

Characterisation of lignosulphonate and its changes during purification

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Abstract

The world needs an environmentally friendly renewable resource that could satisfy future energy needs and lower the impact on climate change. This need has driven many countries to fund research into biomass and biomass derivatives due to their renewability and abundance. This has caused lignosulphonate to become a topic of interest due to its potential benefits of its use. Valorisation of lignosulphonate necessitates the removal of impurities, such as sodium and sulphur, which prevent the use of technical lignosulphonate for high-value applications. The current methods that are used to purify lignosulphonate use expensive ion exchange resins which make it less feasible to incorporate at a larger-scale industrial level.

This research study led to the development of a more affordable purification method that can be easily scaled up for commercial application and does not call for expensive machinery or incur high running costs. Three variables were investigated, namely concentration, temperature, and pH, to determine their influence on the purification of lignosulphonate. Whether lignosulphonate underwent any significant changes under different conditions was also investigated.

The research study first investigated different purification methods to find the most suitable method for the purification of lignosulphonate. A literature review was conducted of the three most used methods of purifying lignosulphonate, namely ultrafiltration, ion exchange and solvent extraction. Both ultrafiltration and ion exchange methods were found to be effective for purifying lignosulphonate; however, both have disadvantages that solvent extraction can overcome, such as expensive filtration equipment, membrane fouling, expensive resins, and the requirement of regular plant section shutdown.

Solvent extraction was selected as the purification method because it showed more potential in being a less expensive process and more easily scaled up for industry. Solvent extraction can be accomplished by two methods, either reflux or Soxhlet extraction with a specific solvent such as ethanol or methanol. To ascertain whether reflux or Soxhlet would be a better choice and whether methanol or ethanol are better solvents, an experimental examination or pre-experimentation was necessary. The pre-experiments were conducted, and it was found that Soxhlet solvent extraction with ethanol as its solvent, resulted in a lower mass loss and significant ash content removal.

The above-mentioned investigation was used to construct a modified solvent extraction method. The modified solvent extraction route included two steps: acidification and washing. In the

acidification step, hydrochloric acid (HCl) was added to the solution to lower the pH value. The lignosulphonate sample was then washed (Soxhlet extraction method) using ethanol as the solvent to remove the impurities.

The next step of the study was to determine the influences of the three variables (concentration, temperature, and pH) on the purification method. To determine the influence of the three variables, it was necessary to characterise the physicochemical properties of lignosulphonate both before and after purification. The characterisation of the sample specifically focused on the ash (proximate analysis*), carbon (elemental analysis*), sodium and sulphur content (inductively coupled plasma analysis*) and was verified by a registered analysis company through an X-ray fluorescence analysis, which included the determination of the molecular weight and number (gel permeation chromatography analysis*) and functional group analyses (Fourier transform infrared spectroscopy*). The assessment of the sodium and sulphur removal, the carbon mass loss and the structural changes led to the discovery of the optimal conditions. The study found that 150 g/L, 25 °C, and a pH of 1 were the best conditions for lignosulphonate purification.

* In-house analysis

Keywords: Lignosulphonate, characterisation, purification, Soxhlet extraction.

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List of abbreviations

Abbreviations

Abbreviation	Explanation
ΔE	Energy required for collisions formation and separation of particles
FTIR	Fourier transform infrared spectroscopy
GPC	Gel permeation chromatography
HPLC	High-performance liquid chromatography
ICP	Inductively coupled plasma
ICP-OES	Inductively coupled plasma optical emission spectroscopy
Mn	Number average molecular weight
Mw	Weight average molecular weight
PDI	Polydispersity index
RID	Refractive index detector
SAPPI	South African Pulp and Paper Industries
XRD	The X-ray diffraction

Periodic elements

Abbreviation	Explanation
C	Carbon
Ca	Calcium
K	Potassium
Mg	Magnesium
Na	Sodium
O	Oxygen
S	Sulphur

Molecular compound

Abbreviation	Explanation
HCl	Hydrochloric acid

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Chapter 1: Introduction

The research study will be introduced in Chapter 1, by giving a short background and motivation for the research in the first section.

In the second section, the problem statement, aim and objectives will be discussed to provide insight into and give structure to the research study. In the last section of Chapter 1, the research scope of the study will be outlined.

1.1 Background and motivation

The environment is under strain due to climate change. This strain has been worsened through the exploitation of natural resources resulting in an increase in greenhouse gas emissions worldwide (Zoghلامي & Paës, 2019). This has instigated many countries to fund research into finding environmentally friendly renewable energy sources (Urban, 2015; McMichael *et al.*, 2006; Höök & Tang, 2013) that mitigate climate change while meeting the world's future energy needs (Bertella & Luterbacher, 2020). Research into biomass has attracted a lot of attention owing to its availability and prospective uses (Mei *et al.*, 2020).

Biomass is a renewable resource and consists of polysaccharides (cellulose and hemicellulose) and aromatic polymers (lignin) (Zoghلامي & Paës, 2019). Biomass in the form of wood has been industrially fractionated to cellulose in the pulp and paper industry for hundreds of years (Bertella & Luterbacher, 2020). However, the full utilisation of hemicellulose and lignin is still under development (Bertella & Luterbacher, 2020). Traditionally, in the pulp and paper industry, black lignin-containing liquors (derived from pulping processes) are burnt to recover energy for the mills and are therefore considered a low-value waste product (Bajpai, 2015). However, lignin has been established as having the potential to be used as a renewable resource for certain high-value applications (Bertella & Luterbacher, 2020).

Lignin is a natural aromatic polymer that is found in the cell walls of plants (Saito *et al.*, 2014). Lignin provides structural support to the plant in the form of a cross-linked network consisting of itself and hemicellulose (Klett, 2017). Lignin has a high carbon content which makes it an exceptional pioneer of certain high-value applications, such as biofuels, carbon fibres, and

adhesives; and also a source of phenolic monomers and fine chemicals (Tagami *et al.*, 2019). The total annual estimation of lignin production worldwide is 1.8 million tons, making it a favourable alternative to petroleum precursors (Aro & Fatehi, 2017). However, the lignin-processing sector faces obstacles such as lignin's unique chemical reactivity, lignin's non-uniform structure and the presence of various organic and inorganic impurities in the solids (Bajwa *et al.*, 2019a).

In the bisulphite pulping industry of wood, lignin is isolated and removed in the form of liginosulphonate (Ruwoldt, 2020). In the process, the complex lignin network is broken down and sulphonate groups are attached to the lignin (Ruwoldt, 2020). After this attachment, the liginosulphonate molecule can separate from the cellulosic fibres (Ruwoldt, 2020). Liginosulphonate can be found in many different applications, such as plasticisers, concrete, coal-slurry, drilling mud thinners, and dye dispersants (Ruwoldt, 2020). Liginosulphonate production is estimated to be 1 million tons per year, dominating the technical lignin market (Stern & Schwarzbauer, 2008). However, before new applications of liginosulphonate can be developed, the characteristics and physicochemical properties need to be better understood.

Liginosulphonate is described as a randomly branched polyaromatic polyelectrolyte that is ionic, water-soluble and contains sulphonate groups (Klett, 2017). A schematic drawing of part of the liginosulphonate structure is given in Figure 1.1.

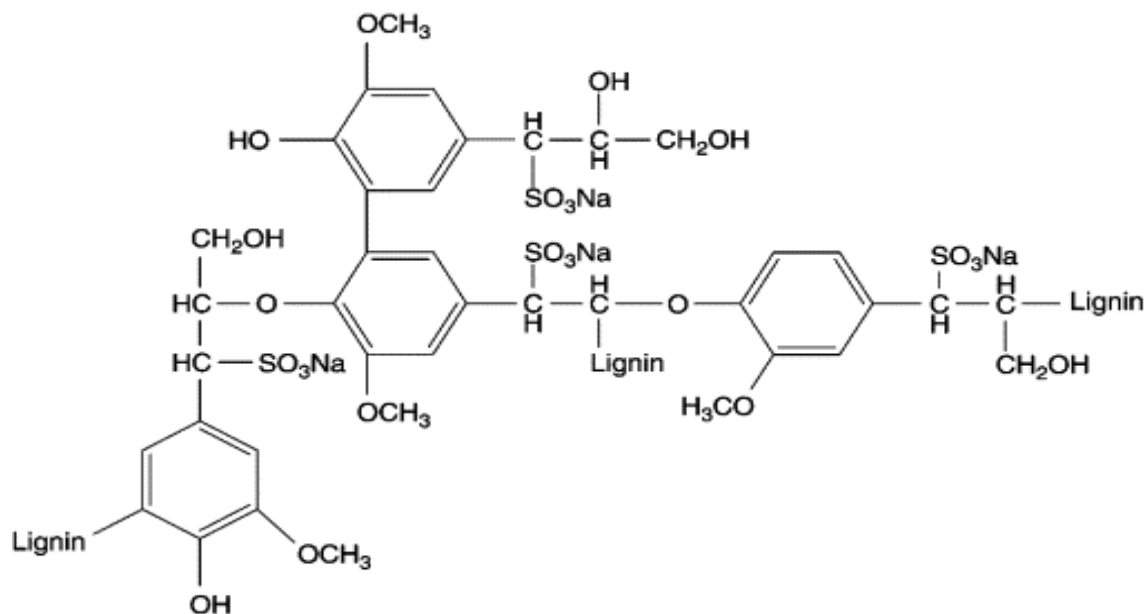


FIGURE 1.1 SIMPLIFIED SCHEMATIC OF A PART OF LIGNOSULPHONATE'S STRUCTURE (Flatt & Schober, 2012).

Before further processing, the lignosulphonate has to be purified to remove certain impurities such as organic acids and inorganic salts (Yang *et al.*, 2015). These impurities in the lignosulphonate can cause difficulties in the production of high-value products and therefore it is necessary to remove them (Klett, 2017). However, this purification procedure should not significantly alter the structure of the lignosulphonate; rather, it should merely eliminate impurities.

1.2 Problem statement, aim and objectives

1.2.1 Problem statement

The pursuit to mitigate climate change while meeting the world's future energy needs has driven research towards environmentally friendly renewable energy sources to be converted to renewable energy. Lignosulphonate has gained attention in this regard due to its abundance and the potential of its utilisation. To date, the full potential of using lignosulphonate as a renewable biomass resource has not been realised due to a lack of knowledge about its structural and chemical changes during purification. Valorisation of lignosulphonate requires the removal of impurities such as sodium and sulphur that inhibit the use of technical lignosulphonate for high-value applications. Most research studies use expensive ion exchange resins to purify lignosulphonate samples by removing undesired cation molecules but resins are too expensive to justify the purification of technical lignin on a large scale.

1.2.2 Aim

This study aims to develop a less expensive purification method to purify lignosulphonate and establish a general insight into and knowledge of the physicochemical changes of technical lignosulphonate during purification resulting from different settings of temperature, pH, and concentration.

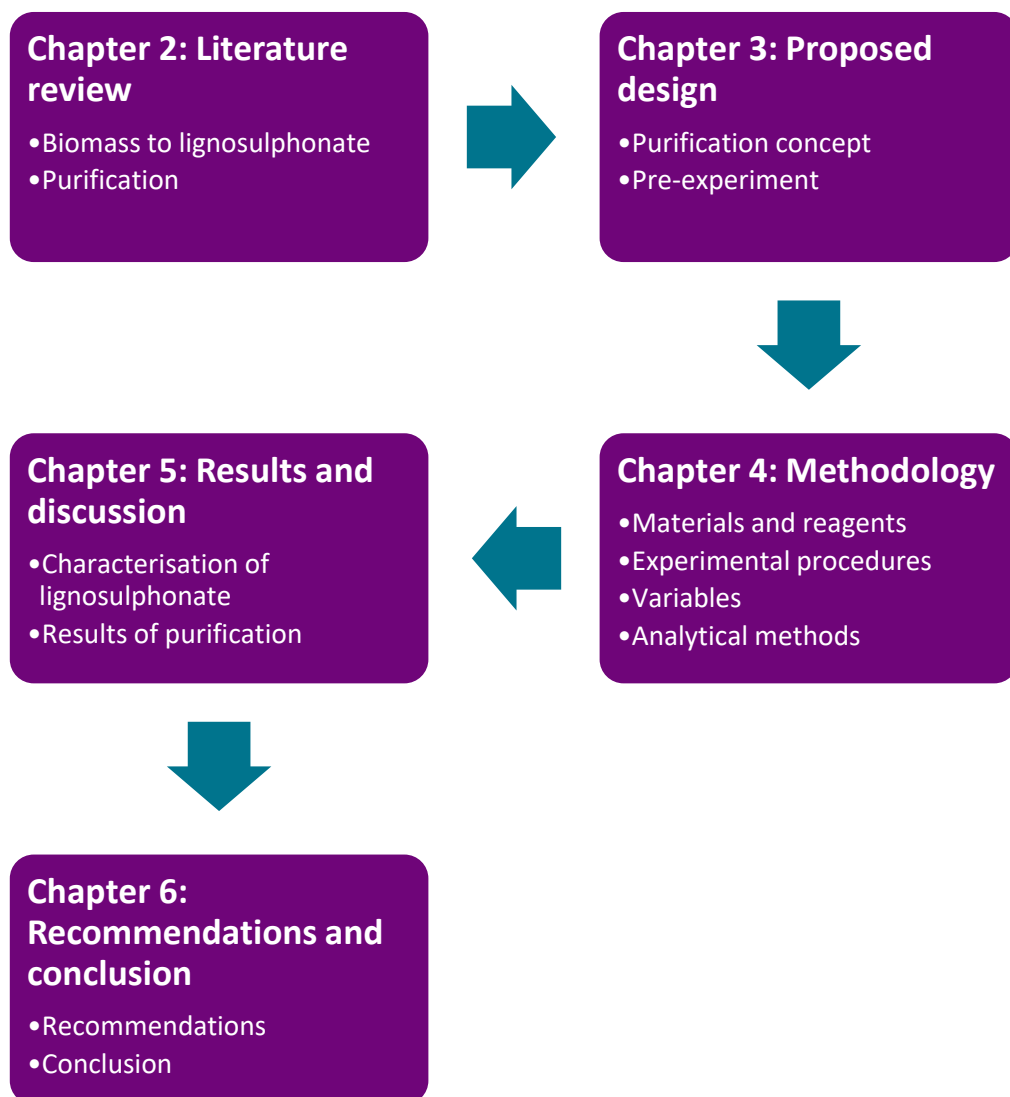
1.2.3 Objectives

The objectives of this study are as follows:

- Assessment of different purification methods to find the highest ash content removal with the least impact on the lignosulphonate structure.

- Assessment of different conditions (concentration, temperature, and pH) for the chosen purification method to obtain a cost-effective purification of technical lignosulphonate. For this, three criteria are required:
 - Complete removal or lowering of sodium and sulphur content.
 - Minimising overall carbon mass loss during purification.
 - Preserving core functionality of the lignosulphonate during purification.
- Assessment of physicochemical characterisation of a technical lignosulphonate sample before and after purification.

1.3 Research scope



Chapter 2: Literature review

Chapter 2 aims to provide insight into the necessary background required to understand the origins of lignosulphonate, and thereby gaining insight into the significance and difficulties of working with lignosulphonate. Chapter 2 is divided into two sections, namely, biomass to lignosulphonate, and purification. In the first section, the origins of lignosulphonate will be explored along with the physicochemical properties of lignosulphonate. The last section will reveal different purification methods currently used in scientific research and their drawbacks.

2.1 Biomass to lignosulphonate

2.1.1 Wood

Wood is one of the most abundant resources that the world has to offer. In addition to being abundant, its composition provides a significant possibility for further valorisation. The chemical makeup of wood changes depending on the type of wood, the location, the temperature, and the soil (Pettersen, 1984). Cellulose and hemicellulose (65–75%), along with lignin (18–35%), are the main chemical constituents of wood, with some trace amounts of organic extractives and inorganic minerals (4–10%) (Pettersen, 1984). Cellulose, hemicellulose, and lignin play complementary parts in the structure of biomasses as illustrated in Figure 2.1.

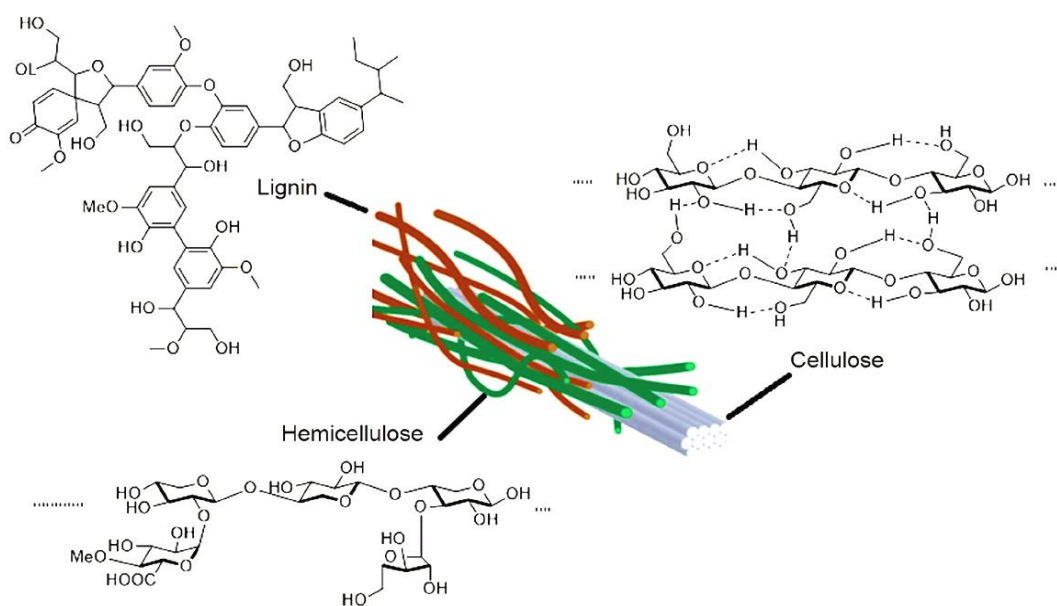


FIGURE 2.1 THE THREE COMPONENTS OF LIGNOCELLULOSE BIOMASS (Li & Takkellapati, 2018).

Wood is comprised of approximately 50% carbon, 6% hydrogen, 44% oxygen, and trace amounts of inorganics (Rowell *et al.*, 2012). These fundamental building components of life make wood a valuable resource in a variety of applications.

Wood has been used for centuries in the pulp and paper industry to cultivate its fibres into paper (Shenoy & Aithal, 2016). In general, pulping refers to the multi-industrial process of converting raw plant material into a fibrous raw material known as pulp (Ince, 2004). To produce cellulose, which is needed to manufacture paper, the pulp is treated and separated (Ince, 2004). Lignin is removed from cellulose and is generally used as a low-value product to generate electricity (Bajwa *et al.*, 2019a). However, lignin has piqued the interest of the global community due to its promise as a renewable resource for some high-value applications (Bertella & Luterbacher, 2020).

2.1.2 Lignin

Lignin was discovered in 1838 by chemical manufacturer, Anselme Payen, in France. Payen discovered that wood contained “cellulose” and an encrusting substance, which was later named “lignin” by a German chemist, Franz Ferdinand Schulze (McCarthy & Islam, 2000). Lignin can be described as a random, amorphous, three-dimensional network polymer that consists of variously linked phenylpropane units (Rowell *et al.*, 2012). This large complex molecule is a crucial part of the structural integrity of the plant cell wall and the stiffness and strength of the stem (Boerjan & Ralph, 2003). Currently, 50–70 million tons of lignin are generated yearly at pulp and paper mills across the world (Bajwa *et al.*, 2019b).

The typical percentage of lignin in wood varies depending on the biomass plant source. Grass, for instance, contains 17–24 wt% lignin, softwood contains 18–25 wt% lignin, and hardwood contains 27–33 wt% lignin (Ragauskas *et al.*, 2014).

Lignin structure

Lignin composition and deposition are affected by environmental factors and various stresses during lignin production (Lourenço & Pereira, 2018). During the biosynthesis of the primary lignin chemical structure, three distinct building block units are interlaced by radical coupling reactions. The building block units are known as monolignol units and consist of *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol (Demuner *et al.*, 2019). The monolignol is called

phenylpropane or C9 units, where the hydroxyl group is linked to the C4, and certain substitutions occur with one or two methoxyl groups at C3 and C4 (see Figure 2.2).

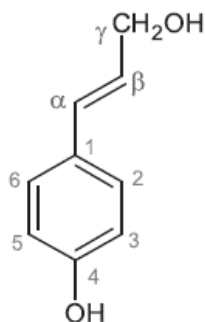


FIGURE 2.2 P-COUMARYL ALCOHOL WITH NUMBERING AND SIDE-CHAIN CARBONS

The side-chain carbons are selected as α-, β- and γ-, with α joined to the aromatic C1. The monolignols consist of corresponding phenylpropanoid monomeric units and are known as p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units, respectively (Abdel-Hamid *et al.*, 2013). The monolignol units can be described as random poly-branched arrangements coupled with oxygen and carbon–carbon bonds, as can be seen in Figure 2.3 (Ruwoldt, 2020).

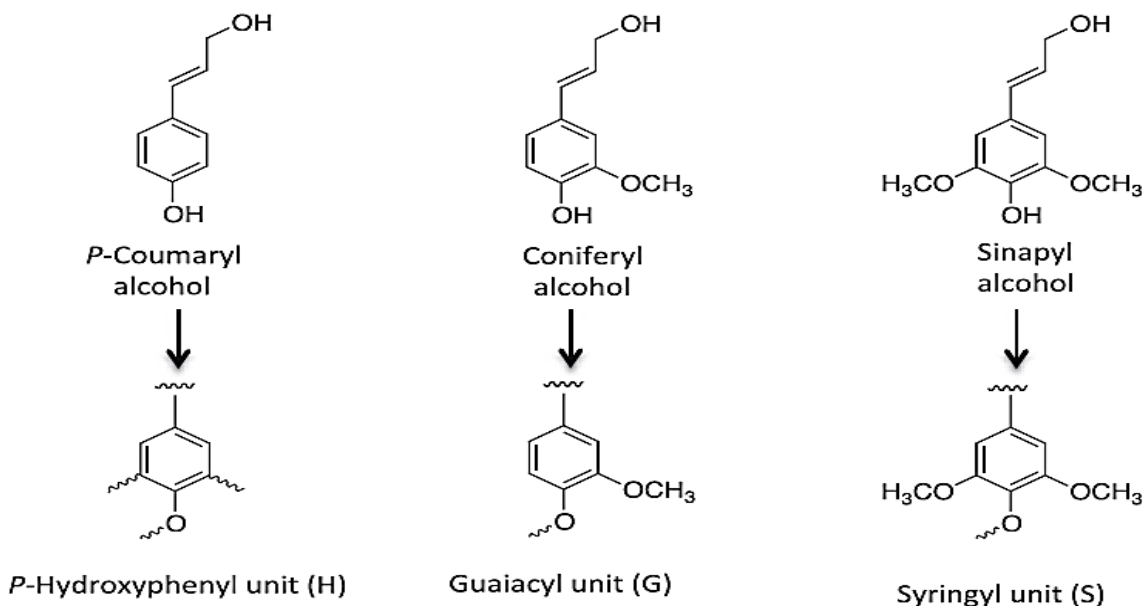


FIGURE 2.3 LIGNIN-BUILDING BLOCKS AND THEIR CORRESPONDING MONOMERIC UNITS (Abdel-Hamid *et al.*, 2013).

The heterogeneity of lignin may be related to enzyme activity that can cause the biosynthetic pathway to branch diversely (Lourenço & Pereira, 2018). However, it is difficult to determine the original lignin structure as it gets changed by harsh chemical and physical treatment (Li & Takkellapati, 2018). Part of the original structure of lignin is preserved during the separation process that removes the lignin from the biomass. This type of processed lignin is called technical lignin and contains chemical bonds and functional groups, such as ketones, ether bonds, hydroxy and methoxy groups (Windeisen & Wegener, 2012). The type of separation or pulping process affects the amount of certain functional groups that are available.

Separation processes

The pulp and paper industry requires short-length cellulose fibre to produce paper (Holtzapfel, 2003). The first step is to produce pulp, the raw paper material, from wood. There are two methods through which pulp is made: mechanical pulping and chemical pulping (Kerr & Hiziroglu, 1998). The mechanical pulping method consists of wood, in the form of wood chips, that is fed into a refiner where it disintegrates into fibre pulp bundles. The lignin structure inside the wood is chemically broken down into a black liquid using certain solvents in the chemical pulping process. Chemical pulping produces higher quality paper while mechanical pulping provides a higher yield of short-length fibres (Kerr & Hiziroglu, 1998). Chemical lignin separating processes can be differentiated into two categories: sulphur-free lignin and sulphur-containing lignin (see Figure 2.4) (Windeisen *et al.*, 2012).

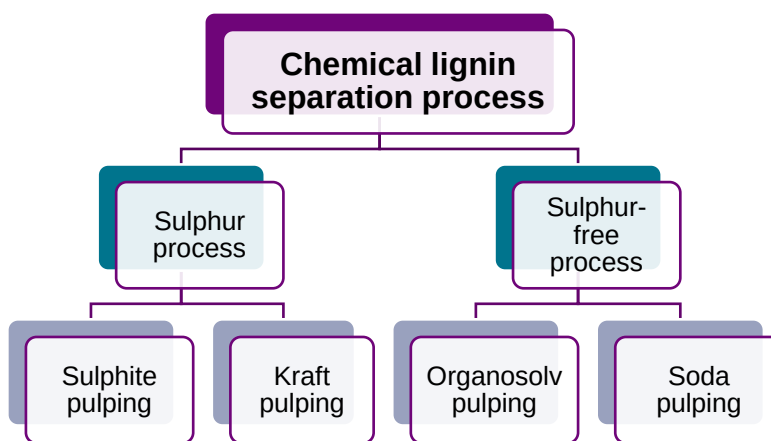


FIGURE 2.4 CATEGORISATION OF THE CHEMICAL LIGNIN SEPARATION PROCESSES (Ruwoldt, 2020).

The sulphur-free category is further subcategorised into organosolv and soda pulping. Organosolv pulping fractionates the biomass component using organic solvents to obtain the black liquor. Organosolv lignin has a relatively low ash content (approximately 1.75%) and a controlled molecular weight which, due to the lack of sulphur, can be made more readily into high-value products (Bajwa *et al.*, 2019a). Soda pulping separates the biomass components through the use of caustic sodium hydroxide as the cooking chemical (Windeisen *et al.*, 2012). The ash content of soda lignin is between 2–4%, which is higher than that of kraft lignin; however, soda lignin is more unmodified than kraft lignin (Windeisen *et al.*, 2012).

The sulphur-containing process subcategories are kraft pulping and sulphite pulping. Kraft lignin processing is the world's dominant pulping process (Demuner *et al.*, 2019). Kraft lignin is created by digesting wood chips under high pressure and temperature in a white liquor solution containing sodium hydroxide and sodium sulphide. The ash content of the kraft lignin is 1–6% (Windeisen *et al.*, 2012). Kraft lignin can be used in fertilisers, carbon fibres, resin, and binders. Kraft lignin can also be used to produce chemicals such as hydroxylated aromatics, quinine, vanillin, aldehydes, and fatty acids (Bajwa *et al.*, 2019a). After purifying kraft lignin, it undergoes sulphomethylation to make sulphonated lignin (Aro & Fatehi, 2017). Sulphonated lignin differs from lignosulphonate on the basis of where the sulphonic groups are found. The sulphonic groups of the lignosulphonate are found on the aliphatic chain, while the sulphonic groups of the sulphonated lignin are attached to the aromatic ring.

In the pulping industry, the sulphite process is less prominent than the kraft process; however, it is still an important process in terms of marketable lignin such as lignosulphonate (Demuner *et al.*, 2019). The wood chips are cooked at a temperature range of 130–145 °C, in a mixture of sulphur dioxide and alkaline solution in which the lignin and hemicellulose are dissolved (Deshpande, 2016). In this process, the sulphonic groups are presented into the partially hydrolysed lignin converting it into a lignosulphonate macromolecule (Windeisen *et al.*, 2012). These molecules are rendered soluble and thus removed from the wood (Deshpande, 2016). In this process, the alkaline solution contains a base cation such as calcium, sodium, magnesium or ammonium (Bajwa *et al.*, 2019a). The reaction is exceedingly dependent on the pH of the reaction medium (Demuner *et al.*, 2019). Calcium is used as the base cation when the bisulphite process has a $\text{pH} \leq 3$, while magnesium is used when the process has a $\text{pH} \leq 5$ (Li and Takkellapati, 2018). Only ammonium and sodium can be used at a higher pH (Li and Takkellapati, 2018). The lignosulphonate produced by the sulphite process contains up to 25% ash (Windeisen *et al.*, 2012).

2.1.3 Lignosulphonate

The versatile character of lignosulphonate gives rise to its many uses in different applications. Not only is lignosulphonate versatile but it also accounts for 90% of the technical lignin in the world market today, with an annual production of 1.8 million tons per year (Li & Takkellapati, 2018).

In the past, the industrial application of lignosulphonate could be grouped into four main functions. These functions included plastic properties (dispersant), adhesive properties (binders), chelation properties (sequestrant) and surface-stabilising properties (emulsifier) (Li & Takkellapati, 2018). Lignosulphonate has sparked interest due to its adaptability and possible applications in the petroleum field as a potential biomass resource (Yan *et al.*, 2010). Lignosulphonate valorisation is hindered by two main factors: Firstly, lignosulphonate is an extremely complex molecule that lacks a primary structure, as its specific composition is severely affected by botanical origin and location, various monomer ratios and their linking modes. Secondly, industrially available lignosulphonate is highly variable and heterogeneous, largely due to the different processes required for its isolation.

Chemical composition

Lignosulphonate is a water-soluble anionic polyelectrolyte polymer and has a similar chemical composition and structure as its predecessor, lignin. The exact structure of lignosulphonate differs due to factors such as wood type and processes involved (such as the processes mentioned in Separation processes in section 2.1.2) . However, it is generally accepted that lignosulphonate contains both hydrophobic (aromatic and aliphatic groups) and hydrophilic groups (sulphonate, carboxyl and phenolic hydroxyl group) (Yan *et al.*, 2010).

Lignosulphonate also contains polar and non-polar functional groups. Some of the polar functional groups, namely, ketones, aldehydes, and methoxy groups, are not hydrophilic groups (Ruwoldt, 2020). However, the aliphatic hydroxyl and ether groups can be hydrophilic (Valencia *et al.*, 2015). Along with these functional groups, lignosulphonate also contains counterions that are the remnants of the pulping process, such as sodium, calcium, magnesium, or ammonia, which facilitate dissociation in an aqueous solution (Ruwoldt, 2020).

The counterions are known to determine the physicochemical properties of lignosulphonates, such as affecting the polymer configuration (Valencia *et al.*, 2015). Lignosulphonate has a complex chemical structure with a near-infinite lignin network as is depicted in Figure 2.5. It has been long suggested that lignosulphonate should be considered as a statistical entity rather than a classical chemical, due to its dispersed structure and molecular weight (Whistler, 1961)

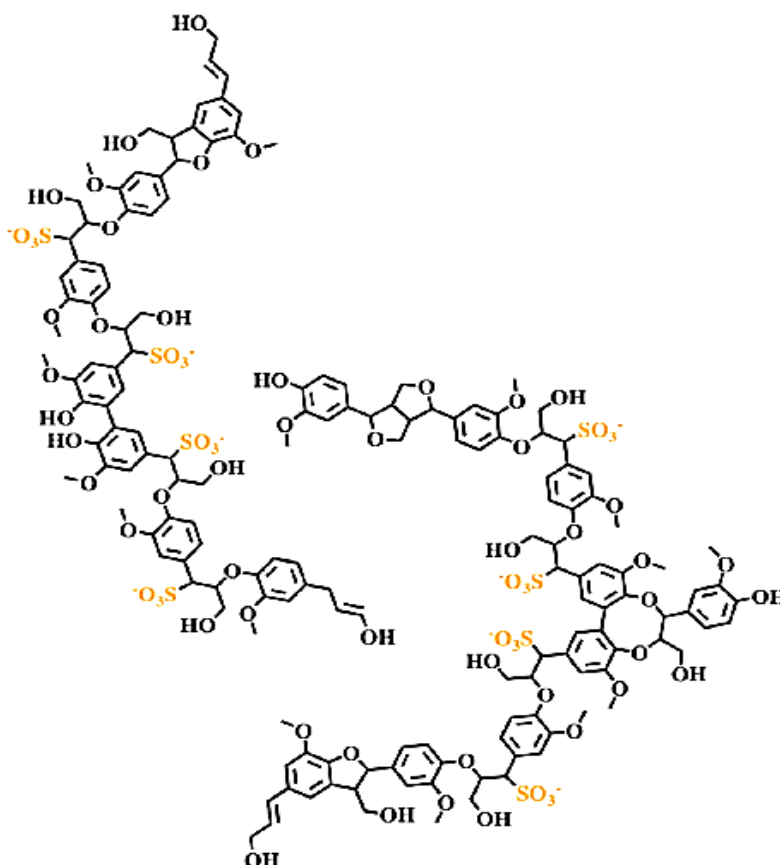


FIGURE 2.5 SCHEMATICAL DRAWING OF LIGNOSULPHONATE IN AQUEOUS FORM (FIORANI *ET AL.*, 2020).

The molecular weight of lignosulphonate is another important factor that determines the properties and behaviour of the molecules. The lignosulphonate molecules have a large molecular weight and a broad distribution of this molecular weight (Vishtal & Kraslawski, 2011). Lignosulphonate's molecular weight may range from less than 1000 g/mol to over 400,000 g/mol (Fredheim *et al.*, 2003). Molecular weight is linked to molecular dimensions and the diffusion coefficient (Kontturi, 1988). High molecular weight imposes slower diffusion and therefore can cause slower adsorption or desorption rates. It has been reported that large molecular weights of lignosulphonate

molecules have shown a lower degree of sulphonation and vice versa (Fredheim *et al.*, 2002). This phenomenon could be attributed to higher molecular weight lignosulphonate being more hydrophobic than lower molecular weight. The degree of sulphonation (millimolar of sulphonic acid per gram of lignosulphonate) is an important structure parameter that affects the physicochemical properties of lignosulphonates such as water solubility, surface activity, dispersing performance, and complexation ability (Li *et al.*, 2019). Degree of sulphonation of commercial lignosulphonate is 1.38 mmol/g (Alwadani & Fatehi, 2018).

Solubility

The solubility of lignosulphonate gives insight into the interaction of lignosulphonate and certain solvents. Lignosulphonate poses a good solubility in water due to the abundance of sulphonate groups on the organic molecule along with plenty of counterions (Rojas & Salager, 1994). Not only is lignosulphonate soluble in water, but it has shown a good solubility in ethylene glycol, propylene glycol, dimethyl sulphoxide (DMSO), as well as in dioxane-water and methanol-water blends with more than 20% water (Myrvold, 2016). However, limited solubility was reported for methanol, dimethyl formamide, acetic acid, and cyclohexylamine (Myrvold, 2014).

Shape and conformation

The description of the shape of lignosulphonate has changed over the years. An early model of lignosulphonate was described as a microgel model and was developed by Rezanowich and Goring (1960). These authors further proposed that the free charges were only located on the surface of the spherical molecule; however, these assumptions were later refuted by another research study (Myrvold, 2008) which determined that the best way to describe lignosulphonate was as a randomly branched polyelectrolyte (Myrvold, 2008). Myrvold's research has shown that in an aqueous solution, the molecule coils to become more ball-shaped with the sulphonic groups enriched on the surface, different from a microgel structure (Myrvold, 2008). This suggested that the lignosulphonate is not a microgel structure as has been previously proposed. However, the ball-like shape has only been estimated based on low molecular weight lignosulphonate. At high molecular weight, it has been better estimated as an elongated shape (Myrvold, 2008). Therefore, the lignosulphonate in an aqueous solution is better described as an oblate spheroid shape. The conformation of lignosulphonate in an aqueous solution is affected by pH, temperature, the concentration of other electrolytes, and the presence of organic solvents (Ruwoldt, 2020).

The lignosulphonate molecule expands at low salinity and concentration due to the electrostatic repulsions between the anionic groups (Myrvold, 2007). This expansion depends on the ionic strength of lignosulphonate. Another factor that affects the expansion of lignosulphonate is the pH-dependant dissociation (Ruwoldt, 2020). It was reported that an increase in pH from 2 to 10, increased the molecular dimensions, viscosity, and pseudo plasticity (Myrvold, 2007). It was also reported that an increase in temperature results in a decrease in molecular dimensions (Li *et al.*, 2015). The entropy at high temperatures results in larger quantities of potential conformation and therefore reduces the average molecular dimensions (Li *et al.*, 2015).

Aggregation

Lignosulphonate has been used in many fields for its specific properties and characteristics. One of the main properties that lignosulphonate has is that it can reduce surface tension and is therefore used as an interfacial additive in various applications (Qiu *et al.*, 2010). Due to its surfactant property, the aggregation behaviour of lignosulphonates cannot be ignored.

It has been reported that many surfactants can easily aggregate in a very dilute solution when their concentration exceeds the critical micelle concentration (Norgren *et al.*, 2002). Micelles are molecules that arrange themselves in a spherical form in aqueous solutions. It was reported that the critical aggregation concentration of lignosulphonate was between 0.05 g/L and 0.38 g/L (Yan *et al.*, 2010; Qiu *et al.*, 2010). Above these values, the micelles formed and grew with increasing concentrations of lignosulphonate, as shown in Figure 2.6.



FIGURE 2.6 GROWING MODEL OF LIGNOSULPHONATE AS THE CONCENTRATION INCREASES (QIU *ET AL.*, 2010).

The specific orientation of the aggregation has long been suggested to be the result of hydrophobic interactions (Rezanowich *et al.*, 1964). The hydrophobic moieties are oriented towards the aggregate core and the hydrophilic moieties are on the aggregate surface

(Rezanowich *et al.*, 1964). The geometry of the aggregates deviated in reports. One of these reports stated that lignosulphonate aggregates are closely spherical (Rezanowich *et al.*, 1964), whereas another report suggested a more hollow shape (Qiu *et al.*, 2010). The molecular structure of the lignosulphonate were studied by Valencia *et al* (2015), and the study produced a graphical representation (in vacuum conditions with no electrical charge). The study showed that the sodium lignosulphonate closes in on itself rather than stretching out.

It has been established that aggregation and disaggregation of lignosulphonate are highly dependent on the preparation method and parameters, such as temperature, pH, equilibration time, and concentration (Myrvold, 2015). The aggregation of lignosulphonate can be induced by increasing the lignosulphonate or salt concentration, increasing pH, adding alcohol, and increasing the temperature (Tang *et al.*, 2015a; Vainio *et al.*, 2012; Qiu *et al.*, 2010). The increase in the concentration of lignosulphonate or another added electrolyte will increase the ionic strength. This can facilitate hydrophobic interactions, which can lead to aggregation (Myrvold, 2007). Similar results have been obtained by adding an alcohol solvent to the aqueous solution (Vainio *et al.*, 2012).

Influencing factors

The characteristics of lignosulphonate are significantly influenced by several variables, such as temperature, pH, and concentration.

Temperature increases have been shown to produce an increase in polyelectrolyte expansion. It was reported that an increase in temperature to 38 °C results in lignosulphonate aggregation along with a reduction in zeta potential; and therefore resulting in a lower degree of dissociation (Qian *et al.*, 2014; Kontturi, 1988). The decrease in zeta potential also results in the decrease of the surface charge due to the charged groups (sulphonic groups and carboxylic groups) that move from the surface into the interior (Qian *et al.*, 2014). The reason for the specific temperature of 38 °C, is that the lignosulphonate molecule tends to aggregate at this temperature due to the weakening of electrostatic repulsion and strengthening of the hydrophobic interactions. Above 38 °C, the absolute value of the zeta potential increases due to modification of the molecular aggregation and conformation (Qian *et al.*, 2014).

The pH can affect the dissociation of anionic functional groups in lignosulphonates. An increased pH tends to induce larger changes in zeta potential due to the higher degree of ionisation of the functional groups of lignosulphonate (Ruwoldt, 2020). The ionisation extent of the ionisable groups of lignosulphonate is affected by the pH values of the solution (Yan *et al.*, 2010). Therefore,

the behaviour of lignosulphonate solution may change in solutions with different pH values (Yan *et al.*, 2010). It was reported that at a pH below 4.19, the surface negative charges of lignosulphonate increase with increasing pH, mainly as a result of the ionisation of sulphonic groups (that mainly reside on the surface of the lignosulphonate molecule) (Tang *et al.*, 2015a). Between a pH of 4.19 and 8.31, the surface negative charges are almost unchanged despite the ionisation of carboxyl groups at a pH below 7.229 (due to the carboxyl groups mainly residing in the cores of lignosulphonate molecules) (Tang *et al.*, 2015a). Above a pH of 8.31, the surface negative charges further increase (as result of the ionisation of phenolic hydroxyl groups) (Tang *et al.*, 2015a). The disaggregation of sodium lignosulphonate occurs above a pH of 10.34, when smaller-sized aggregates form and the degree of aggregation decreases (Tang *et al.*, 2015a). It has therefore been concluded that as the pH increases the electrostatic repulsions and interactions of molecules both increase, which leads to the swelling of the aggregates, and thus enhanced viscosity, thixotropy and elasticity (Tang *et al.*, 2015a). Overall, the aggregation and de-aggregation of lignosulphonate is a kinetic process that is particularly affected by the origin and composition of the sample (Myrvold, 2015).

The concentration of the lignosulphonate solution influences the conductivity of the solution. It was found in a study done by Tang *et al.* (2015) that the conductivity of the solution decreases as the concentration of the lignosulphonate increases at 20 °C. The higher concentration of lignosulphonate leads to a decrease in the ionisation of lignosulphonate and causes an increase in the migration resistance of ions (mainly Na⁺ and SO₄²⁻) and consequently a reduction in the conductivity (Tang *et al.*, 2015). The negative lignosulphonate ions have little effect on the conductivity due to the large size of the molecule and very slow migration.

2.2 Purification

To further process lignosulphonate, the sample needs to be purified by removing impurities (such as salts and low molecular weight compounds) and the sodium cation that is attached to the lignin macromolecule.

There are a few ways in which a sample can be purified, however in this study only three methods were evaluated namely; ion exchange, ultrafiltration, and solvent extraction. Only these three methods were evaluated due to the common use of these methods in scientific research as a purification method of lignosulphonate. Also, the study is the groundwork for future study and

therefore the more elementary processes were evaluate. Each of the methods were discussed in this section.

2.2.1 Ultrafiltration

In more recent years, the development of semipermeable membranes led to the use of ultrafiltration in many fields, including the purification of lignosulphonate (Sumerskii *et al.*, 2015). Ultrafiltration is a pressure-driven filtration technique that has been proven to be useful for industrial and analytical purposes (Ringena & Saake, 2005).

The ultrafiltration method uses a variety of membrane filtration layers in which forces, such as pressure or concentration gradients, lead to a separation through a semipermeable membrane. Dissolved material of high molecular weight is kept in the retentate, while water and other low molecular weight material pass through the membrane in the permeate. This separation process is usually used in industry and research areas for purifying and concentrating macromolecular solutions (such as polymers). Ultrafiltration is mainly based on size exclusion or particle capture. The membrane material comprises ceramics or polymers.

Previous studies have shown that ultrafiltration produces a significant percentage yield of purified lignosulphonate (Sumerskii *et al.*, 2015). It can also be noted that the use of different membranes with different molecular weight cut-offs can provide preliminary information on molecular weight distribution of the sample (Sumerskii *et al.*, 2015). A combination of ultrafiltration and nanofiltration has been shown to be viable in the production of pure lignin fractions (Arkell *et al.*, 2014). The Jönsson *et al.* (2008) research paper described purification experiments with a combination of ultrafiltration and nanofiltration. Ultrafiltration can be used to reduce the polydispersity of the purified lignosulphonates (Fredheim *et al.*, 2002; Ringena & Saake, 2005). Parameters that affect the final product in ultrafiltration are transmembrane pressure, feed temperature, cross-flow velocity, and the Reynolds number (Humpert *et al.*, 2016).

Ultrafiltration has the possibility of easy upscaling to industrial level and process control through applied pressure (Sumerskii *et al.*, 2015). Membrane technology is an excellent purification step due to its exceptional fractionation capability, few chemical requirements and low energy demand (Jönsson *et al.*, 2008). The main drawbacks of ultrafiltration are a decline in flux across the membrane, membrane fouling, and formation of a gel layer (Ringena & Saake, 2005).

2.2.2 Ion exchange

Ion exchange is the preferred method to purify and separate compounds from solution especially in water treatment and protein purification (Bajpai, 2018). This method is preferred more than most other methods due to its durability, adsorption capacity, selectivity, and limited toxicity (Sumerskii *et al.*, 2015). Ion exchange is a reversible chemical reaction within which dissolved ions are removed from solution and replaced with ions of the same or similar electrical charge. The ion exchange process allows the less desired compounds to be swapped for those that are considered more desirable.

The ion exchange method mainly consists of a synthetic cross-linked network of polymeric resin that acts as a physical medium that facilitates the ion exchange reactions. The resin consists of organic polymers that form a cross-linked network of hydrocarbons. Throughout the cross-linked network there are ion exchange sites where either positively charged ions (cations) or negatively charged ions (anions) are attached. The exchange occurs between the undesirable ions (in solution) and a more desirable ion that the resin has to offer. Most often the ion exchange focuses on the exchange of positive and negative ions in water with hydronium (H^+) and hydroxide ions (OH^-).

Ion exchange has been successfully used in many purification processes of lignosulphonate (Fredheim *et al.*, 2002; Sumerskii *et al.*, 2015; Gawluk *et al.*, 2017; Parto *et al.*, 2018). Sodium lignosulphonate can be purified through the exchange of the sodium ion for the hydrogen ion from the resin. Ion exchange resin can be used to remove the low molecular weight organic acid, inorganic salt, and other impurities from samples (Yang *et al.*, 2007).

One of the main advantages that ion exchange has over other methods is its capability to be regenerated and repeatedly applied. However, as ion exchange resin is sensitive to pollutant it requires frequent replacement which could result in a plant shutdown. Additionally, the resin has a relatively high operational cost.

2.2.3 Solvent extraction

Solvent extraction (also known as liquid-liquid extraction) is a process in which compounds are separated from each other based on their relative solubilities in a particular solvent. The solvent penetrates the solid matrix and dissolves the solute which is a certain part of the sample. The solute is then diffused out of the solid matrix and is collected.

The selection of the solvent is a crucial part of the solvent extraction. Therefore, it is essential to consider the selectivity, solubility, cost, and safety of the particular solvent for the extraction process (Zhang *et al.*, 2018). The solvent should be able to dissolve at least one component to a greater extent than the rest of the components in the mixture. Solvents with similar polarity values as the solute are likely to perform better than those with less similarity. Alcohols (ethanol and methanol) are known as the universal solvents in solvent extraction (Zhang *et al.*, 2018). Lignosulphonate can be purified from inorganic salts using the solvent extraction method.

The technique of Soxhlet extraction can be used to carry out solvent extraction procedures. Soxhlet extraction is a simple and effective procedure, traditionally used for solid samples with a limited span of solubility in different solvents (Kim *et al.*, 2012). This method makes it possible to remove impurities from the sample without excessive interference with the structure of the sample. According to Fang *et al.* (2015), who conducted purification experiments to determine the most efficient method in purifying kraft lignin, the Soxhlet extraction experiment should be conducted with a different ratio of solvents. The chemical composition of the sample after such a purification process suggests that more than 80% of the inorganics are removed.

Soxhlet extraction is inexpensive, easy to handle, and has a good solvent recovery capacity (Patel *et al.*, 2019). There are drawbacks to Soxhlet extraction such as long drying periods and the lack of automation (Patel *et al.*, 2019).

Chapter 3: Proposed design

In Chapter 3, the proposed design in terms of how the concept was assembled will be discussed. Chapter 3 contains two sections, namely the purification concept and the pre-experiments. In the purification concept discussion, the choice of the specific method along with the steps of the method and the factors influencing them are addressed. In the last section, the expedition of the pre-experiments is discussed to show how this set of experiments influenced the choice of the setup of the final experiment.

3.1 Purification concept

The behaviour of lignosulphonate in purifying procedures is examined in this study. The assembly of a suitable experimental setup requires literature research and pre-experiments to understand the potential experimental outcomes and limitations. Literature has shown that lignosulphonate is affected by certain variables under certain conditions. To get a better understanding of the effect of these variables, a few pre-experiments are required. The research and results of the pre-experiments would help to build an experimental setup to more specifically investigate the behavioural changes that lignosulphonate undergoes under certain conditions.

The three types of purification methods were discussed in the literature review resulting in the choice to use a modified solvent extraction path for this study. Ultrafiltration and ion exchange methods are both excellent processes to purify lignosulphonate; however, both have some drawbacks that solvent extraction can overcome.

Ultrafiltration requires specific filtration equipment and poses the risk of gels forming when lignosulphonate is processed under certain conditions. Ultrafiltration can be easily scaled up for industrial uses, but membrane fouling is a probable occurrence that would need regular section or plant shutdowns to replace the membrane.

The ion exchange method is a very effective method and is often used by researchers to purify their lignosulphonate sample; however, it is a very expensive resin and would require regular replacement in the industry.

The modified solvent extraction path entails an acidification step and a wash step. Acidification uses hydrochloric acid (HCl) for pH adjustment and a source of hydrogen ion. In the final step the lignosulphonate sample is washed with solvent to separate the impurities from the sample.

3.1.1 Acidification and influencing factors

The aqueous lignosulphonate sample should be acidified with HCl to encourage the removal of the impurities. Under various situations, the lignosulphonate molecule shows diverse behaviours, which hold the key to eliminating contaminants from the system. Therefore, these conditions will be investigated to determine their effect on lignosulphonate.

Temperature has an impact on the aggregation of the lignosulphonate molecule in the aqueous phase. At higher temperatures, the charged groups (sulphonic groups and carboxylic groups) move from the surface of the lignosulphonate molecules into the interior (Qian *et al.*, 2014). To ensure that charged groups remain on the surface of the lignosulphonate molecule, the temperature should not exceed 38 °C. This is to ensure that the charged groups do not move to the interior of the molecule and therefore make it exceedingly more difficult to remove the groups. Another reason for keeping investigating temperatures below 38 °C is that intermolecular aggregates can form above this critical temperature (Li *et al.*, 2015). Due to the decrease of electrostatic repulsion and the increase of hydrophobic interactions, lignosulphonate molecules have a tendency to aggregate (Qian *et al.*, 2014). These aggregates will hinder removal of impurities.

As was stated before, the dissociation of lignosulphonate is dependent on the pH. At high pH, the negatively charged molecules are associated with sodium counterions. High pH will also cause the lignosulphonate molecule to swell. With increasing pH the molecular hydrophobic core swells and the aggregate size increases (Tang *et al.*, 2015a). However, if the pH drops to the acidity range of the phenolic groups ($pK_a = 10$), their degree of protonation increases while at the same time hydrophobic forces (such as van der Waals forces) increase and the molecules precipitate partially (Zhu, 2015). It had also been determined that the pH can influence the assembly of the lignosulphonate molecule (Yan *et al.*, 2010).

Therefore, if the lignosulphonate sample is acidified well below the pK_a of lignin (below a pH of 4) it could theoretically result in the protonation of hydroxyl and carboxyl groups and the dissociation of sulphonic groups and production of an impurity-free sample.

Concentration plays a significant role in the behaviour of lignosulphonate. Higher concentrations of lignosulphonate lead to a decrease in the degree of ionisation (Zhu, 2015). Therefore, keeping the concentration as low as possible could have a positive impact on the degree of ionisation and result in more effective removal or exchange of sodium ions. A high concentration of lignosulphonate molecules can aggregate more easily and therefore obstruct the purification

process. The concentration where the lignosulphonate molecules start to aggregate is very low (0.38 g/L) (Xueqing *et al.*, 2010). Therefore, at practical concentrations, the lignosulphonate would be in an aggregate state. The aggregates can further aggregate under certain conditions. The specific concentration at which this happens is called a turning concentration and is dependent on the pH. Below this concentration the aggregates are independent of each other; however, above the turning concentration, the aggregates start to aggregate with crosslinked networks and become denser (Tang *et al.*, 2015a). It was found that at pH values of 2.89 and 10.34 the turning concentrations were 60% and 56%, respectively (Tang *et al.*, 2015a). Hence, concentration values below 60% were chosen.

The study will therefore focus on how lignosulphonate behaves at different temperatures, pH and concentration. The physicochemical characteristics of a lignosulphonate sample under these different conditions will give deeper insight into the purification of lignosulphonate for further fractionation.

3.1.2 Wash cycle

The wash cycle is necessary to wash the lignosulphonate sample after the acidifying processes. This process would make it possible to remove smaller molecules and impurities from the lignosulphonate sample. These smaller molecules could be sodium and a small fraction of the lignosulphonate molecules.

Reflux and Soxhlet extraction can be used to wash the lignosulphonate sample after the acidifying processes. The reflux extraction involves continuous contact between the lignosulphonate sample and the wash solution. This entails that the lignosulphonate is heated along with the wash solution. While in the Soxhlet extraction process the lignosulphonate sample is not in continuous contact with the wash solution while being heated.

Ethanol and methanol were the chosen wash solutions that were investigated in the pre-experiment. Lignosulphonate is insoluble in both ethanol and methanol (Myrvold, 2016). However, lignosulphonate is a bit more soluble in methanol than ethanol (Myrvold, 2016). Both these solvents could facilitate the removal of the impurities and therefore further investigation was required.

3.2 Pre-experiments

The pre-experiments were conducted to determine a purification setup for lignosulphonate. It also revealed certain behaviours of the lignosulphonate sample under certain conditions. The pre-experiments shows the conceptualising and the thought process behind the construction of the actual study. It shows why certain choices were made and the reasoning behind it. These pre-experiments were to test out theories and see what would happen to the lignosulphonate under certain conditions. These pre-experiments focused on mainly mass changes and ash removal.

The basic outline of these pre-experiments was as follows: certain amount of lignosulphonate was mixed with deionised water. This solution was then acidified with HCl to a certain low pH. The solution was then dried over a couple of days to ensure there was no more water in the processed sample. The sample was then subjected to a wash process in which the impurities could be washed from the sample after which the sample was dried for analysis. The respective analysis of each pre-experiment can be seen in Appendix A.

3.2.1 Pre-experiments 1 and 2

The first two pre-experiments were conducted to see what effect ethanol and methanol would have on the acid-processed lignosulphonate sample in a reflux wash step. The lignosulphonate solution underwent acidification, while being heated, to a pH below 1 to ensure enough hydrogen ion for the exchange. After this step, the wash step was conducted where ethanol and methanol were used separately (experiments 1 and 2, respectively) in the reflux setup (see Figure 3.1).

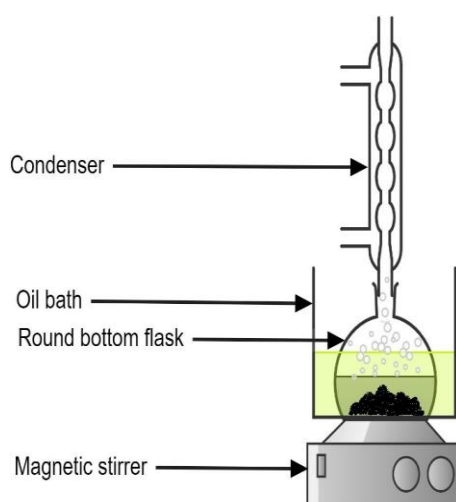


FIGURE 3.1 REFLUX SETUP

The wash step of experiment 1 was conducted for one hour, while it was only done for half an hour in experiment 2 due to the higher solubility of lignosulphonate in methanol. The wash step was repeated three times.

Results and discussion

The results of the two experiments showed that experiment 1 resulted in approximately 42% total mass loss, while experiment 2 resulted in approximately 83% total mass loss. In experiment 1, a 6.1% gain in ash was observed while experiment 2 removed approximately 52.8% ash from the system. From the results, it was concluded that ethanol was a better solvent to use in the wash step due to the lesser loss of mass in comparison to methanol. Experiment 2 showed a larger ash removal; however, the mass loss was rather significantly higher in comparison to the mass loss of experiment 1.

A few obstacles arose in the experiments during reflux. Firstly, the wash solution and the sample needed to be separated after the experiment. This was done using a filter that resulted in the solid sample merging with the filter paper, making it difficult to separate the two. Reflux is not a practical method to purify the lignosulphonate sample. Soxhlet extraction is suggested to be a better wash step since the lignosulphonate sample and boiling wash solution are separate.

3.2.2 Pre-experiment 3

The third experiment was conducted to see the effect that Soxhlet extraction would have on the sample. The lignosulphonate sample underwent acidification, while being heated, to a pH below 1. After this step, the wash step was conducted through Soxhlet extraction (see Figure 3.2) where ethanol was the wash solution. The wash step was continued for 24 hours to ensure a successful wash (repeated 3 times).

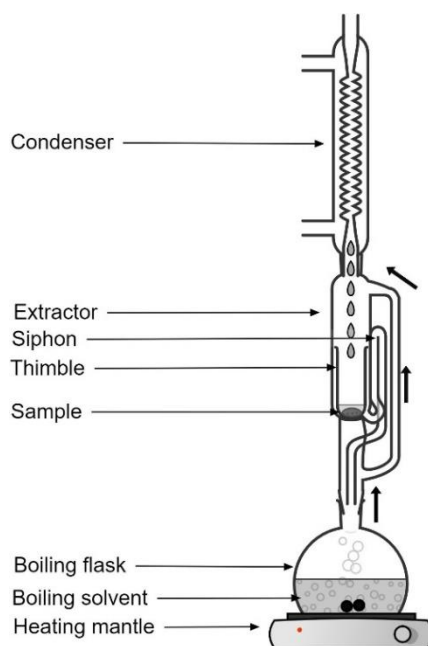


FIGURE 3.2 SOXHLET SET UP

Results and discussion

The results of the experiments showed that the sample experienced approximately 23.97% total mass loss while the ash removal was determined to be 50.3%. From the results, it was concluded that the Soxhlet extraction was a better option for a wash step than the reflux, based on reduced mass loss for the Soxhlet extraction.

3.2.3 Pre-experiments 4 and 5

The fourth and fifth experiments were conducted to determine whether the pH and temperature would have any effect on the purification of lignosulphonate. The lignosulphonate sample underwent acidification *without* being heated (room temperature) to a pH below 0.5 (experiment 4) and a pH of 2 (experiment 5). The samples of both experiments were washed in the Soxhlet extraction setup for 24 hours.

Results and discussion

The results of the experiments showed that experiment 4 experienced approximately 9.55% total mass loss, while experiment 5 experienced approximately 5.9% total mass loss. The ash removal in experiments 4 and 5 was 43.8% and 20.6%, respectively. From these results, it was suggested that the pH and temperature played a significant role in the purification process and therefore required further investigation.

Chapter 4: Methodology

Chapter 4 is divided into four sections. In the first section, the different materials required for the experiments are discussed. The experimental procedure for the experiments are discussed in the second section and the different variables chosen for the experiments in the third section. The different analytical methods used are discussed in the final section.

4.1 Materials and reagents

The sample that is used in the experiment is sodium lignosulphonate, which is called HANSA 101, from SAPPI (Tugela mill). The sodium lignosulphonate was produced through a sulphite pulping processes. The reactants that are used in the experiments and their specifications are listed in Table 4.1.

TABLE 4.1 REAGENT FOR THE EXPERIMENT

Reagent	Specification	Supplier/ Equipment
Deionised water	0.05 uS/cm	Milli-Q
Ethanol	99%; MW 46.07	Glassworld
Hydrogen chloride (HCl)	32%; MW 36.46	Associated chemical supplies

The thimble that is used in the experiments is shown in Figure 4.1. Further details of the thimble can be found in Appendix B.

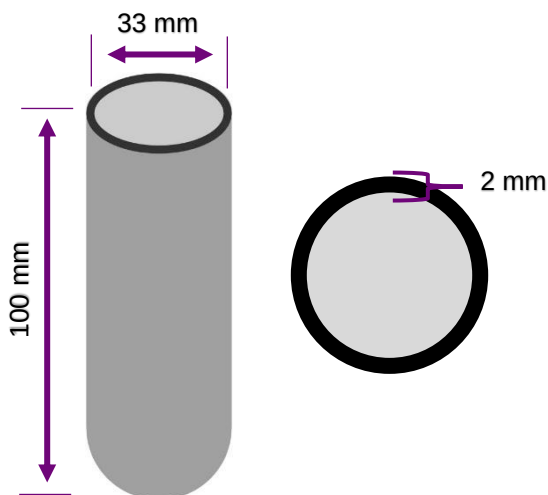


FIGURE 4.1 THE DIMENSIONS OF GRADE 603 STANDARD CELLULOSE EXTRACTION THIMBLE

4.2 Experimental procedures

The experimental procedure involves two steps, namely the acidification step and the wash step. These two steps will be further discussed in this section.

4.2.1 Acidification

The acidification procedure entails placing 50 g of lignosulphonate powder in a beaker. The powder is diluted to a specific concentration with deionised water. The pH of the solution is changed to a specific pH by adding HCl to the solution. The solution is then placed in a mixing chamber at a specific temperature for an hour. The solution is then placed in an oven at 45 °C for 4–6 days to remove the water without creating an environment for other unwanted reactions to occur. Just before the water is completely removed from the solution, the solution is poured into a thimble and placed back into the oven until all water is removed.

4.2.2 Wash cycle

The thimble is then placed into the Soxhlet extraction unit (see Figure 3.2). The ball flask of the Soxhlet is filled with 500 ml ethanol. The heating mantle is turned on to a temperature between

75 °C and 80 °C. The wash starts when the ethanol starts to boil softly and continues for 24 hours. After 24 hours the heating mantle is turned off and the unit cools down. The thimble and solution in the ball flask are then placed into an oven at 45 °C to remove the ethanol. The mixture in the thimble is weighed and sent for analytics procedures.

4.3 Variables

The variable chosen for the experiment was based on literature research. The variables that play a significant role in the behaviour of lignosulphonate are pH, temperature, and concentration. The ranges for these variables were chosen to avoid agglomeration as far as possible because it makes it more difficult to remove the impurities.

These variables will be:

- Concentration of lignosulphonate solution
 - 150 and 250 g/L
- The temperature at which the reaction occurs between lignosulphonate and hydrogen chloride
 - 20, 25 and 30 °C
- pH of the lignosulphonate solution
 - pH of 1, 2, 3 and 4

The experimental run outline is shown in Appendix C.

4.4 Analytical methods

Analytical methods are used to characterise the lignosulphonate sample. The characterisation of the sample before and after purification forms a critical part of understanding the dynamics according to which lignosulphonate operates under certain conditions. This information provides insight into how the structure of the lignosulphonate sample would break down and could promote valorising lignosulphonate effectively.

In the pursuit of characterising lignosulphonate, the following analytical methods were used: proximate and ultimate analyses, inductively coupled plasma analysis (ICP), gel permeation chromatography (GPC), Fourier transform infrared spectroscopy (FTIR) and chloride concentration. The full equipment specification can be seen in Appendix D.

4.4.1 Proximate and elemental analyses

Proximate analysis determines the amount of moisture, solids, volatile matter, ash, and fixed carbon in each sample. The amount of moisture indicates the percentage of water present in the sample and is determined according to the SANS 5925:2007 standard method (sample is placed in a crucible and loaded in the furnace overnight at 105°C, after which the mass is recorded). The solids are the difference in total mass and the moisture mass content. The volatile matter indicates the percentage of non-water gases formed from a sample and determined according to the SANS 50:2011 standard method (sample in the crucible is covered with a lid and then loaded into a furnace oven at 900°C for 7 min, after which the mass is recorded). The ash content is the percentage of the non-combustible inorganic residue that is left after complete combustion and determined according to the NREL/TP-510-42622 standard method (sample in the crucible is loaded in furnace overnight at 815°C, after which the mass is recorded). Fixed carbon was determined by the difference (100% - moisture% - volatile% - ash%).

The elemental analysis produces more comprehensive results than the proximate in which the elemental composition of the sample is determined such as carbon, hydrogen, nitrogen and inorganics. Elemental analysis was done according to the SANS 17247:2017 standard method using a CE-440 elemental analyser (based on thermal conductivity detection).

4.4.2 Inductively coupled plasma analysis

ICP analysis detects the minerals and heavy metals in the sample. The ICP was specifically used in this analysis to provide insight into the amount of sulphur and sodium content in the sample. The analysis was done using inductively coupled plasma optical emission spectroscopy (ICP-OES). The make analyser was the Agilent Technologies 725-ES ICP-OES with a radial torch.

4.4.3 Gel permeation chromatography

GPC, also known as size-exclusion chromatography, characterises the molecular mass size distribution of materials such as polymers where the molecules' molar mass varies across a range. GPC gives the average molecular number, average molecular weight, and the polydispersity index (PDI) of the polymer. The analysis was done with a GPC analyser. The make

analyser was the PerkinElmer Flexar HPLC (high-performance liquid chromatography) with RID (refractive index detector).

4.4.4 X-ray diffraction analysis

The X-ray diffraction (XRD) non-destructive technique provides detailed information about the chemical composition and physical properties of materials. The XRD analysis also gives insight into the composition of the ash of the sample. The XRD analysis was done by XRD Analytical and Consulting cc company using a Malvern Panalytical Empyrean diffractometer with a PIXcel^{3D} detector and fixed slits with Fe-filtered Co-K α radiation.

4.4.5 Fourier transform infrared spectroscopy

FTIR is a non-destructive qualitative and quantitative method to characterise the functional groups in a sample. FTIR gives insight into the functional groups of lignin in the sample. The analysis was done with a Shimadzu IRAffinity-1 Fourier transform infrared spectroscopy analyser.

Chapter 5: Results and discussion

In this chapter the results of the purification experiment, as described in Chapter 4, are discussed. The chapter is divided into two sections. In the first section, the results of the characterisation of the lignosulphonate sample is discussed. This will give a base to work from to compare the results of the purified samples. In the second section, the results obtained after purification are discussed and then compared to the original sample. In this section, the overall mass loss, impurities removal and structural changes will be explored. The optimal condition will also be determined.

5.1 Characterisation of lignosulphonate

The lignosulphonate sample was obtained from SAPPI Tugela Mill. The sample was characterised by the analytical methods as stated in Section 4.4 (Analytical methods).

5.1.1 Proximate and elemental analyses

The results of the proximate and elemental analyses of the lignosulphonate sample are shown in Table 5.1. See Appendix G (Proximate analysis original lignosulphonate) and Appendix I (Elemental analysis original lignosulphonate) for a full description of the proximate analysis and elemental analysis respectively.

TABLE 5.1 PROXIMATE AND ELEMENTAL ANALYSES OF THE LIGNOSULPHONATE SAMPLE

Proximate analysis (air dry basis, mass %)	Value ^a
Solids	96.7 ± 4.2
Moisture	3.3 ± 0.1
Ash	22.8 ± 1.0
Volatile matter	53.2 ± 2.3
Fixed carbon (by difference)	19.0 ± 0.8
Elemental analysis (mass %)	Value
Carbon	34.2 ± 1.4

Hydrogen	4.0 ± 0.2
Nitrogen	0.3 ± 0.01
Oxygen	22.6 ± 0.9
Inorganics (by difference)	38.84 ± 1.6

^a Error in analysis is indicated by 1x standard deviation of the value

5.1.2 Inductively coupled plasma analysis

The results of the ICP are shown in Table 5.2. Only components detected at a concentration above 1 mg/L are reported. Error in analysis is indicated by 1x standard deviation of the value.

TABLE 5.2 THE RESULTS OF THE INDUCTIVELY COUPLED PLASMA ANALYSIS OF THE LIGNOSULPHONATE SAMPLE

Inductively coupled plasma analysis (mass %)	Value ^a
Calcium ion (Ca²⁺)	0.05 ± 0.002
Potassium ion (K⁺)	0.17 ± 0.007
Magnesium ion (Mg²⁺)	0.08 ± 0.003
Sodium ion (Na⁺)	12.0 ± 0.5
Sulphur (S²⁻)	6.3 ± 0.3
Other	0.05 ± 0.002

^a Error in analysis is indicated by 1x standard deviation of the value.

5.1.3 Gel permeation chromatography analysis

The results of the GPC analysis are shown in Table 5.3. The distribution of the molecular weight can be seen in Figure 5.1.

TABLE 5.3 THE RESULTS OF THE GEL PERMEATION CHROMATOGRAPHY ANALYSIS OF THE LIGNOSULPHONATE SAMPLE

Gel permeation chromatography analysis	Value
Weight average molecular weight ($\overline{M}_w$)	2437 g/mol
Number average molecular weight ($\overline{M}_n$)	1005 g/mol
Polydispersity index (PDI)	2.4

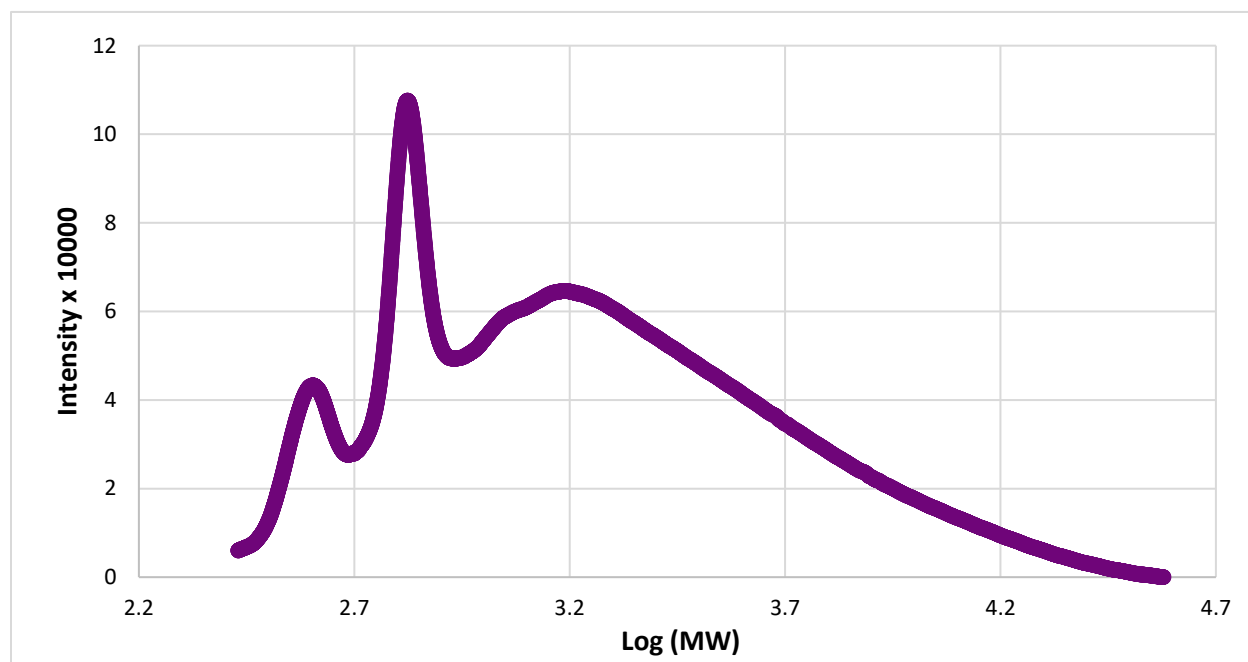


FIGURE 5.1 MOLECULAR WEIGHT DISTRIBUTION OF LIGNOSULPHONATE SAMPLE

5.1.4 X-ray diffraction analysis

The results of the XRD analysis were provided by Bureau Veritas (a certified analysis company) and are shown in Table 5.4. Only components with a content higher than 1 mass% are shown (see a more detailed report in Appendix E).

TABLE 5.4 THE RESULTS OF THE X-RAY DIFFRACTION OF ASH OF LIGNOSULPHONATE SAMPLE

X-Ray diffraction of ash (mass %)	Value ^a
SO ₃	38.4
Na ₂ O	44.5
SiO ₂	14.4

^a Only components with a content higher than 1 mass% are shown

The XRD analysis can be used to verify the ICP results (see Table 5.5).

TABLE 5.5 XRF VERIFY ICP DATA ON SULPHUR AND SODIUM FOR THE LIGNOSULPHONATE SAMPLE

	Mass (g) based on 100 g sample	
	ICP	XRF
Sulphur	6.1	4.3
Sodium	11.6	9.2

5.1.5 Fourier transform infrared spectroscopy

The result of the FTIR of the sample is shown in Figure 5.2 with the transmittance shown as a percentage on the y-axis and the wavenumber on the x-axis. The FTIR results show that there are 4 major functional groups that can be identified; hydroxyl (3600-3100 cm⁻¹), Methyl and methylene (2942 cm⁻¹), C=C Aromatic methyl (1580, 1522, 1421 cm⁻¹) and C-O stretch groups (1046 cm⁻¹). The peak with the corresponding group is tabulated in Table 5.6.

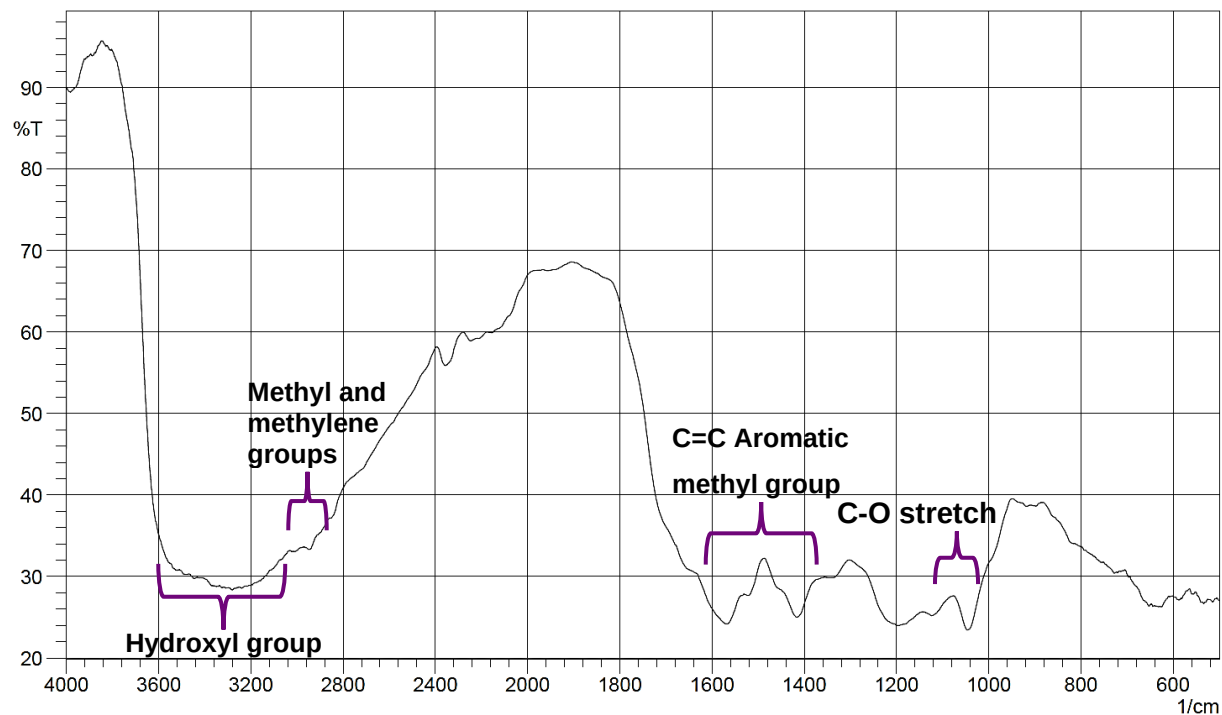


FIGURE 5.2 FTIR OF THE LIGNOSULPHONATE SAMPLE

TABLE 5.6 FTIR RESULTS OF THE PEAK WITH THE CORRESPONDING GROUP OF THE LIGNOSULPHONATE

Peak	Corresponding group	Reference
3600-3100 (broad peak)	Hydroxyl groups (phenolic and carboxylic acids)	(Guo <i>et al.</i> , 2008) (Rodríguez-Lucena <i>et al.</i> , 2009) (Abdel-Salam <i>et al.</i> , 2018)
2942	Methyl and methylene groups	(Abdulkhani <i>et al.</i> , 2019)
1580, 1522, 1421 (three peaks)	C=C Aromatic methyl group vibrations	(Guo <i>et al.</i> , 2008) (Shen <i>et al.</i> , 2008) (Rodríguez-Lucena <i>et al.</i> , 2009) (Abdulkhani <i>et al.</i> , 2019)
1046	C-O stretch (cellulose , hemicellulose and lignin)	(Abdulkhani <i>et al.</i> , 2019)

5.2 Results of purification

In this section, the results of the purification experiment will be discussed. In the first section, the physicochemical changes that have occurred during purification will be assessed. In the next section, the optimal conditions for the purification method based on the criteria set in Chapter 1 (Objectives) will be determined. The full analysis results of the purified samples can be seen in appendices F–N.

5.2.1 Physicochemical changes

The evaluation of the physicochemical changes gives insight into the behaviour of the lignosulphonate molecule under predetermined conditions. Lignosulphonate is a large and very complicated molecule and is known for unconventional behaviour under certain conditions. It is vital to evaluate the effect of the variables on the purified samples and how their physicochemical properties are changed. The physicochemical changes that will be assessed are overall mass loss, impurity removal and structural changes during purification. The two concentrations will be assessed separately.

Overall mass loss

The total mass loss of the sample after purification gives a general indication of any significant changes in the sample. To have an effective purification method, the amount of mass loss should be minimal. In the purification experiment, all 24 experimental runs had a mass loss percentage of less than 10% as can be seen in Table 5. 7 (see Appendix F). This indicates that the general structure of lignosulphonate in each run did not vary significantly. However, this does not necessarily imply that there have been no alterations to the lignosulphonate structure.

TABLE 5. 7 OVERALL MASS LOSS OF ALL RUNS

Run	m _R % (%)	Run	m _R % (%)	Run	m _R % (%)	Run	m _R % (%)
Run 1	2.85	Run 7	2.84	Run 13	3.85	Run 19	2.35
Run 2	6.22	Run 8	2.77	Run 14	2.71	Run 20	2.23
Run 3	6.70	Run 9	3.74	Run 15	2.60	Run 21	2.86
Run 4	4.55	Run 10	3.76	Run 16	2.43	Run 22	2.49
Run 5	5.19	Run 11	3.93	Run 17	4.54	Run 23	2.12
Run 6	4.87	Run 12	3.95	Run 18	2.47	Run 24	3.00

Impurity removal

As indicated in the objectives, the ash removal and, more particularly, the sodium and sulphur removal will be examined to evaluate the impurity loss that occurred during purification.

The impurities that are associated with the lignosulphonate molecule are sodium and sulphur. The processes used to remove sodium and sulphur from the lignosulphonate sample are not well understood. There are, however, two known occurrences namely, dissociation and ionisation. The sodium ion dissociates from the lignosulphonate molecule when the sample is mixed with water. Lignosulphonate is very soluble in water and would readily dissociate under most conditions. The next known occurrence in the process is ionisation due to the lowering of the pH of the solution to below 4. The sulphonic groups that cover the surface of the lignosulphonate molecule start to ionise at a pH below 4 (Yan *et al.*, 2010; Tang *et al.*, 2015).

The influence of the temperatures and pH is difficult to distinguish due to their strong influences on lignosulphonate (Yan *et al.*, 2010; Li *et al.*, 2013; Qian *et al.*, 2014; Zhao *et al.*, 2017). The increase in temperature can cause the lignosulphonate molecule to aggregate and also lose surface charge. While an increase in pH (in the range of 1–4) can increase the surface charge and change the lignosulphonate conformity. These variables do not only influence the lignosulphonate molecule but also influence the behaviour of the impurities such as sodium. It is therefore difficult to establish which variables are having the most impact on the purification process due to their contradicting influences on the lignosulphonate sample.

The full results of the ash removal, and sodium and sulphur removal can be found in Appendix H and Appendix L, respectively.

Impurity removal at 150 g/L

The ash removal gives a general view of the impurities associated with the lignosulphonate molecule. The first observation, as seen in Figure 5.3, is that there was generally a higher ash removal at lower pH values and lower temperatures. As expected, at higher pH and higher temperature values the ash removal was lower. This correlates with the possibility that at higher pH values other parts of the lignosulphonate molecule starts to ionise creating more available sites for other molecules to bind and lowering the overall ash removal. Due to their significant effects on lignosulphonate, it is difficult to discern the effects of temperature and pH, as was stated previously.

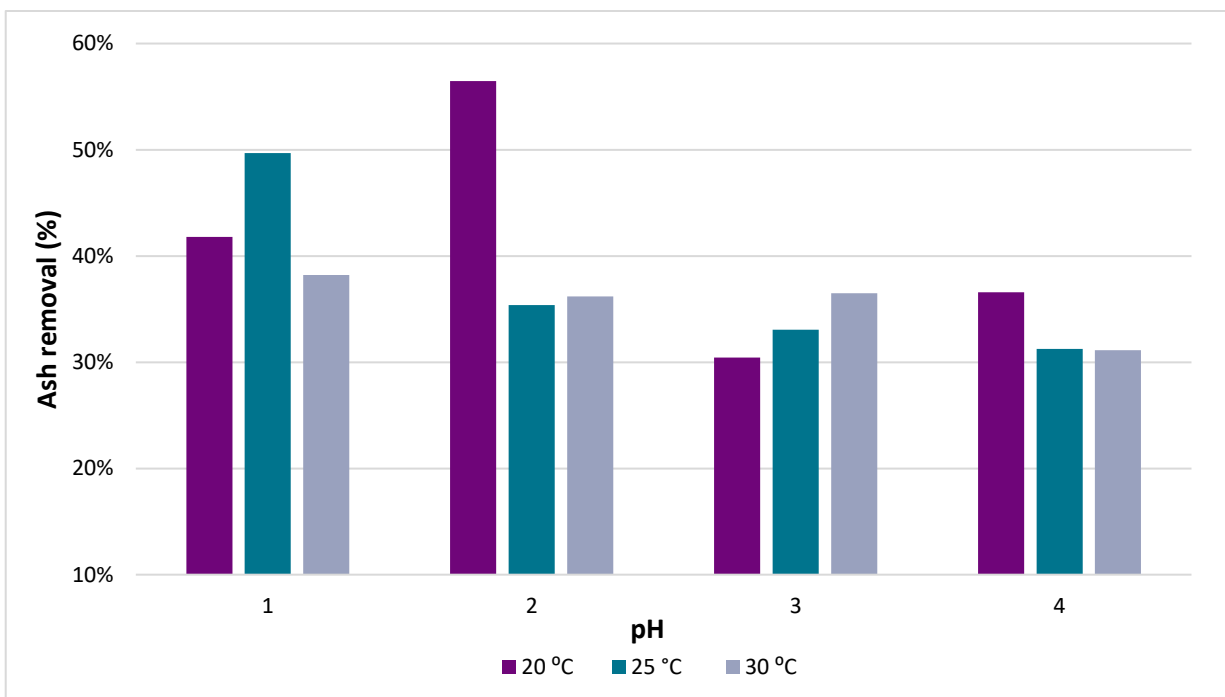


FIGURE 5.3 PERCENTAGE OF ASH REMOVED DUE TO DIFFERENT PH AT DIFFERENT TEMPERATURE AT 150 G/L

Figure 5.4 and Figure 5.5 show the sodium and sulphur removal at 150 g/L. The sodium removal (Figure 5.4) decreased as the pH value increased for all temperature values which correlated with the ash removal trends.

The sulphur removal was low to insignificant at 20 °C and between 95 and 98% at 25 °C for all pH values. This event is supported by the fact that the activation energy (ΔE) of lignosulphonate at 20 °C is 16.25 kJ/mol, yet at temperatures above 20 °C, the ΔE value is 2.85 kJ/mol (Tang *et al.*, 2015b). This has also been seen in a study done by Kontturi and Kontturi (1988), which showed that the lignosulphonate molecule at low pH values and 20 °C had a rather insignificant dissociation of sulphonate groups. Therefore, less energy is required to assist in sulphur breaking its bonds with lignosulphonate at temperatures above 20 °C than below 20 °C.

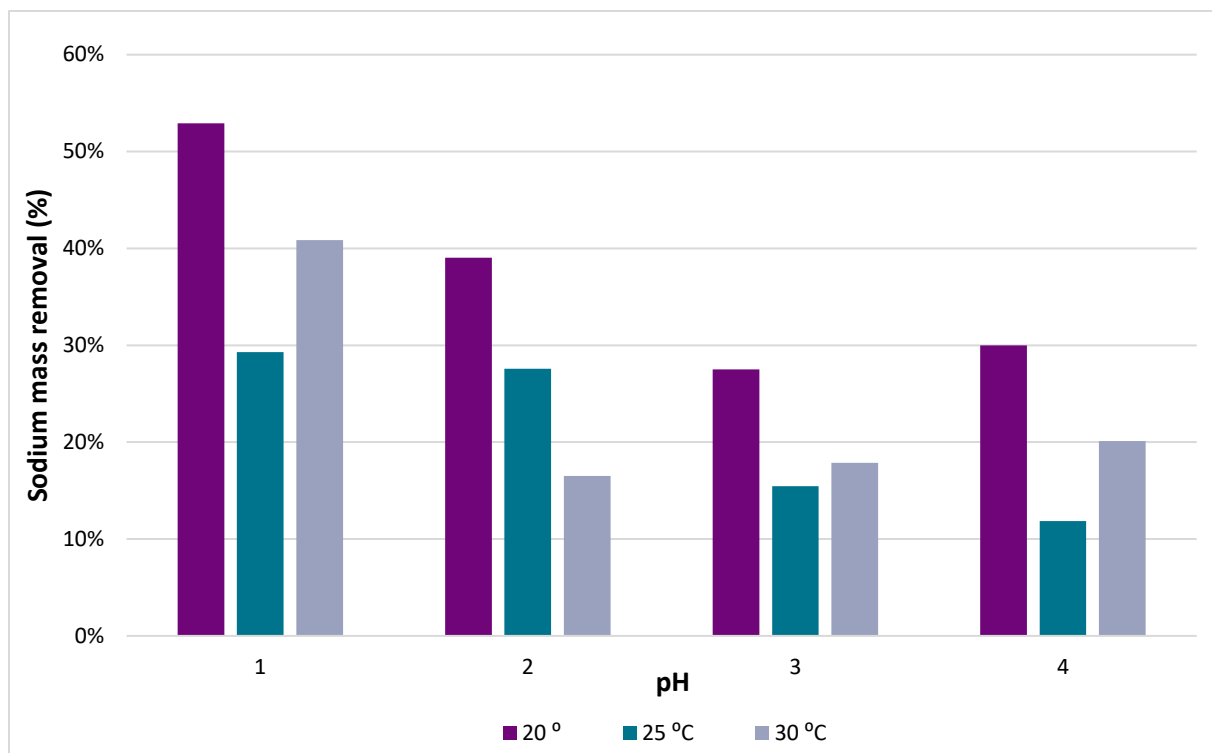


FIGURE 5.4 PERCENTAGE OF SODIUM REMOVED DUE TO DIFFERENT pH AT TEMPERATURE AT 150G/L

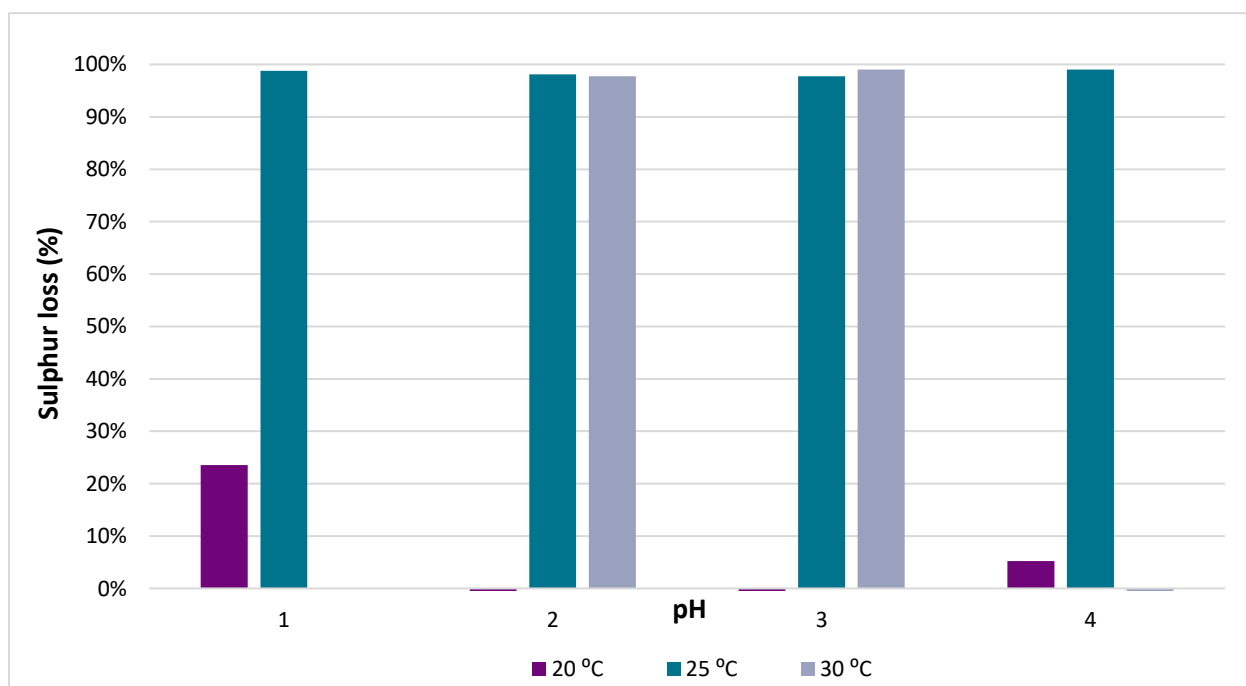


FIGURE 5.5 PERCENTAGE OF SULPHUR REMOVED DUE TO DIFFERENT pH AT TEMPERATURE AT 150G/L

Impurity removal at 250 g/L

As mentioned in the section above, the removal of the ash provides a comprehensive picture of the contaminants linked to the lignosulphonate molecule. The first observation from Figure 5.6 for the ash removal shows a downward trend as the pH increases for all temperatures. The highest ash removal was at lower pH values. Due to their significant effects on lignosulphonate, temperatures and pH effects are difficult to separate, as was mentioned in the preceding section. The 20 °C dataset had a gradual decrease as the pH increased while 30 °C had a more abrupt decrease. The 25 °C dataset presented a more conflicted trend which might have been the result of the conflicting influences of pH and temperature. The ash removal only reflected a portion of the sample's inorganics. As a result, the specific impurities required additional examination.

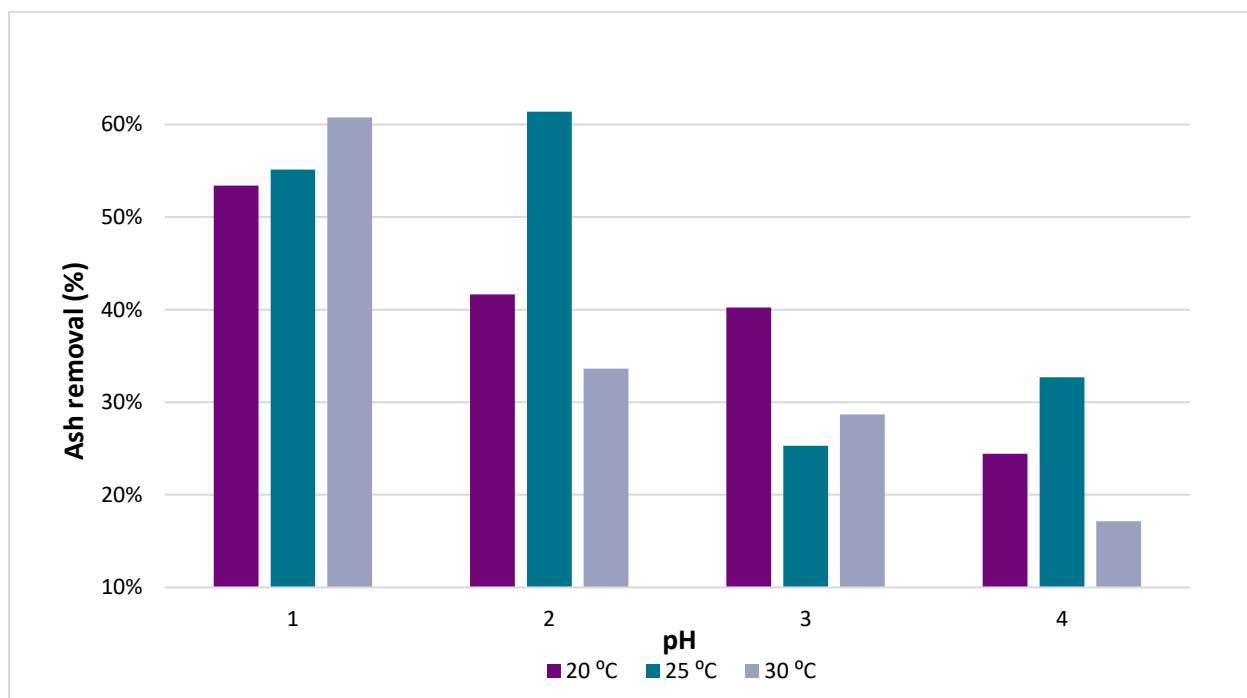


FIGURE 5.6 PERCENTAGE OF ASH REMOVED DUE TO DIFFERENT pH AT DIFFERENT TEMPERATURE AT 250 g/L

Figure 5.7 and Figure 5.8 present the sodium and sulphur removal at 250 g/L. The sodium removal showed a general decreasing trend as the pH increased for all temperatures. This was also in line with the ash removal at 250 g/L and was also similar to the tendency of ash and sodium removal for the 150 g/L datasets. However at higher temperature, the sodium removal was higher, which contrasted with the 150 g/L sodium data set. The higher concentration suggested that the

lignosulphonate molecules had more aggregates than at the lower concentration. It is evident that this altered the behaviour of the lignosulphonate molecule towards the changes in conditions.

For pH values of 1–2, the sodium removal increased as the temperature increased. For pH values of 3–4, the sodium removal trend was still decreasing; however, there was less of a tendency with the increase in temperature. This might be because at this pH value range, the lignosulphonate molecule starts to ionise even more which allows for possible reactions to take place on the lignosulphonate molecule. The 20 °C and 30 °C datasets had a gradual decrease as the pH increased. The 25 °C dataset seemed to simulate the opposite tendency to that of the other temperature datasets.

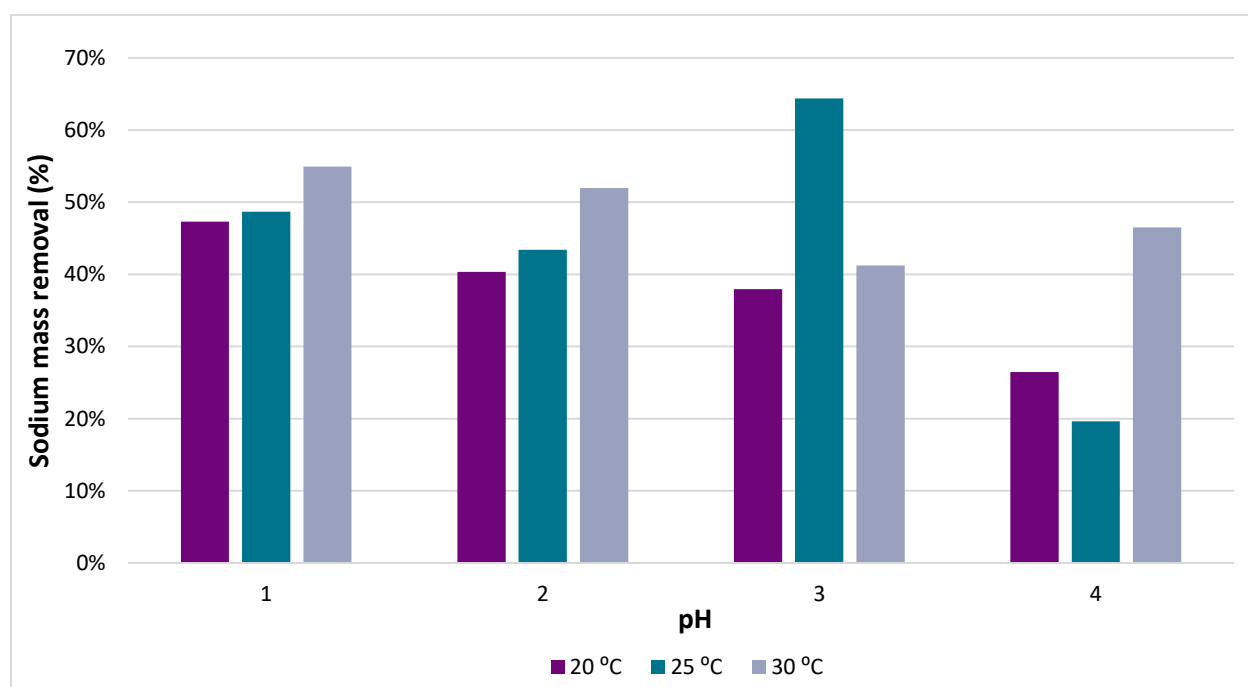


FIGURE 5.7 PERCENTAGE OF SODIUM REMOVED DUE TO DIFFERENT PH AT DIFFERENT TEMPERATURE AT 250 G/L

The sulphur removal (see Figure 5.8) was only evident at a pH of 3 and at 25 °C and gradually at 30 °C as the pH increased. This suggested that with the increase in concentration the lignosulphonate molecules were packed more closely together which induced the molecules to aggregate more readily once in solution. This would have made it difficult for the sulphurs to be removed once the HCl was added and the lignosulphonate molecules started to ionise.

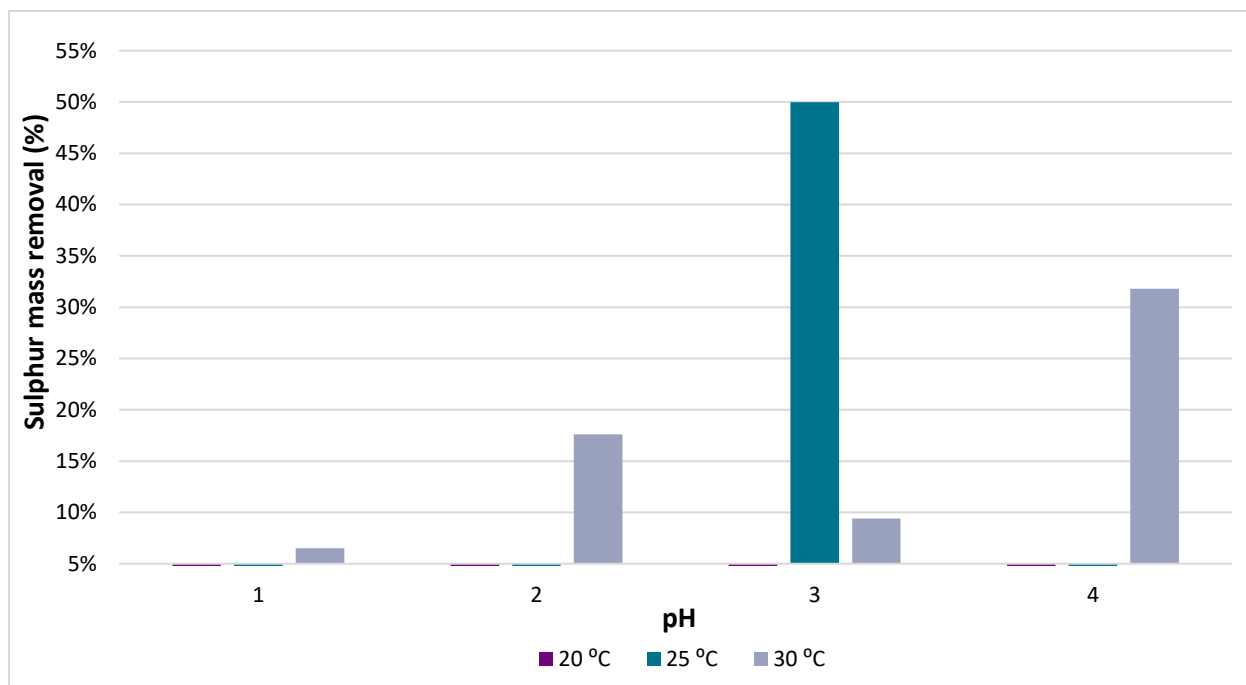


FIGURE 5.8 PERCENTAGE OF SULPHUR REMOVED DUE TO DIFFERENT pH AT DIFFERENT TEMPERATURE AT 250 G/L

Other impurities

The main purpose of the addition of HCl was to lower the pH value. This not only resulted in a higher concentration of hydrogen ions but also of chloride ions. The chloride ion is an anion and could either associate with the lignosulphonate molecule (where the sulphur was removed) or with the sodium ion.

Structural changes

One of the desired outcomes of the study was to ensure that minimal changes occurred to the structure of the lignosulphonate molecules. In this part of the current section, the changes that did occur are explored.

The lignosulphonate molecule is typically an aggregation of many monomeric lignosulphonate units. It is known that the lignosulphonate molecule has a variety of differently sized molecules and therefore has a PDI that is usually larger than 1 (Vishtal & Kraslawski, 2011). Thus, it is necessary to assess the changes to the $\overline{M}_w$ and $\overline{M}_n$. The changes might provide information on the general structure of the lignosulphonate molecule. The $\overline{M}_w$ gives insight into the lignosulphonate molecule with more monomeric units while $\overline{M}_n$ gives insight into the compound with fewer monomeric units. The carbon mass loss gives insight into the carbon chain loss. This could suggest a modification to the hydrophobic inner part of the lignosulphonate molecule. The FTIR results will give insight into some of the main functional groups of lignosulphonate and the changes that these groups undergo. The three main groups that will be investigated are methyl and methylene groups (2940 cm^{-1}), C=C aromatic groups ($1640, 1520, 1460\text{ cm}^{-1}$), and the carbonyl group (1046 cm^{-1}).

The error bars on the $\overline{M}_w$ and $\overline{M}_n$ graphs is based on first standard deviation of the triplicated GPC analysis. The error bars gives insight into the validity of the analysis and how well the average value of the analysis represent the $\overline{M}_w$ and $\overline{M}_n$ value as a whole.

This section will consider the structural changes that occurred for the 150 g/L and 250 g/L datasets due to the different conditions for purification. A pH of 1 and 2 will be examined in the first part of each section, followed by a pH of 3 and 4 in the second part. This is done to examine the structural changes of the data with the highest ash removal (at a pH of 1–2) in comparison with the lower ash removal (at a pH 3–4).

Structural changes at 150 g/L

pH values of 1 and 2

The $\overline{M}_w$ results did not change while the $\overline{M}_n$ results underwent significant loss for a pH of 1 and 2 (see Figure 5.9). Smaller molecule aggregates are usually the first to break apart instead of the larger molecule aggregates. However, at a pH of 1 and a temperature of $20\text{ }^{\circ}\text{C}$ (see Figure 5.9A) and at a pH of 2 and a temperature of $25\text{ }^{\circ}\text{C}$ (Figure 5.9B), the $\overline{M}_w$ and $\overline{M}_n$ results were different

compared to the others. At a pH of 1 and a temperature of 20 °C the $\overline{M}_n$ results were unchanged which suggested that at lower concentration and this condition, the structure of the lignosulphonate molecules was significantly unchanged. At a pH of 2 and a temperature of 25 °C the $\overline{M}_w$ results showed an increase suggesting that the monomeric units could have bonded with the larger molecules and thereby caused the $\overline{M}_w$ increase.

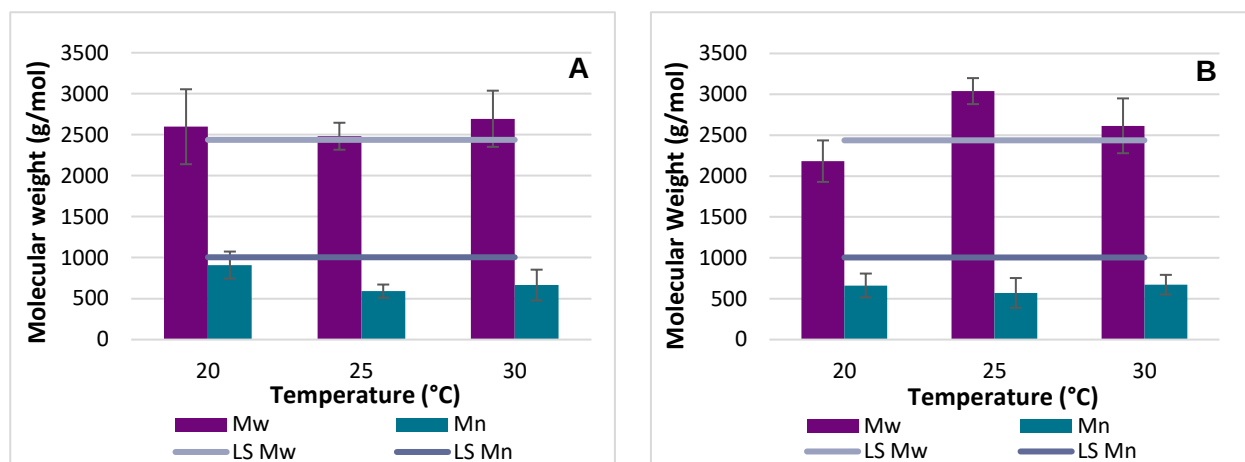


FIGURE 5.9 $\overline{M}_w$ AND $\overline{M}_n$ AT DIFFERENT PH AND DIFFERENT TEMPERATURES AT 150 G/L. (A) AT 1 PH AND (B) AT 2 PH. LS REFERS TO THE ORIGINAL LIGNOSULPHONATE

The carbon mass loss (see Table 5.8) for a pH of 1 was insignificant while at a pH of 2 there was a definite increase in carbon mass loss as the temperature increased. The highest mass loss for pH values of 1 and 2 and a lower concentration was at a pH of 2 and a temperature of 30 °C. The higher temperature would cause more carbon chains to break off from the main molecule.

TABLE 5.8 PERCENTAGE CARBON MASS REMOVED AT 1 AND 2 PH AND DIFFERENT TEMPERATURES AT 150 G/L.

pH	1			2		
Temperature (°C)	20	25	30	20	25	30
Carbon mass removal (%)	10%	4%	10%	14%	12%	22%

The FTIR results for pH values of 1 and 2 can be seen in Figure 5.10 and Figure 5.11. The three main peak groups were sharper and broader than for the original lignosulphonate. From Figure

5.10 (for a pH of 1) the methyl and methylene groups (2940 cm^{-1}) were more defined; however, at $25\text{ }^{\circ}\text{C}$ (green) the peak was a bit shorter than for the other two temperatures. The aromatic groups ($1640, 1520, 1460\text{ cm}^{-1}$) were more distinct with longer peaks and the carbonyl group (1046 cm^{-1}) peak was more intense for all temperatures. These FTIR results for a pH of 1 and a temperature of $25\text{ }^{\circ}\text{C}$ can be explained by the higher ash removal.

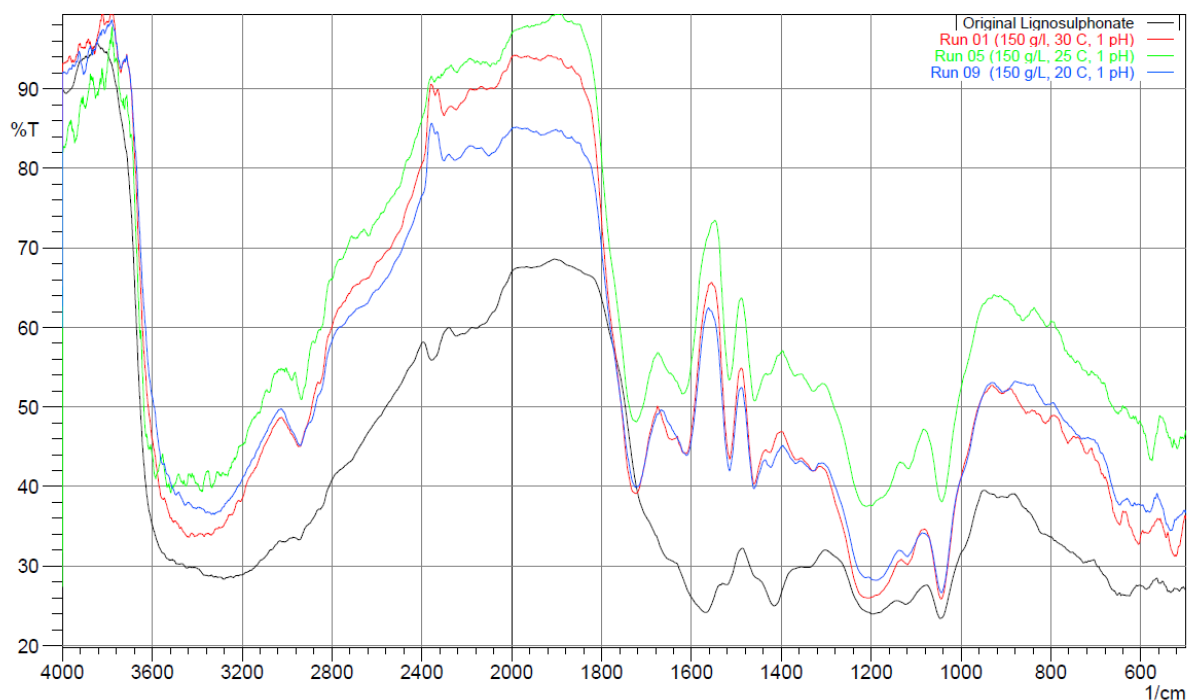


FIGURE 5.10 FTIR RESULTS OF 150G/L AT 1 PH FOR ALL THREE TEMPERATURES

From Figure 5.11 (for a pH of 2) the methyl and methylene groups (2940 cm^{-1}) at $25\text{ }^{\circ}\text{C}$ (green) and $30\text{ }^{\circ}\text{C}$ (red) were shorter than at $20\text{ }^{\circ}\text{C}$ (blue). The aromatic groups ($1640, 1520, 1460\text{ cm}^{-1}$) had longer and more distinct peaks; however, as the temperatures increased from $20\text{ }^{\circ}\text{C}$ to $30\text{ }^{\circ}\text{C}$ the size of the three peaks became smaller and less distinct. The carbonyl group (1046 cm^{-1}) peak was more intense for all temperatures. This FTIR results for a pH of 2 could be explained by the higher ash removal at $20\text{ }^{\circ}\text{C}$ and the lower ash removal at $25\text{ }^{\circ}\text{C}$ and $30\text{ }^{\circ}\text{C}$.

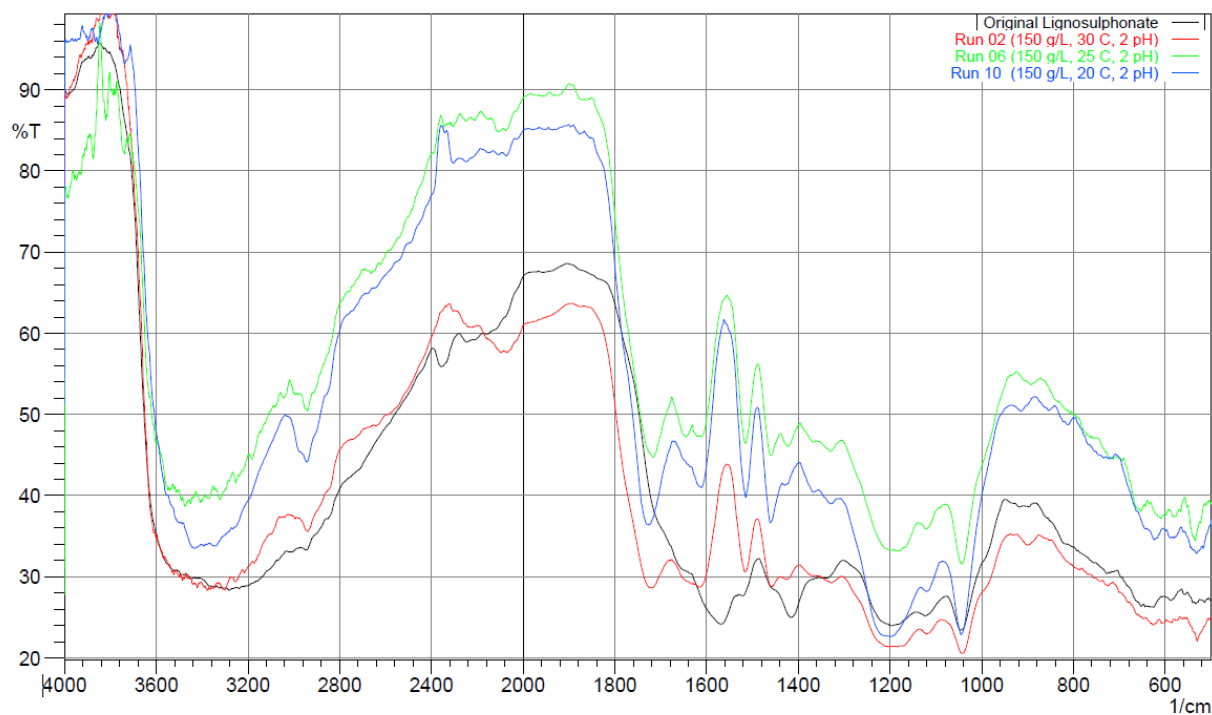


FIGURE 5.11 FTIR RESULTS OF 150G/L AT 2 PH FOR ALL THREE TEMPERATURES

pH values of 3 and 4

From Figure 5.12 the $\overline{M}_w$ and $\overline{M}_n$ results were generally unchanged for pH values of 3 and 4. However at 30 °C for pH values of 3 and 4, the $\overline{M}_n$ value decreased significantly. Therefore, at 20 °C and 25 °C for large and small molecules, the main structures were unaffected by the conditions while at 30 °C the temperature was high enough to break down the small molecules into smaller units.

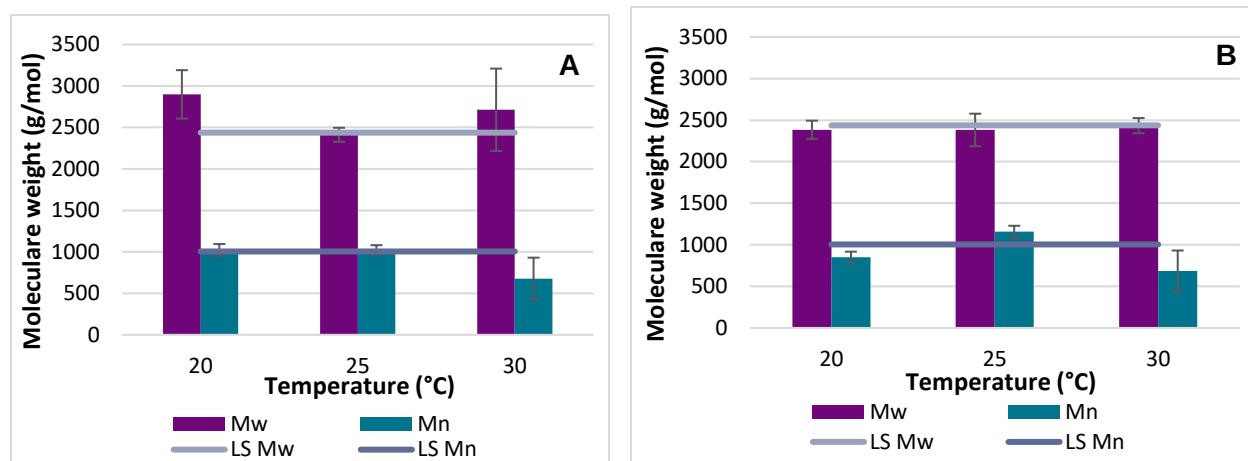


FIGURE 5.12 $\overline{M}_w$ AND $\overline{M}_n$ AT DIFFERENT PH AND DIFFERENT TEMPERATURES AT 150 G/L. (A) AT 3 PH, (B) AT 4 PH. LS REFERS TO THE ORIGINAL LIGNOSULPHONATE

The carbon mass loss (see Table 5.9) for pH values of 3 and 4 were higher than what was observed at pH values of 1 and 2. The higher carbon loss indicated that more carbon chains were removed. This coincided with the fact that at around a pH of 3 the lignosulphonate molecule starts to stretch out and untangle from its coiled-like shape and therefore exposes more carbon chain to the surface (Deng *et al.*, 2010).

TABLE 5.9 PERCENTAGE CARBON MASS REMOVED AT 3 AND 4 PH AND DIFFERENT TEMPERATURES AT 150 G/L

pH	3			4		
Temperature (°C)	20	25	30	20	25	30
Carbon mass removal (%)	19%	21%	22%	20%	12%	24%

The FTIR results for pH values of 3 and 4 can be seen in Figure 5.13 and Figure 5.14. The three main peak groups were sharper and broader than for the original lignosulphonate. From Figure 5.13 (at a pH of 3) the methyl and methylene groups (2940 cm^{-1}) were more defined. The aromatic groups ($1640, 1520, 1460\text{ cm}^{-1}$) were more distinct but smaller in size than those at a pH of 1. The carbonyl group (1046 cm^{-1}) peak was more intense for all temperatures. The FTIR results for a pH of 3 could be explained by the low ash removal at this pH value which would have caused the peaks to be less distinct than those with higher ash removals.

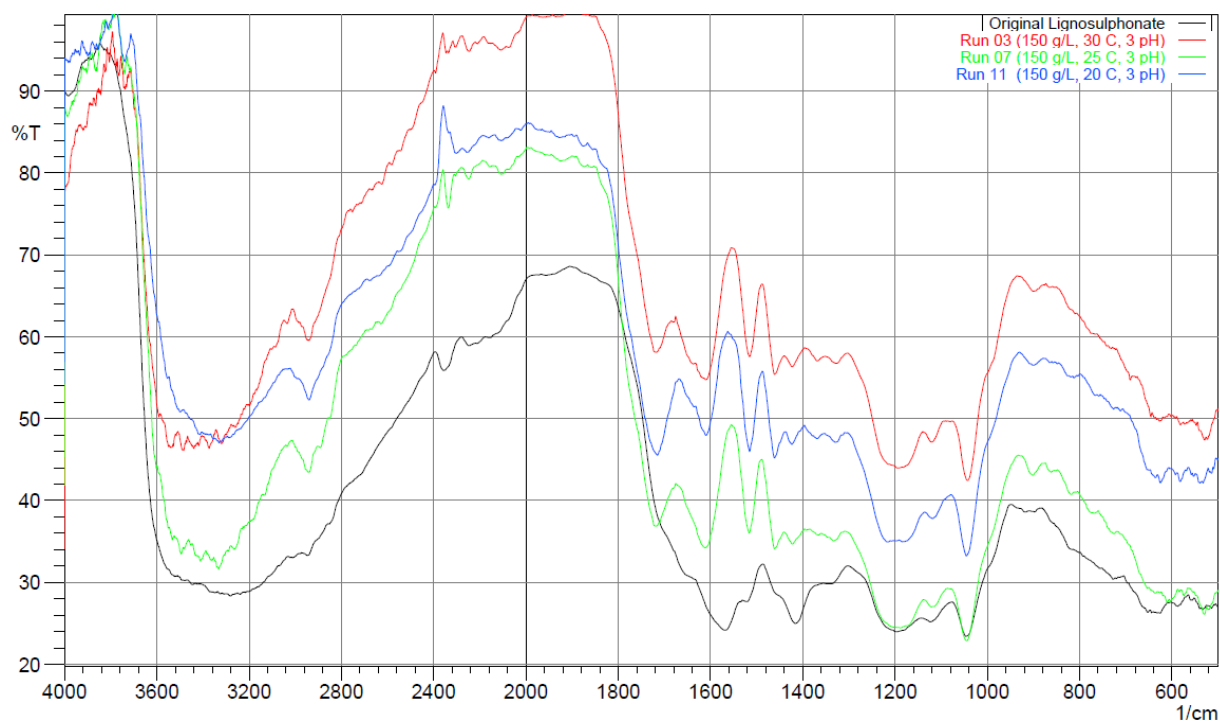


FIGURE 5.13 FTIR RESULTS OF 150G/L AT 3 PH FOR ALL THREE TEMPERATURES

From Figure 5.14 (at a pH of 4) the methyl and methylene groups (2940 cm^{-1}) were more defined but smaller in size. The aromatic groups ($1640, 1520, 1460\text{ cm}^{-1}$) were distinct; however, much smaller and less rounded than at the other pH values. The carbonyl group (1046 cm^{-1}) peak was more intense for all temperatures. The FTIR results at a pH of 4 were explained, just as at a pH of 3, by the low ash removal at this pH. At a pH of 4 the least amount of ash was removed which caused the peaks to be less distinct.

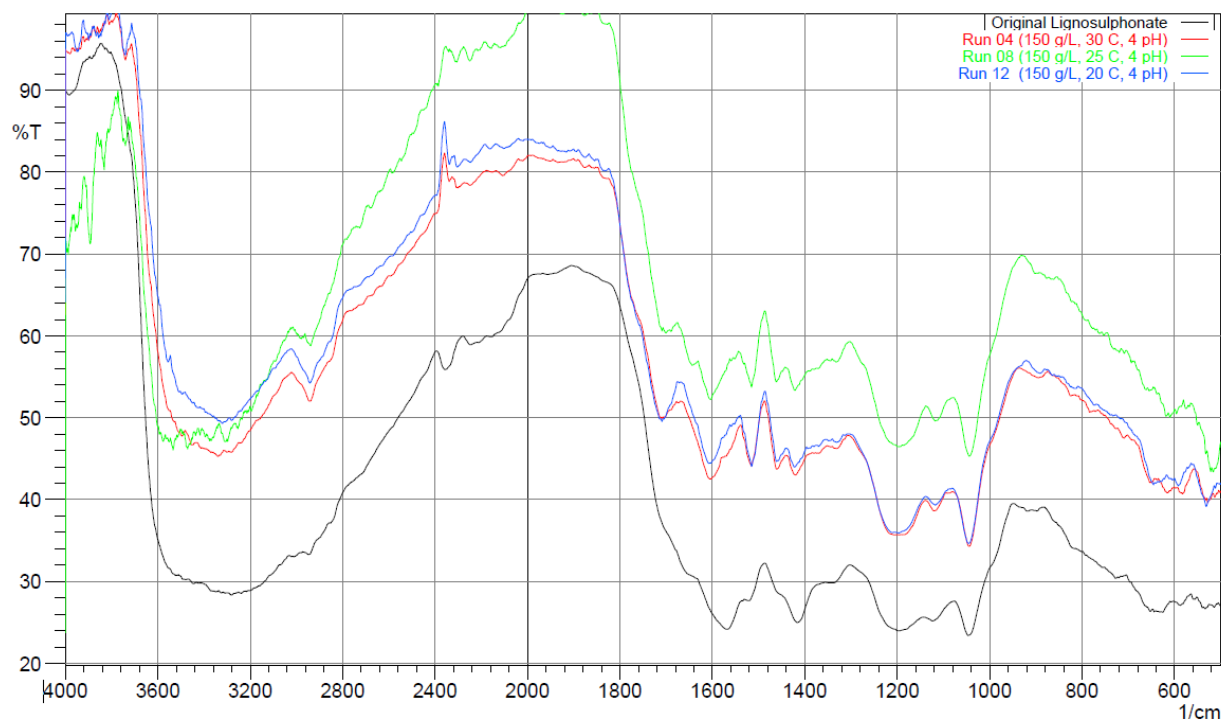


FIGURE 5.14 FTIR RESULTS OF 150G/L AT 4 PH FOR ALL THREE TEMPERATURES

The results obtained for the 150 g/L dataset have shown that generally the $\overline{M}_w$ results were unchanged while the $\overline{M}_n$ results varied based on the conditions. It was suggested that at higher temperatures, the smaller molecules of the lower concentration sample broke apart into a smaller state. The carbon chain loss was only significant at higher pH values and higher temperatures. It is suggested that the lignosulphonate particle existed as a colloidal particle at a pH below approximately 3 at low concentration and above this pH value, the particle started to dissociate due to the decline of hydrophobic interaction. The FTIR results revealed that for all the conditions the structure in essence stayed relatively the same. It is worth noting that the peaks at the three main peak groups were more distinct at lower pH values and lower temperatures than they were at higher pH values and temperatures. Therefore, the lack of impurities would in effect have caused the FTIR results to be clearer.

Structural changes at 250 g/L

In this section, the structural changes that occurred due to the different conditions for purification for the 250 g/L dataset will be considered. In the first part, the results for pH values of 1 and 2 will be examined and in the next part, the results for pH values of 3 and 4 will be examined.

pH VALUES OF 1 AND 2

Figure 5.15 shows that the $\overline{M}_w$ results generally did not change except for two accounts while the $\overline{M}_n$ results underwent significant loss at a pH of 1; however, none at a pH of 2. Figure 5.15A shows that for a pH of 1 the $\overline{M}_n$ results underwent significant loss; however, the $\overline{M}_w$ results were unchanged which suggested the same as in the section for 150 g/L: that smaller lignosulphonate molecules break apart more readily than the large molecules at this pH value and these temperatures. Figure 5.15B shows that for a pH of 2 the $\overline{M}_w$ value at 20 °C was significantly higher and gradually decreased as the temperature decreased until at 30 °C the result proved to be unchanged. However, the $\overline{M}_n$ underwent no significant change. The $\overline{M}_w$'s significantly high results at a pH of 2 suggested that some of the smaller lignosulphonate molecules might have been associated with the larger molecules under these conditions. Lignosulphonate is prone to aggregate as the concentration is increased (Yan *et al.*, 2010; Tang *et al.*, 2015a; Ruwoldt, 2020) and a pH of 2 is approximately the pH value where the sulphonic groups start to ionise (Tang *et al.*, 2015a).

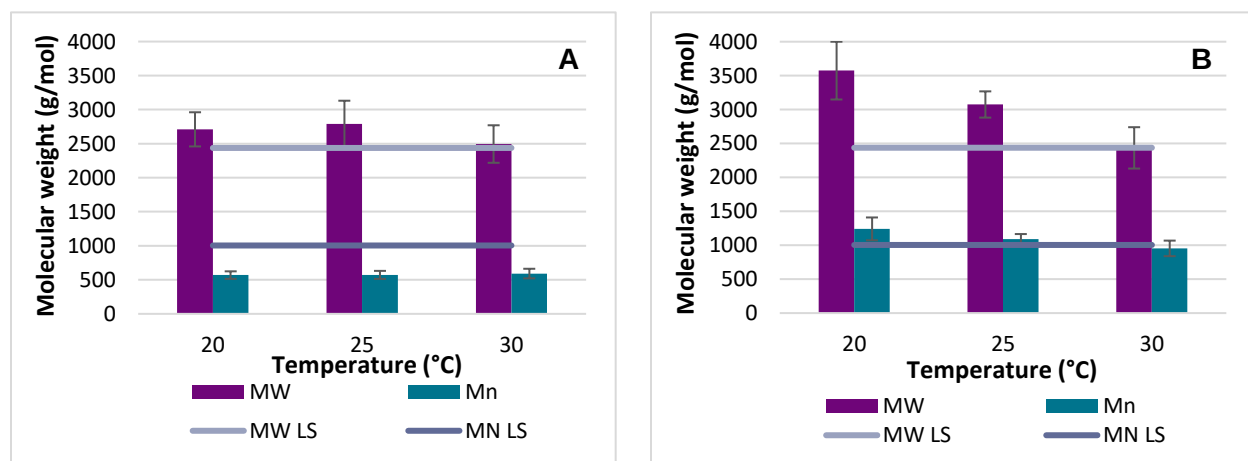


FIGURE 5.15 $\overline{M}_w$ AND $\overline{M}_n$ AT DIFFERENT pH AND DIFFERENT TEMPERATURES AT 250 G/L. (A) AT 1 PH AND (B) AT 2 PH. LS REFERS TO THE ORIGINAL LIGNOSULPHONATE

The carbon mass loss (see Table 5.10) for pH values of 1 and 2 was insignificant except at a pH of 2 and a temperature of 20 °C. The carbon mass loss was low even at higher temperatures which might have been due to the higher concentration. The lignosulphonate molecules were closer to one another at higher concentrations and, therefore, despite higher temperatures the carbon chain was not broken apart as seen for the 150 g/L.

TABLE 5.10 PERCENTAGE CARBON MASS REMOVED AT PH VALUES OF 1 AND 2 AND DIFFERENT TEMPERATURES AT 250 g/L

pH	1			2		
Temperature (°C)	20	25	30	20	25	30
Carbon mass removal (%)	13%	9%	11%	18%	11%	12%

The FTIR results for pH values of 1 and 2 can be seen in Figure 5.16 and Figure 5.17. The three main peak groups were sharper and broader than for original lignosulphonate for both a pH of 1 and 2 and all temperatures. From Figure 5.16 (at a pH of 1) the methyl and methylene groups (2940 cm^{-1}) were more defined, the aromatic groups (1640 , 1520 , 1460 cm^{-1}) were more distinct with longer peaks and the C-O (1046 cm^{-1}) peak was more intense for all temperatures. These FTIR results at a pH of 1 can be explained by the higher ash removal for all three temperatures.

From Figure 5.17 (for a pH of 2) the methyl and methylene groups (2940 cm^{-1}) were sharper and distinct, and the aromatic groups (1640 , 1520 , 1460 cm^{-1}) had longer and more distinct peaks. It is worth noting that the FTIR results at 25 °C had longer peaks than at the other temperatures. The carbonyl group (1046 cm^{-1}) peak was more intense for all temperatures. The FTIR results for a pH of 2 and a temperature of 25 °C were explained by the higher ash removal in comparison to ash removal at temperatures of 20 °C and 30 °C.

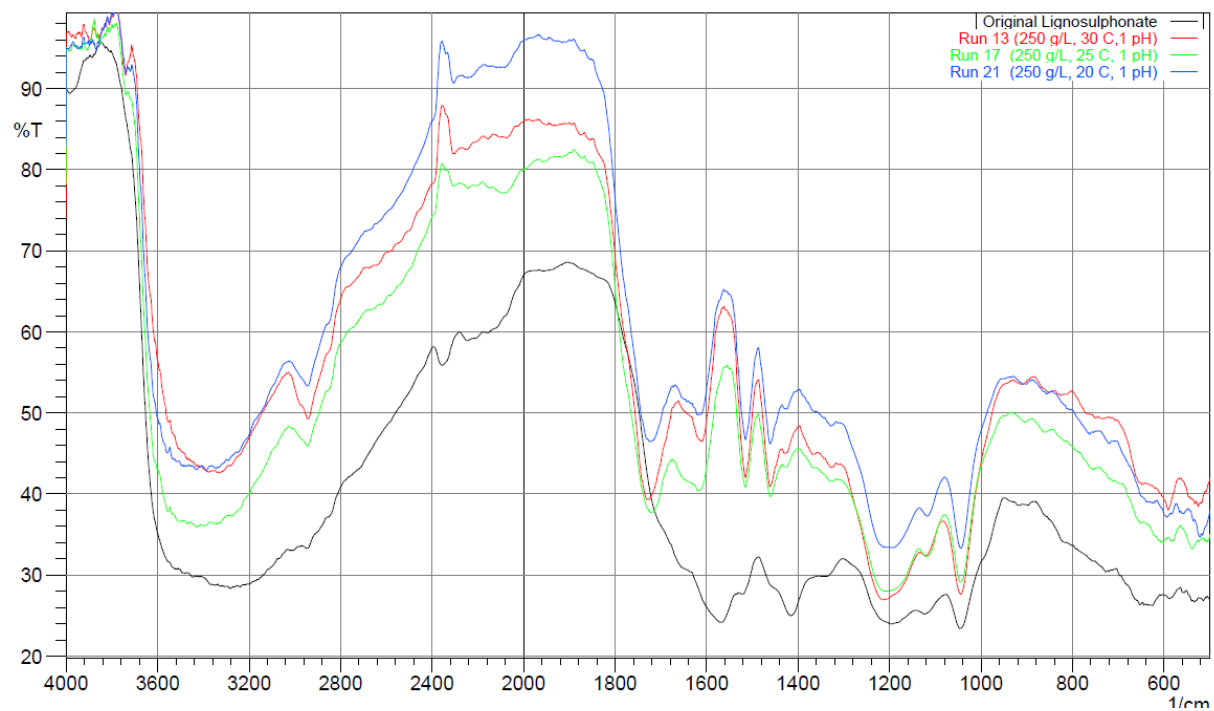


FIGURE 5.16 FTIR RESULTS OF 250G/L AT 1 PH FOR ALL THREE TEMPERATURES

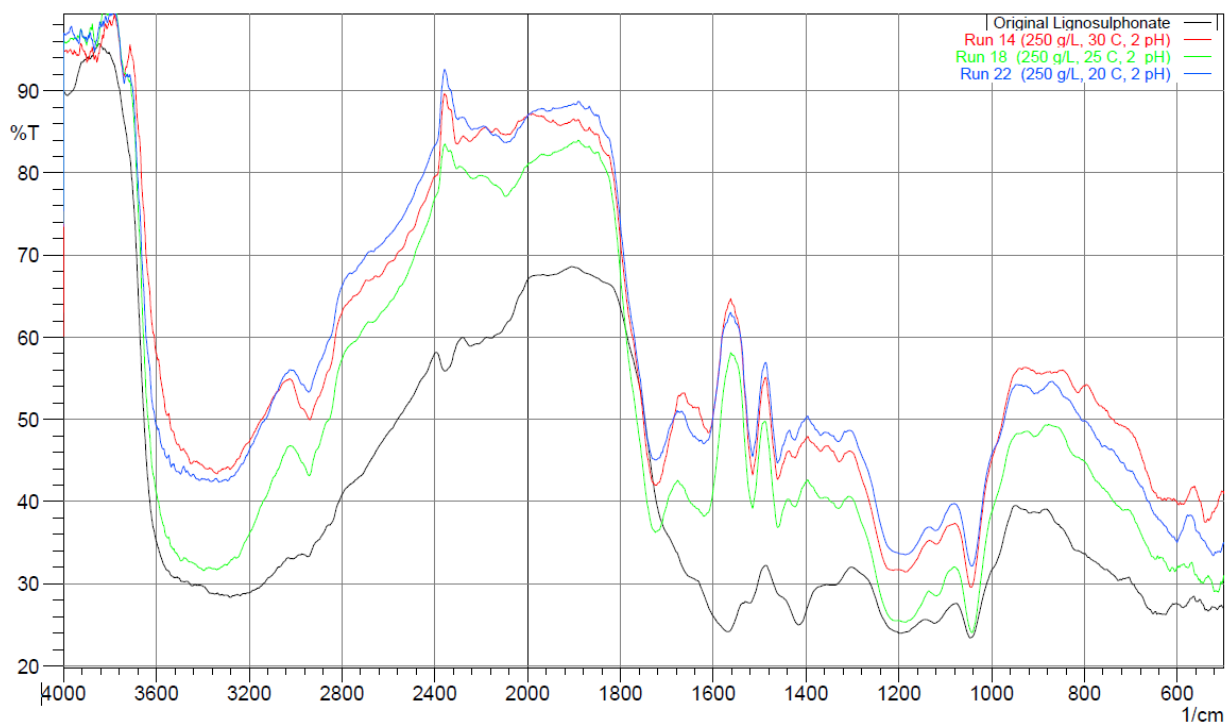


FIGURE 5.17 FTIR RESULTS OF 250G/L AT 2 PH FOR ALL THREE TEMPERATURES

pH VALUES OF 3 AND 4

From Figure 5.18A and Figure 5.18B the $\overline{M}_w$ and $\overline{M}_n$ results were unchanged for pH values of 3 and 4 except at a pH of 3 and a temperature of 20 °C. Therefore, both larger and smaller molecules' main structures were unaffected by the conditions except at a pH of 3 and a temperature of 20 °C when the $\overline{M}_w$ was significantly higher. This suggests the same as stated for a pH of 2 and temperatures of 20 °C and 25 °C, at which the smaller lignosulphonate molecules might have been associated with the larger molecules.

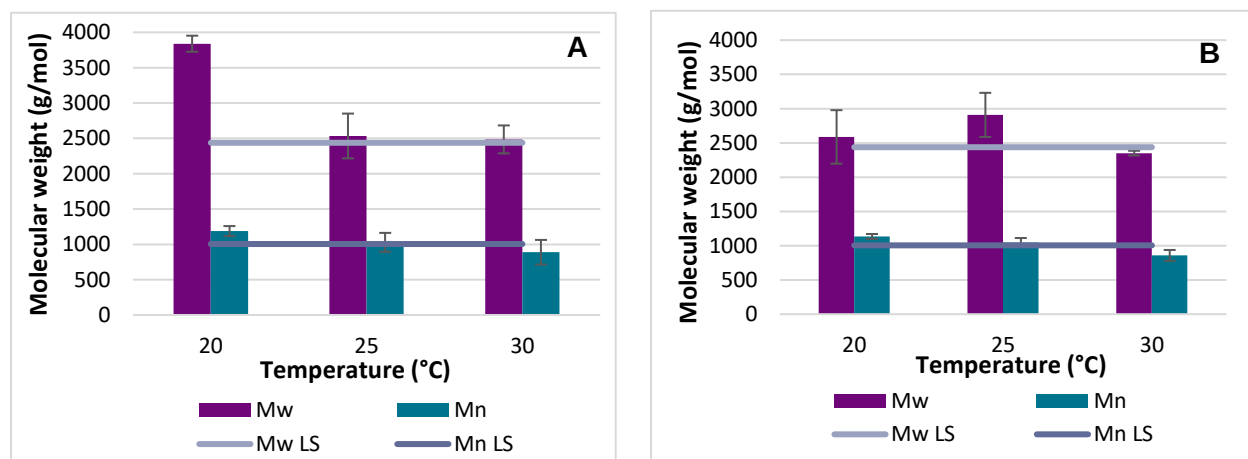


FIGURE 5.18 $\overline{M}_w$ AND $\overline{M}_n$ AT DIFFERENT pH AND DIFFERENT TEMPERATURES AT 250 g/L. (A) AT 3 PH, (B) AT 4 PH

The carbon mass loss (see Table 5.11) for pH values of 3 and 4 was significant but lower than what it was at 150 g/L. This suggests that at higher concentrations lignosulphonate molecules were closer to one another and fewer of the carbon chains were removed than were removed at 150 g/L (Tang *et al.*, 2015a). The higher concentration also hindered the disentanglement of the molecule from its coiled-like shape.

TABLE 5.11 PERCENTAGE CARBON MASS REMOVED AT 3 AND 4 PH AND DIFFERENT TEMPERATURES AT 250 g/L

pH	3			4		
Temperature (°C)	20	25	30	20	25	30
Carbon mass removal (%)	16%	17%	14%	19%	13%	14%

The FTIR results for pH values of 3 and 4 can be seen in Figure 5.19 and Figure 5.20. The three main peak groups were sharper and broader than for original lignosulphonate. From Figure 5.19 (at a pH of 3) the methyl and methylene groups (2940 cm^{-1}) were more defined. The aromatic groups ($1640, 1520, 1460\text{ cm}^{-1}$) were more distinct but smaller in size than those for pH values of 1 and 2. The C-O (1046 cm^{-1}) peak was more intense for all temperatures. The FTIR results for a pH of 3 can be explained by the very low ash removal at this pH value which would have caused the peaks to be less distinct than those with higher ash removals.

In Figure 5.20 (at a pH of 4) the methyl and methylene groups (2940 cm^{-1}) were more defined, but much smaller in size than at the other pH values. The aromatic groups ($1640, 1520, 1460\text{ cm}^{-1}$) were distinct, however much smaller than at the other pH values. The C-O (1046 cm^{-1}) peak was more intense for all temperatures. The FTIR results of 4 pH could be explained by the extremely low ash removal at a pH of 4 resulting in smaller peaks.

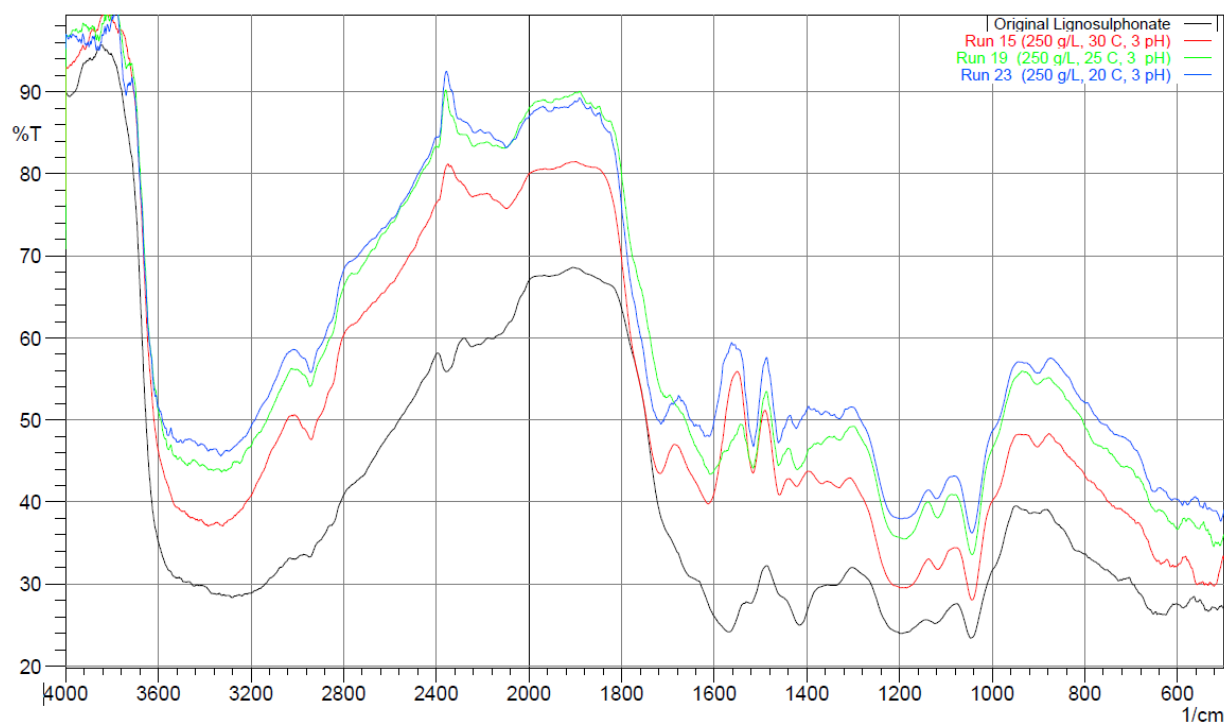


FIGURE 5.19 FTIR RESULTS OF 250G/L AT 3 PH FOR ALL THREE TEMPERATURES

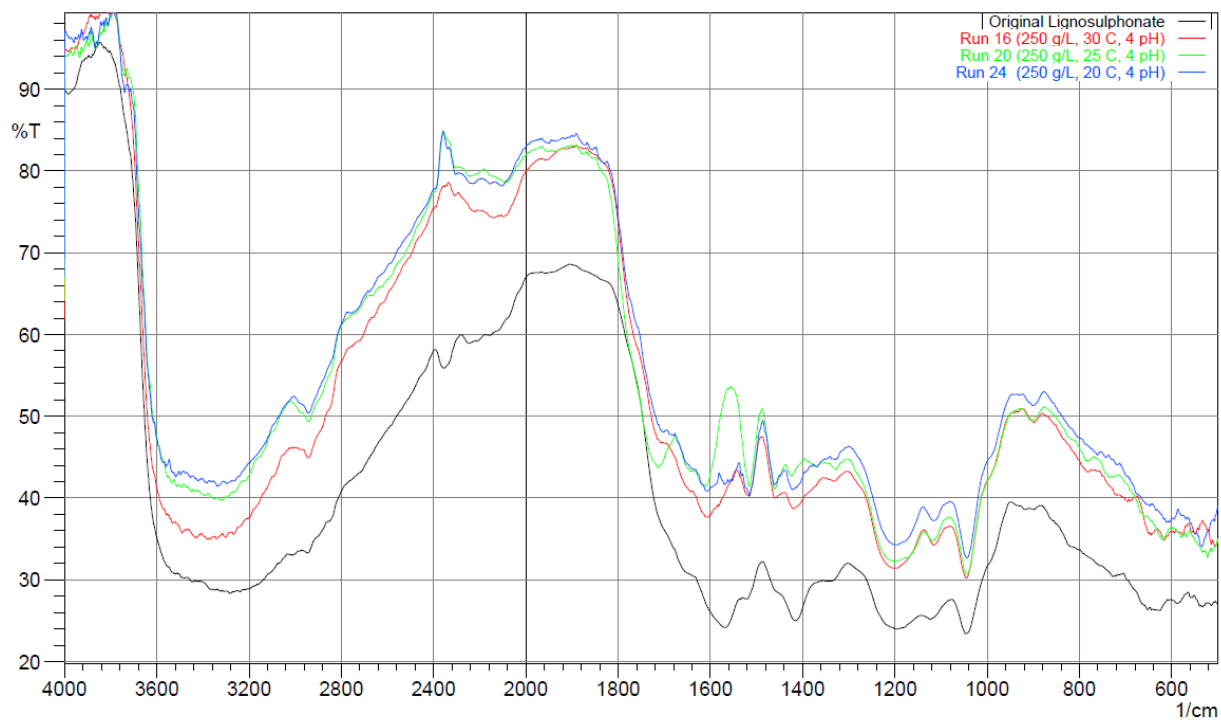


FIGURE 5.20 FTIR RESULTS OF 250G/L AT 4 PH FOR ALL THREE TEMPERATURES

5.2.2 Optimal conditions

From the previous sections, the purification of liginosulphonate was dependent on the pH, temperature, and concentration. In this section, the optimal conditions will be determined systematically based on the relevant criteria for a cost-effective purification of technical liginosulphonate as stated in the Objectives section of Chapter 1.

The first criterion is the complete removal or lowering of sodium and sulphur content. The first evaluation will consider sulphur due to the greater need to remove it from the liginosulphonate molecule. The main form in which sulphur resides in the liginosulphonate molecule is sulphonate which can result in forming SO_2 gas in future processes. Figure 5.21A and Figure 5.21B present the sulphur removal of the two concentration values evaluated, 150 g/L and 250 g/L, respectively. The sulphur removal was generally higher at the concentration value of 150 g/L. The highest sulphur removal at 250 g/L was only 50%.

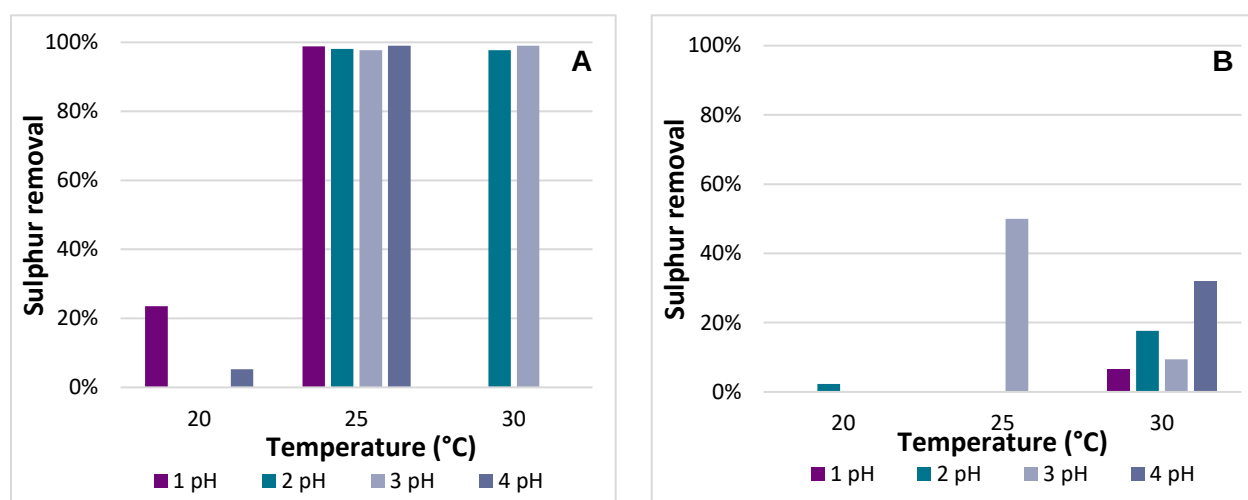


FIGURE 5.21 SULPHUR REMOVAL (%) DUE TO DIFFERENT TEMPERATURES AND PH VALUES AT 150G/L (A) AND 250G/L (B)

The next impurity to evaluate is sodium removal. Sodium interference in future reactions is less problematic than the interference sulphur can create. However, sodium is still considered an impurity to be removed. Figure 5.22A and Figure 5.22B present the sodium removal of the two concentration values evaluated, 150 g/L and 250 g/L, respectively. There was generally a higher removal of sodium at the higher concentration than at the lower concentration. The higher concentration also showed a higher sodium removal at higher temperatures while the lower concentration had a lower sodium removal at higher temperatures.

However, from both concentrations, it is evident that the low pH values resulted in higher sodium removal.

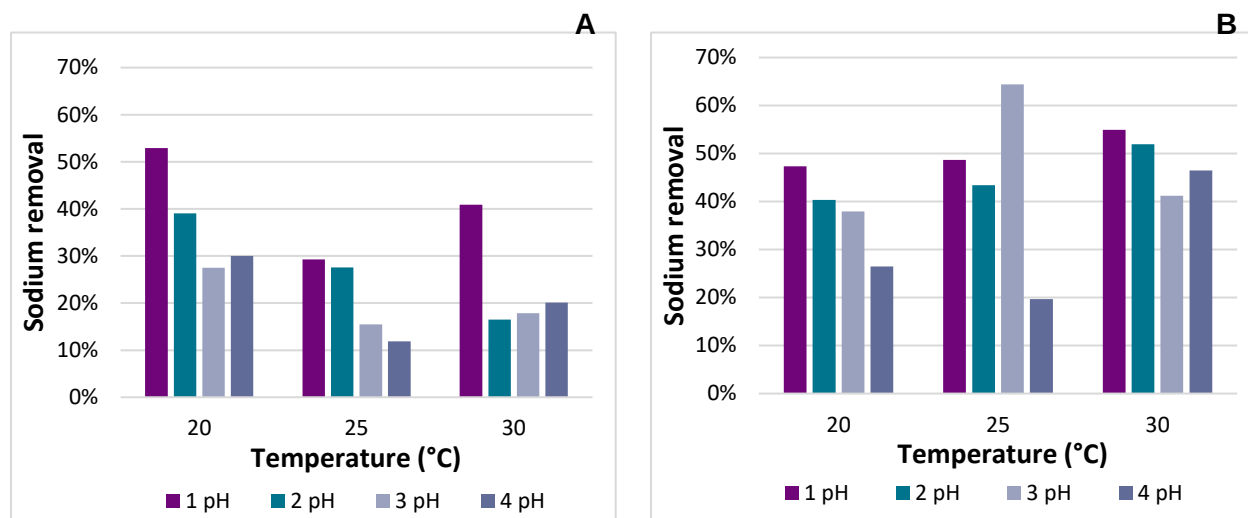


FIGURE 5.22 SODIUM REMOVAL (%) DUE TO DIFFERENT TEMPERATURES AND PH VALUES AT 150G/L (A) AND 250G/L (B)

From the figures for sulphur and sodium, it is evident that lower concentrations favoured sulphur removal and higher concentrations favoured sodium removal. However, due to the greater need to remove sulphur, lower concentrations will be evaluated further. Sulphur had the higher removal at 25 °C (at all pH values) and 30 °C (only at pH values of 2 and 3) at 150 g/L. Sodium had a higher removal at 25 °C than at 30 °C at 150 g/L. The lower pH values produced not only a higher sodium removal but as can be seen from previous ash removal data, a higher ash removal as well. Therefore, in the next evaluation, the dataset of 25 °C, 150 g/L and pH values of 1 and 2 will be assessed.

The next criterion was the minimising of the overall carbon mass loss during purification. The carbon loss for 25 °C at 150 g/L and at pH values of 1 and 2, was 4% and 12%, respectively. Both these values were substantially lower.

The last criterion was preserving the core functionality of the lignosulphonate during purification. The $\overline{M}_w$ and $\overline{M}_n$ values could indicate whether the core of the lignosulphonate molecule underwent any severe changes. The $\overline{M}_w$ and $\overline{M}_n$ of the two conditions are presented in Figure 5.23. The $\overline{M}_w$ value of the condition at a pH of 1 did not change; however, the $\overline{M}_n$ value significantly decreased, thereby suggesting that the larger molecules in the sample were not significantly affected by the purification. However, the smaller molecules underwent a significant reduction. The $\overline{M}_w$ value of the condition at a pH of 2 increased while the $\overline{M}_n$ value decreased,

thereby suggesting that some of the monomeric lignosulphonate molecules started to bind to the larger molecules. This suggests that the molecules started to aggregate.

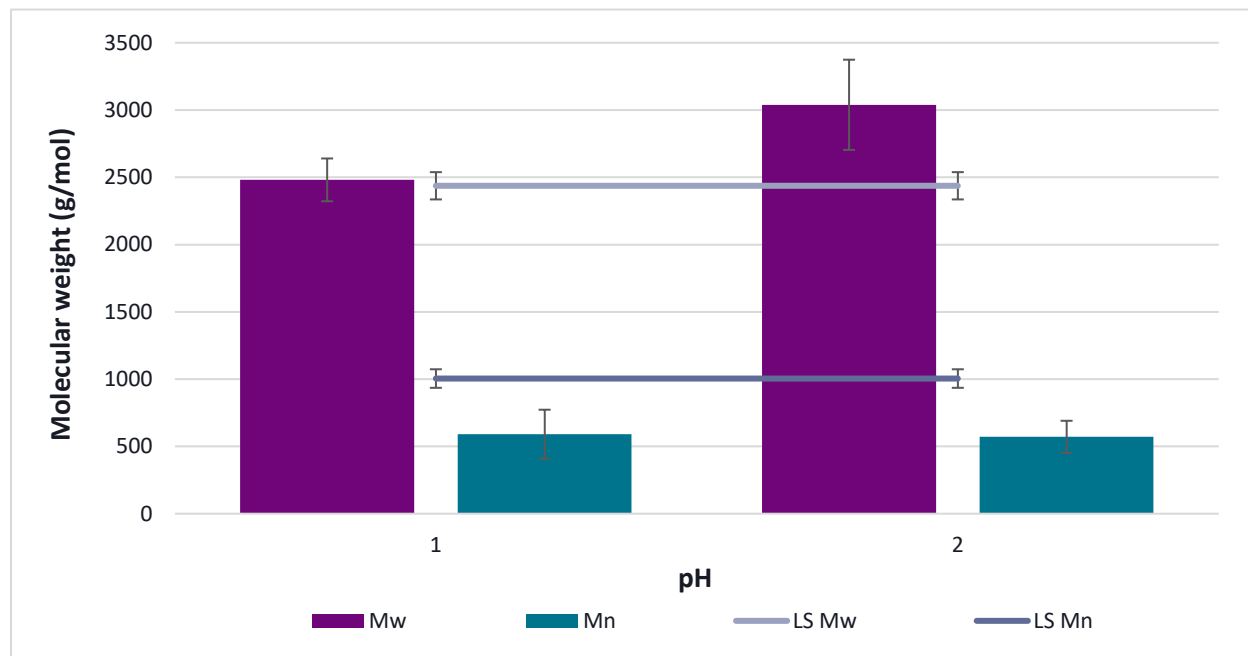


FIGURE 5.23 THE $\overline{M}_w$ AND $\overline{M}_n$ OF THE OPTIMAL CONDITIONS. LS REFERS TO THE ORIGINAL LIGNOSULPHONATE

The FTIR analysis gives insight into the structure after purification at pH values of 1 and 2 (at 25 °C and 150 g/L). In Figure 5.24 the FTIR of the two optimal conditions is shown in comparison with the original sample. The two optimal conditions had more prominent peaks at 2880 cm⁻¹, 1640–1400 cm⁻¹ and 1040 cm⁻¹ in comparison with the original lignosulphonate. This suggests that the impurities that were removed due to the purification, caused a shielding effect in the original lignosulphonate sample. This made the peaks less clear for the FTIR to detect their full presence as can be seen after purification.

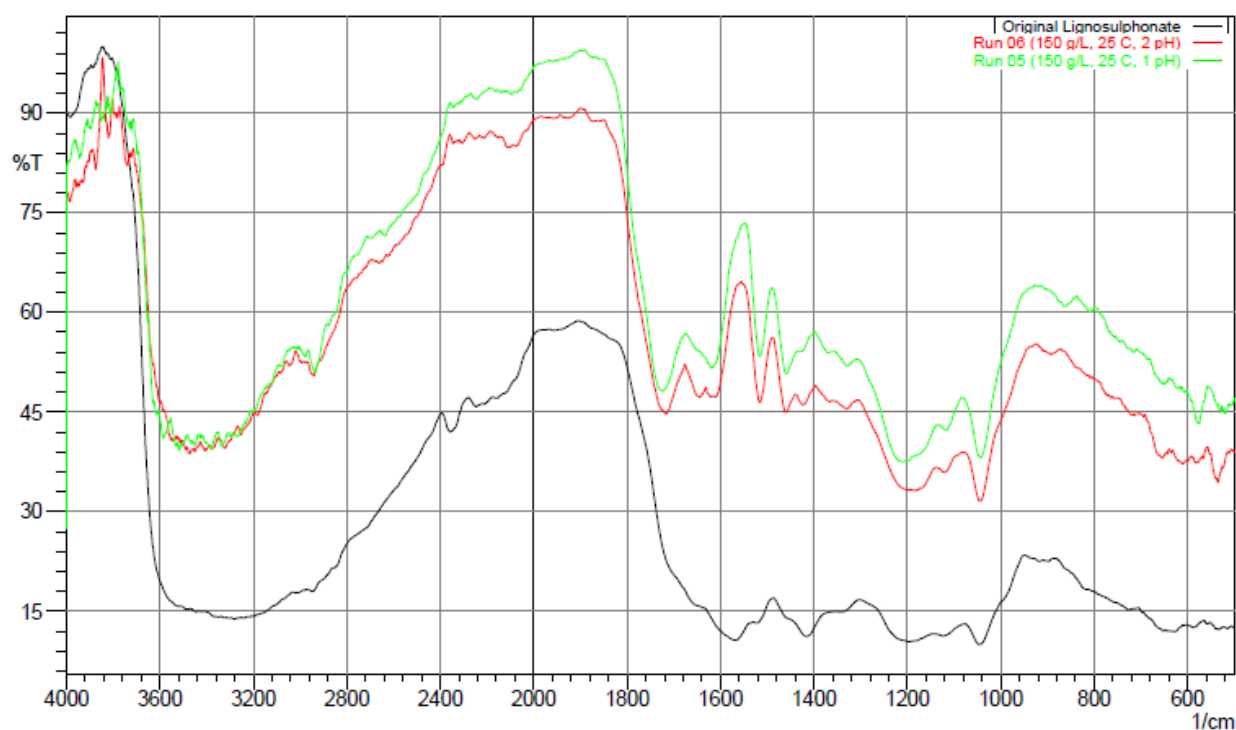


FIGURE 5.24 FTIR RESULTS OF THE OPTIMAL CONDITION

The criteria that were stated in the objectives have led to the conclusion that the optimal conditions of this study were at 150 g/l, 25 °C and low pH values (between 1 and 2). However, when the ash removal is considered, it can be seen that a pH of 1 had substantially higher loss in ash than a pH of 2 and therefore the optimal conditions for this study can be concluded to be 150 g/L, 25 °C and a pH of 1.

In Table 5.12, the purified sample is compared with kraft lignin in terms of ash and sulphur content. The ash content for the purified sample was a bit higher than for the kraft lignin; however, the sulphur content was lower. Further development of the purification method can produce a sample that can be more closely related to kraft lignin.

TABLE 5.12 COMPARISON BETWEEN THE PURIFIED AND COMMERCIAL KRAFT LIGNIN

	Optimal condition for purification	(Namane <i>et al.</i> , 2016)
	150 g/L, 25°C and 1 pH	Commercial kraft lignin
Ash (solid wt%)	14.5	12.6
Sulphur (wt%)	0.08	2.8

Provisional patent

A provisional patent has been filled on this purification process in the United Kingdom by the North West University (see Appendix O for the filling receipt of the provisional patent application). The inventors listed are Prof Sanette Marx, Dr Roelf Venter and Leane Naude.

Chapter 6: Conclusion and recommendation

6.1 Conclusion

The study's purpose evolved into discovering a less expensive method of purifying lignosulphonate and a provisional patent has been filled in the United Kingdom.

The purification method of solvent extraction was chosen based on a literature study. Further investigation was required to determine whether reflux or Soxhlet extraction would be a more suitable option. Through a set of pre-experiments, it was determined that Soxhlet solvent extraction was the most suitable method because the results showed a higher ash removal and lower mass loss.

The physicochemical characterisation of lignosulphonate before and after purification proved vital. This characterisation made it possible to assess the ash, sodium, and sulphur content and also the structural changes. This assessment led to the discovery of the optimal conditions. The study concluded that the optimal conditions for the purification of lignosulphonate occurred at 150 g/L, 25 °C and a pH of 1.

6.2 Recommendations

This study laid the groundwork for further investigation into the affordable purification of sodium lignosulphonate. This study explored how the change in the variables (temperature, pH, and concentration) in the purification process of lignosulphonate influenced the sample. It was also explored how these variables caused changes in the behaviour and structure of the sample. There is a need for further studies into various aspects of purification. More comprehensive studies could lead to a better understanding of this marvel molecule and its behaviour under certain conditions, for example:

- ❖ A more in-depth study of the structural changes of lignosulphonate during purification to obtain a better understanding of the mechanisms at hand and the conformation behaviour of lignosulphonate.

- ❖ An investigation into specifically the 1–2 pH range exploring different temperatures and concentration combinations to obtain a better understanding of the molecular changes that the lignosulphonate molecule undergoes.
- ❖ A study into the kinetics of the possible reactions that occur can also be insightful and provide vital information about the energies involved.
- ❖ Research into the possible reactions that occur and the mechanisms involved in this process would give a better understanding of the purification process.

Further development of the purification concept is required to fully optimise the potential of lignosulphonate. A possible two-step process could be developed to maximise the sodium and sulphur removal. In such a concept, the first step should be conducted at 250 g/L, 30 °C and a pH of 1 as sodium removal is at a maximum under these conditions. The second step should be conducted at 150 g/L, 25 °C and a pH of 1 which would favour sulphur removal. On a calculated basis (see Appendix P), this two-step process can theoretically remove 68% of sodium, 98% of sulphur and 80% of ash content.

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Appendixes

Explanation of the calculation for Appendix F-M

Symbol	Term	Description	Formula
Appendix F: Total Mass loss			
m_L	Mass of the original lignosulphonate (g)	Total mass reported before purification of the original lignosulphonate mass	
m_{AP}	Mass after purification (g)	Total mass reported after purification	
m_R	Mass removal (g)	The total mass removed from the sample due to the purification	$m_R = m_L - m_{AP}$
$m_{R\%}$	Mass removal (%)	The total mass was removed as a percentage of the original mass.	$m_{R\%} = \frac{(m_L - m_{AP})}{m_L}$
Appendix G: Proximate analysis			
Proximate analysis original lignosulphonate			
	Proximate analysis (%)	The proximate reported mean data for the original lignosulphonate for: solids, moisture, ash, volatile	$X_{Lsolids}$ = solids mean data $X_{Lmoisture}$ =moisture mean data X_{Lash} =ash mean data $X_{Lvolatile}$ =volatile mean data <i>L: Original lignosulphonate</i>
	Analysis (g)	The proximate mass content for original lignosulphonate based on the proximate reported mean data for: solids, moisture, ash, volatile	Mass of solids and moisture: $m_{Lsolids} = \frac{X_{Lsolids}}{100} \times m_L$

			$m_{L_{moisture}} = \frac{x_{L_{moisture}}}{100} \times m_L$ Mass of ash and volatile : $m_{L_{ash}} (g) = \frac{x_{L_{ash}}}{100} \times m_{L_{solids}}$ $m_{L_{volatile}} (g) = \frac{x_{L_{volatile}}}{100} \times m_{L_{solids}}$ <i>m: mass</i> <i>L: Original lignosulphonate</i>
Proximate analysis after purification			
	Reported analysis (%)	The proximate reported mean data for the lignosulphonate after purification for: solids, moisture, ash, volatile	$X_{AP_{solids}}$ = solids mean data $X_{AP_{moisture}}$ = moisture mean data $X_{AP_{ash}}$ = ash mean data $X_{AP_{volatile}}$ = volatile mean data <i>AP: After purification lignosulphonate</i>
	Analysis (g)	The proximate mass content for lignosulphonate after purification based on the proximate reported mean data for: solids, moisture, ash, volatile	Analysis of solids and moisture: $m_{AP_{solids}} = \frac{x_{AP_{solids}}}{100} \times m_{AP}$ $m_{AP_{moisture}} = \frac{x_{AP_{moisture}}}{100} \times m_{AP}$ Analysis of ash and volatile : $m_{AP_{ash}} = \frac{x_{AP_{ash}}}{100} \times m_{AP_{solids}}$ $m_{AP_{volatile}} = \frac{x_{AP_{volatile}}}{100} \times m_{AP_{solids}}$ <i>m: mass</i>

			AP: After purification lignosulphonate
	Standard deviation (%)	The standard deviation of the proximate reported data.	
Appendix H: Ash removal analysis			
$m_{L_{ash}}(g)$	Original lignosulphonate (g)	Ash mass content of the original lignosulphonate mass.	
$m_{AP_{ash}}$	After purification (g)	Ash mass content of the lignosulphonate after purification.	
$m_{R_{ash}}$	Removal (g)	The total ash mass removed after purification.	$m_{R_{ash}} = m_{L_{ash}} - m_{AP_{ash}}$
R_{ash}	Removal (%)	The ash content removed after purification as a percentage.	$R_{ash} = \frac{m_{R_{ash}}}{m_{L_{ash}}}$ R: Removal L: Original lignosulphonate
Statistical analysis of ash removal part 1			
$x_{ash_{rep}}$	Ash reported data (%)	The ash reported data from each of the proximate analysis samples after purification	
$m_{ash_{rep}}$	Ash reported data (g)	The ash mass content after purification based on ash reported data	$m_{ash_{rep}} = \frac{x_{ash_{rep}}}{100} \times m_{AP_{solids}}$
$m_{RR_{ash}}$	Removal of reported ash data (g)	The ash content removed after purification	$m_{RR_{ash}} = m_{L_{ash}} - m_{ash_{rep}}$
Statistical analysis of ash removal part 2			
STD_{ash}	Standard deviation of the removal (g)	Standard deviation of the grouped sampled for each run set.	$STD_{ash} = \sqrt{\frac{\sum (x_i - \mu)^2}{N}}$ x_i=Each value of samples of the same run

			μ =The mean of each value of samples of the same run N =the number of samples
$STD_{ash\%}$	Standard deviation of the removal (%)	Standard deviation of the grouped sampled for each run set as a percentage.	$STD_{ash\%} = \frac{STD_{ash}}{m_{Rash}}$
Appendix I: Elemental analysis			
Elemental analysis original lignosulphonate			
	Elemental analysis (%)	The elemental reported mean data for the original lignosulphonate for: Carbon (C), hydrogen (H), nitrogen (N), other (R)	X_{LC} = Carbon mean data X_{LH} =Hydrogen mean data X_{LN} =Nitrogen mean data X_{LR} =Other mean data <i>L: Original lignosulphonate</i>
	Elemental analysis (g)	The elemental mass content for original lignosulphonate based on the elemental reported mean data for: Carbon (C), hydrogen (H), nitrogen (N), other (R)	Analysis of carbon, hydrogen, nitrogen and other. $m_{LC} = \frac{x_{LC}}{100} \times m_L$ $m_{LH} = \frac{x_{LH}}{100} \times m_L$ $m_{LN} = \frac{x_{LN}}{100} \times m_L$ $m_{LR} = \frac{x_{LR}}{100} \times m_L$ <i>m: mass</i> <i>L: Original lignosulphonate</i>
Elemental analysis after purification			
	Elemental analysis (%)	The elemental reported mean data for the lignosulphonate after purification for: Carbon (C), hydrogen (H), nitrogen (N),	X_{AP_C} = Carbon mean data X_{AP_H} =Hydrogen mean data X_{AP_N} =Nitrogen mean data

		other (R)	x_{AP_R} =Other mean data <i>AP: After purification lignosulphonate</i>
	Elemental analysis (g)	The elemental mass content for lignosulphonate after purification based on the elemental reported mean data for: Carbon (C), hydrogen (H), nitrogen (N), other (R)	Analysis of carbon, hydrogen, nitrogen and other. $m_{AP_C} = \frac{x_{AP_C}}{100} \times m_{AP}$ $m_{AP_H} = \frac{x_{AP_H}}{100} \times m_{AP}$ $m_{AP_N} = \frac{x_{AP_N}}{100} \times m_{AP}$ $m_{AP_R} = \frac{x_{AP_R}}{100} \times m_{AP}$ <i>m: mass</i> <i>AP: After purification lignosulphonate</i>
	Standard deviation of the after-purification data (%)	The standard deviation of the elemental reported data.	

Appendix J: Carbon removal analysis

Carbon removal

m_{LC}	Original lignosulphonate (g)	Carbon mass content of the original lignosulphonate.	
m_{AP_C}	After purification (g)	Carbon mass content of the lignosulphonate after purification.	
m_{RC}	Removal (g)	The total carbon mass content removed after purification.	$m_{RC} = m_{LC} - m_{AP_C}$
R_C	Removal (%)	The carbon content removed after purification as a percentage.	$R_C = \frac{m_{RC}}{m_{LC}}$ <i>R: Removal</i>

			<i>L: Original lignosulphonate</i>
Statistical analysis of carbon removal part 1			
x_{Crep}	Carbon reported data (%)	The carbon reported data from each of the elemental analysis samples after purification	
m_{Crep}	Carbon reported data (g)	The carbon mass content after purification based on elemental reported data	$m_{Crep} = \frac{x_{Crep}}{100} \times m_{AP}$
m_{RRC}	Removal of reported carbon (g)	The carbon content removed after purification	$m_{RRC} = m_{LC} - m_{crep}$
Statistical analysis of carbon removal part 2			
STD_C	Standard deviation of the removal (g)	Standard deviation of the grouped sampled for each run set.	$STD_C = \sqrt{\frac{\sum (x_i - \mu)^2}{N}}$ x_i=Each value of samples of the same run μ=The mean of each value of samples of the same run N=the number of samples
$STD_{C\%}$	Standard deviation of the removal (%)	Standard deviation of the grouped sampled for each run set as a percentage.	$STD_{C\%} = \frac{STD_C}{m_{RC}}$
Appendix K: ICP analysis			
ICP analysis original lignosulphonate			
	ICP analysis (%)	The ICP reported mean data for the original lignosulphonate for: calcium (Ca), potassium (K), magnesium (Mg), sodium (Na), sulphur (S) and Other . Only components detected at a	x_{LCa} = calcium mean data x_{LK} = potassium mean data x_{LMg} = magnesium mean data x_{LNa} =sodium mean data

		concentration above 0.001% is reported the rest is summed together under Other.	x_{LS} =sulphur mean data x_{LOther} =other mean data <i>L: original lignosulphonate</i>
	ICP analysis (g)	The ICP mass content for original lignosulphonate based on the ICP reported mean data for: calcium (Ca), potassium (K), magnesium (Mg), sodium (Na), sulphur (S) and Other . Only components detected at a concentration above 0.001% is reported the rest is summed together under Other.	Analysis of calcium, potassium, magnesium, sodium, sulphur and other: $m_{L_{Ca}} = \frac{x_{L_{Ca}}}{100} \times m_L$ $m_{L_K} = \frac{x_{L_K}}{100} \times m_L$ $m_{L_{Mg}} = \frac{x_{L_{Mg}}}{100} \times m_L$ $m_{L_{Na}} = \frac{x_{L_{Na}}}{100} \times m_L$ $m_{L_S} = \frac{x_{L_S}}{100} \times m_L$ $m_{L_{Other}} = \frac{x_{L_{Other}}}{100} \times m_L$ <i>m: mass</i> <i>L: Lignosulphonate</i>
ICP analysis after purification			
	ICP analysis (%)	The ICP reported mean data for the lignosulphonate after purification for: calcium (Ca), potassium (K), magnesium (Mg), sodium (Na), sulphur (S) and Other . Only components detected at a concentration above 0.001% is reported the rest is summed together under Other.	x_{APCa} = calcium mean data x_{APK} = potassium mean data x_{APMg} = magnesium mean data x_{APNa} =sodium mean data x_{APS} =sulphur mean data $x_{APOther}$ =other mean data

			AP: After purification lignosulphonate
	ICP analysis (g)	The ICP mass content for lignosulphonate after purification based on the ICP reported mean data for: calcium (Ca), potassium (K), magnesium (Mg), sodium (Na), sulphur (S) and Other . Only components detected at a concentration above 0.001% is reported the rest is summed together under Other.	Analysis of calcium, potassium, magnesium, sodium, sulphur and other: $m_{APCa} = \frac{x_{APCa}}{100} \times m_{AP}$ $m_{APK} = \frac{x_{APK}}{100} \times m_{AP}$ $m_{APMg} = \frac{x_{APMg}}{100} \times m_{AP}$ $m_{APNa} = \frac{x_{APNa}}{100} \times m_{AP}$ $m_{APS} = \frac{x_{APS}}{100} \times m_{AP}$ $m_{APOther} = \frac{x_{APR}}{100} \times m_{AP}$ m: mass AP: After purification lignosulphonate
	Standard deviation of the after-purification data (%)	The standard deviation of the ICP reported data.	
Appendix L: Sodium and sulphur removal analysis			
Sodium and sulphur removal			
m_{LNa}	Sodium lignosulphonate (g)	Sodium mass content of the original lignosulphonate.	
m_{APNa}	Sodium after purification (g)	Sodium mass content of the lignosulphonate after purification.	
m_{RNa}	Sodium removal (g)	The total sodium mass content removed after purification.	$m_{RNa} = m_{LNa} - m_{APNa}$

R_{Na}	Sodium removal (%)	The sodium content removed after purification as a percentage.	$R_{Na} = \frac{m_{RNa}}{m_{LNa}}$ <i>R: Removal</i> <i>L: Original lignosulphonate</i>
m_{LS}	Sulphur lignosulphonate (g)	Sulphur mass content of the original lignosulphonate.	
m_{AP_S}	Sulphur after purification (g)	Sulphur mass content of the lignosulphonate after purification.	
m_{RS}	Sulphur removal (g)	The total sulphur mass content removed after purification.	$m_{RS} = m_{LS} - m_{AP_S}$
R_S	Sulphur removal (%)	The sulphur content removed after purification as a percentage.	$R_S = \frac{m_{RS}}{m_{LS}}$ <i>R: Removal</i> <i>L: Original lignosulphonate</i>
Statistical analysis of sodium removal part 1			
$x_{Na_{rep}}$	Na reported data (%)	The sodium reported data from each of the ICP analysis samples after purification	
$m_{Na_{rep}}$	Na reported data (g)	The sodium mass content after purification based on ICP reported data	$m_{Na_{rep}} = \frac{x_{Na_{rep}}}{100} \times m_{AP}$
m_{RRNa}	Removal of Na reported mass (g)	The sodium content removed after purification	$m_{RRNa} = m_{LNa} - m_{Na_{rep}}$
Statistical analysis of sodium removal part 2			
STD_{Na}	Standard deviation of the removal (g)	Standard deviation of the grouped sampled for each run set.	$STD_{Na} = \sqrt{\frac{\sum (x_i - \mu)^2}{N}}$ <i>x_i=Each value of samples of the same run</i>

			μ =The mean of each value of samples of the same run N =the number of samples
$STD_{Na\%}$	Standard deviation of the removal (%)	Standard deviation of the grouped sampled for each run set as a percentage.	$STD_{Na\%} = \frac{STD_{Na}}{m_{RNa}}$
STD_{Na}	Standard deviation of the removal (g)	Standard deviation of the grouped sampled for each run set.	$STD_{Na} = \sqrt{\frac{\sum (x_i - \mu)^2}{N}}$ x_i =Each value of samples of the same run μ =The mean of each value of samples of the same run N =the number of samples
Appendix M: GPC analysis			
$\bar{x}$	Mean reported data (g/mol)		
STD	Standard deviation of the reported data (g/mol)	1x standard deviation of the value	
Max	Maximum (g/mol)	Maximum of the reported data based on 1x standard deviation of the value	$Max = \bar{x} + STD$
Min	Minimum (g/mol)	Minimum of the reported data based on 1x standard deviation of the value	$Min = \bar{x} - STD$

Appendix A: Pre-experiment analysis

Purifi. = purification

	Lignosulphonate	Exp 1			
	Analysis (%)	Before purifi. mass (g)	After purifi. (%)	After purifi. mass (g)	Mass loss (%)
Mass loss		118.3		68.5	42
Elemental analysis					
Carbon	34.327	40.61	36.097	24.73	39.1
Hydrogen	3.893	4.61	3.850	2.64	42.7
Nitrogen	0.423	0.50	0.180	0.12	75.4
R	61.353	72.58	59.873	41.01	43.5
Proximate analysis					
Solids	96.712	114.41	91.524	62.69	45.2
Moisture	3.288	3.76	8.476	5.31	-41.3
Ash	23.191	26.53	44.909	28.16	-6.1
Volatile	54.190	62.00	40.069	25.12	59.5
Fixed Carbon	19.331	22.12	6.547	4.10	81.4
GPC	Before purifi. (g/mol)				After purifi. (g/mol)
Mw	2437.20				5423.90
Mn	1004.49				1978.15
PDI	2.43				2.74

	Lignosulphonate	Exp 2			
	Analysis (%)	Before purfi. mass (g)	After purfi. (%)	After purfi. mass (g)	Mass loss (%)
Mass loss		109.7		18.239	83
Elemental analysis					
Carbon	34.327	37.66	18.407	3.36	91.1
Hydrogen	3.893	4.27	1.727	0.31	92.6
Nitrogen	0.423	0.46	0.167	0.03	93.5
R	61.353	67.30	79.700	14.54	78.4
Proximate analysis					
Solids	96.712	106.09	100.235	18.28	82.8
Moisture	3.288	3.61	-0.235	-0.04	101.2
Ash	23.191	24.60	63.491	11.61	52.8
Volatile	54.190	59.45	35.886	6.55	89.0
Fixed Carbon	19.331	21.21	0.858	0.16	99.3
GPC	Before purfi. (g/mol)				After purfi. (g/mol)
Mw	2437.20				2328.81
Mn	1004.49				665.55
PDI	2.43				3.50

	Lignosulphonate	Exp 3			
	Analysis (%)	Before purifi. mass (g)	After purifi. (%)	After purifi. mass (g)	Mass loss (%)
Mass loss		71.858		54.634	23.97
Elemental analysis					
Carbon	34.327	24.67	32.557	17.79	27.9
Hydrogen	3.893	2.80	4.420	2.41	13.7
Nitrogen	0.423	0.30	0.327	0.18	41.3
R	61.353	44.09	62.700	34.26	22.3
Proximate analysis					
Solids	96.712	69.50	87.632	47.88	31.1
Moisture	3.288	2.36	12.368	6.76	-186.0
Ash	23.191	16.12	16.734	8.01	50.3
Volatile	54.190	38.94	75.010	40.98	-5.2
Fixed Carbon	19.331	13.89	0.000	0.00	100.0
GPC	Before purifi. (g/mol)				After purifi. (g/mol)
Mw	2437.20				2970.12
Mn	1004.49				734.53
PDI	2.43				4.06

	Lignosulphonate	Exp 4					
	Analysis (%)	Beginning (g)	Before purfi. mass (g)	Before purif. mass loss (%)	After purfi. (%)	After purfi. mass (g)	Mass loss (%)
Mass loss		50.015	33.621	32.78		30.4095	9.55
Elemental analysis							
Carbon	34.327	17.17	11.54	32.8	31.573	9.60	16.8
Hydrogen	3.893	1.95	1.31	32.8	4.207	1.28	2.3
Nitrogen	0.423	0.21	0.14	32.8	0.310	0.09	33.8
R	61.353	30.69	20.63	32.8	63.900	19.43	5.8
Proximate analysis							
Solids	96.712	48.37	32.52	32.8	83.324	25.34	22.1
Moisture	3.288	1.64	1.11	32.8	16.676	5.07	-358.8
Ash	23.191	11.22	7.54	32.8	16.722	4.24	43.8
Volatile	54.190	27.10	18.22	32.8	65.638	19.96	-9.6
Fixed Carbon	19.331	9.67	6.50	32.8	0.964	0.29	95.5
GPC	Before purfi. (g/mol)						After purfi. (g/mol)
Mw	2437.20						2835.58
Mn	1004.49						744.92
PDI	2.43						3.81

	Lignosulphonate	Exp 5					
	Analysis (%)	Beginning (g)	Before purfi. mass (g)	Before purif. mass loss (%)	After purfi. (%)	After purfi. mass (g)	Mass loss (%)
Mass loss		50.008	33.9618	32.09		31.94	5.9
Elemental analysis							
Carbon	34.327	17.17	11.66	32.1	29.980	9.58	17.9
Hydrogen	3.893	1.95	1.32	32.1	3.947	1.26	4.7
Nitrogen	0.423	0.21	0.14	32.1	0.483	0.15	-7.4
R	61.353	30.68	20.84	32.1	65.590	20.95	-0.6
Proximate analysis							
Solids	96.712	48.36	32.85	32.1	91.418	29.20	11.1
Moisture	3.288	1.64	1.12	32.1	8.582	2.74	-145.5
Ash	23.191	11.22	7.62	32.1	20.717	6.05	20.6
Volatile	54.190	27.10	18.40	32.1	60.956	19.47	-5.8
Fixed Carbon	19.331	9.67	6.56	32.1	9.745	3.11	52.6
GPC	Before purfi. (g/mol)						After purfi. (g/mol)
Mw	2437.20						3114.05
Mn	1004.49						1073.53
PDI	2.43						2.90

Appendix B: Whatman standard cellulose extraction thimbles

Parameter Grade 603 Standard Cellulose Extraction Thimble, 33 × 100 mm, thickness 1.5 mm	
Grade	603
Material	Cellulose
Wall Thickness	1.5 mm
Operating temp. max.	130 °C
i.d.	33 mm
Length	100 mm

Data sources from: <https://www.cytivalifesciences.com/en/us/shop/whatman-laboratory-filtration/thimbles/cellulose-thimbles-standard/standard-cellulose-extraction-thimbles-p-00276#overview>

Appendix C: Experimental run outline

Run	Concentration (g/L)	Temperature (°C)	pH
1	150	30	1
2	150	30	2
3	150	30	3
4	150	30	4
5	150	25	1
6	150	25	2
7	150	25	3
8	150	25	4
9	150	20	1
10	150	20	2
11	150	20	3
12	150	20	4
13	250	30	1
14	250	30	2
15	250	30	3
16	250	30	4
17	250	25	1
18	250	25	2
19	250	25	3
20	250	25	4
21	250	20	1
22	250	20	2
23	250	20	3
24	250	20	4

Appendix D: Instrument specification

Instrument / Method	Make	Information
Inductively Coupled Plasma Optical Emission spectroscopy (ICP-OES)	Agilent Technologies 725-ES ICP OES with radial torch	Power: 0.90 kW Plasma Argon flow: 15.0L/min Auxiliary Argon flow: 1.50 L/min Nebulizer Argon flow: 0.75 L/min Viewing height: 12 mm Replicates: 3 Replicate read time: 15.0 s Instrument stabilization delay: 15 s The ICP principle is based on the fact that atoms and ions can absorb energy to move electrons from the lower ground state to a higher excited state. In ICP-OES, the source of that required energy is the heat from an argon plasma (operates at 10,000 kelvin). As an electron returns from the higher energy level to a lower energy level (usually the ground state) it emits light with a very specific wavelength. The wavelength is determined by the type of atom or ion (referring to specific elements), and the energy levels the electron is moving between. The Beer Lambert law describes the relationship between the light intensity and concentration of the specific element. Meaning that the amount of light that is released at each wavelength is proportional to the number of atoms or ions making the conversion.

Instrument / Method	Make	Info
Gel Permeation Chromatography (GPC)	PerkinElmer Flexar HPLC with RID	Column: 2 x Agilent technologies Polargel-L 300 x 7.5 mm. Columns connected in series. Column temp: 55 °C Mobile phase: DMSO/Water (9:1 v/v) containing 0.05 mol/dm⁻³ LiBr Injection volume: 100 µL Sample preparation: 8 mg/mL sample in mobile phase. Samples must be stirred and filtered through a 0.45 µm PALL Acrodisc, GxP/GHP filter prior to injection. GPC is used to characterise the molecular mass size distribution of materials such as polymers. GPC is especially used where the molecules' molar mass varies across a range, as opposed to a compound with a single specific molar mass. The instrument functions similar to that of the HPLC (High Performance Liquid Chromatography), with the difference being in the type of columns used. GPC columns separate the molecules of a sample based on their physical size. The small molecules take a longer time to move through the GPC columns than the larger molecules of the same sample. The current instrument in operation is mostly used to characterise bio-oils, biomass and lignin.
Fourier Transform Infrared Spectroscopy (FTIR)	Shimadzu – IRAffinity-1	FTIR spectroscopy, is an analysis that tells us more about what kind of molecules that are present in a solid or liquid. The processes involve an infrared beam of different wavelengths projected onto a sample. The atoms within the sample absorb specific wavelengths of the infrared beam. However, the wavelengths that are not absorbed by the sample, pass through a detector that generates a specific signal. These signals are transformed into a spectrum using Fourier transform (mathematical procedure). The characteristic traits of particular groups of molecules are identified from the generated spectrum based on specific peaks that occur at certain wavelengths.

Instrument / Method	Make	Info
Elemental Analysis	Exeter CE-440 Elemental Analyser	The elemental analyser is used for the analysis of organic compounds such as polymers to determine the Carbon (C), Hydrogen (H), Nitrogen (N) , and inorganics (R) content of the sample. The CE440 Elemental Analyser gives dependable results and maximum throughput with unparalleled accuracy and precision.
Proximate Analysis	Determination of Ash in Biomass	NREL/TP-510-42622 NREL/TP-510-42621

Appendix E: Qualitative and (quantitative) XRD Certification of XRD Analysis



Bureau Veritas Testing and
Inspections South Africa
Sunderland Ridge
Reg N° 2002/003217/07



North West University
For Attention: Rene Bekker
Email: rene.bekker@nwu.ac.za

Ref No:	2122-826
Date Received:	04/10/2021
Contact Person:	Willem Swanepoel
Report Status:	FINAL
Report Date:	18/10/2021

308 Barolong Street
Icon Industrial Park
Sunderland Ridge X10
PO Box 11498
Wierda Park South 0057
Tel: +27(0)12 940 0911
Fax: +27(0)86 631 4743

CERTIFICATE OF ANALYSIS

Sample Identification		LIGNEX SAMPLE
Mass	(g)	258
Proximate Analysis	% Inherent moisture content (air-dried)	5.0
	% Ash content (air-dried)	26.6
	% Ash content (dry basis)	27.9
	% Volatile Matter (air-dried)	51.3
	% Volatile Matter (dry basis)	54.0
	% Fixed carbon (by calculation) (air-dried)	17.1
% Total sulphur (air-dried)		7.29
Ultimate Analysis	% Carbon Content (air-dried)	34.20
	% Hydrogen Content (air-dried)	4.01
	% Nitrogen Content (air-dried)	0.31
	% Oxygen Content (calculation) (air-dried)	22.64
Forms of Sulphur	% Pyritical Sulphur (air-dried)	Not possible to analyse, due to sulphonate compound
	% Sulphatic Sulphur (air-dried)	
	% Organic Sulphur (air-dried)	
Ash Composition (XRF)	Al ₂ O ₃ %	0.25
	CaO %	0.70
	Cr ₂ O ₃ %	0.04
	Fe ₂ O ₃ %	0.19
	K ₂ O %	0.82
	MgO %	0.87
	MnO %	0.03
	Na ₂ O %	44.50
	P ₂ O ₅ %	0.28
	SiO ₂ %	14.43
	TiO ₂ %	0.02
	V ₂ O ₅ %	nd
	ZrO ₂ %	0.01
	BaO %	nd
	SrO %	nd
	ZnO %	nd
	SO ₃ %	38.39

These samples were analysed using coal standard methods

Description	Procedure / Test Method
Sample preparation	ISO 13909-4: 2016
Moisture content (%)	ISO 1172: 2013
Ash content (%)	ISO 1171: 2010
Volatile matter content (%)	ISO 1562: 2010
Total sulphur (%)	ISO 15579: 2006
Ultimate analysis	Based on ISO 12902 - CHN Instrumental method (Subcontracted Test)
Ash composition	ASTM D4326 XRF - By fusion bead (Subcontracted Test)

Results reported are only representative of the sample received for testing. Sample preparation will deviate from ISO 13909-4: 2001(E) Table 1 (Minimum Mass of Samples After Division) where insufficient material was supplied or generated due to the nature of the requirements. While every endeavour has been made to ensure that the results reported are accurate, Bureau Veritas Testing and Inspections South Africa shall not be liable for any error nor for any damage or loss what so ever that may arise from the issuing of this certificate. This certificate may not be reproduced in part or full without written permission from the Technical Managers of Bureau Veritas Testing and Inspections South Africa. Please note that samples will be discarded three months after date of Final Report unless instructed otherwise by client.

C.W. Swanepoel
Technical Signatory



T0469



Dr Sabine Verryn

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XRD Analytical and Consulting cc
75 Kafue Street, Lynnwood Glen,
0081, South Africa

CLIENT: Bureau Veritas

DATE: 07 October 2021

SAMPLES: 1 Sample

ANALYSIS: Qualitative and (quantitative) XRD

The material was prepared for XRD analysis using a backloading preparation method. Diffractograms were obtained using a Malvern Panalytical Empyrean diffractometer with PIXcel detector and fixed slits with Fe filtered Co-K α radiation. The phases were identified using X'Pert Highscore plus software.

Comment:

- In case the results do not correspond to results of other analytical techniques, please let me know for further fine tuning of XRD results.
- Mineral names may not reflect the actual compositions of minerals identified, but rather the mineral group.
- Due to preferred orientation and crystallite size effects, results may not be as accurate as shown.
- **Traces of additional phases may be present. The sample seems mainly amorphous with traces of the identified compound.**

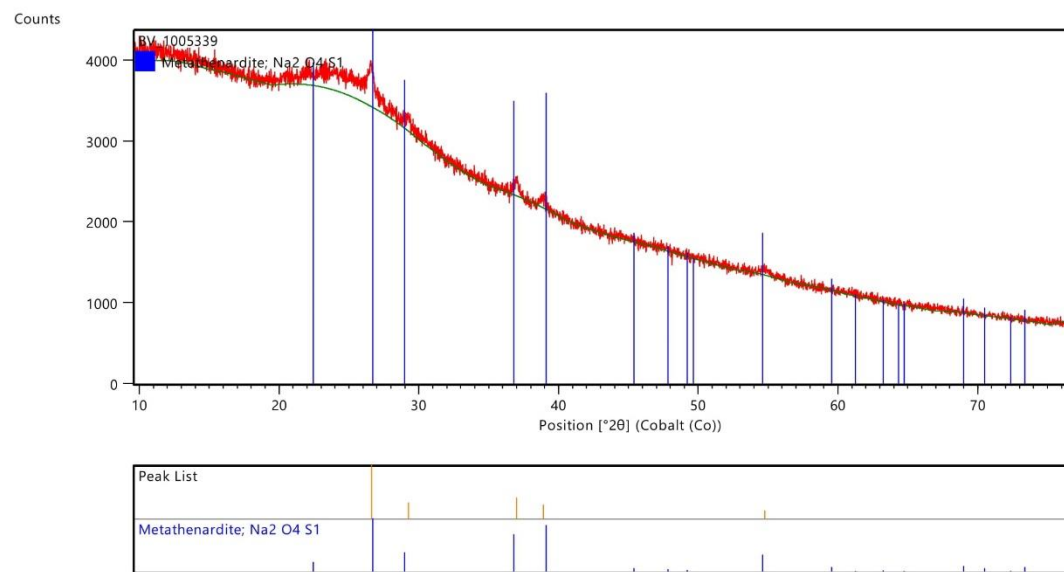
If you have any further queries, kindly contact me.

Dr. Sabine Verryn (Pr.Sci.Nat)

Samples will be stored for 3 months after which they will be discarded.

Limitation of Liability: Although every effort is made to provide reliable and accurate results, by use of the results the client agrees that "XRD Analytical and Consulting cc" and/or its staff can only be held liable for the cost of the analysis.

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0 = n.d. – not detected above the detection limit of 0.5-3 weight per cent

Limitation of Liability: Although every effort is made to provide reliable and accurate results, by use of the results the client agrees that "XRD Analytical and Consulting cc" and/or its staff can only be held liable for the cost of the analysis.

Verification calculation of XRD and ICP

XRF results		
ash_{XRF}	Ash (%) air dried	27.90
$X_{\text{Na}_2\text{O}}$	Na ₂ O (%)	44.5
X_{SO_3}	SO ₃ (%)	38.39

ICP results		
m_{solids}	Solids(%)	96.71
X_{Na}	Na (%)	12.02
X_{S}	S (%)	6.27

100 g of Sample		
XRF		
	Mass (g)	
Ash	27.90	Air dried
	Mass (g)	Mol
SO ₃	10.7	0.13
S	4.3	0.13
Na ₂ O	12.4	0.2
Na	9.21	0.4

100 g of Sample		
ICP		
	Mass (g)	
Solids	96.71	Proximate analysis
S	6.07	
Na	11.63	

XRF calculation

Mass of the ash is determined by the XRF analysis of ash based on dried air analysis. This calculation is based on 100 g sample.

$$m_{\text{ash}} = \frac{\text{ash}_{\text{XRF}}}{100} \times 100$$

The SO₃ mass is then calculated:

$$m_{\text{SO}_3} = \frac{x_{\text{SO}_3}}{100} \times m_{\text{ash}}$$

The SO₃ mol amount is determined by multiplying the m_{SO_3} with its molecular weight (MW of SO₃ is 80.06 g/mol)

$$\text{mol}_{\text{SO}_3} = \frac{m_{\text{ash}}}{80.06}$$

$$\text{mol}_{\text{S}} = \text{mol}_{\text{SO}_3}$$

The Sulphur mass can be calculated by multiplying the sulphur mol amount with its molecular weight (MW of S is 32.07 g/mol)

$$m_{\text{S}} = \text{mol}_{\text{S}} \times 32.07$$

The Na₂O mass is then calculated:

$$m_{Na2O} = \frac{x_{Na2O}}{100} \times m_{ash}$$

The Na₂O mol amount is determined by multiplying the m_{Na2O} with its molecular weight (MW of Na₂O is 61.98 g/mol)

$$mol_{Na2O} = \frac{m_{ash}}{61.98}$$

$$mol_{Na} = mol_{Na2O}$$

The sodium mass can be calculated by multiplying the sodium mol amount with its molecular weight (MW of Na is 22.99 g/mol)

$$m_{Na} = mol_{Na} \times 22.99$$

ICP calculation

The mass amount of sulphur and sodium:

$$m_S = \frac{x_S}{100} \times m_{solids}$$

$$m_{Na} = \frac{x_{Na}}{100} \times m_{solids}$$

Appendix F: Total Mass loss

	m_{LS} (g)	m_{AP} (g)	m_R (g)	m_R% (%)
Run 1	44.1593	42.9011	1.258	2.85
Run 2	42.3428	39.7081	2.635	6.22
Run 3	47.6209	44.4316	3.189	6.70
Run 4	44.8082	42.7716	2.037	4.55
Run 5	48.9148	46.3778	2.537	5.19
Run 6	46.329	44.0721	2.257	4.87
Run 7	47.7394	46.3858	1.354	2.84
Run 8	46.8926	45.5938	1.299	2.77
Run 9	43.6245	41.9932	1.631	3.74
Run 10	44.0976	42.4390	1.659	3.76
Run 11	44.5838	42.8295	1.754	3.93
Run 12	45.9805	44.1624	1.818	3.95
Run 13	44.2352	42.5321	1.703	3.85
Run 14	41.7397	40.6072	1.132	2.71
Run 15	44.8513	43.6840	1.167	2.60
Run 16	46.1645	45.0432	1.121	2.43
Run 17	41.124	39.2571	1.867	4.54
Run 18	44.0806	42.9920	1.089	2.47
Run 19	44.6985	43.6460	1.053	2.35
Run 20	46.0848	45.0561	1.029	2.23
Run 21	43.8678	42.6132	1.255	2.86
Run 22	44.9199	43.8018	1.118	2.49
Run 23	47.5487	46.5396	1.009	2.12
Run 24	46.6873	45.2844	1.403	3.00

Appendix G: Proximate analysis

Proximate analysis original lignosulphonate

	Proximate analysis (%)			
	Solids	Moisture	Ash	Volatile
Lignosulphonate	96.71	3.29	23.19	54.19

	Proximate analysis (g)			
	Solids	Moisture	Ash	Volatile
Run 1	42.7	1.5	9.9	23.1
Run 2	41.0	1.4	9.5	22.2
Run 3	46.1	1.6	10.7	25.0
Run 4	43.3	1.5	10.1	23.5
Run 5	47.3	1.6	11.0	25.6
Run 6	44.8	1.5	10.4	24.3
Run 7	46.2	1.6	10.7	25.0
Run 8	45.4	1.5	10.5	24.6
Run 9	42.2	1.4	9.8	22.9
Run 10	42.6	1.4	9.9	23.1
Run 11	43.1	1.5	10.0	23.4
Run 12	44.5	1.5	10.3	24.1
Run 13	42.8	1.5	9.9	23.2
Run 14	40.4	1.4	9.4	21.9
Run 15	43.4	1.5	10.1	23.5
Run 16	44.6	1.5	10.4	24.2
Run 17	39.8	1.4	9.2	21.6
Run 18	42.6	1.4	9.9	23.1
Run 19	43.2	1.5	10.0	23.4
Run 20	44.6	1.5	10.3	24.2
Run 21	42.4	1.4	9.8	23.0
Run 22	43.4	1.5	10.1	23.5
Run 23	46.0	1.6	10.7	24.9
Run 24	45.2	1.5	10.5	24.5

Proximate analysis after purification

	Reported analysis (%)				Analysis (g)				Standard deviation (%)			
	Solids	Moisture	Ash	Volatile	Solids	Moisture	Ash	Volatile	Solids	Moisture	Ash	Volatile
Run 1	86.421	13.579	15.683	61.653	37.08	5.83	5.81	22.86	0.45	0.45	2.13	2.16
Run 2	84.305	15.695	18.105	60.945	33.48	6.23	6.06	20.4	3.18	3.18	1.88	3.94
Run 3	84.305	15.695	18.105	60.945	37.46	6.97	6.78	22.83	4.21	4.21	5.34	2.74
Run 4	82.354	17.646	19.648	64.292	35.22	7.55	6.92	22.65	1.39	1.39	3.79	4.16
Run 5	82.117	17.883	14.489	64.611	38.08	8.29	5.52	24.61	0.39	0.39	1.96	2.31
Run 6	84.891	15.109	17.949	63.432	37.41	6.66	6.72	23.73	1.28	1.28	2.79	3.37
Run 7	83.967	16.033	18.403	63.812	38.95	7.44	7.17	24.85	0.46	0.46	2.19	6.78
Run 8	81.458	18.542	19.47	55.47	37.14	8.45	7.23	20.6	0.76	0.76	4.95	9.56
Run 9	82.638	17.362	16.415	59.189	34.7	7.29	5.7	20.54	0.20	0.20	1.66	3.66
Run 10	83.175	16.825	12.195	68.516	35.3	7.14	4.3	24.19	3.07	3.07	2.40	9.73
Run 11	80.939	19.061	20.064	60.41	34.67	8.16	6.96	20.94	0.47	0.47	1.70	4.61
Run 12	81.1	18.9	18.264	64.558	35.82	8.35	6.54	23.12	1.50	1.50	4.14	4.11
Run 13	80.5	19.5	11.374	69.281	34.24	8.29	3.89	23.72	0.70	0.70	4.38	11.32
Run 14	81.605	18.395	18.748	62.257	33.14	7.47	6.21	20.63	0.78	0.78	2.43	4.96
Run 15	84.389	15.611	19.462	60.305	36.86	6.82	7.17	22.23	2.43	2.43	0.32	3.81
Run 16	83.691	16.309	22.758	61.343	37.7	7.35	8.58	23.12	0.73	0.73	0.19	1.57
Run 17	82.356	17.644	12.806	70.055	32.33	6.93	4.14	22.65	1.37	1.37	5.97	13.96
Run 18	82.671	17.329	10.745	70.676	35.54	7.45	3.82	25.12	0.98	0.98	5.19	12.45
Run 19	81.42	18.58	21.077	62.227	35.54	8.11	7.49	22.11	0.88	0.88	0.88	6.76
Run 20	82.309	17.691	18.756	57.018	37.09	7.97	6.96	21.15	0.73	0.73	2.42	3.59
Run 21	81.484	18.516	13.209	64.724	34.72	7.89	4.59	22.47	1.47	1.47	6.12	9.86
Run 22	81.29	18.71	16.507	61.908	35.61	8.2	5.88	22.04	0.10	0.10	0.52	0.52
Run 23	82.405	17.595	16.621	61.741	38.35	8.19	6.37	23.68	1.49	1.49	2.00	13.20

Run 24	82.739	17.261	21.118	61.239	37.47	7.82	7.91	22.94	0.75	0.75	0.74	2.53
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Appendix H: Ash removal analysis

Ash removal

	Original lignosulphonate (g)	After purification (g)	Removal (g)	Removal (%)
Run 1	9.905	5.815	4.09	41.3
Run 2	9.497	6.061	3.44	36.2
Run 3	10.681	6.782	3.90	36.5
Run 4	10.050	6.921	3.13	31.1
Run 5	10.971	5.518	5.45	49.7
Run 6	10.391	6.715	3.68	35.4
Run 7	10.707	7.168	3.54	33.1
Run 8	10.518	7.231	3.29	31.3
Run 9	9.785	5.696	4.09	41.8
Run 10	9.891	4.305	5.59	56.5
Run 11	10.000	6.955	3.05	30.5
Run 12	10.313	6.542	3.77	36.6
Run 13	9.921	3.894	6.03	60.7
Run 14	9.362	6.213	3.15	33.6
Run 15	10.060	7.175	2.89	28.7
Run 16	10.354	8.579	1.78	17.1
Run 17	9.224	4.140	5.08	55.1
Run 18	9.887	3.819	6.07	61.4
Run 19	10.025	7.490	2.54	25.3
Run 20	10.336	6.956	3.38	32.7
Run 21	9.839	4.586	5.25	53.4
Run 22	10.075	5.878	4.20	41.7
Run 23	10.665	6.374	4.29	40.2
Run 24	10.471	7.91	2.56	24.4

Statistical analysis of ash removal part 1

Run	Sample	Ash reported data (%)	Ash reported data (g)	Removal of reported ash data(g)
Run 1	Sample 1	13.765	5.07	4.83
Run 1	Sample 2	15.313	5.69	4.21
Run 1	Sample 3	17.972	6.69	3.22
Run 2	Sample 1	18.574	6.25	3.24
Run 2	Sample 2	17.184	6.12	3.38
Run 2	Sample 3	21.189	6.88	2.61
Run 2	Sample 4	16.667	5.47	4.02
Run 2	Sample 5	16.913	5.55	3.95
Run 3	Sample 1	20.665	8.34	2.34
Run 3	Sample 2	19.205	6.82	3.87
Run 3	Sample 3	21.476	7.86	2.83
Run 3	Sample 4	13.636	4.92	5.76
Run 3	Sample 6	20.786	7.63	3.05
Run 4	Sample 1	22.861	8.20	1.85
Run 4	Sample 2	14.534	5.04	5.01
Run 4	Sample 3	22.161	7.89	2.16
Run 4	Sample 4	19.035	6.62	3.43
Run 5	Sample 1	12.279	4.66	6.31
Run 5	Sample 2	15.189	5.77	5.20
Run 5	Sample 3	16.000	6.13	4.84
Run 6	Sample 1	14.136	5.22	5.17
Run 6	Sample 2	19.384	7.29	3.10
Run 6	Sample 3	20.531	7.82	2.57
Run 6	Sample 4	17.747	6.57	3.82
Run 7	Sample 1	18.832	7.30	3.41
Run 7	Sample 2	16.031	6.24	4.47
Run 7	Sample 3	20.346	7.97	2.74
Run 8	Sample 1	12.386	4.66	5.86
Run 8	Sample 2	19.762	7.28	3.24
Run 8	Sample 3	22.695	8.45	2.06
Run 8	Sample 4	23.039	8.50	2.02
Run 9	Sample 1	17.659	5.99	3.79
Run 9	Sample 2	17.051	6.04	3.74
Run 9	Sample 3	14.535	5.05	4.74
Run 10	Sample 1	11.739	4.21	5.68
Run 10	Sample 2	8.451	3.13	6.76
Run 10	Sample 3	14.994	5.32	4.57

Run 10	Sample 4	13.091	4.41	5.48
Run 10	Sample 5	12.701	4.37	5.52
Run 11	Sample 1	18.790	6.53	3.47
Run 11	Sample 2	19.402	6.68	3.32
Run 11	Sample 3	21.999	7.65	2.35
Run 12	Sample 1	18.878	6.64	3.68
Run 12	Sample 2	14.742	5.32	5.00
Run 12	Sample 3	13.398	4.91	5.41
Run 12	Sample 4	23.123	8.12	2.20
Run 12	Sample 5	21.180	7.65	2.66
Run 13	Sample 1	9.946	3.37	6.55
Run 13	Sample 2	11.738	4.00	5.93
Run 13	Sample 3	17.331	5.99	3.93
Run 13	Sample 4	12.619	4.36	5.56
Run 13	Sample 5	5.238	1.79	8.13
Run 14	Sample 1	16.730	5.56	3.80
Run 14	Sample 2	18.063	6.03	3.33
Run 14	Sample 3	21.452	7.03	2.33
Run 15	Sample 1	19.554	7.10	2.96
Run 15	Sample 2	19.729	7.14	2.92
Run 15	Sample 3	19.104	7.28	2.78
Run 16	Sample 1	22.824	8.53	1.82
Run 16	Sample 2	22.546	8.58	1.78
Run 16	Sample 3	22.903	8.63	1.72
Run 17	Sample 1	3.911	1.25	7.97
Run 17	Sample 2	16.323	5.33	3.89
Run 17	Sample 3	14.796	4.86	4.36
Run 17	Sample 4	16.193	5.13	4.09
Run 18	Sample 1	5.240	1.84	8.04
Run 18	Sample 2	12.545	4.50	5.39
Run 18	Sample 3	9.097	3.22	6.66
Run 18	Sample 4	18.774	6.78	3.11
Run 19	Sample 1	20.066	7.16	2.86
Run 19	Sample 2	21.521	7.62	2.41
Run 19	Sample 3	21.643	7.69	2.34
Run 20	Sample 1	16.910	6.21	4.13
Run 20	Sample 2	17.868	6.67	3.67
Run 20	Sample 3	21.490	8.00	2.34
Run 21	Sample 1	19.205	6.88	2.96
Run 21	Sample 2	3.028	1.04	8.80
Run 21	Sample 3	13.308	4.62	5.22

Run 21	Sample 4	16.717	5.80	4.04
Run 21	Sample 5	17.680	6.00	3.84
Run 22	Sample 1	8.520	2.96	7.11
Run 22	Sample 2	16.137	5.75	4.32
Run 22	Sample 3	16.878	6.00	4.07
Run 23	Sample 1	14.456	5.67	4.99
Run 23	Sample 2	14.471	5.46	5.20
Run 23	Sample 3	18.332	7.08	3.59
Run 23	Sample 4	17.509	6.76	3.91
Run 23	Sample 5	18.337	6.89	3.77
Run 24	Sample 1	20.945	7.93	2.54
Run 24	Sample 2	20.481	7.64	2.83
Run 24	Sample 3	21.929	8.17	2.3

Analysis

$$\text{Ash content (g)} = \frac{\text{Ash content (\%)}}{100} \times \text{Mass after purification(g)}$$

$$\text{Ash removal (g)} = \text{Ash original lignosulphonate} -$$

Statistical analysis of ash removal part 2

	Standard deviation of the removal (g)	Standard deviation of the removal (%)
Run 1	0.81	19.9
Run 2	0.58	16.7
Run 3	1.34	37.6
Run 4	1.44	46.2
Run 5	0.76	14.0
Run 6	1.13	30.8
Run 7	0.87	24.7
Run 8	1.80	54.7
Run 9	0.56	13.7
Run 10	0.78	13.9
Run 11	0.61	20.0
Run 12	1.40	37.1
Run 13	1.53	25.4
Run 14	0.75	23.8
Run 15	0.09	3.2
Run 16	0.05	2.8
Run 17	1.94	38.1
Run 18	2.10	36.1
Run 19	0.28	11.2
Run 20	0.93	27.6
Run 21	2.29	46.0
Run 22	1.69	32.6
Run 23	0.75	17.4
Run 24	0.27	10.4

Appendix I: Elemental analysis

Elemental analysis original lignosulphonate

	Elemental analysis (%)			
	Carbon	Hydrogen	Nitrogen	Other
Lignosulphonate	34.33	3.89	0.42	61.35

	Elemental analysis (g)			
	Carbon	Hydrogen	Nitrogen	Other
Run 1	15.1	1.8	0.1	17.2
Run 2	14.5	1.7	0.1	16.4
Run 3	16.3	1.9	0.1	18.5
Run 4	15.3	1.8	0.1	17.4
Run 5	16.7	2.0	0.2	19.0
Run 6	15.8	1.9	0.1	18.0
Run 7	16.3	1.9	0.1	18.5
Run 8	16.0	1.9	0.1	18.2
Run 9	14.9	1.7	0.1	16.9
Run 10	15.1	1.8	0.1	17.1
Run 11	15.2	1.8	0.1	17.3
Run 12	15.7	1.8	0.1	17.9
Run 13	15.1	1.8	0.1	17.2
Run 14	14.3	1.7	0.1	16.2
Run 15	15.3	1.8	0.1	17.4
Run 16	15.8	1.9	0.1	17.9
Run 17	14.1	1.6	0.1	16.0
Run 18	15.1	1.8	0.1	17.1
Run 19	15.3	1.8	0.1	17.4
Run 20	15.8	1.8	0.1	17.9
Run 21	15.0	1.8	0.1	17.0
Run 22	15.4	1.8	0.1	17.4
Run 23	16.3	1.9	0.1	18.5
Run 24	16.0	1.9	0.1	18.1

Elemental analysis after purification

	Elemental analysis (%)				Elemental analysis (g)				Standard deviation of the after-purification data (%)			
	C	H	N	R	C	H	N	R	C	H	N	R
Run 1	31.62	4.52	0.00	64.30	13.6	1.9	0.00	27.6	0.91	0.12	0.00	0.84
Run 2	28.52	3.90	0.08	67.51	11.3	1.6	0.03	26.8	0.12	0.24	0.07	0.23
Run 3	28.69	4.08	0.15	67.07	12.8	1.8	0.07	29.8	0.11	0.44	0.07	0.51
Run 4	27.41	4.10	0.02	69.06	11.7	1.8	0.01	29.5	0.38	0.64	0.03	1.54
Run 5	34.52	4.68	0.22	60.59	16.0	2.2	0.10	28.1	1.01	0.25	0.06	1.23
Run 6	31.47	4.09	0.15	64.29	13.9	1.8	0.07	28.3	0.91	0.25	0.05	1.20
Run 7	27.85	3.89	0.09	68.18	12.9	1.8	0.04	31.6	0.29	0.24	0.10	0.65
Run 8	30.94	3.81	0.17	65.08	14.1	1.7	0.08	29.7	0.35	0.13	0.02	0.43
Run 9	31.85	4.59	0.03	63.97	13.4	1.9	0.01	26.9	0.42	0.37	0.05	1.45
Run 10	30.62	3.95	0.00	66.51	13.0	1.7	0.00	28.2	1.59	0.21	0.00	1.29
Run 11	28.94	3.58	0.00	68.36	12.4	1.5	0.00	29.3	0.49	0.16	0.00	0.73
Run 12	28.33	3.46	0.00	69.26	12.5	1.5	0.00	30.6	0.33	0.11	0.00	0.45
Run 13	31.77	3.83	0.00	65.51	13.5	1.6	0.00	27.9	0.42	0.28	0.00	0.63
Run 14	31.04	3.84	0.00	65.97	12.6	1.6	0.00	26.8	0.27	0.42	0.00	1.10
Run 15	30.06	3.51	0.00	67.35	13.1	1.5	0.00	29.4	1.08	0.65	0.00	2.18
Run 16	30.06	3.51	0.00	67.35	13.5	1.6	0.00	30.3	0.27	0.17	0.00	0.20
Run 17	32.66	4.83	0.05	62.49	12.8	1.9	0.02	24.5	0.14	0.11	0.06	0.24
Run 18	31.08	4.18	0.02	65.14	13.4	1.8	0.01	28.0	1.29	0.31	0.03	1.50
Run 19	29.23	4.56	0.03	66.40	12.8	2.0	0.01	29.0	0.31	0.50	0.05	0.93
Run 20	30.34	3.88	0.00	66.18	13.7	1.8	0.00	29.8	0.92	0.32	0.00	0.43
Run 21	30.58	4.30	0.00	65.37	13.0	1.8	0.00	27.9	0.17	0.39	0.00	0.65
Run 22	28.67	4.16	0.00	67.33	12.6	1.8	0.00	29.5	0.10	0.39	0.00	0.37
Run 23	29.18	3.83	0.00	67.23	13.6	1.8	0.00	31.3	3.29	0.38	0.00	3.50

Run 24	28.39	4.00	0.00	67.80	12.9	1.8	0.00	30.7	0.24	0.56	0.00	0.69
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Elemental reported data

Sample Date 01-Dec-21
Student Leane Naude
 prof Sanette Marx
Report date 01-Dec
Sample Lignex

EXETER DATA SHEET							
DATE	01-Dec-21						
No	Mass	Description	Sample Type	% C	% H	% N	% R
Std		Acetonitrile		71.07	6.74	10.42	11.78
Std	Microgram	Acetonitrile		71.08	6.73	10.38	11.81
	1080	Run 2 (S)	Solid	28.43	4.12	0.14	67.31
	1247	Duplicate		28.48	3.94	0.11	67.47
	668	Triplicate		28.65	3.64	0	67.76
		Standard deviation		0.12	0.24	0.07	0.23
		Average		28.52	3.90	0.08	67.51
	1180	Run 3 (S)	Solid	28.77	3.64	0.08	67.51
	1687	Duplicate		28.56	4.09	0.15	67.19
	3688	Triplicate		28.74	4.52	0.22	66.52
		Standard deviation		0.11	0.44	0.07	0.51
		Average		28.69	4.08	0.15	67.07
	3565	Run 5 (S)	Solid	35.34	4.97	0.27	59.41
	1124	Duplicate		34.82	4.54	0.16	60.49
	1960	Triplicate		33.39	4.52	0.24	61.86
		Standard deviation		1.01	0.25	0.06	1.23
		Average		34.52	4.68	0.22	60.59
	2342	Run 6 (S)	Solid	32.03	4.32	0.2	63.46
	1054	Duplicate		31.96	4.13	0.16	63.75
	1046	Triplicate		30.42	3.82	0.1	65.66
		Standard deviation		0.91	0.25	0.05	1.20
		Average		31.47	4.09	0.15	64.29
	908	Run 7 (S)	Solid	27.71	3.77	0.07	68.45
	3029	Duplicate		28.19	4.17	0.19	67.44
	700	Triplicate		27.66	3.74	0	68.66
		Standard deviation		0.29	0.24	0.10	0.65
		Average		27.85	3.89	0.09	68.18

	1846	Run 8 (S)	Solid	31.27	3.96	0.16	64.62
	1170	Duplicate		30.99	3.7	0.15	65.16
	1523	Triplicate		30.57	3.78	0.19	65.46
		Standard deviation		0.35	0.13	0.02	0.43
		Average		30.94	3.81	0.17	65.08
		Acetonitrile		70.83	6.46	10.32	12.36
<i>Note: Always finish with a Check and a Blank.</i>							
STD1 Accepted values		Acetanilide		71.09	6.71	10.36	11.84

Report Completed

01-Dec-21

Signed

R Bekker

**NORTH WEST UNIVERSITY
SCHOOL FOR CHEMICAL AND MINERALS
ENGINEERING**



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NOORDWES-UNIVERSITEIT
POTCHEFSTROOM CAMPUS

**Bio-Fuels
Centre of Excellence in C-Based Fuels**

Sample Date 28-Feb-22

Report Date 07-Mar-22

**Number of
Samples** 10

Compiled by: René Bekker

Approved by: Prof Sanette
Marx

Requestor Leané Naude

EXETER RESULTS

No	Mass	Description	Sample Type	% C	% H	% N	% R
Std		Acetonitrile		71.07	6.74	10.42	11.78
Std	Microgram	Acetonitrile		71.08	6.73	10.38	11.81
	1327	Redo Run 1 (S)	Solid	32.48	4.49	0	63.65
	2919	Duplicate		30.66	4.41	0	65.25
	2700	Triplicate		31.73	4.65	0	64
		Standard deviation		0.91	0.12	0.00	0.84
		Average		31.62	4.52	0.00	64.30
	3535	Redo Run 4 (S)	Solid	27.85	4.12	0	68.3
	1336	Duplicate		27.19	4.72	0.05	68.05
	1137	Triplicate		27.18	3.45	0	70.84
		Standard deviation		0.38	0.64	0.03	1.54
		Average		27.41	4.10	0.02	69.06
	4263	Run 9 (S)	Solid	32.03	4.72	0	63.43
	1307	Duplicate		31.37	4.18	0	65.62
	1660	Triplicate		32.15	4.88	0.09	62.87
		Standard deviation		0.42	0.37	0.05	1.45
		Average		31.85	4.59	0.03	63.97

	2797	Run 10 (S)	Solid	28.83	3.91	0	67.69
	1338	Duplicate		31.86	4.18	0	65.14
	975	Triplicate		31.18	3.76	0	66.7
		Standard deviation		1.59	0.21	0.00	1.29
		Average		30.62	3.95	0.00	66.51
	1477	Run 11 (S)	Solid	28.39	3.46	0	69.18
	1593	Duplicate		29.3	3.52	0	68.12
	2039	Triplicate		29.14	3.76	0	67.78
		Standard deviation		0.49	0.16	0.00	0.73
		Average		28.94	3.58	0.00	68.36
	2015	Run 12 (S)	Solid	28.03	3.59	0	69.07
	1484	Duplicate		28.69	3.42	0	68.94
	1140	Triplicate		28.28	3.38	0	69.78
		Standard deviation		0.33	0.11	0.00	0.45
		Average		28.33	3.46	0.00	69.26
	942	Run 13 (S)	Solid	32.23	3.54	0	66
	2325	Duplicate		31.66	4.1	0	64.8
	1532	Triplicate		31.42	3.86	0	65.73
		Standard deviation		0.42	0.28	0.00	0.63
		Average		31.77	3.83	0.00	65.51
	1880	Run 14 (S)	Solid	31.33	3.92	0	65.51
	1165	Duplicate		30.8	3.38	0	67.22
	3012	Triplicate		30.98	4.21	0	65.18
		Standard deviation		0.27	0.42	0.00	1.10
		Average		31.04	3.84	0.00	65.97
	3292	Run 15 (S)	Solid	31.07	4.23	0	65.02
	1318	Duplicate		30.19	3.31	0	67.69
	3012	Triplicate		28.93	2.98	0	69.34
		Standard deviation		1.08	0.65	0.00	2.18
		Average		30.06	3.51	0.00	67.35
	1564	Run 16 (S)	Solid	30.79	3.6	0	66.59
	1556	Duplicate		30.59	3.57	0	66.84
	2363	Triplicate		30.25	3.87	0	66.45
		Standard deviation		0.27	0.17	0.00	0.20
		Average		30.06	3.51	0.00	67.35
		Acetonitrile		70.83	6.46	10.32	12.36
Note: Always finish with a Check and a Blank.							
		Acetanilide		71.09	6.71	10.36	11.84

Report Completed
Signed

07-Mar-22
R Bekker

**NORTH WEST UNIVERSITY
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POTCHEFSTROOM CAMPUS

**Bio-Fuels
Centre of Excellence in C-Based Fuels**

Sample Date 23-Mar-22
Report Date 24-Mar-22
Number of Samples 8
Requestor Leané Naude

Compiled by: René Bekker

Approved by: Prof
Sanette Marx

EXETER RESULTS

No	Mass	Description	Sample Type	% C	% H	% N	% R
Std		Acetonitrile		71.04	6.55	9.91	12.51
Std	Microgram	Acetonitrile		70.86	6.43	9.79	12.91
	2412	Run #17	Solid	32.77	4.76	0	62.56
	2610	Duplicate		32.5	4.77	0.04	62.69
	5314	Triplicate		32.72	4.96	0.12	62.22
		Standard deviation		0.14	0.11	0.06	0.24
		Average		32.66	4.83	0.05	62.49
	1077	Run #18	Solid	29.59	4.08	0	66.77
	2070	Duplicate		31.7	4.52	0.05	63.81
	776	Triplicate		31.94	3.93	0	64.84
		Standard deviation		1.29	0.31	0.03	1.50
		Average		31.08	4.18	0.02	65.14
	1418	Run #19	Solid	29.16	4.73	0	66.42
	1454	Duplicate		28.97	4	0	67.32
	2599	Triplicate		29.57	4.96	0.09	65.46

		Standard deviation		0.31	0.50	0.05	0.93
		Average		29.23	4.56	0.03	66.40
	658	Run #20	Solid	31.39	3.65	0	65.79
	1340	Duplicate		29.95	3.74	0	66.64
	2403	Triplicate		29.67	4.25	0	66.12
		Standard deviation		0.92	0.32	0.00	0.43
		Average		30.34	3.88	0.00	66.18
	1643	Run #21	Solid	30.77	4.59	0	64.84
	2022	Duplicate		30.52	4.45	0	65.16
	1254	Triplicate		30.44	3.86	0	66.1
		Standard deviation		0.17	0.39	0.00	0.65
		Average		30.58	4.30	0.00	65.37
	1841	Run #22	Solid	28.58	3.85	0	67.71
	2220	Duplicate		28.78	4.03	0	67.29
	1711	Triplicate		28.64	4.59	0	66.98
		Standard deviation		0.10	0.39	0.00	0.37
		Average		28.67	4.16	0.00	67.33
	1107	Run #23	Solid	31.28	3.9	0	65.24
	2405	Duplicate		25.39	3.42	0	71.27
	1575	Triplicate		30.86	4.18	0	65.19
		Standard deviation		3.29	0.38	0.00	3.50
		Average		29.18	3.83	0.00	67.23
	2054	Run #24	Solid	28.63	3.99	0	67.51
	2836	Duplicate		28.16	4.56	0	67.3
	1189	Triplicate		28.37	3.45	0	68.58
		Standard deviation		0.24	0.56	0.00	0.69
		Average		28.39	4.00	0.00	67.80
		Acetonitrile		70.84	6.12	10.12	12.92
Note: Always finish with a Check and a Blank.							
		Acetanilide		71.09	6.71	10.36	11.84

Report Completed
Signed

24-Mar-
22
R Bekker

Appendix J: Carbon removal analysis

Carbon removal

	Carbon (g)			Carbon (%)
	Lignosulphonate	After purification	Removal	Removal
Run 1	15.102	13.567	1.54	10.17
Run 2	14.481	11.325	3.16	21.80
Run 3	16.286	12.747	3.54	21.73
Run 4	15.324	11.722	3.60	23.51
Run 5	16.729	16.008	0.72	4.31
Run 6	15.845	13.869	1.98	12.47
Run 7	16.327	12.920	3.41	20.87
Run 8	16.037	14.108	1.93	12.03
Run 9	14.920	13.375	1.54	10.35
Run 10	15.081	12.996	2.09	13.83
Run 11	15.248	12.396	2.85	18.70
Run 12	15.725	12.513	3.21	20.43
Run 13	15.128	13.512	1.62	10.68
Run 14	14.275	12.603	1.67	11.71
Run 15	15.339	13.133	2.21	14.38
Run 16	15.788	13.541	2.25	14.23
Run 17	14.064	12.823	1.24	8.83
Run 18	15.076	13.360	1.72	11.38
Run 19	15.287	12.759	2.53	16.54
Run 20	15.761	13.669	2.09	13.28
Run 21	15.003	13.030	1.97	13.15
Run 22	15.363	12.557	2.81	18.27
Run 23	16.262	13.579	2.68	16.50
Run 24	15.967	12.855	3.11	19.49

Statistical analysis of carbon removal part 1

Run	Sample	Carbon reported data (%)	Carbon reported data (g)	Removal of reported carbon (g)
Run 1	Sample 1	32.48	13.93	18.55
Run 1	Sample 2	30.66	13.15	19.33
Run 1	Sample 3	31.73	13.61	18.87
Run 2	Sample 1	28.43	11.29	19.37
Run 2	Sample 2	28.48	11.31	19.35
Run 2	Sample 3	28.65	11.38	19.28
Run 3	Sample 1	28.77	12.78	18.95
Run 3	Sample 2	28.56	12.69	19.04
Run 3	Sample 3	28.74	12.77	18.96
Run 4	Sample 1	27.85	11.91	16.52
Run 4	Sample 2	27.19	11.63	16.80
Run 4	Sample 3	27.18	11.63	16.80
Run 5	Sample 1	35.34	16.39	12.09
Run 5	Sample 2	34.82	16.15	12.33
Run 5	Sample 3	33.39	15.49	12.99
Run 6	Sample 1	32.03	14.12	14.53
Run 6	Sample 2	31.96	14.09	14.56
Run 6	Sample 3	30.42	13.41	15.24
Run 7	Sample 1	27.71	12.85	15.92
Run 7	Sample 2	28.19	13.08	15.69
Run 7	Sample 3	27.66	12.83	15.94
Run 8	Sample 1	31.27	14.26	14.30
Run 8	Sample 2	30.99	14.13	14.43
Run 8	Sample 3	30.57	13.94	14.62
Run 9	Sample 1	32.03	13.45	15.29
Run 9	Sample 2	31.37	13.17	15.57
Run 9	Sample 3	32.15	13.50	15.24
Run 10	Sample 1	28.83	12.24	15.61
Run 10	Sample 2	31.86	13.52	14.33
Run 10	Sample 3	31.18	13.23	14.62
Run 11	Sample 1	28.39	12.16	15.03
Run 11	Sample 2	29.30	12.55	14.64
Run 11	Sample 3	29.14	12.48	14.71
Run 12	Sample 1	28.03	12.38	14.80
Run 12	Sample 2	28.69	12.67	14.51
Run 12	Sample 3	28.28	12.49	14.69

Run 13	Sample 1	32.23	13.71	21.63
Run 13	Sample 2	31.66	13.47	21.87
Run 13	Sample 3	31.42	13.36	21.98
Run 14	Sample 1	31.33	12.72	22.10
Run 14	Sample 2	30.80	12.51	22.31
Run 14	Sample 3	30.98	12.58	22.24
Run 15	Sample 1	31.07	13.57	19.82
Run 15	Sample 2	30.19	13.19	20.20
Run 15	Sample 3	28.93	12.64	20.75
Run 16	Sample 1	30.79	13.87	18.16
Run 16	Sample 2	30.59	13.78	18.25
Run 16	Sample 3	30.25	13.63	18.40
Run 17	Sample 1	32.77	12.86	19.10
Run 17	Sample 2	32.50	12.76	19.20
Run 17	Sample 3	32.72	12.84	19.12
Run 18	Sample 1	29.59	12.72	17.70
Run 18	Sample 2	31.70	13.63	16.79
Run 18	Sample 3	31.94	13.73	16.69
Run 19	Sample 1	29.16	12.73	14.98
Run 19	Sample 2	28.97	12.64	15.07
Run 19	Sample 3	29.57	12.91	14.80
Run 20	Sample 1	31.39	14.14	14.05
Run 20	Sample 2	29.95	13.49	14.70
Run 20	Sample 3	29.67	13.37	14.82
Run 21	Sample 1	30.77	13.11	14.55
Run 21	Sample 2	30.52	13.01	14.65
Run 21	Sample 3	30.44	12.97	14.69
Run 22	Sample 1	28.58	12.52	18.75
Run 22	Sample 2	28.78	12.61	18.66
Run 22	Sample 3	28.64	12.54	18.73
Run 23	Sample 1	31.28	14.56	16.43
Run 23	Sample 2	25.39	11.82	19.17
Run 23	Sample 3	30.86	14.36	16.63
Run 24	Sample 1	28.63	12.96	17.61
Run 24	Sample 2	28.16	12.75	17.82
Run 24	Sample 3	28.4	12.8	17.72
Run 20	Sample 1	81.47	36.7	7.9
Run 20	Sample 2	82.83	37.3	7.3
Run 20	Sample 3	82.63	37.2	7.3
Run 21	Sample 1	84.08	35.8	6.6
Run 21	Sample 2	80.75	34.4	8.0

Run 21	Sample 3	81.40	34.7	7.7
Run 21	Sample 4	81.45	34.7	7.7
Run 21	Sample 5	79.62	33.9	8.5
Run 22	Sample 1	79.42	34.8	8.7
Run 22	Sample 2	81.36	35.6	7.8
Run 22	Sample 3	81.22	35.6	7.9
Run 23	Sample 1	84.33	39.2	6.7
Run 23	Sample 2	81.07	37.7	8.3
Run 23	Sample 3	82.96	38.6	7.4
Run 23	Sample 4	82.93	38.6	7.4
Run 23	Sample 5	80.74	37.6	8.4
Run 24	Sample 1	83.61	37.9	7.3
Run 24	Sample 2	82.35	37.3	7.9
Run 24	Sample 3	82.26	37.2	7.9

Statistical analysis of carbon removal part 2

	Standard deviation of the removal (g)	Standard deviation of the removal (%)
Run 1	0.39	2.07
Run 2	0.05	0.24
Run 3	0.05	0.27
Run 4	0.16	0.98
Run 5	0.47	3.75
Run 6	0.40	2.71
Run 7	0.14	0.86
Run 8	0.16	1.11
Run 9	0.18	1.15
Run 10	0.67	4.54
Run 11	0.21	1.41
Run 12	0.15	1.00
Run 13	0.18	0.81
Run 14	0.11	0.49
Run 15	0.47	2.32
Run 16	0.12	0.67
Run 17	0.06	0.29
Run 18	0.56	3.26
Run 19	0.13	0.90
Run 20	0.42	2.86
Run 21	0.07	0.50
Run 22	0.04	0.24
Run 23	1.53	8.78
Run 24	0.11	0.60

Appendix K: ICP analysis

ICP analysis original lignosulphonate

	ICP analysis (%)					
	Ca	K	Mg	Na	S	Other
Lignosulphonate	0.05	0.17	0.08	12.02	6.27	0.05

	ICP analysis (g)					
	Ca	K	Mg	Na	S	Other
Run 1	0.02	0.08	0.04	5.31	2.77	0.02
Run 2	0.02	0.07	0.03	5.09	2.66	0.02
Run 3	0.02	0.08	0.04	5.73	2.99	0.03
Run 4	0.02	0.08	0.04	5.39	2.81	0.02
Run 5	0.02	0.08	0.04	5.88	3.07	0.03
Run 6	0.02	0.08	0.04	5.57	2.91	0.02
Run 7	0.02	0.08	0.04	5.74	3.00	0.03
Run 8	0.02	0.08	0.04	5.64	2.94	0.03
Run 9	0.02	0.08	0.04	5.24	2.74	0.02
Run 10	0.02	0.08	0.04	5.30	2.77	0.02
Run 11	0.02	0.08	0.04	5.36	2.80	0.02
Run 12	0.02	0.08	0.04	5.53	2.89	0.02
Run 13	0.02	0.08	0.04	5.32	2.78	0.02
Run 14	0.02	0.07	0.03	5.02	2.62	0.02
Run 15	0.02	0.08	0.04	5.39	2.81	0.02
Run 16	0.02	0.08	0.04	5.55	2.90	0.02
Run 17	0.02	0.07	0.03	4.94	2.58	0.02
Run 18	0.02	0.08	0.04	5.30	2.77	0.02
Run 19	0.02	0.08	0.04	5.37	2.80	0.02
Run 20	0.02	0.08	0.04	5.54	2.89	0.02
Run 21	0.02	0.08	0.04	5.27	2.75	0.02
Run 22	0.02	0.08	0.04	5.40	2.82	0.02
Run 23	0.02	0.08	0.04	5.72	2.98	0.03
Run 24	0.02	0.08	0.04	5.61	2.93	0.03

ICP analysis after purification

	ICP analysis (%)						ICP analysis (g)						Standard deviation of the after-purification data (%)				
	Ca	K	Mg	Na	S	Other	Ca	K	Mg	Na	S	Other	Ca	K	Mg	Na	S
Run 1	0.05	0.24	0.10	0.59	0.62	0.07	0.02	0.10	0.04	0.25	0.27	0.03	0.43	0.96	0.79	0.27	CNC
Run 2	0.03	0.17	0.08	0.44	0.43	0.05	0.01	0.07	0.03	0.18	0.17	0.02	0.61	0.91	0.24	0.22	CNC
Run 3	0.05	0.22	0.09	0.75	0.60	0.06	0.02	0.10	0.04	0.33	0.27	0.03	0.78	0.43	1.09	0.28	CNC
Run 4	0.05	0.20	0.09	0.83	0.59	0.07	0.02	0.09	0.04	0.35	0.25	0.03	1.47	0.74	0.56	0.21	CNC
Run 5	0.06	0.29	0.12	0.67	0.78	0.08	0.03	0.14	0.05	0.31	0.36	0.04	0.45	0.50	1.07	0.33	CNC
Run 6	0.06	0.24	0.10	0.76	0.66	0.06	0.02	0.10	0.04	0.33	0.29	0.03	0.93	1.50	0.10	0.36	CNC
Run 7	0.03	0.20	0.08	0.70	0.53	0.06	0.02	0.09	0.04	0.33	0.25	0.03	0.40	0.75	1.24	0.19	CNC
Run 8	0.04	0.22	0.09	0.87	0.60	0.07	0.02	0.10	0.04	0.39	0.27	0.03	0.73	0.41	0.32	0.77	CNC
Run 9	0.08	0.26	0.13	8.49	6.98	0.08	0.03	0.11	0.05	3.56	2.93	0.04	0.67	0.61	1.12	0.23	CNC
Run 10	0.19	0.25	0.12	6.61	6.53	0.08	0.08	0.11	0.05	2.81	2.77	0.03	0.28	0.29	1.50	0.37	CNC
Run 11	0.07	0.24	0.11	7.39	6.22	0.08	0.03	0.10	0.05	3.17	2.66	0.03	0.32	0.43	1.30	0.49	CNC
Run 12	0.07	0.20	0.11	7.26	5.38	0.06	0.03	0.09	0.05	3.21	2.37	0.03	0.49	0.73	0.50	0.25	CNC
Run 13	0.05	0.18	0.07	4.71	4.65	0.06	0.02	0.08	0.03	2.00	1.98	0.03	0.26	0.15	1.09	0.40	CNC
Run 14	0.08	0.16	0.09	4.82	4.20	0.06	0.03	0.07	0.04	1.96	1.71	0.02	0.61	0.82	0.90	0.20	CNC
Run 15	0.07	0.20	0.10	7.04	5.15	0.07	0.03	0.09	0.04	3.08	2.25	0.03	0.71	0.78	1.26	0.24	CNC
Run 16	0.06	0.18	0.09	6.74	4.67	0.07	0.03	0.08	0.04	3.03	2.10	0.03	0.86	0.84	0.72	0.27	CNC
Run 17	0.08	0.25	0.14	0.66	0.69	0.08	0.03	0.10	0.06	0.26	0.27	0.03	1.27	1.51	2.06	0.37	1.96
Run 18	0.08	0.24	0.13	0.69	0.65	0.07	0.04	0.10	0.05	0.29	0.28	0.03	0.51	0.30	2.08	0.12	3.95
Run 19	0.05	0.11	0.08	0.44	0.32	0.04	0.02	0.05	0.03	0.19	0.14	0.02	0.09	0.90	0.72	0.44	7.58
Run 20	0.08	0.24	0.14	0.76	0.67	0.07	0.04	0.11	0.06	0.34	0.30	0.03	0.07	0.46	1.21	0.53	0.92
Run 21	0.05	0.23	0.11	0.62	0.62	0.07	0.02	0.10	0.05	0.26	0.27	0.03	0.26	0.59	0.45	0.20	2.67
Run 22	0.15	0.22	0.13	0.68	0.58	0.06	0.07	0.10	0.06	0.30	0.26	0.03	0.19	0.27	1.60	0.12	4.08
Run 23	0.07	0.24	0.12	0.74	0.63	0.07	0.03	0.11	0.06	0.35	0.29	0.03	0.34	0.35	0.58	0.38	2.28
Run 24	0.09	0.20	0.10	0.78	0.77	0.06	0.04	0.09	0.05	0.35	0.35	0.03	0.50	0.32	0.92	0.29	2.27

CNC : Could Not Compute due to technical difficulties

Ca : Calcium

K : Potassium

Mg : Magnesium

Na : Sodium

S : Sulphur

Other : Sum of chemical elements < 0.001%

ICP reported data

Sample Lignex test work

Date 01-Dec-21

Sample ID	Sample Mass (g)	Vol (ml)	Ca mg/l	K mg/l	Mg mg/l	Na mg/l	S mg/l	Al mg/l	Ba mg/l	Cd mg/l	Co mg/l	Cr mg/l
Run2 (S) Raw Data	0.1724	100	0.148	0.347	0.159	21.590	2.575	0.008	0.001	0.00011	0.0013	ND
Run2 (S) Calculated Data			858.8	2015.4	922.5	125229	1493	46.59	5.25	0.65	7.46	ND
			1x	1x	1x	10x	1x	1x	1x	1x	1x	1x
Run3 (S) Raw Data	0.1879	100	0.082	0.448	0.184	19.884	1.227	0.006	0.001	0.00003	0.00018	ND
Run3 (S) Calculated Data			437.7	2384.1	978.1	105823	653	30.97	2.86	0.13	0.93	ND
			1x	1x	1x	10x	1x	1x	1x	1x	1x	1x
Run5 (S) Raw Data	0.1576	100	0.145	0.388	0.207	14.133	1.252	0.006	0.001	0.00027	0.002	ND
Run5 (S) Calculated Data			920.6	2460.0	1315.3	89674	794	41.09	8.27	1.69	13.21	ND
			1x	1x	1x	10x	1x	1x	1x	1x	1x	1x
Run6 (S) Raw Data	0.2255	100	0.087	0.504	0.199	20.636	2.842	0.008	0.0004	0.00015	0.002	ND
Run6 (S) Calculated Data			386.7	2233.8	883.2	91510	1260	35.25	1.87	0.68	9.05	ND
			1x	1x	1x	10x	1x	1x	1x	1x	1x	1x
Run7 (S) Raw Data	0.1338	100	0.138	0.296	0.166	13.996	1.960	0.008	0.0004	0.00015	0.004	0.00043
Run7 (S) Calculated Data			1032.7	2210.9	1237.8	104603	1465	60.92	2.82	1.11	27.17	3.20
			1x	1x	1x	10x	1x	1x	1x	1x	1x	1x
Run8 (S) Raw Data	0.2083	100	0.142	0.440	0.215	22.700	1.290	0.006	0.0004	0.00013	0.003	ND
Run8 (S) Calculated Data			618.8	2112.7	1032.4	108978	619	26.58	2.04	0.63	13.02	ND

* N.D No Detection

Reported By: R Bekker

Sample	Lignex test work												
Date	01-Dec-21												
Sample ID	Sample Mass (g)	Vol (ml)	Cu mg/l	Fe mg/l	Li mg/l	Mn mg/l	Ni mg/l	P mg/l	Pb mg/l	Si mg/l	Ti g/l	V mg/l	Zn mg/l
Run2 (S) Raw Data	0.1724	100	0.002	0.012	0.00046	0.009	ND	0.049	ND	0.006	0.00030	ND	0.00005
Run2 (S) Calculated Data			14.12	68.77	2.67	53.23	ND	286.98	ND	34.17	1.75	ND	0.29
			1x	1x	1x	1x	1x	1x	1x	1x	1x	1x	1x
Run3 (S) Raw Data	0.1879	100	-0.004	0.017	ND	0.011	0.00028	0.052	ND	0.020	0.00026	0.00004	ND
Run3 (S) Calculated Data			ND	91.61	ND	57.96	1.46	276.49	ND	103.97	1.40	0.23	ND
			1x	1x	1x	1x	1x	1x	1x	1x	1x	1x	1x
Run5 (S) Raw Data	0.1576	100	0.002	0.017	0.00002	0.008	0.001	0.040	0.00022	0.013	0.00035	ND	0.005
Run5 (S) Calculated Data			12.85	110.09	0.15	53.33	8.01	251.43	1.39	81.71	2.23	ND	33.44
			1x	1x	1x	1x	1x	1x	1x	1x	1x	1x	1x
Run6 (S) Raw Data	0.2255	100	0.000	0.018	0.00008	0.011	0.001	0.060	ND	ND	0.00028	ND	0.002
Run6 (S) Calculated Data			0.43	80.07	0.37	48.31	4.79	264.57	ND	ND	1.26	ND	7.51
			1x	1x	1x	1x	1x	1x	1x	1x	1x	1x	1x
Run7 (S) Raw Data	0.1338	100	0.000	0.013	0.0005	0.008	0.00025	0.037	ND	0.015	0.00028	ND	0.009
Run7 (S) Calculated Data			5.78	95.80	4.00	56.33	1.83	273.20	ND	108.86	2.08	ND	70.83
			1x	1x	1x	1x	1x	1x	1x	1x	1x	1x	1x
Run8 (S) Raw Data	0.2083	100	0.001	0.017	0.00041	0.011	0.00041	0.055	0.006	0.026	0.00026	0.00007	ND
Run8 (S) Calculated Data			4.08	83.78	1.97	51.64	1.96	266.27	30.39	123.36	1.26	0.34	ND
* N.D	No Detection												
Reported By:	R Bekker												

Sample Lignex
Date 22-Feb-22

Sample ID	Sample (g)	Volume (ml)	Dilution	Ca mg/l		K mg/l		Mg mg/l		Na mg/l		S mg/l		Al mg/l		Ba mg/l		Cd mg/l	
				Orig.	Calc.	Orig.	Calc.	Orig.	Calc.	Orig.	Calc.	Orig.	Calc.	Orig.	Calc.	Orig.	Calc.	Orig.	Calc.
Run 1 (S)	0.2058	100	1x	1.26	613.17	5.64	2740.14	2.21	1075.16	15.06	73181.6	13.80	67067.5	0.20	95.44	0.02	7.63	0.01	3.00
Run 4 (S)	0.199	100	1x	1.65	830.18	4.65	2338.26	2.34	1175.75	20.03	100631.0	13.60	68319.7	0.03	16.11	0.01	4.18	0.00	2.51
Run 9 (S)	0.2071	100	1x	1.69	818.11	5.40	2605.86	2.61	1260.77	17.47	84350.4	14.36	69341.9	0.10	46.91	0.01	5.42	0.01	2.44
Run 10 (S)	0.1906	100	1x	3.81	2001.25	5.23	2745.26	2.41	1262.33	13.61	71392.2	13.43	70460.9	0.05	26.46	0.01	5.55	0.00	2.13
Run 11 (S)	0.1885	100	1x	1.51	801.55	4.85	2574.83	2.32	1228.47	15.21	80686.7	12.80	67917.9	0.06	32.44	0.01	4.70	0.00	1.93
Run 12 (S)	0.1699	100	1x	1.49	875.47	4.13	2430.34	2.23	1309.86	14.94	87943.6	11.06	65112.9	0.07	41.03	0.01	3.22	0.00	2.37
Run 13 (S)	0.1371	100	1x	1.07	780.88	3.76	2739.81	1.52	1105.34	9.70	70728.4	9.57	69811.6	0.05	38.34	0.01	6.09	0.01	4.19
Run 14 (S)	0.1285	100	1x	1.64	1275.56	3.35	2603.58	1.82	1414.53	9.92	77227.2	8.65	67289.3	0.05	37.27	0.01	4.10	0.01	4.19
Run 15 (S)	0.1578	100	1x	1.46	926.35	4.18	2646.81	2.11	1340.10	14.49	91810.1	10.61	67220.5	0.04	27.82	0.01	6.33	0.00	2.12
Run 16 (S)	0.1464	100	1x	1.23	842.97	3.70	2528.18	1.90	1299.66	13.87	94712.8	9.61	65630.1	0.04	28.97	0.00	3.28	0.01	4.87

* N.D No Detection *Calc. Calculated *Orig. Original

Dilution 10x

Reported By: R Bekker

Sample Lignex
Date 22-Feb-22

Sample ID	Sample (g)	Volume (ml)	Dilution	Co mg/l		Cr mg/l		Cu mg/l		Fe mg/l		Li mg/l		Mn mg/l		Ni mg/l	
				Orig.	Calc.	Orig.	Calc.	Orig.	Calc.	Orig.	Calc.	Orig.	Calc.	Orig.	Calc.	Orig.	Calc.
Re Do Run 1 (S)	0.2058	100	1x	0.01	5.30	0.008	3.96	0.01	6.85	0.23	111.30	ND	ND	0.12	60.39	ND	ND
Re Do Run 4 (S)	0.199	100	1x	0.05	23.83	ND	ND	0.04	19.98	0.18	88.72	ND	ND	0.11	56.58	ND	ND
Run 9 (S)	0.2071	100	1x	0.06	28.12	0.003	1.29	0.02	7.74	0.23	109.31	0.00	0.22	0.12	59.16	ND	ND
Run 10 (S)	0.1906	100	1x	0.02	11.98	0.004	2.00	ND	ND	0.23	122.40	0.00	1.18	0.11	56.16	ND	ND
Run 11 (S)	0.1885	100	1x	0.02	10.84	0.004	2.00	ND	ND	0.18	95.84	0.00	0.82	0.11	57.74	ND	ND
Run 12 (S)	0.1699	100	1x	0.01	6.02	ND	ND	ND	ND	0.16	94.60	0.00	2.08	0.10	58.48	ND	ND
Run 13 (S)	0.1371	100	1x	0.01	5.14	ND	ND	0.00	1.59	0.14	101.46	ND	ND	0.07	54.49	ND	ND
Run 14 (S)	0.1285	100	1x	0.03	26.96	0.013	9.83	0.01	5.76	0.14	106.26	0.00	2.71	0.07	55.21	ND	ND
Run 15 (S)	0.1578	100	1x	0.04	23.12	0.012	7.36	ND	ND	0.16	102.02	0.00	0.13	0.10	60.61	ND	ND
Run 16 (S)	0.1464	100	1x	0.04	30.19	ND	ND	0.02	10.29	0.15	103.46	0.00	2.71	0.09	60.73	ND	ND

* N.D No Detection *Calc. Calculated *Orig. Original

Reported By: R Bekker

Sample Lignex
Date 22-Feb-22

Sample ID	Sample (g)	Volume (ml)	Dilution	P mg/l		Pb mg/l		Si mg/l		Ti g/l		V mg/l		Zn mg/l	
				Orig.	Calc.	Orig.	Calc.	Orig.	Calc.	Orig.	Calc.	Orig.	Calc.	Orig.	Calc.
Re Do Run 1 (S)	0.2058	100	1x	0.64	309.55	0.01	4.49	0.25	121.39	0.00	2.06	0.01	6.10	0.03	16.36
Re Do Run 4 (S)	0.199	100	1x	0.79	395.90	0.02	10.30	0.27	136.01	0.00	1.40	0.02	7.86	0.05	26.18
Run 9 (S)	0.2071	100	1x	0.87	419.18	0.00	1.58	0.23	111.94	0.00	1.26	0.01	6.85	0.08	38.33
Run 10 (S)	0.1906	100	1x	0.87	458.57	ND	ND	0.24	124.72	0.00	1.34	0.01	6.66	0.10	51.40
Run 11 (S)	0.1885	100	1x	0.89	474.75	0.00	1.01	0.23	119.93	0.00	1.13	0.01	6.57	0.04	20.60
Run 12 (S)	0.1699	100	1x	0.60	354.80	0.01	4.65	0.20	116.06	0.00	0.92	0.01	8.75	0.03	19.61
Run 13 (S)	0.1371	100	1x	0.82	599.71	0.00	0.74	0.15	109.10	0.00	1.40	0.02	12.85	0.05	34.23
Run 14 (S)	0.1285	100	1x	0.62	485.93	0.01	6.28	0.15	114.06	0.00	1.31	0.01	11.16	0.03	21.59
Run 15 (S)	0.1578	100	1x	0.75	473.32	ND	ND	0.19	123.56	0.00	1.84	0.01	9.24	0.04	22.51
Run 16 (S)	0.1464	100	1x	0.78	530.97	0.01	10.01	0.17	119.32	0.00	1.23	0.01	8.86	0.08	55.34

* N.D No Detection *Calc. Calculated *Orig. Original

Reported By: R Bekker

Sample Lignex
Date 14-Mar-22

Sample ID	Sample (g)	Volume (ml)	Dilution	Ca mg/l		K mg/l		Mg mg/l		Na mg/l		S mg/l		Al mg/l		Ba mg/l		Cd mg/l	
				Orig.	Calc.	Orig.	Calc.	Orig.	Calc.	Orig.	Calc.	Orig.	Calc.	Orig.	Calc.	Orig.	Calc.	Orig.	Calc.
Run #19 (S)	0.1777	100	1x	0.96	541.66	1.89	1062.43	1.42	797.01	7.79	43863.2	5.71	32135.6	0.04	20.99	0.00	1.72	0.00	1.55
Run #20 (S)	0.1367	100	1x	1.44	1054.27	4.29	3134.96	2.49	1821.86	13.51	98809.0	11.89	86964.7	0.05	36.98	0.01	4.27	0.00	0.36
Run #23 (S)	0.1736	100	1x	1.26	728.33	4.21	2424.37	2.12	1220.18	13.23	76190.2	11.11	64018.9	0.05	31.26	0.01	3.16	0.00	0.48
Run #24 (S)	0.1548	101.3	1x	1.56	1020.49	3.47	2270.51	1.77	1157.48	13.93	91148.4	13.67	89460.1	0.03	16.41	0.01	3.45	0.00	0.34
Run #17 (S)	0.1809	100	1x	1.49	821.66	4.50	2487.02	2.50	1382.11	11.69	64602.9	12.26	67775.9	0.05	26.76	0.01	5.81	0.00	0.68
Run #18 (S)	0.1747	100	1x	1.48	847.95	4.29	2454.87	2.23	1274.24	12.19	69760.2	11.51	65905.3	0.07	38.16	0.01	5.84	0.00	1.98
Run #21 (S)	0.1686	100	1x	0.81	480.47	4.14	2454.50	1.93	1146.68	10.99	65200.3	11.07	65654.7	0.04	21.24	0.01	3.79	0.00	-0.26
Run # 22(S)	0.1646	100	1x	2.64	1605.84	3.89	2365.34	2.35	1430.68	12.10	73533.1	10.35	62898.1	0.05	32.95	0.01	3.23	0.00	1.84

* N.D No Detection *Calc. Calculated *Orig. Original

Dilution 10x

Reported By: R Bekker

Sample Lignex
Date 14-Mar-22

Sample ID	Sample (g)	Volume (ml)	Dilution	Co mg/l		Cr mg/l		Cu mg/l		Fe mg/l		Li mg/l		Mn mg/l		Ni mg/l	
				Orig.	Calc.	Orig.	Calc.	Orig.	Calc.	Orig.	Calc.	Orig.	Calc.	Orig.	Calc.	Orig.	Calc.
Run #19 (S)	0.1777	100	1x	0.01	4.27	0.002	1.25	0.02	11.59	0.06	36.28	ND	ND	0.05	28.82	0.014	7.66
Run #20 (S)	0.1367	100	1x	ND	ND	0.013	9.76	0.01	9.06	0.18	133.96	ND	ND	0.10	74.46	0.010	7.59
Run #23 (S)	0.1736	100	1x	0.06	36.91	0.014	8.00	0.02	12.82	0.15	88.18	ND	ND	0.10	56.17	0.053	30.40
Run #24 (S)	0.1548	101.3	1x	ND	ND	0.000	0.06	0.019	12.19	0.16	106.47	ND	ND	0.09	57.07	0.015	9.49
Run #17 (S)	0.1809	100	1x	0.06	32.67	0.009	4.78	0.018	9.95	0.19	102.42	ND	ND	0.09	51.06	0.015	8.11
Run #18 (S)	0.1747	100	1x	0.00	1.60	0.007	3.80	0.015	8.53	0.19	108.48	ND	ND	0.09	51.97	0.042	24.01
Run #21 (S)	0.1686	100	1x	ND	ND	0.012	7.36	0.01	3.38	0.18	105.94	ND	ND	0.08	49.50	0.013	7.81
Run # 22(S)	0.1646	100	1x	0.00	1.34	0.010	6.18	0.00	1.28	0.16	98.44	ND	ND	0.08	51.44	0.014	8.53

* N.D No Detection *Calc. Calculated *Orig. Original

Reported By: R Bekker

Sample Lignex
Date 14-Mar-22

Sample ID	Sample (g)	Volume (ml)	Dilution	P mg/l		Pb mg/l		Si mg/l		Ti g/l		V mg/l		Zn mg/l	
				Orig.	Calc.	Orig.	Calc.	Orig.	Calc.	Orig.	Calc.	Orig.	Calc.	Orig.	Calc.
Run #19 (S)	0.1777	100	1x	0.27	149.89	0.00	-0.70	0.14	77.25	0.00	0.43	ND	ND	0.02	10.51
Run #20 (S)	0.1367	100	1x	0.57	416.99	0.02	11.97	0.28	202.86	0.00	0.51	ND	ND	0.03	24.00
Run #23 (S)	0.1736	100	1x	0.58	334.59	0.01	4.63	0.18	101.69	0.00	-0.03	ND	ND	0.07	41.73
Run #24 (S)	0.1548	101.3	1x	0.49	321.78	0.010	6.31	0.14	88.98	0.00	1.35	ND	ND	0.06	42.19
Run #17 (S)	0.1809	100	1x	0.69	382.37	0.02	12.42	0.22	122.69	0.00	1.80	ND	ND	0.02	9.98
Run #18 (S)	0.1747	100	1x	0.62	356.44	0.00	-0.06	0.26	147.85	0.00	0.60	ND	ND	ND	ND
Run #21 (S)	0.1686	100	1x	0.71	423.29	0.00	-1.15	0.11	65.91	0.00	1.11	ND	ND	ND	ND
Run # 22(S)	0.1646	100	1x	0.65	393.45	0.01	7.09	0.11	67.32	0.00	0.61	ND	ND	0.04	23.72

* N.D No Detection *Calc. Calculated *Orig. Original

Reported By: R Bekker

Appendix L: Sodium and sulphur removal analysis

Sodium and sulphur removal

	Sodium (g)			Sodium (%)	Sulphur (g)			Sulphur (%)
	Lignosulphonate	After purification	Removal	Removal	Lignosulphonate	After purification	Removal	Removal
Run 1	5.309	3.140	2.17	40.86	2.771	2.877	0.00	0.00
Run 2	5.091	4.250	0.84	16.51	2.657	0.059	2.60	97.77
Run 3	5.725	4.702	1.02	17.88	2.988	0.029	2.96	99.03
Run 4	5.387	4.304	1.08	20.10	2.812	2.922	0.00	0.00
Run 5	5.881	4.159	1.72	29.28	3.069	0.037	3.03	98.80
Run 6	5.570	4.033	1.54	27.59	2.907	0.056	2.85	98.09
Run 7	5.740	4.852	0.89	15.46	2.996	0.068	2.93	97.73
Run 8	5.638	4.969	0.67	11.87	2.942	0.028	2.91	99.04
Run 9	5.245	2.469	2.78	52.92	2.737	2.094	0.64	23.52
Run 10	5.302	3.232	2.07	39.05	2.767	2.911	0.00	0.00
Run 11	5.360	3.886	1.47	27.51	2.798	2.972	0.00	0.00
Run 12	5.528	3.870	1.66	29.99	2.885	2.734	0.15	5.23
Run 13	5.318	2.395	2.92	54.96	2.776	2.595	0.18	6.51
Run 14	5.018	2.411	2.61	51.96	2.619	2.158	0.46	17.61
Run 15	5.392	3.169	2.22	41.23	2.814	2.550	0.26	9.40
Run 16	5.550	2.969	2.58	46.50	2.897	1.975	0.92	31.80
Run 17	4.944	2.536	2.41	48.71	2.581	2.661	0.00	0.00
Run 18	5.300	2.999	2.30	43.41	2.766	2.833	0.00	0.00
Run 19	5.374	1.914	3.46	64.38	2.805	1.403	1.40	49.99
Run 20	5.541	4.452	1.09	19.65	2.892	3.918	0.00	0.00
Run 21	5.274	2.778	2.50	47.32	2.753	2.798	0.00	0.00
Run 22	5.401	3.221	2.18	40.36	2.819	2.755	0.06	2.26

Run 23	5.717	3.546	2.17	37.97	2.984	2.979	0.00	0.14
Run 24	5.613	4.128	1.49	26.46	2.930	4.051	0.00	0.00

Analysis

$$Removal (\%) = \frac{removal}{Lignosulphonate}$$

Statistical analysis of sodium removal part 1

Run	Sample	Na reported data (%)	Na reported data (g)	Removal of Na reported mass (g)
Run 1	Sample 1	7.30	3.13	2.18
Run 1	Sample 2	7.34	3.15	2.16
Run 1	Sample 3	7.32	3.14	2.17
Run 2	Sample 1	12.55	4.98	0.11
Run 2	Sample 2	12.50	4.96	0.13
Run 2	Sample 3	12.52	4.97	0.12
Run 3	Sample 1	10.57	4.70	1.03
Run 3	Sample 2	10.62	4.72	1.01
Run 3	Sample 3	10.56	4.69	1.03
Run 4	Sample 1	10.04	4.29	1.09
Run 4	Sample 2	10.07	4.31	1.08
Run 4	Sample 3	10.08	4.31	1.08
Run 5	Sample 1	9.00	4.17	1.71
Run 5	Sample 2	8.95	4.15	1.73
Run 5	Sample 3	8.95	4.15	1.73
Run 6	Sample 1	9.17	4.04	1.53
Run 6	Sample 2	9.17	4.04	1.53
Run 6	Sample 3	9.11	4.02	1.55
Run 7	Sample 1	10.44	4.84	0.90
Run 7	Sample 2	10.46	4.85	0.89
Run 7	Sample 3	10.48	4.86	0.88
Run 8	Sample 1	10.97	5.00	0.64
Run 8	Sample 2	10.92	4.98	0.66
Run 8	Sample 3	10.81	4.93	0.71
Run 9	Sample 1	8.41	3.53	1.71
Run 9	Sample 2	8.44	3.54	1.70
Run 9	Sample 3	8.45	3.55	1.70
Run 10	Sample 1	7.12	3.02	2.28
Run 10	Sample 2	7.13	3.02	2.28
Run 10	Sample 3	7.17	3.04	2.26
Run 11	Sample 1	8.09	3.47	1.89
Run 11	Sample 2	8.02	3.44	1.92
Run 11	Sample 3	8.09	3.46	1.90
Run 12	Sample 1	8.77	3.87	1.66
Run 12	Sample 2	8.81	3.89	1.64
Run 12	Sample 3	8.81	3.89	1.64
Run 13	Sample 1	7.10	3.02	2.30

Run 13	Sample 2	7.04	3.00	2.32
Run 13	Sample 3	7.07	3.01	2.31
Run 14	Sample 1	7.71	3.13	1.89
Run 14	Sample 2	7.72	3.13	1.88
Run 14	Sample 3	7.74	3.14	1.88
Run 15	Sample 1	9.20	4.02	1.38
Run 15	Sample 2	9.16	4.00	1.39
Run 15	Sample 3	9.19	4.01	1.38
Run 16	Sample 1	9.47	4.27	1.28
Run 16	Sample 2	9.45	4.25	1.30
Run 16	Sample 3	9.50	4.28	1.27
Run 17	Sample 1	6.43	2.53	2.42
Run 17	Sample 2	6.48	2.54	2.40
Run 17	Sample 3	6.47	2.54	2.40
Run 18	Sample 1	6.98	3.00	2.30
Run 18	Sample 2	6.97	2.99	2.30
Run 18	Sample 3	6.98	3.00	2.30
Run 19	Sample 1	4.36	1.90	3.47
Run 19	Sample 2	4.40	1.92	3.45
Run 19	Sample 3	4.39	1.92	3.46
Run 20	Sample 1	9.83	4.43	1.11
Run 20	Sample 2	9.88	4.45	1.09
Run 20	Sample 3	9.94	4.48	1.06
Run 21	Sample 1	6.52	2.78	2.49
Run 21	Sample 2	6.51	2.77	2.50
Run 21	Sample 3	6.53	2.78	2.49
Run 22	Sample 1	7.36	3.22	2.18
Run 22	Sample 2	7.34	3.22	2.18
Run 22	Sample 3	7.36	3.22	2.18
Run 23	Sample 1	7.59	3.53	2.18
Run 23	Sample 2	7.61	3.54	2.17
Run 23	Sample 3	7.65	3.56	2.16
Run 24	Sample 1	9.09	4.12	1.50
Run 24	Sample 2	9.11	4.12	1.49
Run 24	Sample 3	9.14	4.14	1.47

Statistical analysis of sodium removal part 2

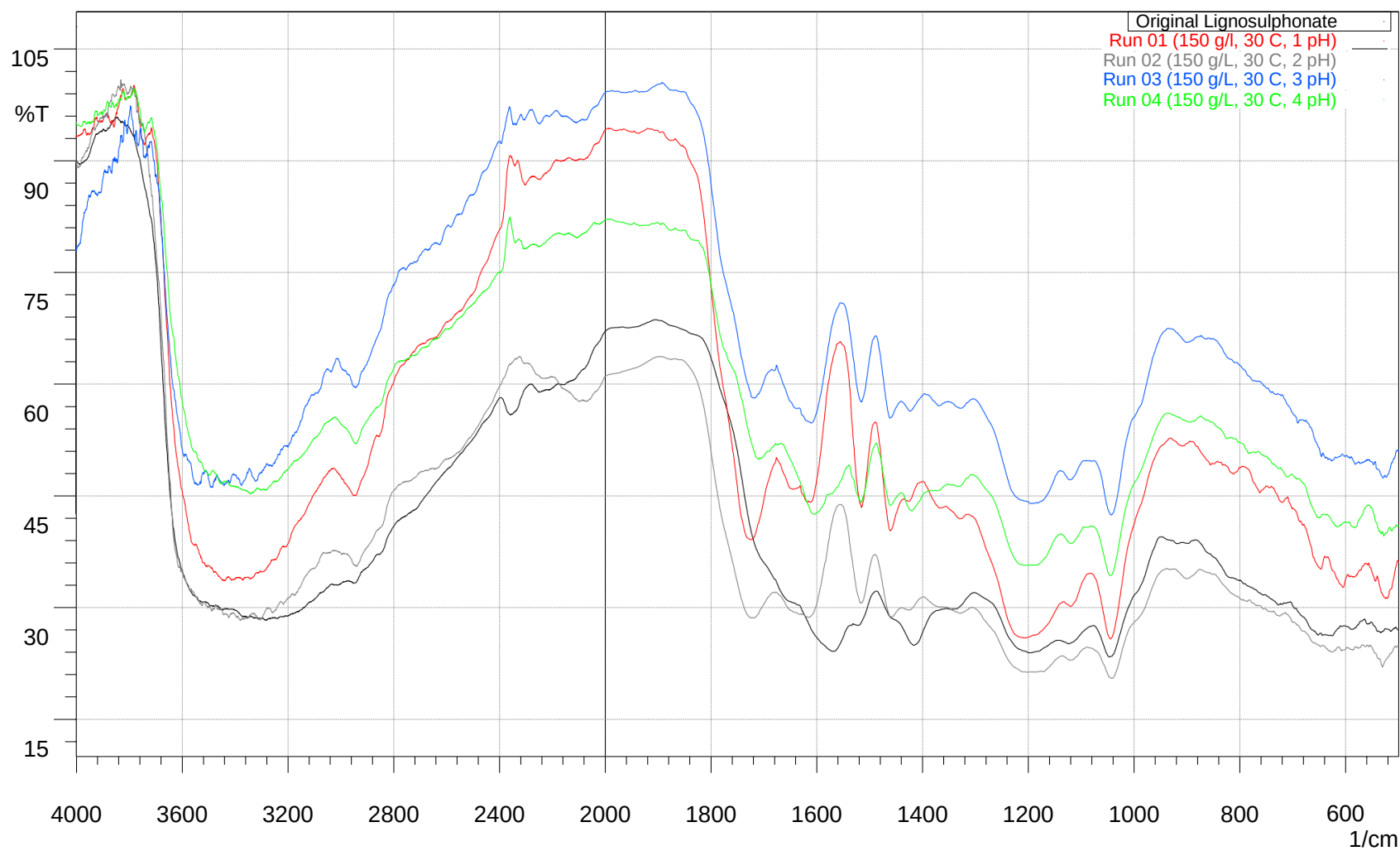
	Standard deviation of the removal (g)	Standard deviation of the removal (%)
Run 1	0.01	0.4%
Run 2	0.01	9.3%
Run 3	0.01	1.3%
Run 4	0.01	0.8%
Run 5	0.01	0.8%
Run 6	0.01	0.9%
Run 7	0.01	1.0%
Run 8	0.04	5.7%
Run 9	0.01	0.5%
Run 10	0.01	0.5%
Run 11	0.02	0.9%
Run 12	0.01	0.6%
Run 13	0.01	0.5%
Run 14	0.01	0.3%
Run 15	0.01	0.7%
Run 16	0.01	0.9%
Run 17	0.01	0.4%
Run 18	0.00	0.2%
Run 19	0.01	0.2%
Run 20	0.02	2.2%
Run 21	0.01	0.2%
Run 22	0.00	0.2%
Run 23	0.01	0.6%
Run 24	0.01	0.8%

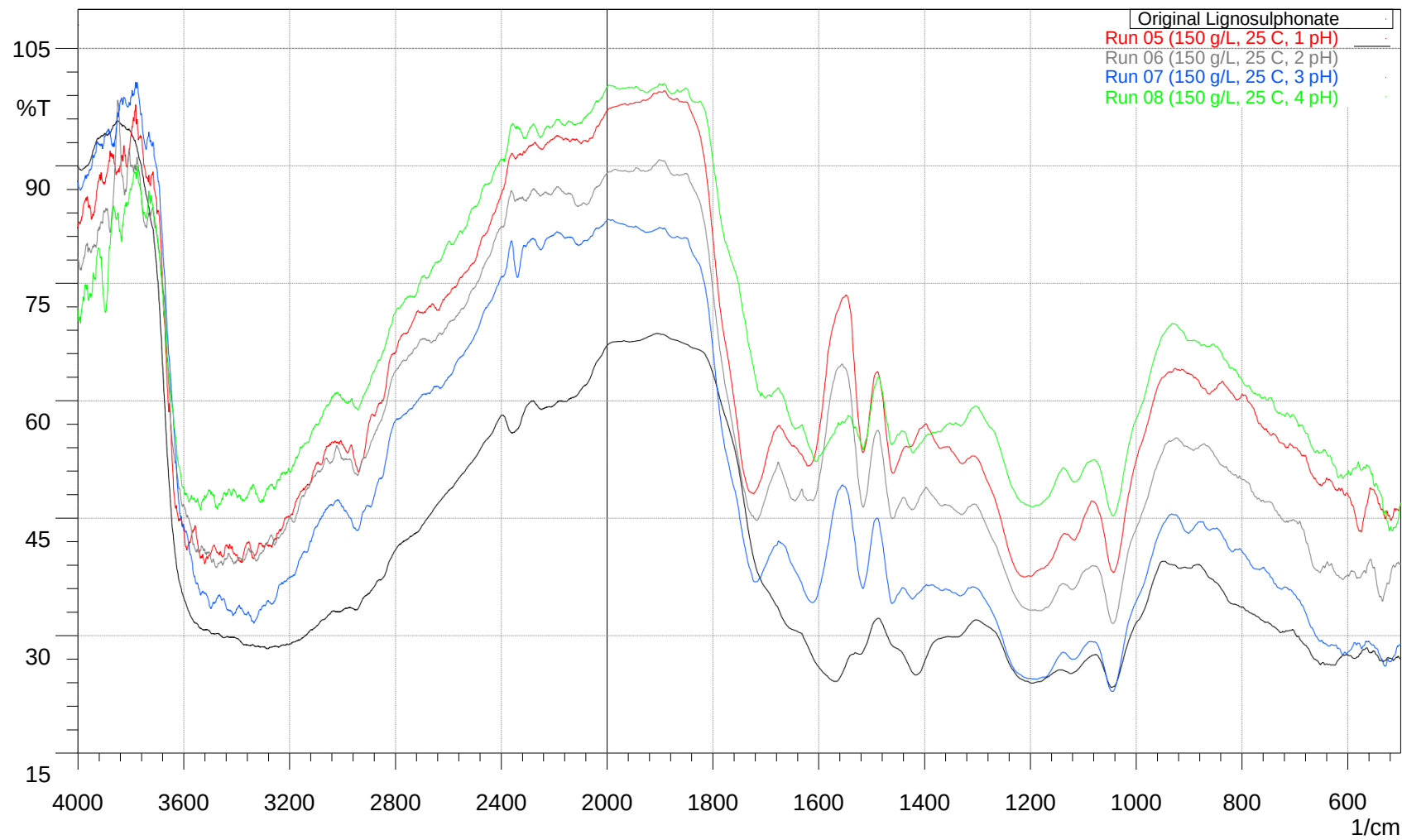
Appendix M: GPC analysis

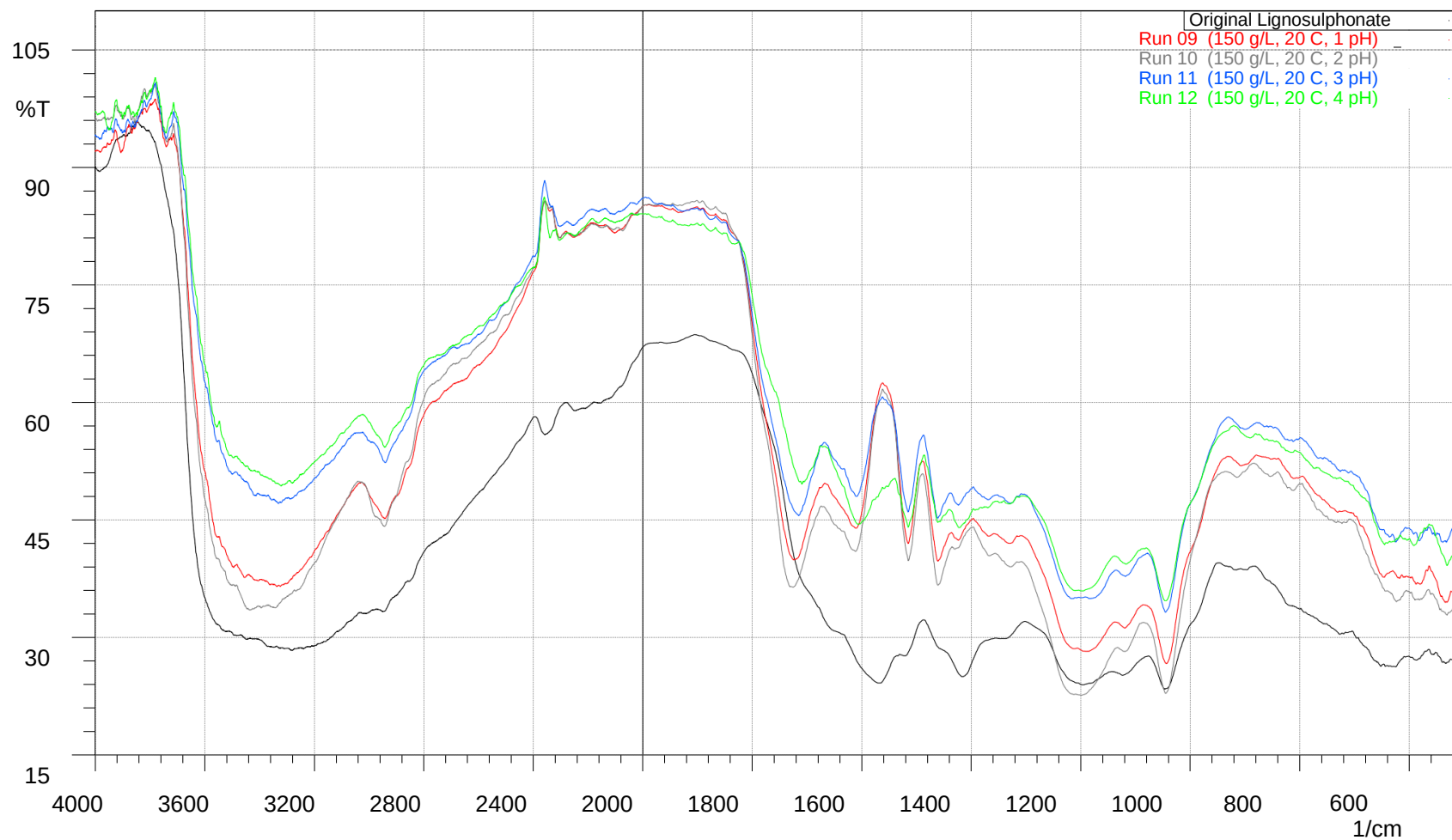
Original lignosulphonate							
Weight average molecular mass (Mw)				Number average molecule mass (Mn)			
$\bar{x}$ (g/mol)	STD (g/mol)	Max (g/mol)	Min (g/mol)	$\bar{x}$ (g/mol)	STD (g/mol)	Max (g/mol)	Min (g/mol)
2437.20	101.40	2538.60	2335.80	1004.49	69.03	1073.52	935.46

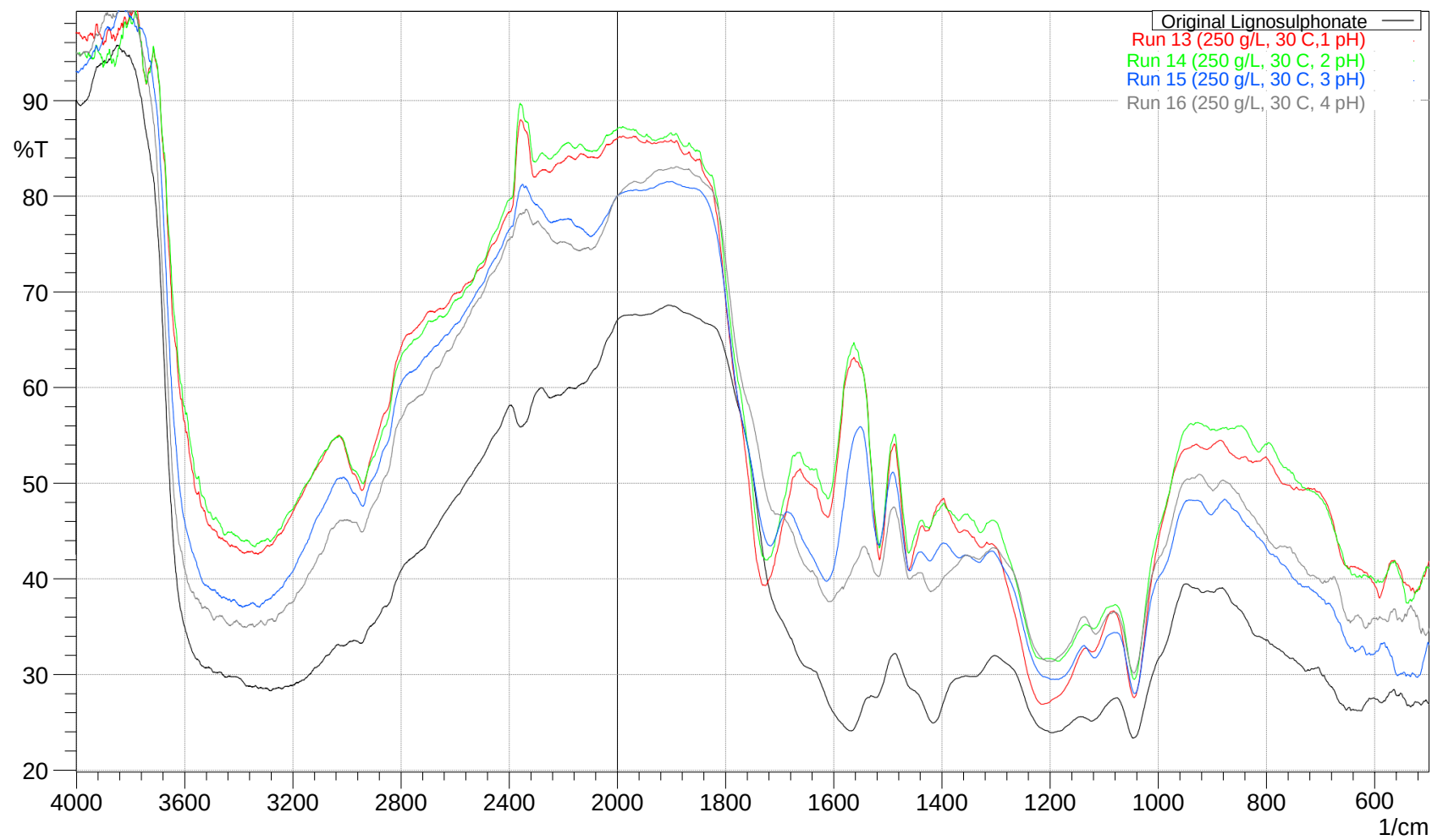
	Lignosulphonate after purification							
	Weight average molecular mass (Mw)				Number average molecule mass (Mn)			
	$\bar{x}$ (g/mol)	STD (g/mol)	Max (g/mol)	Min (g/mol)	$\bar{x}$ (g/mol)	STD (g/mol)	Max (g/mol)	Min (g/mol)
Run 1	2694.38	457.25	3151.63	2237.13	665.09	164.85	829.94	500.24
Run 2	2614.67	164.58	2779.25	2450.09	671.75	80.84	752.59	590.91
Run 3	2712.26	342.8	3055.06	2369.46	676.69	188.05	864.74	488.64
Run 4	2433.58	253.72	2687.3	2179.86	684.91	145.98	830.89	538.93
Run 5	2481.2	158.98	2640.18	2322.22	590.65	182.22	772.87	408.43
Run 6	3039.07	335.28	3374.35	2703.79	570.74	119.79	690.53	450.95
Run 7	2411.24	291.71	2702.95	2119.53	1024.10	72.00	1096.1	952.1
Run 8	2381.86	84.50	2466.36	2297.36	1158.07	56.34	1214.41	1101.73
Run 9	2597.49	497.01	3094.5	2100.48	909.33	253.34	1162.67	655.99
Run 10	2182.49	109.29	2291.78	2073.2	661.62	65.41	727.03	596.21
Run 11	2898.58	195.48	3094.06	2703.1	1022.22	71.01	1093.23	951.21
Run 12	2384.32	91.32	2475.64	2293	851.89	246.57	1098.46	605.32
Run 13	2494.59	275.51	2770.1	2219.08	591.98	70.27	662.25	521.71
Run 14	2435.11	304.77	2739.88	2130.34	953.78	114.48	1068.26	839.3
Run 15	2485.19	197.65	2682.84	2287.54	888.2	174.17	1062.37	714.03
Run 16	2350.64	34.26	2384.9	2316.38	858.4	79.03	937.43	779.37
Run 17	2791.69	339.20	3130.89	2452.49	572.39	58.82	631.21	513.57
Run 18	3074.63	193.55	3268.18	2881.08	1092.6	72.62	1165.22	1019.98
Run 19	2533.56	316.92	2850.48	2216.64	1028.96	133.38	1162.34	895.58
Run 20	2908.72	322.15	3230.87	2586.57	1047.31	64.19	1111.5	983.12
Run 21	2710.52	250.85	2961.37	2459.67	569.32	55.23	624.55	514.09
Run 22	3574.08	425.79	3999.87	3148.29	1241.03	168.35	1409.38	1072.68
Run 23	3839.26	113.76	3953.02	3725.5	1187.11	71.30	1258.41	1115.81
Run 24	2587.46	390.55	2978.01	2196.91	1134.6	35.97	1170.57	1098.63

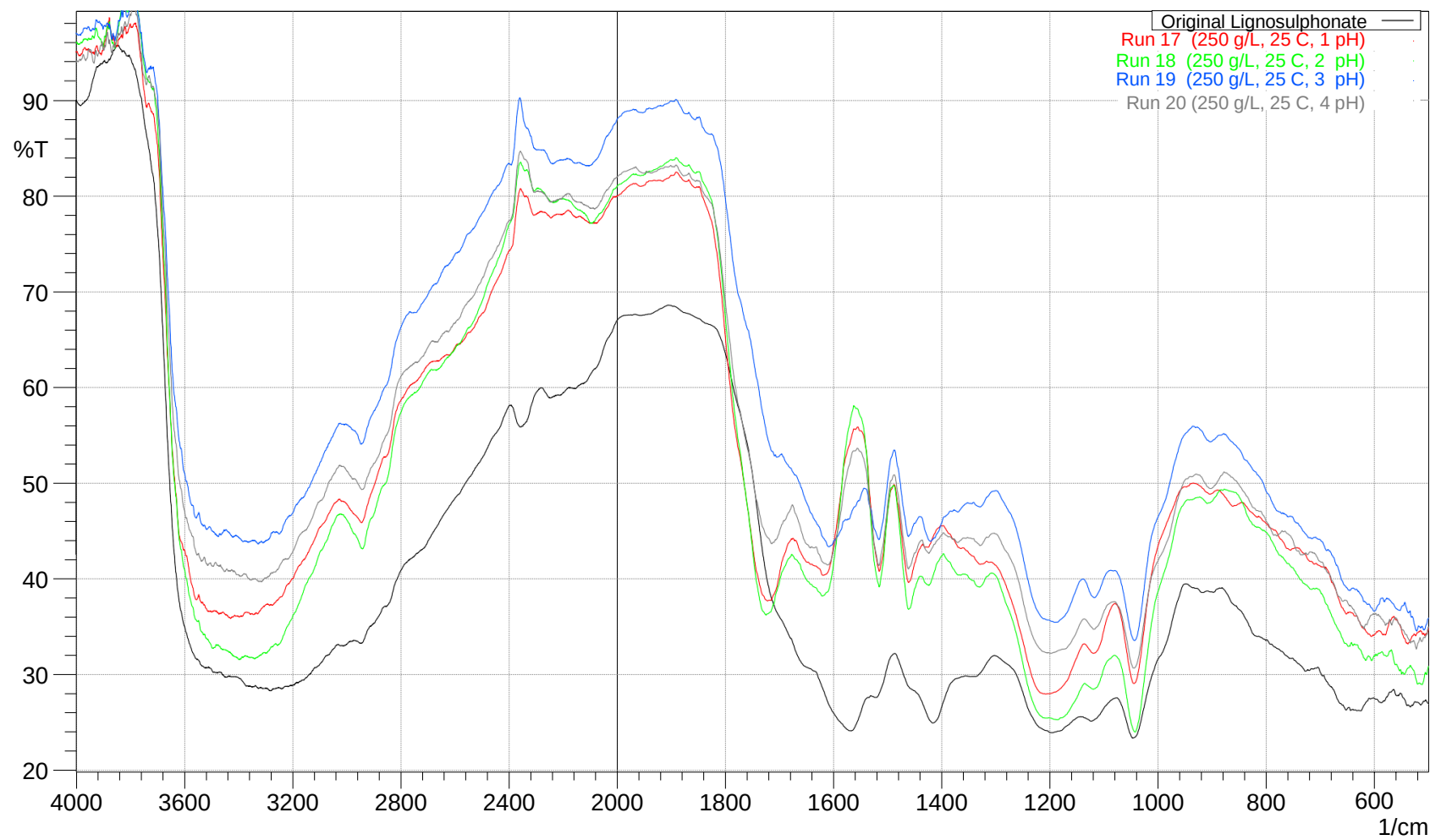
Appendix N: Fourier Transform Infrared Spectroscopy Analysis

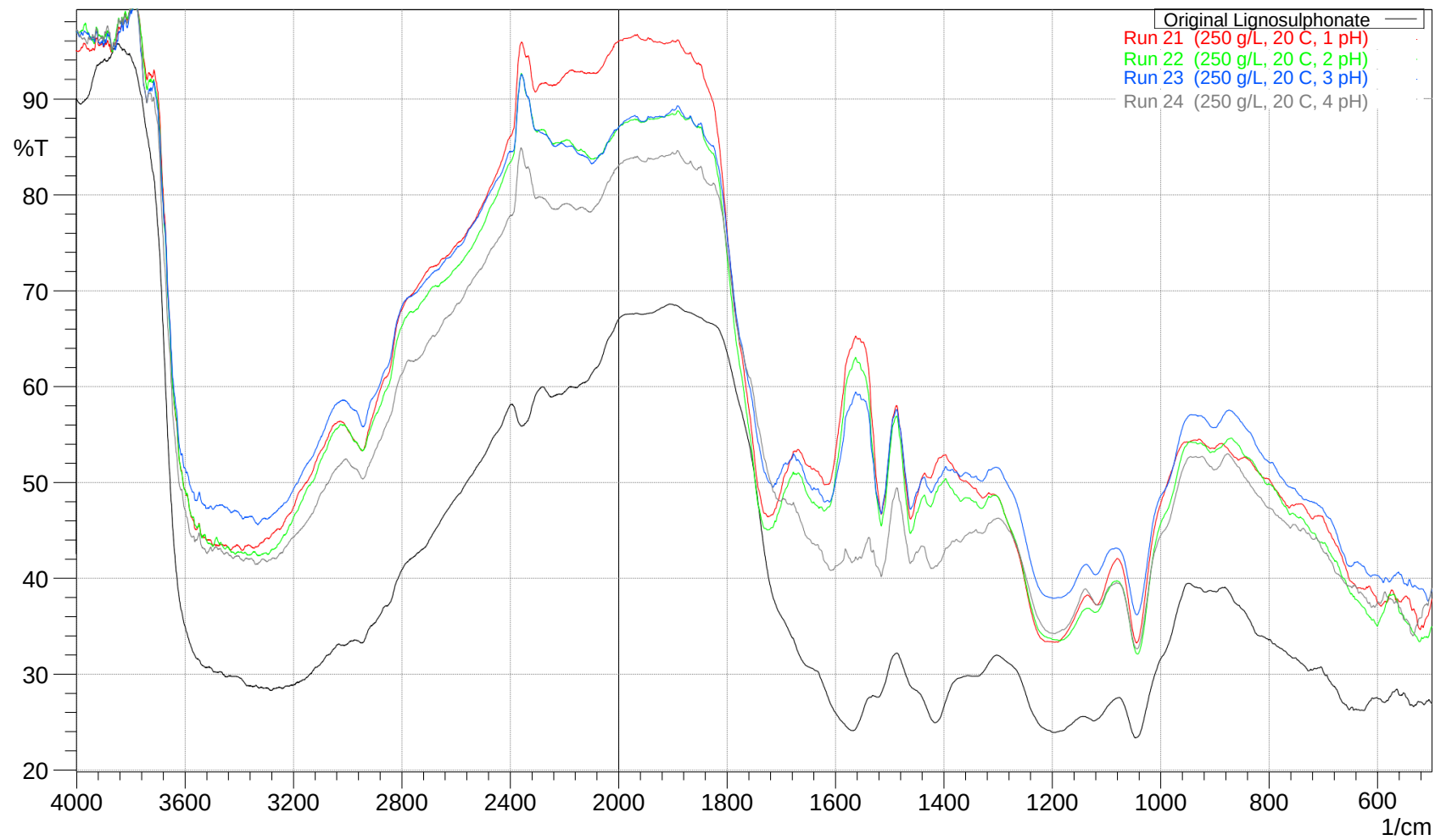












Appendix O: Provisional patent application

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Number of Pages:

2

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Attention: Dr Mesuli Mbanjwa

1 September 2022

Dear Sirs,

**The United Kingdom: Provisional Patent Application No. 2211729.5
In the name of: NORTH-WEST UNIVERSITY
Entitled: LIGNOSULPHONATE PURIFICATION**

We are pleased to inform you that the abovementioned provisional patent application was filed with the following details:-

JURISDICTION	:	The United Kingdom
APPLICANT	:	NORTH-WEST UNIVERSITY
INVENTORS	:	MARX, Sanette VENTER, Roelof Jacobus NAUDE, Leane
TITLE	:	LIGNOSULPHONATE PURIFICATION
FILING DATE	:	11 August 2022

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DM Kisch Inc. Reg. No.: 1979/000871/21 | Kisch Africa Inc. Reg. No.: 2018/068342/21 (B-BBEE Level 2 Contributor) | Kisch Global Ltd. Reg. No.: 128869 (Jersey, Channel Islands)
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01/07/2022

APPLICATION NO. : 2211729.5

COMPLETION DEADLINE : 11 August 2023

EXAMINATION : The application is subjected to examination.

SEARCH : The official IPO search was requested upon filing.

Please find enclosed copies of the electronic filing receipt, statement of inventorship and of right to grant of a patent, as well as our invoice as cover for disbursements incurred and services rendered for your kind attention.

Kindly note that the declaration of inventorship, indicating that the right belongs to the University by virtue of employment was filed in support of the application.

We shall keep you advised of further developments in respect of this patent application.

Thank you for having instructed us in this matter.

Yours faithfully

KISCH IP
Per: Foreign Patent Department
P125AB

Appendix P: Recommendation two-step calculation

Original Lignosulphonate

	Weight based (%)	Weight based (g)
Begin mass (g)		100.0
Solids	96.71	96.7
Ash (solid wt%)	23.2	22.4
Na	12.0	12.0
S	6.3	6.3

First purification results : 250 g/L, 30°C and 1 pH

	Removal (%)	Results after purification (g)
Mass (g)	3.85	96.2
Solids	19.97	77.4
Ash (solid wt%)	60.7	8.8
Na	55.0	5.4
S	6.5	5.9

Second purification results : 150 g/L, 25°C and 2 pH

	Removal (%)	Results after purification (g)	Overall Removal (%)
Mass (g)	5.19	91.16	8.84
Solids	19.49	62.3	35.57
Ash (solid wt%)	49.7	4.4	80.26
Na	29.3	3.8	68.15
S	98.8	0.1	98.88

$$\text{Weight based (g)} = \frac{\text{Weight based (\%)}}{100} \times \text{Begin mass (g)}$$

$$\text{Mass (First purification results)(g)} = \text{Begin mass (g)} \left(1 - \frac{\text{Removal(\%)}}{100}\right)$$

$$\text{Mass (Second purification results)(g)}$$

$$= \text{Mass (First purification results) (g)} \left(1 - \frac{\text{Removal(\%)}}{100}\right)$$

$$\text{Ash (solids wt\%)} (g) = \frac{\text{Removal (\%)}}{100} \times \text{Solids (g)}$$

$$\text{Results after purification for A} = \frac{A(\%)}{100} \times \text{Mass (g)}$$

A : Solids, Na, or S

$$\text{Overall removal (\%)} = \frac{\text{Original Lignosulphonate (g)} - \text{Second purification results (g)}}{\text{Original Lignosulphonate (g)}} \times 100$$