EFFECT OF MECHANICAL AND CHEMICAL PULPING ON IONIC LIQUID FRACTIONATION OF WOOD CHIPS

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PREFACE

The work presented in this thesis was undertaken by the researcher under the supervision of Prof. Nirmala Deenadayalu at Durban University of Technology, Durban, South Africa, co- supervisors: Prof. Bruce Sithole and Mr. Jerome Andrew from the Council for Scientific and Industrial Research's (CSIR), Biorefinery Industry Development Facility (BIDF), from 2014 – 2017. The study presents original work by the researcher and has not been submitted in any form to another university. Where use is made of the work of others, it has been clearly referenced accordingly.

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ABSTRACT

In this study, a comparison of two pulping methods namely mechanical and chemical, on the dissolution of *Eucalyptus grandis (E. grandis)* wood chips was undertaken. The wood chip pulp was treated with an ionic liquid (IL): 1-allyl-3-methylimidazolium chloride to extract the cellulose. The IL was mixed with unbleached mechanical pulp (UBMP), bleached mechanical pulp (BMP), unbleached kraft pulp (UBKP) and bleached kraft pulp (BKP) in ratios of 10%, 20%, 30%. Each solution contained IL, wood pulp and 2-mL of 16 v/v % of dimethyl sulfoxide (DMSO). The 30 % IL pretreatment was the most effective IL pretreatment. The cellulose yield at 30 % IL pretreatment for UBMP, BMP, UBKP and BKP was 65.12%, 63.82%, 67.43%, 67.15%, respectively. This indicated that the kraft pulping method was more effective than the mechanical pulping method for the yield of cellulose after the IL pretreatment. The CrI value at 30 % IL pretreatment was highest for UBMP (72.03%) indicating that the pretreatment used was the least effective in reducing the cellulose crystallinity. The fractions of *E. grandis* wood chip namely, lignin, regenerated cellulose and hemicelluloses before and after the IL pretreatment, were characterized by a variety of analytical techniques such as High-Performance Liquid Chromatography (HPLC) (carbohydrates), Fourier Transform Infra-Red Attenuated Total Reflection (FTIR-ATR) (functional groups), Pyrolysis-Gas Chromatography /Mass Spectroscopy (Py-GC/MS) (lignin fractions), Ultraviolet/Visible spectroscopy (UV/Vis) (acid soluble lignin), Thermo Gravimetric Analysis (TGA) (degradation of pulp), X-Ray Diffraction (XRD) (crystallinity) and high resolution Scanning Electron Microscopy (SEM) (morphology). Kraft pulping was the most effective method for the yield of cellulose after the [AMIM][Cl]/DMSO pretreatment. The 30% [AMIM][Cl]/DMSO pretreatment gave the highest S/G ratio indicating that minimal bleaching was required.

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[AMIM][Br]	1-Allyl-2,3-dimethylimidazolium bromide
[AMIM][Br]	1 -Allyl-2,3-dimethylimidazolium bromide
[AMIM][Cl]	1-Allyl-3-methylimidazolium chloride
[BMIM][Br]	1-Butyl-3-methylimidazolium bromide
[BMIM][Cl], [C_4MIM] [Cl]	1-Butyl-3-methylimidazolium chloride
[BMIM][OAc]	1-Butyl-3-methylimidazolium acetate
[C_2MIM][Cl]	1-Ethyl-3-methylimidazolium chloride
[C_2MIM][MeoPO_2]	1-Ethyl-3-methylimidazolium methyl phosphate
[EMIM][BA]	1-Ethyl-3-methylimidazolium benzoate
[EMIM][Cl]	1-Ethyl-3-methylimidazolium chloride
[EMIM][OAc]	1-Ethyl-3-methylimidazolium acetate
[EMIM][DEP]	1-Ethyl-3-methylimidazolium diethyl phosphate
CS_2	Carbon disulphide
DP	Degree of polymerization
DS	Degree of substitution
DSC	Differential scanning calorimetry
FTIR-ATR	Fourier transform infrared spectroscopy
IL	Ionic liquid
HPLC	High performance liquid chromatography
MCC	Microcrystalline cellulose
NMMO	N-methyl-morpholine-N-oxide
NMR	Nuclear magnetic resonance

TGA	Thermo gravimetric analysis
SEC	Size exclusion chromatography
SEM	Scanning electron microscopy
XRD	X-ray diffractometer
TUBK	Treated unbleached kraft pulp
TUBM	Treated unbleached mechanical pulp
TBKP	Treated bleached kraft pulp
TBMP	Treated bleached mechanical pulp

Definitions

Total alkalinity: Total of all “available “sodium alkali compounds**:**

$NaOH + Na_2S + Na_2CO_3 + Na_2SO_4 + Na_2S_2O_3 + Na_2SO_3$

Total titratable alkalinity (TTA): Total of **$NaOH + Na_2S$**

Effective alkalinity (EA): Total of **$NaOH + \frac{1}{2} Na_2S$**

Causticity: Ratio o**f $NaOH$ to $NaOH + Na_2CO_3$**

Sulphidity: Ratio o**f Na_2S to AA (or TTA)**

Chapter 1

INTRODUCTION

1.1 Background

South Africa has a large pulp and paper industry that contributes almost 6% to the country's Gross Domestic Product (GDP). However, the industry is in decline even on a worldwide basis due mainly to reduced usage of paper due to the advent of digital technology (Balat, 2009). In 2007 global paper production was 157.4 million metric tons and in 2016 it was 122.6 million metric tons, a reduction in paper usage of 22 % (Statistics, 2016).

A potential solution to increasing the use of the pulp and paper biomass is the introduction of lignocellulosic biomass in a bio-refinery as an alternative sustainable energy/chemical source. Which can be converted and further used to produce chemicals, biofuels, and paper related products. The bio-refinery concept has been applied throughout the past few decades as a way to help revive the pulp and paper industry. The concept involves extracting and producing valuable products such as fiber, fuels and alcohols from biomass (Huber, 2006).

Biomass is organic material derived from living or recently dead creatures and plants. The structural framework contains carbon and a mixture of elements such as hydrogen (H), oxygen (O_2) and nitrogen (N_2). Also present are particles such as salt and non-acidic earth metals in low quantities (Field, Campbell and Lobell, 2008).

The carbon that forms biomass comes from CO_2 (Canadell and Schulze, 2014), and is consumed during the processes of photosynthesis. Figure 1.1 below shows the different biomass source.

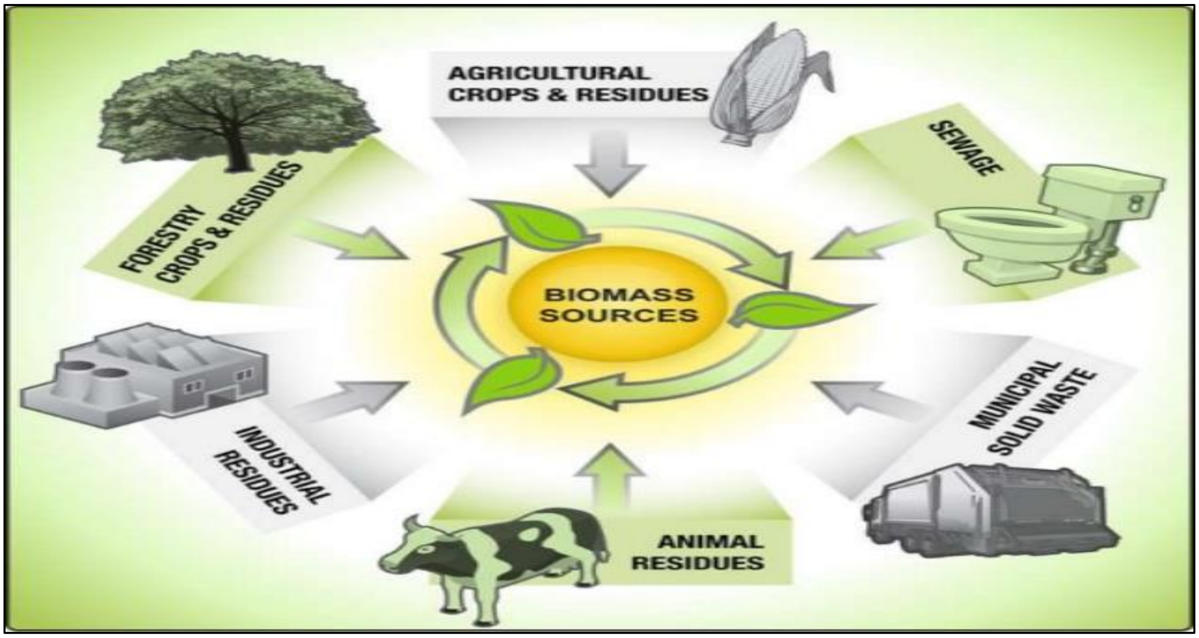

Figure 1:1: Biomass source cycle, (Zafar, 2011)

Plant life that is not consumed by scavengers or harvested for industrial uses is degraded by inter alia, small scale creatures or rough weather. During degradation the biomass releases carbon into the ecosystem. Usually, this carbon is released in the form of carbon dioxide (CO_2) or methane (CH_4) gases. All these different agricultural or industrial processes as illustrated in Figure 1.1 produce residue that contribute to biomass sources (Aresta, 2013).

Lignocellulose biomass consists primarily of three components namely: lignin, hemicellulose and cellulose. Cellulose is the primary component of plant cell fibers that is constituted by a series of linear D-glucose chain units. It is water-insoluble and is a primary source for pulp production. However, due to the presence of lignin and hemicellulose layers which are bonded to each other it makes it difficult to access cellulose (Vitz, 2009). As such, the paper and pulp production industries have since undertaken several pretreatment methods for the removal of lignin, hemicellulose and extractives from wood so that the cellulose is accessible for transformation into useful products.

Pretreatment methods used are: enzyme technology, mechanical and chemical pulping (Bajpai, 2013), steam explosion (Kumar, 2009), alkaline solutions (He, 2005), carbon dioxide (CO_2) explosion (Agbor, *et al*., 2011), dilute acid (Lee, 1999), and white rot fungi (Isroi, *et al*., 2011). Even though the extraction processes are very effective, they have their own shortcomings such as release of toxic greenhouse gasses, pathogens, radiation toxicity as well as chemical misuse and disposal. Furthermore, all these contribute to an increasing rate of global warming (Huber, 2006). As such, the concept of green chemistry was introduced by (Anastas, *et al.*, 2008), which stated that chemical processes should use minimum and recyclable chemicals.

The introduction of ionic liquid (IL) pretreatment has shown promising results in lignin, hemicellulose and cellulose fractionation from biomass. As a result, ILs are now widely recommended as green solvent for global green chemistry technology (Roselli, *et al.*, 2014).

Wood dissolution by ionic liquids is highly beneficial in paper and bio-fuel production. In order to reduce production costs, new technology is required for low energy consumption in the extraction processes and disposal of toxic waste (Miljić, 2016). In these dissolutions, the removal of lignin and hemicellulose composition in biomass is easily achieved without deteriorating cellulose fibers within the wooden structure (Poletto, 2014).

Not only can ILs extract and remove lignin and hemicellulose with success, they also show a significant advantage over other pretreatment methods mentioned above. ILs have well-known unique properties, namely:

- low melting point
- high solubility for polar and non-polar substances
- wide electrochemical stability
- good electrical conductivity
- high ionic mobility (Dzyuba and Bartsch, 2002).

Moreover, ionic liquids are recyclable and less hazardous when compared to the use of other chemicals and enzymes. They are considered as bio-degradable organic solvents that are actively applicable at room temperature (Somers, *et al.*, 2013). In addition, ILs have the potential to completely separate lignocellulosic material into regenerated cellulose, hemicellulose, and lignin. Figure 1.2 below illustrates the overviews of possible products from lignocellulosic biomass.

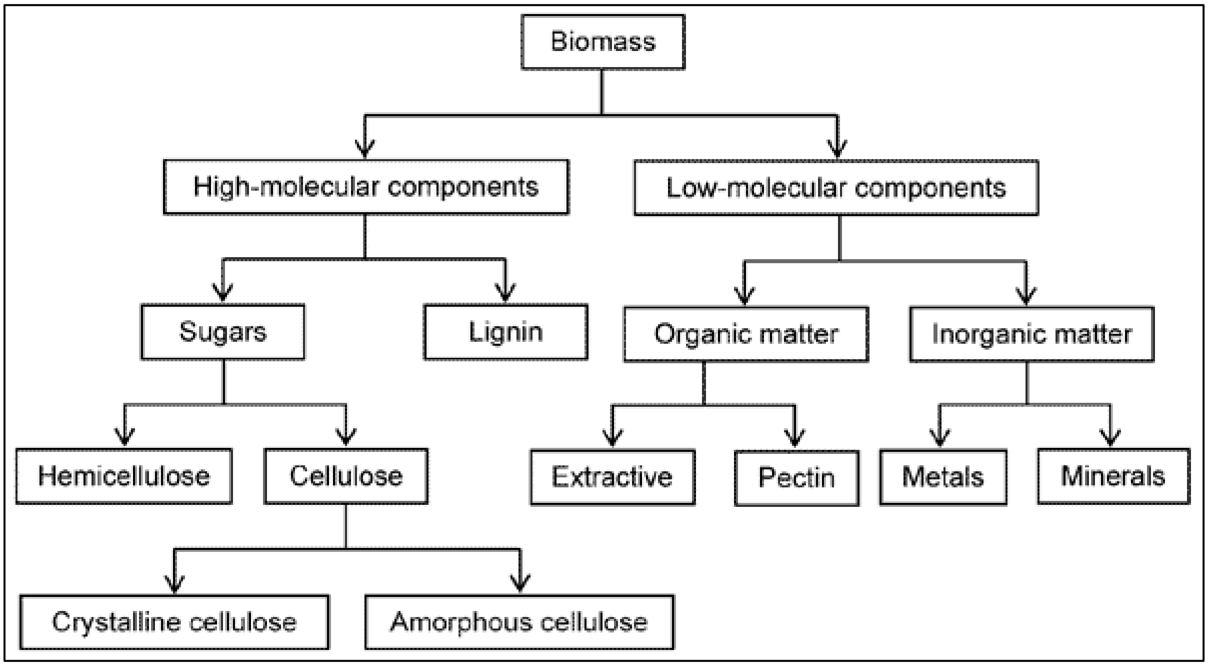

Figure 1.2: Overview of possible products from lignocellulosic biomass (Nanda, 2016)

1.2 Lignocellulosic biomass

Lignocellulosic biomass can be obtained from different sources, namely: wood, grass, forest waste, and agricultural waste (Hoogwijk, 2003; Kumar, *et al.*, 2009). It comprises of polysaccharides (cellulose 40%-55%, hemicellulose 24%-50%) and between 24%-30% of lignin yield which are illustrated in Figure: 1.3 below. Lignocellulosic biomass is also composed of proteins, triglyceride, ash and some extractives depending on the species of biomass. Polysaccharides constitute 80% of the biomass, these may be converted to fuel alcohols by fermentation/ fermented to fuel alcohols (Brandt, 2010).

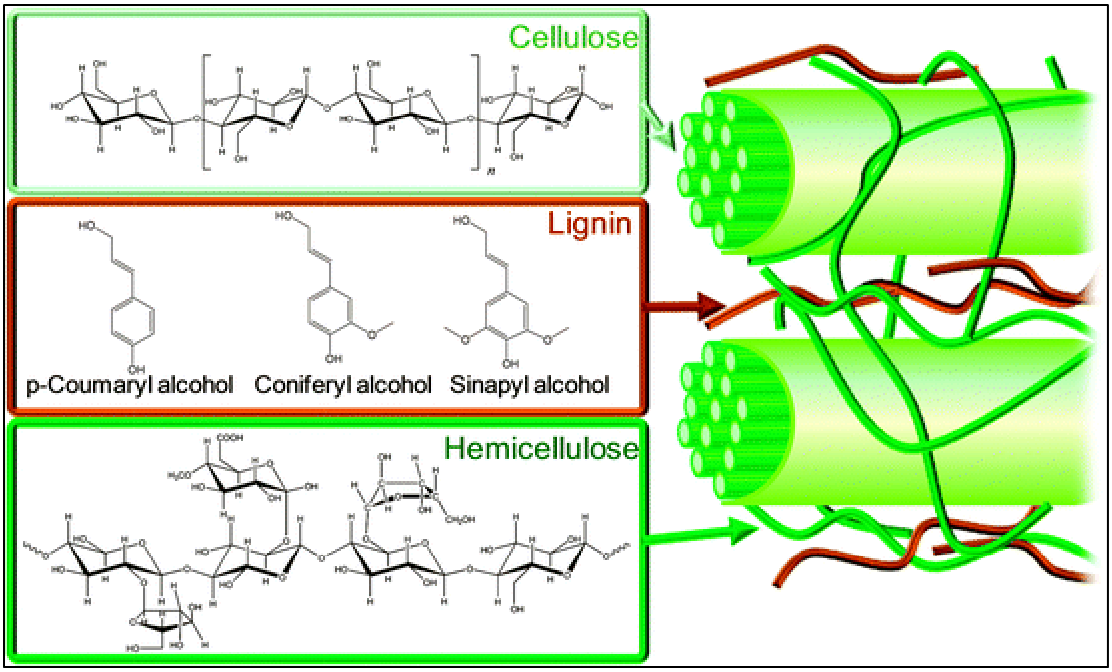

Figure 1.3: Three major components of lignocellulose biomass structure, available: http://pubs.rsc.org (accessed 2015/06/06)

The lignin fraction of the lignocellulosic biomass material is not only burnt for energy but also has the possibility to be used for the production of valuable materials. The use of lignocellulosic biomass is more complicated because the polysaccharides are more stable, tightly bonded and pentose sugars are not readily fermentable. Cellulose and hemicellulose by nature are well known to be naturally impermeable to compound attack due to the presence of lignin (Hinman, 1989). To convert lignocellulosic biomass to biofuels, polysaccharides must first be hydrolyzed to simple sugars using either acid, enzymes or green solvents. Figure 1.4 below illustrates the hydrolysis of lignocellulosic material (Kumar, 2009).

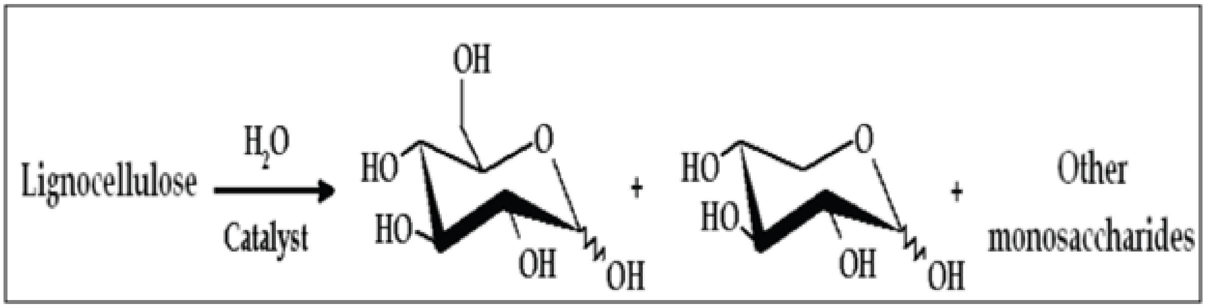

Figure 1.4 Hydrolysis of lignocellulosic material (Kumar, 2009)

1.3 Conventional dissolution methods of the lignocellulosic biomass *Eucalyptus grandis* hardwood

The kraft process liberates the pulp fibres by dissolution of the lignin from the *E. grandis* lignocellulose biomass. Mechanical process degrades lignocellulose biomass into mechanical pulp. Acid hydrolysis isolates klason lignin from lignocellulose biomass and enzymatic hydrolysis uses fungi to fractionate cellulose from lignocellulose biomass (Moshkelani, *et al.*, 2013). These extraction processes are still being utilized in various industries to produce pentose sugars. Enzymatic and acid hydrolysis pretreatment has been successful in the past towards dissolving cellulose, hemicellulose and degrading wood. However, it has been observed that these extraction processes have some short comings: non-renewable, adverse effects to the environment, human health and are expensive (Pérez, *et al.*, 2002).

As such, new chemical technologies are being developed to counteract such drawbacks which includes less-corrosive, bio-degradable and less harmful treatments for the dissolution of lignocellulosic biomass into fractions of lignin, hemicellulose and cellulose.

As much as enzymatic hydrolysis, chemical and acid hydrolysis are well established and profitable, in comparison with ILs pretreatment green chemistry, they have setbacks such as: high CO_2 emission, greenhouse gas effect, high chemical cost, hazardous effects towards environment and human health. ILs pretreatment have excellent characteristics such as: robustness, non-volatile, recyclable, can be used at low temperatures (Fadeev and Meagher, 2001).

1.4 Research problem statement

General problems in *E. grandis* hardwood dissolution are:

- Mechanical pulp fibres are generally stiff and difficult to dissolve due to the presence of lignin, which restricts fibres from swelling during pulping.
- After chemical pulping any remaining hemicelluloses in the cellulose pulp will affect the strength of the pulp fibre.
- Chemical pulp is the largest contributor to the world pulp market and is used to produce approximately all paper products (Food and Agriculture Organization, 2001). This process involves alkaline or acidic pulping processes, including bleaching steps. In this pulping process high yield of cellulose pulp is obtained.

Chemical pulping has disadvantages such as: hazardous chemical waste disposal and expensive chemical costs (Gierer,1985). Since ILs are non-flammable, non-volatile and recyclable, they are known as green solvents.
Due to their excellent properties such as: solvating potential, thermal stability and low vapour pressure they are considered favourable substitutes for conventional solvents (Ghandi, 2014).

1.5 Aim

This research investigates the effects of mechanical and chemical pulping on IL fractionation of wood chips

1.6 Objectives of the study

The objectives of this study are to:

- Understand the impacts of ionic liquid pretreatment on hardwood *Eucalyptus grandis* pulp after kraft and mechanical pulping.
- Remove hemicellulose and lignin from *Eucalyptus grandis* wood pulp using 1-allyl-3-methylimidazolium chloride IL treatment after kraft and mechanical pulp processes.
- Evaluate the efficacy of 1-allyl-3-methylimidazoluim chloride for *Eucalyptus grandi's* wood pulp dissolution.

1.7 Research significance

The research significance of the work presented was to use IL pretreatment on *E. grandis* biomass to dissolve lignin and hemicellulose and recover cellulose. IL pretreatment was used to introduce a green chemistry approach which was different from the current industrial pulping process (acid and enzyme hydrolysis, chemical and mechanical processes). This ILs pretreatment green chemistry approach would reduce CO_2 emission, chemical cost, hazardous effects on the environment and human health.

1.8 Delineation and limitation

The bleaching treatment on hardwood *E. grandis* wood chips in the mechanical and chemical streams is performed to enhance the de-lignifying and brightness of the pulp to produce a lignin-free regenerated cellulose pulp. The decolourisation of the lignin in the mechanical pulp was to give a *white-lignin touch,* while avoiding loss of pulp yield, especially in the mechanical pulp. The lignin content is considered an important part in the quality of pulp yield achieved. Nevertheless, quantifying and understanding the role of bleaching in this research was not of any significance, but merely a precursor to producing high yield regenerated cellulose.

Chapter 2

LITERATURE REVIEW

2.1 Wood chemistry

Wood is a naturally occurring material used for many global and national purposes such as fuel, paper, wood coal, furniture and healing herbs production. The structure of wood is displayed in Figure 2.1 where the average wood diameter is 1dm, a wood fibre width is 1 mm and a cell width of 1 µm. South African wood is produced by Forest Stewardship Council (FSC) certified producers. Wood is expensive and takes time to produce. An alternative biorefinery resource such as lignocellulose biomass, wood waste by-products can be recycled and re-used instead of wood. These biorefinery resources do not require high costs. They can be salvaged from wood waste, which make them abundant and cost effective. As a result, the environment is further preserved and protected, which is aligned with FSC regulations. Not only does biorefinery facility produce pulp, more valuable products can result from its by-products (vanillin, lignosulphonate etc.) which will be profitable, beneficial to pulp and paper production. The pulp and paper industry is one of the major contributors to the South African GDP (Mayers, Evans and Foy, 2001).

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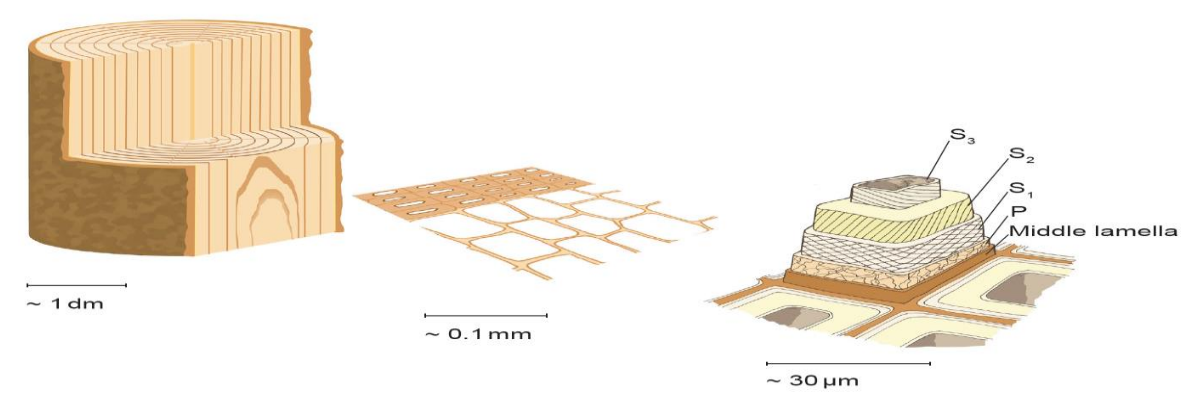

Figure 2.1: Wood structures showing wood fiber walls built up in several layers, available: https://www.doitpoms.ac.uk (accessed 2016/04/06)

Wood consists mainly of the component's hemicellulose, cellulose, and lignin. These components are polymers and esters and are regarded as the building blocks of plant stems and wood structures. Wood is categorized into two groups: softwoods (conifers) and hardwood (angiosperms). The vertical structure of softwood consists mainly of long, elongated cells called tracheids. In other species, vertical resin channels are also present (Strunck, 1990). Hardwood consists of both relatively long, narrow cells called libriform fibers and very short cell fibers. The fibers that originate from hardwood are porous in cross- sectional view with long grooves on vertical surfaces. Hardwood also has vertical parenchyma, horizontal or ray parenchyma orientation (Salmen, 1984). The different types of hardwood species are: avodire, birch, etimoe, maple, redwood, swiss pearwood, sassafras, walnut burl, white oak and *Eucalyptus grandis*. A photograph of a *Eucalyptus grandis* wood logs is illustrated in Figure 2.2. The tree trunks (logs) are stored or stacked in a clearing or in the forest until they are needed at the sawmill.

Figure 2.2: Photograph of a *Eucalyptus grandis* wood logs, available: http://businessoffers.gilltimbers.com/eucalyptus-grandis-round-logs/ (accessed 12/05/16)

This also allows for the 'free' water to evaporate, reducing the weight of the logs. Industrial hardwood and other wood species usually undergo pulping by one or two methods, namely chemical or mechanical pulping.

2.2 Cellulose, hemicellulose and lignin derivatives

2.2.1 Cellulose

Cellulose is a polysaccharide, organic compound, which has a linear chain consisting of many β(1→4) connected D-glucose-units illustrated in Figure 2.3 (Updegraff, 1969; Crawford, 1981). Cellulose is embedded between the lignin and hemicellulose structure with the formula of ($C_6H_{10}O_5$). Cellulose is an abundant natural polymer which is used as the main resource in paper making and cotton production (Piotrowski, 2011).

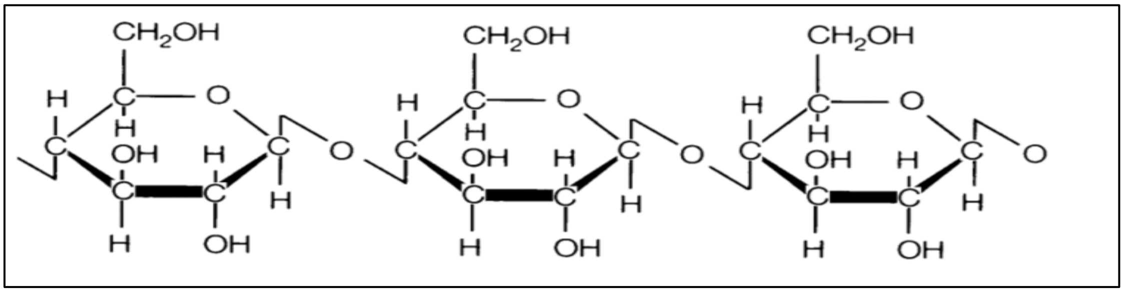

Figure 2.3: Segment of a cellulose chain, available: http://sci.waikato.ac.nz/farm/content/plantstructure.html (accessed 2016/03/16)

2.2.2 Hemicellulose

Hemicellulose consist of several heteropolymers (Hosseinaei, 2012). Hemicellulose is a polysaccharide connected to cellulose and comprises 20% - 40% of the biomass in most plants (Shambe and Kennedy, 1985). Hemicellulose is a short-chained polysaccharide that has a parent structure of β-(1→4)-glucose linkages linked with mannose, xylose, and glucose in an equatorial formation. They are mostly distinguished as side groups: 2-linked 4-methyl α-D-glucuronic acid units and 3-linked α-L-arabinofuranosylcytosine as (arabinose) units. Mannose is mostly found in small land plants, such as lycophytes xyloglucans and mosses (Gibson, 2013).

2.2.3 Lignin

It is covalently linked to hemicellulose, therefore crosslinks different plant, polysaccharides, covering the whole plant structure (Lin, 2015). Lignin is a polymer which consist of complex aromatic linkage chains and insoluble physical properties that proves a waterproofing, structural layer that is resistance to biological and physical attack on the carbohydrate cell walls of undeveloped plant tissues. It is a covering layer on carbohydrate in a form of strong impenetrable fibers. It is amorphous and highly-polymerized which bids the fibers together (Salmén 1984). The lignin is an aromatic compound containing phenolic groups, It is a heterogeneous polymer and second abundant polymer on earth (Argyropoulos D.R. 2000). The scheme diagram of thermal degradation behavior of lignin and the lignin structure are illustrated in Figure 2.4 and Figure 2.5 below. Primarily, lignin has three monomer derivatives: coniferyl, sinapyl and *p*-courmaryl alcohols (Cheng *et.al.* 2010). as illustrated in Figure 2.7 below. The monomer derivatives get their substitution patterns from the broken down polymer (Del Río 2001).

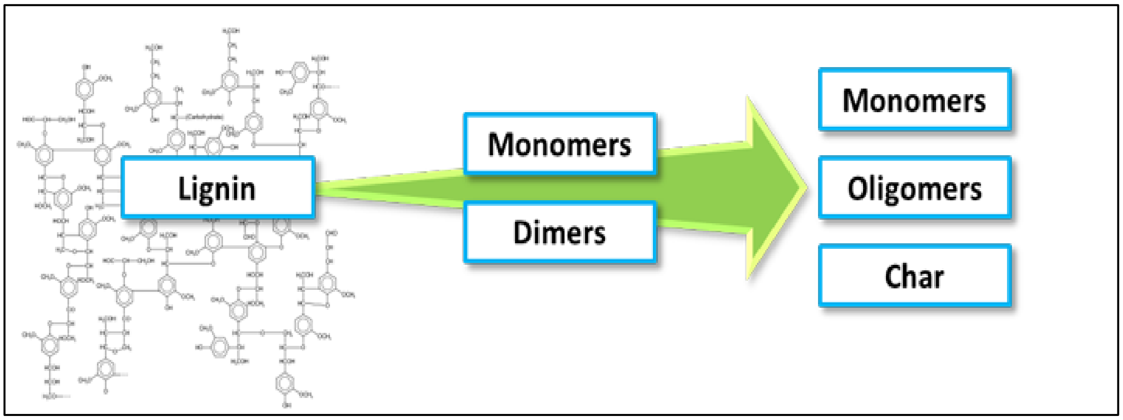

Figure 2.4: Scheme diagram of thermal degradation behaviour of lignin, available: https://www.cset.iastate.edu/files/2013/02/lignin_figure1.png

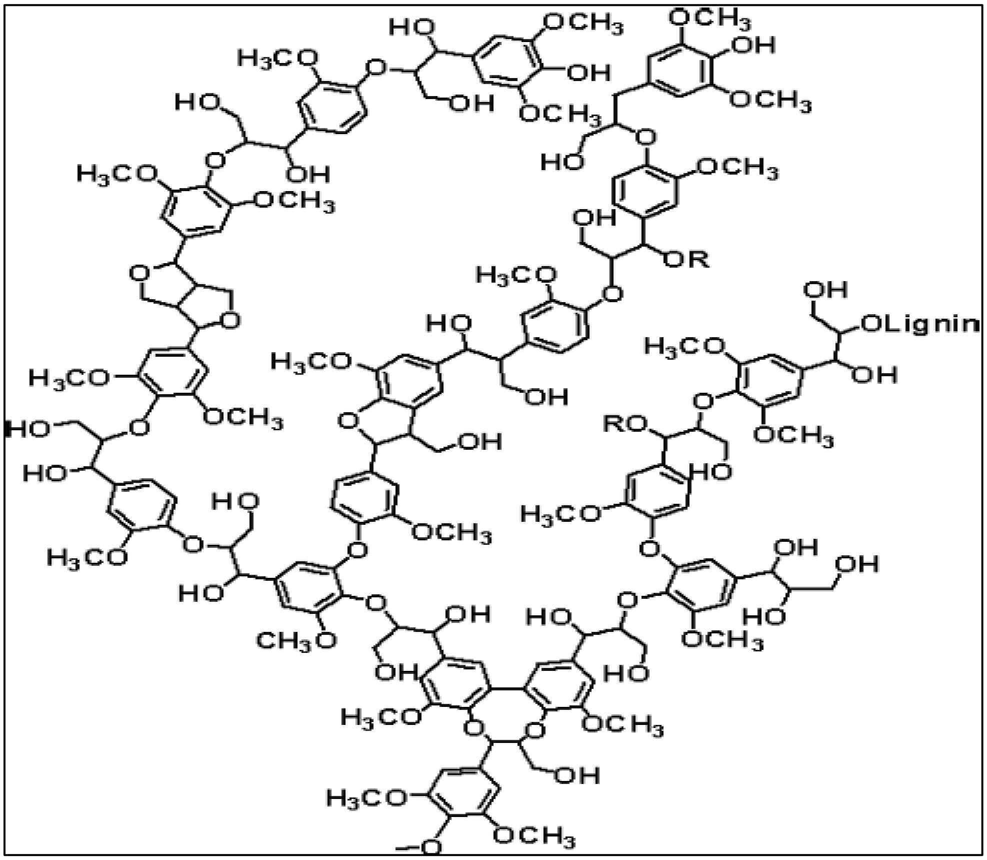

Figure 2.5: Lignin structure, available: https://www.e-education.psu.edu/egee439/node/665 (accessed 2016/05/04)

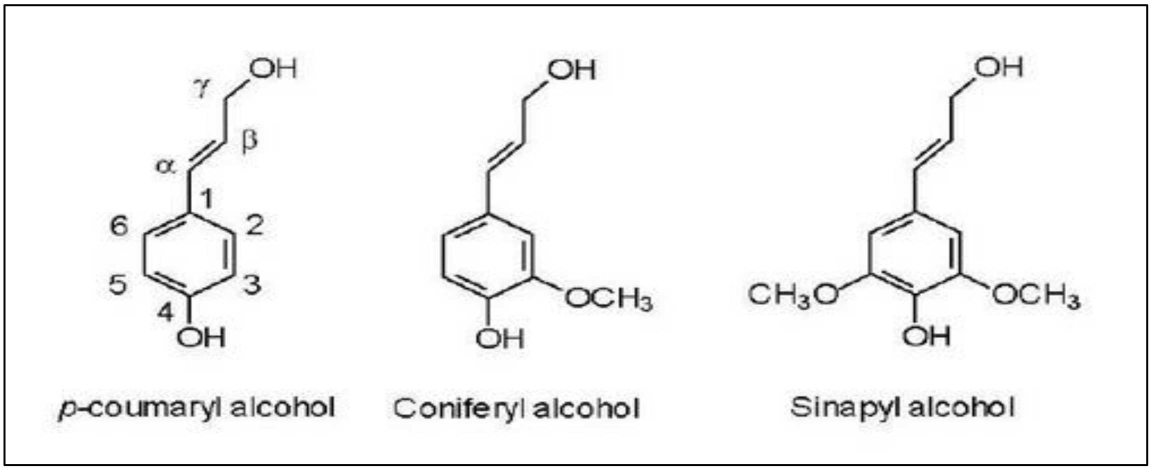

Figure 2.6: Phenolic groups; *p*-coumaryl alcohol, coniferyl alcohol, sinapyl alcohol (Crawford, 1981)

In the pyrolysis of *Eucalyptus* wood, lignin beta-o-4 aryl ether linkages are broken down into a range of products, typical ones are methoxy groups, phenolic groups, guaiacol and syringol derivatives (Oudia 2007). The most important groups are guaiacyl (G) and syringyl (S) functional groups (Nunes, 2010), as illustrated in Figure 2.7 below. The guaiacyl lignin (GL) has a largely polymerization product of coniferyl alcohol. Pulp with high GL is harder to digest, but with higher syringyl lignin (SL) is easier to pulp, the GL occurs in almost all softwoods. Hardwood on the other hand has a guaiacyl-syringyl lignin, this type of lignin is a co-polymer of coniferyl and sinapyl alcohol (Harman-Ware *et al.* 2013). The G-S lignin is the result of the dehydrated coniferyl alcohol and sinapyl alcohol with a content of lignin between 17 % –23 % (Gao, 1996). The ratio of syringyl propane to guaiacyl propane is 0.5: 1, *Eucalyptus urophylla* lignin: syringyl-units is 58.10 % and guaiacyl-units is 18.75 % (Gao, 1996), in comparison to *Eucalyptus grandis* lignin the ratio is (syringyl/ guaiacyl) is 4.3. *Eucalyptus grandis* lignin also contains 7%–12 % % ester groups, *p*-Coumaryl alcohol in it is linked to lignin in the form of ester (Zheng, *et al*. 2005). The syringyl units: 4-ethly syringol, 4-vinyl-syringol, homo-syringaldehyde, acetosyringone) and the guaiacyl units: guaiacol, 4-methly guaiacol, 4-vinyl guaiacol, vanillin (Nunes 2010). *Eucalyptus* wood with a high S/G ratio produce high pulping yields and are easier to delignify during chemical pulp process (González-Vila *et al.,* 1999; Del Río et al., 2005). The syringyl/guaiacyl (S/G) ratio are determined by dividing the sum of peak areas from syringyl units by the sum of the peak areas of guaiacyl units of the which are selected (Harman-Ware *et al.* 2013), obtained by integration of the peak areas and considering the total peak area as 100% (Lourenço *et al.* 2012). The S/G ratio is calculated using equation 2.1 below.

$$\frac{S}{G} ratio\ (estimated\ Lignin\ ) = \frac{Syringyl\ unit\ area\ \%}{Guaiacy\ unit\ area\ \%} \tag{2.1}$$

According to Samuel, *et, al.* (2010), *Eucalyptus* hardwood pulp has a higher amount of S-lignin than G-lignin. Which makes *Eucalyptus* lignin a good study of ILs pretreatment on the dissolution of biomass and its components. Hence, a decrease and increase in the S/G ratio of the *Eucalyptus* lignin will predict the ease of delignification and released of carbohydrates in the pulp. Kraft pulp has a low to none lignin content presence, but mechanical pulp has a largest amount of lignin content retained within the pulp fibres. Therefore, S/G ratio determination for mechanical pulp indicates the effectiveness of the IL pretreatment on the removal of lignin from biomass.

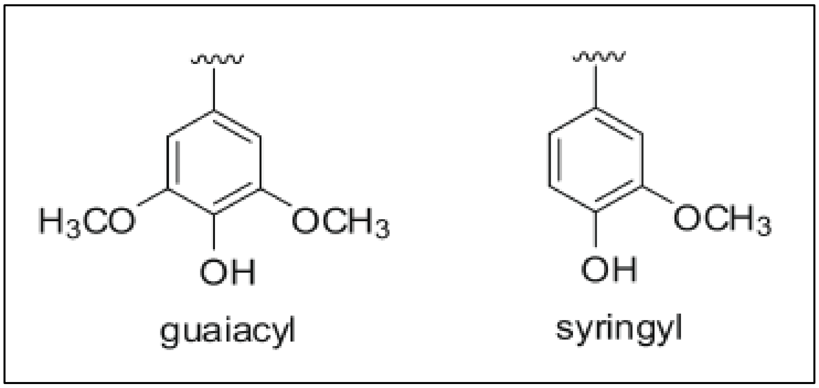

Figure 2.7: Guaiacyl (G) and syringyl (S) structures (Nunes, 2010)

2.3 Chemical Pulping

2.3.1 Kraft process pulping

The *E. grandis* hardwood wood chips are mixed and homogenized with "white liquor" (a solution of sodium hydroxide, NaOH, and sodium sulphide, Na_2S) in a heated pressurized digester between 150°C - 160°C (Howard, 1992). There are also several types of chemical pulping: kraft process, sulfite process, and soda pulping. Kraft process has two to three cooking stages which present different pH levels to improve the removal of hemicellulose and lignin (Um, 2013). Equations: 2.2, 2.3 and 2.4 below demonstrate the reactions that occur between the wood chips and the white liquor during the digestion process (Dryden, 2008: Kirk, 2001).

The main chemical reactions in the cooking process can be
described as:

$$\text{NaOH} + \text{NaS}_2 + \text{Wood} \rightarrow \text{Na-wood.} + \text{S-wood.} + \text{NaHS} \qquad (2.2)$$

The wood represents many different organic compounds such as:
lignin, cellulose, hemicellulose and resins (Chakar, 2004).

The solution of sodium sulphite and sodium hydroxide in water is generating an equilibrium as follows:

$S_2^- + H_2O \rightarrow SH^- + OHSH$ (2.3)

$H_2O \rightarrow S_2H + OH$ (2.4)

The first part has a neutral to slightly acidic cooking solution, in which lignin is sulfonated, but still kept in a solid phase where most reactive groups are protected by sulfonation at high temperatures (Gonzalez-Serrano, 2004). Washing with water under high pressure results in the disintegration of wood chips to pulp fibres. In the second part the solid phase is condensed with pinosylvine to form black liquor, the conversion of black liquor is described by the following equations: 2.5, 2.6 and 2.7 below (Sixta, 2006; Sjoström, 1981).

Black liquor (burning)

$Na_2O + CO_2 \rightarrow Na_2CO_3$ (2.5)

$Na^+ + H^+ + S_2 \rightarrow NaHS$ (2.6)

$Na^+ + OH \rightarrow NaOH$ (2.7)

After the reaction, the black liquor is decanted and collected for lignosulphonate analysis. While the pulp produce is screened, washed with warm water until all chemicals are removed (Smook, 1994). As a result, *E. grandis* wood chips are converted into chemical pulp. An industrial schematic overview of the kraft pulp process, is illustrated in Figure 2.8 below.

The advantages of chemical pulping are:

- high quality wood pulp produced with longer and stronger fibre that contain fewer impurities
- waste lignin from the process can be burnt as a fuel and oil substitute

The disadvantages of chemical pulping are:

- Disposal of chemical waste and cellulose deterioration

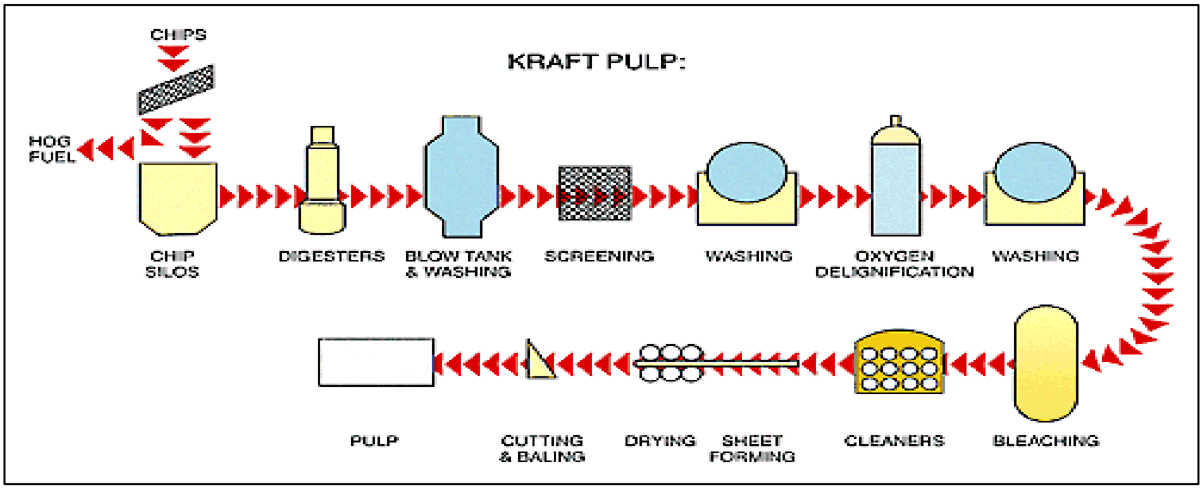

Figure 2.8: Industrial schematic overview of kraft pulp process (Moshkelani *et al*., 2013)

2.4 Mechanical puling

2.4.1 Refiner-mechanical pulping

Figure 2.9 below is a schematic overview of an industrial mechanical pulp process. There are several types of mechanical pulping which are as follows: stone ground wood (SGW) process, pressure ground wood (PGW) process, refiner mechanical pulp (RMP) procedure, thermomechanical process (TMP) process, chemi-mechanical (CMP) and chemi-thermomechanical (CTMP), some processes involve several and different bleaching stages. Mechanical pulping is a rapidly growing industrial process for the manufacture of pulp and paper, particularly newsprint (Zavatta, 1993). In the production of mechanical pulping, either refiner mechanical pulping or thermo-mechanical pulping process is used. Refiner mechanical pulping (RMP) and thermo-mechanical pulping (TMP) convert wood chips into pulp fibers. The thermo-mechanical pulping process uses bar along high water pressure at high temperatures. The refiner mechanical pulping process uses blade discs.

There are three types of refiners used to make mechanical pulps:

- Single disc: one of the first, still used in new installations. Lowest capital cost and has smaller capacities than others (Dodd, 1995).
- Double disc: high intensity refining, less energy to obtain the same Freeness (Dodd, 1995).
- Twin disc: more like a large single disc. Low intensity possible because of large refining surface (Garasimowicz, 1998).

Refiner

During the passage of wood chips through a refiner, the wood chips are crushed and grinded into much smaller fibres. The smaller fibres are developed from the removal of outer parts of the cell wall (lignin) and by flexibilization created by the motion of the spinning bars (Howard, 1992). Bar spins further break the fibres down and the pulp fibres is produced.

To achieve the pulp stage, there is a coarse breaker bar section in the inner radius of the refiner where most of the breaking down takes place (Taylor, 2005). Followed by a middle bar section patterns, here most of the pulp fibre are produced. The process takes between 1-10 minutes (Smook, 1994). Consequently, *E. grandis* wood chips are converted to mechanical pulp.

Pulp washing and screening

After the pulp is manufactured from the mechanical process, the pulp is washed with warm water and screened using Sommerville screen which have a dot size of 0.15 mm. Un-processed wood rejects and pulp residue remains on the surface of shives (Cort, 1991).

The main advantages of mechanical pulping are:

- yields 90% of wood pulp
- can be further bleached to produce higher value-added products

The disadvantages of mechanical pulping are:

- Paper from mechanical pulp can also turn yellow in colour when exposed to bright lights due to high lignin content

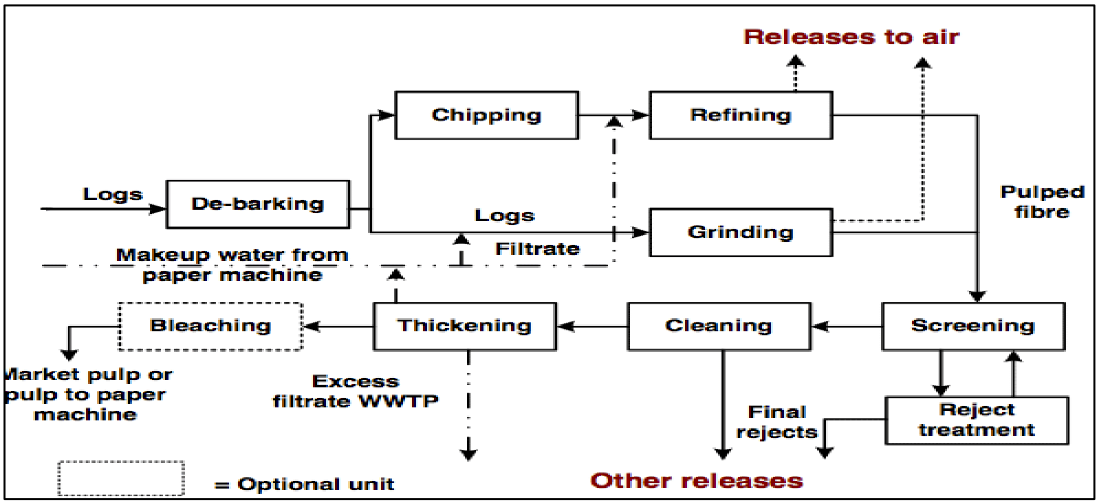

Figure 2.9: Industrial schematic overview of the mechanical pulp process, available: http://ietd.iipnetwork.org/content/mechanical-pulping (accessed 2016/05/06)

2.5 Lignocellulosic biomass dssolution

The pulp and paper production industries have shown considerable interest in alternative approaches, such as bio refinery concepts to maximize resource utilisation. Hence, the lignocellulosic biomass acting as an alternative raw starting material for the industrial production of pulp and paper, has lowered the over use of wood. As a result, less financial use, less machinery labour for forestry and wood haverst is reqiured (Cherubini, 2010). The hemicellulose and lignin composition need to be removed from lignocellulose biomass, without extensively depolymerizing the cellulose fiber embedded within the biomass structure. Lignin's protective layer shield limits the exposure of cellulose composition within the biomass structure. The hemicellulose's hydrophilic nature, sponge-like membrane absorbs water into the wood cell fibers inversely softening and weaking the strength of the fibres (Ganan, *et al.*, 2004). There are well established pulp process and pretreatment to remove lignin, hemicelulose and produce regenerated cellulose. These pulp pretreatments and processes are as follow: biological pulping, chemical hydrolysis, enzymatic hydrolysis, sulphite kraft pulping, mechanical pulping and coventional solvent pretreatments.

Biological pulping on wood chips to degrade lignin and hemicellulose, the fungi pretreatment is conducted before the pulping process. Since the fungi pretreatment extracted a part of the lignin in the wood chips (Lumme, 1999). The chemical or mechanical pulp end up requiring less retention time and less energy usage, while the paper strength improvement increase (Gamble, 1996).

Economical, the biological pulping process is not harmful to the environment, due to benign materials begin used, with no additional waste streams being generated (Reid, 1991; Akhtar, *et al.*, 1998; Highley and Dashek, 1998), but not cost effective and none recyclable in comparison to ILs. Chemical hydrolysis use chemicals such as: sodium carbonate, sodium hydroxide, magnesium and calcium carbonate to hydrolyze biomass into pulp fibre (Rowell, 2005). The disadvantage of chemical hydrolysis, the disposal of chemical waste is a great concern to global enviromental health (Moshkelani, 2013). Mechanical pulping process use high powered motors, mechanical pulp has a tendency to turn yellow in colour when exposed to bright lights due to high lignin content.

A few traditional solvents are able to dissolve cellulose, such as N, N-dimethylacetamide/lithium chloride (DMAc/LiCl) and nitrogen methyl morpholine nitrogen-oxide (NMNO). The drawbacks of such solvents is attributed to their nitro-group connection, which are highly toxic and non-stable, even though these solvents tend to denature cellulose structure to some degree (Aver, 2014). These traditional pretreatment and solvent processes solvents are designed to dissolve and remove undesired extracts to access the primary cellulose structure for paper production (Gomes, 2014. Nevertheless, these pretreatments and processes are responsible for major financial and health concerns in the pretreatment of lignocellulose biomass. Alternatively, ionic liquid pretreatment in cellulose dissolution tends to cause degradation on other cell fiber components in the wood structure.

For some decades, the green chemistry project has proposed the use of green solvents known as ionic liquids, as alternative means to counteract such problems caused by traditional extraction pretreatments (Rogers and Seddon, 2002). Dissolving solvents that require minimal energy usage while dissolving wood biomass and many other wood materials at low temperatures as well as being recyclable and re-usable for more than one experiment at a time.

Ionic liquid (ILs) are organic salts that comprise of organic cations and inorganic anions as illustrated in Figure 2.10 below. As an example, cation structures include large organic structures such as;- imidazolium, pyrrolidinium, pyridinium or phosphonium moieties (George, 2011). The synthesizing of imidazolium cation salt with ethyl – or allyl- groups, eliminates the presence of nitro-group which decreases toxicity much greater than pyrrolidinium, pyridinium or phosphonium moieties. ILs usually melt, boil or dissolve at 100ºC and in some instances even react at lower than 100 ºC temperatures depending on their physical properties. ILs can also be used in different chemistry fields such as liquid-liquid extraction process, replacements for aprotic solvents, catalytic cracking, and catalysis for artificial organic chemistry and in radical polymerization. Also, ionic liquid can draw powerful microwave irradiation and can be used in microwave-assisted preparations, having a short reaction time compared to traditional solvents. Ionic liquid solubility strength is dependent on the interaction that takes place in the biopolymer matrix, which forms hydrogen bonds from hydroxyl groups that link to the anion of the solvent (Swatloski, 2002).

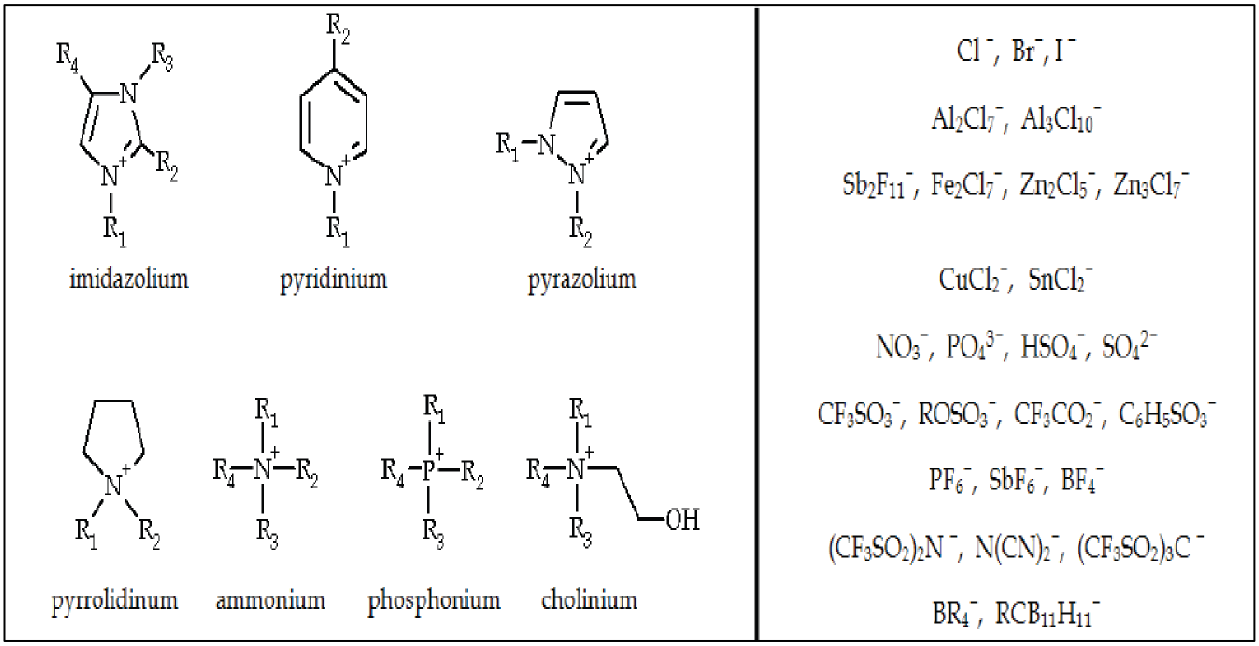

Figure 2.10: Ionic liquid cations and anions, available: https://www.intechopen.com/books/ionic-liquids-new-aspects-for-the-future/the-structure-of-supported-ionic-liquids-at-the-interface (accessed 2015/06/05)

Another limitation to the efficiency of ionic liquid is the effect of water. Water, even in small quantity can highly affect ILs physical and chemically properties, by decreasing melting point, lowering viscosity and density (Seddon, 2000; Chen, 2010; Fendt, 2011; Anantharaj, 2012). Water is known to reduce the dissolution of wood and create unwanted precipitation of molecules dissolved. A decrease in the solubility of carbohydrates is due to more than one H_2O molecules involved, per molecule of [AMIM][Cl] (Ding ,2012). As a result, the involvement of water in cellulose dissolution treated with IL, tend to weaken the hydrogen bonds linked between the $[AMIM]^+$ and the $[Cl]^-$ halide.

The presence of carboxylic acid moieties in hemicellulose and interaction with the ILs usually cause degradation reactions, although ionic liquids on their own tend to display catalytic behaviour under acidic conditions. Chloride based imidazolium ILs have an imidazole ring that consists of a proton that functions as a hydrogen bond donor, whilst the role the chloride act as a hydrogen bond acceptor.

This orientation often stimulates the hydroxyl groups of the carbohydrates as they are dissolved by the IL (Moulthrop, 2005; Mazza, 2009). Ionic liquid solvation efficiency often decreases when there is a decrease in the acidity of protons caused by the presence of electronegative atoms. A solution to this problem is the addition of dimethyl sulfoxide (DMSO) which is used as a co-solvent. This co-solvent (DMSO) usually enhances the solubility and reduces the viscosity of the ionic liquid, making the dissolution of wood more effective (Andanson, 2014; Shi, 2014). Consequently, ionic liquids are shown to be an ideal approach for the extraction of lignin and hemicellulose content from biomass, due to their unique properties namely: low melting points, high solvation capacity for both polar and non-polar substances , relatively extensive electrochemical stability, good electrical conductivity, high ionic mobility (Tao, 2011; Ding, 2012). As a result, ionic liquids have become a great asset towards the pulp production industry, in extracting unwanted extractives in lignocellulosic biomass in order to produce paper.

ILs limits the interference of degradation level in fiber strength while giving a high yield in pulp. Most crucial, is its cost effectiveness towards the economy by operating in reactors of moderate size using minimal heat power requirements (Ab Rani, 2011).

2.6 Cellulose, hemicellulose and lignin dissolution by ([AMIM][Cl]) ionic liquid pretreatment

According to Mäki-Arvela (2010), using [AMIM][Cl] to dissolve cellulose, lignin, and hemicellulose is an excellent IL pretreatment approach. There is a strong bond between the properties of imidazolium salts and their dissolution capacity in dissolving biomass, such as polarity, solubility, physical conditions. The impact of Hildebrand solubility parameter and hydrogen bond basicity are correlated with the dissolution of lignocellulosic material. A structure of 1-allyl-3-methlyimidazolium chloride with a molecular mass of 158.62 g/mol and molecular formula: $C_7H_{11}ClN_2$ as illustrated in Figure 2.11 below.

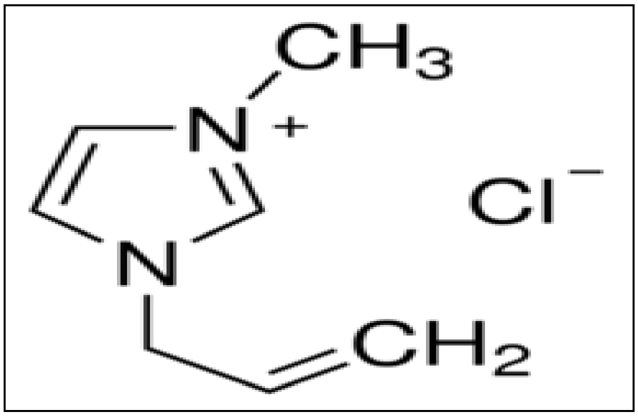

Figure 2.11: Structure of 1-allyl-3-methylimidazolium chloride ionic liquid (Sigma-Aldrich Co. LL, 2016)

2.7 *E. grandis* lignocellulose biomass lignin dissolution by [AMIM][Cl] ionic liquid

There were changes observed in several lignin structures after dissolution in imidazolium based ILs at 120°C for 3 hours (George, 2011). Results indicated a reduction in the molecular mass of the ascending order, dimethyl phosphate < chloride < acetate < lactate < sulfate in conversion of lignin into smaller fragments. According to Kilpeläinen (2007), in the family of imidazolium salts,1-butyl-3-methylimidazolium chloride and 1-allyl-3-methylimidazolium chloride are both excellent green solvents even though both have different amount of dissolution *of E.Grandis* material.
While the alkyl-group of 1-allyl-3-methlimidazolium chloride is a substituent ($-CH_2R$) and consists of a methylene bridge ($-CH_2$)-, the allyl-group facilitates a beta-interaction with the aromatic lignin structure faster than the butyl-group. As a result, 1-allyl-3-methylimidazolium chloride has a significant advantage over 1-butyl-3-methylimidazolium chloride. Thus, a faster degradation of lignin occurs from the biomass. A bond cleavage takes place between the carboxylic acid, methoxy group of the lignin. A beta-carbon from the lignin interacts with the allyl-group of the [AMIM][Cl]. This reaction is known as the reversed menschutkin reaction. Furthermore, this reaction is a type of nucleophilic substitution that can occur as an SN_1 and SN_2 mechanism simultaneously (Edwards, 1954; Kolthoff, 1961). It is displayed in Figure 2.12 below.

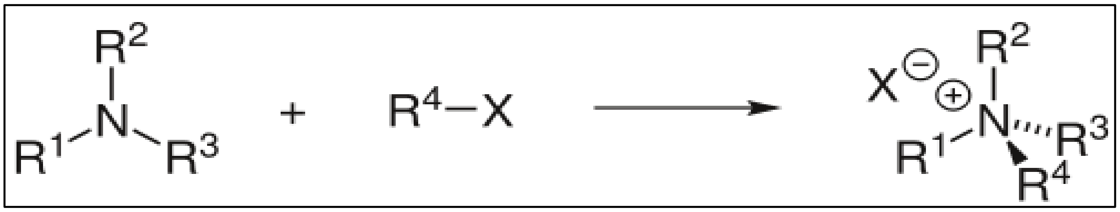

Figure 2.12 : Mechanism of a faster degradation of cellulose using 1-allyl-3-methylimidazolium chloride compare to 1-butyl-3-methylimidazoluim chloride via reversed menschutkin reaction (Wooster, *et al.,* 2006)

2.8 *E. grandis* lignocellulose biomass cellulose dissolution by [AMIM][Cl] ionic liquid

The cellulose dissolution by an ionic liquid is based on the disruption of the intermolecular, as well as the inter-hydrogen bonds of cellulose. This is inclusive of the formation of hydrogen bonds found between the hydroxyl protons of the carbohydrates and the IL anions (Remsing, 2006; Youngs, 2007; Santos, *et al.*, 2013).

The important factors usually reconsidered before any attempt of cellulose dissolution are depolymerization and crystallinity of the cellulose. High crystallinity of cellulose implies that the dissolution of cellulose is more difficult. As such, the solubility strength, temperature, reaction time of the ionic liquid depends entirely on these factors.

Cellulose in wood is a semi-crystalline biopolymer, which means that a fraction of the molecules is tightly packed forming crystalline zones (Park, 2010).

Hydrophilic ionic liquid interferes with the solubility of cellulose, compared to hydrophobic ionic liquid which yields optimal dissolution levels (Vitz, 2009). Table 2.1 below, illustrates the summary of different ionic liquids pretreatment of the dissolution of cellulose, followed by a typical illustration of a dissolution mechanism of cellulose in [AMIM][Cl], as displayed in Figure 2.13 below. The $[AMIM]^+$ from the [AMIM][Cl] IL attacks one of the O-H groups from the cellulose structure. This phenomenon results in a bond cleavage, where one hydrogen from the cellulose structure is released to form a new bond with the Cl^- anion of the IL, whilst the nitrogen group of the IL interacts with the O^- from the cellulose structure.

Table 2.1: Summary of dissolution of cellulose in different types of ILs

Cellulose	Ionic Liquid	Time: hours	Temperature	Solubility %wt	Reference
Pulp	[BMIM][Cl]	-	100°C	10	(Heinze, 2005)
Pulp	[BMIM]][Cl]	12	83°C	18	(Erdmenger, 2007)
Pulp	[BMIM][Cl]	-	85°C	13.6	(Kosan, 2008)
Pulp	[EMIM][Cl]	-	85°C	15.8	(Kosan, 2008)
Pulp	[EMIM][OAc]	-	85°C	13.5	(Kosan, 2008)

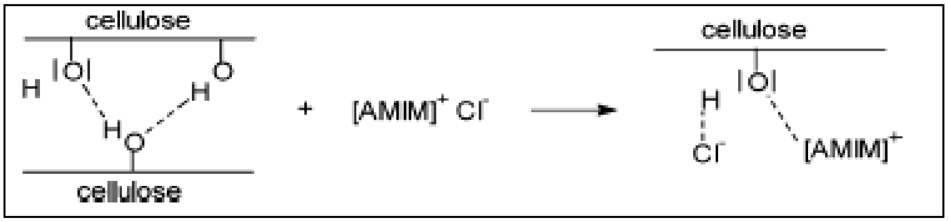

Figure 2.13 : Dissolution mechanism of cellulose in [AMIM][Cl] (Feng, 2008)

2.9 *E. grandis* lignocellulose biomass hemicellulose dissolution by [AMIM][Cl] ionic liquid

Hemicellulose shares a similar trait pattern with cellulose, but the difference is that cellulose chain structure is much longer than the hemicellulose structure and less stiff. As a result, there is not much of a difference in the dissolution processes between cellulose and hemicellulose (Lindman, 2010). Ionic liquids that dissolve cellulose are capable of dissolving hemicellulose as well. Hemicellulose usually depolymerizes under IL pretreatment (Arora, 2010). This phenomenon is due to the IL's anion nature. For example, if the anion is $[HSO_4]^{-,}$, it will cause the hemicellulose to depolymerize completely to form furfural (Brandt, 2011).

2.10 Summary of literature review

The use of *E. grandis* lignocellulosic materials, in a biorefinery approach, can replace the misuse of non-renewable resources by producing a sustainable energy source for industrial and public use. However, there are various challenges in using lignocellulosic materials properties, because of different physical and chemical characteristics. As a result, they would need suitable pretreatment technology to extract the desired and undesired lignocellulosic materials by–products. The efficiency of lignocellulose pretreatment is one of the most significant factors in a successful conversion of the originally low-cost material chemicals into biofuels or biofuel products.

Cellulose crystallinity, protective lignin shield and the layer of hemicelluloses make it resistant to enzymatic and chemical hydrolysis. The separation of cellulose by using ionic liquids has provided a platform towards providing a complete application of lignocellulosic material extraction in green chemistry. The advantage of ionic liquids ability to disrupt hydrogen bonds reduces cellulose crystallinity in the biomass structure. Similarly, the exceptional chemical and physical properties of ILs make them effective and rapidly reacting cellulose solvents. This allows ideal ionic liquids to be recommended for extraction applications above traditional solvents.

Ionic liquids possess properties such as broad liquid regions, high thermal stabilities, and negligible vapor pressure. Ionic liquid solubility strength is dependent on the interaction that takes place in the biopolymer matrix, which forms hydrogen bonds with hydroxyl groups that link to the anion of the solvent (Swatloski, 2002).

Mass transfer is negatively affected by the viscosity of the ionic liquid. As a result, further research should be undertaken with relation to the conditions and performance of ionic liquids.

Enzymatic and chemical setbacks compared to ionic liquid pretreatment:

Enzymatic hydrolysis:

- longer reaction time
- high cellulase cost
- low yield of cellulose (Chandra, 2007)

Acid hydrolysis

- use of strong acids
- low yield of hemicellulose (Yu, 2004)
- high financial cost for acid resistant equipment

The presence of Cl^- anions in [AMIM][Cl] is important as they are small hydrogen bond acceptors which makes them a good selection in lignin and cellulose interaction (Dadi, 2006; Lee, 2009). Experimental investigations observed that, after 24 hr at 80°C, chloride-based ILs dissolved both wood and lignin (Ji, 2012). According to Ji (2012), solvation mechanism between the lignin and anion of the ionic liquid can be observed through the interaction between the bulky lignin model compounds and [AMIM][Cl]. The above study noted that the imidazolium ILs dissolution strength for dissolving lignin in wood depended entirely on the strength of the halide electronegativity.

The presence of electronegative atoms on the cation decreases the acidity of the protons, causing a decrease in the solvation efficiency. The chloride anion (with non-bonding electrons), in combination with the $[AMIM]^+$ cation, forms an IL that exhibits the ability to interact with π-systems molecules. Chloride based imidazolium ILs have an imidazole ring that consists of a proton that functions as a hydrogen bond donor, whilst the role function chloride acts as a hydrogen bond acceptor. This orientation often stimulates the hydroxyl groups of the carbohydrates as they are dissolved by [AMIM][Cl] ionic liquid (Moulthrop, 2005; Mazza, 2009). The active chloride ions in the [AMIM][Cl] ionic liquid would disrupt the hydrogen-bonding interactions present in the wood structure.

This occurrence leads to a viscous, hazy solution. However, the addition of co-solvents such as DMSO (dimethyl sulfoxide) in a wood/[AMIM][Cl] pretreatment, makes the mixture less viscous. As result , this provides good results of lignin, hemicellulose dissolution (Andanson, 2014). According to Mäki-Arvela (2010), 1-ethyl-3-methylimidazolium acetate and 1-allyl-3-methylimidazolium chloride serves as good solvents to dissolve lignin and hemicellulose. Although the allyl group link chain of [AMIM][Cl] promotes the ethylene in the structure to facilitate beta- interactions with the aromatic lignin structure much faster the ethyl or butyl group is linked to imidazolium cation.

2.11 Instrumentation techniques

2.11.1 Thermo gravimetry (TGA)

Thermal analysis includes a group of techniques in which a physical property of a substance is measured as a function of temperature while the substance is subjected to a controlled temperature program. A complete modern thermal analysis instrument measures temperature of transitions, mass losses in materials, energies of transitions, dimensional changes, and viscoelastic properties (Poletto, 2014). Thermogravimetric analysis (TGA) provides the analyst with a quantitative measurement of any mass change associated with a transition. TGA curves are characteristic for a given compound or system because of the unique sequence of physicochemical reactions which occur over definite temperature ranges and at rates that are a function of the molecular structure. The changes in mass are a result formation of various physical and chemical bonds at elevated temperatures that lead to the evolution of volatile products or the formation of heavier reaction products. Data obtained from the thermograms, relates to the thermodynamics and kinetics of the various chemical reactions, reaction mechanisms, and the intermediate and final reaction products. The usual temperature range is from ambient to 1200 ˚C with inert or reactive atmospheres. The derivative in the TGA is often used to pinpoint completion of the mass loss steps or to increase resolution of overlapping mass loss occurrences (Willard, 1986). A thermo gravimetric analysis schematic diagram is illustrated in Figure 2.14 below.

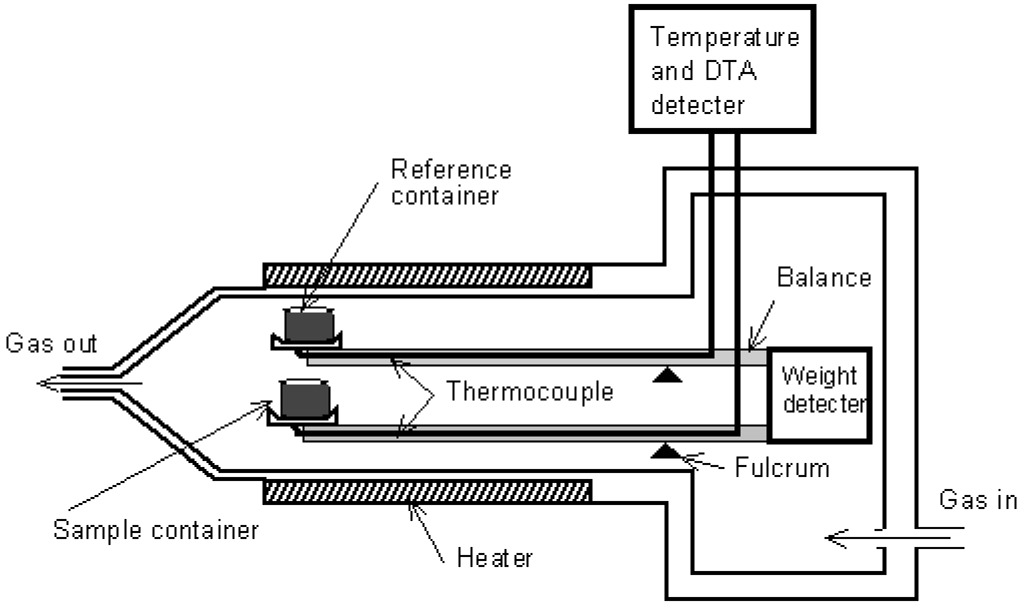

Figure 2.14: Schematic diagram of a thermo gravimetric analyser (TGA)

2.11.2 Scanning electron microscopy (SEM)

The basic principle of SEM is that a beam of electrons is generated by a suitable source, in most cases a tungsten filament or a field emission gun (Popescu, 2011). The electron beam is energized using a high voltage and passing through a system of spaces and electromagnetic lenses to produce a thin beam of electrons. Subsequently, the beam scans the surface of the sample material by means of scan coils. The electrons become excited and are emitted from the electrical conductivity of the coated samples, which results in a light scanning beam across the sample. The scan is then collected by an angle-positioned electron detector. The beam scanning the sample surface is synchronized with the angle whereby the overall morphology is viewed. A schematic diagram of a scanning electron microscope in illustrated in Figure 2.15 below.

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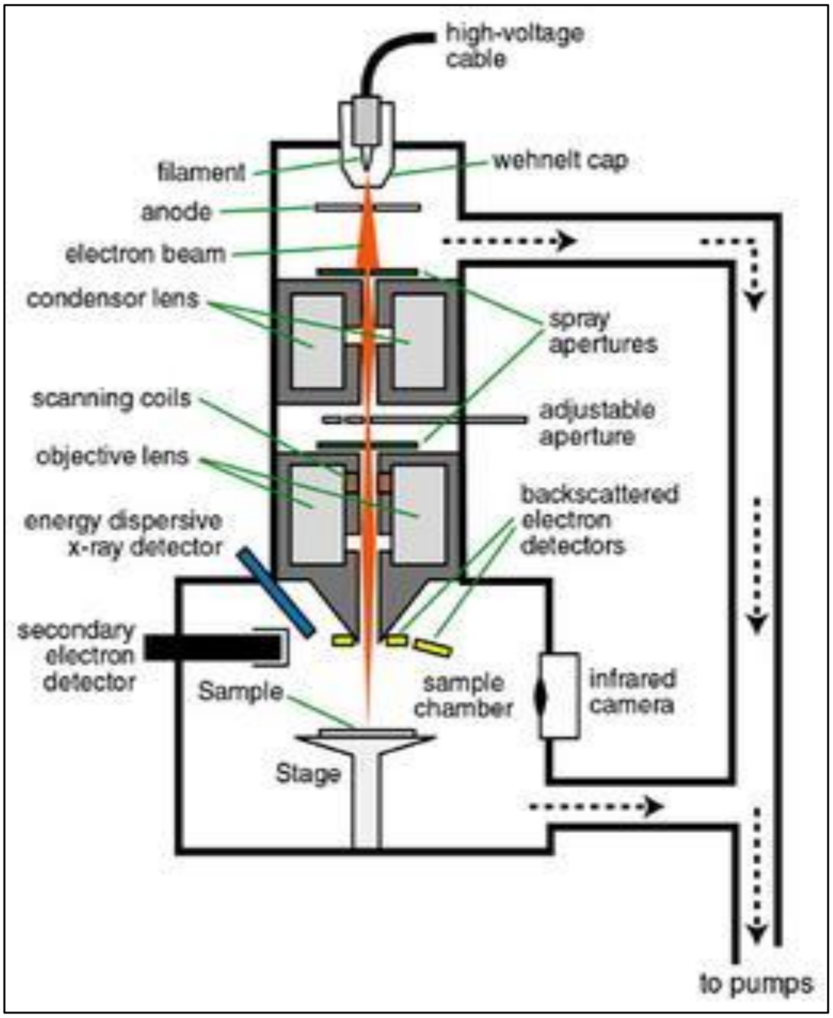


Figure 2.15: Schematic diagram of scanning electron microscope (SEM), available: http://faculty.engineering.asu.edu/neithalath/laboratory/ (accessed 2016/10/12)

There are three types of electron lens namely: objective lens, condenser lens and scanning electron lens. The first two is often common and the third gives the highest resolution image above all. A backscattered electron image is used for background correction purposes. The brightness of the back scattered electron is rested on the objective lens (Willard, 1986).

2.11.3 Fourier transmittance infra-red (FTIR) attenuated total reflectance (ATR)

ATR is a FTIR analytical technique that gives excellent quality data in combination with the best possible reproducibility of any IR sampling technique. It has transformed IR solid and liquid sampling through rapid sampling while improving sample-to-sample reproducibility and minimizing multiple separation spectral variation. As displayed in Figure 2.16, an attenuated total reflection compartment is attached to a normal FTIR instrumentation, illustrated in Figure 2.17 below. This is an advantage as the measurements of the changes occur within the reflected infrared beam for both liquid and solid samples. When the light scattering beam comes into contact with a sample, the beam is focused onto an optically dense crystal with a high refractive index at a precise angle. This internal reflectance produces an evanescent wave that spreads beyond the surface of the crystal into the sample in contact with the crystal (Kalmodia, *et al.*, 2015). In order to achieve a good contact between the sample and the crystal surface, the sample must be at least a few microns (0.5 μ - 5 μ) for a beam wave to pass through. The evanescent wave will be attenuated or altered in the regions where the sample energy is absorbed in the infrared spectrum. This phenomenon gives an overall infra-red spectrum of the analyzed samples according to their absorption bands and wavelengths.

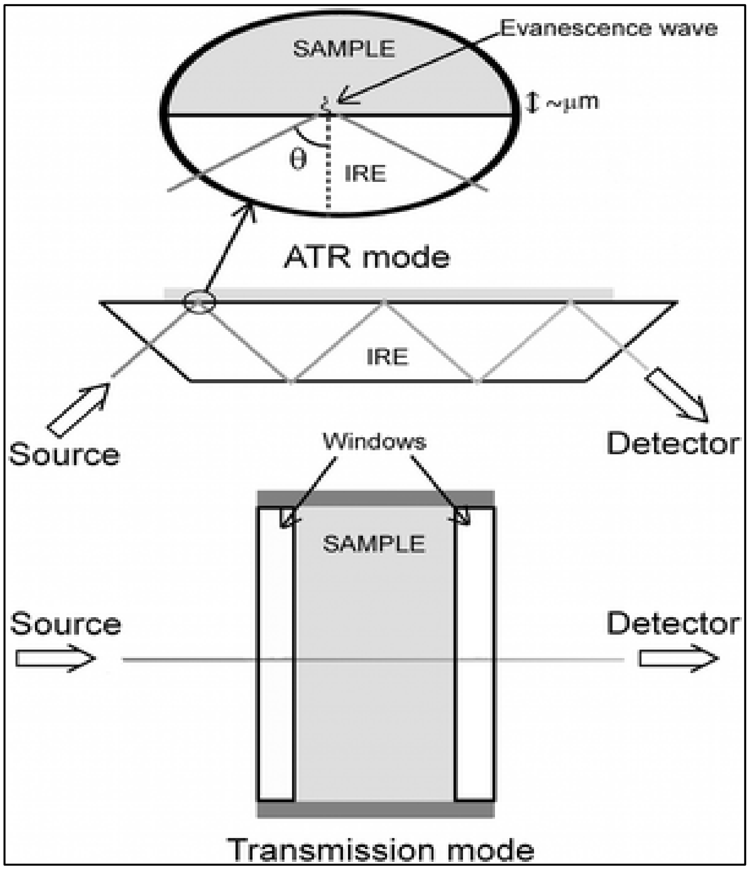


Figure 2.16: Schematic diagram of an attenuated total reflectance analyser (ATR), available: https://upload.wikimedia.org/wikipedia/commons/thumb/3/36/ATR-Halterung.jpg/1200px-ATR-Halterung.jpg (accessed 2016/12.06)

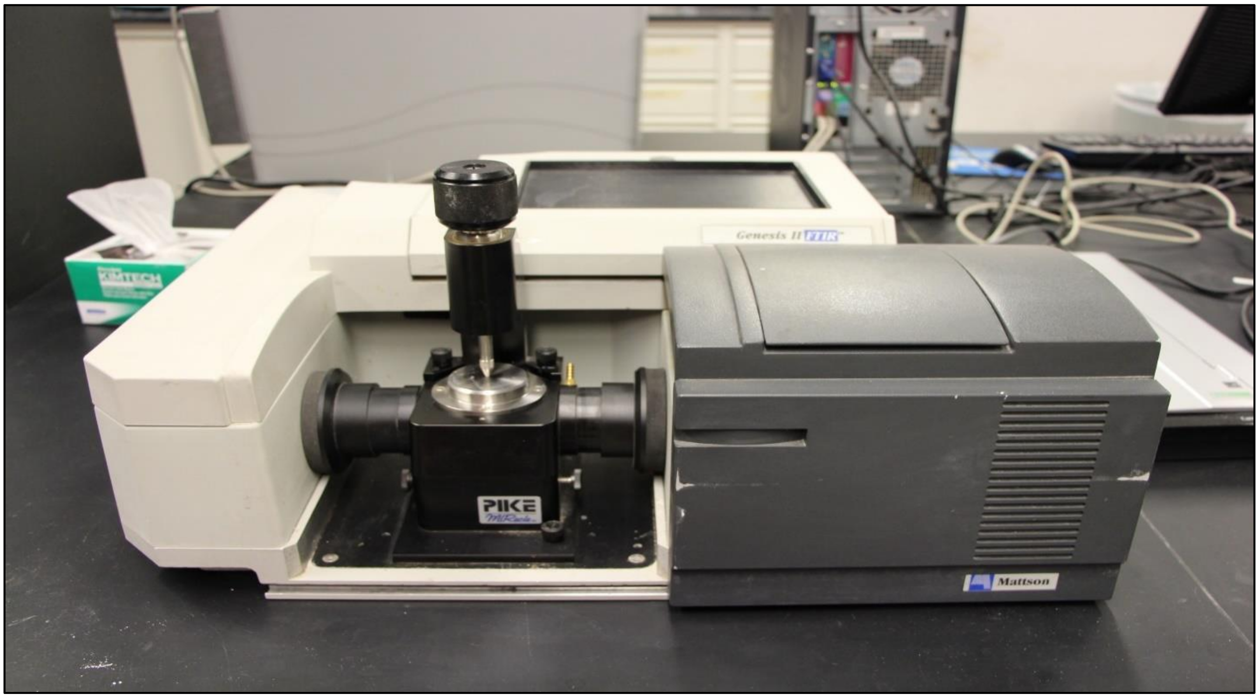


Figure 2.17: Photograph of a Fourier transmittance infra-red-attenuated total reflectance (FTIR-ATR), available: http://faculty.engineering.asu.edu/neithalath/laboratory/ (accessed 2016/10/12)

2.11.4 X-ray diffraction (XRD)

The x-ray diffraction is one of the main techniques used to characterize materials, producing structural information without being affected by the size of the crystallite, even in very small amounts of sample, across a single crystal x-ray diffraction method. The x-ray diffraction is based on constructive interference of monochromatic x-rays and crystalline sample (Mansikkamäki, 2005).

It is a rapid and non-destructive technique where a finely crushed, homogenous sample is analyzed to give a unique crystalline pattern, and finger print identification of various solid materials. The XRD is also used to determine the spaces between atoms and their alignment in crystalline materials. These X-rays are produced by a cathode ray tube, filtered to produce monochromatic radiation, accurately set alignment of light beams directed towards the sample. The interaction of the incident rays with the sample produces constructive interference, along with a diffracted ray when the alignment is met and the conditions are suitable. The Bragg's Law ($n\lambda = 2d \sin \theta$) equation is to determine the crystalline structure of the material. An XRD ray diffraction schematic diagram in Figure 2.18, is illustrated below.

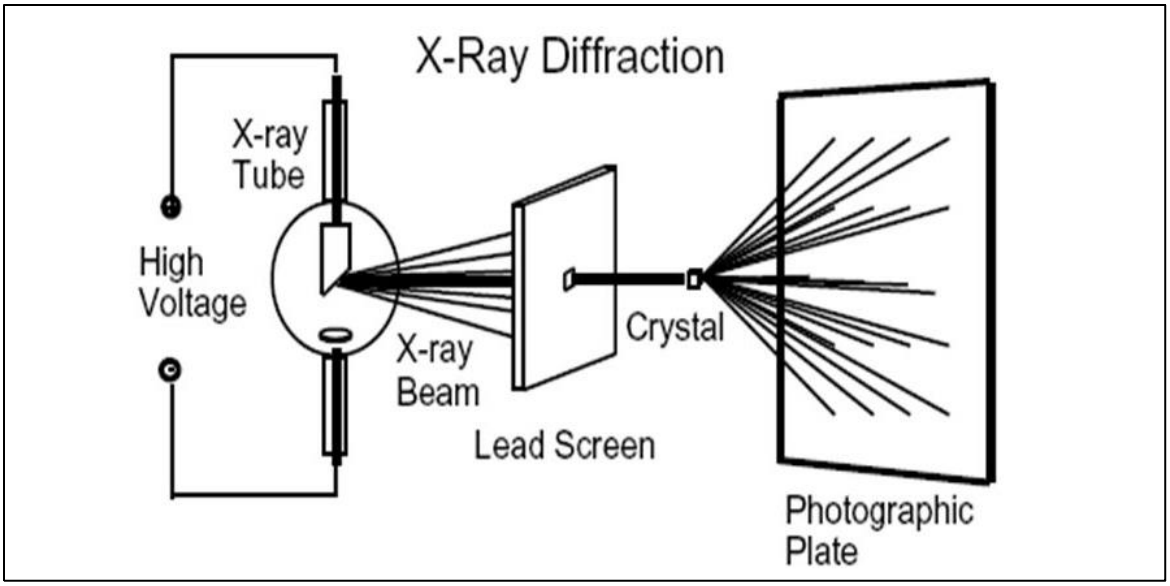


Figure 2.18: Schematic diagram of an x-ray diffraction (XRD), available: http://faculty.engineering.asu.edu/neithalath/laboratory/ (accessed 2016/10/12)

2.11.5 Ultra-violet/visible spectroscopy (UV/Vis)

The ultraviolet–visible spectroscopy (UV/Vis) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. This means it uses light in the visible and adjacent ranges. A beam of light from a visible and UV light source is separated into its component wavelengths by a prism or diffraction grating. In turn, each monochromatic beam is split into two equal intensity beams by a half-mirrored device (Yelle, 2008). When a sample is exposed to light energy that matches the energy difference between a possible electronic transition within the molecule, a fraction of the light energy would be absorbed by the molecule and the electrons would be promoted to the higher energy state orbital. A spectrometer records the degree of absorption by a sample at different wavelengths and the resulting plot of absorbance (A) versus wavelength (λ) is known as a spectrum. The absorbance of the sample is calculated or determined by using an equation called the Beer-Lambert law. The Beer – Lambert law is the linear relationship between absorbance and concentration of an absorbing species (Ferraz, 2008). The general Beer-Lambert law is usually written as: $A = a(\lambda) \times b \times c$. Where (A) is the measured absorbance, a (λ) is a wavelength-dependent absorptivity coefficient, b is the path length, and (c) is the analyte concentration (Calloway, 1997). A photograph of a ultra-violet/vis spectrophotometer (UV-Vis) in is illustrated in Figure 2.19 below.

Figure 2.19: Photograph of an ultra-violet spectrophotometer (UV/Vis)

2.11.6 Pyrolysis gas chromatography /mass spectroscopy (Py-GC/MS)

A pyrolysis gas chromatograph/mass spectrometer (Py-GC/MS) schematic diagram is shown in Figure 2.20 below. Py-GC/MS is the transformation of non-volatile material into degradation products by a rapid heating in the absence of oxygen (Harmanware, 2013)

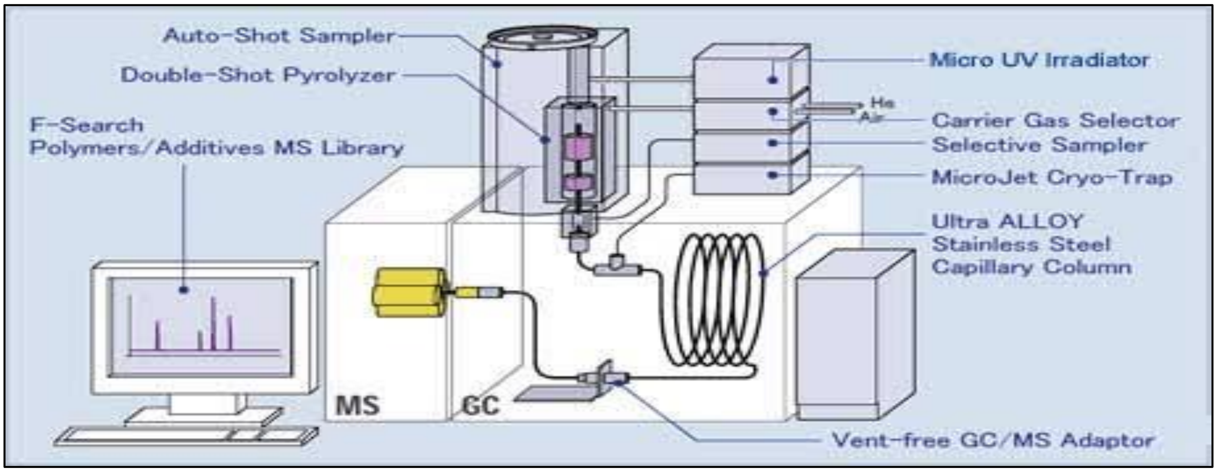


Figure 2.20: Schematic diagram of pyrolysis gas chromatograph/mass spectrometer (Py-GC/MS) (Han, *et al.*, 2015)

A wood material is used as an example to explain the internal mechanism of the technique. The technique pyrolyzes pulp material into its gaseous phase by means of atomization and sublimation processes. The pyrolyzing furnace in the pyrolysis chamber atomizes and breaks down the wood or pulp structure into fragments of polysaccharides or oil products found in the wood material. The gaseous wood fragment which is bombarded by the pyrolyzer at very high temperatures ranging between of 350-600 °C is then introduced into the stationary phase of the GC column. The wood analytes elute separately due to their different retention times giving several peaks that are used to deduce the concentration of the sample. At this juncture, the MS compartment interprets the molecular mass of each analytes by giving an idea of the structural information of the sample. All this information is read via a pyrogram scan.

2.11.7 High performance liquid chromatography (HPLC)

Chromatography is a technique used to separate mixtures of substances into their components based on their molecular structure and molecular composition. This involves a stationary phase (solid or liquid supported on a solid) and a mobile phase (liquid or gas). The mobile phase flows through the stationary phase and carries the components of the mixture with it. Sample components that display stronger interactions with the stationary phase will move more slowly through the column than components with weaker interactions. This difference in rates cause the separation of various components. Chromatographic separations can be carried out using a variety of stationary phases, including immobilized silica on glass plates (thin-layer chromatography), volatile gases (gas chromatography), paper (paper chromatography) and liquids (liquid chromatography). High performance liquid chromatography (HPLC) is basically a highly improved form of column liquid chromatography, instead of a solvent being allowed to drip through a column under gravity. It is forced through under high pressures of up to 400 atmospheres, through isothermal elution or gradient elution. This makes the sample elution occur much faster and separate into its constituent parts. This is due to the difference in the relative polarity of different molecules for the mobile phase and the stationary phase used in the separation (Snyder, 2012). This is used to determine the concentration of the sample. A schematic diagram of high-performance liquid chromatograph (HPLC) is illustrated in Figure 2.21 below. The mixed standards are run from lowest concentration to highest concentration to avoid matrix effect interference. A linear graph of concentration versus retention time is plotted for the whole standards.

Accordingly, the retention times and concentrations of mixed standards are compared to those of the sample. The concentration of the samples is determined using equation (2.8) illustrated below, which is extrapolated from the mixed standard graph equation, with a good correlation co-efficient not less than ≤ 0.9 value.

$$y = mx + c \tag{2.8}$$

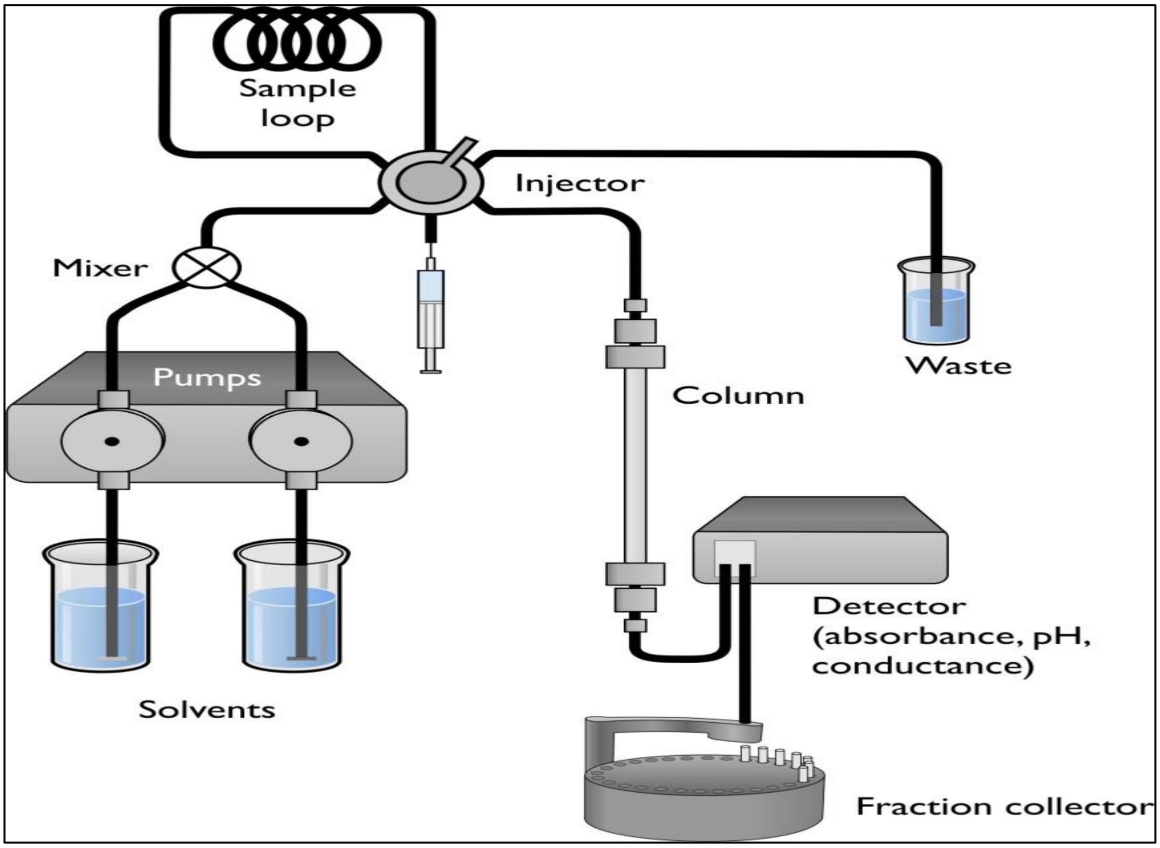


Figure 2.21: Schematic diagram of high performance liquid chromatograph (HPLC), available: http://laboratoryinfo.com/wp-content/uploads/2015/07/High-performance-liquid-chromatograph-hplc.jpg (accessed 15/06/16)

Chapter 3

EXPERIMENTAL

PART A PRETREATMENT

3.1 Materials and methods

3.1.1 Materials

The hardwood *E. grandis wood* chip samples used in this study were obtained from Mondi forest, KZN, South Africa. The chemicals used in this study were purchased from Sigma Aldrich and listed in Table 3.1 below.

Table 3.1: Chemicals and solvents that were used for pretreatment of *Eucalyptus grandis* wood chips

Chemicals	**Purity**
Sodium sulphide solution (Na_2S)	-
Caustic pellets (NaOH)	98.5%
1-allyl-3-methylimidazolium chloride	> 95 wt.%
Chlorine dioxide (ClO_2)	-
Potassium permanganate ($KMnO_4$)	-
Starch solution	-
Hydrogen peroxide (H_2O_2)	30% v/v
Sulphuric acid (H_2SO_4)	72 % v/v, 98%
Ammonium hydroxide (NH_4OH)	25%
Silica oil	-
Dimethyl sulfoxide co-solvent (DMSO)	16 % v/v
Acetone	99.5% Assay
Calcium carbonate powder ($CaCO_3$)	-
HPLC carbohydrates C_1-C_2 standards (rhamnose, mannose, xylose, galactose, glucose, sucrose)	≥95 %

3.2 Experimental procedure

The hardwood *E. grandis* wood chips underwent two streams of pulping namely mechanical and chemical. A portion of the pulp then underwent bleaching. All the pulp namely: unbleached mechanical pulp (UBMP), bleached mechanical pulp (BMP), unbleached kraft pulp (UBKP) and bleached kraft pulp (BKP) underwent ionic liquid pretreatment for the removal of lignin and hemicellulose. The experimental procedure for the dissolution of *Eucalyptus grandis* hardwood wood chips is depicted in Figure 3.1 below.

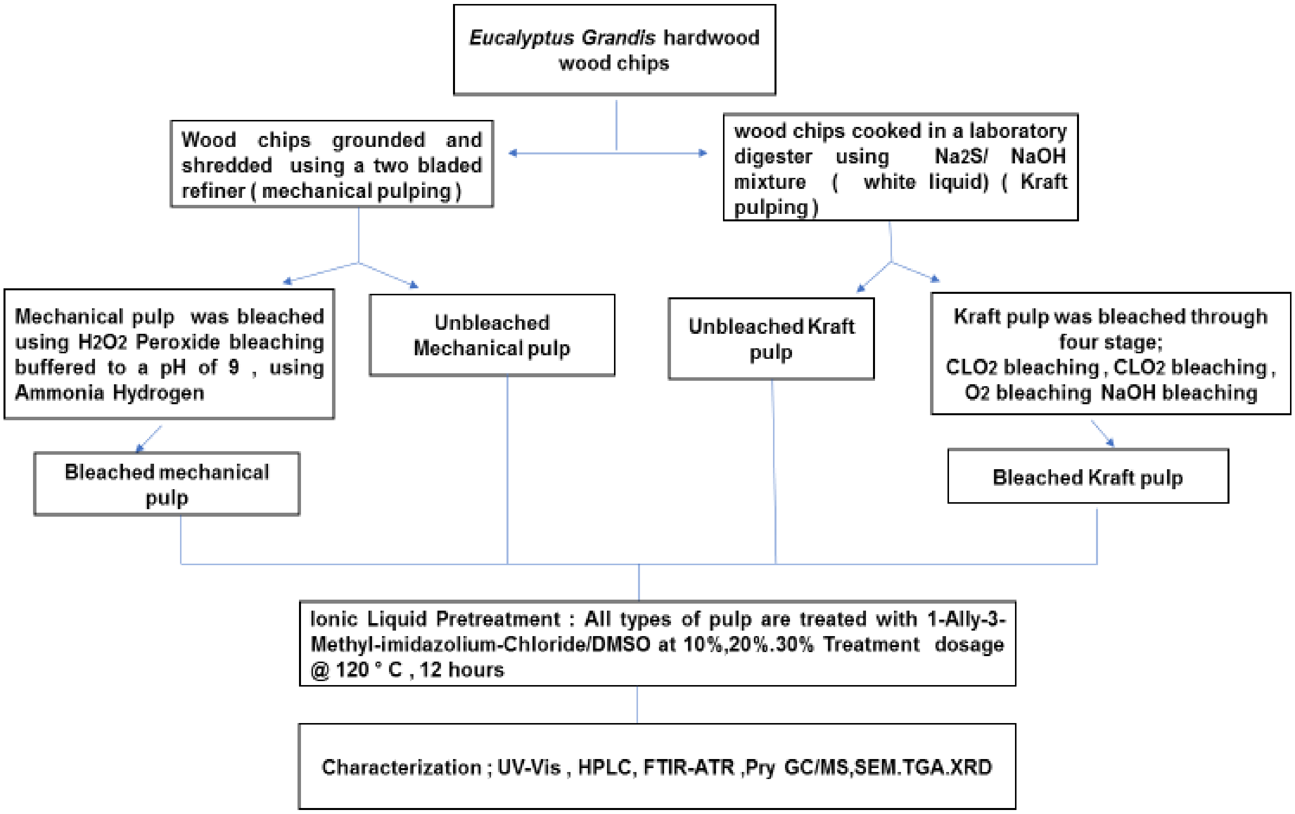


Figure 3.1*:* **Experimental procedure for the dissolution of *Eucalyptus grandis* hardwood wood chips**

3.2.1 Moisture content and total dry solids

Moisture and ash content were determined by NREL methods for the untreated wood chips before and after pretreatment.

Triplicate samples of 926 g of *E. grandis* (air dry solids) were weighed quantitatively on an analytical balance, then transferred into a ceramic crucible and dried overnight at 150 °C, using a furnace oven. After drying *E. grandis,* the sampled wood chips were weighed out again (Sluiter, 2008). The moisture content and total dry solids were calculated by using NREL methods (3.1) and (3.2).

$$Moisture\ \% \ = \frac{crucible\ \ + dried\ wood}{crucible + wood\ chips}\ \ x\ 100 \tag{3.1}$$

$$Dry\ solids\ \% \ = \ 100 - moisture\ \% \tag{3.2}$$

3.2.2 Ash content

Triplicate samples of 0.302 g of *E. grandis* hardwood pulp were weighed quantitatively on an analytical balance using a ceramic crucible and dried in dry oven at 180°C for 12 hours. The ash samples were removed and placed in a desiccator to cool. The crucibles with the samples were weighed and masses were recorded accordingly.

The samples were placed back into the oven dry and ashed to constant mass which represented a change less than ± 0.3 mg in the mass after 1.5 hours of reheating the crucible (Sluiter, 2008). The NREL methods were used to determine the ash content (3.3).

$$Ash\ content\ \% = \frac{crucible\ +\ dried\ ash}{crucible + air\ dry\ wood\ chip}\ x\ 100 \tag{3.3}$$

3.3 Pulping procedure

The following cooking procedure was conducted on wood chips used for both chemical and mechanical pulping:

The *E. grandis wood* chips with a size of 5 mm in length x 5 mm in width were weighed quantitatively on a top loading balance to a mass of 926 grams. The wood chips were introduced into a laboratory rotary digester with a ramp time of 90 minutes and heated to 120°C (Poletto, 2014). The system was purged for any air bubble formation or non-condensable gasses which may have been present. The temperature was then held constant for 40 minutes for the wood chips to fully cook (Smook, 1994). After the cooking process, a laboratory rotary digester displayed in Figure 3.2, was degassed the second time at 140°C during blow down time (Area, 2001). The cooking parameters for chemical pulping and mechanical pulping conditions are given in Table 3.2 below.

Figure 3.2: Photograph of a laboratory rotary digester

The results may be given in units of substance concentration (moles per litre) or grams of sodium hydroxide per litre. To obtain the results in moles per litre, they were calculated using the following equations below:

$$\text{NaOHconc} = \frac{\text{no of moles of NaOH}}{\text{Volume of NaOH}} \qquad (3.4)$$

$$\text{NaOHmoles} = \frac{\text{mass of NaOH}}{\text{Molecular mass NaOH}} \qquad (3.5)$$

Total alkalinity: Total of all “available “sodium alkali compounds:

$NaOH + Na_2S + Na_2CO_3 + Na_2SO_4 + Na_2S_2O_3 + Na_2SO_3$

Total titratable alkalinity (TTA) g/L →Total of concentration of NaOH + Na_2S (3.6)

Effective alkalinity (EA) g/L → Total of $NaOH_{conc}$ + ½ Na_2S (3.7)

Causticity → Ratio of NaOH to NaOH + Na_2CO_3 (3.8)

Sulphidity % → Ratio of Na_2S: AA or (TTA) (3.9)

If sodium hydroxide per litre was required in grams, the values were multiplied 40 g/mol (the relative molecular mass of NaOH and reported to the nearest 0.01 mol/l or to the nearest 1 g/l. Liquor to wood ratio was described as (4 x volume of liquor: 5 x volume of wood). The kraft pulp parameters were determined using method: 3.4, 3.5, 3.6, 3.7, 3.8 and 3.9 respectively.

Table 3.2 Cooking parameters for mechanical and chemical pulping

Parameters	Mechanical pulp	kraft pulp
Liquor to wood ratio	-	4.5
Active alkali/ oven dried	-	18%
Wood chips (g)	926	926
Cooking volume	-	1111 mL
Volume of water	3473 mL	2362 mL
Total alkalinity	-	140.70 g/L
Active alkalinity	-	12.60 g/L
Sulphidity percentage	-	27.20%.

3.3.1 Refiner mechanical pulping

Before, the *E. grandis* wood chips with a mass of 926 g were introduced into the mechanical refiner, the wood chips were cooked in the laboratory digester using distilled water with a volume of 3473 mL. No addition of white liquor (NaOH / Na_2S) was added.

The purpose of the initial step was to soften and loosely unpacked the fibres before they were introduced to the refiner. The degassing of non-condensable gasses took place during a blowdown time of 20 minutes cook (Smook, 1994), not all wood chips were entirely dissolved. The digested wood chips were removed from the digester and transferred into a mechanical refiner, as illustrated in Figure 3.3 below. The mechanical refiner consists of two fast-rotating, grating blades spinning on opposite directions.

Figure 3.3: Photograph of a mechanical refiner

The wood chips were fed into the refiner mechanical at constant hot tap water passed between the blades to avoid any form of explosion from dry friction. The new pulp sample was screened using two screeners with different porous sizes of 0.15 mm and 0.3 mm.

Pulp which did not pass through the screeners during washing were considered as "rejects”. The mechanical pulp was dried overnight at 90°C in a dry oven. After drying, the moisture content %, oven dried pulp mass % and ash content % was determined using methods (3.1), (3.2) and (3.3), respectively.

3.3.2 Kraft process pulping

The *E. grandis* wood chips were mixed with a 1:1 ratio white liquor ($NaOH$ / Na_2S) solution in the laboratory rotary digester and cooked under the cooking parameters given in Table 3.2 above. After cooking, the black liquor supernatant ($NaOH$ / Na_2S mixed solution + residue) was discarded. The soft discoloured chemical pulp was collected and vigorously washed with tap water several times and pass through two different porous size screeners of 0.15 mm and 0.3 mm. The pulp was dried overnight at 90 °C in a dry oven. After drying, the moisture content %, chemical (kraft) pulp mass % and ash content % was determined using methods (3.1), (3.2) and (3.3), respectively.

3.3.3 Kappa number

Kappa number is the common parameter for the determination of lignin content. A value ranging between (12-17) is considered a reasonable kappa number for kraft pulping process (Costa, 2007). The consumption of $KMnO_4$ reagent (titrant) is measured against the presence of lignin, hexeneuronic acids, as well as other small compounds involved in the wood matrix composition aliquot during a titration (Gellerstedt,1998).

kappa number determination test is based on TAPPI standard test methods T230 om-94 and T236 cm85 respectively. Kappa number determination is only done for kraft *E. grandis* pulp to quantify for lignin content with respect to pulp yield and bleaching purposes. Mechanical pulp has a high degree of lignin which is the main characteristic of mechanical pulp. Therefore, determining kappa number on the mechanical pulp is of no importance.

3.3.4 Bleaching

Kraft and mechanical pulp underwent various bleaching conditions known as bleaching stages. Kraft pulp bleaching stages were as follow:

The chlorine dioxide delignification stage (D_1), sodium hydroxide NaOH stage (E_1) and chlorine dioxide delignification (D_2) were carried out with a 280 g oven dried pulp sample in polyethylene bags for each stage. The desired amount of chlorine dioxide, hydrogen peroxide and sodium hydroxide were added onto the pulp and thoroughly mixed. The polyethylene bag containing the pulp solution was immersed in a water bath and temperature adjusted to required specifications, pH and time. After completion, the pulp was washed with distilled water. Pulp samples were analyzed according to TAPPI. 236.The bleaching conditions are as follow in Table 3:3 below:

Table 3.3: Bleaching conditions

Bleaching stage	D_1	E_1	EP	D_2
Consistency%	10	10	10	10
Time min	120	120	120	180
Temperature °C	60	70	60	85
End pH	3	8	8	5

Mechanical pulp has a high degree of lignin content which is important towards mechanical pulp yield. As such, it was bleached using H_2O_2 bleaching. The bleaching mixture was buffered using ammonium hydrogen to a pH of 8. Peroxide acted as an effective oxidizing agent, (Haugan, 2006), as it can oxidize lignin chromophores by discolouring the lignin without reducing its concentration or affecting the pulp yield.

3.4 Fractionation of *E. grandis* pulp with 1-allyl-3-methylimidazolium chloride [AMIM][Cl]

The fractionation of *E. grandis* pulp which comprised of unbleached kraft pulp (UBKP), unbleached mechanical pulp (UBMP) and bleached mechanical pulp (BMP) was done using [AMIM][Cl]/DMSO pretreatment to isolate cellulose**.** A 0.301 grams of *E. grandis* pulp was mixed with (3, 6 and 9) grams of ionic liquid and the mixture was quantitatively transferred into a 50 mL round bottom flask. A 2-mL volume of 16 % wt. % of DMSO was added to the mixture to lower the viscosity of the ionic liquid (Casas, 2012).

The experiments were conducted under atmospheric pressure for 16 hours and gradually homogenized with a magnetic stirrer bar placed inside the round bottom flask at 120°C (Li, *et al*., 2010). The 50-mL round bottom flask containing the sample was connected to a condensation reflux apparatus and constantly heated at 120°C, using an electronically adjusted magnetic hot plate (Lab smart Ms – H280 Pro). The temperature was constantly monitored using a glass thermometer, as seen in Figure 3.4 below. The flask was immersed half-way deep in a silicone oil bath enclosed in a beaker placed on the hot plate to reserve heat.

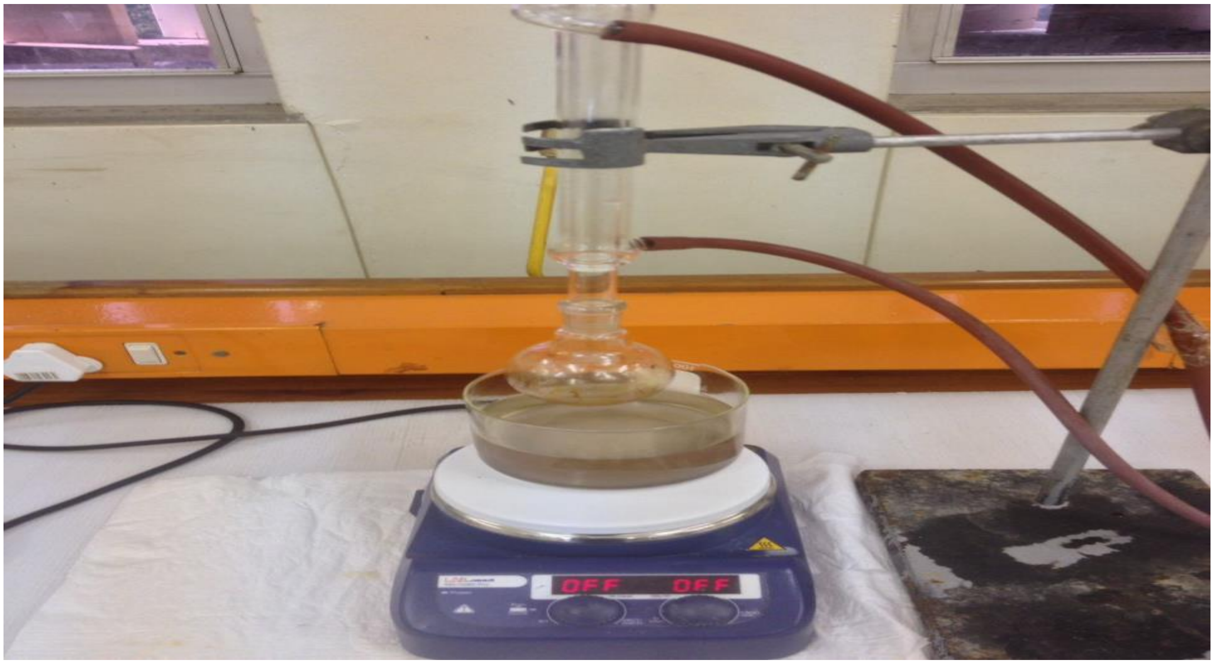


Figure 3.4: Photograph of a reflux/condensation setup, heat magnetic stove and silica oil bath

There was no experimental design, the experiment was randomly done under a set of three increasing IL pretreatment ratios: (10% [3g / 0.301g], 20% [6g / 0.301g], 30% [9g / 0.301g]) * 100 and a constant 2-mL 16% DMSO addition, series of IL/DMSO pretreatment are represented in percentages:

- 10 % (pulp 0.301g / 3g IL) + 2-mL (16 % DMSO Solution)
- 20 % (pulp 0.301g / 6 g IL) + 2-mL (16 % DMSO Solution)
- 30 % (pulp 0.301g / 9 g IL) + 2-mL (16 % DMSO Solution)

3.4.1 Regenerated pulp recovery

After the dissolution process, the UMBP, BMP hot IL mixture from section 3.4 was brown in colour and the UBKP hot IL mixture was light yellowish in colour. It contained cellulose and lignin which was left to cool for 20 minutes at room temperature (Chen, 2010). The slurry composition of biomass + [AMIM][Cl] / DMSO solution was filtered through a 0.45 mm porous sized filter paper using vacuum. Thereafter, it was washed several times with 40-mL portion of 1:1 solution of deionised water and acetone (20-mL deionised water / 20-mL acetone) (Mäki-Arvela, 2010). Retentate 1 (cellulose + IL insoluble lignin) deposited on the filter paper was dried overnight at 90 °C (Brown, 2012). The filtrate (hemicellulose, IL soluble lignin, DMSO, deionised water and acetone), was heated on an electronically hot plate for an hour at 110°C, for the evaporation of water and acetone.

The DMSO solution has a boiling point of 189°C and was considered negligible and not evaporated. Retentate 2 (soluble lignin + hemicellulose) was dried at 90 °C overnight (Socha, 2014). Retentate 1 and retentate 2 recovered from section 3.4, was hydrolyzed by adding 3-mL of 72% H_2SO_4 for 2 hours at 30 °C in a water bath (Roselli, 2014). The 72 % H_2SO_4 mixture was reduced to 4% H_2SO_4 mixture by adding 84 ml deionized water into 50 ml schott bottles (Pedersen, 2010). Retentate 1 was mixed with 4% H_2SO_4 solution and autoclaved for 1 hour for the separation of the cellulose and acid soluble lignin (Li, 2010). The solution was then filtered using a vacuum and the cellulose retained on the filter paper was dried overnight at 90°C. The pulp recovery % was then calculated using equation (3.10) below.

$$\%\,Pulp\ recovery = \frac{Mass\ of\ recovered\ \ cellulose\ pulp}{Mass\ of\ untreated\ pulp} x\ 100 \qquad (3.10)$$

3.4.2 Air dried lignin and acid insoluble lignin recovery

After the evaporation of deionised water from the filtrate, the IL soluble lignin aliquot was used to determine hemicelluloses content via HPLC analysis (Socha, 2014). For UV/Vis analysis, ASL was determined by using equations, (3.11) and (3.12), respectively.

$$\%\,ASL = \frac{UV\ Absorbance\ x\ Filtrate\ Volume\ x\ Dilution\ factor}{Absorptivity\ (e)\ x\ ODW\ (sample) x\ Path\ length} x\ 100 \qquad (3.11)$$

$$\%\,Total\ lignin = \%\,AIL + \%\,ASL \qquad (3.12)$$

PART B CHARACTERISATION

3.5 Characterisation of *E. grandis* cellulose, lignin and hemicellulose

3.5.1 Thermo gravimetry (TGA)

Figure 3.5 below is a photograph of a thermo gravimetric analyzer. Each treated pulp sample with a mass of 10 mg was placed on a platinum sample holder pan for the entire analysis. TGA curves were recorded from 80°C to 700 °C temperature at a rate of 10 °/min under nitrogen flow of 20 ml/min. All results were recorded at optimum conditions. The TGA results were used to distinguish the degree of water loss %, degradation and polymerization of *E. grandis* regenerated cellulose.

Figure 3.5: Photograph of thermo gravimetric analyzer TGA Mettler Toledo TGA/DSC 1 stare system

3.5.2 Scanning electron microscopy (SEM)

Figure 3.6 below, is a photograph of a Zeiss scanning electron microscope. The SEM images of untreated / treated *E. grandis* kraft and mechanical pulp were captured and recorded at optimum magnifications of 3.0 kx. The purpose for the analysis was to distinguish the changes of structural and surface nature before and after IL/DMSO pretreatment of *E. grandis* treated pulp samples. Each sample with a mass of 10 mg was first coated with gold, placed onto a platinum sample holder pan and then covered with copper tape for electrical conductivity then ran on the instrument.

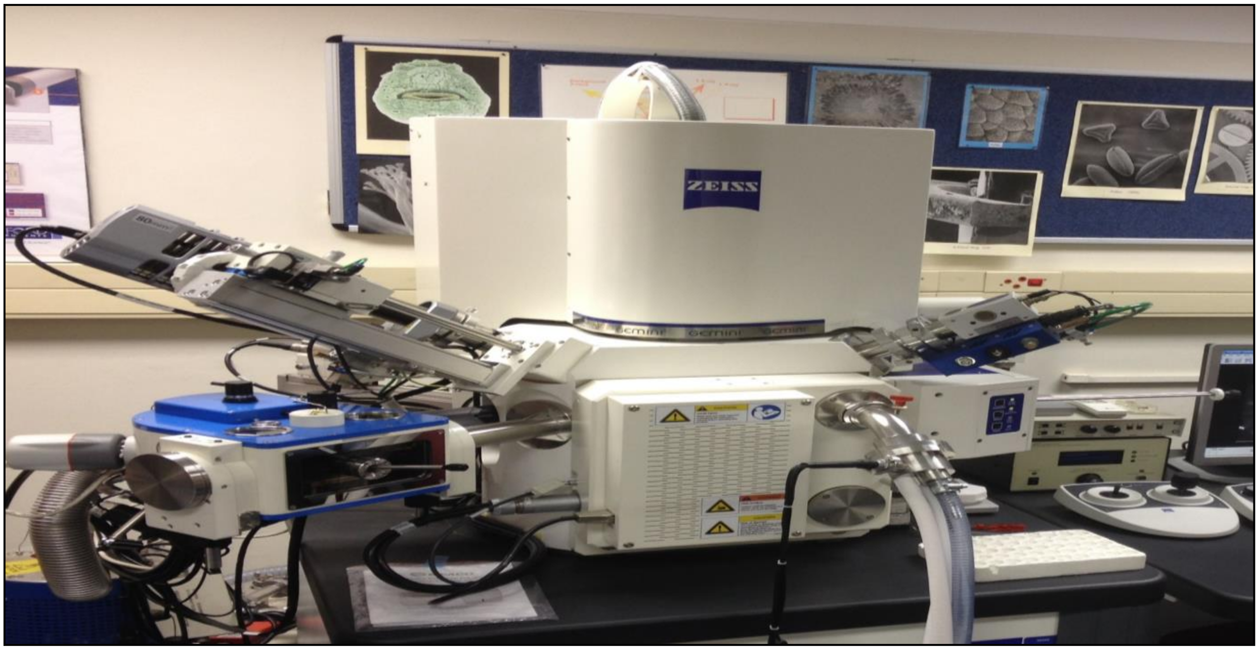


Figure 3.6: Photograph of the Zeiss scanning electron microscopy

3.5.3 Fourier transmittance infra-red-attenuated total reflectance (FTIR) (ATR)

The ATIR-FTIR spectra scans were recorded from 4000 cm^{-1} to 650 cm^{-1}. The regenerated cellulose was compared with the FTIR spectrum of *E. grandis* wood chip pulp sample by using a Varian 800 FTIR spectrometer - Scimitar Series photograph is shown in Figure 3.7, illustrated below.

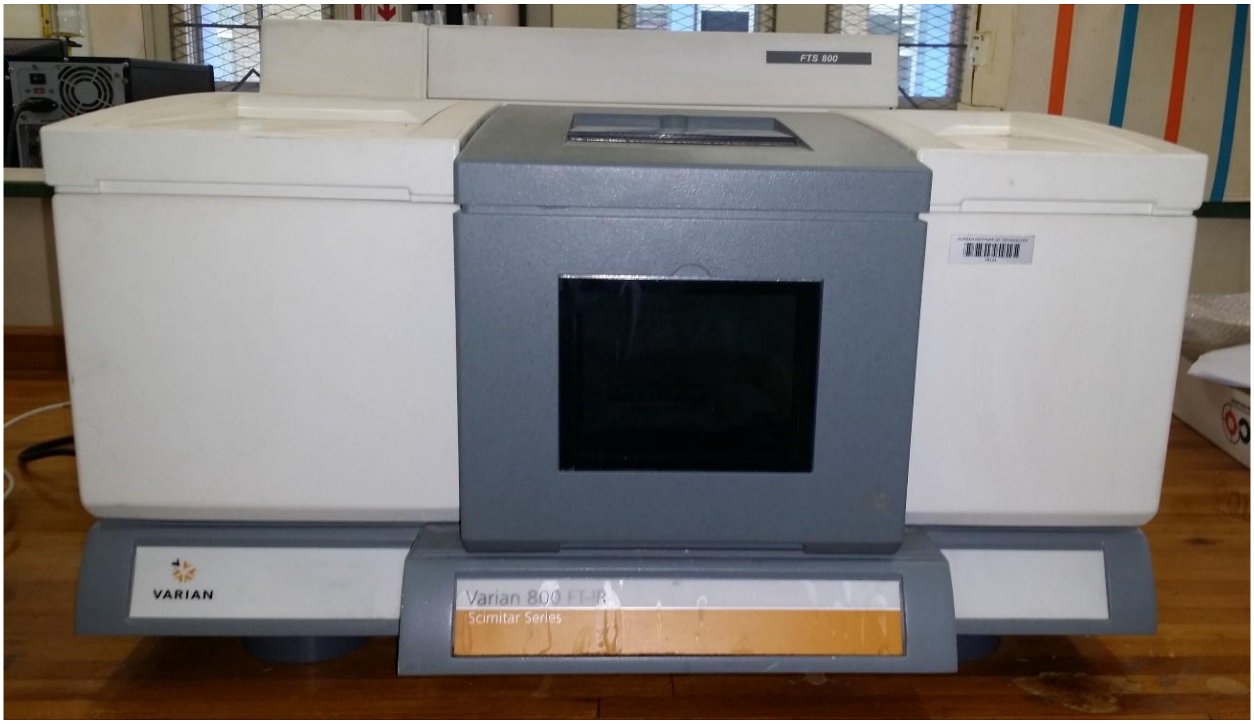


Figure 3.7: Photograph of the Varian Cary 800 ATIR-FTIR spectrometer - Scimitar Series

3.5.4 X-ray diffraction (XRD)

An *E. grandis* recovered cellulose sample with a mass of 0.5 μg was analyzed using x-ray diffraction instrumentation as displayed in Figure 3.8 below. The x-ray diffraction images for untreated / treated *E. grandis* kraft and mechanical pulp scans were recorded. The patterns were recorded using Cu-$\underset{\infty}{\underline{K}}$ radiation at 40 kV and the range for angle of diffraction was 2θ = 10°- 70°. According to Segal (1962), the crystallinity index (CrI) of the regenerated cellulose and MCC should be calculated using Bragg's law equation (3.13) below.

$$CrI = \frac{I_{tot} - I_{am}}{I_{tot}} x\ 100 \qquad (3.13)$$

The crystallinity index (CrI) of the recovered cellulose samples were obtained using the above equation, using the I_{am} and I_{tot} values which derive from the longest peak at 2θ = 23° and shortest peaks at 2θ = 15° and 16° of the cellulose sample.

Figure 3.8: Photograph of x-ray diffraction instrumentation, available: http://faculty.engineering.asu.edu/neithalath/laboratory/ (accessed 2016/10/12)

3.5.5 Ultra violet /visible spectroscopy (UV/Vis)

Lignin shows strong absorption bands in the UV/Vis regions compared to hemicellulose and cellulose. Therefore, the use of a uv spectrophotometry is most crucial in the investigation of lignin (Mongeau, 2001). A 15-mL volume filtrate of soluble lignin solution of was collected for uv analysis.

The analysis was conducted by using a varian cary 50 cons uv-vis spectrophotometer in Figure 3.9, illustrated below, with a 10 mm Quartz cell to determine each pretreated sample absorbance at 280 nm. A 4% H_2SO_4 blank solution was used for background correction. The ASL was determined by using equations (3.11) and (3.12), respectively.

Figure 3.9 : Photograph of Varian Cary 50 conc uv-vis spectrophotometer

3.5.6 Pyrolysis gas chromatography /mass spectroscopy (Py-GC/MS)

The Py-GC/MS thermogram were recorded between (45-250) °C via temperature programming method on a Shimadzu (Py-GC/MS) chromatograph in Figure 3.10, shown below. A 10 mg of each dry *E. grandis* recovered pulp was placed on stainless-steel crucible, pyrolyzed and ran on GC coupled with a mass spectra compartment. All *E. grandis* hardwood pulp samples were analyzed using Py-GC/MS under a pyrolyzer temperature of 550°C, with an elapse time of 30 s. The heating rate of the GC/MS was 20 °C per minute, between 38-42 minutes was required for each pulp sample to reach a temperature of 250 °C, from the initial temperature of 45 °C. The detected products were categorized into acids, alcohols, aldehydes, ketones, furans (mostly abundant in sulfonate lignin), phenols, esters, including hydrocarbons (Nunes, 2010).The S/G ratio for untreated / treated *E. grandis* kraft and mechanical pulp were calculated using area peak % of syringyl units / guaiacol units. As a result, lignin composition for all four types of pulps was estimated using the S/G ratio values obtained from using equation (3.14) shown below.

$$\frac{S}{G} ratio\ (estimated\ Lignin\ ) = \frac{Syringyl\ unit\ area\ \%}{Guaiacy\ unit\ area\ \%} \tag{3.14}$$

Figure 3.10: Photograph of Shimadzu (Py-GC/MS) chromatograph

3.5.7 High performance liquid chromatography (HPLC)

HPLC chromatography was done for both qualitative and quantitative analysis of hemicellulose carbohydrates constituents; glucose, mannose, arabinose, xylose, rhamnose and galactose found in the *E. grandis* treated samples, which were quantified at very low concentrations between 0.1% - 0.4%.

Sample preparation

A 0.3 g of pretreated *E. grandis* pulp sample was weighed using an analytical balance and quantitatively transferred into a test tube. A 3-ml pipette of 72 % H_2SO_4 was transferred into the same test tube. The test tube was then heated in a water bath at temperature of 30 °C, for 2 hours.

A constant stir with a glass rod was done every 15 minutes until complete dissolution. After two hours of heating, the test tube was cooled at room temperature for 20 minutes. The solution was rinsed out from the test tube with deionized water of a volume of 84-ml into a 100 mL schott bottle. The 84-mL volume of deionized water lowered the acidity level from 72 % H_2SO_4 to 4% H_2SO_4 acid solution. The 100-ml Schott bottle with the sampled mixture was autoclaved for a period of 2 hours for the purpose of breaking down sugars within the pulp. Thereafter, the solution was cooled for at least an hour. Subsequently, it was transferred into a 40 ml centrifuge vials and refrigerated for 24 hours.

The HPLC column used for the experiment was sensitive to acidic substance. Hence, the treated samples had to buffer between the pH of 5-9 region using $CaCO_3$ powered before HPLC analysis. The HPLC analysis were performed using HPLC Perkin Elmer 250 pump system, Figure 3.11, illustrated below under specific parameters.

HPLC Perkin Elmer 250 pump system consisting of: a bio-grad organic acid column Aminex HPX-87P, an LC 235 diode array detector as displayed. These were the HPLC parameter used for the present study:

Parameters**:**

- Mobile phase: 5 mM deionised water
- Sample volume: 5 µL
- Column Temperature: 80 - 85 0C
- Flow rate: 0.6 mL/min
- Column type: bio-grad organic acid column Aminex HPX-87

Figure 3.11: Photograph of HPLC Perkin Elmer 250 pump system

Chapter 4

RESULTS AND DISCUSSION

PART A BIOMASS PROCESSING

4.1 Moisture content and dry solids

The results are reported on a dry mass basis (% m/m) and were obtained using NREL methods (3.1) and (3.2). The results are shown in Table 4.1 below.

4.2 Ash content

NREL Method (3.3) was used to determine the ash content of the untreated wood chips and was expresssed in Table 4.1. The % moisture was 13.63% and the % dry solids was 86.37% for the untreated *E. grandis* wood chips. The % moisture of *E. grandis* wood was higher than the literature values, but dry solids had a lower value in comparison to literature values.

Table 4.1: *E. grandis* wood moisture, ash and dry solids %

Sample	WSE	Klason lignin	Polysaccharides	Moisture	Dry solids	Ash Content
E. grandis	-	-	-	13.63	86.37	1.11
**E. grandis* (Spain)	1.60	21.1	75.30	1.70	98.30	0.30

*(Rencoret, Gutierrez and del Rio 2007), Mugabi, (2010) and Oasmaa, *et al.,* (2010)

4.3 Pulping process

4.3.1 Mechanical pulping

Figure 4.1 displays a photograph of the mechanical pulp obtained after the *E. grandis* wood chips were crushed and shredded using a mechanical refiner. The fibres obtained were ± 20 mm in length, 3mm in width and still retained its brown colour.

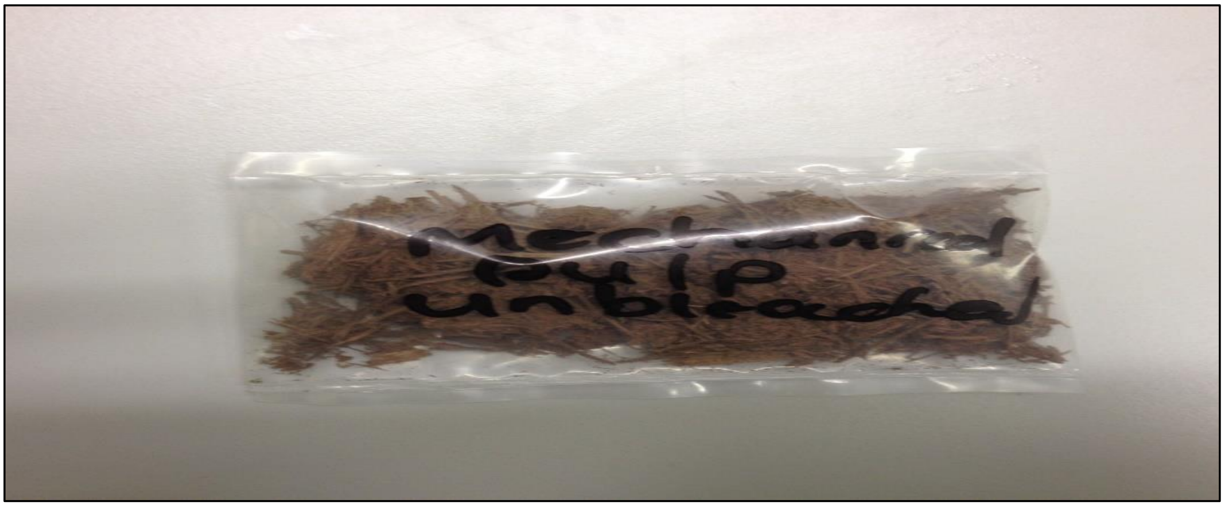


Figure 4.1 : Photograph of mechanical pulp from wood chips

4.3.2 Chemical pulping

Figure 4.2 displays a photograph of unbleached kraft pulp and Figure 4.3 displays a photograph of bleached kraft pulp obtained after *E. grandis* wood chips underwent chemical pulping.

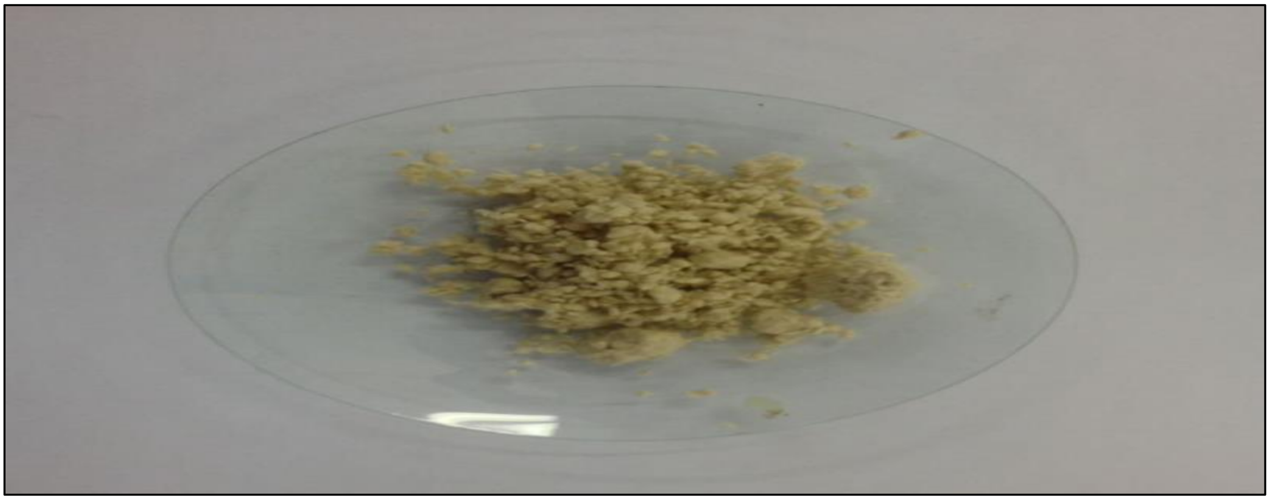


Figure 4.2 : Photograph of unbleached kraft pulp

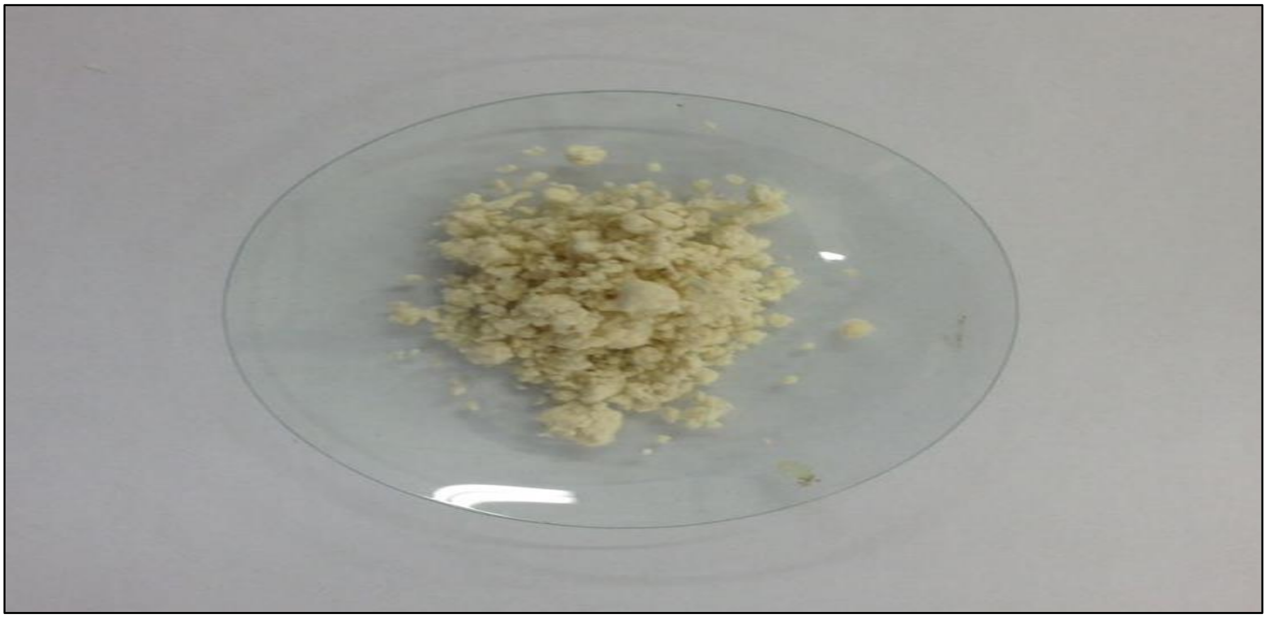


Figure 4.3 : Photograph of bleached kraft pulp

4.4 Kappa number

The lignin content, relative hardness,bleachability or dregree of delignification of the untreated kraft pulp was determined by calculating the kappa number. kappa number determination test was based on TAPPI standard test methods T230 om-94 and T236 cm-85 respectively. According to literature, *E.grandis* pulp requires a low kappa number between 10 - 12 for the pulp to maintain full brightness and good fibre strength , because during bleaching processes, fibre degradation occurs greatly and affects pulp yield. In this work unbleached *E. grandis* kraft Kappa no. was found to be 12.3 ,which is in agreement with literature review kappa range (Gellerstedt, 1998).

4.5 Bleaching

The chlorine dioxide bleaching consumption per kappa number of the hexeneuronic acids is 9.94 mmol (Antti, 2000) and lignin residue is 8.44 mmol (Costa, 2006), per kg of *Eucalyptus* kraft pulp, respectively. Hence, The UBKP with a kappa no. of 12.3, about 153.30 g of residual lignin was removed from wood chips. The phenolic and carbonyl functional group are responsible for the lignin composition in wood pulp. Therefore, the removal of these functional groups inversely increases the quality of pulp yield. According to Rencoret, *et al.,* (2007), about 21.1% of klason lignin is found in *E. grandis* (Table 4.1) and approximately 35%-40% of carbonyl functional groups in lignin are removed during hydrogen peroxide bleaching on UBMP alone (Oliveria, 2006). The wood chip mass was 926 g, 21.1% (195.39 g ±) belonged to lignin. Hence, 35%- 40% (74.24 g ±) of lignin was discoloured after peroxide bleaching. This indicates that the bleaching was effective in discolouring the lignin content on BMP before IL/DMSO pretreatment on *E. grandis* pulp.

4.6 IL/DMSO pretreatment

Table 4.2 below illustrates the literature values of *E. grandis* for different pretreatment and conditions against [AMIM][Cl]/solvent pretreatment below.

Table 4.2: Literature values of *E. grandis* IL pretreatments

Sample	Regenerated cellulose %	Temp	Time	IL	Ref
E. grandis	96	150 °C	24 hr	[AMIM][Cl]	(Li, *et al.,* 2010)
E. grandis	-	150 ◦C	24 hr	[EMIM][OAc]/ ethanol	(Casas,*et al.,* 2012)
E. grandis	43.6	-	24 hr	[EMIM][Cl]	Pezoa, *et al.,* 2010)

4.6.1 Recovery of regenerated cellulose

The highest percent mass recovered for the regenerated cellulose was obtained for the UBKP (67,43%), similar values were obtained for the 20% IL pretreated BKP (67.13%) and 30% IL pretreated BKP (67.15%). As illustrated in Figure 4.4, the graphical trend of pulp recovery obtained at 10%, 20% and 30% IL pretreatment.

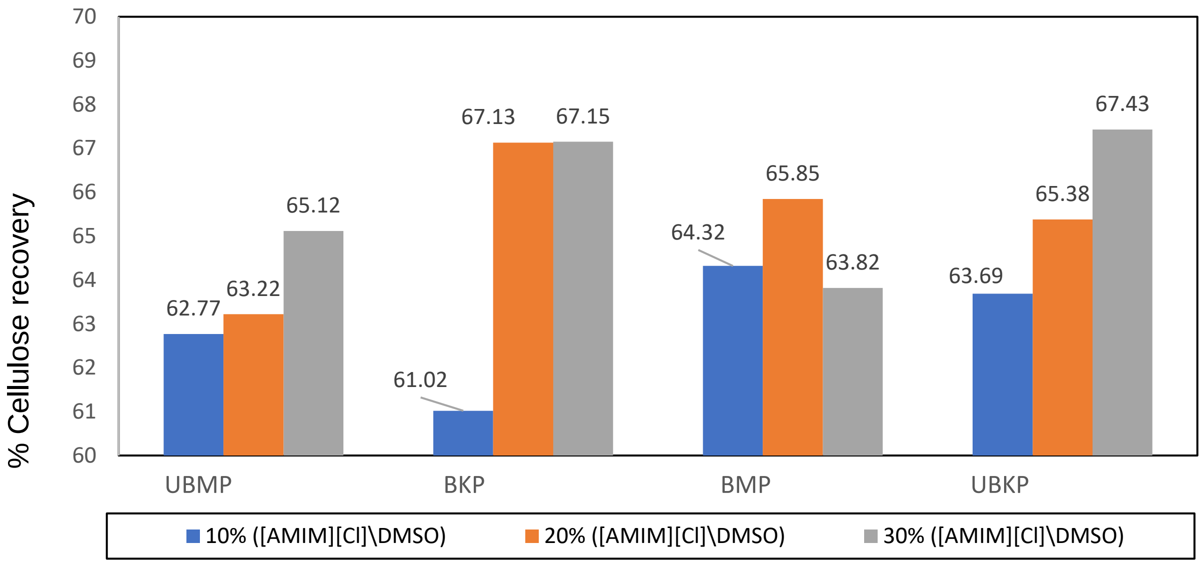


Figure 4.4: Recovery of regenerated cellulose

According to Twaybi (2014), percentage yield of regenerated cellulose after dissolution of unbleached, bleached dissolving pulp samples with [EMIM][OAc]/DMSO and [EMIM][OAc]/DMF at 120°C for 12hr, are as follow: the unbleached and bleached pulp pretreated with [EMIM[OAc]/DMSO regenerated cellulose yield were 15.25%, 41.88%, respectively. The unbleached and bleached pulp pretreated with [EMIM][OAc]/DMF regenerated cellulose yield were 36.25%, 49.89%, respectively. According to Pezoa (2010), percentage yield of regenerated cellulose using [EMIM][Cl] for 24hr was 43.6%. In comparison, the highest regenerated cellulose yield was obtained from 30% [AMIM][Cl]/DMSO at 120°C for 16hr, the UBKP (67.43%) and BKP (67.15%).

The pulp recovery values were higher than the literature review values, a positive indication of high pulp yield under 30% [AMIM][Cl]\DMSO pretreatment for both chemical and mechanical pulp samples. Figure 4.5 below, illustrates the regenerated cellulose recovery % for each type of *E. grandis* treated pulp at the most optimum condition of 30 % IL/DMSO pretreatment.

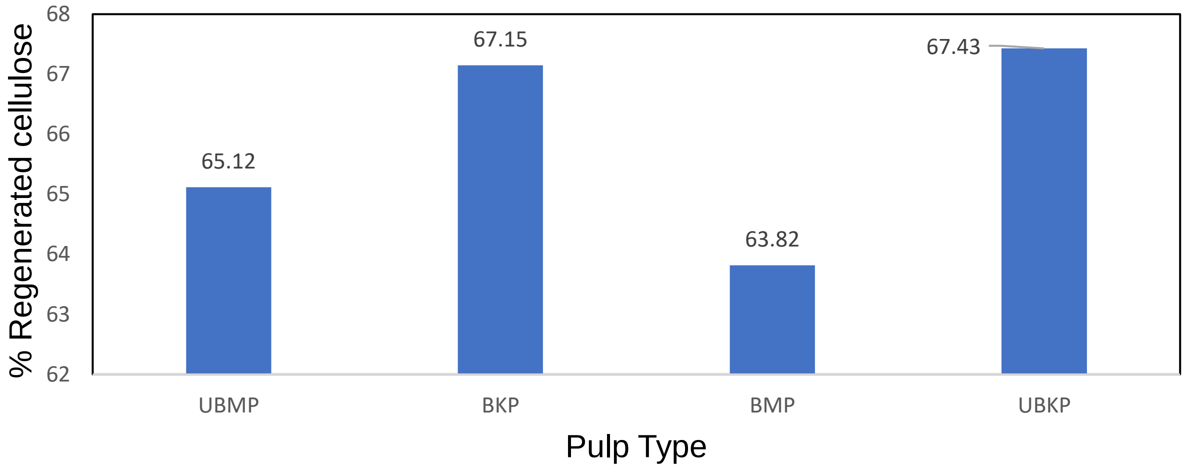


Figure 4.5: Regenerated cellulose average mass recovery % for each type of *E. grandis* treated pulp at the most optimum condition of 30 % IL/DMSO pretreatment

4.6.2 Hemicellulose recovery

According to Xu (2016), after pretreatment of milled *Eucalyptus* with [AMIM][Cl], [BMIM][Ace], [BMIM][Br], [BMIM][Cl] and [EMIM][Cl] at 120°C for 3 hr., the hemicellulose recovery was 0.78%, 2.13%, 0.88%, 1.10%, 0.98% and 1.02%, respectively. The highest hemicellulose% recovery was obtained for the UBMP pretreated 10%, 20% and 30% IL/DMSO pretreatment at 120°C for 16hr, 6.79%, 6.41% and 9.13%, respectively. The BMP (3.36%) pretreated at 20% IL/DMSO pretreatment and the BKP (3.28%) pretreated at 20% IL/DMSO pretreatment. The results values were higher then the literature values. A postive indication of hemicellulose removal at 20% and 30% [AMIM][Cl]\DMSO pretreatment for UBMP, BMP and BKP samples. Possibly, high hemicellulose recovery was due to longer IL/DMSO pretreatment time on the pulp samples. Figure 4.6 illustrated the graphical trend of hemicelluloses recovery obtained at 10%, 20% and 30% IL pretreatment.

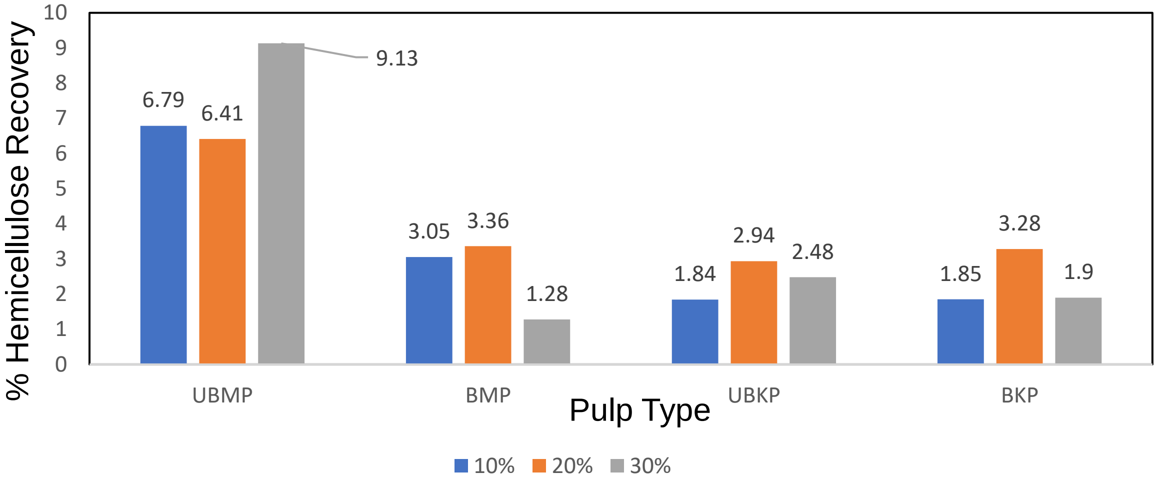


Figure 4.6: Hemicellulose recovery

4.6.3 Lignin recovery

According to Mkhize (2016), after pretreatment of sugar bagasse pulp with [EMIM][OAc] at 120°C for 12hr, lignin % recovery was 28.88%. hardwood oak and maple pulp were pretreated with [EMIM][$MeCO_2$] at 120°C for 12hr and at 110°C for 16hr, respectively. The lignin recovery % was 35% and 26%, respectively. The highest liginin % recovery was obtained at 30% IL/DMSO pretreatment for UBMP (29.23%), followed by BMP at 20% and 30% IL/DMSO pretreatment: 27.12% and 27.53%, respectively. The UBMP at 30% IL/DMSO pretreatment had a higher liginin % recovery then literature values. The differences in value were ± 0.35 %, in comparsion to sugar bagasse pulp pretreated with [EMIM][OAc] at 120°C for 12hr. A positive indication of lignin removal at 30% [AMIM][Cl]\DMSO pretreatment UBMP.

The lowest amounts of lignin was obtained at 10% pretreated UBKP (25.68%) and 30% IL/DMSO pretreatment BKP (25.19%). Both UBKP and BKP lignin % recoveries were lower then the lowest literature values (26%). Figure 4.7 illustrated the graphical trend of lignin recovery obtained at 10%, 20% and 30% IL pretreatment.

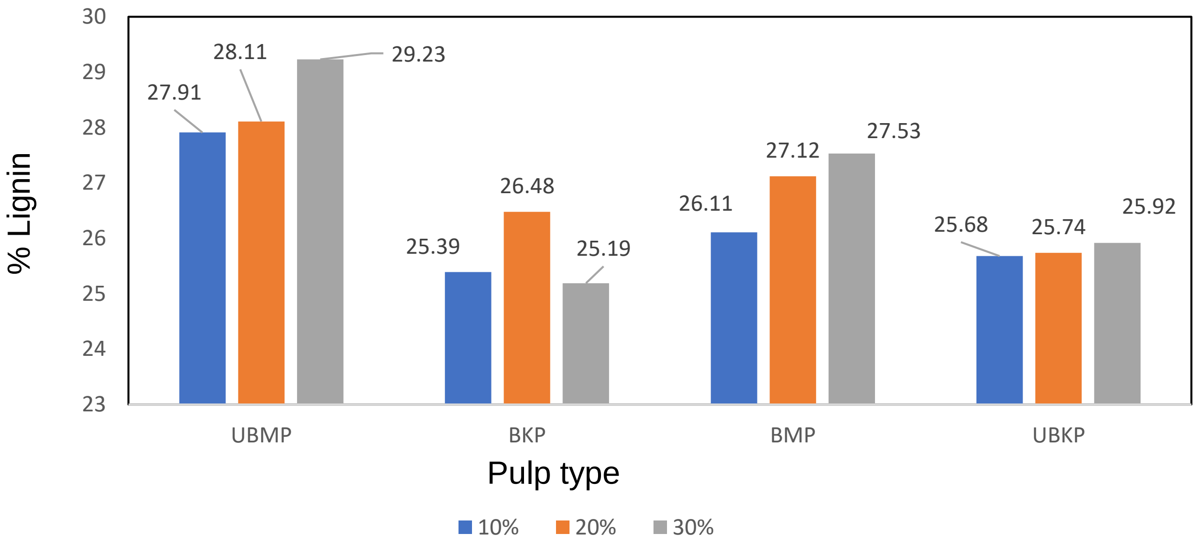


Figure 4.7: Lignin recovery

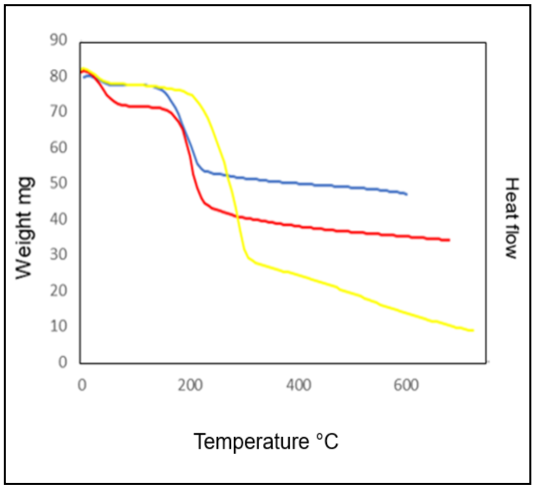
PART B CHARACTERISATION

4.7 Characterization of *E. grandis* treated samples

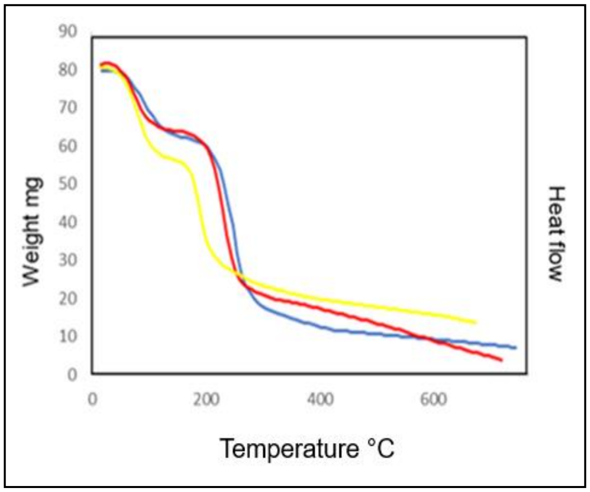
4.7.1 TGA of *E. grandis* treated samples

The TGA/DSC scans for the *E. grandis* IL/DMSO treated pulp are given in Figure 4.8 (a) - (d) below.

(a)



(b)



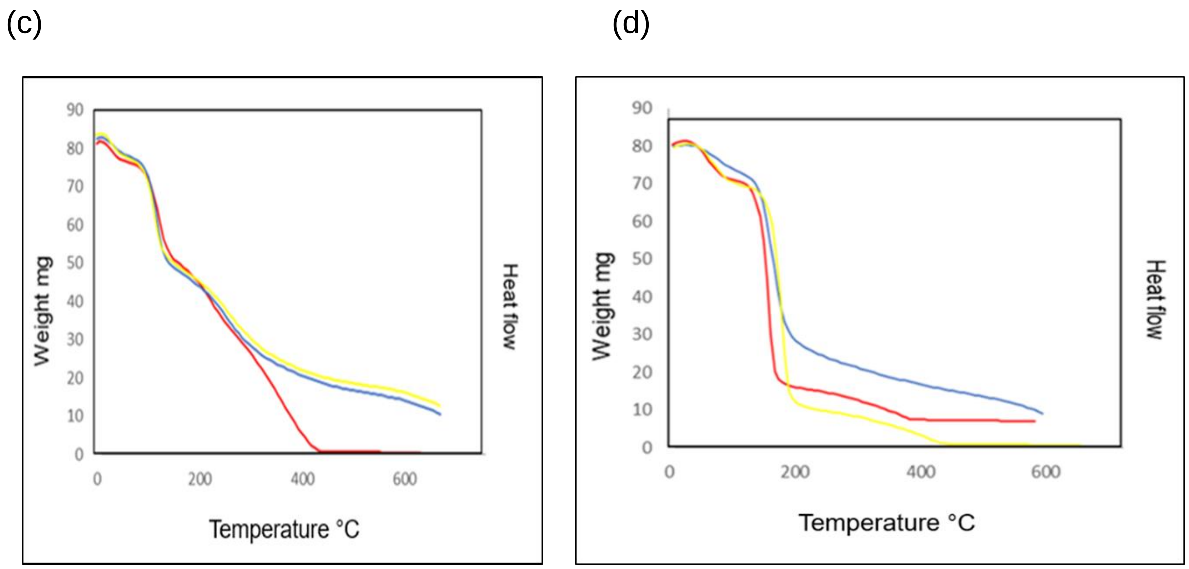


Figure 4.8: **(a) *E. grandis* BKP pretreated (10% (red), 20 % (blue) and 30% (yellow) of [AMIM][Cl]/ DMSO) at 120 °C, 12 h, (b) *E. grandis* UBKP pretreated in 10 % (red), 20 % (blue) and 30% (yellow) of [AMIM][Cl]/ DMSO at 120 °C, 12 h)**
(c) *E. grandis* BMP pretreated in (10 % (red), 20 % (blue) and 30% (yellow) of [AMIM][Cl]/ DMSO) at 120 °C, 12 h, (d) *E. grandis* (red) UBMP pretreated (10% (red), 20 % (blue) and 30% (yellow) of [AMIM][Cl]/ DMSO) at 120 °C, 12 h.

In Figure 4.8 (a) the thermogram of *E. grandis* bleached kraft pulp treated at 10 %, 20 %, 30 % [AMIM][Cl] / DMSO pretreatment is illustrated. There was a common trend of three mass loss steps for all three [AMIM][Cl]/DMSO pretreatment conditions. This was similar to the results obtained by (Poletto, 2010). The initial mass loss of the *E. grandis* sample occurred at 100 °C, due to the evaporation of water adsorbed in the sample.

A slightly slow degradation and decomposition of lignin was observed between 210°C - 300°C. Cellulose degradation occurred between 250°C -500°C (Kim, *et al*., 2006). Between 275°C -350 °C all pulp samples had a curve peak which indicated a cleavage of glyosidic linkage of cellulose (Kim, *et al*., 2006). The third curve caused by char oxidation, which occurred between 400 °C (10%) to 600°C, prior to the formation of CO_2, H_2O, and CO (Barneto, *et al*., 2011 ; Soares, *et al*., 1995). As a result, the most important mass loss % (s) occurred between 200 °C (75%), 300 °C (30%) and 600°C (10%). The thermal curves observed were associated with thermal degradation of cellulose, hemicelluloses and lignin of the treated pulp. The bleached kraft pulp at 10 % [AMIM][Cl]/ DMSO pretreatment had an average mass loss % of (30%), at 20% [AMIM][Cl]/ DMSO pretreatment with an average mass loss % of (28%) and at 30 % [AMIM][Cl]/ DMSO pretreatment with an average mass loss % of (65%), at temperatures between 275°C -350 °C.

Figure 4.8 (b) illustrates the thermogram of *E. grandis* unbleached kraft pulp at 10 %, 20 %, 30 % [AMIM][Cl]/ DMSO pretreatment. The thermal curves which are associated with thermal degradation of hemicelluloses and cellulose were observed at 190 °C (65 %), 220 °C (25%) and 600 °C (5%). The unbleached Kraft pulp at 10 % [AMIM][Cl]/DMSO pretreatment had an average mass loss % of (55%), at 20% [AMIM][Cl]/DMSO pretreatment with an average mass loss % of (60%) and at 30 % [AMIM][Cl]/ DMSO pretreatment with an average mass loss % of (35%).

Figure 4.8 (c) illustrates the thermogram of *E. grandis* bleached mechanical pulp treated at 10 %, 20 %, 30 % [AMIM][Cl]/ DMSO pretreatment. The thermal curves which are associated with thermal degradation of hemicelluloses and cellulose were observed at 100 °C (50%), 150 °C (45%), 200 °C (40%) and 300 °C (30%).The treated *E. grandis* bleached mechanical pulp at 10 % [AMIM][Cl]/ DMSO pretreatment had an average mass loss % of (60%), at 20% [AMIM][Cl]/ DMSO pretreatment with an average mass loss % of (65%) and at 30 % [AMIM][Cl]/ DMSO pretreatment with an average mass loss % of (50%).

Figure 4.8 (d) illustrates the thermogram of *E. grandis* unbleached mechanical pulp treated at 10 %, 20 %, 30 % [AMIM][Cl]/ DMSO pretreatment. The thermal curves which are associated with thermal degradation of hemicelluloses and cellulose were observed at 100 °C (72%), 150 °C (72%), 200 °C (68%) and 400 °C (10%). The *E. grandis* unbleached mechanical pulp at 10 % [AMIM][Cl]/ DMSO pretreatment had an average mass loss % of (62%). At 20% [AMIM][Cl]/ DMSO pretreatment with an average mass loss % of (64%). At 30 % [AMIM][Cl]/ DMSO pretreatment with an average mass loss % of (70%). The highest mass % loss was observed in *E. grandis* unbleached mechanical pulp at 30 % [AMIM][Cl]/ DMSO pretreatment with an average mass loss % of (70%), at 20% [AMIM][Cl]/ DMSO pretreatment with an average mass loss % of (64%) and *E. grandis* bleached mechanical pulp at 20% [AMIM][Cl]/DMSO pretreatment with an average mass loss % of (65%), at temperatures between 275°C - 350 °C. Table 4.3 mass losses for each sample at 10, 20 and 30% IL/DMSO.

Table 4.3: Mass losses % for each sample at 10, 20 and 30% IL/DMSO

Pulp name	IL/DMSO dosages		
	10%	20%	30%
UBMP	62	64	70
BMP	60	65	50
UBKP	55	60	35
BKP	30	28	65

4.7.2 SEM of *E. grandis* treated samples

Figures 4.9 – 4.13 illustrate the SEM images of untreated and pre-treated *E. grandis* Kraft and mechanical pulp [AMIM][Cl]/ DMSO. Both IL pretreatment SEM images were recorded at optimum conditions (highest lignin content).

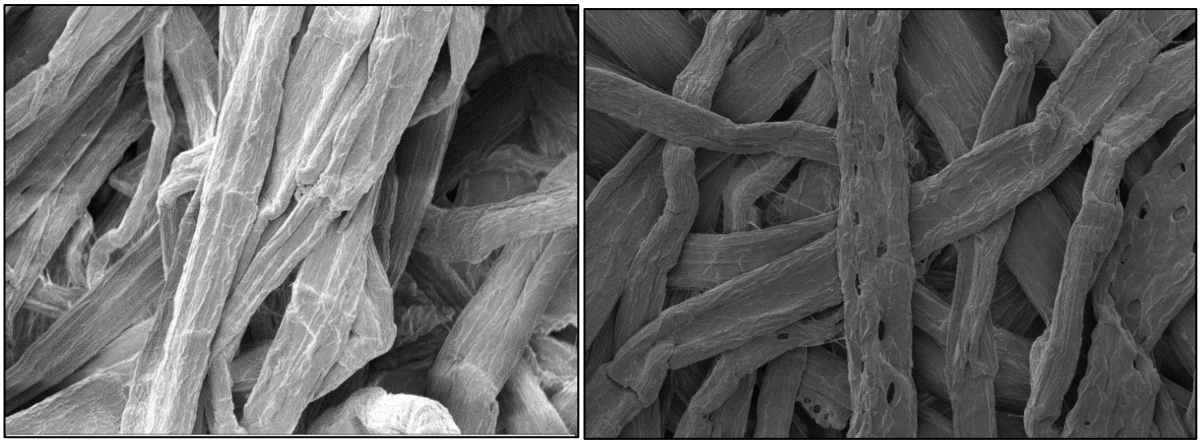


Figure 4.9: SEM images of *E. grandis* (a) bleached and (b) unbleached kraft pulp at different magnifications (500 x, 1.00 kx, 1.05 kx and 3.00 kx)

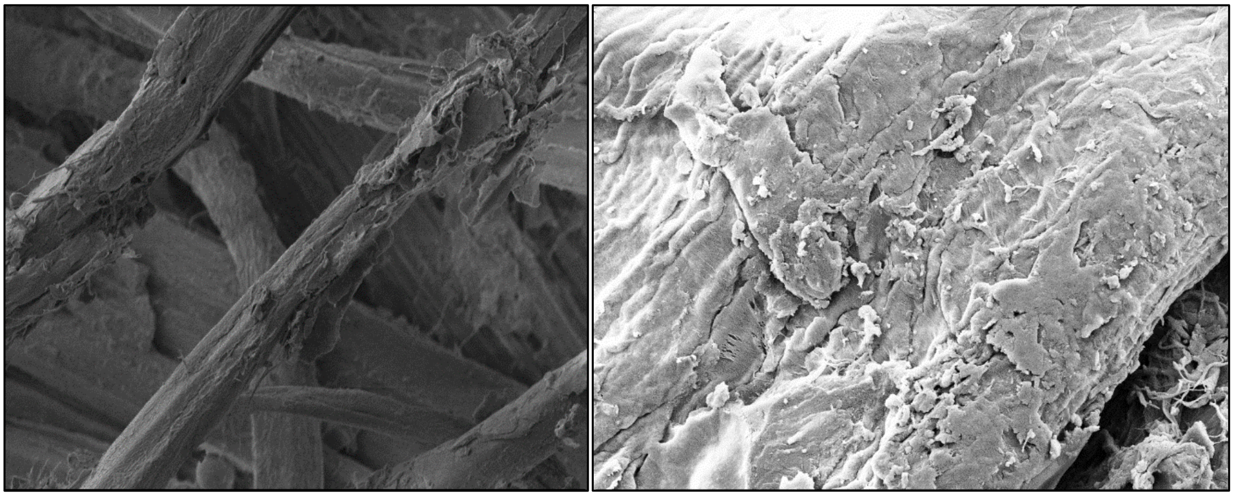


Figure 4.10: SEM images of treated *E. grandis* (c) unbleached and (d) bleached mechanical pulp at optimum conditions at 10 % ([AMIM][Cl]/ DMSO (120 °C, 12 h) at different magnifications (500 x, 1.00 kx, 1.05 kx and 3.00 kx)

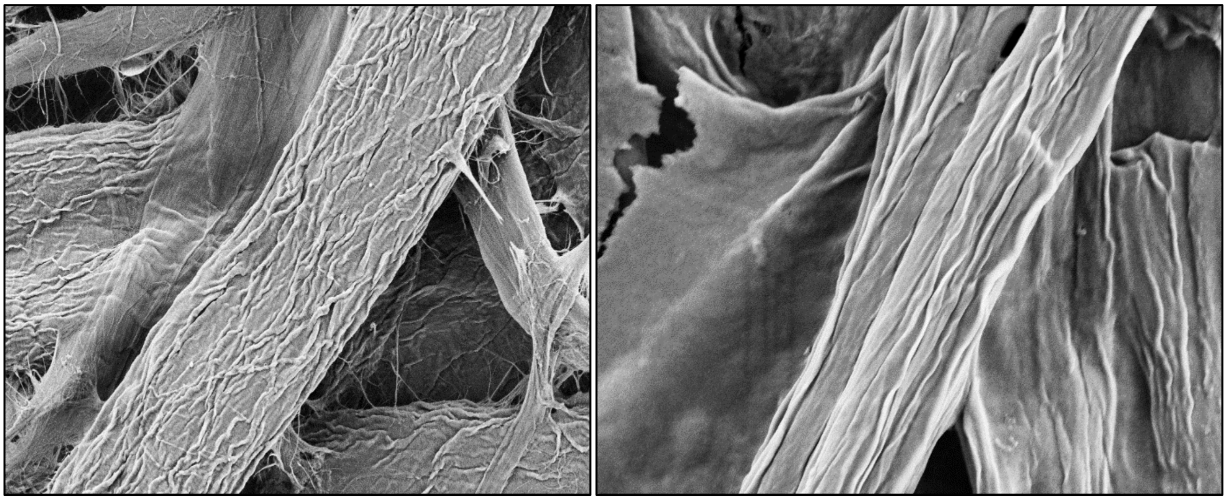


Figure 4.11: SEM images of treated *E. grandis* (e) unbleached and (f) bleached kraft pulp at optimum conditions treated at 20 % [AMIM][Cl]/ DMSO (120 °C, 12 h) at different magnifications (500 x, 1.00 kx, 1.05 kx and 3.00 kx)

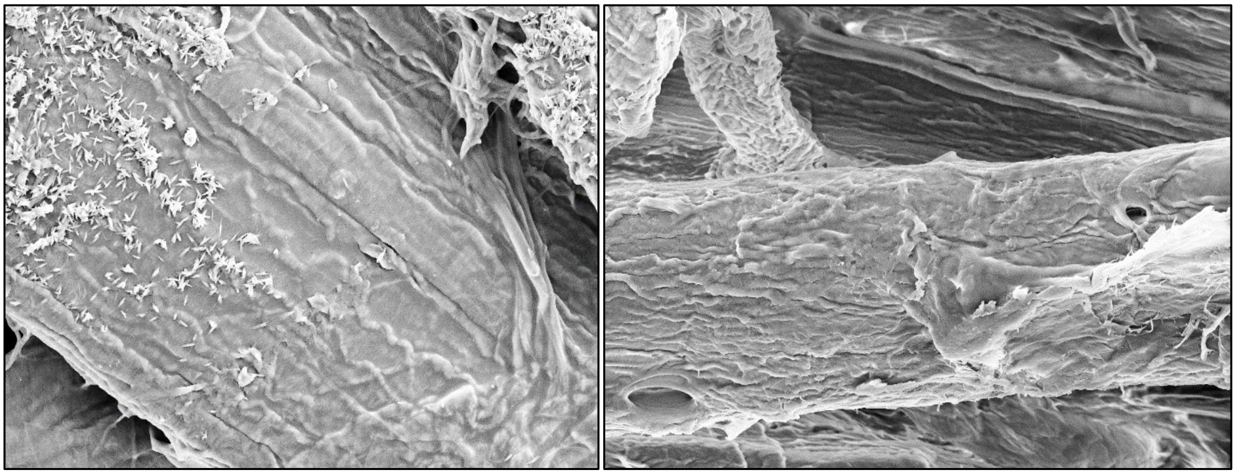


Figure 4.12: SEM images of treated *E. grandis* (g) unbleached and (h) bleached mechanical pulp at optimum conditions treated at (30% [AMIM][Cl]/ DMSO (120 °C, 12 h) at different magnifications (500x, 1.00 kx, 1.05 kx and 3.00 kx)

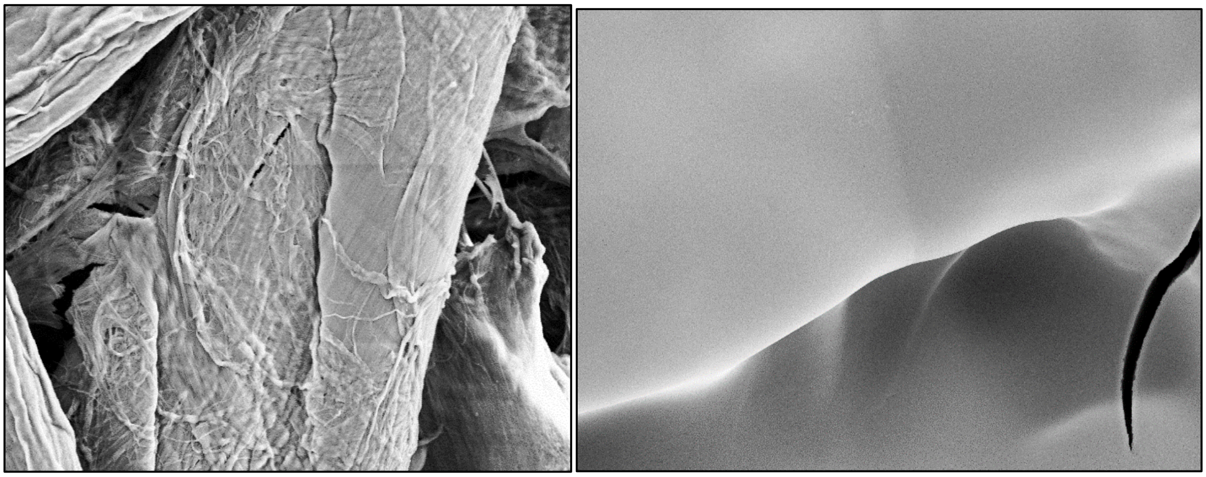


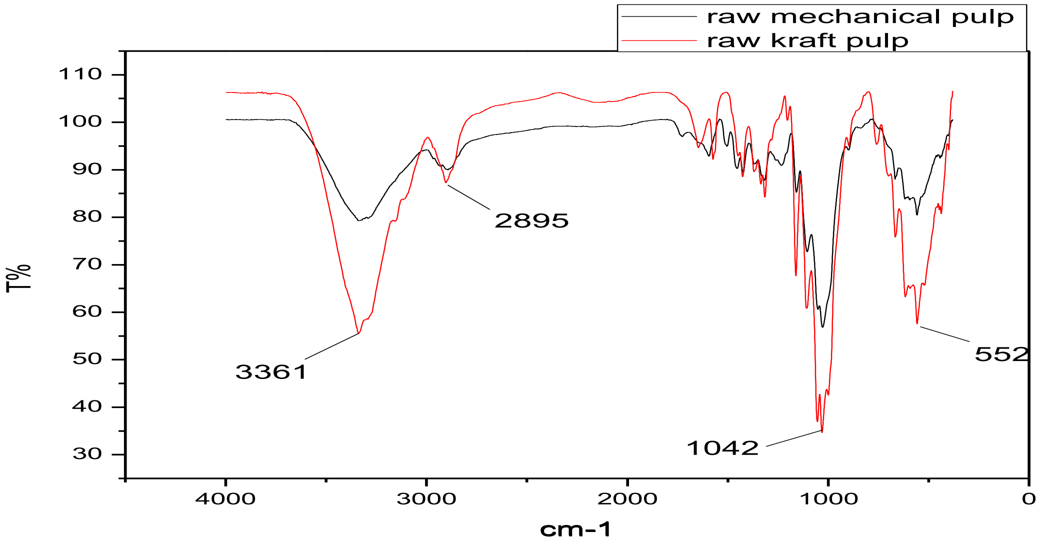
Figure 4.13: SEM images of treated *E. grandis* (i) unbleached kraft pulp and (j) bleached kraft pulp at optimum conditions treated at (30 % [AMIM][Cl]/ DMSO 120°C,12 h) at different magnifications (500 x, 1.00 kx, 1.05 kx and 3.00 kx)

The SEM images of *E. grandis* hardwood (Figure 4.9 – 4.10) showed solid, ordered and inflexible fibril structures. After the dissolution process was completed the unbleached mechanical and bleached kraft pulp samples exhibited huge structural change for 20% and 30% [AMIM][Cl] / DMSO pretreatment. The structural shape for both IL treated UBMP and UBKP samples became loose, untangled disorderedly, showed wavy diminishing fibers and increasing brightness in Figures 4.11 – 4.13. This indicated the removal of lignin and an increase in cellulose crystallinity, which was further confirmed by FTIR-ATR and XRD. The results are similar to the results obtained by Oudia (2007) for biomass. The BKP in comparison to the UKBP, were loosely packed, brighter than the fibers seen in UKBP. There were multiple torn up fibre seen in BKP due to bleaching process and IL/DMSO pretreatment. These observations implied a removal of lignin, as there were no fibre dark in colour.

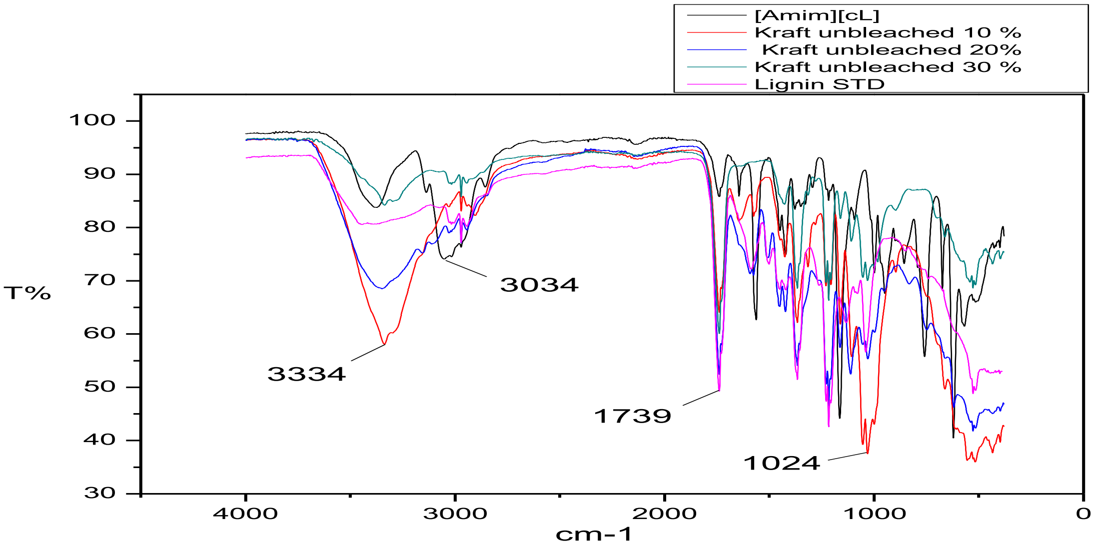
4.7.3 FTIR-ATR of *E. grandis* treated samples

The FTIR-ATR spectrums of untreated *E. grandis* Kraft and mechanical pulp pretreated with [AMIM][Cl] / DMSO are given in Figure 4.14 (a) – (d) below.

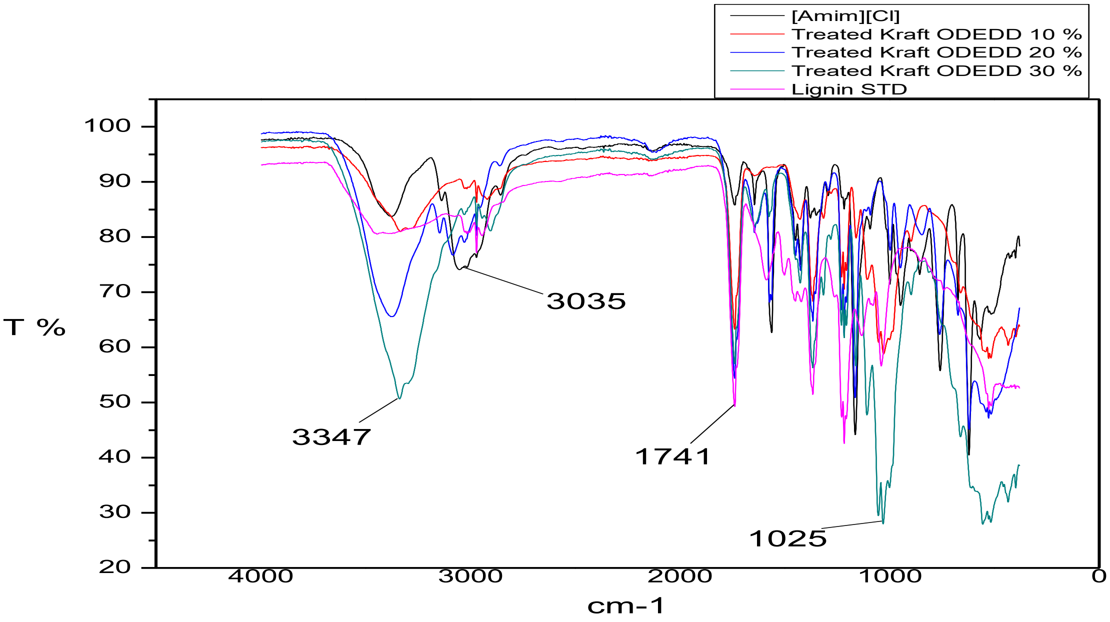
(a)



(b)


[Amim][cL]
Kraft unbleached 10 %
Kraft unbleached 20%
Kraft unbleached 30 %
Lignin STD
T%
100
90
80
70
60
50
40
30
4000
3000
2000
1000
0
cm-1
3334
3034
1739
1024

(c)


[Amim][Cl]
Treated Kraft ODEDD 10 %
Treated Kraft ODEDD 20 %
Treated Kraft ODEDD 30 %
Lignin STD
T %
100
90
80
70
60
50
40
30
20
4000
3000
2000
1000
0
cm-1
3347
3035
1741
1025

(d)

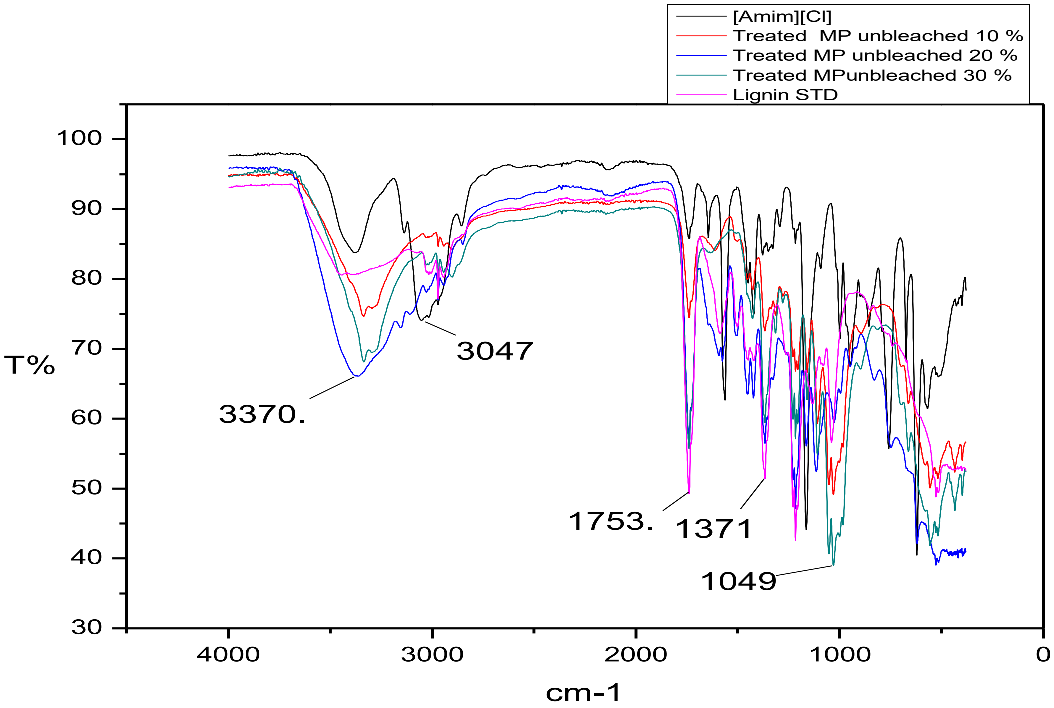


Figure 4.14: (a) *E. grandis* unbleached kraft pulp treated and unbleached mechanical untreated pulp, (b) *E. grandis* unbleached kraft pulp treated (10 %, 20%, 30 %([AMIM][Cl]/ DMSO) at 120 °C, 12 h) and lignin standard. (c) *E. grandis* bleached Kraft pulp treated (10%, 20 %, 30 % ([AMIM][Cl]/ DMSO) at 120 °C, 12 h) and lignin standard. (d) *E. grandis* unbleached mechanical pulp treated at (10 %, 20 %, 30 % ([AMIM][Cl]/ DMSO) at 120 °C, 12 h), and lignin standard

` Figure 4.14 (a), the UBMP and UBKP absorption vibration peaks were observed on identical wavenumber regions even though the UBKP peaks seem to be much broader and narrow compared to UBMP spectra. After the IL/DMSO pretreatment all pretreated sample had a small C-H plane deformation of aromatic, S=O symmetrical stretching vibration seen at 1024 cm $^{-1}$ region identified with a long and partially narrow peak, seem be constant in all treated samples and untreated pulp samples.

In Figure 4.14 (b), a distinct change around 4000 cm^{-1} – 3400 cm^{-1}, the O-H group peak seen at 3334 cm^{-1} regions seem to have decreased rapidly in unbleached UBKP treated at 30% IL/DMSO pretreatment. This significant observation indicated a removal of the phenolic groups' chains coming from the lignin composition. There was also a slight shift of the small peak next to the broad OH phenolic peak at 3334 cm^{-1}. The small peak shifted from 2895 cm^{-1} to 3034 cm^{-1}. This phenomenon is also known as hypochromic shift. This unique peak denoted the presence of C-H stretching of akyls groups.

The ambiguous broadly shaped peak seen at 3334 cm^{-1} regions at 30 % pretreated bleached kraft pulp seemed not to be affected by the IL/DMSO pretreatment.

This occurrence was due to unexpected impurities and contaminations that were not in relation to lignin, hemicellulose and cellulose composition. Some pretreated samples may deposit in a form that contains the solvent as "solvent of crystallization" (Chalmer, 2006).

Figure 4.14 (c), there was a noticeable sharp narrow peak at 1740 cm^{-1} in bleached treated kraft sample, which was not present before the IL/DMSO pretreatment. This peak hinted the presence of C=O non-conjugate stretching vibration in the pretreated pulp. The appearance of this absorption peak was due to the breaking of the lignin layer caused by IL pretreatment. There was low to none intensities detected around 1268 cm^{-1} and 1230 cm^{-1} for all *E. grandis* treated samples. It's presence would have hinted the presence of guaiacyl derivatives (C-O stretch in lignin and C-O linkage in guaiacyl aromatic methoxyl groups (Pandey, 2003), suggestively stating that there was indeed a significant amount of lignin removed after the IL/DMSO pretreatment .

Figure 4.14 (d), the OH functional groups at 3370 cm^{-1}, seem to be much broader and smoother at 20 % IL pretreatment on unbleached mechanical pulp. In comparison to UBKP and BKP, with a slight shift of OH group from 3334 cm^{-1} to 3370cm^{-1}. There was also a lignin removal observed at 30 % IL pretreatment upon UBMP, with comparison to the lignin standard spectra at 1371 cm^{-1}, 1753 cm^{-1} and 3370 cm^{-1} regions. This indicated that 30% IL pretreatment dissolved, broke down the guaiacyl and syringyl functional groups of lignin content in unbleached mechanical pulp with success.

The breaking down of methoxyl, hydroxyl functional groups around the regions; 1371cm^{-1}, 1753 cm^{-1} and 3370 cm^{-1} resulted in weakening the lignin crosslinked chains of the β-O-4 acryl bond in the treated biomass. The syringyl and guaiacyl composition decreased with the decrease in lignin content. There was a low to none intensities detected around 1268 cm^{-1} and 1230 cm^{-1} for all *E. grandis* treated samples. This would have hinted the presence of guaiacyl derivatives (C-O stretch in lignin and C-O linkage in guaiacyl aromatic methoxyl groups (Pandey, 2003), suggestively stating that there was indeed a significant amount of lignin removed after the IL pretreatment . The O-H group absorption peak at (3600 cm^{-1} – 3200 cm^{-1}) for treated kraft pulp were a bit broad and longer compared to the ones observed in mechanical treated pulp. The occurrence was not due to the kraft treated sample having an abundant quantity of phenolic groups or a high lignin content, but merely due to an unexpected presence of impurities or contamination. Residual solvents in the pretreated samples cast from bleaching and kraft process solution was a result of impurities. As a result, attributed absorption bands are usually readily observable and give misleading information about the treated sample.

In some treated samples may deposit in a form that contains the solvent as "solvent of crystallization"(Chalmers, 2006). The [AMIM][Cl] ionic liquid pretreatment 30% was successful at reducing some degree of lignin content contained in unbleached mechanical pulp by attacking and breaking the methoxyl, hydroxyl functional groups around the regions; 1371 cm^{-1}, 1753 cm^{-1} and 3370 cm^{-1}. This resulted in weakening the lignin cross-linked chains of the beta-O-4 acryl bond in the treated biomass. The syringyl and guaiacyl composition decreased with the decrease in lignin content.

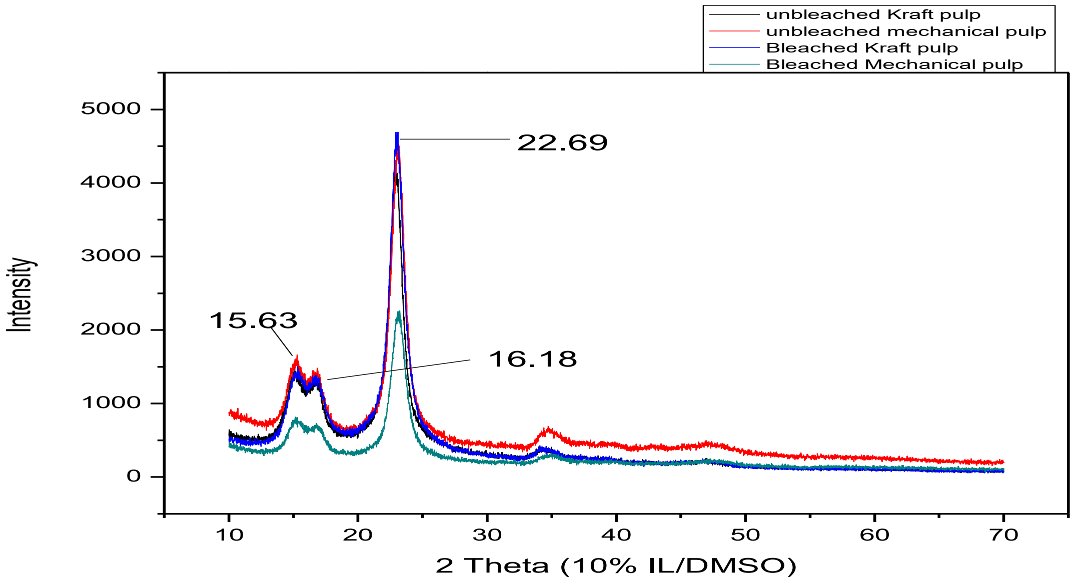
4.7.4 XRD of *E. grandis* treated samples

The XRD diffractograms for UBKP, BKP, UBMP and BMP are given below and, that show the combined XRD diffractograms for all four samples at increasing [AMIM][Cl]/DMSO solution dosage percentage. Figure 4.15 (a), is the illustration of the XRD diffractogram for samples at 10 % IL solution, (b), is the illustration of the XRD diffractogram for pulp samples at 20 % IL solution and (c), is the illustration of the XRD diffractogram for pulp samples at 30 % IL solution. At 10 % IL pretreatment, the characteristic cellulose peaks were observed around 2θ = 15°, 16°, co-elution occurrence of a short intensity and narrow shape peak was seen at 2θ = 23°. At 20 % IL pretreatment, a similar trend of peak elution as well as shape form was seen.

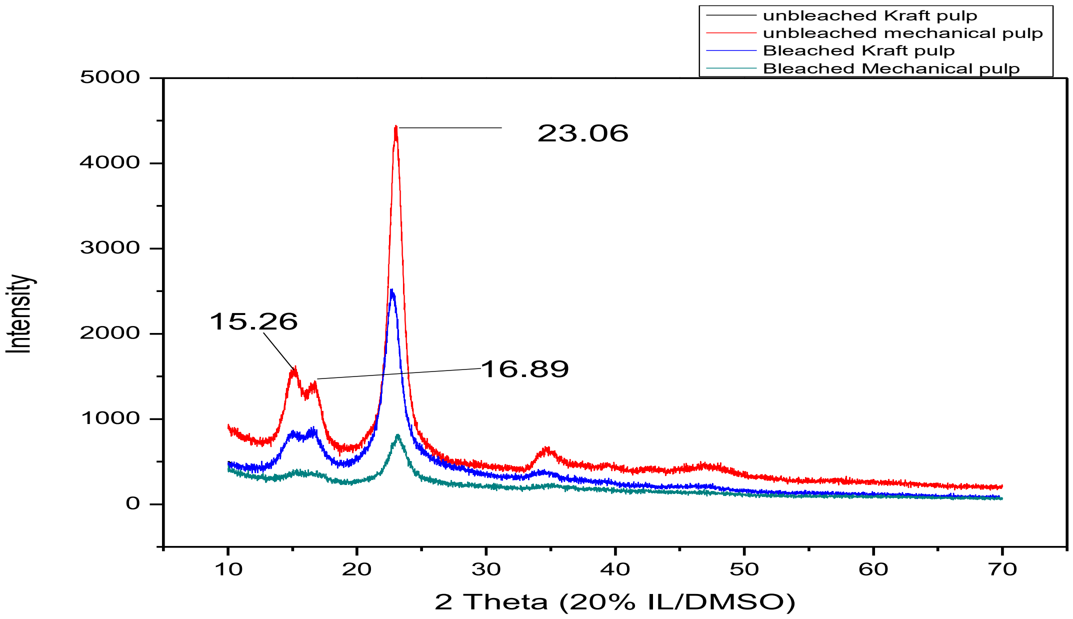
These phenomena suggestively indicated that all pretreated sample have of similar cellulose behaviour around the region of 2θ = 15°, 16°, 23°.

There was also a change and increase in the relative intensity and width of the amorphous peaks which significantly indicated a decreased in the crystallinity.

(a)


unbleached Kraft pulp
unbleached mechanical pulp
Bleached Kraft pulp
Bleached Mechanical pulp
Intensity
5000
4000
3000
2000
1000
0
10
20
30
40
50
60
70
2 Theta (10% IL/DMSO)
22.69
15.63
16.18

(b)


unbleached Kraft pulp
unbleached mechanical pulp
Bleached Kraft pulp
Bleached Mechanical pulp
Intensity
5000
4000
3000
2000
1000
0
10
20
30
40
50
60
70
2 Theta (20% IL/DMSO)
23.06
15.26
16.89

(c)

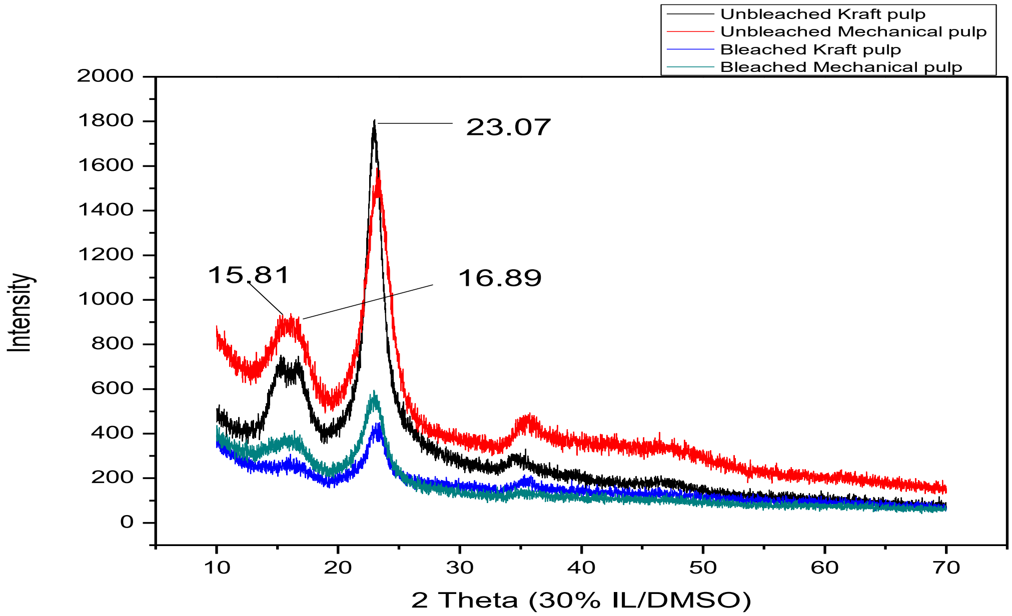


Figure 4.14 (a) ***E. grandis*** **unbleached, UBMP, UBKP, BKP and BMP pretreated (10% [AMIM][Cl] / DMSO) at 120 °C, 12 h, (b)** ***E. grandis*** **UBMP, UBKP, BKP and BMP pretreated (20 % [AMIM][Cl]/DMSO) at 120 °C, 12 h, (c)** ***E. grandis*** **UBMP, UBKP, BKP and BMP pretreated (30 % ([AMIM][Cl]/DMSO) at 120 °C, 12 h**

The alteration of cellulose from cellulose I to cellulose II normally takes place in the amorphous region and slowly becomes crystals as the dimensions gradually become increasingly larger (Okano, 1985). After deconvolution, three bands were observed, namely; 15 °C (2θ) reflection was represented the (101) crystallographic plane, 16° (2θ) reflection was stated as the amorphous phase, which is the cellulose I and the 23° (2θ) was allocated to the cellulose II (Popescu, *et al*., 2007).

Where the lattice diffraction of the maximum intensity of the well-defined peak was expressed as $I_{tot,}$ at theta region 2θ = 23° and the I_{am} which referred to the two broad peaks at 2θ = 15° and 16°. According to (Segal, 1962), the crystallinity index (CrI) of the regenerated cellulose and MCC should be calculated using Bragg's law equation (3.13) below.

$$CrI = \frac{I_{tot} - I_{am}}{I_{tot}} x\ 100 \tag{3.13}$$

As a result, the crystallinity index of the treated regenerated cellulose pulp was determined by using the equation (3.13). The crystallinity index values of 10%, 20 % and 30 % [AMIM][Cl] /DMSO pretreated regenerated cellulose pulp for cellulose I; 10% IL pretreatment of UBMP, BMP,UBKP and BKP are : 68.09% , 52.62%, 62.08% and 67.09 %, respectively. At 20% IL pretreatment of UBMP, BMP,UBKP and BKP are: 68.09 %, 52.62% , 67.09 % and 67.09 % respectively. At 30%: IL pretreatment of UBMP, BMP,UBKP and BKP are: 72.03 %,71.56 %, 72.02 %, 72.02 %, respectively. In literature, *E. grandis* hardwood crystallinity values for cellulose I and cellulose 72.7%, 76.8% (Popescu, *et al.*, 2011), respectively. As a result, IL pretreatment at 30 % crystallinity ranged from 71.56% - 72.03%, there was an agreement with literature crystallinity index values and the regenerated cellulose TGA results.

The highest mass % loss was observed in *E. grandis* unbleached mechanical pulp at 30 % [AMIM][Cl]/ DMSO pretreatment with an average mass loss % of (70%). This was a clear indication of hemicellulose and lignin removal (Kim and Lee, 2005), caused by [AMIM][Cl]/DMSO pretreatment on *E.grandis* pulp.

4.7.5 UV/Vis of *E. grandis* treated samples

The UV/Vis results of *E. grandis* treated samples are reported in Table 4.4 together with amount of AIL and Total lignin.

Table 4.4: UV/Vis results, AIL and Total lignin of *E. grandis* treated samples

Pulp name	ASL %	AIL %	Total lignin%	IL % dosage
UBMP	5.09	22.76	27.85	20
BMP	7.2	18.81	26.01	20
UBKP	10.62	15.05	25.67	20
BKP	16.91	8.11	25.02	20
BMP	7.54	18.55	26.09	20
UBKP	11.84	14.45	26.29	20
UBMP	5.39	25.16	30.55	30
BMP	7.41	20.52	27.94	30
UBKP	10.55	16.39	26.94	30
BKP	15.12	10.16	25.29	30
UBKP	14.01	14.45	28.46	30
UBMP	6.81	22.29	29.10	30
UBMP	7.04	20.99	28.03	10
BMP	8.08	18.75	26.83	10
BKP	19.27	7.67	26.95	10
BKP	12.56	13.4	25.99	10

Figure 4.16 is a photograph of the filtrate obtained from: a) bleached kraft, b) unbleached kraft and c) unbleached mechanical, respectively. The BKP filtrate was clear in colour, the UKBP was yellowish which suggested a presence of low amount of soluble lignin, the UBMP and BMP filtrate was dark brown in colour which indicated a high amount of soluble lignin was present.

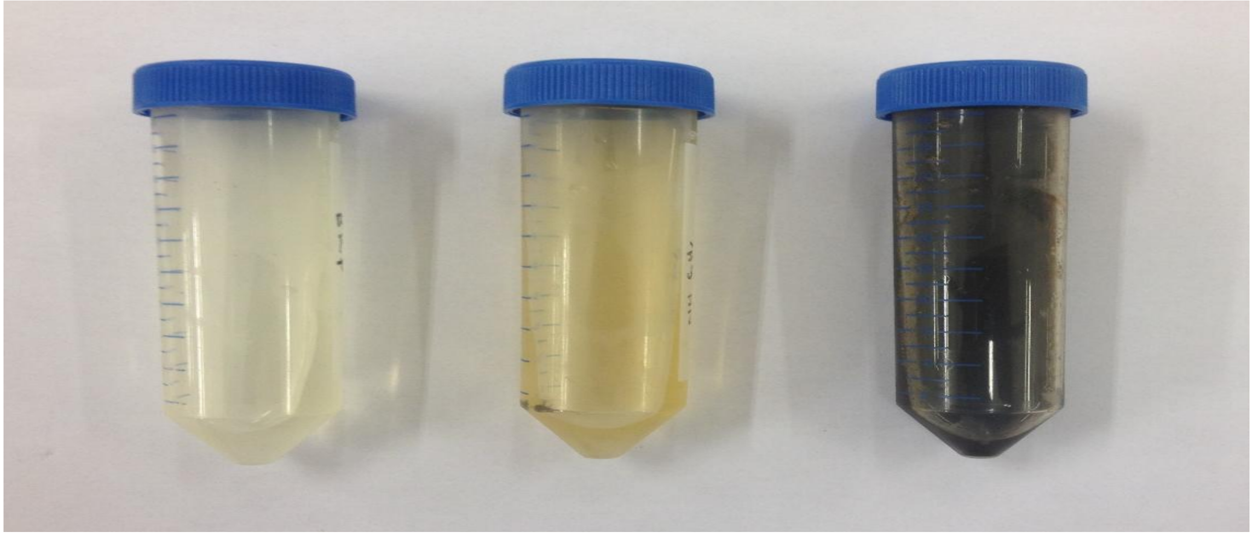


Figure 4.16: Photograph of the filtrate obtained from: a) bleached kraft, b) unbleached kraft and c) unbleached mechanical

The lignin % recovery for UBMP, BMP, BKP and UBKP pretreated samples at 10%, 20% and 30% IL/DMSO pretreatment was compared with literature vaules and properly intrepreted in section 4.6.3.

4.7.6 Py GC/MS of *E. grandis* treated samples

The S/G ratio for all *E. grandis* pulp was calculated using equation (3.14). The ionic liquid pretreatment was divided into three percentage dosage sets 10%, 20% and 30% [AMIM][Cl]/DMSO pretreatment. Table 4.5 below illustrates the literature values of S/G ratio in pretreated *E. grandis* samples. The S/G ratio in each sample was a theoretical indication of how much lignin content was present in all pulp samples composition, as illustrated in Table 4.6 below. Kappa number was done for UBKP samples but not for UBMP and BMP samples. Hence, UBMP and BMP's lignin content had to be quantified by means of S/G ratio determination. In Table 4.7 illustrates the ionic liquid dosage percentage versus total sum of S/G ratio for each sample batch which was done at 550 °C pyrolysis. However, the results obtained for treated mechanical and treated kraft pulp samples S/G ratio in both bleached and unbleached mechanical pulp showed a very high lignin yield compared to bleached and unbleached kraft pulp.

Table 4.5: Literature values of S/G ratio in pretreated *E. grandis* pretreated samples

Sample	Temp	S/G ratio values	Ref
Eucalyptus grandis material	450 C	3.1	(Alves, *et al.,* 2009)
	550°C	2.7.	(Alves, *et al.,* 2009)
	550°C	2.7	(Rencoret, Gutierrez and del Rio, 2007)
		3.0	(Lima, *et al.,* 2008)

Table 4.6: S/G ratio of all pretreated samples

E. grandis sample		unbleached kraft pulp			bleached kraft pulp			unbleached mechanical pulp			bleached mechanical pulp		
Compounds	**origin**	**10%**	**20%**	**30%**	**10%**	**20%**	**30%**	**10%**	**20%**	**30%**	**10%**	**20%**	**30%**
Guaiacol	GL	.96		0.35	6.91	6.91	6.96	2.28			2.18	2.18	0.93
4-Methylguaiacol	GL			0.05				3.68			9.78	2.48	1.64
4-Ethylguaiacol	GL		0.65								1.71	0.65	
3-methoxycatechol	ML		1.25						1.41	1.41			
4-Vinylguaiacol	SL	4				3.82	4	1.36			3.97	1.25	1.06
Syringol	SL	1.4			0.48	1.39	1.4	0.69			1.47		1.11
3,4-Dimethoxyphenol	GL	2.25			2.18	2.18	2.25	0.19			1.44		
Eugenol	GL	0.95	3.21	0.21	2.86	0.95	0.95	0.94			0.98		
cis-Isoeugenol	GL	2.53	2.39	2.1	2.51	6.88	6.93	0.55			0.77	3.21	
Vanillin	GL	1.79		0.7	1.77	1.25	1.26		0.54	0.91	0.41	2.39	
trans-Isoeugenol	GL	0.56		0.38	0.56	1.95	1.96	3.82	0.24		0.51		
4-Methylsyringol	SL	10.16		3.46	10.08	0.56	0.71	0.31	2.42	2.42			4.23
Unidentified												0.78	
Homovanillin	GL	12.84	2.07	2.34	12.75	12.75	12.84	0.35	0.98	0.84	2.39	2.07	0.73
Acetoguaiacone	GL		0.44	0.45				0.87	0.49	0.49	2.86	0.44	0.8
4-Hydroxy-3-methoxyacetophenone													
4-Ethylsyringol	SL	6.81	2.13	3.27	6.75	6.75	6.81						
Guaiacylacetone	GL	2.11		2.68	12.16	1.99	2.11	0.38	7.06	2.36		2.13	
4-Vinylsyringol	SL		0.22	5.18					0.91	0.91		0.5	
4-Allylsyringol	SL	0.31	0.46		0.31	0.31	0.31		3.92	3.06			
4-Propylsyringol	SL	2.28	1.83	8.04	2.27	2.27	2.28	1.22	0.67	0.67		0.22	
cis-4-Propenylsyringol	SL	1.11	7	1.29	1.1	0.82	0.83	3.8	0.67	0.67		0.46	1.01
2- Levoglucosane													
Syringaldehyde	SL			9.55				2.05	0.62	0.62		1.83	0.82
trans-4-Propenylsyringol	SL		0.34		1.5	1.5	1.51	2.51	3.25	3.25		7.01	
homosyringaldehyde	SL	1.51		10.85					4.45	4.45			2.19
Acetosyringone	SL							2.96	0.93	0.93			0.93
Coniferaldehyde	GL		0.65	7.1					1.62	1.62		0.34	1.64
Syringylacetone	SL	1.64	1.25		1.63	1.63	1.64		0.87	1.83			
Propiosyringone	SL								1.71	0.34			
Synapaldehyde	SL	1.13			1.12	1.12	1.13		3.23	3.32			1.06
S/G	Ratio:	1.01	1.14	2.55	0.47	0.58	0.59	1.38	3.67	4.88	0.24	0.74	2.54

Table 4.7: Ionic liquid dosage percentage versus total sum of S/G ratio of treated sample pyrolyzed at 550 °C

Dosage	S/G			
	BKP	UBKP	UBMP	BMP
10 %	0.47	0.24	0.74	1.01
20 %	0.58	1.14	3.67	2.54
30 %	0.59	1.38	4.88	2.55

Lignin determination on kraft pulp was done by kappa number test, but lignin in mechanical pulp needed to be accounted for, hence a S/G ratio determination had to be done with the intention to identify the guaiacyl and syringyl belonging to lignin content, which were present in pulp after IL pretreatment. According to Samuel, *et, al* (2010), *Eucalyptus* milled Amur linden wood: lignin fraction obtained using [EMIM][Cl] at 120°C for 3 hr (MWL), lignin fractions obtained from [AMIM]Cl] pretreatment at 120°C for 3 hr (L_1) and lignin fraction directly extracted by 70% aqueous ethanol containing 1 M NaOH at 75°C for 3 hr without ILs pretreatment (AEL). The S/G ratios obtained from MWL, AEL and L1 were: 2.32, 3.03, and 3.29 respectively. The AEL had a higher S/G ratio than MWL. This suggested that the SL was mostly removed under bleaching and alkaline conditions. A better removal of GL usually occurs at 120°C IL pretreatment. The S/G ratio of L_1 was much higher as compared to MWL and AEL, which points toward a breakdown of GL in comparison to SL during IL pretreatment step (Varanasi *et, al.* 2010). This might be the reason for the slightly higher S/G ratio of L_1 (Xu, *et, al.* 2015).

The S/G values for 10% IL/DMSO pretreatment of BKP, UBKP,UBMP and BMP are: 0.47%, 0.24%, 0.74% and 1.01%, respectively. The highest percent S/G% was obtained for the UBMP (0.74%). The S/G ratio values for 20% IL/DMSO pretreatment of BKP, UBKP,UBMP and BMP are: 0.58%, 1.14%, 3.67% and 2.54%, respectively. The highest percent S/G% was obtained for the UBMP (3.67%). The S/G ratio values for 30% IL/DMSO pretreatment of BKP, UBKP,UBMP and BMP are: 0.59%, 1.38%, 4.88% and 2.55%, respectively. The highest percent S/G% was obtained for the UBMP (3.67%). The S/G ratio of BMP, UBMP at 20% IL/DMSO pretreatment and UBMP at 30% IL/DMSO pretreatment were higher then literature values. Therefore, indicated an effective break down of the GL in the pulp. The BKP and UBKP had lower values in comparison to literature values. The reason maybe, there was a small amount of phenol and alkyl phenols which were identified in the BKP and UBKP during pyrolysis, indicating that few methoxyl groups were removed. Hence, due to higher reactivity of the GL of the UBMP and BMP samples between 20% - 30% ionic liquid pretreatment pulp, the BMP and UBMP are much easier to be delignified pulp. This concurs with the rate of delignification increases with higher S/G ratio, along with an increase in sugar release (Reina, *et al.*, 2014).

Hypothetically, an alternative approach to produce high regenerated cellulose recovery. The *E. grandis* wood chips can be mechanically pulped to loosen the pulp fibres. Afterwards, the pulp is IL pretreated for the delignify of the pulp. As a result, a pulp having a high S/G ratio after IL pretreatment will require minimal bleaching chemical consumption for cellulose pulp production. As a result, minimal usage of toxic costly chemicals and chemical disposal.

4.7.7 HPLC results of *E. grandis* treated samples

The unbleached kraft pulp had an average of 17.38 % of xylose content and an average of 4.84% for unbleached mechanical pulp samples. The concentration % of the pretreated samples were calculated using equation (2.8) and a summarized carbohydrate composition of the *E. grandis* treated sample was illustrated in Table 4.8 below.

Table 4.8: Summary of carbohydrates composition of *E. grandis* treated sample

Carbohydrates	Treatment	Experimental work				Literature review	Reference
		TUBK	TBKP	TBMP	TUBM		
Fucose	Klason test	-	-	-	-	0.12 %	(Lima *et al.,* 2013) Klason test with two steps of HCL %, 4% NaOH Pretreatment
Rhamnose		-	-	-	-	0.34 %	
Arabinose		-	-	-	-	1.14 %	
Galactose		-	-	-	-	1.19 %	
Glucose		16 %	14%		-	39.55 %	
Xylose		7.8	7.7%	5.6%	6.6%	8.64 %	

The 30% [AMIM][Cl]/DMSO pretreatment yield the highest carbohydrates content in pretreated samples. The xylose standards graph gave a reliable correlation co-efficient of $R^2 = 0.9955$. The glucose standards graph gave a correlation co-efficient of $R^2 = 0.9996$, both illustrated in Appendix 1. The carbohydrates content consists of six c-c carbon sugars: fucose, rhamnose, arabinose, galactose, glucose and xylose. From the six sugars, five were either not detectable or below limit of detection and below limit of quantification except for xylose content. The average xylose content of the pretreated *E. grandis* UBKP, BKP, BMP and UBKP were: 7.8%, 7.7%, 5.6% and 6.6%, respectively. In comparison to literature review, the xylose content on all pretreated samples was less by (2-3) % in concentration. This indicated that the [AMIM][Cl]/DMSO pretreatment had a (2-3) % effect on the removal of xylose belonging to the six sugars that make up hemicelluloses' composition. As to, using conventional chemical pretreatment of high cost and toxic disposal, when properly modified and enhance.

Chapter 5

CONCLUSION

The highest recovery of cellulose was obtained for 30% IL pretreated BKP (67.43%). Whereas the highest loss was observed in *E. grandis* unbleached mechanical pulp at 30% [AMIM][Cl]/DMSO pretreatment with an average mass loss of 70%. The structural shape for both IL treated UBMP and UBKP samples became loose, untangled disorderedly, showed wavy diminishing fibers and increasing brightness. This indicated the removal of lignin and increase of cellulose crystallinity. This was further confirmed by FTIR-ATR and XRD. The 30% [AMIM][Cl] ionic liquid pretreatment was seen to be the most successful IL pretreatment at reducing lignin content (29.23%) contained in UBMP by attacking and breaking the methoxyl, hydroxyl functional groups. This resulted in weakening the lignin cross-linked chains of the beta-O-4 acryl bond in the treated biomass. The 30% IL/DMSO pretreatment crystallinity ranged from 71.56 % - 72.03 % and was in an agreement with literature crystallinity index values. The kraft pulp gave the highest CrI for both bleached and unbleached kraft pulp. This was a clear indication of hemicellulose and lignin removal cause by [AMIM][Cl]/DMSO pretreatment on *E. grandis* pulp. The S/G ratio values of pretreated UBMP at 20% and 30 % IL/DMSO pretreatment were much higher than those from literature values. This indicated that after the IL/DMSO pretreatment there was an increase in the ease of delignification of the *E. grandis* samples.

Higher S/G values indicated an increase in sugar released. It was therefore confirmed that at 30% IL/DMSO pretreatment, there was a high recovery of regenerated cellulose, hemicellulose and lignin content. In conclusion the kraft pulping was the most effective method for the yield of cellulose after the [AMIM][Cl]/ DMSO pretreatment.

RECOMMENDATIONS

These finding significantly indicates that at 30% IL/DMSO pretreatment on *E. grandis* dissolution, followed by Klason test may possibly remove high xylose content in *E. grandis* kraft pulp. This showed a good pulp yield, with satisfactory removal of lignin and hemicellulose on unbleached and bleached mechanical pulp. Also, the IL pretreatment for the kraft can be used for higher cellulose yield and also as an alternative approach for the dissolution of biomass, instead of using conventional chemical pretreatment that require high cost purchase and produce toxic disposal.

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Appendix 1

The composition of arabinose, galactose, rhamnose and fucose on both bleached treated kraft samples and bleached treated mechanical pulp was not detectable. Two graphs were plotted using mixed standards of lowest to highest concentration. The xylose standards graph gave a reliable correlation co-efficient of $R^2 = 0.9955$, illustrated in Figure 4.17 below. The glucose standards graph gave a correlation co-efficient of R^2

= 0.9996 illustrated in Figure 4.18. The concentration % of the pretreated samples were calculated using equation (2.4) and a summarized carbohydrates composition of the *E. grandis* treated sample was illustrated in Table 5.12 below.

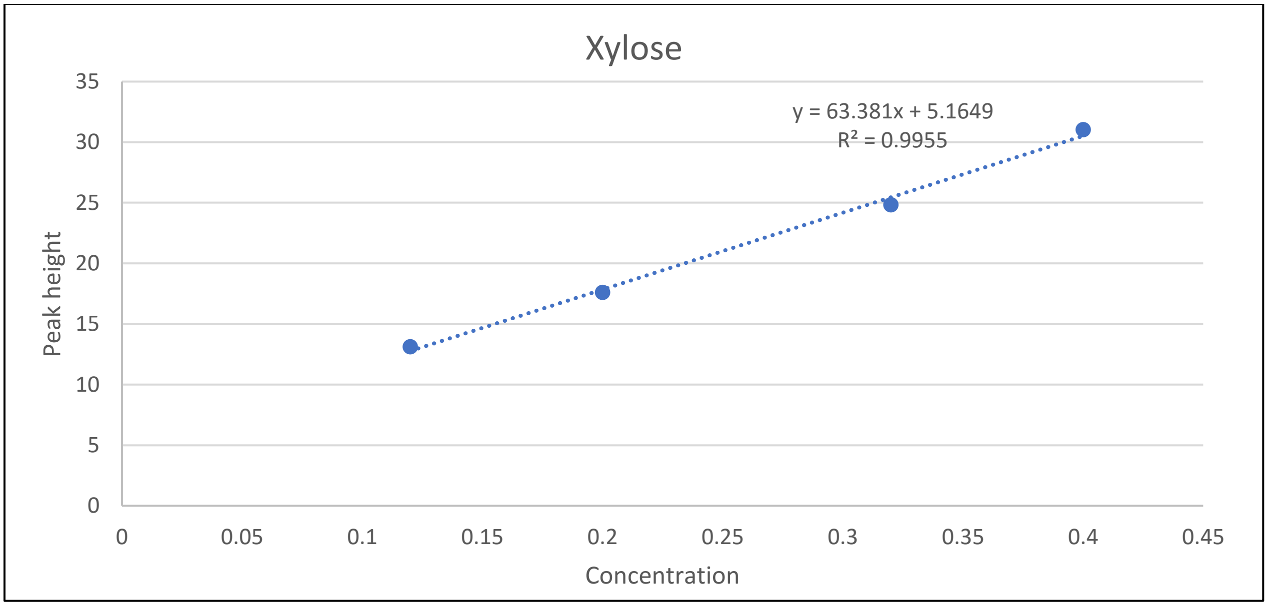

Figure 4.17: Xylose standard peak height versus concentration

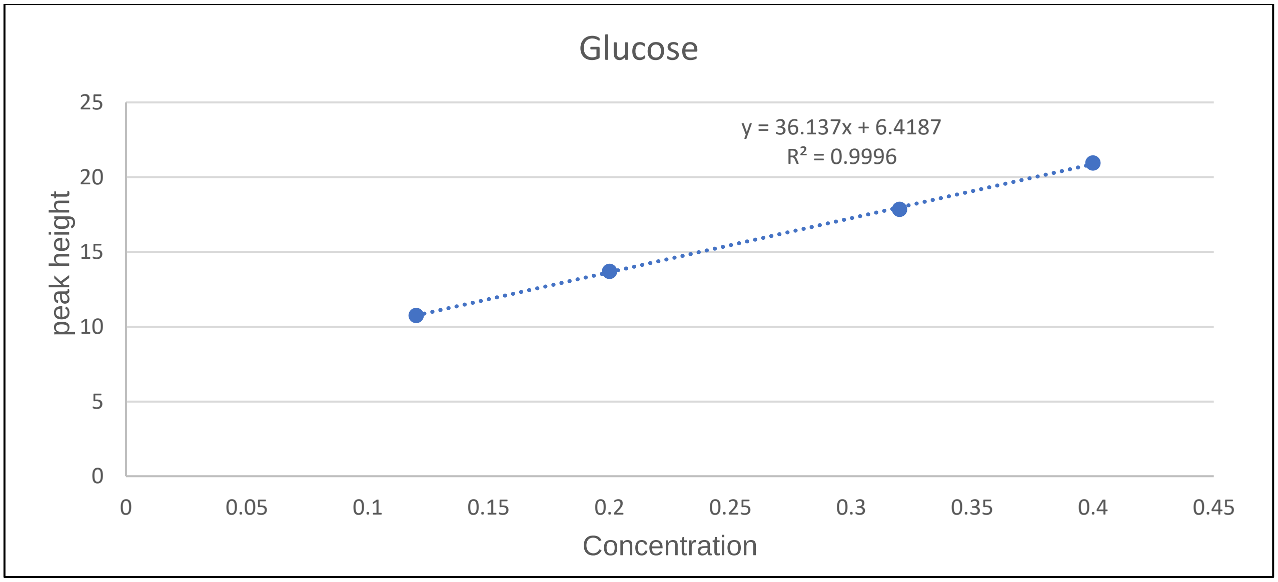

Figure 4.18: Glucose standard peak height versus concentration