking

2. In beds with non-uniform size particles, preferential flow of fluid in particular areas occurs. In addition, the fixed and fluidised regions co-exist within the bed. It has been reported to occur commonly in gas-solid systems. In such instances, the bed appears to be well fluidised but part of its weight may still be sustained by the distributor. This results in the pressure drop being below the expected value. Therefore, the minimum velocity for which the fluid totally supports (v'_{fs}) the bed weight is higher then the expected minimum fluidisation velocity. This is illustrated in Figure 3-3.

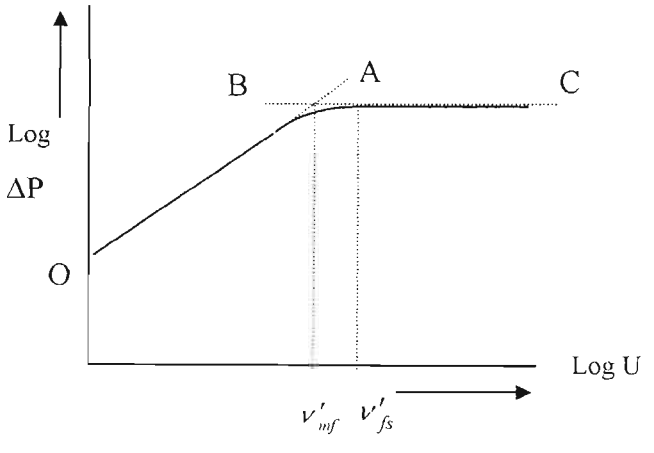


Figure 3 - 3: The Effect of non-uniform particle size distribution on the pressure drop versus velocity curve

Another explanation based on the particle size is offered by Kunii et al. (1991). Increasing the superficial velocity of the gas, the smaller particles slip into the void spaces between

larger particles. These smaller particles fluidise whilst the larger particles remain stationary. This is described by them as partial fluidisation, which results in an intermediate pressure drop.

3. In cases where the bed experiences severe channelling, the remainder of the bed may possibly remain unfluidised. This is due to a high proportion of the fluid flowing through the channels.

4. In some instances the uneven distribution of fluid by the distribution plate may be responsible for inducing channels in the bed.

3.1.2 Minimum Fluidisation Velocity from Pressure Drop versus Velocity Curves

The minimum fluidisation velocity is determined from the pressure drop versus velocity curves as follows. These diagrams provide a rough indication of the quality of fluidisation, especially when visual observations are not possible (Kunii et al, 1991). Richardson (1971), states that considerable amount of information regarding the structure of the bed can be provided.

From Figure 3-2, the minimum fluidisation velocity is obtained by taking the superficial velocity at the highest pressure drop reading i.e. at the hump. This is in accordance with the method by Rhodes (2001) and Kunii et al. (1991).

From Figure 3-3, the minimum fluidisation velocity is obtained by constructing lines OA and BC and reading off the value of the superficial velocity at the point of intersection of these lines (Richardson, 1971 and Kunii et al., 1991)

3.1.3 Geldarts Classification Chart for Particles

Dry (1982), states that this chart (Figure 3-4) gives the best priori prediction of fluidisation behaviour. Kunii et al. (1991), reports that Geldart (1973), observed the fluidisation of all sorts and sizes of solids and determined four clearly recognizable kinds of particle behaviour. These classes are reported by Kunii et al. (1991) as follows.

- "Group C: cohesive or very fine particles. Normal fluidisation is extremely difficult for these solids because interparticle forces are greater than those resulting from the action of the gas.
- Group A: aeratable, or materials having a small mean particle size and/or low particle density ($<\sim 1.4 g/cm^3$). These solids fluidise easily, with smooth fluidisation at low gas velocities and controlled bubbling with small bubbles at higher gas velocities.

- Group B: sand-like, or most particles of size with a mean diameter of 40 $\mu m < \overline{dp} <$ 500 μm and density 1.4 < ρ <4g/cm^3. These solids fluidise well with vigorous bubbling action and bubbles that grow large.
- Group D: spoutable, or large and/or dense particles. Deep beds of these solids are difficult to fluidise. They behave erratically, giving large exploding bubbles or severe channelling, or spouting behaviour if the gas distribution is very uneven."

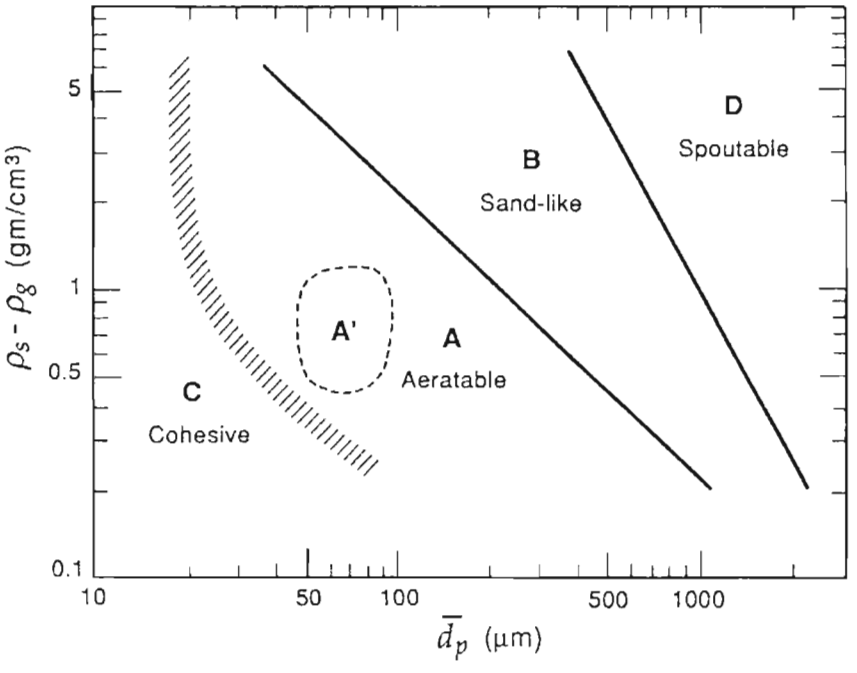


Figure 3 - 4: Geldart's Classification of particle behaviour for ambient conditions as reported in Kunii et al. (1991)

3.1.4 Advantages and Disadvantages of Fluidisation (Kunii et al., 1991)

3.1.4.1 Advantages

- Due to the characteristic liquid like behaviour of bed solids, this ensures continuous automatically controlled operations with ease of solids handling.
- Intense mixing and good gas-solid contact ensures that there are no temperature gradients or hot spots in the bed especially with exothermic reactions.
- A well mixed bed of solids resists rapid temperature change, responds slowly to sudden changes in operating conditions, and gives a large margin of safety in avoiding temperature runaways for highly exothermic reactions.
- Good heat and mass transfer rates between the gas and solids in the bed.

- Fluidised bed operations are suitable for large- scale operations.

3.1.4.2 Disadvantages

- Inefficient contacting for bubbling bed of fine particles especially when high conversion of gaseous reactant is required.
- Non-uniform residence times of solids due to vigorous mixing in the bed.
- Entrainment of friable material which has to be replaced in order to contain the mass balance.
- Internals such as pipes in fluidised bed reactors are likely to erode due to abrasion of bed particles.
- Reduction in temperature which reduces the reaction rate, necessary to accommodate fine particles from sintering and agglomerating.

3.1.5 Determination of Minimum Fluidisation Velocity

3.1.5.1 Experimental Determination

When the mass of solids are at the point of minimum fluidisation, the spaces between the individual particles begin to expand. The term porosity or voidage fraction of the bed (ε) is used to describe this expansion with a minimum voidage (ε_{mf}) attained at minimum fluidisation. The minimum fluidisation velocity can be determined from pressure drop versus velocity curves which are obtained from measurement by experimentally subjecting the bed of solids to increases in superficial velocity. The voidage can be determined in the same way but the bed height measurement is required. (Geankoplis, 1993)

3.1.5.2 Calculation

$$1.75\mathrm{N}_{\mathrm{Re},mf}{}^{2}\frac{1}{\phi_s\varepsilon_{mf}{}^{3}}+150\mathrm{N}_{\mathrm{Re},mf}\frac{(1-\varepsilon_{mf})}{\phi_s{}^{2}\varepsilon_{mf}{}^{3}}-\frac{Dp^{3}\rho(\rho_p-\rho)g}{\mu^{2}}=0 \qquad (3\text{-}2)$$

where

$$\text{Reynolds Number} = \mathrm{N}_{\mathrm{Re},mf} = Dp\,v'_{mf}\,\rho/\mu \qquad (3\text{-}3)$$

Equation 3-2 can be used to determine the minimum fluidisation velocity if the above parameters are known. In the case of irregular shaped particles e.g. aluminium oxide or silica, a factor known as the sphericity factor (ϕ_s) must be included to account for this where Dp is

$$Dp = \phi_s Dp \qquad (3\text{-}4)$$

Sphericity factor is defined as follows:

$$\phi_s = \text{(surface of sphere/ surface of particle)} \qquad (3\text{-}5)$$

Experimentally the mean diameter of non-uniform size particles can be determined by the following.

$$\overline{Dp} = \frac{1}{\sum^{alli} (x / Dp)_i} \qquad (3\text{-}6)$$

When ϕ_s and ε_{mf} are not known, the v'_{mf} can be predicted by the following equations

$$N_{\mathrm{Re}_{mf}} = \left[(33.7)^2 + 0.0408 Ar\right]^{1/2} - 33.7 \qquad (3\text{-}7)$$

$$N_{\mathrm{Re}_{mf}} = \left[(28.7)^2 + 0.0494 Ar\right]^{1/2} - 28.7 \qquad (3\text{-}8)$$

Equations 3-7 and 3-8 were found in Kunii et al. (1991). Kunii et al. (1991) defines the use of these equations according to the nature of the particles. Equation 3-7 is defined for use of fine particles and equation 3-8 for coarse particles.

Others, such as Geankoplis (1993) and Rhodes (2001) define the use of equation 3-7 according to a range of Reynolds number. From their work, this equation holds true in the range $0.01 < \mathrm{Re}_{mf} < 1000$.

3.2 Le Chatelier's Principle

Le Chatelier's principle states that when a closed system, in equilibrium, is subjected to a stress, the equilibrium is disturbed and the system rearranges itself to overcome or reduce the effects of the stress such that equilibrium is re-established. Le Chatelier's principle was used to validate some of the observations made when the product gas composition profiles were discussed.

3.2.1 Effects of Temperature

$$\Delta G^o = -RT \ln K \qquad (3\text{-}9)$$

The above equation shows that the equilibrium constant changes with temperature. As a result, increasing the temperature will cause a new equilibrium to be established in the

direction in which heat is absorbed. However, increasing the temperature increases both forward and reverse reactions but the overall shift in equilibrium will occur from a larger increase in the rate of the endothermic process rather than the exothermic process. (Gray et al., 1967)

3.2.2 Effects of Catalysts

The catalyst does not shift the equilibrium position in any particular direction. It increases the rate of both the forward and reverse reactions by lowering the activation energy.

3.2.3 Effects of Pressure

An increase in pressure will shift the equilibrium position in the direction which favours the formation of the lower number of moles of gas particles and vice versa.

3.2.4 Effects of Concentration

An increase in the concentration will shift the equilibrium position away from the increase and vice versa.

CHAPTER 4:
EQUIPMENT DESCRIPTION

The objective of this chapter is to give a detailed description of the gasification system. The pilot-scale gasifier together with the feed system, the heating system and product gas system is elaborated on. Also, included are details of analytical equipment used for analysis of the product gas. This chapter concludes with illustrations of the spent liquor gasification system, peripheral apparatus and the sampling system used.

4.1 Introduction

A pilot-scale fluidised bed gasifier was designed and constructed at the former University of Natal. The unit was developed to demonstrate an alternative approach to treating spent liquor. The gasifier operates at atmospheric pressure and was designed for operation at temperatures as high as 800°C. In this gas-solid system, excess superheated steam is used as the fluidising gas and inert aluminium oxide grit as bed solids. The product gas is not separated from the excess steam, however; samples of the product gas are.

Prior to experimental work being conducted, necessary additions to the experimental systems was made. The objective behind these additions was to improve the system in terms of performance, operability and reliability, and accuracy of data. These additions included:

- A separator for reducing the carryover in the product gas and for cooling of the product gas.
- An orifice meter was installed to measure the wet product gas flowrate.
- The liquor injection rod was modified to provide easy cleaning and better performance.
- An improved sampling system was implemented.
- A gas chromatograph was used to measure the composition of the product gas.

In order to better understand the process reactions and decisions made for operation of the gasifier, the following information was found in literature:

- The kinetics of the steam-char gasification at temperatures below 1000°C is controlled by the rates of the chemical reactions and the order of magnitude of the reaction rate will be relatively low (stated by Schmal et al., (1982) and reported by Riley (1990)).
- Riley (1990) reports that by supplying an excess of one reactant, the reaction conditions are maintained approximately steady with respect to the excess reactant.

Subsequently, in this study the use of high steam flowrates achieves this with the added advantage of ensuring good mixing of the bed solids.

- Li et al., (1989), reports that gasification of spent liquor char is strongly catalysed by alkali species in the char, and precedes at rates several orders of magnitude higher than those of pure carbon.
- Researchers such as Mansour et al. (2002) and Rockvam (2001) have reported that low temperature gasification processes produce a synthesis gas composed of hydrogen, carbon dioxide, carbon monoxide, methane, hydrogen sulphide and less than 3% of other longer chain hydrocarbons.
- Zeng et al. (1999) indicates that lower carbon conversion and gasification rates are expected in a low temperature gasification process.

4.2 Brief Process Flowsheet Description

The gasification system is shown in a process flow and instrumentation diagram in Figure 4-1 on the next page.

The feed system comprises of the spent liquor storage tank, the hot water storage tank and the injection rod. Pre-heated spent liquor is delivered to the injection rod via a pump, for in bed firing of the liquor. Hot water from the hot water storage tank is used for cleaning and maintenance of the pump, injection rod and connecting piping. It is delivered to the injection rod along the same route as spent liquor.

The heating system comprises of the steam coils, steam manifold, steam spargers, distributor, gas burner and heating element. Steam is supplied from the main boiler via a main supply line. It is superheated in a set of coils, prior to entry into the gasifier. These coils are located in the direct pathway or annulus of the flame generated by the LPG (liquid petroleum gas) burner which ensures a constant heat source for superheating steam. Flue from burning LPG is removed via the LPG flue gas stack connecting the reactor chamber to the outside.

The product gas system comprises of the orifice meter and the separator. Superheated steam enters the reactor and fluidises the inert bed solids. Reactions of char and steam take place to produce gasification products. Thereafter, these products together with the excess steam (the wet product gas), exits the gasifier via the gasifier product gas stack. The wet product gas stream is directed into a separator which reduces the carryover. Thereafter, the product gas exits the separator via the exit stack located at the top of the unit.

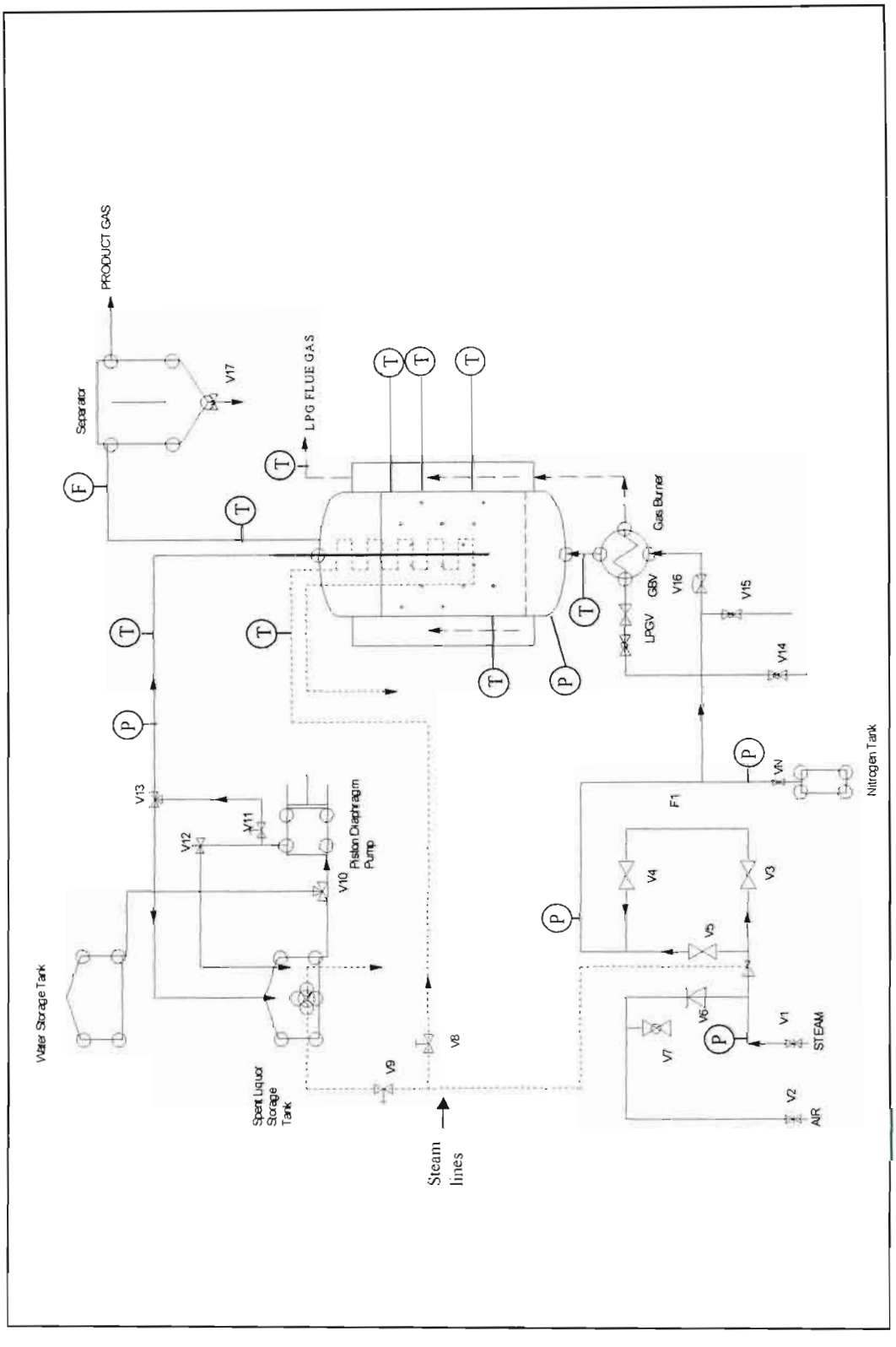


Figure 4 - 1: The Gasification System (PID)

4.3 The Fluidised Bed Reactor Configuration

A sketch of the fluidised bed reactor is shown in Figure 4-2 on the next page with a detailed drawing shown in APPENDIX G. The reactor is cylindrical in shape and is designed such that it is positioned in a compartment with metal partitions. The outside of the compartment is insulated with layers of glass wool. The glass wool is secured in place by a cylindrical shell which forms the external framework or housing of this unit.

The reactor is positioned such that there is adequate space for the steam coils and the flame tube of the LPG burner to be housed in this compartment. There is a set of two steam coils, which are arranged in a helical structure with the exit side attached to a steam manifold. Superheated steam enters the manifold and exits through a sparger type nozzle into the windbox. The sparger ensures that there is a uniform distribution of superheated steam in the windbox of the reactor. The windbox is the region below the distribution plate. Thereafter, the superheated steam enters the bed via a bubble-cap distribution plate. The LPG burner is bolted to the base of the shell such that the flame tube is positioned within the reactor compartment. The flame from the burner provides sufficient energy to superheat steam. The flue gas from burning LPG is vented through a stack that connects the reactor compartment to the outside.

The injection rod system is designed for in-bed firing of the spent liquor. It is screwed onto the lid of the reactor such that the body of the injection rod is in the bed chamber.

Also located within the gasification chamber of the reactor is the heating element. The heating element provides extra energy for the steam-char gasification reactions and ensures better operational control of the reactor.

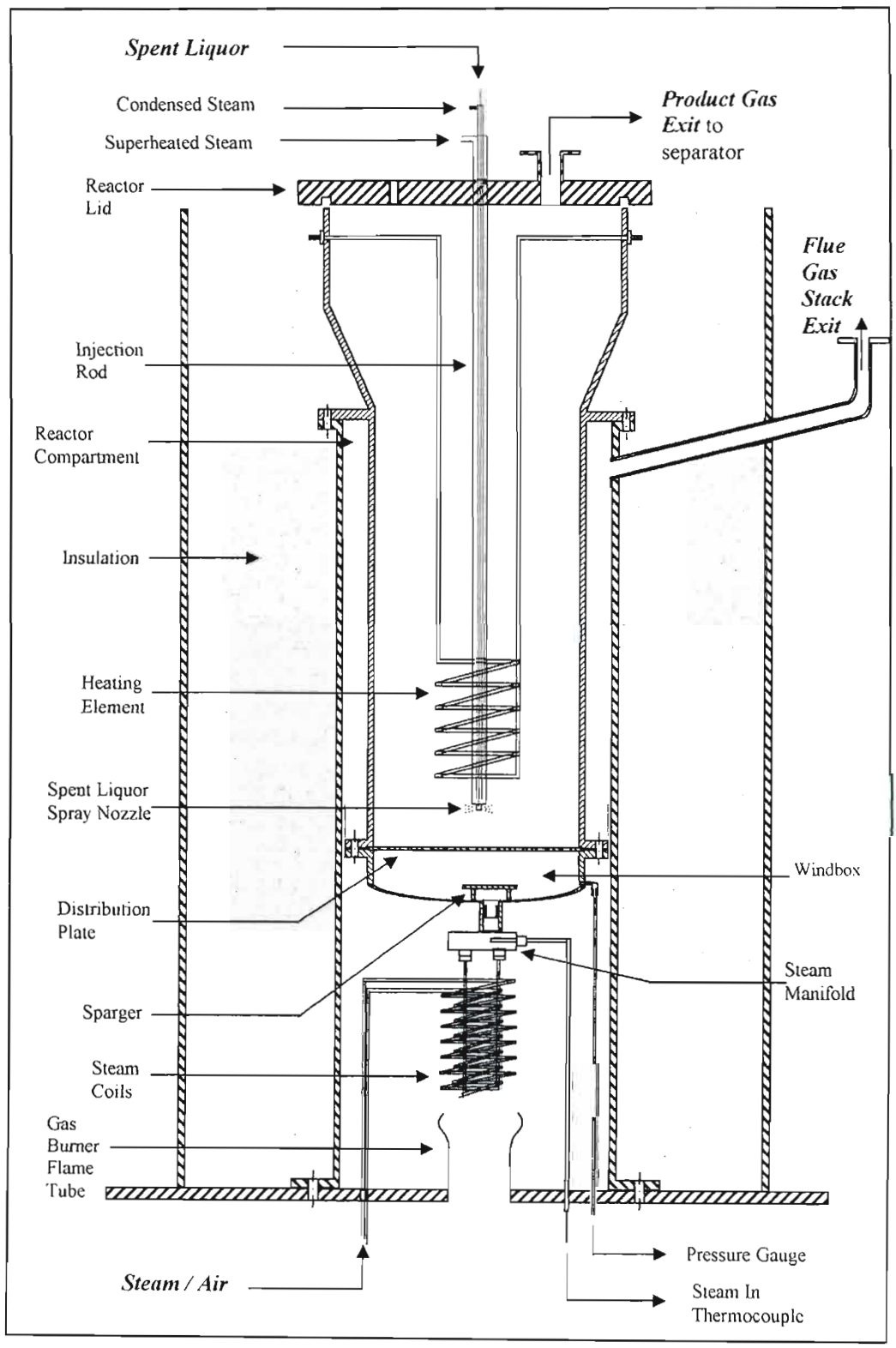


Figure 4 - 2: The Pilot-Scale Gasifier (Drawn by Mr. V. Avidi and modified by the author)

4.4 Details of Peripheral Components of the Gasification System

4.4.1 The Spent Liquor Feed System

The spent liquor feed system comprises of an 8L storage tank, a 10L hot water tank, spent liquor stirring apparatus, a spent liquor feed pump and a spent liquor injection rod with steam cooling.

An 8L stainless steel urn with a 3kW heating element is used as a make-shift storage tank for spent liquor. A temperature controller ensures adequate control over the heating of the spent liquor. In addition to the heating element, a set of ¼ inch heating coils was added to the storage tank. These coils are connected to a common steam off-take line just before the steam delivery line to the reactor. A needle valve on the heating coil line is used to control the heating rate of the spent liquor. The heating coils are positioned within the urn in arrangement that ensures uniform heat distribution in the spent liquor. The coils are spread apart to cover the height of the tank. The heating elements in conjunction with the heating coils are controlled by monitoring the temperature reading made possible by a thermocouple located at the black liquor inlet to the injection rod.

A stirring rod apparatus ensures that the liquor is well mixed at all times and prevents dissolved solids from settling at the bottom of the urn; hence, a uniform solids concentration in the liquor will be injected. In addition, the stirring rod apparatus ensures a uniform distribution of heat to the spent liquor and prevents the formation of soapy film layers at the surface, which is caused by heating without mixing.

Spent liquor is then pumped using a Sera piston diaphragm pump of model type R409.1-8.5KM/14, which is able to deliver spent liquor at a nominal capacity of 8.5L/hr. A second pump was also procured with a nominal capacity of 50L/hr with model type R409.1-50e and was used for higher spent liquor flowrates. Hot water from the storage tank was used to heat the pump before spent liquor injection and for cleaning the pump pressure valves after spent liquor injection. The piping network connecting the spent liquor storage tank to the pump and injection rod were wrapped with nichrome wire used for electrical heating or heat tracing of these lines. This prevents high solid concentration spent liquors from solidifying in these lines.

An injection rod with steam cooling is used to inject spent liquor into the fluidised bed. It is 900mm in length with a diameter of 30mm and made of mild steel. It is shown in Figure 4-3 below. The innovative design can be simply described as a rod with three compartments. The outer two are linked for heat removal whilst the inner compartment is a ¼ inch continuous tube for spent liquor delivery to the bed.

Hot water from condensed steam is supplied to the injection rod from a common steam off-take line as described earlier. It flows into the compartment surrounding the spent liquor and as it flows down, evaporates and then gets superheated. The superheated steam then flows up the outer compartment to be removed from the rod. This design ensures that the spent liquor does not dry out in the rod due to high temperature exposure. The rod has been modified so that in an event of a blockage or rupture of the spent liquor tube due to high temperature exposure or no cooling condensate, the rod can be disassembled with ease. With the original design, this was not possible as the different components of the rod were welded together.

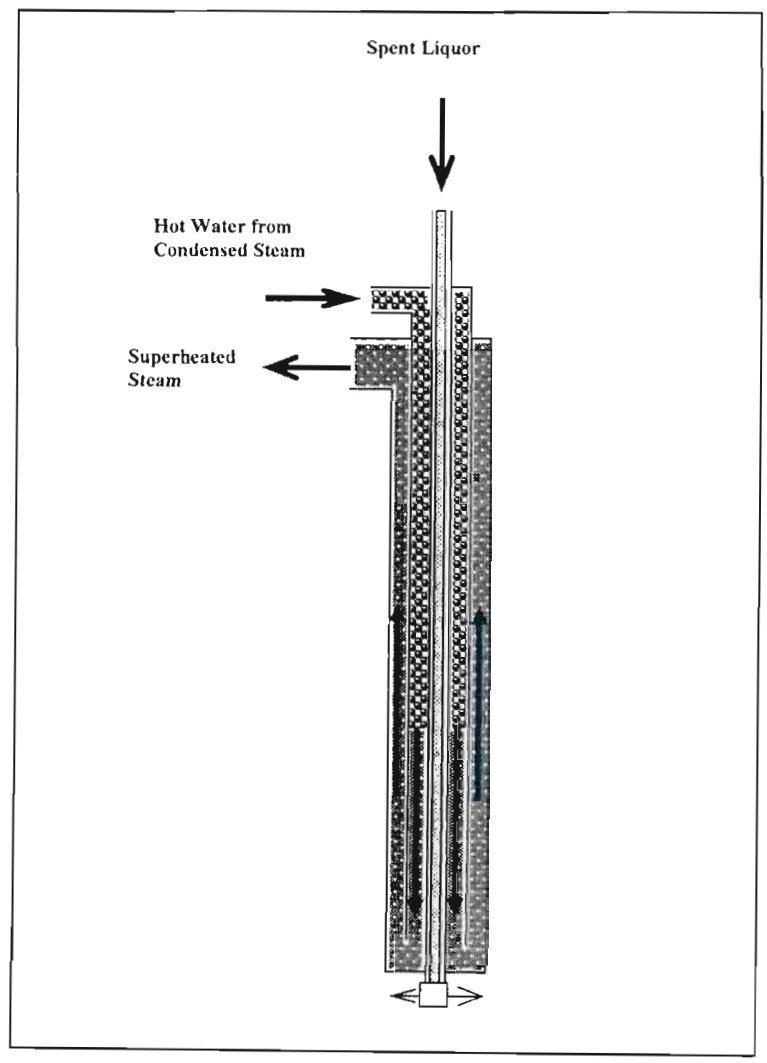


Figure 4 - 3: The Injection Rod

4.4.2 The Heating System

The heating system is comprised of the liquid petroleum gas (LPG) burner, two sets of steam coils, steam manifold, spargers, distributor and heating elements.

A Klockner forced draft gas burner (KL20.1G) is used to superheat steam flowing through stainless steel steam coils. A set of two ½ inch stainless steel coils are arranged in a helical arrangement and are positioned over the flame tube and in the annulus of the flame generated by the burner. Liquid petroleum gas (LPG) fuels the gas burner. LPG is a mixture of propane, propylene, n-butane, butylenes and iso-butane.

Superheated steam then flows into a steam manifold and out sparger tubes into the windbox. The sparger tubes ensure uniform distribution of steam to the windbox which then flows via the distributor into the bed of solids. The distributor is a bubble cap plate with the 12 active bubble caps arranged on a triangular pitch. In addition to the heating system is a 4kW heating element that is connected to a thermocouple which in turn is connected to a temperature controller. However, a manual switch is used to operate the heating element. The heating element provides extra energy, which is required for endothermic gasification reactions. It is also used for finer temperature control.

4.4.3 The Product Gas System

This system comprises of an orifice meter and the separator unit.

The orifice meter is installed into the product gas line exiting the gasifier; hence, measuring the product gas flowrate. The orifice meter is attached to a glass manometer filled with water. Readings from the manometer are taken at regular intervals during a run.

An old cyclone was added to the system. It was closed off at the bottom with a valve and used as a separator. The unit is 1.4m in height with a 10inch diameter. It is used to remove particulates from the product gas stream. Insulation in the form of glass wool is wrapped tightly around the separator so as to prevent the condensation of the product gas from the gasifier.

4.4.3.1 The Orifice Meter

An eccentric orifice meter (Figure 4-4) was designed and fabricated for the purposes of measuring the flowrate of the wet product gas exiting the Gasifier. The reason for such a design was that it was believed that solids entrained in the product gas would collect in front of the conventional concentric orifice meter (Perry, 1999). Therefore, the eccentric orifice meter was designed (APPENDIX C) with the squared edged opening, on the lower side of the orifice plate.

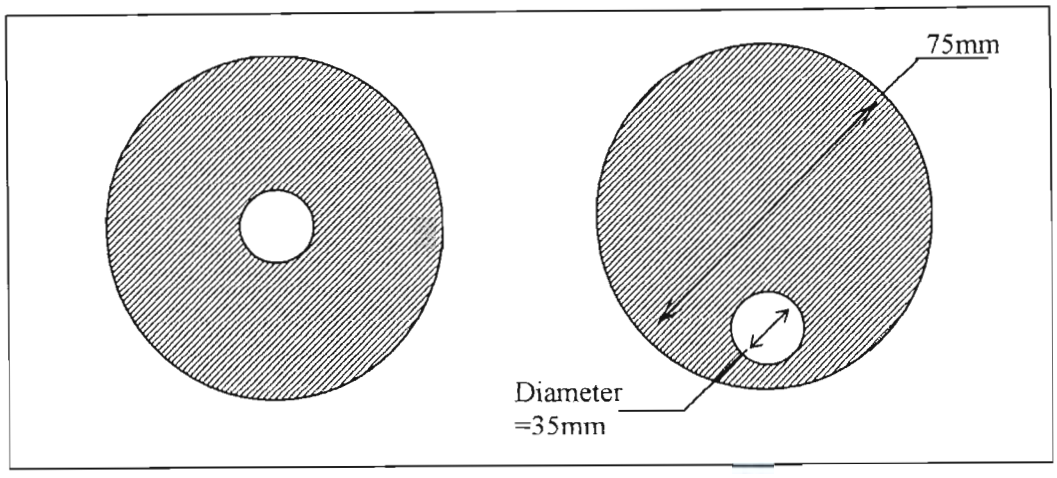


Figure 4-4: Concentric orifice meter (left) & Eccentric orifice meter (right)

The orifice meter is essentially a piece of material that is held in position by flanges welded to the pipe ends. It was important to select the appropriate material for the orifice plate and mild steel was chosen. Mild steel would be able to withstand the high temperatures (greater than 450°C) and would not be corroded by the components in the product gas.

The orifice meter is designed such that the pressure drop across the plate could be measured. This is achieved by the radius taps that were positioned at calculated positions upstream and downstream of the orifice plate. Perry (1999) suggests that in the case of the eccentric orifice plate, the taps must be positioned on the opposite side of the opening of the orifice plate as seen in Figure 4-5 below. The radius taps were positioned one pipe diameter upstream and half a pipe diameter downstream with the thickness of the plate being one eight the diameter of the orifice (Perry, 1999).

The orifice meter was calibrated before experimental work began. It was connected to the product gas stack of the gasifier and calibrated with superheated steam. The objective of this calibration was to determine an experimental discharge coefficient (Cv). Since the product gas was composed of mainly superheated steam, it was decided to calibrate using superheated steam. Superheated steam at experimental operating temperatures was used for this calibration (Figure 4-6).

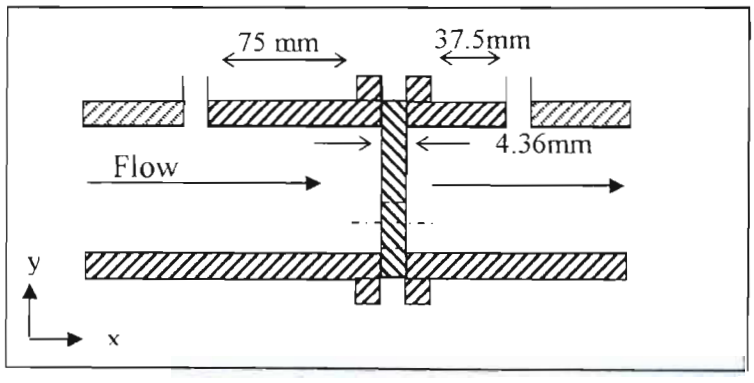


Figure 4-5: Cross section of orifice meter

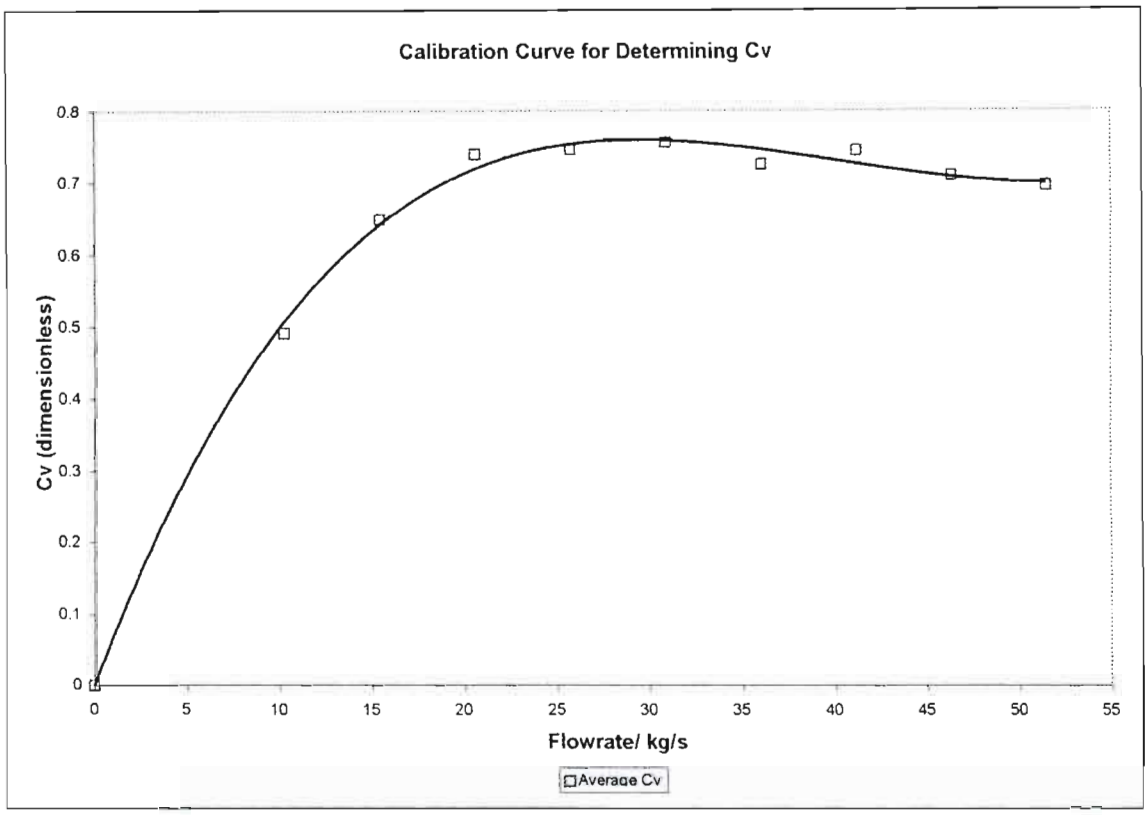


Figure 4-6: Calibration for orifice meter

Readings were obtained from a water manometer with a ruler measure. Stainless steel ¼ inch pipes made up half of the distance from the orifice meter taps to the manometer with polyurethane tubes forming the rest of the distance. Readings obtained from the manometer were consistent and stable for the most part with the exception of a pulsation occasionally. Perry (1999) recommends pressure transducers with flush-mounted diaphragms in conjunction with high-speed recording equipment, to provide accurate records of the pressure profiles at the radial taps. The water manometer for these experiments was adequate.

4.5 The Gas Sampling System

A sample of the wet product gas (Figure 4-7) is taken from an off-take on the exit pipe of the separator. A vacuum pump with an air regulator is used to draw a sample through. The sample is drawn through coils of a condenser unit and is cooled by crushed ice to condense the steam in the sample. Condensate is removed in a catch pot (knockout pot) and dry product gas exits at the top of the catch pot. Thereafter, the product gas enters a dryer which is a cylindrical glass column filled with silica gel crystals to remove any moisture present. After a period of 30-60s, valve VS is closed so that the sample can be taken at atmospheric pressure. A sample is removed at a septum which is then analysed using gas chromatography.

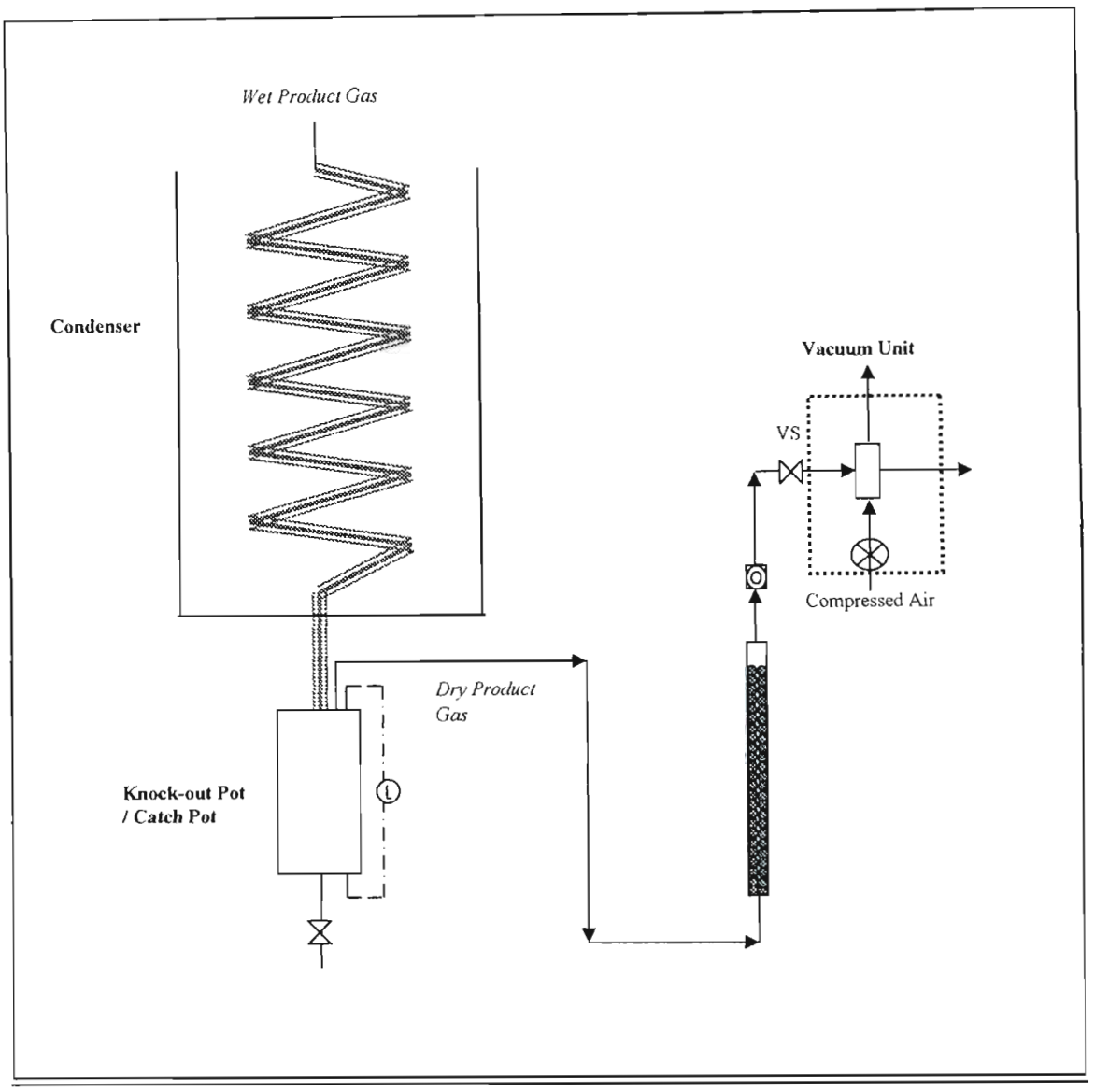


Figure 4 -7: The Gas Sampling System

4.6. Lab-scale Fluidisation Apparatus

A simple lab-scale fluidisation apparatus (Figure 4-8) was used to conduct fluidisation experiments with sodium carbonate and aluminium oxide bed material. The objective of these experiments was to determine the characteristic pressure drop versus velocity curves for these materials.

The fluidisation apparatus consists of a cylinder with a distribution plate at the closed end. Compressed air is delivered to the cylinder via a copper piping network with valves, a rotameter, and a water trap. A water manometer is used to measure the pressure drop across the bed.

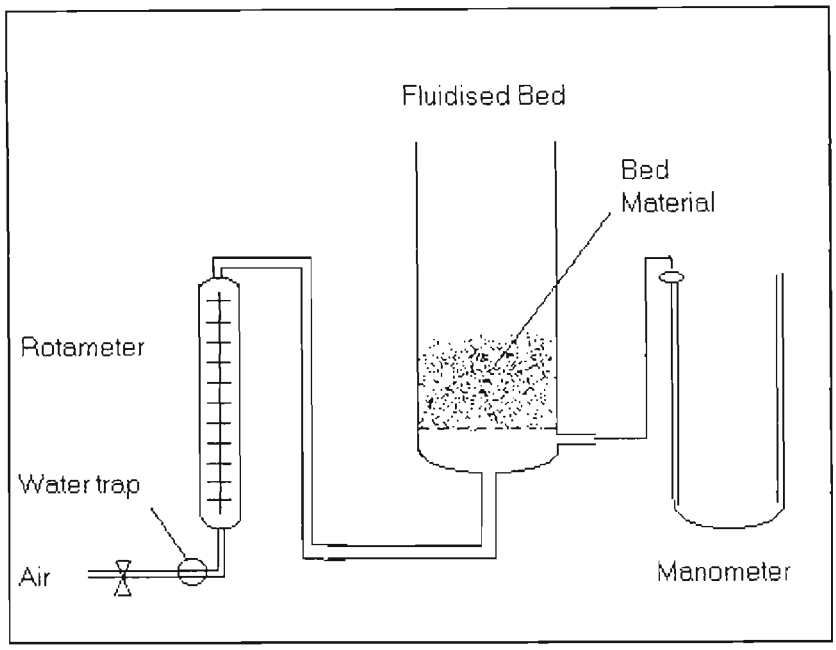


Figure 4 -8: The Lab-scale Fluidisation Apparatus

4.7 Gas Analysis Equipment

The method of gas analysis used in the analysis of the dry product gas is gas chromatography. A series 150 Gow Mac gas chromatograph (GC) was used. This unit has two channels for two chromatographic columns but they both use the same detector. The detector used in this GC is a thermal conductivity detector (TCD).

In the course of this study, two columns were purchased and both installed in the gas chromatograph. A molecular sieve 5A and a carboxen 1004 were purchased. The molecular sieve 5A was used to quantify hydrogen, carbon monoxide and methane and the carboxen column was used to quantify the carbon dioxide in the product gas.

The molecular sieve 5A traps carbon dioxide and hydrogen sulphide from the injected gas sample and prevents it from passing through the column. Therefore, this column has to be regenerated regularly at 300°C for 16hours to release the trapped gases. In addition, the molecular sieve 5A column is sensitive to moisture; therefore every attempt to dry the gas properly must be made.

The carrier gas used was instrument grade helium. The reason for this choice was based on the higher thermal conductivity of helium which would give a better response and the fact that it has low moisture content. The flowrate of helium was set 29.5ml/min. The oven temperature was maintained at 37°C with the TCD filament current set at 100mA. Integrator software was installed on a computer to generate peaks. Data Apex CSW32 software was purchased.

4.8. Temperature Control of the Gasification System

4.8.1 The Gasifier

Temperature probes or thermocouples within the reactor were crucial to the operating of the gasifier. Therefore, four K-type thermocouples of differing lengths, incased in ceramic tubes with stainless steel outer sheathing, were positioned within the reactor. There were four temperature zones, namely; the reactor hot zone, the reactor middle zone, the reactor top zone and the wall temperature zone. The wall temperature zone was linked to an independent controller whereas the other three were linked via an interface card to a real time computer. The signals from these temperature probes were displayed as readings and a temperature-time plot (temperature profiles) was generated by a software programme.

The most important operating temperatures were the wall temperature and the reactor hot zone temperature which were located within the bed. These temperatures were good indicators of the fluidisation in the bed.

4.8.2 Peripheral Temperature Management

A number of thermocouples were located in the spent liquor gasification system. A PT-100 thermocouple, a flexible wire type of thermocouple, was used to measure the temperature of the steam in the reactor. Smaller K-type thermocouples were used to measure the following: the product gas directly out of the reactor, the LPG flue gas, the spent liquor feed entering the injection rod and the injection rod cooling condensate temperature. Figure 4-9, is an example of a common temperature profile obtained during a run. The main temperature control was made by adjusting the LPG intake valve of the burner. The erratic STEAM IN response (3) in Figure 4-9 illustrates the main temperature control. The temperature of the bed was controlled to within 10°C of the operating temperature.

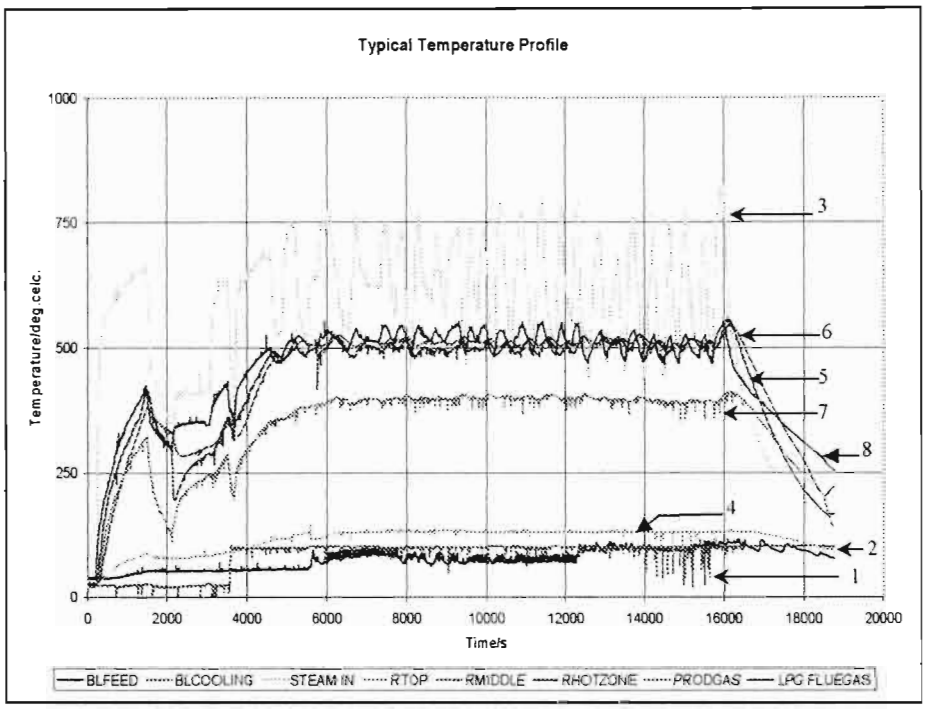


Figure 4 -9: An example of a typical temperature profile

In Figure 4-9, the numbers denote the following temperatures.

1. BLFEED - Spent liquor feed temperature.
2. BLCOOLING - Steam condensate temperature for cooling of injection rod.
3. STEAM IN - Superheated steam temperature.
4. RTOP - Reactor top temperature.
5. RMIDDLE - Reactor middle temperature.
6. RHOTZONE - Reactor hot zone temperature.
7. PRODGAS - Product gas temperature.
8. LPG FLUEGAS - LPG flue gas temperature.

It is recommended that a basic feedback control system consisting of a sensor, transmitter, controller and control element (Luyben, 1990) be installed. The control system would be employed to control the LPG flowrate by monitoring the bed temperature according to a setpoint. Furthermore, the installed control system will automatically control the bed temperature. This time-saving benefit allows for greater focus on sampling of the product gas and taking measurements from the system.

4.10 Maintenance of the Gasifier

The agglomeration of sodium carbonate particles made cleaning and removal of the bed difficult. In fact, some of the bed was so hard that force had to be used to remove it from the gasifier. This was a time consuming activity and risked damaging the vessel. However, with aluminium oxide grit as a bed, none of these problems were experienced.

The most frequent repair made was to the gasket which secured the distribution plate in its position. It required regular replacement due to the damage caused by constant high temperature exposure. These gaskets are located at the bottom of the reactor and prevented the formation of leaks around the distribution plate.

A good indicator of a broken gasket was the pressure gauge which measured the pressure in the windbox (region between the distribution plate and steam entry point). Normally, the pressure in the windbox was virtually the same for all experimental runs as steam flowrate and bed mass was fixed. Any deviations in the pressure would imply a broken or damaged gasket. This required immediate attention as the fluidisation in the bed would be compromised and had to be changed immediately.

4.11 Illustrations

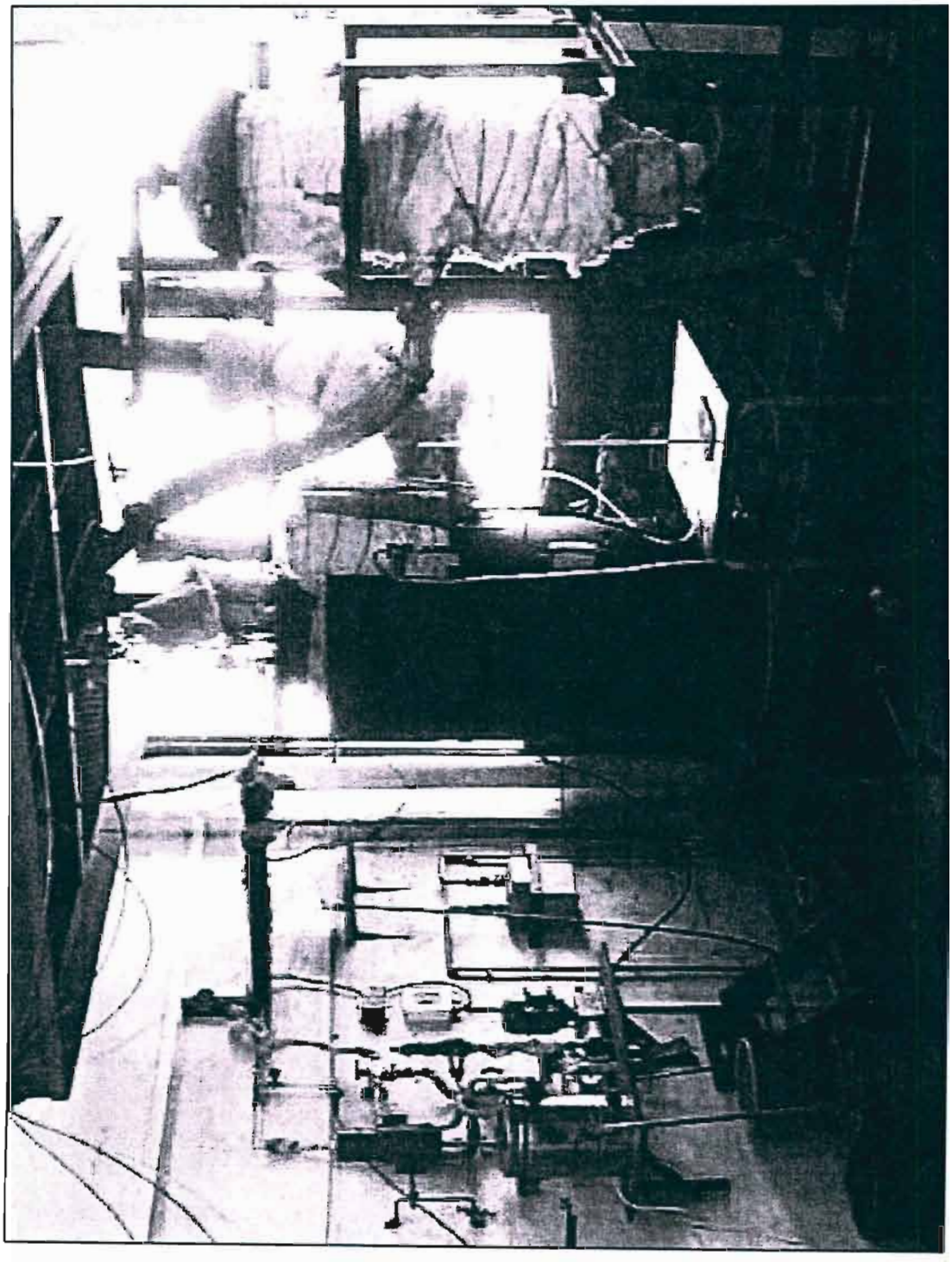


Figure 4 -10: Experimental set-up

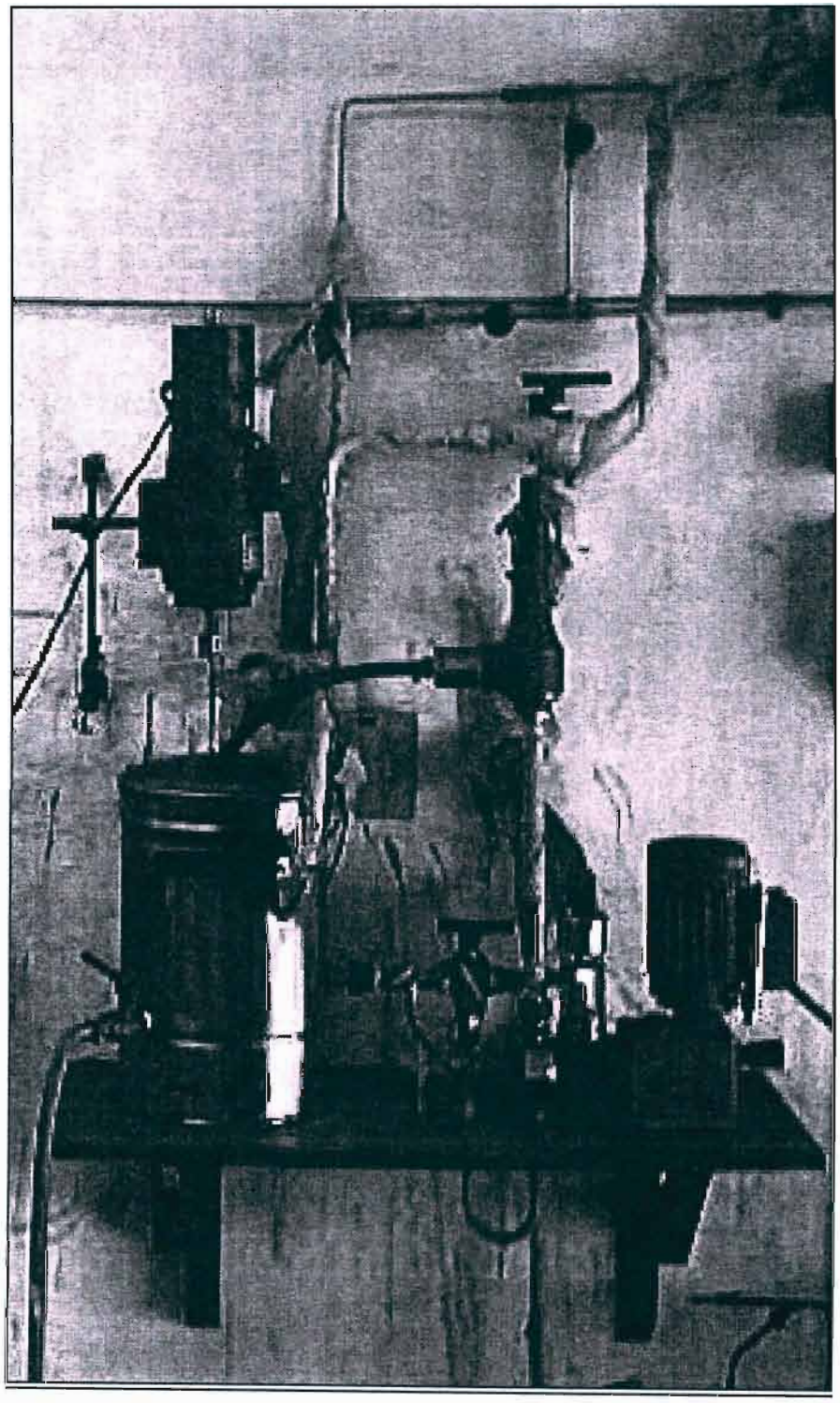


Figure 4 -11: Spent liquor feed system

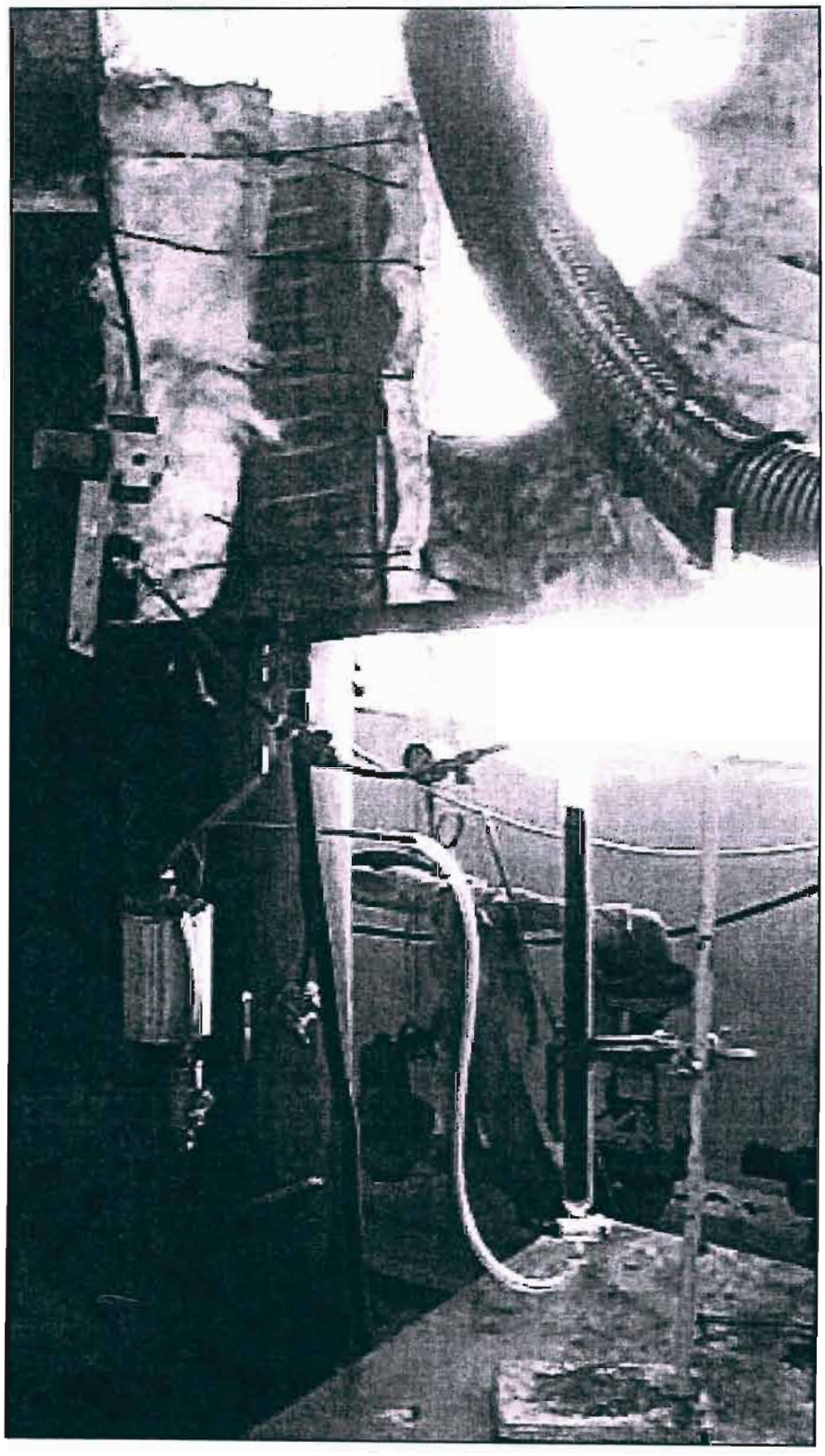


Figure 4 -12: Product gas sampling system

CHAPTER 5:

ANALYTICAL METHODS

In this chapter, details of the analytical methods used in the experimental work are discussed. Analytical methods were used to determine the spent liquor flowrates for both liquors used, the analysis of the bed material after a run, the measurement of species in the product gas and the qualitative analysis of tars in the condensed product gas. Also, elaborated on is the analytical equipment that was used.

5.1 Introduction

The design and construction of the pilot-scale gasifier was completed by Mr. V. Avidi; however, little work was done in the analysis of this system by him. Consequently, no comprehensive mass balance was achieved. Since taking over this project it was realised that in order to facilitate a mass balance, important data and information from the gasification system was required. Therefore, analytical methods to evaluate the following were implemented:

- Spent liquor flowrate
- Dry product gas composition
- Sulphates
- Non-process elements such as silica, potassium and chlorides
- Sodium content
- Organic carbon and inorganic carbon content in bed

Samples from the bed, dry product gas and the condensate from the knock-out pot (catch pot) were analysed.

5.2 Spent liquor flowrate

The spent liquor flowrate was established by calibrating the spent liquor feed pump.The calibration was done on a mass basis as a function of the pump setting for spent soda liquor and SASAQ liquor. This was achieved by measuring the mass of a sample of liquor delivered by the pump for a set period of time. The following calibration chart (Figure 5-1) was obtained.

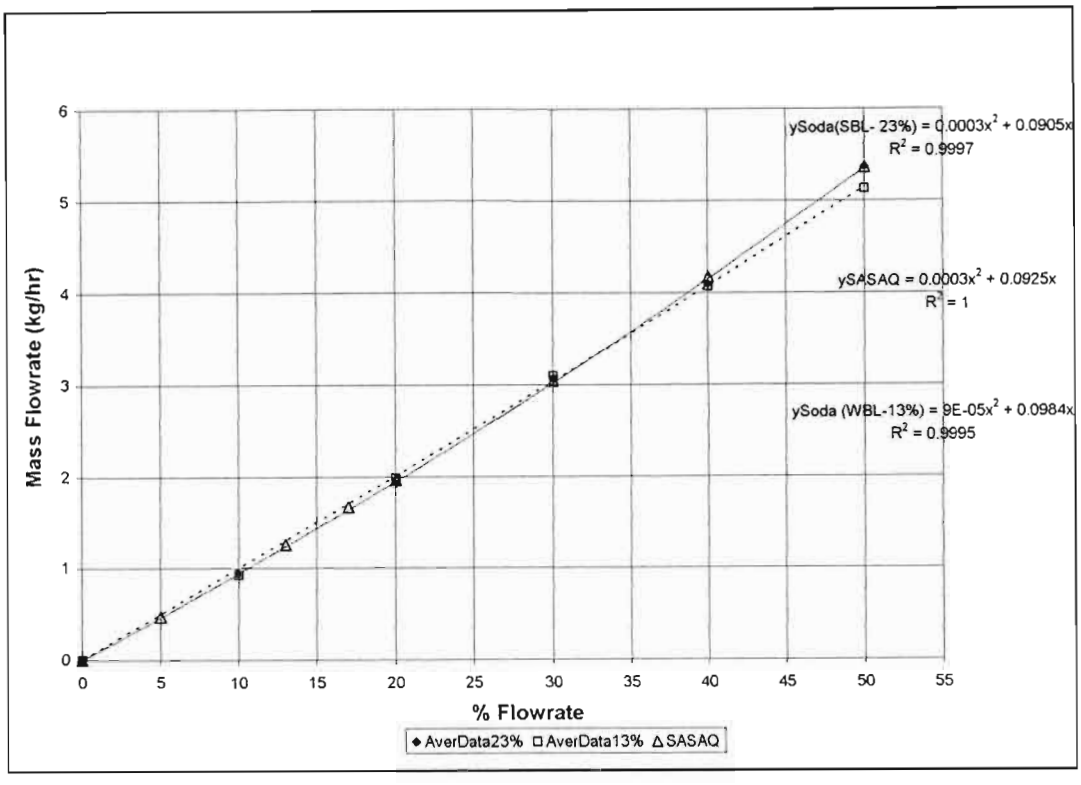


Figure 5-1: Spent Liquor Pump Calibration

5.3 Bed Analysis

The bed grit was quantitatively analysed using X-ray Fluorescence to determine total oxide species of silicon, sulphur, sodium, potassium, chorine and aluminium. These results were reported as total silica, total sulphur, total sodium, total potassium, total chlorine and total aluminium oxide.

5.3.1 X-ray Fluorescence (XRF)

Fluorescence is a process by which a substance gives off light or another form of electromagnetic radiation when they absorb energy. X-rays cause a substance to fluoresce. As a result electrons become excited and this absorbed energy enables them to move into a higher energy level. In XRF, elements absorb energy from x-rays and emit light.

There are two preparation methods used for sample analyses by XRF. Before the samples are prepared, they need to be milled. A ball mill is used for this application. The two methods are the press pellet and fusion disc method. The XRF is then calibrated with accurate standards of the chemical species in the bed material samples.

5.3.1.1 Pressed Pellet method

In this method, about 8g of milled sample is mixed with a binder and poured into a special press apparatus designed to withstand the high pressure of pressing pellets. This apparatus is made up of individual pieces of thick stainless steel that fit together such that a hollow vessel is formed. Smaller discs fit into this hollow vessel and the prepared sample is placed between these discs. Pressure at about 10kPa is applied to these discs for 30-60s by a hydraulic pressing unit. The end result is a solid cylindrical pellet which is then dried in an oven at 110°C. The pellet is then analysed in the XRF unit. The pressed pellet preparation method was used for the analyses of bed material samples.

5.3.1.2 Fusion Disc method

A milled sample of about 3mg is mixed with spectroflux in a specified ratio of spectroflux to sample and weighed into a heat resistant crucible. The crucible with all its contents is then placed in a furnace at 1000°C. At this temperature the contents in the crucible melt and fuse together. The melt is immediately pressed into a thin transparent disc by a press tool. The fusion disc is then analysed in the XRF unit.

5.3.2 The Scanning Electron Microscope and Electron Dispersive Spectroscopy

The scanning electron microscope (SEM) with electron dispersive spectroscopy (EDS) was an important tool in the qualitative and quantitative investigation of the spent liquor coating of the aluminium oxide grit. In this investigation the following aspects were looked at:

- Existence of a coating (SEM).
- Thickness of coating (EDS).
- Structural formations of coating (SEM).
- Elemental analysis of elements on the surface of coatings (EDS).

A LEO 1450 SEM was used for viewing of samples which were prepared by coating the samples with a 10nm layer of gold in a Polaron E5100 SEM Coating Unit. The gold coating makes the sample more conductive. The SEM unit is fitted with a Link ISIS energy dispersive X-ray analysis system for surface elemental analyses. Samples were not coated for EDS analysis.

5.3.2.1 Operating Mechanism of the SEM

A V-shaped tungsten filament is heated, with the result that electrons are emitted. The electron beam is focused and strikes a part of the surface which is demagnified by a series of lenses for better resolution at higher magnifications. The specimen is scanned and as this takes place, the electrons striking the surface throw off secondary electrons. These secondary electrons are collected by a detector which produces a signal that is processed and then

displayed on monitors for viewing. In addition, the EDS feature is able to analyse x-rays which are emitted by the high energy electron beam. These x-rays are characteristic of the elements present on the surface of the sample.

The SEM unit is operated under vacuum conditions to ensure that air molecules are removed, which might otherwise hinder the high energy electron beam to the specimen surface, and ensures the collection of secondary electrons.

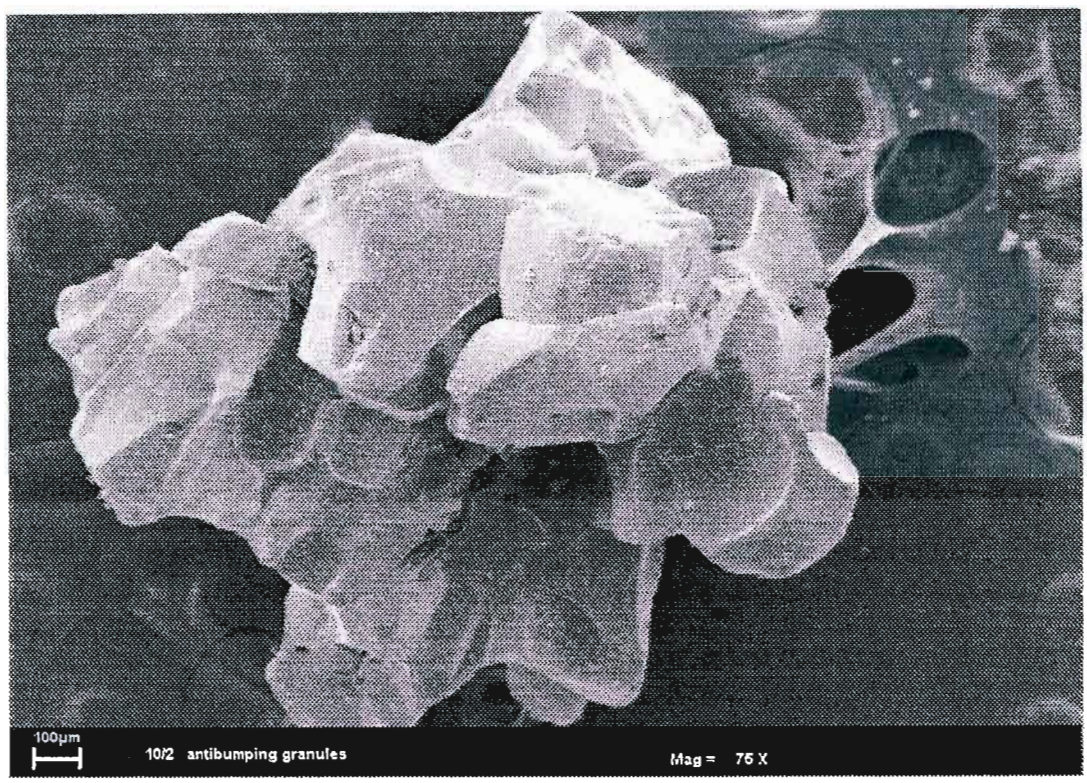


Figure 5-2: Scanning electron micrograph-75X magnified

5.3.3 Silica Analysis of Bed material

Soluble silica was determined using a colorimetric method of analysis. In principle, dissolved silicic acid and phosphate in small quantities react with an ammonium molybdate solution. This occurs at an acidity level (ph) of approximately 1.2 to give heterpoly acids. Heteropoly acids are acids with unequal distribution of charge which are different from semi polar acids. By adding oxalic acid, the molybdophosphoric acid is destroyed leaving the molybdosilicic acid. The addition of aminonaphtholsulphonic acid is used to reduce the yellow molybdosilicic acid to a heteropolar blue. The yellow colour is dependent on the concentration of molybdate reactive silica present.

5.3.3.1 Analysis Instrument – The Spectrophotometer

Light is transmitted through a filter or monochromator for wavelength selection and then through a colour developed sample in a sample container known as a cuvette or cell. Light passes through the cell and the intensity of the transmitted light is measure by a photo detector. The photocurrent produced by the ejection of electrons from the photoemissive surface of the photodetector is amplified and a reading is displayed in a digital or analogue form. Colour development is important as it makes the sample more sensitive for light transmittance through the sample.

The spectrophotometer has to be calibrated with purchased or made-up standards. A concentration range of 0.7-5.5mg/L standards were made up according to Tappi methods with a few lower concentrations (below 0.7mg/L). A wavelength of 650nm was used as per Tappi standard method for the above range.

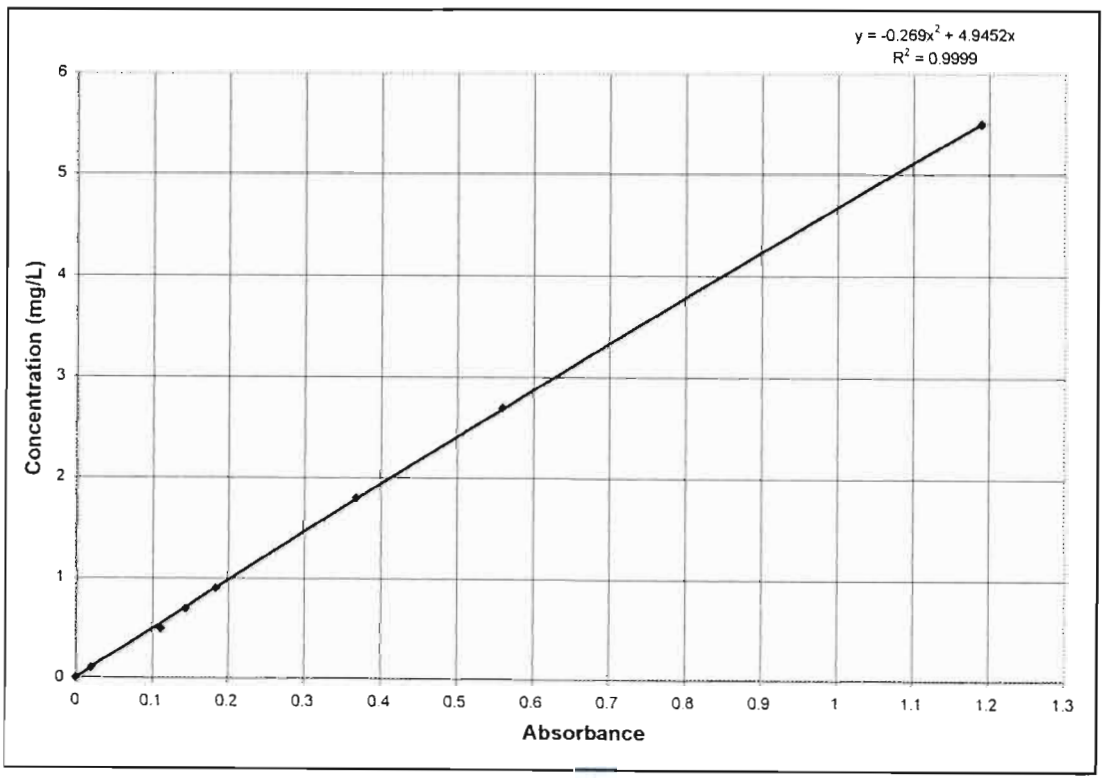


Figure 5-3: Spectrophotometer calibration

5.3.4 Sulphate Analysis

Sulphate in water was determined using a gravimetric method of analysis. In principle, sulphate is precipitated as barium sulphate in an acidic solution of hydrochloric acid with barium chloride addition. This solution is heated to boiling where precipitation takes place.

After a period of at least two hours, digestion is complete. The precipitate is then filtered, washed with water until no chlorides are present, dried and weighed as barium sulphate.

5.3.5 Ash Tests

The bed grit was analysed for organic carbon content. This was achieved by incinerating a sample of bed grit at 800°C for 4hours or until mass of incinerated sample remained constant. This was done in a Labcon muffle furnace. The inorganic carbon content was measured from the mass loss of the original sample by incineration of organics.

5.4 Catch Pot Analysis

The samples from the separator where analysed for silica, sulphate, sodium and potassium of which silica and sulphate where determined by methods stated above.

5.4.1 Sodium and Potassium Analysis

Sodium and potassium where determined using Flame Photometry. In principle, alkali (group 1) and alkaline (group 2) earth metals can be thermally dissociated from compounds in a flame. As a result, the atoms that are produced become excited; with electrons in their orbitals moving to higher energy levels. Since this state is temporary, the electrons return to their ground state, and on doing so emit radiation which lies mainly in the visible region of the spectrum. Radiation will be emitted at a specific wavelength characteristic of elements. In a flame photometer, an optical filter is used to separate the characteristic wavelengths of the elements being analysed. The intensity of this light is measured by a photodetector and an electrical signal is generated which is then processed and displayed as a reading in a digital or analogue form. Similarly, this instrument needs to be calibrated. Calibration graphs of potassium and sodium are shown below (Figure 5-4 & 5-5).

In some instances the intensity of the light emitted is directly proportional to the number of atoms returning to the ground state and in turn is proportional to the metal concentration in the sample. This is limited to low concentration ranges.

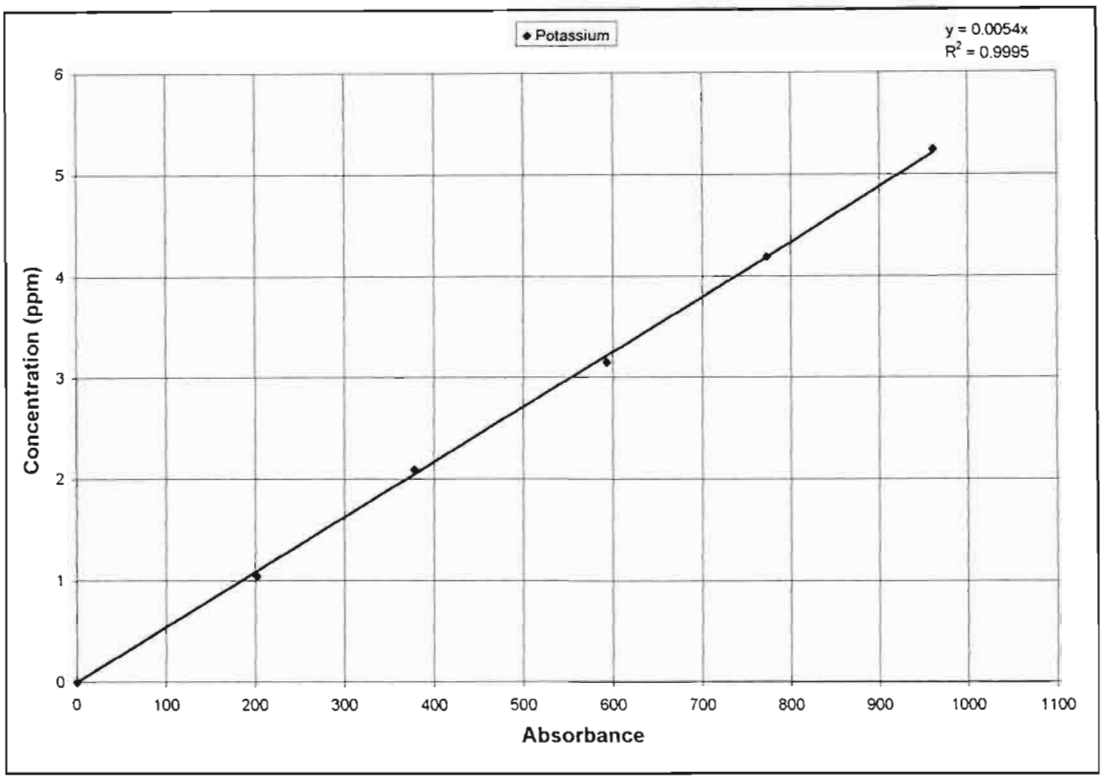


Figure 5 - 4: Potassium calibration

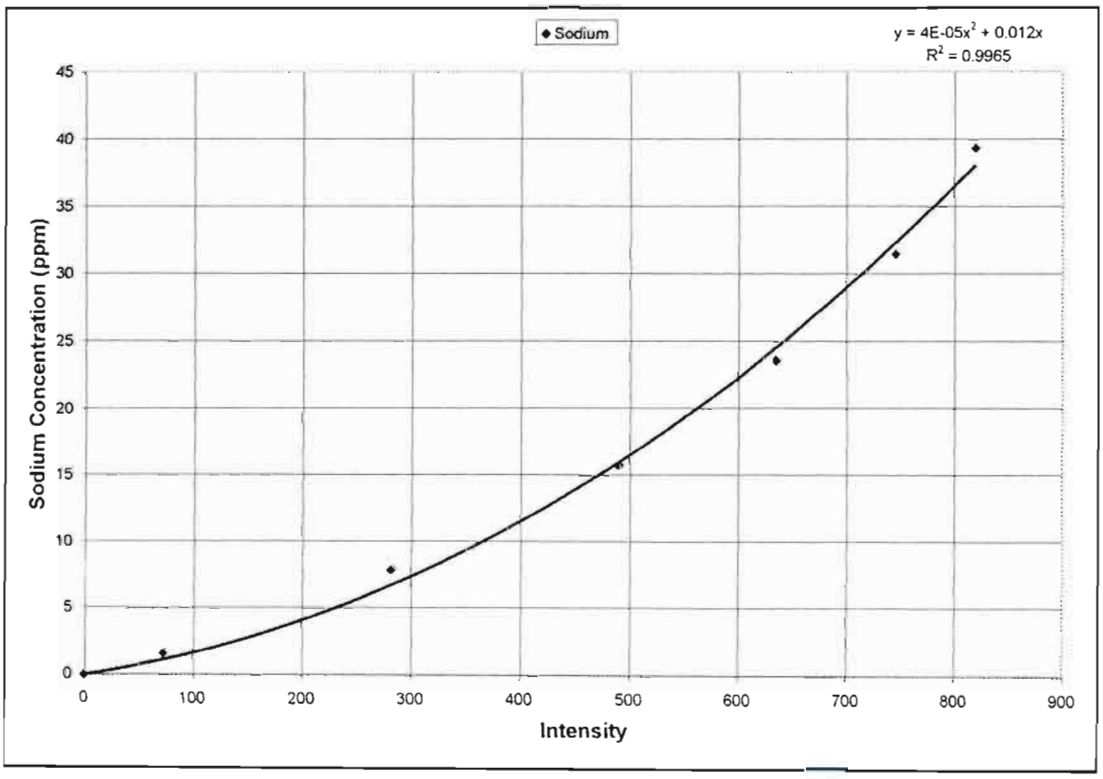


Figure 5 - 5: Sodium calibration

5.5. Product Gas Analysis

5.5.1 Gas Chromatography

Chromatography is a physical method of separation of sample components in which these components distribute themselves between two phases, one stationary and the other mobile. Gas chromatography is a method in which the mobile phase is gas. (Grob, 1995)

Dry product gas was analysed by gas chromatography from the wet product gas stream exiting the separator after water was removed via the condenser system and drying column. Hydrogen, carbon monoxide, carbon dioxide and methane were measured using a gas chromatograph. Calibration graphs are shown below (Figure 5-6:5-9).

During a run, samples were withdrawn by a vacuum pump at regular intervals for a minute. However, hydrogen sulphide produced from SASAQ liquor coated the silica gel crystals. The major concern was that the hydrogen sulphide coating would affect the mass balance for sulphur. Therefore, it was decided to take the hydrogen sulphide measurement using Drager tubes before the drying column. The other concern was that the coated silica gel crystals would not absorb moisture and may damage the column. Therefore, silica gel had to be continuously refilled in the drying columns, which was time consuming and was thought to compromise the sampling system. The other alternative was to reduce the time for sampling to 30s which reduced the coating of hydrogen sulphide. The concern here was that this might affect the concentration of the dry product gas. However, sampling for 30 or 60s had no effect on the dry product gas composition as the sample was being withdrawn at a high flowrate.

Two gas chromatograph columns were installed in a gas chromatograph (GC) unit with a single thermal conductivity detector. In order to cater for both columns, two gas tight syringes were used to take samples of the gas at sampling time. However, they could not be injected at the same time as each column used the same detector.

In order to achieve good separation of the peaks, the GC had to be operated at low oven temperatures with a suitable carrier gas flowrate. Thus, this led to longer residence times of the gas species in the chromatograph columns, which meant that the analysis time would be increased. In addition, only a few samples were taken in a run due to this. The total analysis time for both samples to run on the GC took roughly 15 minutes.

5.5.2 Interference of gas chromatograph columns

A continuous sample of product gas was withdrawn at regular intervals. Water was removed from these samples and then further dried using silica gel crystals in a drying column as a

good and cheap drying agent. The importance of this step is to ensure that no water gets into the GC column since water may interfere or damage the packing found in these column.

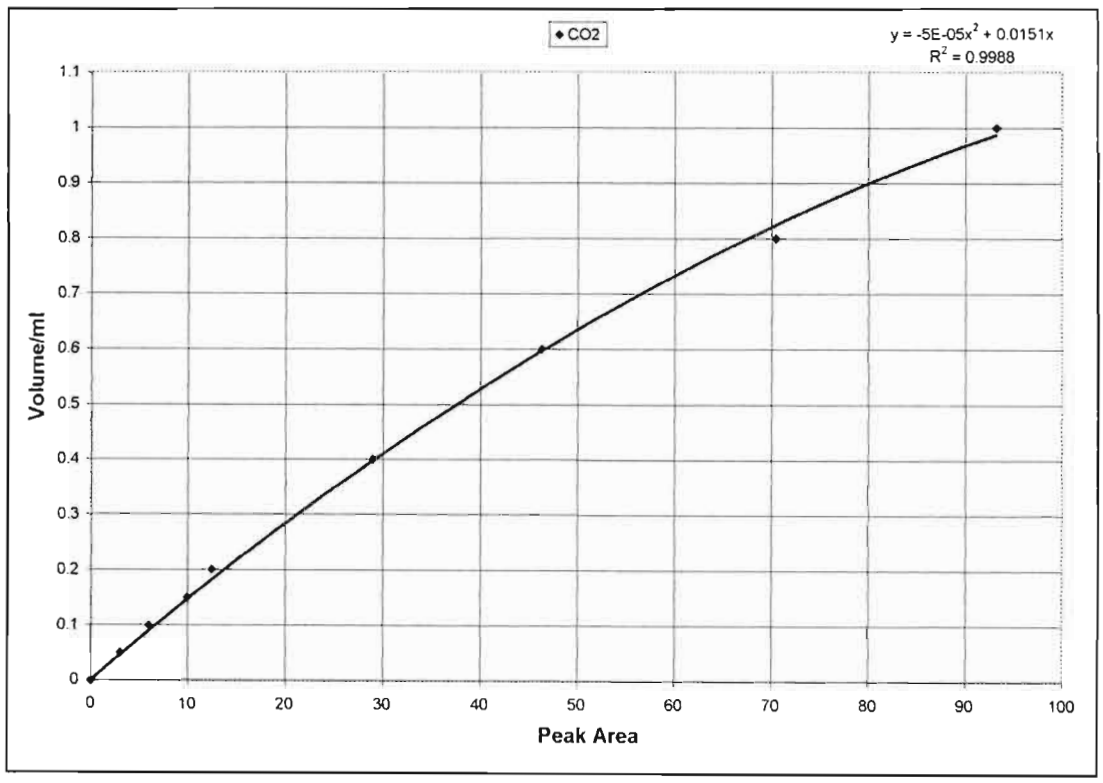


Figure 5 - 6: Calibration of carbon dioxide

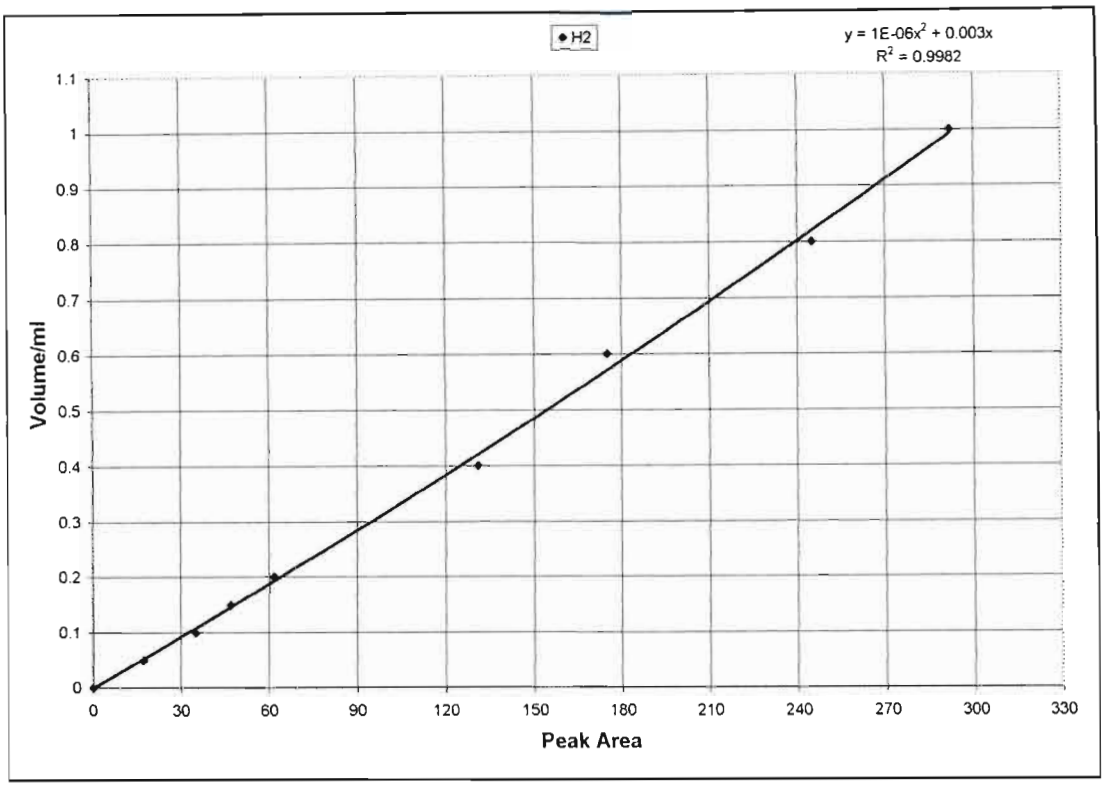


Figure 5 - 7: Calibration of Hydrogen

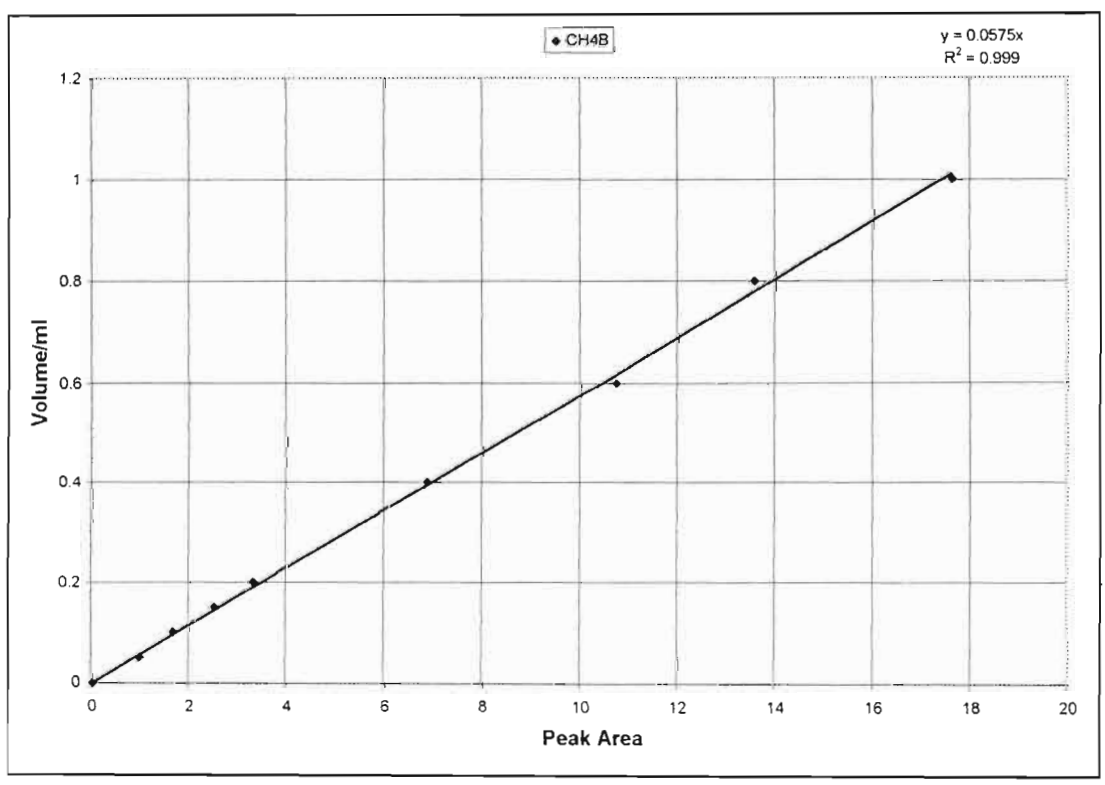


Figure 5 - 8: Calibration of Methane

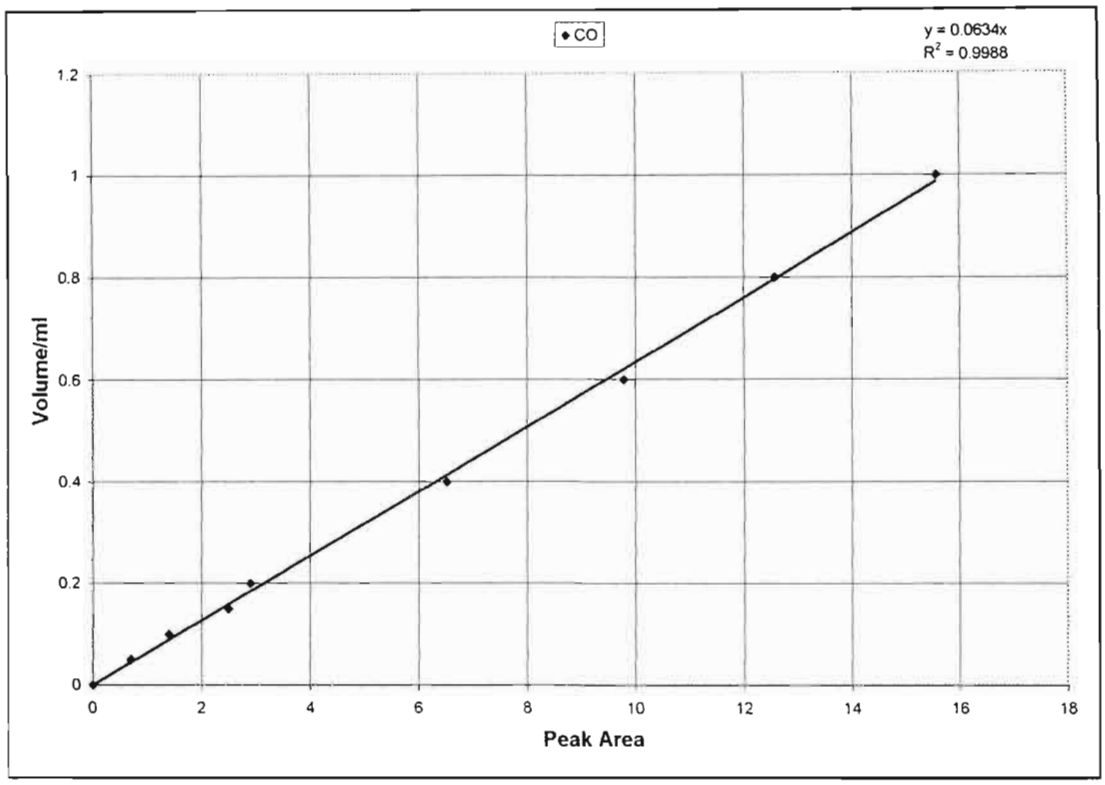


Figure 5 - 9: Calibration of Carbon monoxide

5.5.3 Drager Tubes

Drager tubes were used to measure the concentration of hydrogen sulphide before the silica gel drying columns (Figure 4-7). Two ranges of Drager tubes were purchased: 0.001-0.3 and 0.2-7 volume percent. They have a standard deviation of 10-15%. The drager tubes had to be used in conjunction with a drager tube pump.

They work on the principle of allowing the gas to be pumped into a tube with a hand held pump. The inside of the tube is lined with a packed bed of chemical granules, which undergo a colour change. The colour change is a function of the concentration of the component that is to be analysed.

5.6 Tar samples

Tar samples were qualitatively analysed using a gas chromatograph (GC) fitted with a mass selective (MS) detector. A Perkin Elmer 900 Autosystem XL, with a Perkin Elmer electron impact detector was used. The column used was an Elite capillary column HP. It is a 95% dimethyl, 5% diphenyl column, with a methylpolysiloxane stationary phase. The column dimensions are column length of 30m, diameter of 250μm and thickness of 0.25μm.

In order to achieve sufficient separation of the different components in the sample injected, the following variable settings were implemented.

Variable	Value
Injection Port Temp./ °C	40
Hold Time/ min	2
Ramp Rate/ (°C/min)	10
Final Temp./ °C	240
Hold Time at final Temp./ min	1
Scan Duration/ min	24
MS Interscan Time/ s	0.1
Injection Volume/ (μL)	1

Table 5 - 1: GC/MS settings

As the injected mixture passes through the column, compound separation takes place according to the boiling points of the compounds in the mixture. A chromatogram of the compound separation in the mixture is recorded which can be both qualitatively and quantitavely analysed. By virtue of the MS detector, mass spectral fragmentation patterns of each compound are also recorded for identification purposes. This is then compared to other mass spectral fragmentation patterns found in a mass spectral database for identification of unknown compounds. However, in most instances a number of compound possibilities are identified which may be very misleading. Therefore, caution must be exercised when going through these possibilities.

CHAPTER 6:

RESULTS AND DISCUSSION

The initial discussion focuses on the general aspects of the gasifier operation which discusses the difficulties associated with operating on such a large scale. Also discussed is the familiarisation of the pilot unit and bed material used in operation

Thereafter, fluidisation characteristics with details of the work done in cold testing, devising a means of determining bed fluidisation and the problems encountered by agglomerations will be elaborated on. The next topic of discussion is bed coating where evidence is given to verify this.

Following this, the experimental plan is reviewed with the approach used in the experiments discussed. Since the product gas composition is a vital part of this work, predicted gas compositions is compared to the findings obtained in the experimental work by adjusting the process variables of this system. These are the temperature, the spent liquor to steam ratio, the solids content of the liquor and time for soda and SASAQ liquors. The findings from bed material analysis are shown with the fate of non process elements elaborated upon. A summarised mass balance is also included. Finally, an attempt to consider the catalytic effect of alkali metals on the gasification of carbon is then discussed.

6.1 General Aspects of Gasifier Operation

6.1.1 Pilot-scale Considerations

The fluidised bed reactor used in this study, for a research project of this kind, was larger than those (Li et al., 1991b; Whitty et al., 1995) usually encountered. Therefore, the difficulties experienced when operating on this scale should be mentioned.

A great deal of time was involved in menial tasks like run preparation, maintenance and repairs. To paint a better picture, run preparation took roughly 1 ½ hours and cooling of the reactor took 3-4 hours before it could be cleaned. Some repairs took a maximum of three days. However, the major disadvantage of this size equipment was the great deal of manual labour involved especially during repairs.

6.1.2 Familiarisation

Many months were spent trying to perfect the operation of the unit. This meant dealing with the many problems encountered along the way as they arose. It was in this time that a simple yet effective operating procedure for the unit was developed. The operating procedure is elaborated upon in APPENDIX A.

6.1.3 Bed Material

Spherical particles of sodium carbonate were used as bed material for the pilot-scale unit in preliminary investigations. These porous particles were non uniform in size with particle diameter varying from 0.7 -1.2mm. Backman et al. (1993), reported that sodium salts have a melting interval of 760°C - 795°C and was valid for a system containing no impurities like chlorides or potassium.

Sodium carbonate was used and presented major problems in the fluidised bed operation. The continuous agglomerating of the bed occurred. The fusing of these particles was suspected to be caused by:

- Hot spots in the sodium carbonate bed due to the fluidising behaviour of sodium carbonate particles.
- The presence of non-process elements such as chlorides and potassium in the spent liquor which are reported to lower the melting point eutectics of the inorganic salts. (Backman et al., 1991; Frederick et al., 1991)

Consequently, partial or complete melting of the sodium carbonate particles occurred with subsequent fusion of the individual particles.

Therefore, a new bed material that contained no sodium salts and would be able to withstand the operating temperature and any subsequent temperature fluctuations or hotspots in the bed was sourced out. Two options were considered, namely; white aluminium oxide and sand. However, white aluminium oxide of non-spherical shape, also known as anti-bumping granules, was considered the better choice. The reason for this decision was based on the following:

- The aluminium oxide melting point of 2000°C is more than adequate for operating conditions. It does not contain sodium salts and it is therefore unlikely that fusion may occur in the presence of chlorides and potassium.
- The composition of the material will not form part of the mass balance closure on the system.

Although aluminium oxide grit had many advantages over sodium carbonate, it was speculated at the outset of the project that it would not be coated. However, after the initial experimental work, these speculations were dismissed.

6.2 Fluidisation Characteristics

6.2.1 Bed Behaviour during Cold Tests

Cold tests were conducted on the pilot-scale gasifier and on a lab-scale fluidised bed with air as the fluidising medium. The details of the lab-scale apparatus are in chapter 4. The lab-scale apparatus was used to determine the pressure drop versus velocity diagrams as detailed in chapter 3, from which the minimum fluidisation velocity can be obtained. It was however, not possible to use the gasifier for this purpose as small pressure changes could not be accurately measured by the pressure gauge of the gasifier. Instead, it provided relevant information on the behaviour of the bed with respect to aluminium oxide grit.

The lab-scale apparatus was equipped for easy and reliable measurements of the pressure drop across the bed as a function of the air flowrate. In addition, even the smallest of pressure drops could be measured with great sensitivity using a water-filled manometer. Although an electronic pressure measuring device would ensure greater accuracy, the water manometer sufficed for a rough estimate of the minimum fluidisation velocity of the lab-scale fluidised bed. The following pressure drop versus velocity diagram was obtained from lab-scale cold tests for aluminium oxide and sodium carbonate for increasing air flowrates.

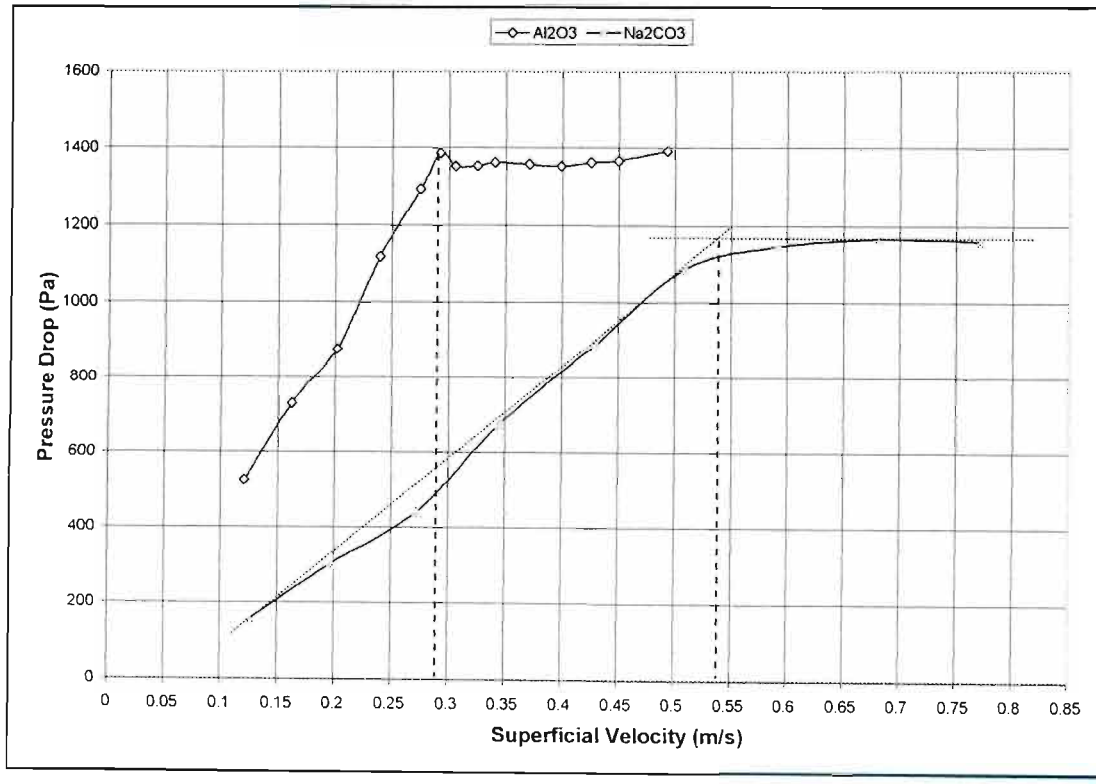


Figure 6 - 1: Characteristic curves for fluidisation behaviour of aluminium oxide (Al_2O_3) and sodium carbonate (Na_2CO_3).

Figure 6-1 illustrates the non-ideal behaviour as discussed in chapter 3. The aluminium oxide curve displays a hump which is reported to be caused by particles interlocking with each other and as a result partial bridging occurs. It is reported to occur in fluidised beds of small diameter, where wall effects are significant and are common to uniform sized particles. Since the aluminium oxide was of uniform size and the fluidised bed diameter was small, this non-ideal behaviour, as reported by Richardson (1971) and Kunii et al. (1991), supports the results obtained in this study.

The sodium carbonate curve displays a different trend which is valid with respect to the non-uniform size distribution of these particles. In theory, it is believed that the fixed and fluidised regions co-exist (see Figure 3-1and 3-3). As elucidated in chapter 3, part of the bed material weight is supported by the distribution plate therefore the pressure drop is below the expected value for non-uniform particles. However, the minimum velocity of the bed is higher than the expected minimum fluidisation velocity. This minimum velocity for a fully supported bed is difficult to determine from these diagrams and the minimum fluidisation value is instead used.

From the pressure drop versus velocity diagram, the minimum fluidisation velocity for both the aluminium oxide grit and the sodium carbonate particles (Figure 6-1) is 0.28m/s and 0.54m/s respectively.

Since it is not possible to determine the minimum fluidisation velocity on the gasifier, a suitable equation (Equation 3-7 and 3-8) was used. Considering that the aluminium oxide grit is non-spherical in shape and may be regarded as coarse particles, similar to sand but finer, it should be mentioned that many authors who have cited equations for the calculation of this value, define its use by either the nature of the particle whether coarse or fine (Kunii et al., 1991), or by the Reynolds number range (Geankoplis, 1993). However, for the purposes of this study, the choice of the equation will be based on the nature of the particles. From equation 3-8, the minimum fluidisation velocity of aluminium oxide was calculated to be 0.12m/s using the sphericity of sand (0.67) (Kunii et al., 1991). Sodium carbonate particles are spherical in nature (mean diameter of 0.91mm) and can be classified as fine particles. Equation 3-7 was used to calculate the minimum fluidisation velocity. This was determined as 0.49m/s using a sphericity of 1.00.

From experimental values, it is apparent that the minimum fluidisation velocity of sodium carbonate compares well with its predicted value. It should be mentioned that the measurement of this value from the pressure-drop versus velocity diagram may not represent the true value of a fully supported bed. The poor comparison for aluminium oxide grit could be due to the sensitivity of equation 3-8 to sphericity and voidage, which provide good results for materials for which this equation was derived. It is also believed that the sphericity of 0.67 used was too low but rather than on particle size, the correlations are dependent on particle shape and modification of their empirical constants accordingly should

improve their predictions of the minimum fluidisation velocity. In order to improve the minimum fluidisation velocity, the sphericity factor may require a more accurate determination. This in turn will require the determination of the fractional voidage and the frictional pressure drop of the bed (Kunii et al., 1991). In order to facilitate this sort of an investigation, a more precise experimental apparatus is needed but for the purposes of this study, the sphericity of sand will suffice.

From the calculated value of the minimum fluidisation velocity of aluminium oxide, it suggests that determining this velocity for superheated steam fluidisation will not be accurately predicted. Therefore, by using the minimum fluidisation velocity of aluminium oxide for air fluidisation as a correction factor, the minimum fluidisation of aluminium oxide grit under superheated steam conditions can be estimated.

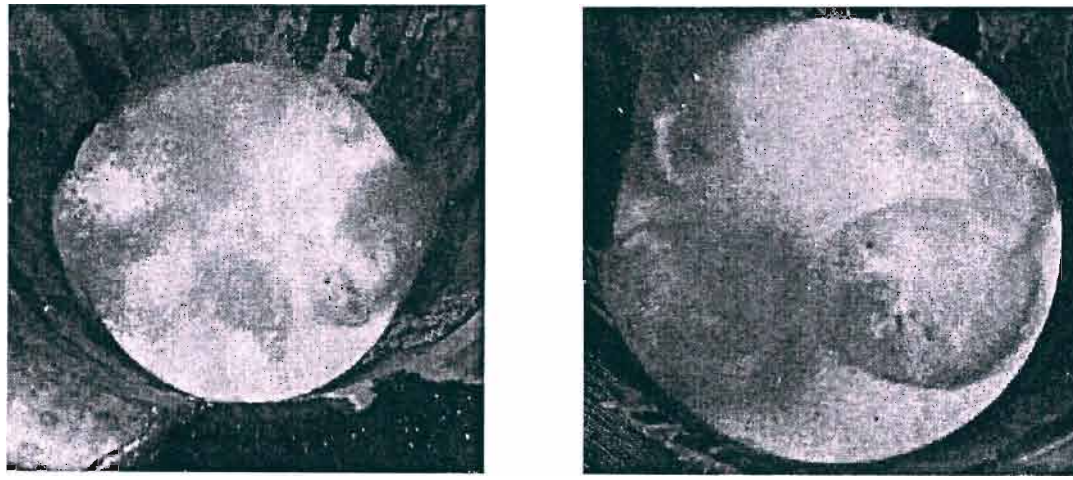


Figure 6 - 2: Fluidisation Behaviour of the bed with air

Figure 6-2 illustrates the type of behaviour characteristic of aluminium oxide grit in our unit during cold tests. From this figure, it is apparent that bubbling bed behaviour is dominant. The dark patches represent bubbles that have either reached the surface or collapsed.

According to Geldarts Classification of particle behaviour (Figure 3-4), aluminium oxide can be classified as Group B particles. Group B particles are reported in theory (Chapter 3) to be well fluidised particles that display dynamic bubbling action with the formation of large bubbles. This confirms the behaviour apparent in Figure 6-2.

Information of this nature is relevant as it gives an idea of the expected fluidisation characteristics during steam fluidisation of the aluminium oxide grit in the gasifier. This information is even more important when one considers that it is impossible to determine fluidisation characteristics visually under operating conditions.

6.2.2 Temperature Distribution as Fluidisation Indicator

The main flaw of this fluidised bed operation is the lack of a measurement system to assess whether fluidisation is in fact taking place. This was of concern because physical data such as the bulk particle density during fluidisation and bed height is required to improve the quality of fluidisation, and improved fluidisation in turn means better mixing. Since pressure drop is a function of density and height, the bulk particle density can be measured by virtue of the pressure drop across a fixed distance in the bed. By knowing this and the pressure drop across the bed, the height of the fluidised bed can be determined. Although this information is necessary, a fluctuation of the pressure drop across the bed is enough to indicate fluidisation.

In other fluidised bed studies (Du Preez, 1985), DP cells were used to measure the pressure drop across the bed. The DP cells were connected in a series configuration across sections of the bed. Du Preez (1985) states that the fluctuations of the pressure drop as bubbles moved through the bed was one of the most reliable ways of determining whether the bed was in the fluidised state.

In order to measure the pressure drops in the pilot unit, modifications will first need to be made. Since one of the objectives of this project was to evaluate the capability of the pilot unit as it is, this modification was recommended for further work. Therefore, another method was required. Kunii et al. (1985) stated that in a bubbling bed or turbulent bed operation, the temperature distribution is uniform throughout the bed. Following this, the only way of determining whether the bed is being fluidised in this operation was to monitor the distribution of temperature in the bed.

Several thermocouples are located at different positions in the system. Four of which are located in the bed chamber at different levels with two of them located in the bed as depicted in Figure 6-3. This enables us to determine the temperature distribution in the bed and in the freeboard region (region above the bed). Figure 6-4, illustrates the temperature distribution in the bed and in the freeboard region during a test with spent liquor. The freeboard region is depicted by the reactor middle temperature. The wall and reactor hot zone thermocouples are located at roughly 50cm and 97cm above the distribution plate respectively. It is apparent in Figure 6-4 that the bed temperature distribution is almost equal as the bed reaches operating temperature. This, by Kunii et al. (1991), indicates that the bed is being fluidised. After spent liquor is injected, noted by the dip in temperatures, the temperature readings are virtually the same except for the reactor middle temperature which is roughly 5-6^{0}C lower. The uniform temperature in the bed confirms the mixed nature of the bed. Rehmat et al. (1984) used the same approach to determine temperature distribution and to confirm the mixed nature of the bed.

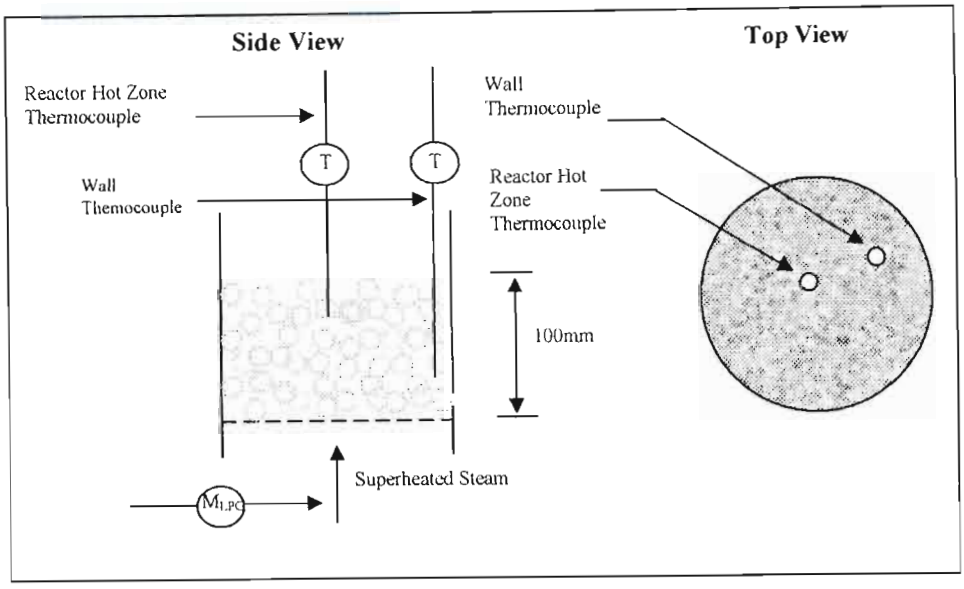


Figure 6 - 3: Sketch of Thermocouples in the bed

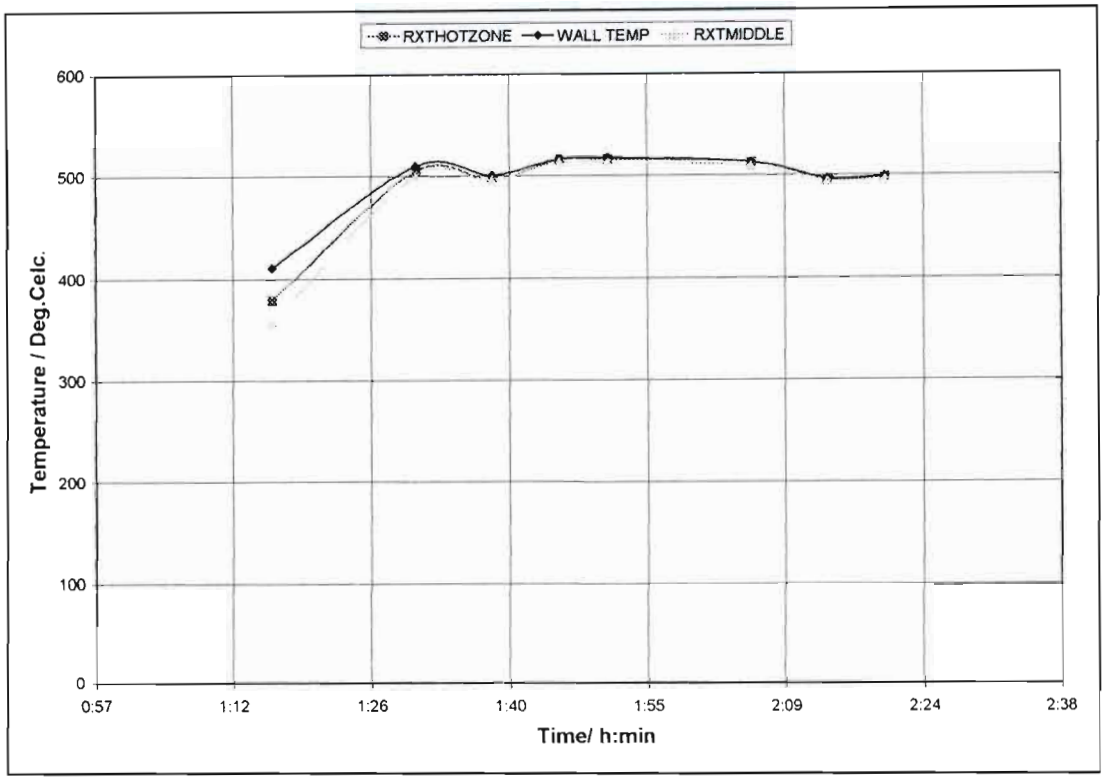


Figure 6 - 4: Temperature distribution in bed and freeboard

The lid of the gasifier is fitted with a small, circular quartz viewing window, which may have been intended for visually establishing the fluidisation status. However, this proved very dangerous. The lid of the reactor reaches high temperatures, usually above 300^0C. Even if the proper precautions were taken, determining whether the bed was fluidising was next to impossible to do because of poor visibility in the gasifier. Alternate means of determining

whether the bed was being fluidised was required. The use of laser equipment was investigated but was found to be very expensive. The idea behind it was that the laser was to reflect off metal balls in the bed and the intensity of the reflected light measured. However, this idea was complicated and coating of these balls would prove problematic. In conclusion, the simplest, cheapest and easiest way to monitor bed fluidisation was to measure temperature distribution in the bed.

6.2.3 Solids Agglomeration

Initially, sodium carbonate was used as bed material in the gasifier. As mentioned previously, agglomeration due to the melting of the sodium carbonate particles posed a major problem. It was believed that hot spots due to dead zones and the presence NPE's were responsible for this. Agglomeration in a fluidised bed may vary in intensity from barely perceptible interparticle sintering to an extreme state where surface fusion of particles occur (Whitehead, 1971).

According to the cold tests conducted, it was apparent that the fluidisation behaviour as observed in the gasifier, demonstrated spouting behaviour. This behaviour was confined to the centre of the bed and may have been caused by channelling. As a result, little or no movement was observed around the edges. According to Geldarts Classification (Figure 3-4) for particle behaviour, sodium carbonate particles exhibit Class D particle behaviour. This assessment was based on the mean diameter and density differences as per the parameters of the Geldarts classification.

Class D particle behaviour (Section 3.1.3), are believed to display spouting behaviour and these particles are regarded as difficult to fluidise. Furthermore, this class of particles are said to behave erratically causing severe channelling. This type of behaviour, according to Geldarts Classification, will also occur during superheated steam fluidisation.

In order to improve the fluidisation behaviour, the distribution plate was modified with the addition of several bubble caps, so that the dead zones could be reduced. Although this would compromise the existing design by reducing the overall pressure drop, this modification was based on the presumption that an increase in superficial velocity of superheated steam would counteract the change. During cold model testing of the modified plate, it was apparent that the bed was uniformly fluidised. As expected, the superficial velocity had to be increased.

The option of modifying the distribution plate was chosen due to the time constraints. It was approximated that making up a new distributor would be time consuming when designing, procuring, in-house fabrication and testing considerations were taken into account. There was also the possibility that the new distribution plate may not work. Due to financial constraints an outside company could not be approached to fabricate the distribution plate.

The distribution plate was tested in a full test run with aluminium oxide. Immediately during bed start-up with air, temperature gradients within the bed were observed. An increase in the superficial velocity resolved this problem. Similarly with superheated steam, fluidisation had to be controlled by the superficial velocity.

When spent liquor was injected, poor bed fluidisation behaviour was immediately apparent when the bed temperatures were monitored. A temperature reduction of approximately 10°C at the beginning of liquor injection was expected but the temperature of the reactor hot zone continually decreased and a large difference between the wall temperature and the reactor hot zone temperature was evident. This occurred due to the formation of agglomerates in the bed. The bed then defluidised and behaved like a fixed bed. This was noted by the large temperature gradients in the bed (Kunii et al., 1991). Further increases in the superficial velocity reduced the size of the agglomerates in the bed but did not eliminate it. Large agglomerates, of diameters up to 10cm (Figure 6-5), were formed.

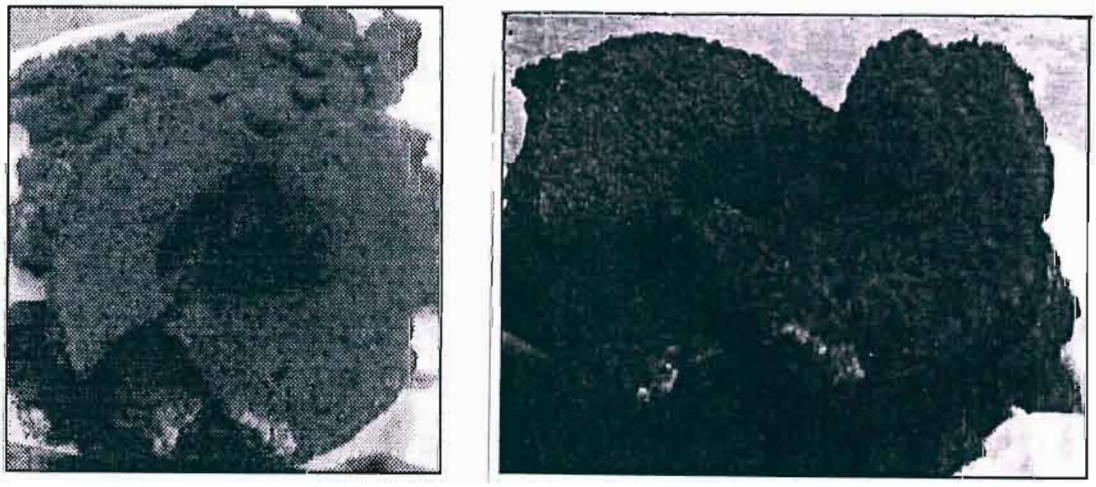


Figure 6 - 5: Top and Side View of Agglomerate

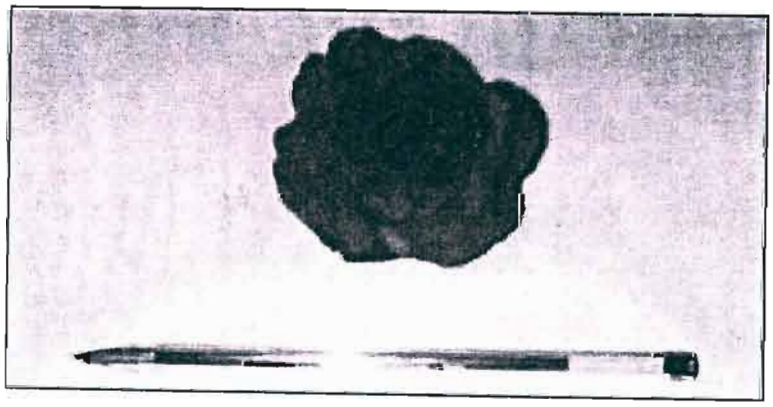


Figure 6 - 6: Smaller Agglomerate with increased superficial velocity

Many fluidised bed gasification studies were reviewed and it was found that in these studies agglomeration was also encountered (Olazar et al., 2002; Dickenson et al., 1998). These studies were conducted on a bench-scale level.

Olazar et al (2002) reported that particle agglomeration and the resulting bed defluidisation may be due to the high particle density common in fluidised bed reactors. They used soda liquor from straw pulping for treatment in a bench-scale fluidised bed and spouted bed reactor. The fluidised bed reactor was operated at a superficial velocity of seven times the minimum fluidisation velocity. Our unit operates at twice the minimum fluidisation velocity. The soda liquor used in this study is similar to the soda liquor used in the study by them, except that the chloride, potassium and silica levels in the liquor that they had used were much higher. The agglomeration problems were concentrated in the fluidised bed reactor and not in the conical spouted bed reactor. In the spouted bed reactor, the agglomerations are broken up by the vigorous movement of the solids. Subsequent bed defluidisation was reported to be due to the swelling properties of spent soda liquor.

Dickenson et al. (1988) conducted a more detailed study of Kraft spent liquor gasification with a mixture of air, nitrogen and steam at similar operating temperatures. From their study, they concluded that low temperature gasification was possible in a bubbling bed mode. Agglomerates of char and sand, with diameters between 10 to 25mm, were reported. They believed that the subsequent defluidisation was due to the settling of the agglomerates on the distributor.

The conclusion drawn from these studies is that vigorous movements of solids are required to breakdown agglomerates and that the modified distribution plate did not achieve this. This is especially important when dealing with sticky spent liquor like soda liquor.

It seemed that the agglomeration problems encountered may lie in the poor interaction of the solids in the bed. Subsequently, when the spent liquor goes through a sticky stage, the solids in the bed begin to agglomerate. Increasing the superficial velocity may resolve this problem but the higher steam flowrate required may prove to be uneconomical.

Therefore, by plugging the holes of the added bubble caps, more vigorous bubbling bed behaviour for aluminium oxide was created. This ensured that the agglomerates would be broken down as soon as they were formed and thus be removed. Since aluminium oxide grit was the permanent feature of the gasifier, fluctuations in temperature would not be a problem.

6.3 Spent Liquor Coating

Aluminium oxide grit has an irregular shape and its crystal form is classified as rhombohedral class. By means of the scanning electron microscope, the shape and surface of aluminium oxide grit was viewed (Figure 6-7).

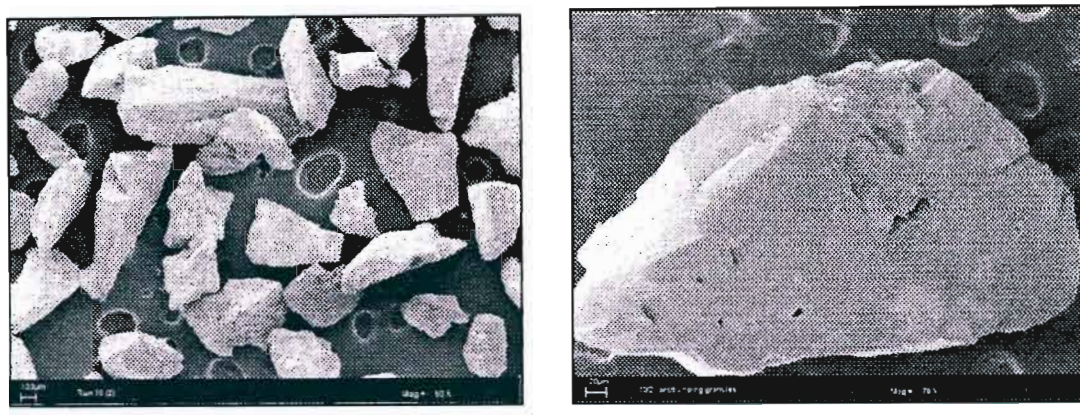


Figure 6 - 7: Aluminium Oxide Grit

The major concern of using aluminium oxide grit was that the liquor would not adhere to its surface. In addition, the char coating would be worn away during fluidisation due to the natural attrition of particles in a fluidised bed. However, sufficient evidence was obtained from experimental work to allay these fears. Scanning electron microscope (SEM) micographs, electron dispersive spectroscopy (EDS) and X-ray fluorescence (XRF) provide sufficient evidence to establish that aluminium oxide grit can be coated.

On inspection of the grit it was noted that the coating became lighter with increased temperature. This was due to the increased organic carbon conversion with less organic carbon remaining in the bed at higher temperatures.

Sodium was used as a tracer element to quantitatively evaluate the extent of the coating (Figure 6-8). Apart from being the second highest constituent of the spent liquors used, it is believed to deposit in the bed (Rockvam, 2001). The following sodium results were obtained from XRF analysis of a bed of aluminium oxide that was continuously used in experiments with spent soda liquor of different concentrations. In addition, the temperature was varied with each run an hour long.

Figure 6-8, illustrates the loading of sodium onto the aluminium oxide bed. Samples were taken in duplicate from a well mixed bed and analysed by means of XRF. The results depicted in the figure indicate that sodium was, in fact, deposited in the bed. This can only be achieved if more liquor makes contact and dries on the aluminium oxide grit thus increasing the sodium content. At higher temperatures, these results indicated that more sodium was loaded onto the bed.

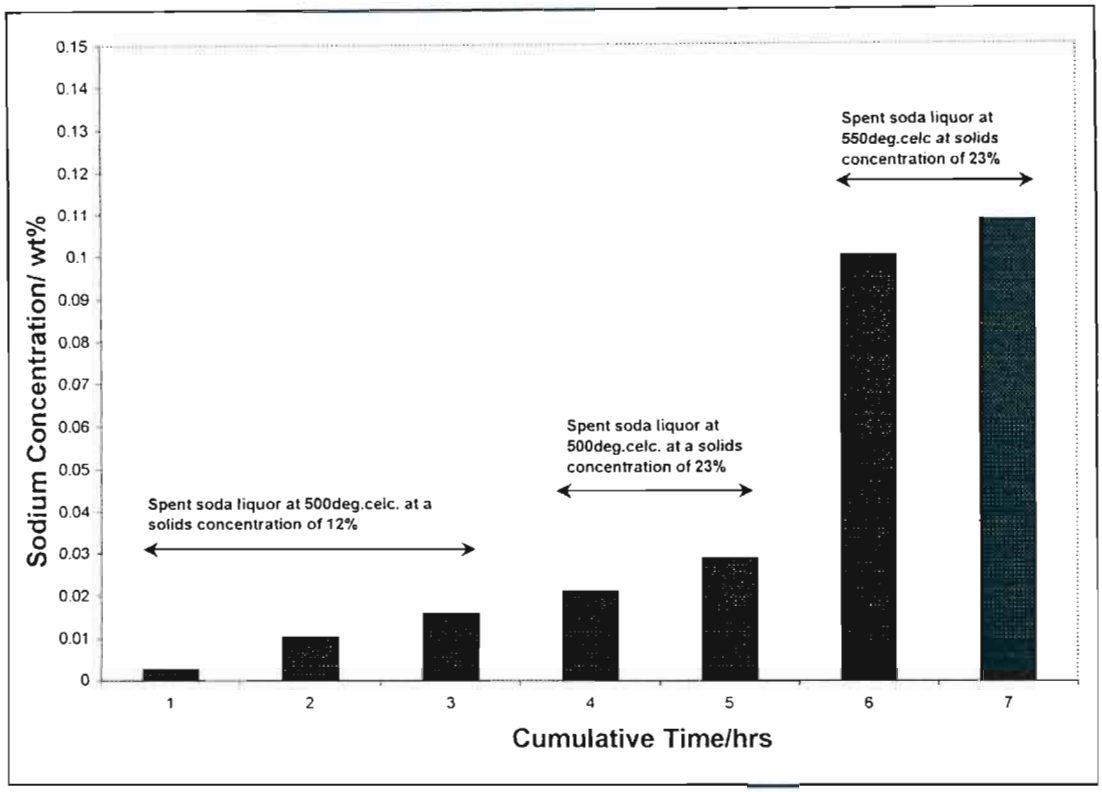


Figure 6 - 8: Sodium used as a tracer to determine bed loading

Further evidence of aluminium oxide grit coating is given in the following SEM micrographs. From Figure 6-9, it is apparent that the grit is coated. Char particles are seen (A).

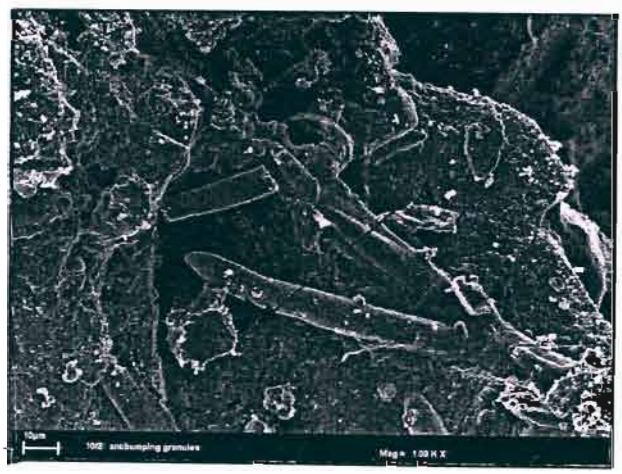


Figure 6 - 9: Micrograph of the surface morphology of aluminium oxide grit from the gasification of spent SASAQ liquor

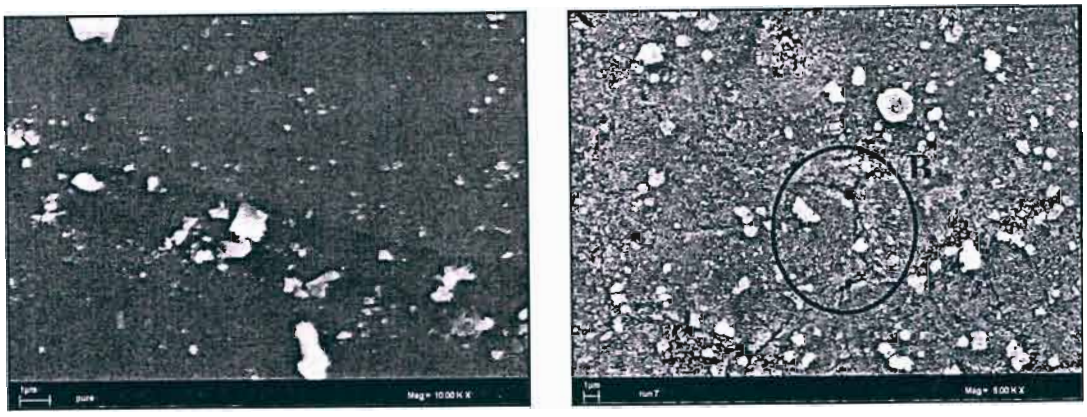


Figure 6 - 10: Micrograph of the surface morphology of aluminium oxide grit from the gasification of spent soda liquor compared to a non-coated grit (left)

Figure 6-10 shows that spent liquor has coated the surface of the grit and this is seen by the crack (point B) in the coating. The crack can be identified as char. The natural curling structure of the char is evident.

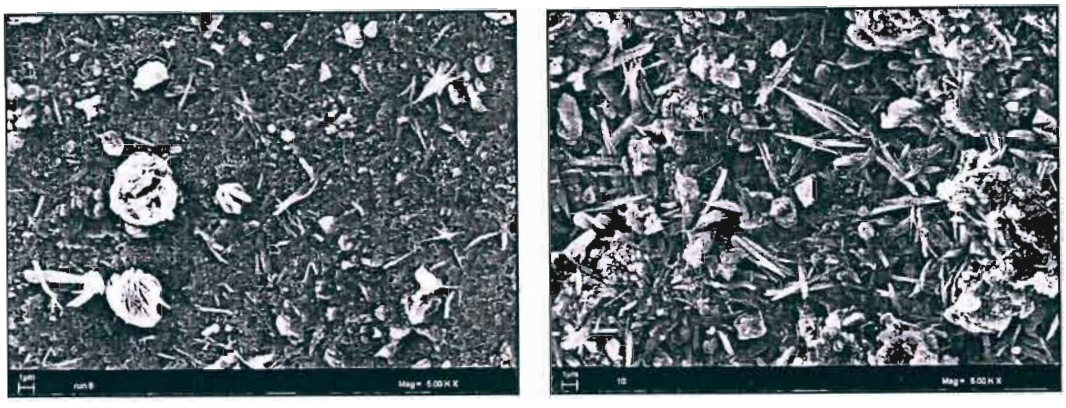


Figure 6 - 11: Micrograph of more coated grit

The micrographs in the figures 6-9 to 6-11 reveal that the coating on the surface of the grit is made up of crystal structures with unique forms. Details of which will be discussed in a later section.

Analysis by electron dispersive spectroscopy (EDS) provided the results of surface analyses of the aluminium oxide grit. This indicated that the surface coating is composed of a high concentration of aluminium, oxygen with carbon and sodium at lower concentrations. It is reasonable to assume that the high concentration aluminium and oxygen is due to the chemical composition of the aluminium oxide grit whereas carbon and sodium are from the coating of spent liquor. The carbon indicated represents both organic and inorganic carbon present. The weight percentage of carbon to sodium is greater than 2:1. The mere presence of aluminium oxide according to this surface may indicate that the grit is not uniformly coated.

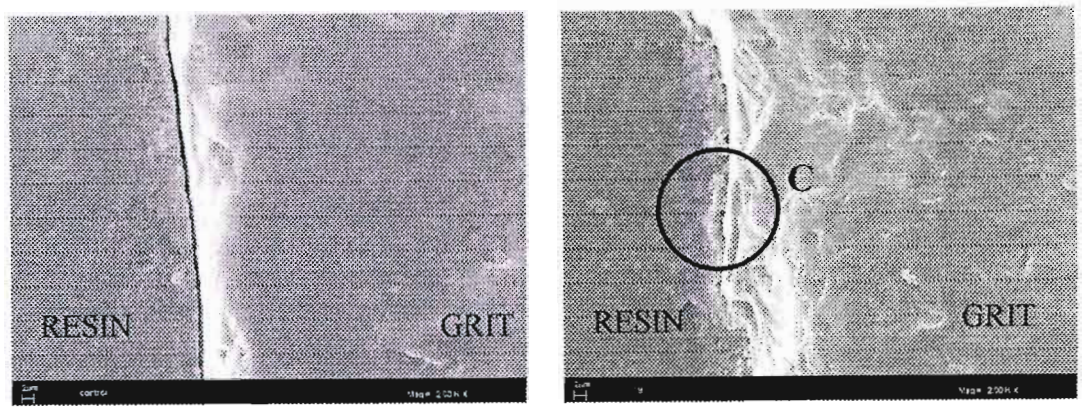


Figure 6 - 12: Coated grit (right) and control (left)

The micrographs in Figure 6-12 are that of a grit sample that was set in resin and polished down so that the thickness of the coating could be evaluated. However, it is difficult to deduce the thickness of the coating as it is evident that the coating is not uniform (point C). The coating at point C is clearly visible at the interface attached to the grit. The EDS analysis of this point indicated that carbon and sodium were present. High concentrations of sodium were found. Therefore, the presence of the sodium must be from the coating of the spent liquor.

6.4 Cleaning of Coating

Warm to hot water was used to remove the coating from the aluminium oxide grit but with little success. It seemed as if the coating formed a permanent bond to the surface of the grit. This could have been due to the formation of the unusual crystal structures apparent in the above micrographs (Figure 6-9, Figure 6-11).

However, fluidising a coated bed with superheated steam at a temperature of 600°C for an hour completely removed the coating. Since no spent liquor was injected into the bed in this run, it was believed that the organic carbon present in the coating was entirely gasified at 600°C. Furthermore, XRF analysis of the grit from the run indicated that sodium was present and may have been in the form of sodium carbonate. Ash tests of coated aluminium oxide grit at 1000°C proved that the coating had been removed but sodium was still present on the surface of the grit. It was speculated that inorganic carbon in the form of sodium carbonate bonds to the surface of the grit once the organic carbon is gasified and the crystal structures that form on the surface are in fact sodium carbonate.

This discovery was useful because it provided a way for re-using bed material. This proved very cost effective, but since the bed was to be re-used, it became necessary to analyse the bed before a run. This ensured that accurate results from bed analyses were obtained.

6.5 Experiments

Numerous experiments were conducted using the gasifier illustrated in Chapter 4. The primary objective of the experiments was to evaluate the gasification capability of this fluidised bed with respect to process variables, process species of interest and non-process elements.

A proposed plan for the experimental work was designed, which involved investigating the effect of operating variables such as temperature, spent liquor (L) to steam (S) ratio [L:S], spent liquor solids content (Solids) and time. There were two types of spent liquor used in this study, namely; soda and sulphite liquor (SASAQ), both of which were obtained from the pulping of bagasse. In the case of the SASAQ liquor, this investigation was limited to temperature and time. SASAQ liquor of 20 % solids content was available for this investigation. The experiments were based on the following experimental design:

Independent Variables	**Data Set A**	**Data Set B**	**Data Set C**	**Data Set D**
L:S	V	C	C	C
Temperature	C	V	C	C
Time	C	C	V	C
Solids	C	C	C	V

Table 6 - 1: Experimental design for Spent Soda Liquor.

Legend: C-constant; V-variable

Independent Variables	**Data Set E**	**Data Set F**
Temperature	C	V
Time	V	C

Table 6 - 2: Experimental plan for Spent Sulphite Liquor (SASAQ)

Legend: C-constant; V-variable

The elemental analysis for both spent liquors is given in Table 2-1. It should be noted that these values were given as a generalised elemental analysis from the sponsors of this project. Initially, the analysis of the soda and sulphite liquors were conducted by outside laboratories but these results proved to be unsatisfactory and was therefore not used.

The generalised elemental analysis was used to conduct mass balances on the system. However, this analysis does not take into account the fact that the spent liquor compositions may have varied considerably as the spent liquor samples used in this study were received from Sappi-Stanger Mill at different times. Consequently, this may have had a major impact on the results and the interpretation there of.

6.5.1 Approach for Experiments

The general approach used in this study was to:

- change one of the process variables of interest
- keep the remaining variables constant and
- study the effect.

This was easily achieved since each variable was independent. Many of the runs were done in duplicate for verification purposes. Duplicate runs were important as it ensured some degree of confidence in the results obtained. A set of average data is located in APPENDIX H for the composition profiles of the experimental runs conducted. Although, there are many limitations on the data, we should not lose sight of the fact that the gasifier is a useful instrument to study the chemistry of spent liquor gasification.

In the case of the spent liquor to steam ratio (L:S), it was decided that the spent liquor was to be varied and the steam flowrate to be kept constant. The reason for this is that in varying the steam flowrate, fluidisation and mixing will be affected. Consequently, heat and mass transfer effects must be accounted for if steam flowrate were to be changed. Therefore, it was decided best to keep the steam flowrate constant and vary the spent liquor flowrate.

6.5.2 Description of Experimental Runs

The general approach to a run was to preheat the bed with air until the temperature in the bulk of the bed was uniform. Thereafter, air was switched over to superheated steam which then takes the bed up to gasification temperatures. This was found to be the most effective method for gasifier operation.

After the operating temperature was reached, a further period of 10 minutes was required before spent liquor was injected. Thereafter, the bed temperature dropped by 5-10°C. Only once steady state with respect to the temperature profiles in the bed, spent liquor and steam flowrates was reached, did analysis of the product gas begin.

Gas chromatography was used in the analysis of the product gas. Fixed volume samples of the product gas were then injected into the gas chromatograph (GC) unit. Prior to injection, water from the wet product gas had to be completely removed and to protect the columns in the GC. Water was knocked out in a condenser system and the sample gas further dried in a drying column.

6.6 Predicted Equilibrium Gas Compositions

The equilibrium concentrations were calculated for temperatures of 500-600°C. The following independent reactions were considered in this equilibrium calculation. The calculations are reported in the APPENDIX B.

$$C + H_2O \leftrightarrow CO + H_2 \quad (A)$$
$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (B)$$
$$C + 2H_2 \leftrightarrow CH_4 \quad (C)$$

	500°C	550°C	600°C
K_A	0.024	0.086	0.269
K_B	5.755	3.669	2.718
K_C	2.586	1.000	0.449

Table 6 - 3: Equilibrium Constants for Reactions A, B, C (Smith et al., 1996)

Components	500°C	550°C	600°C
H_2O	0.326	0.273	0.203
CO	0.032	0.073	0.139
H_2	0.240	0.322	0.392
CO_2	0.253	0.228	0.196
CH_4	0.149	0.104	0.069

Table 6 - 4: Predicted Composition of Wet Product Gas (mol%)

	500°C	550°C	600°C
CO	0.0481	0.1007	0.1747
H_2	0.3560	0.4430	0.4926
CO_2	0.3750	0.3137	0.2459
CH_4	0.2210	0.1426	0.0869

Table 6 - 5: Predicted Composition of Dry Product Gas (mol%)

The data reported in Table 6-4 and Table 6-5 above show:

1. Hydrogen and carbon monoxide increased with temperature.
2. Methane and carbon dioxide decreased with temperature.

6.7 Experimental Product Gas Compositions

6.7.1 Spent Soda Liquor

Spent soda liquor has low sulphur content (0.03%). Therefore, its contribution to the formation of hydrogen sulphide is negligible. The only source of sulphur that comes into the pulp and papermaking process is from bagasse and not from the pulping chemicals used. In the case of soda pulping of bagasse, sulphur may be referred to as a non-process element.

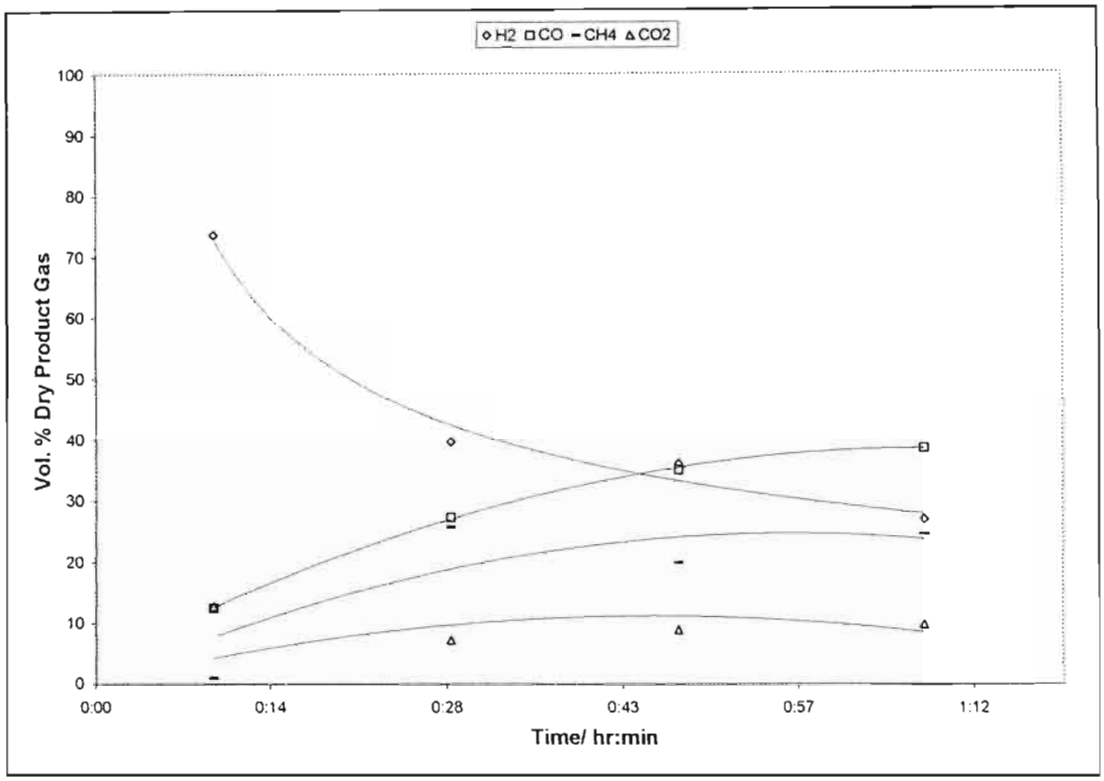


Figure 6 - 13: An example of a typical dry product gas distribution at 500°C with L: S of 0.06 for 23% solids liquor.

Figure 6-13 illustrates the trends that were observed in the dry composition profiles of the syngas from the gasifier. A product gas consisting of hydrogen, carbon monoxide, carbon dioxide and methane was produced. This product was the result of the following reactions (Li et al., 1991b):

$C + H_2O \leftrightarrow CO + H_2$ <6-1>steam-carbon gasification reaction

$CO + H_2O \leftrightarrow CO_2 + H_2$ <6-2>water-gas shift reaction

$C + 2H_2 \leftrightarrow CH_4$ <6-3>methane formation reaction

The main reaction was considered to be the water-gas shift reaction.

In addition, it is clear that the dry product gas species approached equilibrium. When one considers that the gasifier system was continuous with respect to the reactants and product gas, then the abovementioned trend is an acceptable description of the species in the product gas. However, it is surprising that it takes so long to reach equilibrium considering the quick reaction rates and short residence time in the reactor of the steam. A possible explanation is that the gasification was affected by the extent of the coating on the aluminium oxide and perhaps the coating reaches an equilibrium thickness during firing of the liquor.

Furthermore, it is apparent from Figure 6-13 that hydrogen was the principle constituent of the dry product gas at the initial stages of the run. However, with time, the compositions of the remaining gases gradually increased with a decrease in hydrogen. This can be explained by looking at the devolatilisation (pyrolysis) stage, the second stage in the conversion of spent liquor (Figure 2-4). In this stage the organic matter in the liquor degraded to form combustible gases from volatile substances with the formation of hydrogen and carbon monoxide. The initial presence of very high hydrogen concentrations may be due to the fact that the burning stages (spent liquor conversion stages) overlapped to varying degrees (Whitty et al., 1997). This implied that the char burning stage may have overlapped with the devolitisation stage. The hydrogen concentration was significantly higher than the carbon monoxide concentration at the initial stages of this run. This may suggest that more hydrogen formed than carbon monoxide.

An alternative explanation is that the carbon monoxide was consumed via the water-gas shift reaction <6-2> to form more hydrogen. Towards the end of the run, the shift in the reaction favoured the formation of carbon monoxide rather than hydrogen.

6.7.1.1 The Effect of Temperature

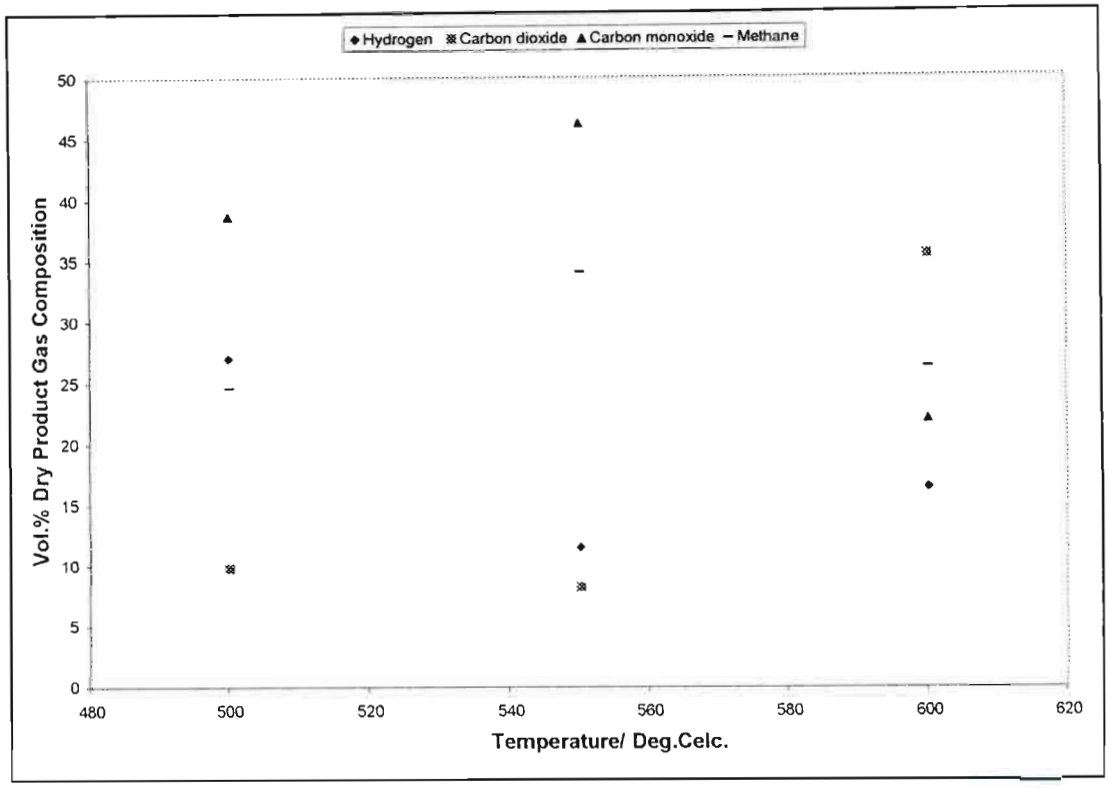


Figure 6 - 14: Effect of temperature on the product gas compositions

The effect of temperature on the product gas distribution was investigated by increasing the gasification temperature. The effect of temperature in the range of 500-600°C with a constant L: S ratio, solids content and time. The L: S ratio was constant at 0.06, with 23% solids spent liquor used in a 70 minute run. In some instances, the run was a few minutes longer to allow for an extra set of samples, which was required when the reliability of data was questioned. From the product gas composition profiles, the increase in time by a few minutes had no significant effect on the product gas distribution.

The temperature was limited to a maximum of 600°C and was based on the eutectic considerations of the system rather than a random choice. This decision was based on the NPE's (chlorides and potassium) present in the spent liquor which was reported to reduce the melting points of alkali salts (Backman et al., 1993; Frederick et al., 1991).

As was discussed in section 6.7.1., a similar trend to Figure 6-13 in the composition profiles at different temperatures was observed. It is quite evident that temperature is an important process variable and its significance on the product gas distribution should be noted.

From the predicted gas compositions, carbon monoxide and hydrogen were expected to increase with temperature; however experimental data proved contrary. In fact, carbon

monoxide and hydrogen decreased with an increase in temperature and the carbon dioxide composition increased with a increase in temperature (Figure 6-14). High concentrations of carbon dioxide are recorded at 600°C, at levels of over 35%. In addition, methane was predicted by calculations to be 22.1% at 500°C and predicted to decrease to about 8% at 600°C. However, this was not the case.

The experimental results can be explained by Le Chatelier's principle. According to Le Chatelier, the water-gas shift reaction will favour the formation of carbon dioxide and hydrogen at high temperatures, and the formation of carbon monoxide and steam at lower temperatures. This is true as carbon dioxide observed from Figure 6-14 was above 35% at 600°C and lower than 10% at 500°C. Carbon monoxide was at its highest concentration at 500°C and at its lowest at 600°C. Furthermore, the formation of hydrogen was observed to decrease with increasing temperature and may be due to the formation of methane via the consumption of hydrogen.

When considering the methane formation reaction <6-3> and equilibrium constants of this reaction, it was found that the equilibrium constant <6-4> at atmospheric pressure decreased with temperature and was almost negligible at 600°C. In fact, a rough estimate of the equilibrium constant was found to be 2 times lower at 600°C than at 500°C. This indicated that the methane content should be significantly lower than the compositions reported in this study. However, methane was recorded to be roughly 25% at 500°C and 600°C but increased to 35% at 550°C.

$$K = \frac{Y_{CH_4}}{Y_{H_2}^2} = \frac{P_{CH_4}}{P_{H_2}^2} \qquad \text{<6-4>}$$

Kohan (1981) stated that the gasifier methane yields may be difficult to solely predict from equilibrium considerations and that this may depend on the reactivity of the feedstock and the type of gasifier.

6.7.1.2 The Effect of the Spent Liquor to Steam Ratio

The spent liquor to steam ratio (L: S) is an important process variable. L: S ratios would be preferable when considering the economics of plant operation. Subsequently, lower steam wastage per kg of organic carbon gasified would be the ideal case.

However, not much information is known about the effects of this variable on spent liquor gasification. In order to evaluate this ratio, it was decided to vary the spent liquor flowrate whilst maintaining a constant steam flowrate and temperature of 500°C. The following ratios were investigated: 0.06 and 0.12.

By maintaining a fixed steam flowrate, it was possible to evaluate the effects of increasing the spent liquor flowrates without having to consider the mass transfer effects. Arbitrary ratios were chosen to investigate this process variable.

It was postulated that by increasing the spent liquor flowrate, the product gas distribution will favour the formation of more hydrogen and carbon dioxide. This was found to be incorrect. Although the carbon dioxide concentration did increase, it was still lower than the carbon monoxide concentration. This suggested that temperature has a significant effect on product gas composition no matter how much of spent liquor is added. The increase was limited to carbon dioxide only, and carbon monoxide and methane remained virtually unchanged. A twofold increase in carbon dioxide concentration was noted towards the end of the run when compared to the L: S ratio of 0.06 (Figure 6-15). Figure 6-16 illustrates the effect of the increased spent liquor flowrate on the CO_2/CO ratio as a function of time. A plausible explanation of the increase in carbon dioxide is the higher organic carbon available for gasification with steam.

Figure 6-15 illustrates the effect of L: S on the dry product gas composition profile. Subtle increases in the carbon monoxide and methane compositions were noted with a significant increase in composition of carbon dioxide. However, a decrease in hydrogen concentration was recorded, with an increase in the spent soda liquor flowrate.

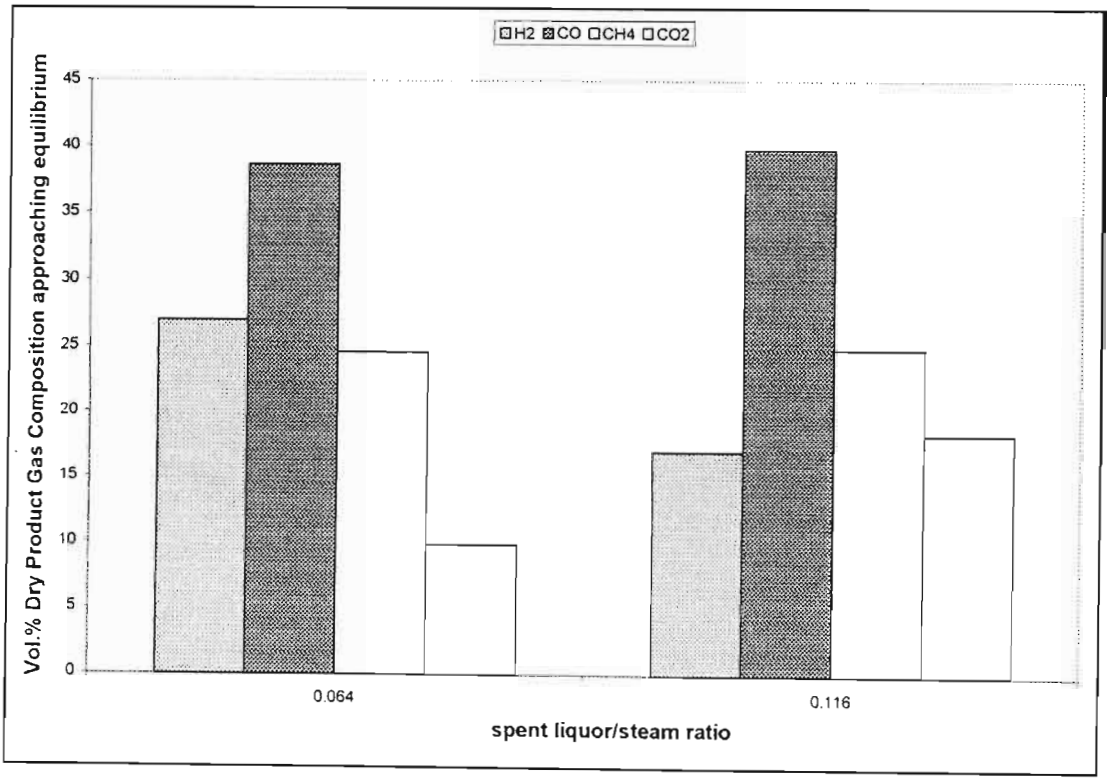


Figure 6 - 15: Effect of spent liquor to steam ratio on product gas composition at 500°C

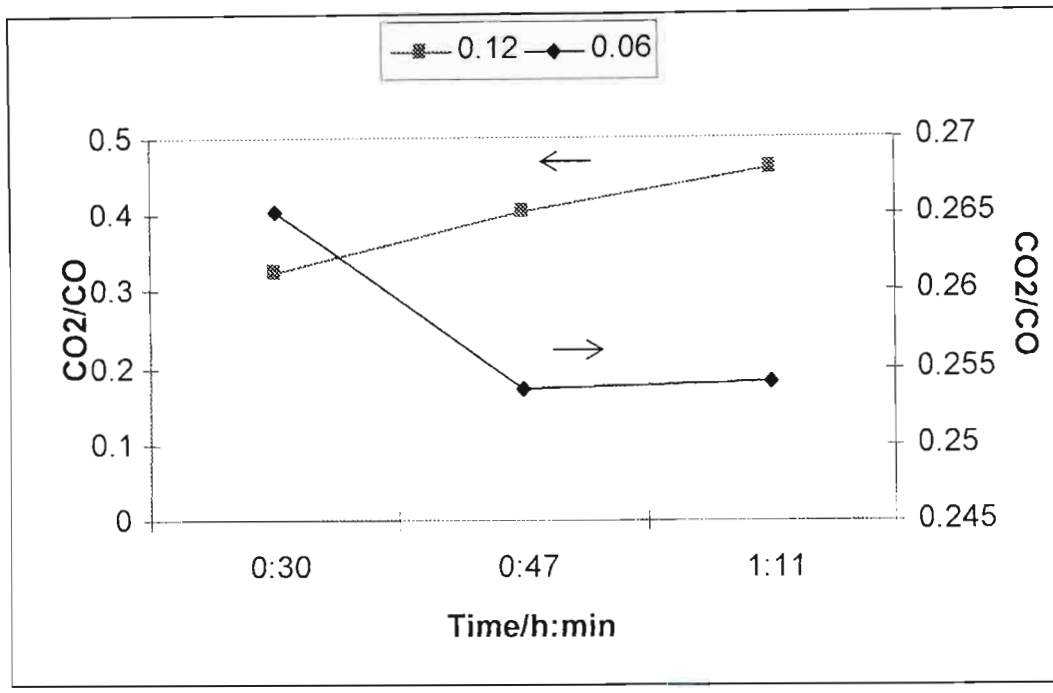


Figure 6 - 16: Effect of soda liquor to steam ratio at 500°C

6.7.1.3 The Effect of Increasing the Solid Content of the Feed

In a full scale plant operation, spent liquor has to be highly concentrated before being injected into the gasifier. Firstly, this would reduce the heat load of the unit which is used to evaporate water in the drying process. Secondly, the spent liquor has to contain a sufficiently high concentration of organic material to sustain gasification reactions, which can then be efficiently utilised by the low water content. It is reported that low concentrated liquors will require more energy to combust than it can provide (Kocurek, 1989).

The spent soda liquor available to this study was of 13%, 23% and 40% solids concentration. The only sulphite liquor that was available had a concentration of 20% solids. Therefore, this investigation focused on spent soda liquor. The L: S ratio and the temperature where maintained at 0.06 and 500°C, respectively.

Initially, gasifying highly concentrated liquor was of concern as the probability of agglomeration was high. This was based on the fact that highly concentrated liquor has a lower heat transfer coefficient in comparison with lower concentrated liquors due to their varying physical properties with changing concentrations (Bremford et al., 2000). It was expected that spent liquor would overload the bed and with the low residence time of the gas, less organic carbon would be gasified. Another concern was that the pump would struggle to pump 40% concentrated liquor as the viscosity was too high.

However, attempts to use highly concentrated liquors of 40% solids content failed. It was difficult to pump such highly concentrated liquor as the liquor was very viscous and "sticky". Olazar et al. (2002), states that liquor viscosity increases exponentially with solid content. Secondly, problems with continuous blockages where encountered. This occurred along the liquor piping network, in the injection rod and at the nozzle. Although the liquor piping network was heat traced to prevent the liquor from losing heat to the surroundings and getting blocked, blockages still occurred.

As was expected, when liquor was injected into the bed, agglomeration was encountered. It was believed that the sticky nature of the liquor and the greater gasification load was responsible for this. These experiments lasted only a few minutes due to blockages encountered. Although this proved difficult in this pilot-scale system, a full-scale plant design will be able to cater for highly concentrated liquor.

Due to the abovementioned problems, it was decided that 13% and 23% concentrated liquors would be used in this investigation. From the figures below, it is apparent that an increase in the water content in the feed has a significant effect on the product gas composition. On comparison of the 23% solids content liquor with the 13 % liquor, higher hydrogen concentrations were recorded in the 13% solids liquor.

The equilibrium of the system with a change in the solids content was observed to approach equilibrium; however, it was predicted to take a longer time. This is illustrated in Figure 6-17. Based on the water-gas shift reaction, an increase in concentration of water vapour should shift the equilibrium towards the formation of hydrogen and carbon dioxide but this was not so. The reason for this was that the water in the 13% concentrated liquor at the low spent liquor flowrates used in this study had a negligible affect on changing the position of the water-gas shift reaction when one considered the high steam flowrates used. The excess steam maintained a steady reaction condition (Riley, 1990). The contributing factor to shifting the equilibrium of the water-gas shift reaction was still the reaction temperature.

However, the extra water in the spent liquor was a burden on the energy balance of the process since it had to be either vaporised or reacted (White et al., 1981). Therefore, it was an important process parameter. In addition, equilibrium would probably take a longer time to occur. This is apparent in Figure 6-17. Therefore, it is important to reduce the water content in liquor especially in a commercial operation.

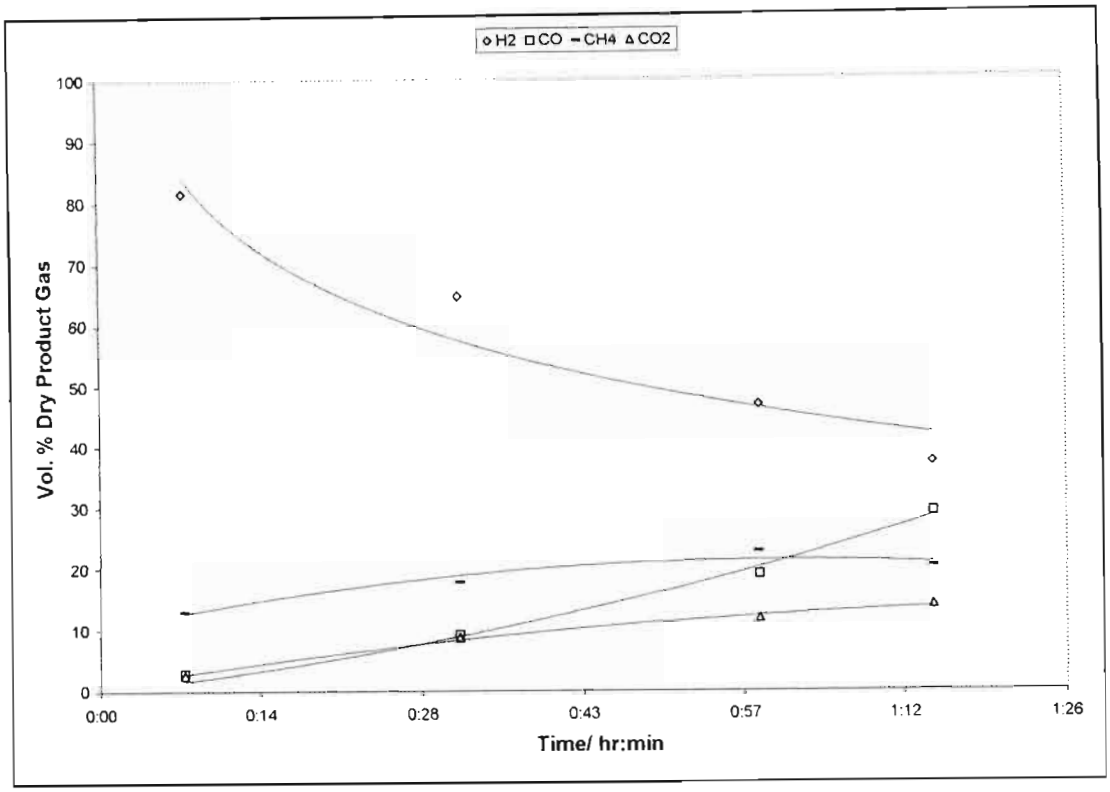


Figure 6 - 17: Effect of solids content of spent soda liquor (13% solids content at constant L: S ratio)

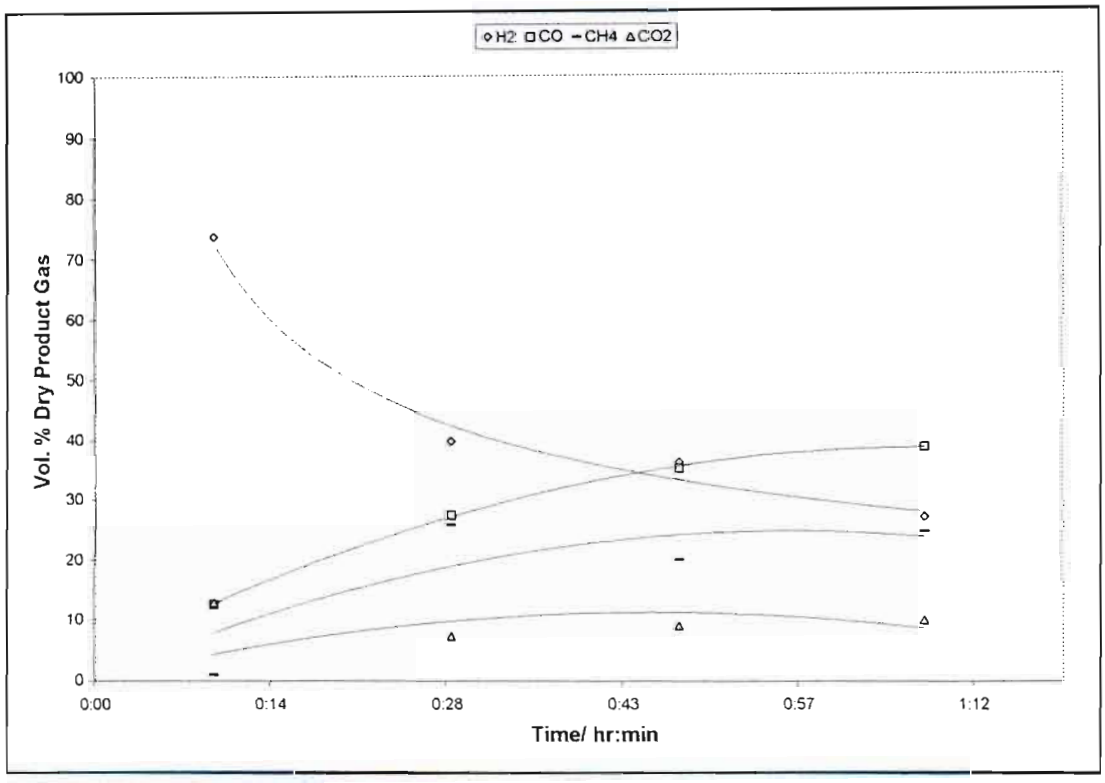


Figure 6 - 18: Effect of solids content of spent soda liquor (23% solids content at constant spent L: S ratio)

6.7.1.4 The Effect of Time

The residence time of the solids was increased to 3 hours in this set of experiments. From the figure below, it is evident that equilibrium was achieved. When compared to the shorter run (Figure 6-13) at the same conditions, a similar profile was obtained. This validates the reproducibility of the experimental work accomplished in this study.

In the figure below, it is apparent that the methane reaction does not reach equilibrium immediately. As illustrated in this figure, methane went through a period of increased yield and then dropped off to settle at equilibrium. However, due to time constraints the reason for this was not determined. It is therefore recommended for further work.

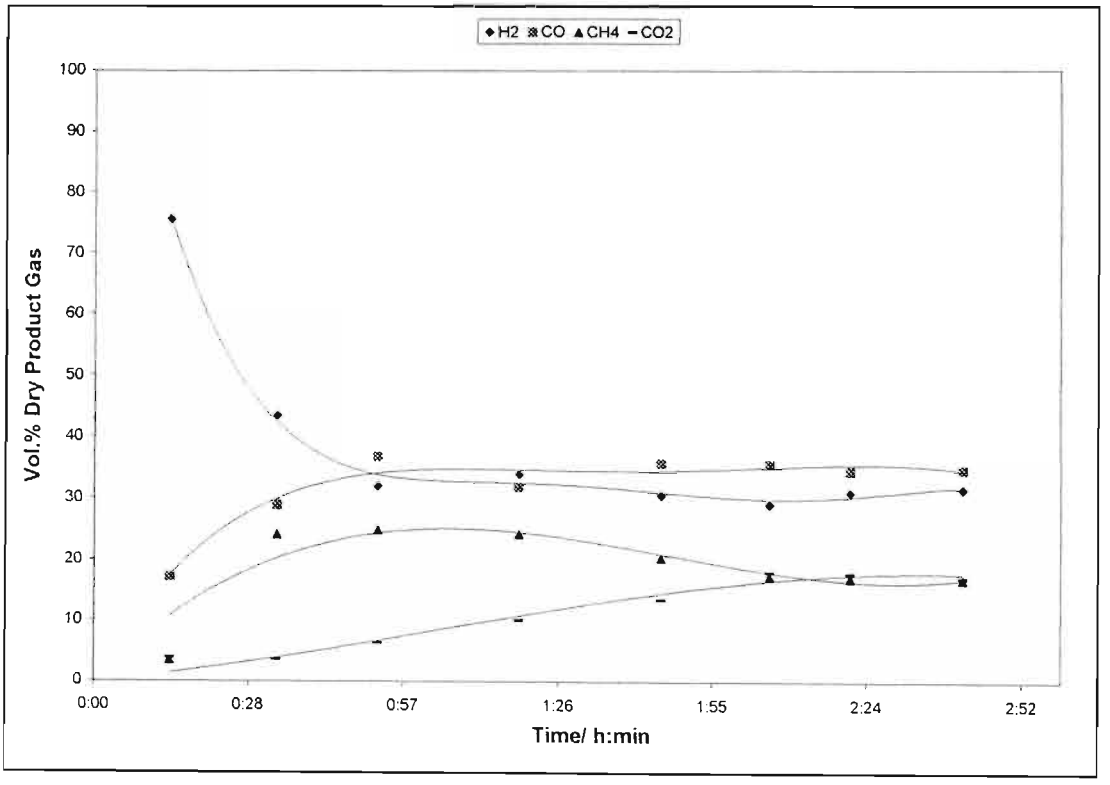


Figure 6 - 19: The effect of time on the product gas compositions. T = 500°C

6.7.2 Semi-Alkaline Sulphite Spent Liquor (SASAQ)

The semi-alkaline sulphite spent liquor was obtained from the pulping of bagasse. The pulping chemistry consists of a catalyst known as anthraquinone which is believed to increase yield and paper quality. However, no suitable chemical recovery system for spent SASAQ liquor exists and gasification is being explored to provide one.

SASAQ liquor has high sulphur content. This is due to the chemical make-up of the pulping liquor which utilises sulphur compounds. Consequently, hydrogen sulphide is expected to form part of the product gas.

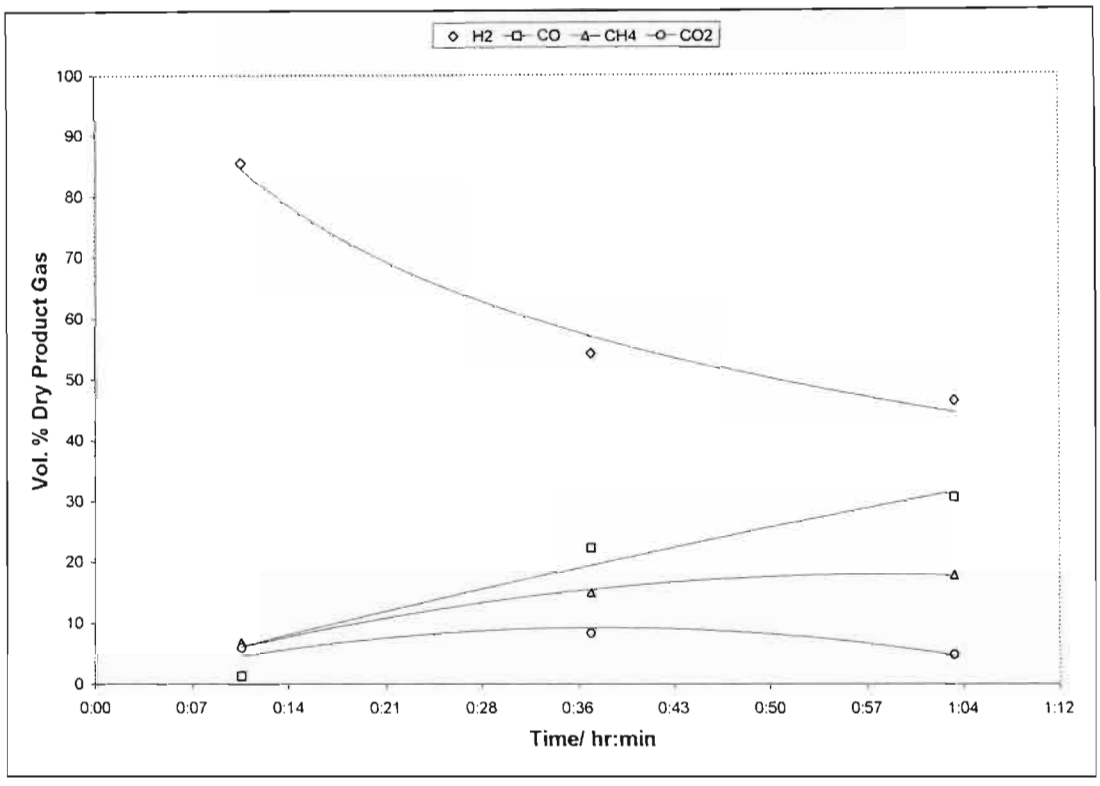


Figure 6 - 20: General trend of product gas compositions of SASAQ liquor

The general trend (Figure 6-20) of the product gas composition profiles for the variables investigated for spent SASAQ liquor indicated that the chemical species in the product gas approached equilibrium. This is similar to the product gas compositions profiles of the soda liquor reported in previous sections. It should be mentioned that using drager tubes very low concentrations of hydrogen sulphide in the range of 0.1-0.4% by volume (APPENDIX HD7) were measured.

6.7.2.1 The Effect of Temperature and Time

A similar trend in the product gas composition profiles is observed for the SASAQ gasification experiments. However, in these experiments hydrogen production was generally higher than those results obtained from the gasification of spent soda liquor.

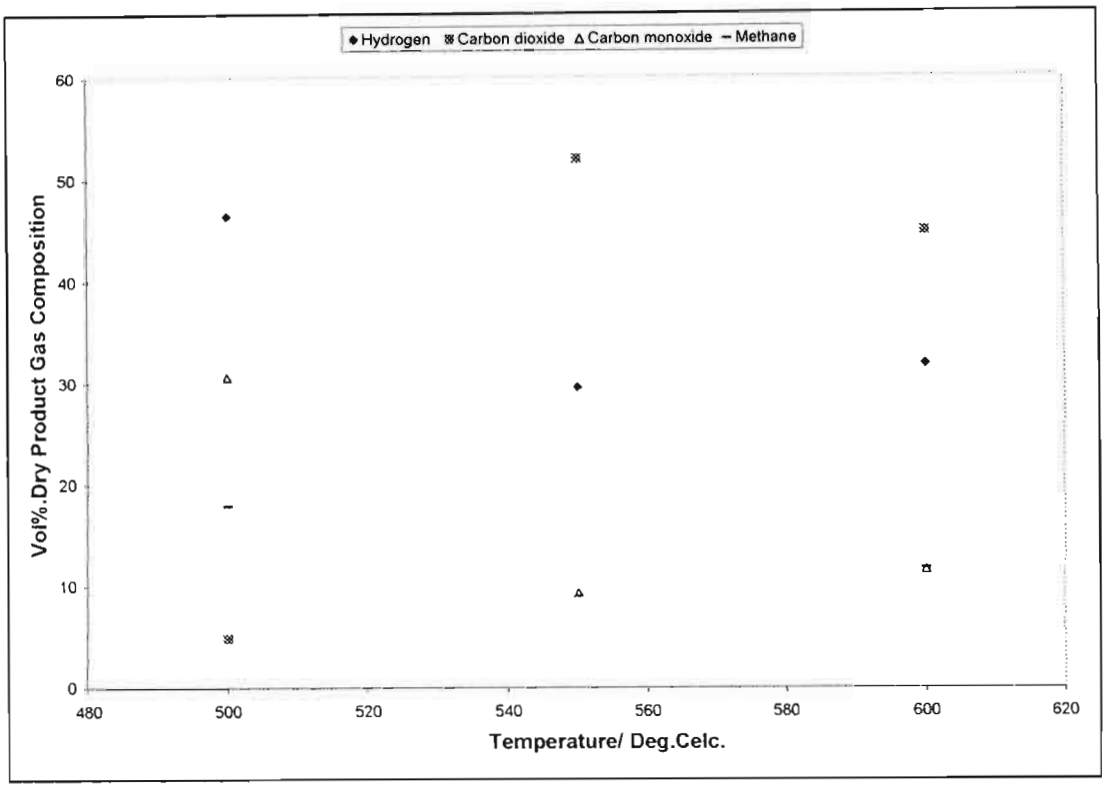


Figure 6 - 21: Effect of temperature on the dry product gas composition

Based on a similar discussion for spent soda liquor, Le Chatelier's principle validates the observations apparent in Figure 6-21. At high temperatures the forward reaction of the water-gas shift reaction was favoured and this validates the high concentration of carbon dioxide. At lower temperatures the reverse reaction was favoured with the formation of more carbon monoxide than carbon dioxide.

In Figure 6-21, a high concentration of hydrogen at 500°C is observed. Similar results were noted in Figure 6-17 when 13% solids concentration spent soda liquor was gasified. Equilibrium of the SASAQ liquor was also predicted to take a longer time to be reached. Therefore the effect of extra water in the feed had a significant effect on the product gas distribution and equilibrium of the system. In addition, low concentrations of hydrogen sulphide were measured (APPENDIX HD 7-9) at 500, 550 and 600°C.

Also investigated was the effect of time on the product gas composition profile to determine whether equilibrium was in fact established. This was done in a 3hr long run at a temperature of 500°C and at an L: S ratio of 0.06.

From Figure 6-22 below, it is clearly evident that some sort of equilibrium was established. This is similar to the spent soda liquor experiments conducted. Hydrogen and carbon monoxide are clearly dominant at equilibrium. At this temperature lower concentrations of carbon dioxide and methane were recorded. This was consistent with previous product gas composition profiles for that temperature. Methane apparently increased initially, reached a high point and than began to decrease to an equilibrium composition. A similar finding was made for spent soda liquor gasification. The hydrogen sulphide measured (APPENDIX HD10) in the 3hr runs were extremely low.

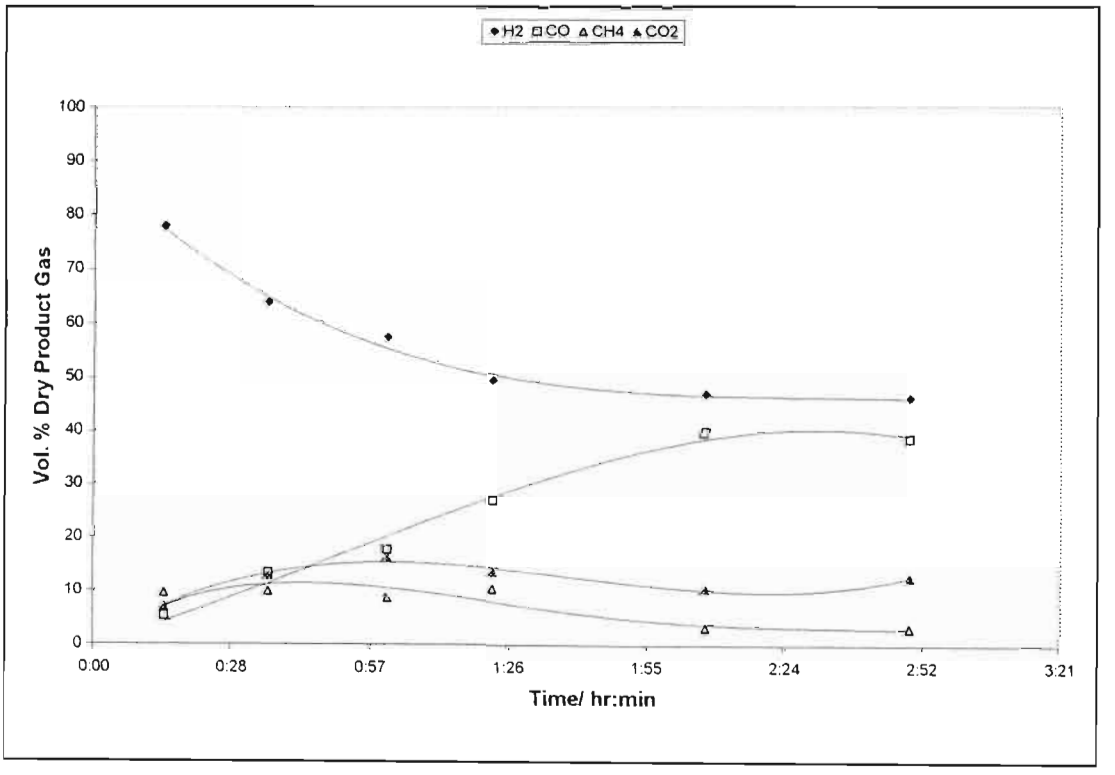


Figure 6 - 22: The effect of time on the product gas composition profile. T=500°C

6.8 Bed Material Analysis

6.8.1Organic Carbon Content

The organic carbon content of the bed was measured by carrying out ash tests on samples of the bed material from the experiments conducted. It was found that at lower temperatures, more organic carbon remained in the bed for both spent soda and SASAQ liquors. This confirmed that gasification was temperature dependent.

The following table shows the organic carbon conversion which was calculated based on the mass of organic carbon in the bed. The alternative way to calculate the conversion of organic carbon was to determine the mass of carbon in the form of carbon dioxide, carbon monoxide and methane in the product gas relative to the total mass of organic carbon in the feed. According to Durai-Swamy et al. (1991), it is inappropriate to do so as the theoretical gasification limit of 100% will still result in the carbon in the product solids due to the formation of sodium carbonate. As a result, they define gasification efficiency as the organic carbon remaining in all solid products relative to the total organic carbon in spent liquor solids.

Temperature / °C	**Spent Soda Liquor/ %**	**Spent SASAQ Liquor**
	Organic in liquor = 65%	*Organic content in liquor = 30%*
500	11.60	13.84
550	16.37	26.58
600	41.50	35.89

Table 6 - 6: Carbon conversion (organic) or gasification efficiency

Comparatively, spent soda liquor had a higher carbon conversion than spent SASAQ liquor as shown in Table 6-6 under similar run conditions. From these results, lower temperatures reduced carbon conversion. It may be possible to increase carbon conversion further by increasing the operating temperature but the effect of inorganic salts melting would restrict the use of high temperatures. In the presence of non-process elements (NPE's) such as chlorides and potassium, the inorganic solids eutectic melting point would be reduced.

Although spent soda liquor has a much higher melting temperature than say spent Kraft liquor, the melting point of soda liquor can be extended with the use of autocausticising agents such as titanium dioxide and sodium borate (Chapter 2). Zeng et al. (2000), reports melting points of 900°C is possible when sodium combines with titanium dioxide to form sodium titanates in a low temperature gasification process. This will be an advantage and a great benefit to fluidised bed gasification processes as higher temperatures imply higher carbon conversion. It is recommended that further work is conducted with the use of autocausticising agents.

In the 3 hour run, the carbon conversion was determined to be 42.19% for spent soda liquor gasification and 28.06% for spent SASAQ liquor. This is low and the reason for this is that the run was at 500°C. However, this is still higher than those reported for the shorter runs at the same temperature. Therefore, it is possible that an increased residence time of the solids has an effect on increased conversion.

6.8.2 Mass Balances

Mass balances were based on the overall system, which includes the gasifier unit and the separator. The results reported in the following tables are represented as percentages of the spent liquor feed. Samples of the bed material and product gas were analysed. The mass balance was closed by assuming a full closure (100%) of the system since no samples were taken from the separator bottoms. Therefore, the percentage of the species ending up in the separator, in relation to the species in the feed was calculated by difference.

The results are averages based on replicate runs conducted on the system. Chloride analysis was limited to the bed as chlorides in the product gas were found to be too low for wet chemistry methods. Inductive Coupled Plasma (ICP) analysis was found to be the best method for such low levels of chlorides however it was too costly to do.

500°C	**Bed Material Sample %**	**Product Gas Sample %**	**Separator Sample %***
Na	97.15	< 1	1.85
S	9.98	84.30	5.72
K	1.94	< 1	97.06
Cl	41.00	-	-
550°C			
Na	94.59	<1	4.41
S	8.65	89.03	2.32
K	2.40	<1	96.60
Cl	49.00	-	-
600°C			
Na	88.04	<1	10.96
S	3.00	94.76	2.24
K	2.09	<1	96.91
Cl	40.32	-	-

Table 6 - 7: Summary of Mass balance for SASAQ gasification

500°C	Bed Sample %	Product Gas Sample %	Separator Sample %*
Na	89.46	<1	9.54
K	47.87	<1	51.13
Cl	75.35	-	-
550°C			
Na	77.28	<1	21.72
K	53.08	<1	45.92
Cl	70.32	-	-
600°C			
Na	75.60	<1	23.4
K	56.39	<1	42.61
Cl	62.52	-	-

Table 6 - 8: Summary of Mass balance for soda liquor gasification

500°C	Bed Material Sample %	Product Gas Sample %	Separator Sample %*
Na	71.65	<1	27.35
S	8.52	87.81	3.67
K	4.69	<1	94.31
Cl	81.12	-	-

Table 6 - 9: Summary of mass balance for SASAQ liquor for 3hr run

500°C	Bed Material Sample %	Product Gas Sample %	Separator Sample %*
Na	60.96	<1	38.04
K	41.64	<1	57.36
Cl	68.86	-	-

Table 6 - 10: Summary of mass balance for Soda liquor for 3hr run

6.8.3 The Fate of Non-process Elements: Chlorides and Potassium

From the mass balance of Table 6-7 to Table 6-10 for spent SASAQ and soda liquor respectively; a large concentration of chlorides deposit in the bed. To suggest that temperature has an effect on the depositing of chlorides in the bed may be a bit presumptuous, since further work is required to validate this statement. However, from the results obtained for the spent SASAQ liquor, it seems that more chloride is deposited at a lower temperature. This observation, however, cannot be made for the spent soda liquor.

The fate of potassium, as seen in these tables, suggest that for soda liquor more then 40% of the potassium in the feed is deposited in the bed. However, far lower concentrations of potassium are observed to deposit in the bed for spent SASAQ liquor gasification. The reason for this is unknown and due to the limited time, was not investigated.

The reason as to why these non-process elements deposit in the bed in the way that they do is beyond the scope of this study. Further, investigation on a lab-scale study to evaluate the mechanisms for this occurrence is recommended. However, it is possible to infer from these results that these non-process elements will in fact hinder the fluidised bed operation especially if alkali metal salts are to be used as bed material. As mentioned previously, these non-process elements are known to reduce the melting point of inorganic salts and the correct operating temperature is important in bed fluidisation if say sodium carbonate particles were to be used.

6.8.4 The Fate of Non-process Elements: Silica (SiO_2)

The main difficulty in recovering chemicals and energy from spent liquor from non-wood pulping is the high silica content. Silica in the form of silicate is responsible for the fouling of heat transfer surfaces and possibly the very high viscosity of spent liquor after concentration.

This occurs mainly in soda pulping and is dependent on the hydroxide concentration and pH. The following reaction occurs:

$$NaOH + SiO_2 \rightarrow Na\ SiO_{3\,(ppt)} \text{ (at high pH levels 12-14)} \quad <6\text{-}5>$$

As a result, the silica in the bed material is required to be low and preferably in the form of silica. At higher pH levels the silica is converted to silicate and it is this form that is responsible for fouling and scaling problems in evaporators and recovery boilers.

However, with sulphite pulping, this hydroxide concentration will be reduced due to the nature of pulping chemicals used. However, small concentration of silicates possibly sodium silicates may be present. In this study, it was not possible to determine the silicate content

but soluble silica was determined. Low concentration of soluble silica was found to be deposited in the bed (Table 6-11), which may suggest that silica in the feed is deposited as insoluble silica in the bed. It is highly unlikely that silica will pass out in the product gas. In a commercial gasification process, silica is expected to be low and will be removed by means of filtration. The rest of the silica deposits as insoluble silica on the bed material or possibly reduced to silicate. However, reduction to silicate maybe highly unlikely as silica must react with hydroxide ions at high pH's to occur.

Temperature / °C	Soda Liquor / %*	SASAQ Liquor / %*
500	0.25	0.45
550	0.22	0.32
600	0.27	0.25

Table 6 - 11: Soluble Silica in the bed represented as percentage of total silica in the feed

* % = {soluble silica in bed / Total silica in feed liquor} *100

6.8.5 Sulphates

The following results were obtained for the sulphate content of the bed.

	Soda /ppm	SASAQ/ppm
500	1.64	67.71
550	2.23	32.52
600	5.57	25.31

Table 6 -12: Sulphate present in the bed

Spent soda liquor has lower sulphur content and therefore, the sulphate in the bed was expected to be lower than the SASAQ liquor. This low sulphate content especially in the higher sulphur liquor was an important result as sulphate in current chemical recovery make up the dead load in the system.

Due to the low sulphur in the bed, it is presumed that the sulphur is removed as hydrogen sulphide. Rockvam (2001) reports that sulphate reacts with steam and carbon dioxide to form sulphur in the sulphide form.

$$NaSO_4 + H_2O + CO_2 \leftrightarrow Na_2S \leftrightarrow Na_2CO_3 + H_2S \quad \text{(Li et al., 1994)} \ <6\text{-}6>$$

However he states that the sulphide is unstable and forms hydrogen sulphide and sodium carbonate.

This is validated by the mass balances performed (Table 6-7), which indicates that most sulphur is removed in the product gas as hydrogen sulphide. The low concentration of sulphate in the bed and the high concentration of sulphur in a gaseous form validate the work done by Rockvam (2001).

6.9 Alkali Metal Salts as Catalysts

Li et al (1991b), reports that alkali-metal salts are among the oldest known additives that markedly increase the rate of steam gasification of carbonaceous materials. Alkali metal salts as catalysts have the remarkable ability of increased reactivity with better catalyst dispersion. The effects of these catalysts have been well studied with numerous mechanisms documented (Sams et al., 1986; McKee et al., 1975; Li et al., 1991b).

The spent liquors used in this study have high carbon contents and consist of alkali metal salts in the form of sodium and potassium salts. During the literature survey, sufficient evidence was found to suggest that alkali metal salts influence the rate of steam gasification of carbonaceous materials. Although, this investigation was of minor importance, an attempt to consider the catalytic effect of sodium and potassium, by re-using a coated bed during gasification experiments, was thought to be interesting.

This investigation was based on the effects of sodium and potassium salts as catalysts when the spent liquor coated the grit and the effect that these alkali salts would have when the bed material was continuously re-used. The effect on the composition profiles of the dry product gas and the morphology of the coating was looked at. Since this was not a kinetic study, the investigation into the effect of alkali metals as catalysts was limited to general observations and deductions. Also due to the limited time, verification of results in this section of the experimental work was not possible and is recommended for future work.

A bed was continuously used and Figure 6-23 and Figure 6-24 below are examples of the dry product gas composition profiles. In Figure 6-23, an unusually high concentration of methane was recorded relative to carbon monoxide and hydrogen, at 500°C. This may suggest that the methane was also influenced by the alkali metal catalysts. However, research work suggests that methane formation should not be affected by the alkali metal catalysts (Du Preez, 1985).

In Figure 6-24, carbon dioxide reaches values of 70%. Miura et al (1986) conducted lab-scale investigations and reported that sodium, potassium and calcium greatly promotes the carbon dioxide formation but have less influence on carbon monoxide formation. This in conjunction with the higher temperature promotes and favours carbon dioxide formation. From considering both figures, it can be said that the continuous use of a bed creates abnormal behavioural changes in the composition profiles. The only constant in these composition profiles is that hydrogen decreases as the run goes on.

It is recommended that sodium or potassium compounds should be added to the liquor to investigate the effect of increased concentration on organic carbon conversion. However, due to limited time, this investigation was not conducted. Also of interest would be to investigate the effect of a mixed bed i.e. sodium carbonate mixed with aluminium oxide grit.

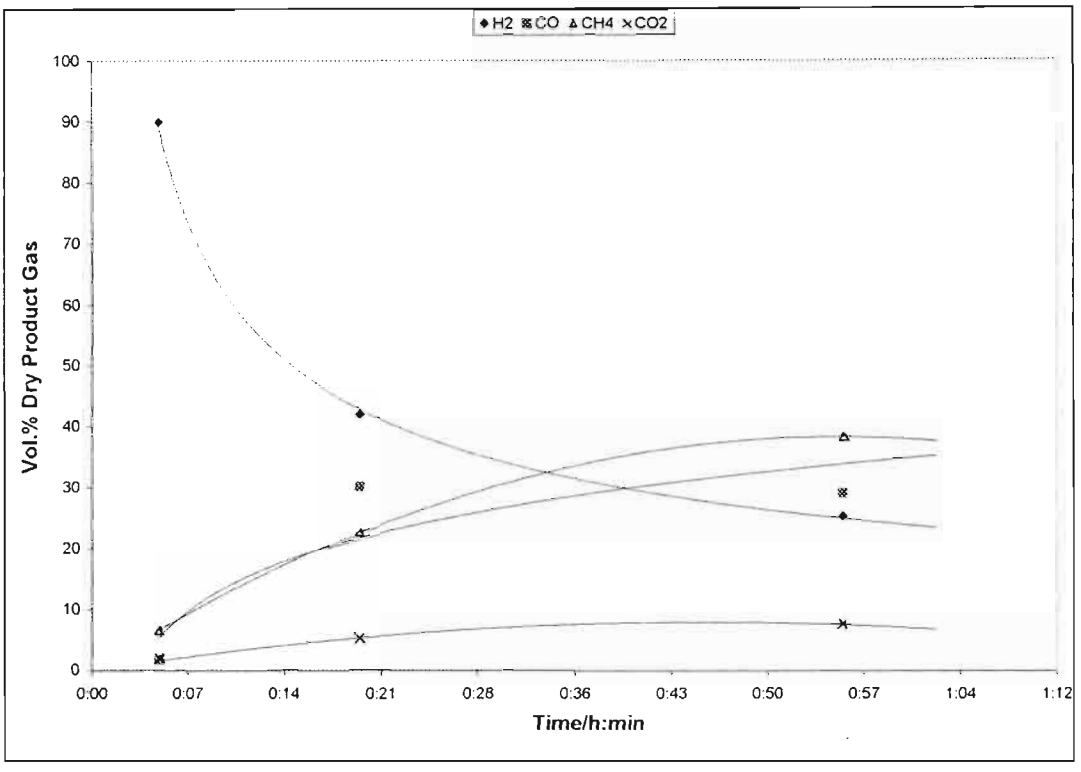


Figure 6 - 23: Effect of continuous bed usage with spent soda liquor (23%) at 500°C

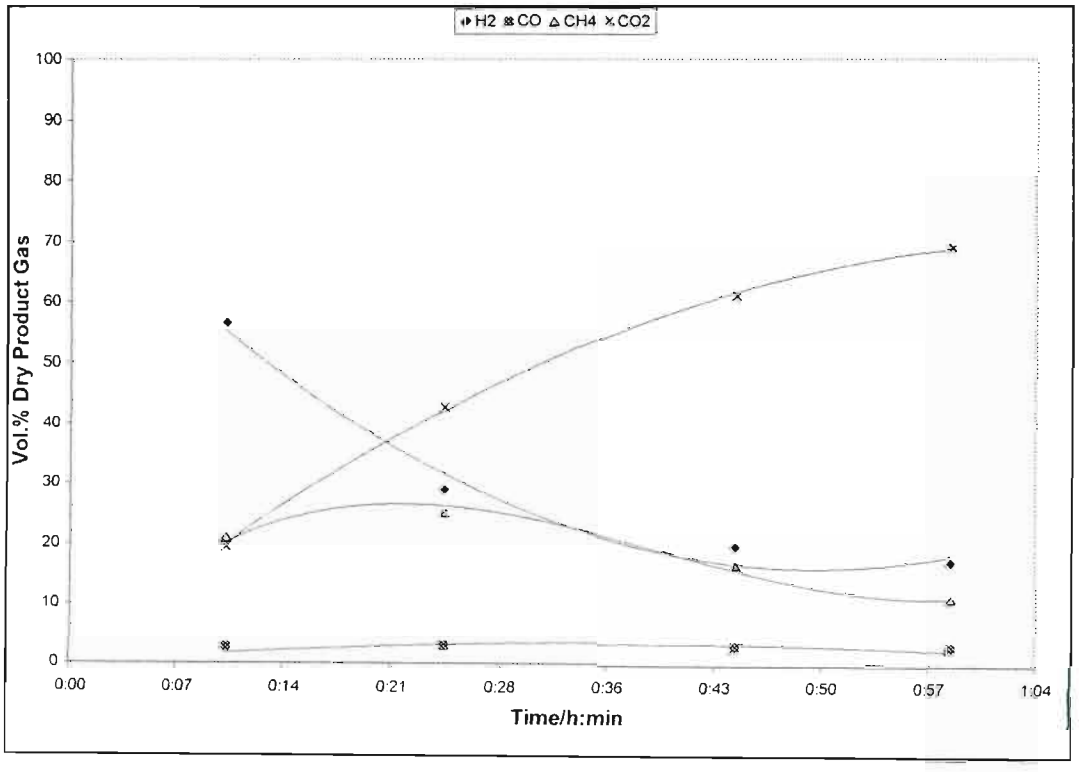


Figure 6 - 24: Effect of continuous bed usage with spent soda liquor (23%) at 550°C

The surface structure of the coated aluminium oxide grit for the different runs were analysed by means of the scanning electron microscope. Micrographs of the bed grit for some of the catalysed runs are shown below for continuous bed usage.

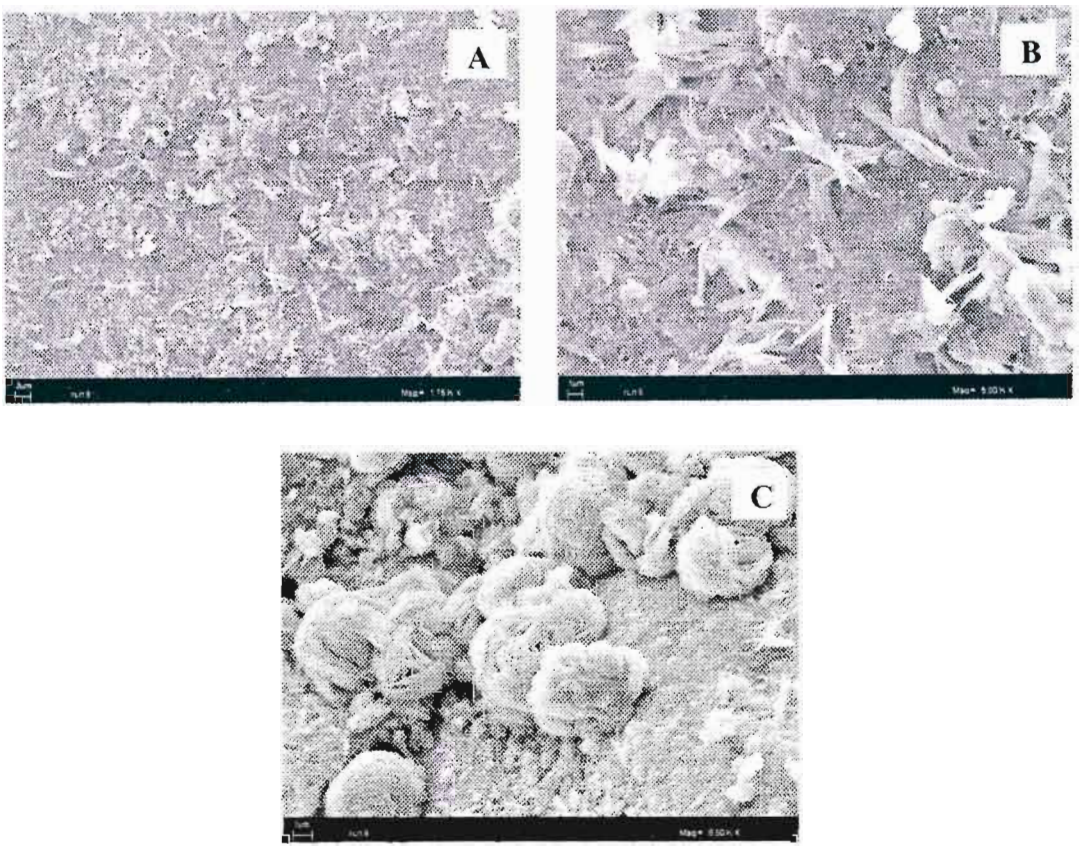


Figure 6 - 25: Spent soda liquor (13% solids) at 550°C

Branched crystal structures were identified on the surface of a coated grit after a period of continuous bed usage. These structures can be described as dendritic in form and it is apparent that they are well dispersed on the surface of the grit. A closer examination of the surface, in the frame C of Figure 6-25, revealed cluster type arrangement of spherical crystals also present.

Electron dispersive spectroscopy (EDS) was used to determine the nature of these crystal structures. EDS scans of these structures indicated high concentrations of sodium present relative to the areas where these structures were not present. This confirms that these structures were sodium salt crystals. Li et al. (1990a), reports dendritic structures (Figure 6-26) were observed when spent liquor char was gasified with carbon dioxide in a thermogravimetric unit at temperatures of 600-800°C. It was believed by them that fine dispersion of sodium present in the carbon matrix was responsible for high gasification rates.

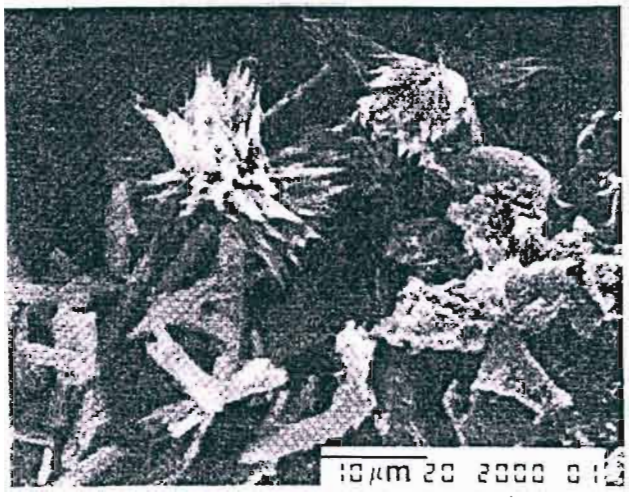


Figure 6 - 26: SEM reported by Li et al. (1990)

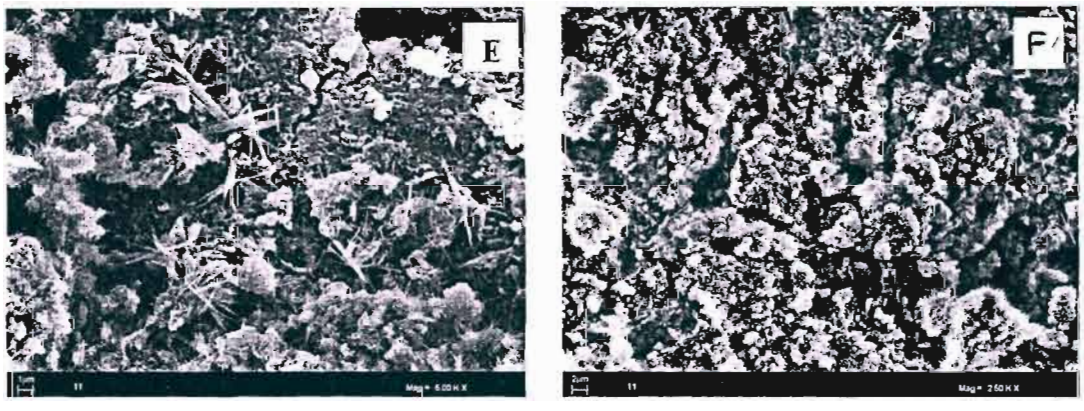


Figure 6 - 27: Spent soda liquor (23%) at 500°C

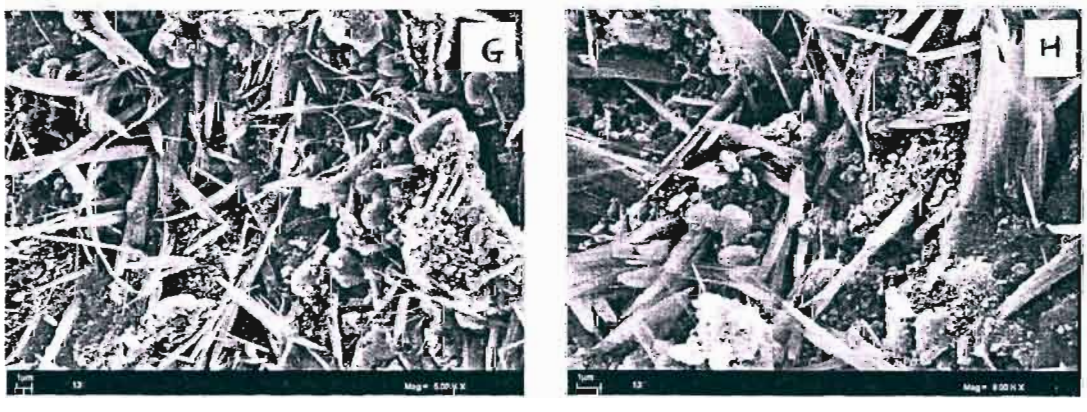


Figure 6 - 28: Spent soda liquor at 550°C

Spent soda liquor at 23% solids concentration was also gasified using the same bed. The bed grit was examined under the scanning electron microscope. At a temperature of 500°C, the char morphology was different (Frame E of Figure 5-27) and exhibited round crystal

structures from which very fine dendritic structures appeared. These round structures seemed to be flaky and translucent. High values of sodium and carbon were reported in the EDS analysis of these structures.

6.10 Tar Compounds

6.10.1 Analysis of Tars

Low temperature biomass and spent liquor gasification are prone to the formation of tar compounds. Tars contaminate the synthesis gas produced in gasification processes which are used as fuel in gas turbines. Tars are also responsible for the contamination of gas clean up operations and represent a potential loss of chemical and fuel. In addition, tars cause contamination problems in chemical recovery of spent liquor gasification processes. (Sricharoenchaikul et al, 2002b)

In this study, condensed samples of product gas were analysed to qualitatively investigate the presence of complex compounds called tars. As explained in the analytical methods chapter, the samples had to be prepared before injection into the GC/MS. A quantitative analysis was thought to be irrelevant when considering the objectives of this study but it should be kept in mind that it is certainly vital to any full scale plant operation. In addition, these complex compounds identified by the GC/MS would require the purchase of expensive calibration standards which were not financially feasible in this study.

Compounds	**Boiling Points/°C**
Toluene	111
Phenol	182
2,6-dimethyl phenol	234
2-ethyl phenol	207
2,5 –dimethyl phenol	211.5
4-ethyl phenol	219
3,4 – dimethyl phenol	225
1,2,3 trimethoxy-benzene	247

Table 6 - 13: Tar compounds found in the product gas (Lide, 1992)

Condensate samples from experimental work with soda and SASAQ spent liquor were analysed by the GC/MS. Table 6-13 is an analysis from a soda liquor run at 600°C showing the tars identified. The condensed samples were removed after the run and analysed. SASAQ condensate sample analysis showed similar compounds for gasification at the same

temperature. The condensate samples had a light brown discolouration and were turbid. Upon closer examination of the condensed samples, minute droplets of oil were visible at the surface. In addition, fine black to dark brown material was present in the sample. These observations were also reported by Dickenson et al. (1998).

The fine material may be attributed to the entrainment of char fines from the bed due to attrition. The presence of these fines was limited to small quantities that were visible in the samples extracted. Adherence of the fines to the walls of the sample cylinders was noticeable. A plausible explanation for this is based on the composition of these fines. Since char fines are composed of residual organic carbon that may have not been completely gasified, the fines may have adhered to the surface of materials, to such an extent that the carbon is absorbed. Interestingly enough, when the sample cylinders were rinsed with hot water, the adhered material was not easily removed. Glass and plastic cylinders were used to store these samples, and the fine material present in these samples firmly adhered to the walls of these cylinders.

The condensate samples were affected by light. This was apparent when the samples which were stored in glass cylinders changed colour when exposed to light. A noticeable colour change from light brown to a mauve colour was observed. It can be inferred from this observation that the organics present in these samples react when exposed to light.

Condensate from the soda liquor run produced a condensate with an obnoxious aromatic smell. When exposed to light for long period of time these smells dissipated. In the case of the SASAQ liquor, the smell of sulphur was present. Work done by Dickenson et al (1998) reported similar findings with Kraft liquor.

6.10.2 Tar Formation

Hardwood, softwood and grass lignin have similar structures but use different base units. The spent soda and sulphite liquor used in this study was from the pulping of bagasse and therefore the lignin structure present in these liquors is of a grass lignin.

The figure below illustrates a complex lignin structure for softwood lignin, which is similar to the grass lignin of bagasse. This structure may be useful in understanding the formation of tars. From this figure, it is apparent that this structure consists of many aromatic units or clusters. Aromatic compounds are relatively simple structures and are commonly six-carbon units. Many of these six-carbon units pass through chemical reactions unchanged, with alterations made to the rest of the structure in which they are present (Hart et al., 1995).

From Table 6-13, these tar compounds such as toluene and phenol, are characteristically aromatic and are part of the lignin substructures (Figure 6-29). Sricharoenchaikul et al. (2002b), states that these aromatic compounds are believed to have formed due to the

thermal decomposition of lignin and re-formation of the lignin-derived constituents. In addition, it is reported by them that weak bonds connecting the aromatic substructure of lignin may be broken to form light tars during devolatilisation. Also, during this process, re-formation of broken aromatic groups results in heavier multi-ring tars being formed. This may explain the presence of 1,2,3 trimethoxy-benzene. Their work was based on the study of tars from spent Kraft liquor.

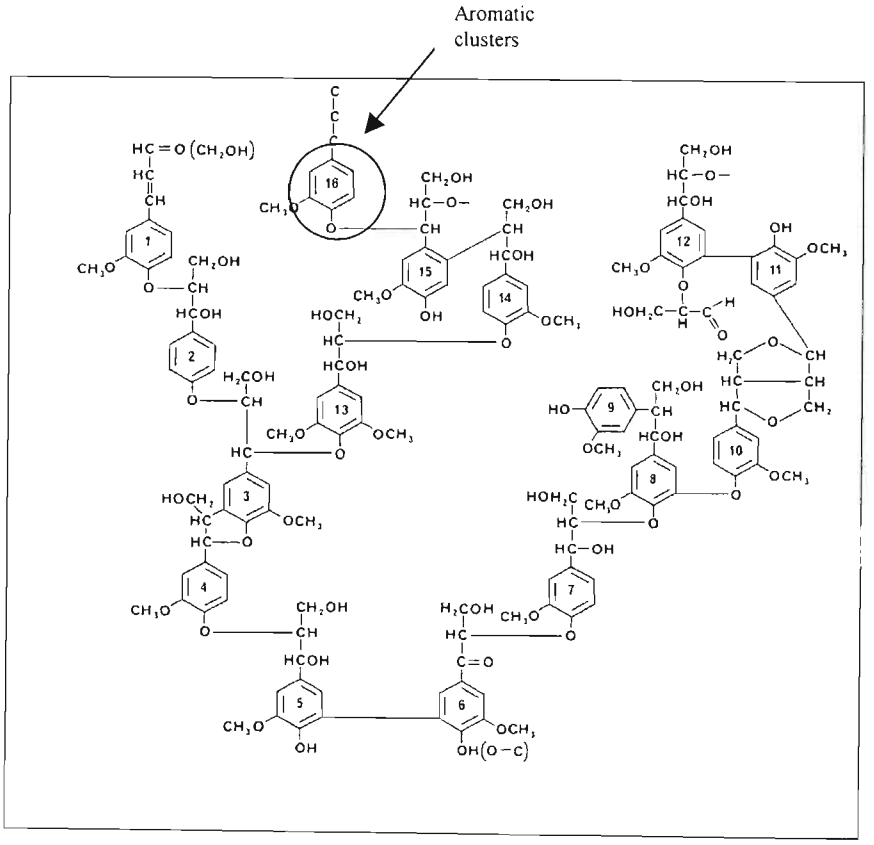


Figure 6 - 29: Lignin structure for softwood lignin (Kocurek, 1989)

CHAPTER 7:
CONCLUSIONS

1. The pilot-scale unit was successfully used to demonstrate an alternative approach to the treatment of spent liquor for the pulping of bagasse.

2. Low temperature gasification technology can therefore be incorporated into or replace current incineration technology in a chemical recovery process in the paper industry.

3. The study demonstrated that gasification technology can be used to treat spent liquor from a semi-alkaline sulphite (SASAQ) pulping chemistry and that gasification may even provide a recovery process for it.

4. This study also showed that aluminium oxide grit can be coated.

5. The operation of the pilot-scale unit has been successful because of a simple yet effective operating procedure.

6. An effective and reliable way to determine whether fluidisation was taking place was to monitor the temperatures in the bed.

7. The problems regarding fluidisation were methodically determined and resolved and eventually the bed was well coated. This indicates that good mixing of the fluidised bed can be achieved.

8. Sodium carbonate particles as a bed material were found to be problematic due to particle agglomeration.

9. The presence of non-process elements may hinder the use of sodium carbonate at high temperatures.

10. It is important to note that designing of a distribution plate does not lie solely in calculations as was initially thought, but rather in the physical behaviour of particles which can be predicted by Geldarts Classification Chart (Section 3.1.3).

11. Poor predictability of the equations used to determine the minimum fluidisation velocity of the aluminium oxide grit was apparent when compared to cold test experimental results.

12. Aluminium oxide grit as bed material was found to be comparatively better than sodium carbonate and well suited for the fluidised bed operation at high temperatures and in the presence of non-process elements.

13. The product gas consists of hydrogen, carbon dioxide, carbon monoxide and methane. Hydrogen sulphide is also present but was only detected in the gasification of spent SASAQ liquor. Hydrogen sulphide was not detected in the gasification of spent soda liquor because of its low sulphur content (0.03%).

14. From the composition profiles of the dry product gas, the species identified approached equilibrium. The product gas composition profile, of a three hour run at 500°C for spent soda liquor gasification, indicated that hydrogen, carbon monoxide, carbon dioxide and methane were present in quantities of approximately 31.5%, 34.7%, 16.8% and 17% respectively at equilibrium. The product gas composition profile for spent SASAQ liquor at the same conditions, were 46.03%, 38.46%, 12.48%, and 3.02% respectively with hydrogen sulphide at 0.01%. The predicted values did not compare well with the experimental results.

15. In spent soda liquor gasification, hydrogen decreased with temperature and reached values as low as 11%. Hydrogen present in the product gas, in spent SASAQ gasification experiments, decreased with temperature and the lowest value reported was roughly 30%.

16. The main process variable that affects the water-gas shift reaction is temperature. Higher temperatures favoured the formation of carbon dioxide production and carbon monoxide production was favoured at the lower temperatures. This was apparent in both spent soda and SASAQ liquor. An increase in the spent liquor to steam reaction indicated that more carbon dioxide was produced but at the temperature studied was not the dominant species. The increase in water content of the spent liquor showed increased species concentrations of hydrogen with equilibrium predicted to take a longer time. Therefore, commercial units will need to increase the concentration of solids in the spent liquor.

17. One of the limitations of the equipment was the inability to use higher concentrated spent liquors.

18. The organic carbon conversion was relatively low and this was due to the temperature range in which it was investigated.

19. The silica in the bed was found to be very low as expected.

20. Tars were found to be mainly aromatic compounds.

20. Tars were found to be mainly aromatic compounds.

21. By the overall mass balance, it was found that most of the sodium remains in the bed with more than 75% and 88% for spent soda and SASAQ liquors respectively. Chlorides were found to deposit in the bed with the lowest concentrations reported for spent SASAQ liquor (40.32%). High concentrations of potassium were found in the bed for spent soda liquor gasification with very low concentrations for spent SASAQ gasification. For the spent SASAQ liquor sulphur seems to partition to the gas phase as hydrogen sulphide and validates the reports in literature (Rockvam, 2001).

CHAPTER 8:
RECOMMENDATIONS AND FUTURE WORK

1. Before each run the lid of the gasifier was sealed with a thick layer of high temperature silicone. This was cumbersome. A better way of sealing the lid without leaks should be found. It is proposed that the reactor lid should be modified to incorporate a gasket and bolts so that the lid is sealed and bolted in position.

2. The graphite gaskets were used to hold the distribution plate in position and to prevent any leaks at the distribution plate from occurring. These were found to be prone to damage. This was due to the high temperature exposure at the distribution plate and these gaskets had to be replaced frequently. The only way to reach these gaskets was to dismantle the gasifier. Dismantling the gasifier was a labour intensive task and was time consuming. Since, this had to be done frequently; a higher temperature type of gasket was sourced out. A steel-graphite type of gasket was found and it is recommended for any future gasket replacements.

3. The distribution plate is currently enclosed in the reactor compartment. To solve the problem of constantly having to dismantle the gasifier to get to the gaskets, it is recommended that the gasifier be modified so that the distribution plate can be exposed at the bottom of the gasifier. This will make it easily accessible when gaskets need to be replaced. In order to facilitate this design, the burner section would have to be located in a separate furnace unit near the gasifier. Commercial fluidised bed reactors have easy access to their distribution plates.

4. A more effective approach to cleaning the product gas would be to purchase a cyclone according to the size of the particulates and conditions of the gasifier. A series of cyclones is recommended for more effective removal of particulates from the product gas stream.

5. In addition, the cyclone should be able to recycle particulate matter to the gasifier. In the pilot unit, a recycle of the separator contents was not achieved due to design limitations. Recycling would increase carbon conversion.

6. The addition of at least one more temperature probe is recommended so that it can be positioned in the bed at a different location from the other temperature probes. The bed temperatures would then be more effectively monitored. However, the addition of more temperature probes may effect fluidisation but that needs to be determined. The easiest

way would be to extend an existing temperature probe that is in the freeboard region of the gasifier.

7. The best way of implementing better control of fluidization would be to measure the pressures across a fixed height in the bed, and across the distributor plate and top of gasifier (just below the lid). A pressure gauge across a fixed height within the bed will give the bulk density of the particles when the bed is fluidised. Another pressure gauge across the distributor plate and above the bed, will give the overall pressure drop. The height of the bed during fluidisation can then be calculated using the overall pressure drop and the bulk density of the fluidised bed. A DP cell would be ideal for low pressure drops which are expected. *The current design may make it difficult to measure the pressure drops in the bed.*

8. For better performance of the bed, the aluminium oxide should be coated with potassium hydroxide or sodium carbonate as it is believed that large amount of alkali metals will catalyse gasification reactions and improve carbon conversion. Otherwise, a mixed bed of aluminium oxide and sodium carbonate should be tried.

9. Further investigations, on a lab-scale, should be considered to determine the effect of chlorides and potassium with respect to concentration and temperature. Furthermore, a phase diagram of a sodium carbonate-chloride-potassium system should be investigated. This will aid in determining a safe operating window with respect to temperature for sodium carbonate bed operation.

10. Verification of the effect of alkali metal salts as catalysts should be done by conducting a lab-scale kinetic study. This will determine the affect of varying the alkali metal salts in spent liquor. There is very little work done in this area. It may be possible to carry out some of these tests on the gasifier by varying the alkali salts in the spent liquor and then determining its effects by monitoring the product gas distribution. Synthetic liquor should be used.

11. A lab-scale investigation into the use of autocausticising agents should be conducted.

12. The use of an inert gas, such as nitrogen (tracer gas method), to more accurately measure the flowrate of the product gas stream out of the gasifier should be implemented. The inert gas would be sampled by a gas chromatograph to provide a direct ratio of nitrogen to the balance of the dry gas species. (Durai-swamy, 1991)

13. A basic feedback control system should be employed to accurately control the bed temperature. This can be achieved by controlling the LPG flowrate to the burner by monitoring the bed temperature according to a setpoint.

14. Since this study was conducted at 500-600°C, it would be best that future investigations be conducted at higher temperatures for increased carbon conversion. In addition, higher temperatures for increased L:S ratios and use of higher solids content liquor should be investigated. Furthermore, longer runs should be conducted to simulate full-scale conditions. The experimental work done in this study was too short and as a result may have been done in an unstable phase.

15. The use of ICP (Inductively Coupled Plasma) emission spectroscopy for the analysis of chlorides should be investigated. In addition, the quantification of tars is recommended for future work.

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APPENDIX A:
GASIFIER OPERATIONAL PROCEDURE

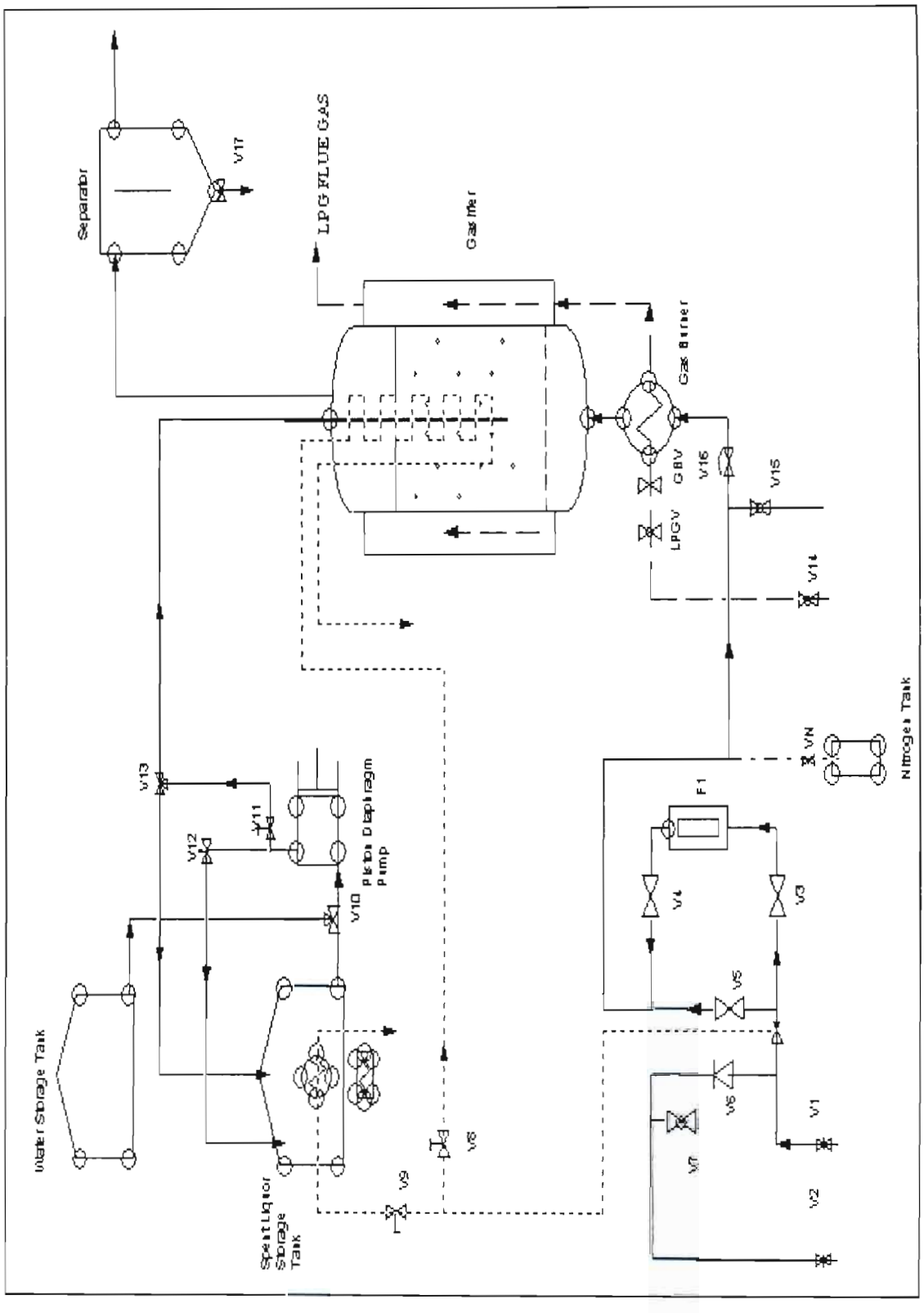

Figure A1: Flowsheet of spent liquor gasification system

1. Safety Check

Before each run the following checks were made:

- The lid of the reactor was positioned properly and the safety chain was hooked onto the reactor lid and locked into position with a padlock.
- Before opening the LPG valve, the extractor was turned on.
- The LPG piping to the gas burner was inspected to ensure that it was properly connected and that there were no cuts or holes along the full length of the piping.
- The heating element wires were checked to ensure that the live, earth and neutral wires were secured in their respective positions.
- A piece of insulation material was placed on the electronic unit of the gas burner to shield it from heat escaping from the piping holes below the reactor. This was to prevent damage to the unit.
- All power cables in direct contact with the unit were removed to prevent short-circuiting.
- The variac or slide regulator used to provide electricity for trace heating of the spent liquor piping was checked, including the electrical wires. The nichrome wires were also checked to ensure that there was no break in the wires and that these wires were not wet. If the wires were wet, they had to be properly dried. This prevented continuous tripping of the main switch due to wet wires.
- In order to prevent any mishaps during operation, the cooling water pipes, spent liquor injection rod, spent liquor pipes and thermocouples were checked to ensure that they were securely in position.
- The LPG and steam thermocouples were also checked.
- In addition, the wall temperature control unit, including the computer programme, was inspected to ensure that they were in working order.

2. Startup

2.1 Spent liquor storage tank

- Before filling the spent liquor storage tank, valves V8 and V9 on the steam off-take line along the walls were closed.
- The spent liquor storage tank was filled to a height that completely submerged the steam coils in the tank.
- Valve V8 was opened to pass condensed steam to the injection rod. The temperature of the condensed steam entering the injection rod was reflected as the cooling water temperature in the computer programme.
- The spent liquor approaching the injection rod was maintained to approximately 80-90°C. The thermostat of the spent liquor storage tank was positioned at

setting 2 and was determined to be sufficient to reach this temperature. The temperature was indicated by the black liquor feed temperature on the computer.

- Thereafter, the stirring apparatus was switched on to ensure proper mixing of the liquor.
- The lid of the spent liquor storage tank was then replaced.

2.2 Water storage tank

- The water storage tank was filled with hot water and the tank lid removed.
- The rubber pipe to the piping network was checked.
- The plastic tap of the tank was left open at all times to prevent damage to the pump when pumping hot water for heating and cleaning of the piping network,.

2.3 Gasifier

2.3.1 Air Startup

- Prior to firing up the gas burner, the ball valve V7 was closed and the main air supply saunders valve V2 and steam/air bypass ball valve V15 were fully opened.
- The bypass valve V5 was opened with valve V3 and V4 closed.
- Steam/air into the gasifier was controlled by valve V16. It was closed to ensure that any water in the piping network was removed (condensation of steam from previous runs) before the air entered the gasifier. The bypass valve V15 was connected to a plastic pipe so water removal could be visually monitored. The removed water was sent to a drain.
- The computer programme was started.
- After a few minutes, the gas burner was started by plugging into the power socket and fully opening the yellow ball valve LPGV. The burner goes through a startup cycle before ignition. If any problems are encountered the burner goes off and an orange light comes on which lights up the reset button on the electronics box.
- To ensure that the gasifier was heating up, the temperature profiles were monitored via the computer programme.
- The manometer was checked to ensure it was properly working by increasing and decreasing valve V16.
- When the reactor hot zone temperature was above 300°C, the LPG ball valve (LPGV) was closed and the burner automatically stopped. This was indicated by an orange light in the electronics box.
- The bed material was fed through an opening at the top which was properly closed with a lid and sealed with high temperature silicon after the bed material was poured in. A glass funnel was used to pour the bed material into the gasifier. Strict safety

precautions were adhered during all of this such as the wearing of gloves and goggles.

- When the bed material was put in, the main air supply valve V2 and the LPGV valve was opened. The reset button of the burner was pressed and the orange light went off. The burner started up after its safety cycle.
- Once the burner was fired up, the temperature distribution in the bed was monitored.
- The bed material was fluidised with air until the reactor hot zone temperature displayed on the computer and the wall temperature, displayed on the temperature control unit, were equal. Thereafter, the burner was shut off by closing the LPG ball valve (LPGV).

2.3.2. Steam startup

- Valve V16 was closed and ball valve V15 was fully opened. This again was to ensure that the condensate that formed in the cold pipes upon entry of steam was removed.
- Valve V5 was closed and valves V3 and V4 were opened. This ensured that the flowmeter was utilised for steam flowrate measurements.
- Valve V7 was opened.
- At this point the main steam supply valve was very hot, so safety glasses and gloves had to be used.
- The initial condensate that formed was removed and valve V8 was opened slightly. The piping network was sufficiently heated up over 3 to 5 minutes.
- The burner was started up by opening valve LPGV and then resetting the burner.
- When the burner started up, valve V16 was slowly opened and valve V15 was closed. There were noticeable fluctuations on the steam flowmeter but this settled down. The steam flowrate was controlled by valveV16.
- The temperatures were monitored once again. As soon as the gas burner was on and the superheated steam delivered to the gasifier, the temperature profiles started to increase.
- In a short period of time, the reactor hot zone and the wall temperature became equal. This suggested that the reactor was fluidising.
- Condensate trapped in the separator was removed by opening ball valve V17. This was done before the spent liquor was injected. This also cleaned the separator.
- Once operating temperature was reached after about 20 minutes, a further 5 minutes were required for the temperature profiles to be stable. The LPG flowrate valve located on the burner (GBV) was adjusted.

2.3.3 Spent liquor injection

- While waiting for the reactor hot zone temperature and wall temperatures to equalise, the piston diaphragm pump was warmed up by circulating hot water. This was done by changing the position of valve V10 to re-route hot water from the hot water storage tank. Valve V13 was in the drain position. A pipe was attached to the end of the drain line for removal of hot water into a bucket.
- A low flowrate was selected for this purpose by changing the pump speed.
- When the pump was warmed up, spent liquor was circulated by changing valve V10 to the appropriate position and allowed the liquor to drain. When spent liquor flowed out of the pipe into a bucket, the attached pipe was removed for recycling of spent liquor into the storage tank. The flowrate of liquor for the run was selected from the calibration graph.
- Valve V13 was changed to deliver spent liquor to the injection rod for injection into the bed.

2. Shutdown

- When spent liquor injection ended, valve V10 was changed so that water was injected into the bed for cleaning of the spent liquor piping network and the injection rod. This took roughly 3-5 minutes. The reactor hot zone temperature then declined.
- The LPG valve was closed and the power socket for the burner was removed from the main electricity supply.
- Steam was left to flow into the reactor until the steam in temperature profile reached roughly 130°C. This took 1-1 ½ hours. The reactor temperatures were observed to increase when steam flowrate into the gasifier seized.
- The nitrogen cylinder was opened and the regulator adjusted to a pressure of 60-100kPa. Nitrogen flow into the gasifier remained turned on for about an hour by opening the ball valve located on that line.
- Valve V16 and the nitrogen cylinder valve were then shut off.

3. Maintenance

- The spent liquor from the spent liquor storage tank was removed and cleaned with water. Hot water was heated up in the spent liquor storage tank.
- Valve V13 was changed to the recycle position so that the pump recycled hot water to the spent liquor storage tank.
- When the gasifier has sufficiently cooled down, the thermocouples and the lid of the gasifier were removed. A vacuum was used to remove the bed material.

APPENDIX B:
EQUILIBRIUM CALCULATIONS

Equilibrium concentrations were calculated for temperatures of 500, 550 and 600°C. The following independent reactions were considered in this equilibrium calculation.

$C + H_2O \leftrightarrow CO + H_2$ (A)

$CO + H_2O \leftrightarrow CO_2 + H_2$ (B)

$C + 2H_2 \leftrightarrow CH_4$ (C)

	500°C	550°C	600°C
K_A	0.024	0.086	0.269
K_B	5.755	3.669	2.718
K_C	2.586	1.000	0.449

Table B1: Equilibrium Constants for Reactions A, B, C (Smith et al., 1996)

These predicted values where calculated using a Generalized Reduced Gradient nonlinear optimization method (Solver application in Excel) where K_j, $v_{i,j}$ are known and ε and y was unknown (equations 1 and 2).

Note: K_j = equilibrium constant

$v_{i,j}$ = stoichiometric coefficients

ε = extent of reaction

y = mole fraction of component i

P = pressure, P_0 = initial pressure

$n_{i,o}$ = initial no. of moles of component i and n = total no. of moles

Equation 1

$$y_i = \left[n_{io} + \sum_j v_{i,j}\varepsilon_j\right] / \left[n_o + \sum_j v_j \varepsilon_j\right]$$

Equation 2

$$K_j * (P / P_0)^{-v_j} = \prod_i (y_i)^{v_{i,j}}$$ **(Smith et al., 1996)**

Conditions:

1. The sum of the mole fractions of the components of the gas phase equals one.
2. The equilibrium constants given in Table B1.

APPENDIX C:

C1: THEORY BEHIND ORIFICE PLATE DESIGN

(GEANKOPLIS, 1993)

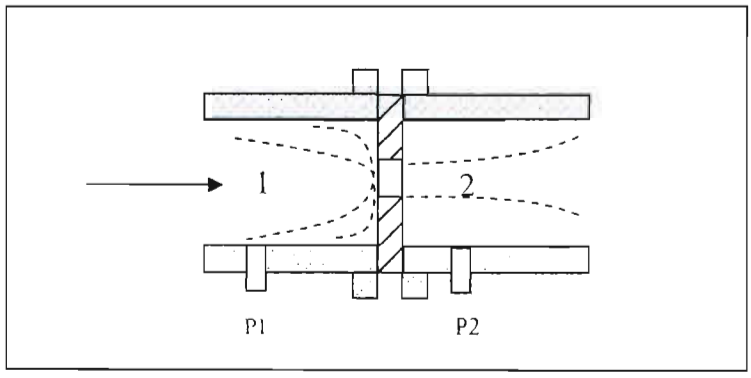

Figure C1 -1: Orifice meter (Geankoplis, 1993)

The mechanical energy balance for an incompressible flow between points 1 and 2 is given below. Friction is neglected with and the pipe is assumed horizontal and turbulent flow.

$$\frac{v_1^2}{2}+\frac{p_1}{\rho}=\frac{v_2^2}{2}+\frac{p_2}{\rho} \qquad \text{(H1)}$$

From the continuity equation

$$v_1\frac{\pi D_1^2}{4}=v_2\frac{\pi D_2^2}{4} \qquad \text{(H2)}$$

Combining the above equations and considering small friction losses, an experimental coefficient C_v is added.

$$v_2=\frac{C_v}{\sqrt{1-\left(D_2/D_1\right)^4}}\sqrt{\frac{2(p_1-p_2)}{\rho}} \qquad \text{(H3)}$$

For compressible flow of gases, the adiabatic expansion from p1 to p2 pressure must be accounted for in the above equation. The dimensionless expansion correction factor Y which is a function of the pressure ratio is added.

$$m = \frac{C_v A Y}{\sqrt{1 - \left(D_2 / D_1\right)^4}} \sqrt{2(p_1 - p_2)\rho} \qquad \text{(H4)}$$

Equation H4 was used to design the orifice meter.

APPENDIX C:

C2:DESIGN-ORIFICE METER CALCULATION

Table C1:Input

Parameter	Nomenclature	Units	Value
Orifice diameter	Do	m	0.035
Pipe diameter	D1	m	0.075
Pressure difference (assumed)	P1-P2	Pa	1400
Properties			
Density	p	kg/m^3	0.30
Viscosity	v	Pa.s	2.65E-05
Cv <pipe diameter less than0.2m		Dim.	0.61
Density of water @ 25deg.cel.	p_w	kg/m^3	997.08
Gravity	g	m/s^2	9.81

Table C2:Output

Parameter	Nomenclature	Units	Value
volumetric flowrate	Q	m^3/s	0.058
velocity at orifice	Vo	m/s	60.389
Reynolds No.	N_{Re}	Dimensionless	23902.701
Height of water in Manonmeter	H	cm	14.313
Thickness of orifice plate	t	mm	4.375
Radius tap upstream		pipe diameter	1
Radius tap downstream		pipe diameter	0.5

Table C3:Calculation

	Units	Values	Definition
Do/D1	Dim	0.467	Ratio
Ao = Pi() * Do^2 / 4	m^2	0.001	Area of orifice
Q=(CvAo)*(2(P1-P2)/*p*)^0.5/((1-(Do/Di)^4)^0.5	m^3/s	0.058	Volumetric flowrate at orifice
Vo = Q / Ao	m/s	60.389	Velocity at orifice
Nre = Do*Vo**p*/*v*	Dim	23903	Reynolds Number
t= 1/8 * Do	m	0.004	Thickness of orifice plate
P1 - P2 = *pw * g *H therefore H =*	m	14.313	Predicted Height of water in manometer

APPENDIX D:
MATERIAL SAFETY DATA SHEET

SPENT SASAQ LIQUOR (RED LIQUOR)

1. PRODUCT IDENTIFICATION

NAME OF CHEMICAL	Red Liquor
DESCRIPTION/USE OF CHEMICAL	Red viscous liquor
SUPPLIER	Sappi – Stanger
ADDRESS	Sappi Fine Papers Gledhow Stanger
CONTACT PERSON	Willie Appelcryn /Thamen Govender
EMERGENCY TEL NO.	**032 437 2174/2149**

2. PRODUCT INFORMATION

TYPE	Spent NSSC Liquor
CHEMICAL COMPONENTS	17% Sodium lignosulphonates and hemicellulose, <1% sodium sulphite, sodium hydroxide and sodium sulphate; balance water.
INCOMPATIBLE MATERIALS:	No hazardous reactions expected
DECOMPOSITION PRODUCTS:	Oxides of sulphur and carbon in fire.

3. PHYSICAL DATA

PHYSICAL STATE	Dark red liquid
DENSITY/S.G.:	?
BOILING POINT	>100°C
FLASH POINT	
ODOUR	Sulphur type
Ph	10-12
SOLUBILITY	
SOLIDS	18-20%
CORROSIVE	No
OXIDISING AGENT	No

REDUCING AGENT	No
STABLE	Yes
SPONTANEOUS COMBUSTION	No
HAZARDOUS POLYMERISATION	No
EXPLOSIVE	No

4. STORAGE CONDITIONS

Store in closed containers under normal warehouse conditions.

5. ECOLOGICAL AND TOXICOLOGICAL DATA

No information

6. HAZARDS AND RISKS

PHYSICAL HAZARDS:	No information
HEALTH HAZARDS:	Irritant to eyes and skin

7. FIRST AID PROCEDURES

SPLASHES IN THE EYES:	Wipe excess away from eye with a soft cloth. Flush eye with water (or normal saline solution if available) for at least fifteen minutes. Seek medical attention as a precautionary measure.
CONTACT WITH SKIN:	Immediately remove contaminated clothing and wash affected area with lots of soap and water. If irritation persists seek medical attention. If injected through the skin immediately seed medical attention.

MOUTH CONTACT OR EATEN:	Do not induce vomiting. Rinse mouth and drink plenty of water or milk. Donot drink alcohol. Seek medical attention.
INHALATION:	Remove to fresh air, rest and keep warm. Seek medical attention if symptoms persist or if exposure was prolonged.

8. EMERGENCY ACTION FOR FIRES AND SPILLS

FIRE FIGHTING:	Determined by surrounding fire. Breathing apparatus should be worn.
SPILLAGE:	Flush away with large quantities of water to effluent drain, or if this is not possible recover into drums for disposal avoid contaminating natural water systems.
DISPOSAL:	Dispose by incineration or biological treatment.

9. PERSONAL PROTECTIVE EQUIPMENT

PROTECTIVE EQUIPMENT:	Gloves; goggles; normal industrial protective clothing.

10. **ADDITIONAL COMMENTS:**	pH ca.9. Ecological effects are unknown but expected to be harmful due to the increase in the COD of the water system. Product will burn once excess water is evaporated. Product does not require labelling for shipping purposes.

APPENDIX E

MATERIAL SAFETY DATA SHEET

SPENT SODA LIQUOR (STRONG BLACK LIQUOR)

1. PRODUCT IDENTIFICATION

NAME OF CHEMICAL	Strong Black Liquor
DESCRIPTION/USE OF CHEMICAL	Used for the production of Soda Ash
SUPPLIER	Sappi – Stanger
ADDRESS	Sappi Fine Papers Gledhow Stanger
CONTACT PERSON	Willie Appelcryn /Thamen Govender
EMERGENCY TEL NO.	**032 437 2174/2149**

2. PRODUCT INFORMATION

TYPE	Spent soda liquor
CHEMICAL COMPONENTS	Sodium carbonate, Sodium silicates, Sodium sulphates and Sodium chlorides, residual sodium hydroxide, lignin
INCOMPATIBLE MATERIALS:	No hazardous reactions expected
DECOMPOSITION PRODUCTS:	No information
MATERIALS TO AVOID:	Oxidising agents, acids (will cause precipitation of solids)

3. PHYSICAL DATA

PHYSICAL STATE	Dark brown liquid
DENSITY/S.G.:	~1.18
BOILING POINT	>100°C
FLASH POINT	>100°C
ODOUR	Distinctive
Ph	11.5-12.5
SOLUBILITY	100% in water
SOLIDS	22%-30%

PHYSICAL DATA (cont.)	
CORROSIVE	No
OXIDISING AGENT	No
REDUCING AGENT	No
STABLE	Yes
SPONTANEOUS COMBUSTION	No, but decomposition will liberate oxides of carbon
HAZARDOUS POLYMERISATION	No

4. STORAGE CONDITIONS

Stored in specifically designed tanks as part of process conditions. Should the need arise to store in a non-dedicated tank, obtain permission from plant superintendent.

5. ECOLOGICAL AND TOXICOLOGICAL DATA

ACUTE EFFECTS	LC:50>10ppm. Spills into natural water systems will cause foaming and unsightly appearance, but are unlikely to cause any long-term effects to the ecology. Acute fish mortality may be possible as a result of oxygen depletion due to the high COD of the liquor.
IRRITANT EFFECTS	Product is expected to be corrosive to eyes due to residual caustic levels.Irritation to skin is expected on prolonged or repeated exposure, resulting in dermatitis. Oral toxicity is not known. But is not expected to be highly toxic.
SENSITIZATION EFFECTS	None
CARCINOGENIC POTENTIAL	None
OTHER HEALTH EFFECTS	None

6. HAZARDS AND RISKS

PHYSICAL HAZARDS:	No information
HEALTH HAZARDS:	Irritant to eyes and skin

7. FIRST AID PROCEDURES

SPLASHES IN THE EYES:	Wipe excess away from eye with a soft cloth. Flush eye with water (or nomal saline solution if available) for at least fifteen minutes. Seek medical attention as a precautionary measure. If contact with hot liquor has occurred seek immediate medical attention.
CONTACT WITH SKIN:	Immediately remove contaminated clothing and wash affected area with lots of soap and water. If irritation persists seek medical attention. If injected through the skin immediately seed medical attention. Ifcontact with hot liquor has occurred seek immediate medical attention.
MOUTH CONTACT OR EATEN:	Do no induce vomiting. Rinse mouth and drink plenty of water or milk. Do not drink alcohol. Seek medical attention.
INHALATION:	Not expected to be hazardous. Remove to fresh air, rest and keep warm. Seek medical attention if symptoms persist or if exposure was prolonged.

8. EMERGENCY ACTION FOR FIRES AND SPILLS

FIRE FIGHTING:	Determined by surrounding fire. Breathing apparatus should be worn. Water mist, foam, carbon dioxide, dry powder.
SPILLAGE:	Dam spill with sand/earth to prevent spreading. Pump into
SPILLAGE (cont.)	proper containersfor re-use or disposal. Absorb remainder onto sand/earth. If not fit for re-use,dispose via waste contractor. Contact Environmental Manager or Process Chemist for spill handling procedure if unsure.
DISPOSAL:	Dispose by incineration or biological treatment.

9. PERSONAL PROTECTIVE EQUIPMENT

PROTECTIVE EQUIPMENT:	Gloves (heat resistant); goggles; normal industrial protective clothing. If potential hazard of spilling, use of gumboots and faceshields are necessary including the above mentioned protective measures.

APPENDIX F:
MATERIAL SAFETY DATA SHEET

LIQUEFIED PETROLEUM GAS & PROPANE
BOC GASES-AFROX
EMERGENCY NO: (011) 820 5400 (24HR)

1. PRODUCT AND COMPANY IDENTIFICATION

PRODUCT IDENTIFICATION

Product Name:	LIQUEFIED PETROLEUM GAS (ALL BRANDS)
Chemical Formula:	C_3H_8 and C_4H_{10}
Company identification	African Oxygen Limited 23 Webber Street Johannesburg, 2001 Tel. No: (011) 490-0400 Fax No: (011) 493-8828

2. COMPOSITION/INFORMATION ON INGREDIENTS

Trade Names	HANDIGAS		
	Technical Propane		
	Instrument Grade Propane		
Chemical Name	Butane / Propane / Propylene		
Chemical Family	Aliphatic Hydrocarbon		
CAS No.	Butane	106-97-8	UN No. 1075
	Propane	74-98-6	UN No. 1978
	Propylene	115-07-01	UN No. 1077
Hazchem Code:	2WE		
Hazchem Warning	2A Fammable gas		

3. HAZARDS IDENTIFICATION

Main Hazards

Vapourised liquefied petroleum gas is highly flammable and can form explosive mixtures with air. The vapourised liquid does not support life. It can act as a simple asphyxiant by diluting the concentration of

	oxygen in the air below the levels necessary to support life; it can act as a simple asphyxiant.
Adverse Health effects	The liquefied petroleum gases are non-toxic. Prolonged inhalation of high concentrations has an anaesthetic effect.
Chemical Hazards	Propane and butane (known most extensively in commercial and popular terms as LPgas or LPG) have an extremely wide range of domestic, industrial, commercial, agricultural and internal combustion engine uses. It is estimated that the two gases, un-mixed and in mixtures, have several thousand industrial applications and many more in other fields. Their very broad application stems from their occurrences as hydrocarbons between natural gas and natural gasoline, and from their corresponding properties. As a result of their wide application, misuse could result in serious chemical hazards.
Biological Hazards	Contact with the liquid phase of liquefied petroleum gases with the skin can result in frostbite.
Vapour Inhalation	As the vapourised liquid acts as a simple asphyxiant death may result from errors in judgement, confusion, or loss of consciousness which prevents self-rescue. At low oxygen concentrations, unconsciousness and death may occur in seconds without warning.
Eye Contact	The liquid can cause severe burn-like injuries
Skin Contact	Contact with the liquid phase can cause severe burn-like injuries.
Ingestion	No known effect.

4. FIRST AID MEASURES

Prompt medical attention is mandatory in all cases of overexposure to vapourised liquefied petroleum gas. Rescue personnel should be equipped with self-contained breathing apparatus. In the case of frostbite from contact with the liquid phase, place the frost-bitten part in warm water, about 40-42°C. If warm water is not available, or is impractical to use, wrap the affected part gently in blankets. Encourage the patient to exercise the affected part whilst it is being warmed. Do not remove clothing while frosted. Conscious persons should be assisted to an uncontaminated area and inhale fresh air. Quick removal from the contaminated area is most important. Unconscious persons should be removed to an uncontaminated area, and given mouth-to mouth resuscitation and supplemental oxygen.

Eye Contact	Immediately flush with large quantities of tepid water, (with the liquid phase) or with sterile saline solution. Seek medical attention
Skin Contact (with the liquid phase)	See above for handling of frostbite.
Ingestion	No known effect.

5. FIRE FIGHTING MEASURES

Extinguishing media	Do not extinguish fires unless the leakage can be stopped. DO NOT USE WATER JET – use dry chemical, CO_2 or foam.
Specific Hazards	The rupturing of cylinders or bulk containers due to excessive exposure to a fire could result in a BLEVE (Boiling liquid expanding vapour explosion), with disastrous effects. As the flammability limits in air for the main constituents of liquefied petroleum gas vary between approximately 2 and 11%, extreme care must be taken when handling leaks.
Emergency Actions	If possible, shut off the source of the spillage. Evacuate area. Post notices "NO NAKED

	LIGHTS – NO SMOKING". Prevent liquid or vapour from entering sewers, basements and workpits. Keep cylinders or bulk vessels cool by spraying with water if exposed to a fire. If tanker has overturned, do not attempt to right or move it. CONTACT THE NEAREST BOC (AFROX) BRANCH.
Protective Clothing	Self-contained breathing apparatus. Safety gloves and shoes or boots should be worn when handling containers.
Environmental Precautions	Vapourised liquefied petroleum gas is heavier then air and could form pockets of oxygen-deficient atmosphere in low lying areas.

6. ACCIDENTAL RELEASE MEASURES

Personal Precautions	Do not enter any area where liquefied petroleum gas has been spilled unless tests have shown that it is safe to do so.
Environmental Precautions	The danger of widespread formation of explosive LPG/Air mixtures should be taken into account. Accidental ignition could result in a massive explosion.
Small spills	DO NOT extinguish the fire unless the leakage can be stopped immediately. Once the fire has been extinguished and all spills have been stopped, ventilate the area.
Large spills	Stop the source if it can be done without risk. Contain the leaking liquid, with sand or earth, or disperse with special water / fog spray nozzle. Allow to evaporate. Take the precautions as listed above under "Emergency Actions". Restrict access to the area until

completion of the clean-up procedure. Ventilate the area using forced-draft if necessary. All electrical equipment must be flameproof.

7. HANDLING AND STORAGE

Cylinders containing liquefied pertroleum gas should only be handled and stored in the vertical position. Cylinders should never be rolled. Do not allow cylinders to slide or come into contact with sharp edges and they should be handled carefully. Ensure that cylinders are stored away from other oxidants. Comply with all local legislation. Keep out of reach of children.

8. EXPOSURE CONTROL/PERSONAL PROTECTION

Occupational exposure hazards	As vapourised LPG is a simple asphyxiant, avoid any areas where spillage has taken place. Only enter once testing has proved the atmosphere to be safe.
Engineering control measures	Engineering control measures are preferred to reduce exposure to Oxygen-depleted atmospheres. General methods include forced-draft ventilation, separate from other exhaust ventilation systems. Ensure that sufficient fresh air enters at, or near, floor level. Ensure that all electrical equipment is flameproof.
Personal protection	Self-contained breathing apparatus should always be worn when entering area where oxygen depletion may have occurred. Safety goggles, gloves and shoes or boots should be worn when handling containers.
Skin	Wear loose-fitting overall, preferably without pockets.

9. PHYSICAL AND CHEMICAL PROPERTIES

PHYSICAL DATA

Chemical symbol	Propane C_3H_8 LPG	
Molecular Weight	44.10	
Specific Volume @ 20°C &101.325kPa	547ml/g	471ml/g
Boiling point @ 101.325kPa	-42.1°C	
Vapour pressure @ 20°C	900kPa	+/-750kPa
Auto ignition temperature	480°C	+/-450°C
Calorific value	11900kcal/kg	1185kcal/kg
Density, gas @101,325 KPa & 20°C	183 g/ml	212 g/ml
Density, liquid @ 20°C	0.5kg/litre	0.528kg/litre
Relative density (Air =1) @ 101,325kPa	1,55	+/-1.75
Flammability in air	2.2-9.5%	2.2-9.5%
Critical temperature	96.67°C	+/-95°C
Colour – Liquid	Clear	Clear
Taste	None	None
Odour	Ethyl Mercaptan added	Ethyl Mercaptan added
Specification	SABS 691	SABS 690

10. STABILITY AND REACTIVITY

Conditions to avoid — The dilution of the oxygen concentration in the atmosphere to levels which cannot support life. The formation explosive gas/air mixtures.

11. TOXICOLOGICAL INFORMATION

Acute Toxicity	TLV 1000VPM.
Skin & eye contact	No known effect.
Chronic Toxicity	No known effect.
Carcinogenicity	Severe cold burns can result in carcinoma
Mutagenicity	No known effect.
Reproductive Hazards	No known effect.

APPENDIX G:
DIMENSIONS OF GASIFIER

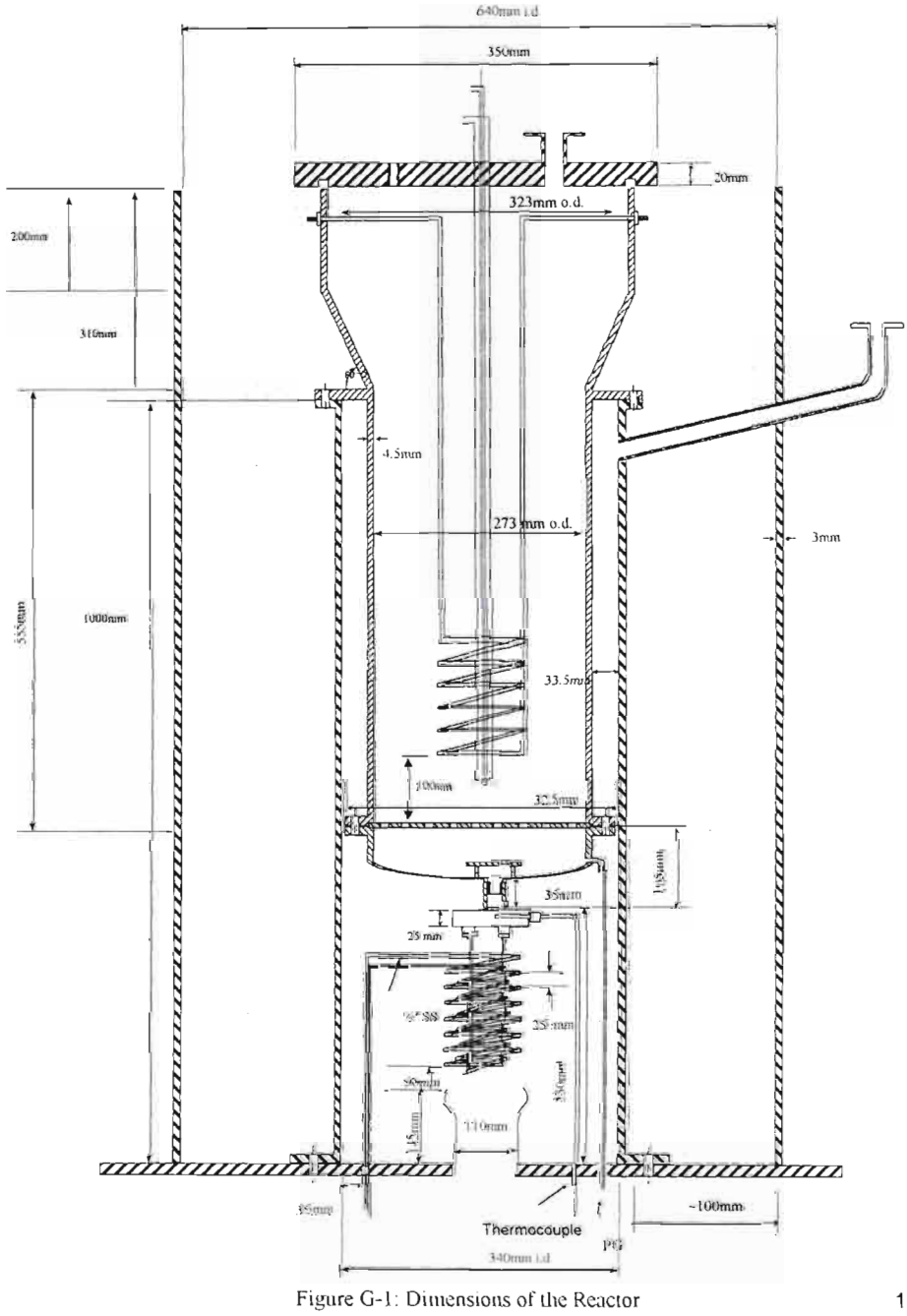

Figure G-1: Dimensions of the Reactor

APPENDIX H:

AVERAGE DATA FROM RUNS - COMPOSITION PROFILES

Soda Experiments - Average Data

HD1

Temperature	500.00	Deg.Celc.
Steam Flowrate	25.00	kg/hr
L: S ratio	0.06	
Solids Concentration	23.00	%

Time/ h:min	H2vol%	COvol%	CH4vol%	CO2vol%
0:09	73.72	12.50	0.98	12.80
0:29	39.71	27.32	25.72	7.25
0:47	36.07	35.12	19.90	8.91
1:07	26.98	38.63	24.58	9.81

HD2

Temperature	550.00	Deg.Celc.
Steam Flowrate	25.00	kg/hr
L:S ratio	0.06	
Solids Concentration	23.00	%

Time/ h:min	NH2vol%	NCOvol%	NCH4vol%	NCO2vol%
0:07	91.45	0.40	8.09	0.06
0:42	31.82	27.82	35.41	4.95
0:58	15.47	42.41	35.32	6.80
1:09	11.51	46.21	34.04	8.24

HD3

Temperature	600.00	Deg.Celc.
Steam Flowrate	25.00	kg/hr
L:S ratio	0.06	
Solids Concentration	23.00	%

Time/ h:min	H2vol%	COvol%	CH4vol%	CO2vol%
0:13	73.49	25.05	1.27	0.19
0:30	39.93	25.82	28.32	5.94
0:48	38.01	23.03	21.67	17.29
1:10	16.36	21.98	26.25	35.41

HD4

Temperature	500.00	Deg.Celc.
Steam Flowrate	25.00	kg/hr
L:S ratio	0.12	
Solids Concentration	23.00	%

Time/ h:min	H2vol%	COvol%	CH4vol%	CO2vol%
0:10	78.95	1.36	5.37	14.32
0:30	19.27	41.79	25.44	13.51
0:47	16.90	40.53	26.16	16.42
1:11	17.00	39.80	24.87	18.33

HD5

Temperature	500.00	Deg.Celc.
Steam Flowrate	25.00	kg/hr
L:S ratio	0.06	
Solids Concentration	13.00	%

Time/ h:min	H2vol%	COvol%	CH4vol%	CO2vol%
0:07	81.44	2.91	13.00	2.64
0:32	64.51	9.14	17.72	8.63
0:58	46.68	18.90	22.74	11.68
1:14	37.12	28.99	20.10	13.78

HD6

Temperature	500.00	deg.Celc.
Steam Flowrate	25.00	kg/hr
L:S ratio	0.06	
Solids Concentration	23.00	%

Time/ h:min	H2vol%	COvol%	CH4vol%	CO2vol%
0:14	75.53	17.16	3.44	3.87
0:34	43.41	28.90	24.12	3.57
0:52	31.98	36.72	24.91	6.38
1:18	33.95	31.86	24.15	10.04
1:45	30.51	35.82	20.28	13.39
2:05	29.07	35.64	17.32	17.98
2:20	30.95	34.43	16.91	17.72
2:41	31.53	34.73	16.74	17.00

SASAQ Experiments - Average Data

HD7

Temperature	500.00	Deg.Celc.
Steam Flowrate	25.00	kg/hr
L:S ratio	0.06	
Solids Concentration	20.00	%

Time/ h:min	H2vol%	COvol%	CH4Bvol%	CO2vol%	H2Svol%
0:10	85.40	1.38	6.84	5.97	0.41
0:37	54.20	22.33	15.03	8.34	0.10
1:04	46.45	30.62	17.91	4.89	0.14

HD8

Temperature	550.00	Deg.Celc.
Steam Flowrate	25.00	kg/hr
L:S ratio	0.06	
Solids Concentration	20.00	%

Time/ h:min	H2vol%	COvol%	CH4Bvol%	CO2vol%	H2Svol%
0:07	70.84	12.10	11.27	5.66	0.13
0:22	45.90	15.76	15.66	22.44	0.24
0:42	38.40	7.29	14.80	39.06	0.45
1:05	29.52	9.28	8.98	51.94	0.27

HD9

Temperature	600.00	Deg.Celc.
Steam Flowrate	25.00	kg/hr
L:S ratio	0.06	
Solids Concentration	20.00	%

Time/ h:min	H2vol%	COvol%	CH4Bvol%	CO2vol%	H2Svol%
0:08	90.95	1.62	6.99	0.25	0.19
0:29	61.39	16.42	15.80	6.10	0.29
0:52	46.28	12.50	16.53	24.48	0.21
1:10	31.76	11.52	11.67	44.83	0.22

HD10

Temperature	500.00	Deg.Celc.
Steam Flowrate	25.00	kg/hr
L:S ratio	0.06	
Solids Concentration	20.00	%
Run Time	3.00	hr

Time/ h:min	H2vol%	COvol%	CH4Bvol%	CO2vol%	H2Svol%
0:14	77.91	5.34	9.57	7.06	0.11
0:36	63.90	13.37	9.88	12.83	0.01
1:01	57.41	17.69	8.65	16.22	0.02
1:23	49.35	26.84	10.32	13.45	0.03
2:07	46.80	39.71	3.10	10.39	0.02
2:50	46.03	38.46	3.02	12.48	0.01

HD11

Catalytic Effect of Alkali Metal Salts - Single Run

Temperature	550.00	Deg.Celc.
Steam Flowrate	25.00	kg/hr
L:S ratio	0.06	
Solids Concentration	20.00	%

Time/h:min	H2vol%	COvol%	CH4Bvol%	CO2vol%
0:10	56.58	2.74	21.30	19.38
0:25	28.96	2.99	25.15	42.91
0:44	19.55	2.82	16.44	61.18
0:59	17.06	2.72	10.95	69.26