Sulfonation of kraft lignin to water soluble value added products

By

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Table of Contents

List of Figures

List of Tables

Abstract

Kraft lignin is water insoluble and has limited end-use applications. The main objective of this MSc studies was to rend kraft lignin water soluble, and various value-added products including dispersants and flocculants. In this work, softwood kraft lignin was supplied from FPInnovations from its pilot facilities in Thunder Bay, ON. It was then modified using BURL lab facilities of Lakehead University. In one alternative, phenolation and hydroxymethylation of kraft lignin were followed as pre-treatment processes to improve the reactivity of lignin. Unmodified kraft lignin, phenolated lignin and hydroxymethylated lignin were then sulfonated through 1) concentrated sulfuric acid and 2) sodium sulfite treatments. All lignin samples treated with sodium sulfite exhibited increased in charge density and solubility. Additionally, sulfuric acid treatment of phenolated lignin yielded soluble product (SAP) with a high charge density (e.g. 3 meq/g). However, sulfuric acid treatment of phenolated lignin was unsuccessful in producing lignin with desired charge density and solubility. The synthesized soluble sulfonated lignin samples (SS, SSH, SSP, and SAP) demonstrated a greater solubility than kraft lignin, but weaker solubility than commercial and industrial lignosulfonates.

The application of sulfonated lignin samples were evaluated as dispersants in cement and kaolinite; adsorbent on kaolinite and calcium carbonate to produce modified fillers for composites and papermaking as well as flocculants for textile industry. The addition of the sulfonated lignin to cement did not increase the fluidity of the cement, but improved the fluidity of kaolinite to some extent.

The adsorption of sulfonated lignins on calcium carbonate and kaolinite were greater than that of kraft lignin, which shows that modified lignin can have a high adsorption capacity to produce modified fillers. The samples, which were phenolated, exhibited a greater adsorption affinity than other samples on calcium carbonate.

In this study, ethyl violet and basic blue solutions were used as model wastewater samples of textile industry. The results showed that, the sulfonated lignin samples were generally able to remove ethyl violet, but were unsuccessful in removing basic blue from solution.

Chapter 1: Introduction

1.1.Overview

Dispersants have a wide range of application in industry. They could be used in cement admixture to reduce fluidity of the mixture, reduce viscosity of ore suspensions in the mining industry or reduce the viscosity of oil-sand mixture for better oil recovery. In the same vein, flocculants have a broad industrial application. They are used in the wastewater of food, mining, oil, pulp and paper as well as textile industries. However, the current industrially used dispersants and flocculants are oil-based, which is environmentally unfriendly, and expensive. There is a strong driving force for the production of bio-based dispersants and flocculants that are more environmentally friendly and inexpensive. In this regard, lignin-based dispersants and flocculants can potentially serve for this purpose.

On the other note, the application of inorganic fillers in papermaking and composites is under investigation for some time. The main challenge of this application is the weak interaction of fillers with the rest of composite or papermaking materials. In this regard, lignin can be adsorbed on fillers in order to modify their surface properties. This would help improve the interaction of fillers with composite or papermaking materials.

Many kraft pulp mills have surplus production of kraft lignin, and they currently incinerate it as there is no industrial application for kraft lignin. The water solubility and basically weak reactivity of kraft lignin are its main challenges. As kraft pulp mills are financially struggling, the production of value-added chemicals from kraft lignin will help these processes. To produce value-added products, kraft lignin should be isolated from spent liquor (black liquor) of pulping processes. FPInnovations and NORAM Ltd developed a process for producing kraft lignin in industrial scale, which facilitates the use of kraft lignin in many applications. In this MSc studies, washed and dried softwood kraft lignin was received from FPInnovations that is produced in its pilot plant facilities in Thunder Bay, ON.

In chapter one of this thesis, which is the current chapter, the overall prospective of this MSc work is discussed. It explains the abstracts of other chapters, hypothesis, objectives and novelty of the proset studies.

In chapter two, the properties, production and modification of lignin to different products were discussed. It also covered literature reviews on the pretreatment and sulfonation of lignin is disused. The methods to characterize the properties of lignin were also stated in this chapter.

In chapter 3, the pre-treatment of kraft lignin is tested via phenolation and hydroxymethylation in order to improve lignin's reactivity toward sulfonation. The impact of process conditions on the phenolation and hydroxymethylation of kraft lignin was investigated in order to produce pretreated kraft lignin with best properties.

In chapter 4, the sulfonation of lignin via sulfuric acid treatment was studied. In this chapter, the impact of process conditions on the sulfonation of unmodified, phenolated and hydroxymethylated lignins was investigated and the conditions to produce the most soluble lignin with a highest charge density were determined. The characteristics of the products were also investigated by means of FTIR, TGA as well as elemental and charge density analyses.

In chapter 5, the sulfonation of lignin via sodium sulfite treatment was studied. In this chapter, the impact of process conditions on the sulfonation of unmodified, phenolated and hydroxymethylated lignins was investigated and the conditions to produce the most soluble lignin with a highest charge density were determined. The characteristics of the products were also investigated by means of FTIR, TGA as well as elemental and charge density analyses. In Chapter 6, the solubility of modified lignins under various pHs and concentrations were investigated. Furthermore, the applications of synthesized sulfonated lignin samples were evaluated. Possible applications of the lignin-based products were dispersants for cement and kaolinite; flocculants for dye solutions. The lignin samples were also adsorbed on kaolinite and calcium carbonate to produce modified fillers.

In chapter 7, the overall conclusions were stated. Furthermore, future works were suggested.

This majority of the work presented in this thesis was solely conducted by John Inwood. However, due to limited time, Kristy Prahila and Nikki Stein helped conduct some experiments of chapter 6 under the supervision of John. Dr. Fatehi was always available throughout this study for guideline and help. This thesis was provided under the guideline of Dr. Fatehi, as the sole supervisor.

1.2. Hypothesis

It is hypothesized that kraft lignin can be modified to be water soluble. Sulfonation provides anionic charge density and improves the water solubility of kraft lignin. Generally, particles with the same charge density in polyelectrolyte repel each other, while those with an opposite charge density attract each other. Dispersants improve the fluidity and reduce viscosity of solution via increasing repulsion between particles in suspension, while flocculants agglomerate particles (precipitates) via reducing repulsion between particles in suspension. It is hypothesized that the produced water soluble sulphonated kraft lignin can be used as a dispersant if the overall charge density of a suspension is anionic and a flocculant if the overall charge density of a suspension is cationic. Also, polymers with adsorb on surfaces with an opposite charge density. The surface modification of particles will modify their properties, which will promote their application. It is further hypothesized that modified lignin can be adsorbed on fillers to produce modified fillers.

1.3. Objectives

This thesis has the following objectives:

1. Overcome the low reactivity of kraft lignin via phenolation and hydroxymethylation
2. Increase the solubility and charge density of unmodified, phenolated, hydroxymethylated softwood kraft lignin through sodium sulfite and sulfuric acid treatments
3. Determine the possible applications of the synthesized sulfonated lignin as dispersants for cement admixture and flocculants for dye solutions.
4. Determine the adsorption performance of sulphonated lignin samples on kaolinite and calcium carbonate.
5. Elucidate the link between the structure, properties and application of modified lignins

1.4. Novelty of study

In this work, the hydroxymethylation and phenolation of industrially produced softwood kraft lignin was assessed, which was not investigated earlier. Also, the sulfonation of hydroxymethylated and phenolated softwood kraft lignin was assessed via sulfuric acid and sodium sulfite treatments. The charge density and solubility were considered for the first time as key factors in determining the properties of products. Furthermore, the applications of produced soluble sulphonated softwood kraft lignin in cement and dye solutions (as model wastewater) were assessed. The production of modified fillers via adsorbing sulphonated lignin on calcium carbonate and kaolinite was also investigated for the first time in this thesis.

Chapter 2: Literature review

2.1. Introduction

Lignin is the most abundant natural polymer, second to cellulose, and is available in both nonwood and wood. Lignin is mainly present within the cell walls of plant , which provides structural rigidity to the plant (Vanholme et al., 2010). Lignin comprises 15-30% of plants biomass (Mansfield et al., 1999; Robert, 1997; Ververis et al., 2004) and is responsible for water impermeability and microbial decay resistance (Saake and Lehnen, 2012). Plant species all contain lignin and softwood species have more lignin than hardwood species (Azadi et al., 2013). Lignin has been a source of interest in research and development since the 1970s due to its abundance and its renewable nature. It was estimated that more than 70 million tons of lignin is produced annually via pulping industry as a by-product (Kamm et al., 2012).

However, only small amounts of industrially produced lignin (2%) were used to create value-added products as of 2005 (Kubo and Kalda, 2005), while the vast majority of produced lignin were utilized as a fuel. While being an abundant fuel source, it has a low yield (almost 25% of fossil-based fuel) (Fengel and Wegener, 1984). However, lignin can be modified and used in many different end-use applications. The modification of lignin to create value-added products is not fully developed yet. To fully understand lignin, its various derivatives, modifications and potential applications, the structure of lignin must be understood.

Lignin has a complicated structure, as its composition is dependent on a various factors such as the species of hardwood and softwood, the growing conditions of the trees and the processing conditions of extracting/producing lignin from wood species.

2.2. Lignin structure

Lignin has a multi-branched three dimensional structure, which are connected through a multitude of ether and carbon-carbon bonds. Figure 1 shows the structure of native lignin. It is observable that the structure is complicated and exhibits none of the repeating structural pattern of synthesized polymers.

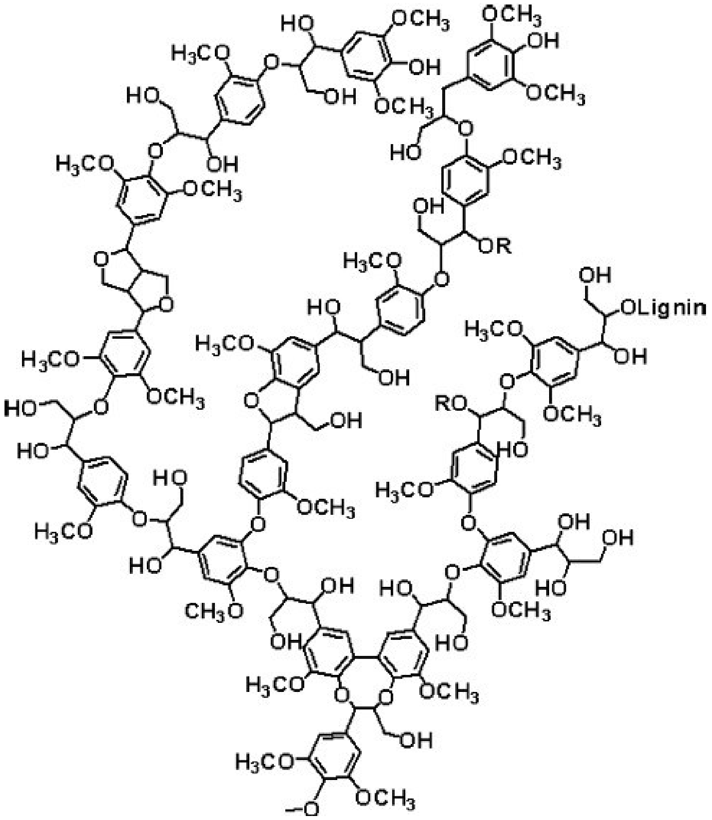

Figure 2.1. Representative structure of native lignin (http://www.lignoworks.ca/content/what-lignin)

However, this complicated structure has three subunits of *P*-hydroxyphenylpropene, guaiacyl, and syringyl (Desch and Dinwoodie, 1996). The phenyl propene subunits are represented quantitatively differently in softwood and hardwood. Hardwood species contain a near equal amount of guaiacyl and syringyl. For example, it was reported that *Fagus sylvatica* L. contained 4 wt.% *P*-Hydroxypehnylpropene, 56 wt.% Guaiacyl and 40 wt.% Syringyl (Choi et al., 2001). On the other hand, softwood species contain a significantly greater amount of guaiacyl. In one study, *Picea abies* L. contained 94 wt.% guaiacyl, 1 wt.% Syringyl and 5 wt.% *p*-hydroxypehnylpropene (Erickson et al., 1973). The individual amount of each subunit differs from species to species, and thus each species requires a varied process optimization for the utilization or modification of lignin.

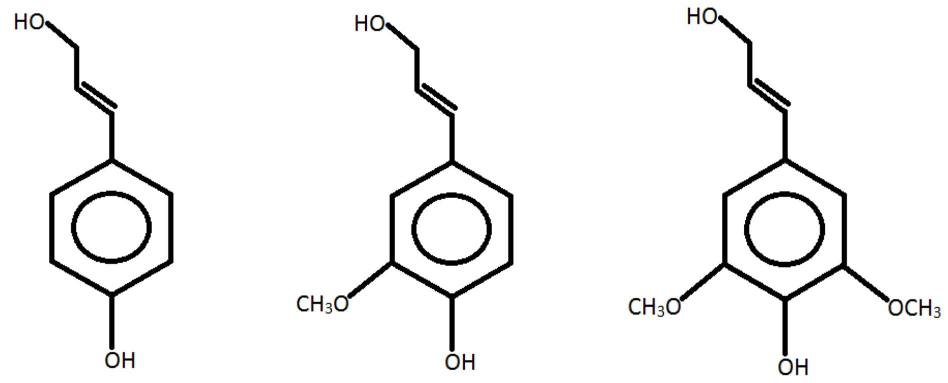

Figure 2.2. Phenyl propene subunits of lignin. *P*-hydroxyphenylpropene, guaiacyl, and syringyl, respectively (from left to right).

These subunits are bonded together with a network of β-O-4 and α-O-4 linkages, making the chemical modification of lignin difficult to conduct and to predict.

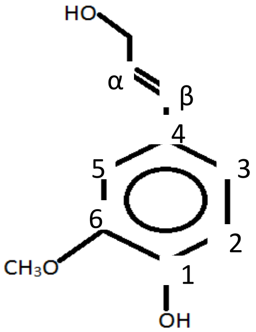

Figure 2.3. Coniferyl phenyl propene subunit with numbered reaction positions

Since the precursors are derivatives of phenolic molecules, an important consideration is the affinity of the molecule toward electrophilic substitution of the pre-existing substituents, namely hydroxide, methoxy and alcohol terminated alkyl chain. The hydroxyl group is a strongly activating substituent as it donates electrons to the aromatic ring, and exhibits an ortho/para directing nature for any reaction on lignin, which is represented by positions 2 and 4 in Figure 3. However, the para position in all of three subunits is already occupied with the alkyl chain, and the ortho position is where the reaction will be directed to the 3 and 5 positions for sinaypl; the 2 and 5 positions for confieryl and the 2 and 6 positions for p-coumaryl (Solomons and Fryhle, 2004). Due to high reactivity in water (pKa of the phenol is 9.95), the hydroxide group at position 1 on all three of the different subunits (p-coumaryl, coniferyl and sinapyl) provides the most reactive site and will react with reagents quickly. Methoxy substituents (present at the 6th position on the ring for coniferyl and the 2nd and 6th positions for the sinapyl alcoholic precursor) activate, slightly less than the hydroxyl group, and are para/ortho directing (represented by position 3 and 5 in Figure 3). The third substituent is represented by an alkene chain in all three precursors shown in Figure 1. However, the β and α linkage hydrogenated with the double bond to render it an alkyl group. Alkyl groups only weakly activate and correspondingly they have only a slight directing capability toward 3 and 5 positions shown in Figure 3 (the para position is already occupied with the hydroxide group).

The difference in phenyl propene subunits fails to fully represent the complete variability of lignin's polymeric structure as seen in Figure 1. Aryl ether bonds link the lignin monomers together in an amorphous manner, these ether bonds are classified as β-O-4, α-O-4 and 4-O-5. The amount of aryl ether bonds are known to fluctuate. Amongst these ether linkages, β-O-4 bonds comprises the majority with 60% and 50% for softwoods and hardwoods, respectively (Alder, 1977).

The respective amount of these ether bonds differs between softwood and hardwood. Softwood is represented with percentages of 46%, 6–8%, and 3.5- 4%, for β-O-4, α-O-4 and 4-O-5 bonds, respectively. Hardwood has generally 60%, 6-8%, and 6.5%, for β-O-4, α-O-4 and 4-O-5 ether bonds, respectively (Azadi et al., 2013). The phenyl propene subunits of lignin are linked not only through ether bonds, but also through covalent bonds between the phenyl propene lignin subunits, which are classified as β-5-phenylcoumaran, β-1-(1,2-diarylpropane), β-β-resinol and 5-5-biphenyl. Softwood has an average breakdown of interconnecting covalent bonds of 9-12%, 7%, 2% and 9.5-11%, for β-5, β-1, β-β and 5-5 covalent bonds, respectively. Covalent bonds within hardwood present different ratios of 6%, 7%, 3% and 4.5% for β-5, β-1, β-β and 5-5 covalent bonds, respectively (Azadi et al., 2013).

The determination of lignin structure is complicated as the different lignin production processes affect the structure lignin. For example, ball-mills have been shown to decrease the amount of B-O-4 linkages with an increase in process intensity (i.e. mechanical grinding) (Fugimoto et al., 2005; Guerra et al., 2006; Hu et al., 2006).

2.3. Lignin production

Lignin is mostly produced via sulfite and kraft pulping processes. The traditional method of pulping is the sulfite pulping, which was patented in 1866 (Tilghman, 1866) and is conducted under acidic conditions (Smook, 2002).The sulfite process can be described as three separate stages from lignin removal point of view: the synthesis of lignosulfonic acid from the reaction between lignin and sulfuric acid; the formation of semi-soluble lignosulfonates with various cations (NH_4^+, Mg or Na); and finally the fragmentation of lignosulfonates (Alen, 2000). The sulfite process is usually conducted in the temperature range of 140 °C and 160 °C and a pH range of 1.5-5 (Smook, 2002). The sulfite pulping pprocess produces a highly soluble, cross-linked lignosulfonate with an average sulfur content of 5% that exhibits two polar groups: sulfonated (Hawley and Wise, 1926) and phenolic hydroxyl groups (Alen, 2000; Wong, 1980). It was reported that the variations in the metal content of sulfite pulping produce lignosulfonate with different characteristics: an extended linear lignosulfonate polymer is observed when sodium is present in pulping and a more condensed lignosulfonate is produced when calcium is present (Alen, 2000; Wong, 1980).

The sodium sulfite pulping process separates lignin from the other parts of woody materials (cellulose and hemicellulose) by the cleavage of the α-ether and β-ether linkages existing in native lignin (Alen, 2000). In comparison with alkaline delignification, a decreased amount of cleavage in the side chain of lignin is observed in sulfite pulping. Condensation reactions may occur through the S_N2 mechanism, as the cleavage of aryl ether bonds can form a benzylic carbocation and carbocation is responsible for condensation (Doherty et al., 2011). The S_N2 mechanism is a bimolecular nucleophilic substitution reaction and can be characterised by the nucleophilic attack on the back side (directly opposite of the leaving group) of the partially positive carbon atom (Solomons and Fryhle, 2004). The leaving group is the atom or compound, which was replaced by the added nucleophile. Another cause of condensation may be the formation of a carbon-carbon bond via benzylic carbocation with a carbon of high electron density present within aromatic rings or the formation of inter/intramolecular bonding due to the protonation of the benzylic oxygen during sulfite pulping on the derivatives of lignosulfonates.

Kraft pulping, also known as the sulfate process, is currently the most prevalent pulping process, and produces the greatest amount of lignin in the world (Smook, 2002). Ether bonds in lignin are cleaved through the use of sodium hydroxide and sodium sulfide in kraft process. The produced kraft lignin is hydrophobic , as they lack the sulfonate ion observed in lignosulfonates, and thus lignin must be modified to increase its reactivity (Hu et al., 2011b). During kraft process, the β-1-4 linkage in cellulose is cleaved by the alkaline hydrolysis. Also, the ether linkages in lignin are cleaved by base-induced hydrolysis. The α-ethyl bonds are more susceptible to cleavage than the β-aryl ether bonds, if there is a free phenolic hydroxide group present (all of the phenyl propene subunits present in lignin contain this group) (Baucher et al., 2003; Sakakibara et al., 1966). The α-ethyl bonds linking the phenyl propene subunits can be cleaved ether a quinone methide intermediate or through nucleophilic substitution by S_N2 mechanism by heating (Chakar and Ragauskas, 2004). The quinone methide intermediate is a cyclohexadiene molecule that contains both a carbonyl and methylene group to an external carbon. The formation of the reactive quinone methide intermediate is the rate determining step in delignification (Brogdan and Dimmel, 1996). Similar to the sulfite process, the kraft process also creates lignin that marginally contains sulfur (1-2 wt.%), which is less than the lignosulfonate (Doherty et al., 2011). However, the sulfur is present as aliphatic thiol groups in kraft lignin.

In the kraft process, condensation occurring in alkaline conditions presents a competing reaction between the nucleophiles, i.e. the anionic phenols and carbon anions (Olm and Tisdat, 1979). The driving force toward condensation is dependent on the initial organic structures. Condensation is the less dominant reaction if β-carbon is bonded to a good-leaving group (such as weak bases), as the cleavage of the β-aryl ether bonds between lignin's phenyl propene subunits will dominate (Chakar and Ragauskas, 2004).

2.4. Lignin purification

In sulfite pulping, the purification of lignosulfonate from pulping spent liquor is important, as pulping spent liquors contain lignosulfonate, sugars and the residual of pulping chemicals. In order to isolate and purify the lignosulfonate from spent liquors ultrafiltration was proposed, and its efficiency was evaluated (Neytzell-De Wilde, 1987). The dilute nature (less than 10 wt.%) of lignosulfonate in spent liquors presents difficulties in ultrafiltration. In the literature, the ultrafiltration followed by evaporation was proposed to increase the lignosulfonate concentration to 30 wt.% (Bansal and Wikey, 1975). Furthermore, ultrafiltration was shown to be inefficient in removing lignosulfonate from pulping spent liquors, and thus a combination of ultrafiltration and reverse osmose was used to collect more lignosulfonate from spent liquors (Restolho et al., 2009). Ultrafiltration is used in industry with the polysulphone and fluropolymer filters of medium sizes (Bhattacharya et al., 2005). Amine extraction (Lin et al., 1992) and Pekilo process (fermentation followed by ultrafiltration) (Fross et al., 1979) were also used to isolate lignosulfonate from sulfite lignin. These alternative methods have difficulties, due to the high variability of lignosulfonate structure and long processing times.

The spent liquor of kraft pulping (which is called black liquor), similar to that of sulfite pulping, contains kraft lignin, sugars, pulping chemicals and decomposed organic materials, such as acids and methanol (Zhu and Chai, 1999). Recovering kraft lignin from black liquor, can be accomplished by lowering the pH of the pulping liquor to 10,or lower with either sulfuric acid or carbon dioxide (Koljenen et al., 2004). The recovery yield of this process has been improved recently (Courchene, 1998), and the recovery of lignin of various tree species from pulping liquor was assessed in the past (Kordsachia et al., 1999).

The traditional methods for removing lignin from black liquors are based on acidification, which causes lignin precipitation and separation. These separation processes are usually conducted by filters and these filters have blockage problems. A high amount of impurities within the separated lignin is another problem of this method.. A new method to separate lignin from black liquor is the LignoBoost technology (Tomani, 2010). In this process, black liquor is treated with carbon dioxide to reduce its pH to 10, which helps precipitate lignin. The LignoBoost process is slightly different from traditional methods and after acidification with carbon dioxide, the precipiates are dispersed and washed with acid prior to filtration. Compared to the traditional methods, LignoBoost has been found to reduce investment costs by circumventing the need for larger filter areas, reduce the operational costs by lowing the amount of sulfuric acid and is able to increase the yield and purity of produced lignin.

Lignoforce is the newest technology to remove lignin from black liquor (Kouisni et al., 2012). In this system, the black liquor is concentrated, cooled and precipitated with the addition of a mixture of carbon dioxide and oxygen. The lignin is then washed without forming cake and filter pressed. This produces a high purity of kraft lignin, reduces consumption of carbon dioxide and eliminates the H_2S emissions. A pilot plant, built by FPInnovations and NORAM, at the Resolute Thunder Bay mill produces 12.5 kg/h of high quality lignin through Lignoforce technology.

2.5. Lignin modification

Lignosulfonates produced from the sulfite process has long been utilized for various purposes (will be discussed in the following section); however the amount of lignosulfonate produced is very limited.. This is because the number of sulfite pulping processes and the capacity of each of these pulping processes are limited worldwide. For example, there are only two sulfite pulping processes operating in Canada currently. Kraft lignin, while abundant, has very limited industrial application, as it is water insoluble and not reactive, thus it requires modification to increase its potential application. In comparison to other wood based materials, such as cellulose, which can be easily modified (Rajalaxmi et al., 2010), the modification of kraft lignin is challenging due to the structural complexity of kraft lignin. In the absence of any modification, the α position of these phenyl propene subunits in kraft lignin presents the most reactive site (Heden et al., 1936; Holmberg and Svensk, 1935). However, the β-O-4 aryl ether linkages and others interconnecting bonds create significant steric hindrance or occupy the available reactive α site (i.e. α-O-4 aryl ether bonds), which leads to unreactivity of kraft lignin for modification.

Various processes were reported for modifying lignin structure. These methods include demethylation, reduction, oxidation, hydrolysis, phenolation and hydroxymethylation. The demethylation of lignin selectively removes methoxy group blocking the hydroxide group attached to the phenyl propene subunits of lignin, which improves the reactivity of lignin (Okamoto et al., 1996). However, this is accomplished by enzymatic oxidative cleavage (Filley et al., 2002). Although biological processes are selective, the cost and necessarily longer retention time of these processes complicate their industrial applicability. The reactivity of lignin can also be improved through the reduction of lignin. The reduction reaction leads to the conversion of aldehyde and ketone to more reactive alcohol, and lithium aluminum hydride is often used in the reduction process as a catalyst (Meister, 2002). Other metal catalysts have been assessed in the reduction process, but the high cost remains an issue for their application. Furthermore, the purification and recovery of catalysts after the reactions pose difficulties in their industrial applicability. The oxidation of lignin has been utilized to form reactive catechol groups on lignin (Nagieb and Egypt, 1985; Olivares et al., 1988). While being a powerful tool to increase reactivity, the oxidation of lignin must be promoted with the addition of a reducing reagent under a specific reaction condition (i.e. at a certain reaction time), and this sensitivity presents difficulties in the development of oxidation processes. The hydrolysis of lignin increases the reactivity of lignin through cleavage of ether and results in the production of phenolic compounds with a lower molecular weight (Hu et al., 2011a). While hydrolysis does increase the reactivity of lignin, the decrease in molecular weight is undesirable for the synthesis of flocculants and dispersants.

The phenolation and hydroxymethylation reactions were reported to increase the reaction sites, and were capable of increasing the reactivity of lignin in the past (Alonso et al., 2005; Gosselink et al., 2004). The phenolation of lignin increases the reactivity of lignin through grafting a phenol group at the α position on the lignin structure. Grafting reactions can occurs at the α position (if not occupied), and at the *ortho* site relative to the hydroxide group through aromatic substitutions. The phenolation would add two more sites *ortho* relative to hydroxide groups on the attached phenol and would allow for a total of three sites for reaction (e.g. aromatic substitutions of sulfonation). In other words, with attaching a phenol group at the α position), phenolization allows for a potential threefold improvement of aromatic reactive sites when compared to unmodified lignin (on guaiacyl phenyl propene subunit). Hydroxymethylation increases the reactivity of the bonding site *ortho* relative to the hydroxide group on phenyl propene subunit. Hydroxymethylation, through the addition of formaldehyde to the aromatic ring, has been proven to be reactive on the *para* and/or *ortho* positions relative to the hydroxyl group. With the aliphatic chain occupying the *para* position relative to the aromatic ring the formaldehyde would react solely on the *ortho* position (Yasuda et al., 1998)

Hydroxymethylation and phenolation were chosen to increase the reactivity of lignin in this study. It was claimed that phenolation and hydroxymethylation were more effective than reduction, oxidation and hydrolysis on increasing the reactivity of lignin (Hu et al., 2011a). The phenolation and hydroxymethylation reactions increased the reaction sites, and were capable of increasing the reactivity of lignin (Alonso et al., 2005; Gosselink et al., 2004).

2.6. Application of lignin in composites

The application of non-wood based lignin as filler or binder in various products, such as plastic and insulation materials, were explored in the past (Kumar et al., 2009). Methylated softwood ammonium lignosulfate and Eucalyptus lignin derived from bark were also utilized to replace phenol in phenol-formaldehyde composite (Alonso et al., 2004; Khan et al., 2004). The incorporation of lignin into phenol-formaldehyde resins can be performed in different manners: 1) lignin can first react with formaldehyde, which would react to the available positions in aromatic ring of lignin, and sequentially be added to the phenol-formaldehyde resin (Forss and Fuhrmann, 1979). 2) lignin can be added directly to a mixture of phenol and formaldehyde solutions (Khan et al., 2004) and 3) lignin can be pretreated with formaldehyde and/or phenol, which can increase the reactivity of lignin prior to inclusion into the phenol-formaldehyde resin (OH et al., 1994). The incorporation of lignin into phenol formaldehyde was originally performed with the goal of decreasing manufacturing costs, interestingly, it was discovered that lignin inclusion in the formula could also improve the properties of composites. One study reported that non-woody lignin, from the leaf sheaths of a banana plant, could be utilized as a filler (up to 60%) in the epoxy bisphenol a digylcidyl ether resin (DGEBA), which is used in printed electric boards (Oliveira et al., 2004). Other studies were also claimed the use of lignin as a comonomer in the production of adhesives (Olivares et al., 1995).

The application of hydrolytic lignin in a isotactic polypropylene blend was also performed in order to improve the thermal stability of the composites by creating a protective layer of char, which prevented the diffusion of oxygen into the bulk of the polymer (Canetti et al., 2006).The flame retardant nature of hydrolytic lignin under various blending conditions was investigated (Chirico et al., 2003). Alternatively, lignin could completely replace TiO_2 in poly vinyl chloride (PVC) composite (Fledman et al., 1996). The application of lignin in polymers/composites is detailed in an study conducted by Kumar and his associates (Kumar et al., 2009).

Lignosulfonate has a sulfonated group on its structure, which makes it an anionic hydrophilic material. Lignosulfonates can also be introduced into phenol/formaldehyde resin insolation board, based on mineral wool, as an adhesive (Budin et al., 1990). A comprehensive examination of this application was studied at laboratory and industrial scales. It was found that a high molecular weight lignosulfonate (which had been isolated from pulping spent liquor through ultrafiltration) could be incorporated in adhesive that is used for the creation of the insolation board. The incorporation of the lignosulfonate in the adhesives allowed for shorter curing times of isolation board production, which could increase the production rate of insulation boards.

2.7. Application of lignin as a dispersant for cement admixture

In 2009, the sulfonation of alkali lignin (i.e. lignin that is produced in alkaline pulping) was attempted and its properties was evaluated as a dispersing agent in cement (Ouyang et al., 2009). In these reactions, the alkali lignin was first oxidized and then hydroxymethylated in order to improve its reactivity and allow for a sulfonation to occur in less sever reaction conditions. The evaluation of sulfonated alkali lignin as a dispersant for cement determined that it contained improved characteristics when compared to commercial lignosulfonates. The properties that allowed the sulfonated alkali lignin to be considered were a higher sulfonation degree, lower surface tension, and a higher adsorption amount on the cement particles. The effects of sulfonated phenolic resins on concrete workability were also evaluated (Hsu et al., 2000). It was reported that the fluidity of cement (prior to curing) increased as the sulfonation degree of lignin increased until sulfonation reached a degree of 0.36 g/g sulfur/carbon ratio, where a plateau was reached. Furthermore, the performance of the cement material improved as the degree of polymerization of phenols, as the product used in cement, increased. It was determined that a phenolic resin with a molecular weight of 3 x 10^4 g/mol and sulfonation degree of 0.36 g/g S/C yielded the most effective dispersant with respect to workability and compressive strength.

In another study, the incorporation of sulfonated non-wood lignin in cement was practiced in an effort to reduce the amount of water needed in the cement mixture (Li et al., 2011). In this work, wheat straw lignin was produced via ethanol pulping and then lignin was hydroxymethylated and sulphonated with Na_2SO_3 in a formaldehyde solution. It was determined that sulfonated lignin allowed for 14.9% less water usage at a higher compressive strength when compared to commercially available lignosulfonates. The structure of the cement exhibited a much denser structure and exhibited small porosity, which had a twofold benefit of improving concrete strength and increasing the concrete's permeability resistance. An increase in sulfur in lignin has also been linked to greater absorption (Sadowski, 1992) and dispersive ability (Matsushita and Yasuda, 2005).

2.8. Application of lignin as a flocculant or dispersant for wastewater

Flocculants have long been used in industrial practices of fermentation, papermaking, food manufacturing and water treatment in order to remove colloidal particles from solutions (Wei et al., 2008). Commercial flocculants used are alum, ferric or synthetic organic flocculants (Li et al., 2008) . However, they all possess a limitation. The solublity of alum is low, thus when alum flocculants is used, there is residual alum left in solution (Banks et al., 2006). Ferric flocculants are costly and associated with undesirable characteristics (i.e. odor, color and corrosion) (Li et al., 2008) . Synthesized organic materials are not typically biodegradable and their monomers have been shown to be toxic (Shih et al., 2001). Due to the limitations of current flocculants, lignin and other natural polymers have been converted to be used as flocculants, as they degrade naturally into monomers that are not harmful to humans and the environment(You et al., 2009). Lignin has potential to be a dispersant or flocculants due to its large and complex polyphenolic structure (Doherty et al., 2011).

In 1975, lignosulfonate was used as a flocculant in order to aid the separation of insoluble compounds, such as talc ($Mg_3Si_4O_{10}(OH)_3$) and other phyllosilicates, from molybdenum concentrates (Hiscox et al., 1975). It was found that a large amount of lignosulfonate in conjunction with calcium hydroxide (to raise the pH) would depress molybdenite (MoS_2) and allow clays and talc to float to the surface of the suspension, making the separation a simpler process.

Lignin was investigated as a flocculant (previously ammonium salt of lignin was reacted with sodium alginate to create cationic flocculant) (Zhang et al., 2013). This denotes the most common method of the introduction of a cationic group onto lignin to increase its flocculation property (Zhang et al., 2013). The molecular weight and charge density of flocculants presents a major role on its performance (Ahvazi et al., 2011). Similarly, it was reported that an increase in the charge density and molecular weight of lignin-based dispersant improved its dispersing properites (Matsushita and Yasuda, 2005). However, the application of an anionic lignin-based flocculant for wastewater has not yet been investigated and is one of the focuses of this study.

This study focused on the sulfonation of lignin, rather than carboxylation or other grafting techniques, in order to make use of kraft lignin.

2.9. Application of lignin as an adsorbant

Lignin was also modified and used as an adsorbent in various studies. A study in 1992 (Sadowski, 1992) evaluated the effect of sodium lignosulfonate on the adsorption of sodium dodecyl sulfate onto mineral surface, such as calcite and barite. It was shown that the sodium lignosulfonate had a greater negative charge density than did sodium dodecyl sulfate, which competed for adsorbing on the surface of barite. With this competition for a limited amount of surface, the total amount of adsorbed sodium dodecyl sulfate was reduced. In another study, kraft lignin was used as an adsorbent of Ni and V in the oil industry (Pérez et al., 2006).

2.10. Other uses of lignin

Another use of lignin to convert lignin to carbon fiber, which can be used for numerous processes (Kadla et al., 2002) . Carbon fiber with appropriate mechanical properties was obtained from hardwood kraft and Alcell lignin through a two-step process: thermal spinning preceded by carbonization. It has been suggested that kraft lignin has potential as a valuable precursor for the production of general grade carbon fibers.

The production of hydrogen gas presents another use for lignin (Azadi et al., 2013). Theoretically, the production of lignin has a larger hydrogen production selectively than glucose, fructose, cellulose, xylan and bark in supercritical water using metal catalysts (Nickel and ruthenium) 380^{O}C and 230 bar (Azadi et al., 2012). However, it was found that lignin presented difficulties in gasification, when compared to other woody materials due to its increase in intramolecular bonds. While lignin can be used to produce hydrogen gas, a large amount of energy is needed as the reaction is endothermic.

Lignosulfonate were utilized in addressing acid rock drainage in the mining industry (Zhuang and Walsh, 2003). Acidic rock drainage is produced by the oxidation of the processed mine rock (i.e. ore), and is a significant environmental concern. A common method of treating acid rock drainage is the HDS (high density sludge). The HDS relies on the addition of excess amount lime, which neutralizes the acidity, and allows for alkaline conditions. In these alkaline conditions, metal ions are precipitated in their respective hydroxides. The sludge is mixed with the ore in a clarifier, iron chloride is added to further remove metal ions in solution and then the settled sludge removed. A large concentration of metals can be found in the HDS and it can be disposed of properly. The lignosulfonate complexion with metals increases the pH of the solution (as metals acts as lewis acids). Furthermore, lignosulfonate reportedly coats the surface of lime and decreases the lime needed. The results of this study were promising, as the treatment reduced the amount of sludge and improved the sludge's ability to resist metal leaching into solution, which reduces the cost of the process (Zhuang and Walsh, 2003).

Previously, lignin and hemicelluloses dissolved in the prehydrolysis liquor (i.e. spent liquor) of kraft based dissolving pulp process or spent liquor of an neutral sulfite semi chemical pulping process were adsorbed on activated carbon, calcium carbonate, and calcium oxide, and the products were claimed to be used as modified fillers in various application such as papermaking and composites (Fatehi et al., 2013; Fatehi et al., 2010). In the same vein, the kraft lignin can be used for the same purpose if modified to be water soluble.

2.11. Sulfonation of lignin

The sulfonation of lignin provides lignin with unique properties. As stated in previous sections, lignosulfonate was used as dispersants and flocculants in various environments. Therefore, the sulfonation of kraft lignin may render kraft lignin with such properties that are required for dispersion/flocculation application. The sulfonation of lignocellulosic materials was conducted through various pathways. When dealing with Klason treated Pinus densiflora lignin, a phenol group can be grafted to its α-position through phenolation (Matsushita and Yasuda, 2005). Alternatively, methoxy group can be added to aromatic ring of lignin in order to improve its reactivity through hydroxymethylation (Matsushita et al., 2004; Yasuda and Asano, 2000; Yasuda et al., 1999; Yasuda et al., 1998). Previously, sulfuric acid treatment was used as a method to sulfonate alkali lignin and hydroxymethylate alkali lignin derived from olive stone biomass, which were incorporated into a phenol/formaldehyde resin (Zoumpoulakis and Simitzis, 2001).

The reagents and raw materials of several sulfonation reactions of lignin and non-lignin species were tabulated in Tables 1 and 2, respectively. It is inferred from the tabulated data that concentrated sulfuric acid, sodium bisulfate, sodium sulfate, chlorosulfuric acid and sulfur trioxide are capable of sulfonating lignin with a high efficiency. However, each reactant species would exhibit certain benefits and weaknesses. Concentrated sulfuric acid may cause serious corrosion problems due to its very low pH of 0.3 (with a concentration range approximately 70%). Chlorosulfuric acid is a corrosive material, while sulfur dioxide gas is more difficult to use and control in reaction compared with sulfuric acid. Solvent based sulfonation can also present an efficient sulfonation process, and showed to dramatically increase the amount of sulfur present in the produced sulfonated lignin that was derived from Pinus densiflora and treated with 72% sulfuric acid treatment (Browning, 1967). However, it was stated that solvent-based sulfonation presented a more complicated and expensive scenario for applying in industry (Matsushita and Yasuda, 2005).

Table 2.1. Sulfonation alternatives for lignin

Starting material	Reagents	Reference
Phenolated sulfuric lignin	1) 1M NaOH + 37% formalin →1M HCl 2) 40% $NaHSO_3$	(Matsushita and Yasuda, 2005)
Phenolated sulfuric lignin	0.5 M NaOH + $CH_2(OH)SO_3Na$	(Matsushita and Yasuda, 2005)
Phenolated sulfuric lignin	$ClSO_3H$ in $CHCl_3$ (or $CHCl_4$)	(Matsushita and Yasuda, 2005)
Phenolated sulfuric lignin	1) HCHO + 3M NaOH 2) C_2Cl_4 + $ClSO_3H$	(Yasuda and Asano, 2000)
Alkali lignin	1)HCHO 2)Na_2SO_3	(Ouyang et al., 2009)
Wheat Straw hydroxymethyl ethanol lignin	Na_2SO_3 in formaldehyde (CH_2O)	(Li et al., 2011)
Lignin	SO_3^{2-} + CH_2O	(Meister, 2002)

Table 2.2. Sulfonation alternatives for non-lignin species

Starting Material	Reagents	Reference
Starch-phenol formaldehyde	Concentrated H_2SO_4 (Ag_2SO_4 as catalyst)	(Farag, 1995)
Anisole	Concentrated H_2SO_4	(Cerfontain et al., 1985)
Poly (phenylene ether ether sulfone)	H_2SO_4, $N(CH_3)_4OH$	(Al-Omran and Rose, 1996)
Benzene, halogenobenzenes, halogenonaphtalens, chloroanthracenes	SO_3 in CH_2Cl_2 solvent	(Cerfontain et al., 1994)
Phenol	$HOCH_2SO_3Na*H_2O$	(Rober A.M.C., 1987)
Cellosics	1) $NaIO_4$ 2) $NaHSO_3$	(Zhang et al., 2007)

The sulfonation analysis conducted on other woody compounds can also be used as guidelines for the sulfonation of lignin. In one study, the oxidation of the cellulosics materials was performed through the addition of sodium metaperiodate ($NaIO_4$) regent and was then sulfonated by sodium bisulfite ($NaHSO_3$) (Zhang et al., 2007). It was also stated that the oxidation of the cellulosic materials increased their aldehyde content prior to sulfonation in order to improve the sulfonation efficiency.

In another study, it was discovered that the sulfonation of aromatic compounds could be assisted with the addition of sonification in order for regioselective sulfonations to occur (Ziyauddin et al., 2009). In this study, the application of ultrasound improved the reaction rate and selectivity of sulfonation reaction dramatically, as sonification reduced the reaction time from 24 h to 45 min and improved the conversion rate by 6-10%. Thes studies illustrated that the sulfonation of aromatics could be affected through many variables and with altered conditions and different sulfonated products could be synthesized.

2.12. Analyzing the properties of lignin

The amorphous nature of lignin and its inherent complexity presents a great difficulty for characterizing lignin. The sulfonation of these compounds creates even more difficulties and these difficulties will even arise during the separation for sulfonated lignin from other compounds of a reaction (Ede and Ralph, 1996). In the past, a separation method was developed using one and two-dimensional liquid chromatography for the analysis of lignosulfonates and sulfonated kraft lignins (Brudin et al., 2008). Although the study proved to be a step in the right direction to comprehend the nature and separation of complex polymeric species, there is still a need for further development. 2 Dimensional NMR was used to illuminate the primary structure of lignin in one study (Ede and Ralph, 1996). This was accomplished through a development and ^{1}H and ^{13}C NMR utilizing monomeric sulfonated compounds and dimeric sulphonated compounds. In fact, these chemicals can be used as external references to confirm whether sulfonation, the degree of sulfonation and at which locations on the ring grafting occurred (Lutnaes et al., 2008). Furthermore, ^{31}P NMR can be used to determine the amounts of the pheynyl propene subunits of lignin. The different types of ether and carbon-carbon linkages between the phenyl propene groups can also be determined through ^{31}P NMR(Pas et al., 2014).

Other analytical methods were used to determine the functional groups of technical lignin (Mansouri and Savado, 2007). Gas chromatography, aminolysis, UV spectroscopy, and FTIR spectroscopy were also used to specify the structure of lignin in the past (Mansouri and Savado, 2007). Gas chromatography can be used to characterize the composition of the phenyl propene monomers of lignin (Choi et al., 2001). Aminolysis can be used as a pretreatment to UV or FTIR, in order to determine the structural functional groups of lignin (Wegener and Strobel, 1992). While UV can be used to provide an estimation of the amount of functional groups in lignin (phenolic hydroxyl, carbonyl, aldehyde and ketones) (Popescu et al., 2006; Sarkanen and Ludwig, 1971). FTIR presents another method to determine the functional groups attached to lignin and the amount of phenolic hydroxyl group (Faix and Bottcher, 1993).

While lignosulfonates from the sulfite pulping process are soluble, kraft lignin is not and as such the solubility must be increased through various reactions, such as sulfonation, in order to improve its end use in industry.

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Chapter 3: Hydroxymethylation and phenolation of softwood kraft lignin

Abstract

In this work, the modification of softwood kraft lignin through hydroxymethylation and phenolation was investigated. The hydroxymethylation of softwood kraft lignin was investigated with formaldehyde underneath various conditions, i.e. CH_2O/ kraft lignin molar ratio, lignin concentration, temperature and time. The phenolation of softwood kraft lignin was also investigated with liquefied phenol in a sulphuric acid solution underneath various conditions of liquefied phenol/kraft lignin molar ratio, reaction temperature and time. The results showed that hydroxymethylation increased the solubility and charge density of kraft lignin, and phenolation proved to be detrimental to solubility and provided no charge to kraft lignin. Self-condensation of the guaiacyl phenyl propane subunits of lignin during phenolation aided by sulphuric acid catalyst seemed to create a detrimental effect in increasing the reactivity of sulfonation of lignin. The optimum conditions for hydroxymethylation were found to be at 80 °C, 4 h, formaldehyde/lignin molar ratio of 0.55 mol/mol and lignin concentration of 10 g/L. The optimum conditions for phenolation were a phenol/lignin molar ratio of 7.3 mol/mol, 4 h , 80 °C ,reacting in a 90 ml of 60 wt.% H_2SO_4, which was followed by a dilution to 1500 ml of water and boiling for 2 h.

3.1. Introduction

Lignin is the second most abundant natural occurring biopolymer, preceding cellulose and provides an excellent source of inexpensive readily available reactant to create valuable chemicals such as dispersants.

Kraft lignin can be modified to increase its reactivity. Without any modification to the structure of the phenyl propene subunits, sulfonation of the α position of these phenyl propene subunits easily occurs (Heden et al., 1936; Holmberg and Svensk, 1935). Most α position are commonly occupied through α-0-4 bonds and other ether bonds in the macromolecule of lignin. Increasing th*e reactivity of lignin would allow a greater amount of sulfonation to occur and increases the potential of high charge density. Methods to increase the reactively of lignin include phenolation, hydroxymethylation, demethylation, reduction, oxidation and hydrolysis. The demethylation (via biological treatment) of lignin selectively removes methoxy group blocking the hydroxide group attached to the phenyl propene subunits of lignin, which increases its reactivity (Filley et al., 2002; Okamoto et al., 1996). Demethylation is usually conducted via biological processes which are very selective, but is a slow process. The operations with biological enzymes are costly to operate due to larger batch reactors and require substantially longer reaction times. The reduction of lignin (via using lithium aluminum) will reduce the aldehyde and ketone subunit of lignin to more reactive alcohol (Meister, 2002). Other catalysts were also used for reduction reaction of lignin, however, catalysts are expensive and purification of lignin after the reaction (i.e. removal of catalysts) is very difficult. The oxidation of lignin was also experienced to form reactive catechol groups (Nagieb and Egypt, 1985; Olivares et al., 1988). The oxidation of lignin must be performed with a timely addition of reducing reagents and its performance is dependent upon the structure of lignin; this presents difficulties in oxidation reaction due to lignin's non-uniformity. The hydrolysis of lignin increases the reactivity of lignin through cleavage of ether bonds and results in the production of phenolic compounds with lower molecular weights (Hu et al., 2011a). However, a lower molecular weight lignin is not desirable as dispersants (Matsushita and Yasuda, 2005). It was also claimed that phenolation and hydroxymethylation of lignin were more effective than reduction, oxidation and hydrolysis (Hu et al., 2011a). The phenolation and hydroxymethylation reactions increased the reaction sites and were capable of increasing the reactivity of lignin in the past (Alonso et al., 2005; Gosselink et al., 2004).

The phenolation of lignin occurs at the α position, as shown in Figure 3.1. If not occupied, sulfonation can occurs at α position, and at the *ortho* site relative to the hydroxide group through aromatic substitutions. The phenolation would add two more sites *ortho* relative to hydroxide groups on the attached phenol and would allow for a total of three sites for aromatic substitutions of sulfonation. In other words, at the cost of the potential sulfonation at the α position, phenolization allows for a potential threefold degree of sulfonation when compared to kraft lignin.

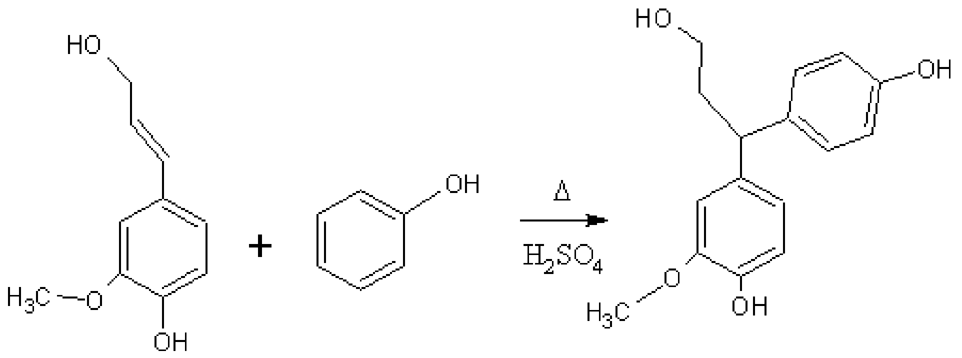

Figure 3.1. The scheme of phenolation of lignin

Hydroxymethylation increases the reactivity of the bonding site of *ortho*, relative to the hydroxide group, on phenyl propene subunit. Hydroxymethylation, through the addition of formaldehyde to the aromatic ring, has been proven to be reactive on the *para* and/or *ortho* positions relative to the hydroxyl group. With the aliphatic chain occupying the *para* position relative to the aromatic ring the formaldehyde would react solely on the *ortho* position (Yasuda et al., 1998). On the hydroxymethylated lignin, a new position can occur for the sulfonation on the newly added methoxy group associated with the aromatic ring, as seen in Figure 3.2.

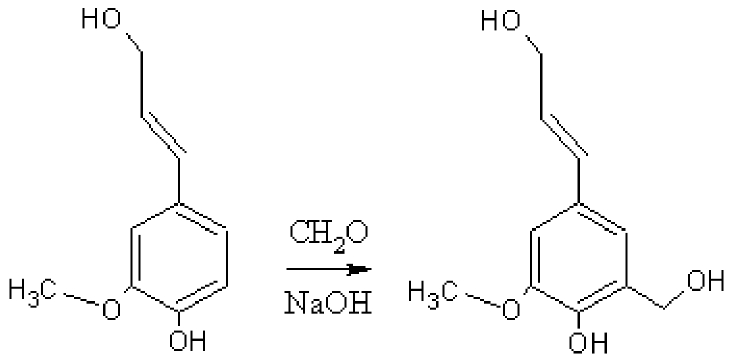

Figure 3.2. The scheme of hydroxymethylation of lignin

The phenolation and hydroxymethylation as pretreatment processes were previously conducted on Klason treated Pinus densiflora lignin prior to sulfonation through sodium sulfite simultaneously (i.e. Chlorosulfoninc acid). The products of this process were used as dispersants for gypsum paste (Matsushita and Yasuda, 2005). However, it is not clear if the changes in properties of lignin are attributed to phenolation and hydroxymethylation. The adsorption qualities of the sulfonated lignin, and cellulose, were investigated in the past for heavy metals

(Gaballah and G., 1998; Lee et al., 2006; Lee et al., 2005; Liang et al., 2013; Pourjavadi et al., 2013; Shet and Wallajapet, 1997). However, the adsorption properties of sulfonated phenolated and hydroxymethylated softwood kraft lignin have not been fully explored. As the properties of lignin affect its modification performance, the results available in literature cannot be expected for different lignin samples.

In this chapter, the hydroxymethylation and phenolation were conducted on softwood kraft lignin under various scenarios. The characteristics of the products were evaluated using the amount of mols grafted onto lignin, a particle charge detector, FTIR, TGA and Hansen solubility parameter. The solubility of the modified lignin samples was also assessed. Based on the results, the conditions that yielded modified lignin samples with the highest efficiency of grafting were determined. As the properties of lignin affect its modification performance, the results available in literature cannot be expected for different lignin samples. The main aim of this chapter was to explore the phenolation and hydroxymethylation of softwood kraft lignin.

3.2. Experimental

3.2.1. Raw materials

In this work, washed and dried softwood kraft lignin was supplied by FPInnovations from its pilot scale facilities in Thunder Bay, ON. Liquefied phenol (>89% purity), formaldehyde solution (30%), 3-(Trimethylsilyl)proionic-2,2,3,3-d acid sodium salt (TSP), and poly (diallyldimethylammonium chloride) solution (PDADMAC) with a molecular weight (MW) of 100,000-200,000 g/mol (20 wt.% in water) were all purchased from Sigma-Aldrich. Sulphuric acid (98% purity) was purchased from ACP, and used as received. Anionic polyvinyl sulfate (PVSK) with a MW of 100,000-200,000 g/mol (98.4 wt.% esterified) was provided by Wako Pure Chem. Ltd. Japan. Tego@trant A100 utilized for Metrohm Ion analysis was supplied by Metrohm.

3.2.2. Hydroxymethylation of kraft lignin

The hydroxymethylation of softwood kraft lignin was performed through the addition of dried kraft lignin (0.5-3g) to 0.3-1.8 g of 37 wt.% formaldehyde solution in a three-neck glass flask, the pH of the solution was adjusted to 10 with the addition of 2.5 M NaOH, and bulked to a final fixed volume of 100 ml with deionized distilled water. The system was charged with a graham condenser and a magnetic stir bar, and reacted at 50-95°C for 1-6 h. The investigated parameters were lignin concentration (0.05-0.3g/ml), CH_2O/lignin ratio (0.1-0.5), reaction temperature (50-95°C) and time (1-6 h). After the reaction, 30 ml sample was taken for determining the amount of reacted formaldehyde with the lignin. The products were cooled to room temperature, then neutralized with 1M $H_2SO_{4(aq)}$ and then underwent membrane dialysis with the MW cut off of 1,000 g/mol for two days, while changing the water every 2 h for the first 6 h and then once a day for 2 days for purification. The purified solution was then dried at 60 °C in an oven so that dried modified lignin was obtained.

3.2.3. Phenolation of kraft lignin

The phenolation of lignin was conducted and the reaction was optimized for various conditions (phenol/ lignin molar ratio, reaction temperature and time) in a three necked flask. At first, 0.5 g of kraft lignin was added to 1-5 ml of liquefied phenol and 90 ml of 60 wt.% H_2SO_4 solutions was added as a catalyst. The system was charged with a stir bar, graham condenser and a thermometer. The reaction was then stirred and heated at 20-95 °C for 1-8 h. The phenolated lignin solution was then quenched with 300 ml of distilled water and boiled for another 2 h. The resulting solution was then cooled to room temperature and preceded by vacuum filtration using a 45 nm nylon filter.

3.2.4. Charge density and solubility of unmodified, hydroxymethylated and phenolated lignin

At first, 1 wt.% solution of lignin samples was prepared by adding the lignin samples to deionized distilled water (pH 7) and room temperature. The solution was shaken for 1 h at 100 rpm at 30 °C. After shaking, the solutions were centrifuged at 1000 rpm for 5 min in order to separate soluble and insoluble parts from the solution. The filtrate part was taken for charge density analysis of soluble lignin, while precipitates were dried in an oven at 60 °C for charge density analysis of insoluble lignin. The charge density of soluble lignin samples were determined by direct titration, while the charge density of insoluble ones was identified by the back titration method. To measure the charge density of soluble samples, 1 to 2 ml of lignin sample solutions were added to the cell of a particle charge detector, Mutek PCD-04 titrator (Herrsching, Germany) and titrated against PDADMAC standard solution (~0.005M).These values were then used to calculate charge density using Equation 3.1. To measure the charge density of insoluble lignin samples, about 0.05 g of dried insoluble lignin samples were mixed with PVSK standard solution (~0.005M) for 1 h at 30 °C. Then, the concentration of PVSK solutions before and after mixing with lignin samples were determined by the titrator using the PDADMAC standard solution, and the charge density of insoluble lignin was determined using Equation 2.

Equation 3.1

(——)

Equation 3.2

3.2.5. Elemental analysis

The elemental analysis of dried kraft lignin and modified lignin samples was conducted using a Vario EL Cube instrument (Germany) as dictated in the literature (Fadeeva et al., 2008). Lignin samples were weighed and loaded in an integrated carousel, and flushed with carrier gas (He). The combustion of lignin samples was carried out, and the combusted gases were reduced in order to be identified by the instrument. The elemental balance of the lignin samples were developed from this data. The elemental analysis helped investigate the theoretical formula of lignin before and after treatment by considering the weight percentage and atomic weight of each element.

3.2.6. Thermo-gravimetric analysis

Thermal performance of the lignin before and after treatment was assessed using a thermo-gravimetreic analysis (TGA). The lignin samples were first dried at 105 °C and subsequently heated with a thermo-gravimetric analyzer (TGA)-i1000 series (instrument Specialist Inc.) using N_2 (30ml/min) with an increment rate of 10 °C/min in the temperature range of 25 °C and 800 ^{o}C (Zhang et al., 2011).

3.2.7. FTIR analysis

Alternatively, the structure of the samples were analyzed using a Tensor 37 Fourier Transform Infrared Spectrophotometer (FTIR) (Bruker,Canada) in order to investigate the functional groups associated with lignin.

3.2.8. Quantification of grafted formaldehyde in the hydroxymethylation

A sample was collected from the three neck flask after the hydroxymethylation reaction (prior to any neutralization and purification). Formaldehyde Vacu-vials Kit (K-4203) was used to determine the initial and final concentrations of formaldehyde in the reaction solutions. In this test, a selective sample of the reaction solution was taken after the reaction, 5 drops of formaldehyde activator solution were added and mixed with a vacuum sealed vial containing a the oxidizing agent of persulfate and Purpald® (developed by Sigma Aldrich). The formaldehyde within the solution reacts with Purpald and forms a purple colored complex, which is produced in proportion with formaldehyde concentration. The intensity of wavelength at 550 nm was measured by a Thermo Scientific Genesys 10S UV vis spectrophotometer, and the concentration of formaldehyde (in mg/L, or ppm, CH_2O) was determined using equation 3. The amount of formaldehyde grafted to lignin was determined using Equation 4.

Equation 3

ppm CH_2O = 6.69(absorbance at 550 nm) – 0.03 (formula obtained from Formaldehyde Vacu-Vials Kit K-4203

Equation 4

$$\frac{((\qquad (—) \qquad (—)) \qquad)}{}$$

3.2.9. Quantification of grafted phenol in the phenolation

At first, samples were taken from the reaction medium (three neck flask). Then, 1.1 ml of reaction medium was combined with 0.4 ml of D_2O and 0.5 ml of a 2.35 x 10^{-5} mol/L 3-(Trimethylsilyl)propanoic acid (TSP) solution. ^{1}H-NMR analysis was conducted on a solution sample before and after the phenolation reaction using a Varian Unity Inova 500. TSP acted as a known standard to determine the amount of phenol present in the solution, and the amount of phenol grafted was determined via Equation 5 and 6.

Equation 5

$$[\qquad] \quad \frac{[\quad]}{}$$

Equation 6

$$\frac{[(\qquad [\qquad](—) \qquad [\qquad] (—)) \qquad]}{} \quad (—)$$

3.3. Results and discussion

3.3.1. Hydroxymethylation of lignin

Figure 3.3 shows the impact of CH_2O/lignin ratio on the grafting efficiency of formaldehyde on lignin. It is noted that as the amount of formaldehyde present in the reactions increases, the greater amount of formaldehyde grafted onto kraft lignin. However, the grafting efficiency was somehow independent of the CH_2O/lignin molar ratio. Lower grafting efficiencies of formaldehyde onto lignin create a reaction with higher costs for reagents and greater need for purification. In the past, formaldehyde was used through the hydroxymethylation in order to increase the reactivity of calcium lignosulfonate in an effort to increase its absorption and foaming ability; (Pang et al., 2008) and in the copolymerization of phenol and/or lignin (Ma et al., 2011). An excess amount of formaldehyde is undesirable in the reaction medium, as the copolymerization of lignin can occur. In this work, CH_2O/lignin molar ratio of 0.55 was chosen as optimal (Zoumpoulakis and Simitzis, 2001). In the literature, a molar ratio ranging 0.55-1.01 was reported as an optimum for hydroxymethylation of sodium lignosulfonate (Yu et al., 2013).

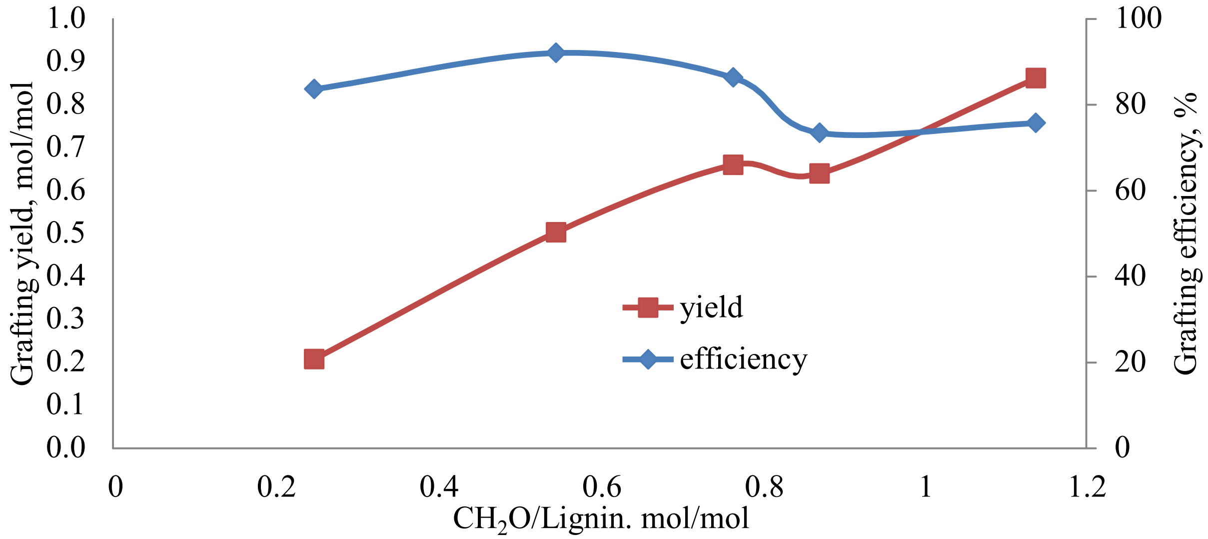

Figure 3.3. Impact of CH_2O/lignin molar ratio on the grafting yield and grafting efficiency. Experiments were conducted at 95°C, 2 h and a lignin concentration of 10 g/L.

The impact of lignin concentration on the grafting efficiency of formaldehyde to lignin is presented in Figure 3.4. It is noted that the amount of formaldehyde grafted onto lignin initially increased from 0.2 to 0.56 mol/mol, as the lignin concentration was increased from 5 g/L to 10 g/L. The grafting amount remained relatively constant as lignin concentration increased form10 g/L to 20 g/L, and increased dramatically at a lignin concentration of 25g /L. The grafting efficiency was the greatest, 86%, at a kraft lignin concentration of 10 g/L and was chosen as the optimum lignin concentration. The results showed that, by increasing the lignin concentration the grafted amount on the lignin was increased. The decrease in the efficiency might be due to increase in the viscosity, i.e. mechanical constrains, of the solution that was most probably hampered the reaction. The greater efficiency of the formaldehyde reaction requires less purification after the reaction. The value of 10 g/L found in this study as the optimized concentration is smaller than literature value of 30 g/L for the hydroxymethylation of calcium lignosulfonate (Pang et al., 2008), and further exemplifies the variability of lignin species.

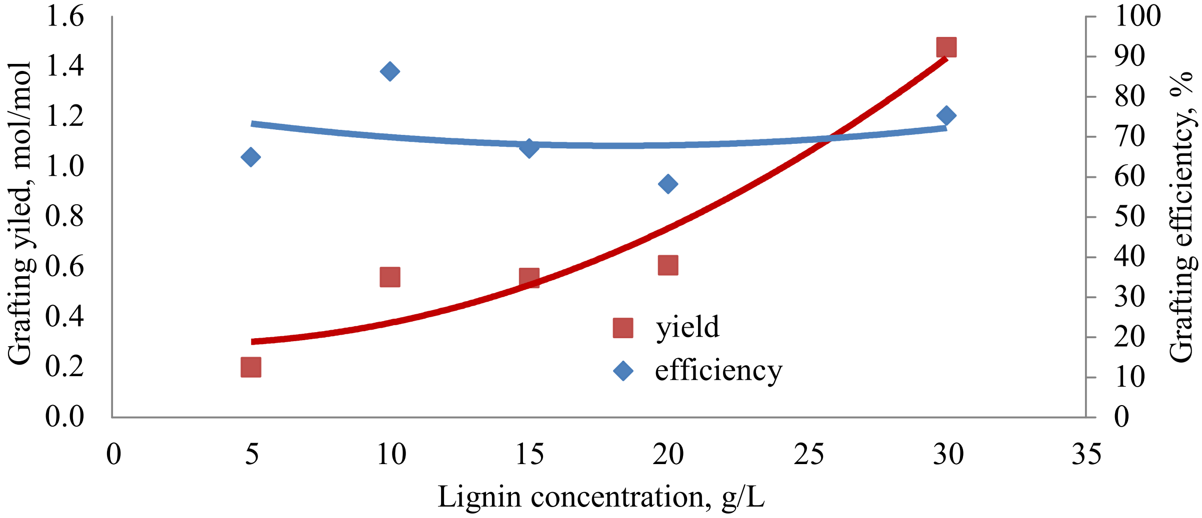

Figure 3.4. Grafting yield CH_2O/lignin and efficiency as a function of the kraft lignin concentration. Experiments were conducted at 95°C, 2 h and a CH_2O/ lignin molar ratio of 0.76.

The impact of reaction temperature on the grafting efficiency of formaldehyde is shown in Figure 3.5. Increasing the reaction temperature of the hydroxymethylation is shown to increase the yield of formaldehyde reacted with kraft lignin. Of the reaction temperature tested (50-95 °C), the highest temperature (95 °C) was chosen as the optimum temperature since the greatest amount of formaldehyde reacted at this temperature. This is a higher reaction temperature than previously reported temperatures for hydroxymethylation of calcium lignosulfonate (80 °C)

(Pang et al., 2008) and for hydroxymethylation of phenolated guaiacyl sulfuric acid (60 °C) (Matsushita and Yasuda, 2005).

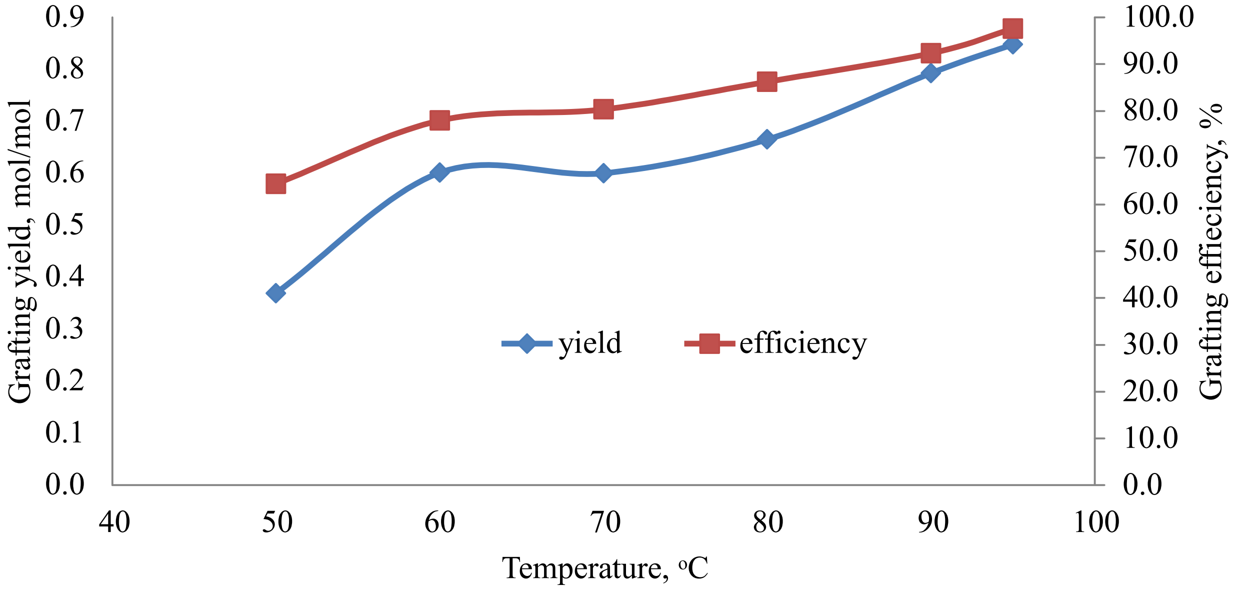

Figure 3.5. Grafting yield CH_2O/lignin and efficiency as a function of the reaction temperature. Experiments were conducted at 2 h, a lignin concentration of 0.1 g/ml and a CH_2O/ lignin molar ratio of 0.76.

The impact of reaction time on the hydroxymethylation of kraft lignin is shown in Figure 3.6. It was observed that time of reaction was limited effect on the reaction yield and efficiency. The optimum reaction time was selected as 4 h. This reaction time is greater than what was reported (i.e. 2 h) for the hydroxymethylation of calcium lignosulfonate (Pang et al., 2008).The hydroxymethylation of phenolated guaiacyl sulfuric acid was reported to be optimized in 4 h of reaction (Matsushita and Yasuda, 2005).

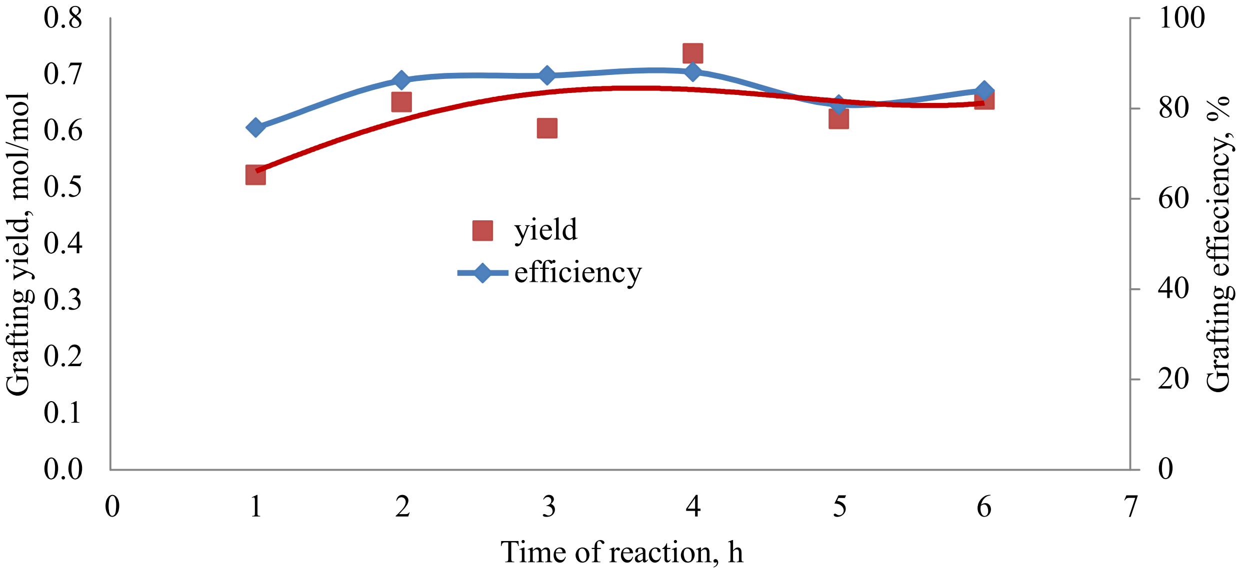

Figure 3.6. Grafting yield CH_2O/lignin and efficiency as a function of the reaction time. Experiments were conducted at 95°C, a lignin concentration of 10 g/L and a CH_2O/ lignin molar ratio of 0.76.

3.3.2. Phenolation of lignin

The phenolation of lignin was performed with 72% and 60% H_2SO_4 in the past (Matsushita and Yasuda, 2003; Yasuda et al., 1980).The less concentrated catalyst was chosen in an attempt to reduce the condensation reaction during phenolation, as this condensation was shown to occur in acidic conditions (Matsushita and Yasuda, 2003; Yasuda et al., 1980). Condensation usually tends to reduce the reactivity of lignin (Matsushita and Yasuda, 2003), which is an undesirable outcome as the phenolation of lignin increases the reactivity of lignin. Figure 3.7 shows the impact of phenol/lignin ratio on the phenolation yield and efficiency of lignin. It was found that increasing the dosage of phenol increased the yield of reaction. At lower phenol/lignin molar ratios, the amount of reacting phenol is very low and the efficiency of the phenolation is less than 25% at a dosage of 4.85 mol/mol. Increasing the phenol/kraft lignin molar ratio from 9.70 to 14.55 mol/mol has reaction efficiencies of 76 and 97%, respectively. Thus, the phenol dosage of14.55 mol/mol was chosen as the optimum molar ratio for the phenolation of kraft lignin, which is similar to previous phenolation studies conditions of a 14.21 molar ratio used in the phenolation of sulfuric acid lignin (Matsushita and Yasuda, 2005) .

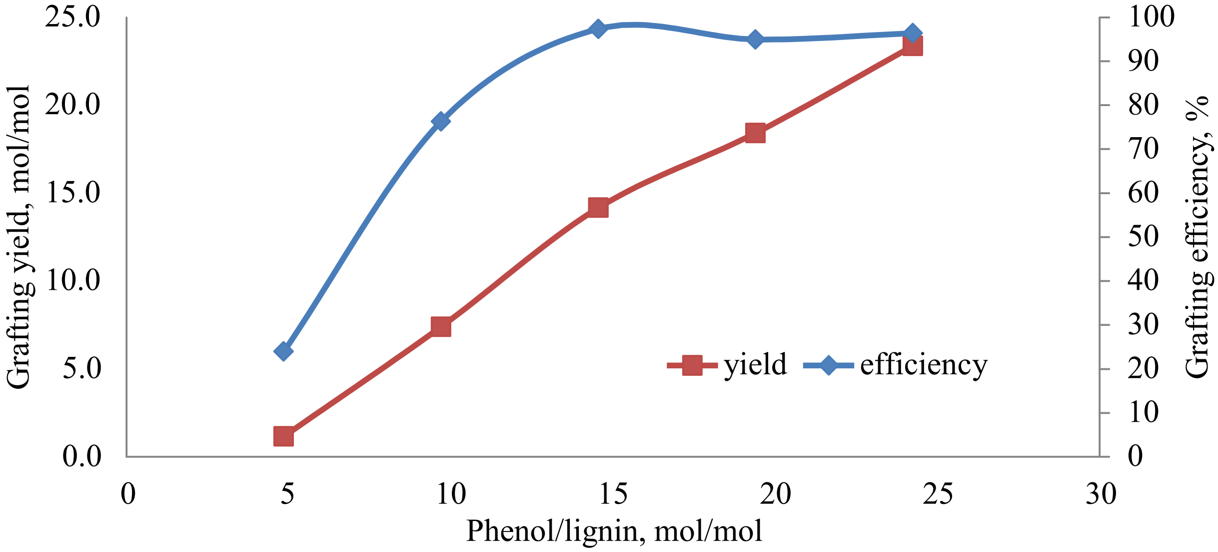

Figure 3.7. Grafting yield phenol/lignin and efficiency as a function of the phenol/ lignin molar ratio. Ratio optimizations were done at 80 °C, and 4 h.

Figure 3.8 presents the effect of reaction temperature on the phenolation of kraft lignin. It can be seen that temperature has a minor effect on the phenolation of kraft lignin. The reason for this is unknown, but may be attributed to the presence of a strong catalyst. The presence of the strong catalyst may lower the activation energy by a sufficient amount to render temperature less important. In the literature, 60°C and 80°C have been used for the phenolation of lignin species (Ma et al., 2011; Matsushita and Yasuda, 2005; Yasuda et al., 1999). The temperature of 80 °C *was chosen, as it was associated with a shorter boiling time after the dilution (Ma et al., 2011).

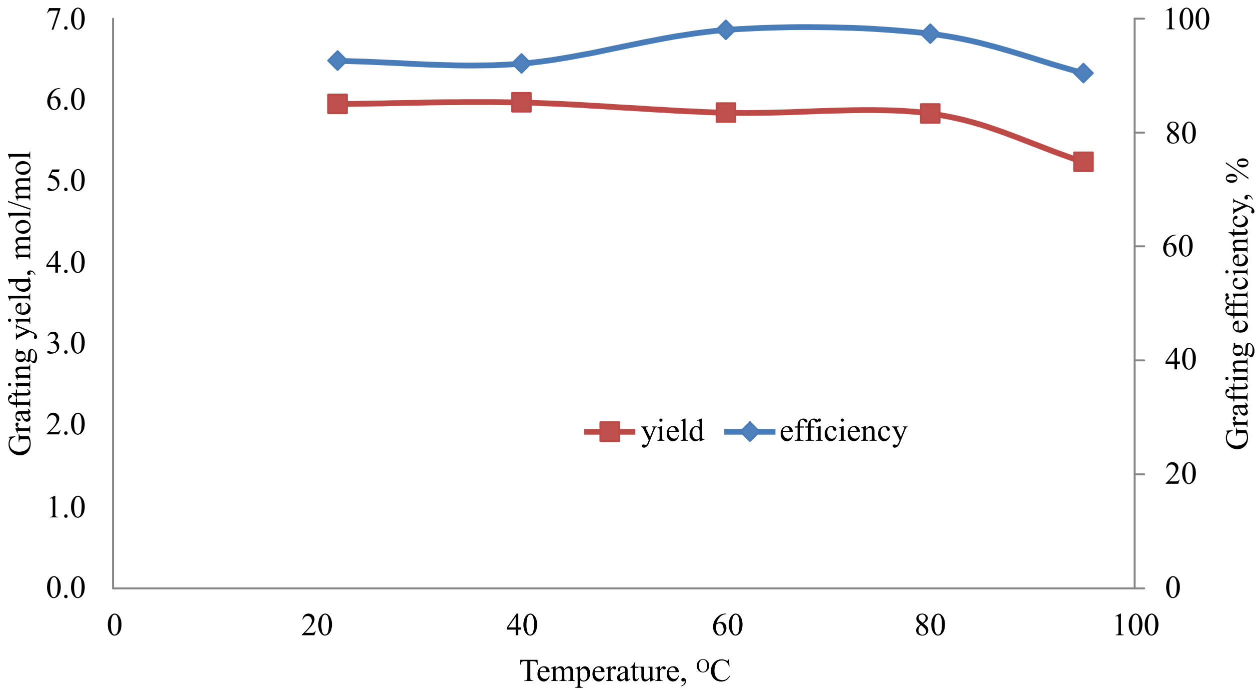

Figure 3.8. Grafting yield and efficiency as a function of the reaction temperature. Temperature optimizations were conducted at phenol/lignin molar 14.55 mol/mol and 4 h)

Figure 3.9 shows the impact of reaction time on the phenolation efficiency. It is seen that reaction time of 4 h is optimum for phenolation even though reaction time has marginal effect on the phenolation efficiency. In the past, a 4 h of reaction was chosen for the phenolation of acid insoluble lignin from rice hull in one study (Ma et al., 2011) and 6 h of reaction for phenolation of sulfuric acid lignin in another study (Matsushita and Yasuda, 2005; Yasuda et al., 1999).

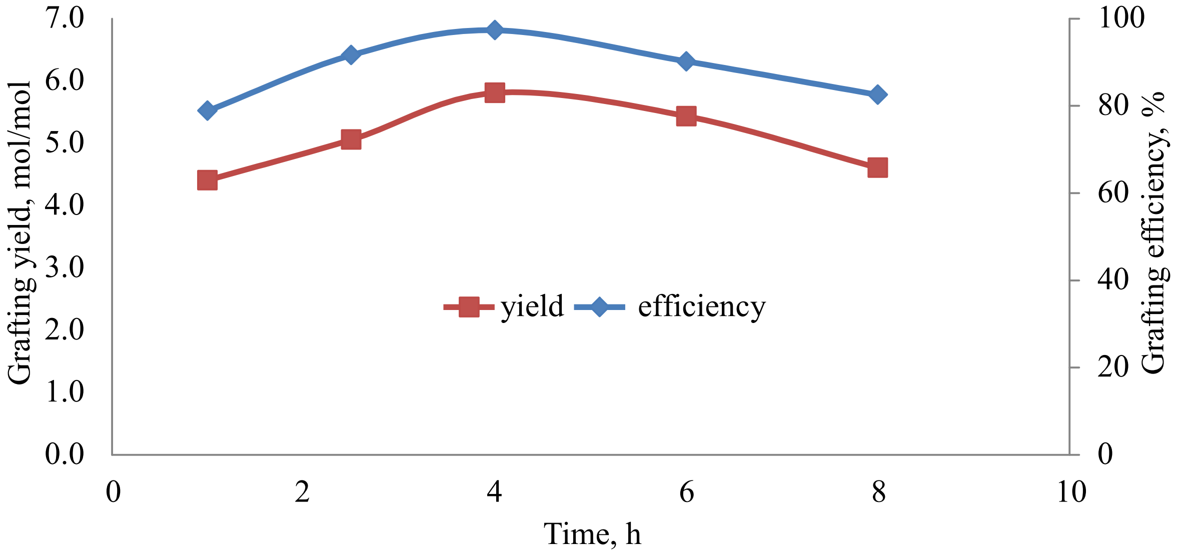

Figure 3.9. Grafting yield phenol/lignin and efficiency as a function of the reaction time. Experiments conducted at a phenol/lignin molar ratio of 14.55 mol/mol and a reaction temperature of 80 °C)

3.3.3. Characterization of kraft, H-lignin and P-lignin

The properties of kraft, H-lignin and P-lignin prepared in this work are shown in Table 3.1. This study determined that unmodified kraft lignin had a Mw of 25,100 and a M_n of 10,681 g/mol, which are higher than reported values and will be attributed to different tree species and pulping process conditions. The molecular weight of lignin present in different tree species is varied, as Pseudotsuga menziesii, Abies concolor and, E. Globulus contain lignin with a molecular weight of 38000, 52000 and 32000 g/mol, respectively (Guerra et al., 2006). In one study, the molecular weight of lignin generated from milled softwood was 10,700 g/mol (Meister, 2002). Another study reported that softwood lignosulfonate had an average molecular weight of 36,000 – 61,000 g/mol. However, hardwood kraft lignin was reported to be in the range of 5,000 to 15,000 g/mol (Luque et al., 1994). The M_W and M_n of softwood kraft lignin recovered by Lignotech from black liquor were reported to be 8,900-11,119 g/mol and 200 to 2755 g/mol, respectively (Baumberger et al., 2007). In another report, the M_W and M_n of softwood kraft lignin were 3,503-13,109 g/mol and of 163-847 g/mol, respectively (Helander et al., 2013). The optimum reaction conditions for the H-lignin prepared in this study were a temperature of 80°C, reaction time of 4.0 h, CH_2O/lignin molar ratio of 0.0.54, and a kraft lignin concentration of 10 g/L. H-lignin was determined to have a MW of 45,540 g/mol and an M_n of 22,710 g/mol, which was determined through light scattering analysis of GPC instrument, and are larger than the molecular weights found for kraft lignin. This verifies that polymerization occurred through the formaldehyde reagent despite optimum conditions designed to discourage this undesirable side reaction. The polymerization of formaldehyde with phenols and/or lignin was reported (Zoumpoulakis and Simitzis, 2001) and this occurs via reacting at the available para or ortho positions of the phenyl propene subunits to form a tertfunctional based network. The optimum conditions for the synthesis of P-lignin were a temperature of 80°C, reaction time of 4.0 h, and a phenol/lignin molar ratio of 14.5. The M_w and M_n of P-lignin could not been measured vie light scattering analysis of the GPC instrument, but were detected by UV analysis and were 4,155 g/mol and 1049 g/mol respectively. The M_w and M_n of kraft lignin were 9,769 g/mol and 2,141 g/mol, respectively. It is evident that condensation was not observed in this study, in contrast to previous studies (Alonso et al., 2005; Xie and Shi, 2011; Yasuda et al., 2001; Yasuda et al., 1980). The decrease in molecular weight can be attributed to the cleaving of ether bonds (Hu et al., 2011b). The reason for this behavior might be due to the fact that impurities can help reduce the effect of condensation and increase the hydrolysis of lignin. As kraft lignin used in this study produced industrially, a level of impurity was expected in kraft lignin, which could accelerate the hydrolysis reaction.

Kraft lignin used in this study was found to have a carbon content of 64.%, which closely correlate with literature values. In the past, the elemental analysis of softwood kraft lignin reported to have 64.88% carbon, 6.3% hydrogen and 1.7 % sulfur (Helander et al., 2013). In another study, softwood kraft lignin contained 61.26% carbon, 5.9% hydrogen and 8.7% sulfur (Helander et al., 2013). Alternatively, biomass lignin contained 47% carbon, 14.3% hydrogen, and 19.6% nitrogen (Lv et al., 2013).

Furthermore, H-lignin and P-lignin contained marginally less carbon than experimental and literature values of 58.61% and 59.50%, respectively (Helander et al., 2013). The hydrogen content of H-lignin and P-lignin were reported to be 5.62 % and 5.53%, respectively, which is marginally lower than the literature values for hydrogen (5.9-6.3%) (Helander et al., 2013), but higher than the hydrogen content of kraft lignin (5.12%). The oxygen content of both H-lignin and P-lignin is expected to increase with grafting formaldehyde and phenol to the phenyl propene subunits of lignin. With an oxygen content of 35.11 % and 32.16% for H-lignin and P-lignin, an increase in the oxygen content (28.5%) of kraft lignin was observed. The sulfur content of kraft lignin, H-lignin and P-lignin in this study were 1.46, 4.2% and 5.92%, respectively. P-lignin has a higher amount of sulfur than does the H-lignin, which is due to the treatment of phenolated lignin with sulfuric acid in the phenolation treatment.

Furthermore, the elemental analysis helped propose chemical formulas for unmodified and modified lignin samples. To allow for ease of comparison, a basis of 9 units of carbon was used. The chemical formula of kraft lignin was determined to be $C_9H_{8.55}O_{2.99}S_{0.075}$. H-lignin and P-lignin were determined to have chemical formulas of $C_9H_{10.29}O_{4.047}S_{0.242}$ and $C_9H_{9.97}O_{3.65}S_{0.335}$. It is noted that the addition of formaldehyde and phenol to lignin increased its hydrogen content. H-lignin and P-lignin exhibit a slight increase in the amount of oxygen present when compared to kraft lignin. The amount of sulfur incorporated into both of these modified lignin samples also increased. The increase in the sulfur content of P-lignin is due to the fact that softwood lignin contains a small amount of sulfur due to the sulfuric acid treatment. The increase in sulfur content of H-lignin is unexpected and may be due to impurities within the sample and/or inaccuracies within the elemental analysis.

Table 3.1. Properties of lignin studied in the work and reported in literature

lignin	Mw, g/mol	Mn, g/mol	Mw/Mn	CHNOS					Charge density, meq/g	SO_3^- group, meq/g	Reference
				C%	H%	N%	O%	S%			
H lignin	14092[3] 45420[4]	3090[3] 22710[4]	4.56[3] 2.0[4]	58.61	562	0.04	35.11	4.21	1.55 ±0.02	0 ±0.01	PS[1]
P-lignin	4155[3] ND[4]	1049[3] ND[4]	3.96[3] ND[4]	59.50	5.53	0.04	32.16	5.92	0±0.01	0 ±0.01	PS
Softwood kraft lignin	3,503-13,109	163-847	NR	64.88	6.3	0.1	NR	1.69	NR[2]	NR	(Helander et al., 2013)
Softwood kraft lignin	NR	NR	NR	61.26	5.89	0.1	NR	8.69	NS	NR	(Helander et al., 2013)
Biomass Lignin	NR	NR	NR	47.65	4.30	2.92	19.60	0.08	NR	NR	(Lv et al., 2013)
Softwood lignosulfonate	8,900-11,119	200-2755	NR	NR	NR	NR	NR	NR	NR	NR	(Baumberger et al., 2007)
Softwood lignosulfonate	36,000-61,000	NR	NR	NR	NR	NR	NR	NR	NR	NR	(Luque et al., 1994)
Hardwood lignosulfonate	5,000-15,00	NR	NR	NR	NR	NR	NR	NR	NR	NR	(Luque et al., 1994)
Kraft lignin	9679[3] 25100[4]	2141[3] 10681[4]	4.52[3] 2.35[4]	64.26	5.12	0.07	28.52	1.46	0 ± 0.03	0± 0.04	PS

[1]PS: Present work, [2]NR: Not reported, [3]UV determined, [4]Light scattering results, [5]ND: Not detected

3.3.4. FTIR analysis

Figure 3.10 presents the FTIR spectra of kraft , H- and P-lignin, while the assignments to the peaks are listed in Table 3.2. It can be seen that there exists a broad signal around 3400 cm^{-1}, which denotes the hydroxide group. In all three lignin samples, the aromatic skeletal vibrations are present and located at the 1400 – 1600 cm^{-1} range. With comparing kraft lignin and modified lignin samples, it can be observed that the absorption intensity is less for H-lignin and greater for P-lignin. Also, the peak at 1371 cm^{-1}, which can be attributed to C-H stretch in methyl groups, is significantly reduced in P-lignin and is less in H-lignin. The absorbance increases drastically for P-lignin at 1240 cm^{-1} peak, which is associated with the stretching of aromatic C-O bond. The addition of phenol increases the amount of aromatic C-O bonds available for stretching in the P-lignin. Another difference is noted due to aromatic substation of the H-lignin at the 835 cm^{-1} peak, which is attributed to aromatic C-H bending, but is not overly present in the H-lignin when compared to kraft and P-lignin. More importantly, the signals at 1040, 1110 and 618 cm^{-1}, which are associated with the sulfate group that is attached to the P-lignin and kraft lignin. H-lignin exhibits less intense peaks associated with sulfate group.

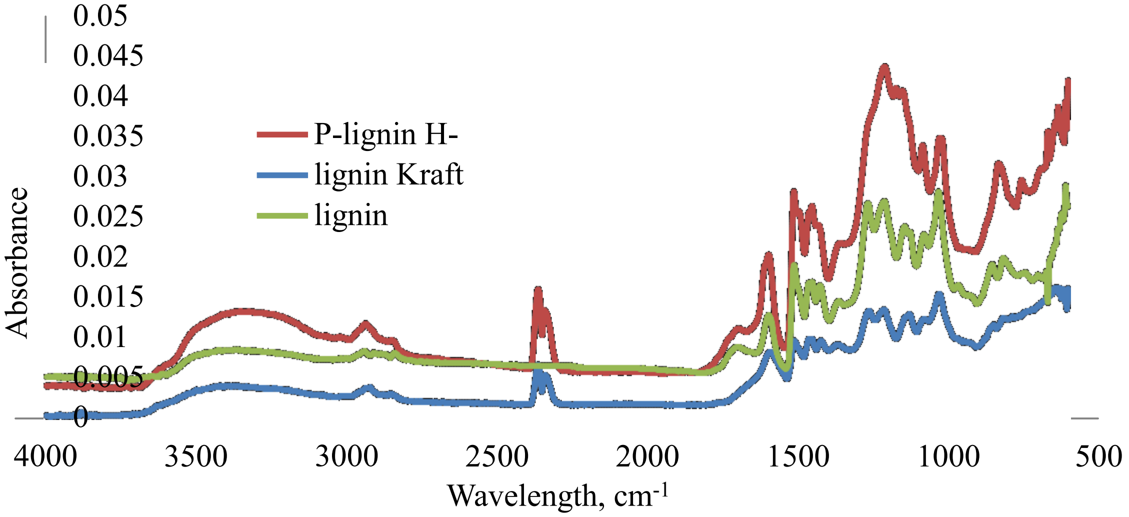

Figure 3.10. FTIR result of kraft lignin, H-lignin and P-lignin

Table 3.2. FTIR spectra assignment (Maria et al., 2002; Peak et al., 1999; Xu et al., 2006)

Wave number (cm^{-1})	Assignment
3429	OH stretching
2945	CH stretching of methyl or methane group
1732, 1726	C=O stretch in unconjugated ketone and carboxyl groups
1660, 1653	C=O stretch in conjugated ketone
1606, 1507, 1434	Aromatic skeletal vibrations
1460	Aromatic methyl group vibrations
1374	Aliphatic C-H stretch in methyl
1328	Syringyl ring C-O stretching
1242	Aromatic C-O stretching
1165	C-O stretch in ester groups
1135	Aromatic C-H in plane deformation in syringyl
1110	Sulfate group
1043	Aromatic C-H in plane deformation in guaiacyl
1040	C-S elongation
855, 844	Aromatic C-H out of plane bending
618	Sulfate

3.3.5. TGA analysis

Figure 3.11 presents the weight loss of lignin samples as a function of temperature. It is observed that kraft lignin was incinerated completely at a temperature of 500 °C, while the H-lignin and P-lignin exhibited thermal resistance at this temperature or higher. The results also showed that 25% and 7 % of the tested mass of the H-lignin and P-lignin remained at 750 °C, respectively. It was noted that lignin had a higher combustion temperature compared to other lignocellusoic materials, which was due to the inter linkage of lignin (Yang et al., 2004).

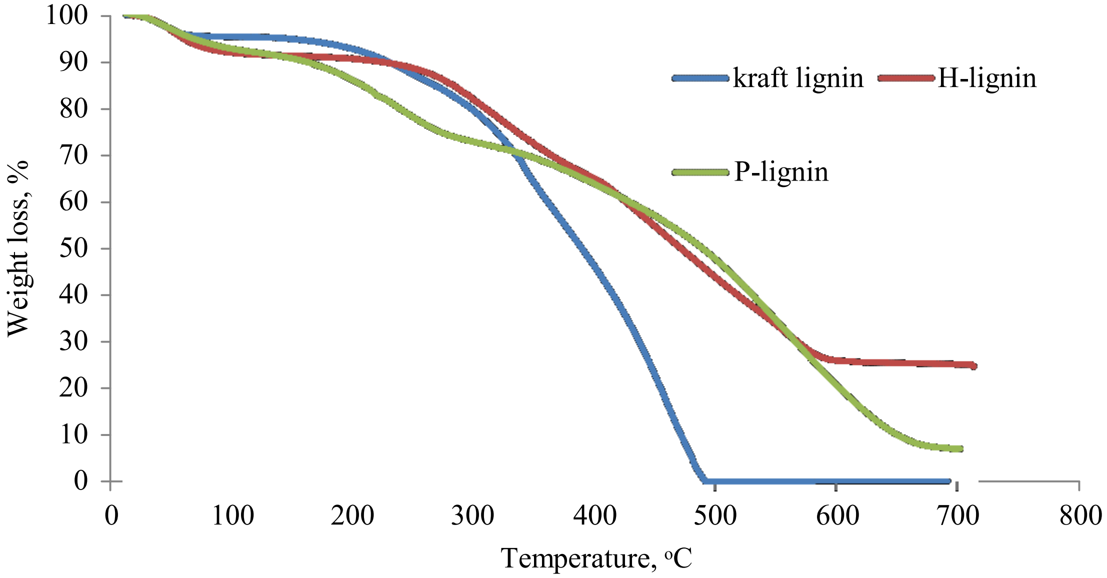

Figure 3.11. Weight loss of kraft lignin, H- and P-lignin obtained under optimized conditions. Experiment conducted in N_2 at 30 ml/min heated at 10 °C/min.

Figure 3.12 presents the weight loss rate of kraft lignin, H-lignin and P-lignin as a function of temperature. It can be seen that a noticeable increase occurred at approximately 300 to 350 °C in kraft and H-lignin, with kraft lignin representing the highest. P-lignin exhibited a similar increase as H-lignin, but at a lower temperature of 250 °C. The decreased thermal resistance can be attributed to the decrease in the molecular weight, as noted in Table 1. The peaks at 350 °C and 450 °C could be due to the decomposition of greater amount of intermolecular bonding. (Zhang et al., 2014).

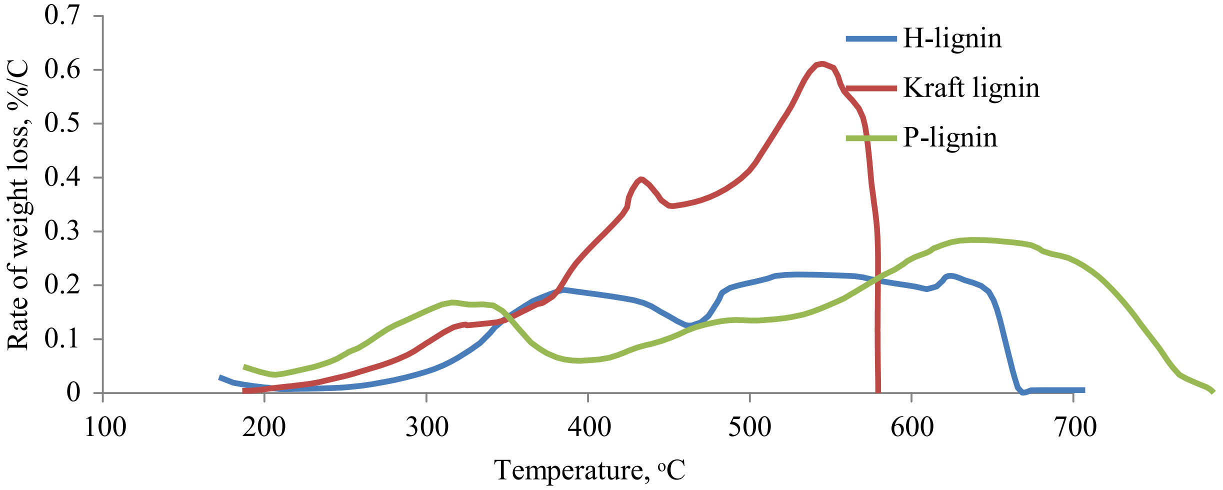

Figure 3.12. Weight loss rate of kraft, H- and P-lignin obtained under optimized conditions. Experiments conducted in N_2 at 30 ml/ min heated at 10 °C/min)

3.3.5 Solubility parameter determination

The change in the solubility of organic materials was correlated with changes in their structures in the literature (Hidlebrand and Scott, 1950). An organic material is soluble in a liquid, if its solubility parameter (δ value) is close to that of the liquid. In other words, the closer the δ values of the lignin samples are to that of water, the greater the solubility of samples is in water. To investigate the impact of hydroxymethylation and phenolation on the solubility of lignin, the change in the δ value of lignin before and after modification should be determined (Hidlebrand and Scott, 1950). The δ value of lignin phenyl propene subunits can be theoretically calculated by considering the molar vaporization energy and the molar volume for the functional groups that comprise the individual chemical compound, as shown in Table 3.3(Quesada-Medina et al., 2010). The δ value can be calculated using equation 7.

Equation 7

$$\Sigma \qquad\qquad \Sigma \qquad\qquad\qquad\qquad (5)$$

It was reported in the literature that the δ value of guaiacyl unit of softwood was 15.04 $(cal/cm^3)^{1/2}$ (Quesada-Medina et al., 2010). This study replicated the calculation and confirmed this δ value presented in the literate as 15.04 $(cal/cm^3)^{1/2}$. As guaiacyl is the dominant form of phenyl propene subunits seen in softwood with a 94 wt.% (Erickson et al., 1973), this unit will be considered as the basis of lignin for comparison. Utilizing the data from the Molar Vaporization Energy and Molar Volume at 25 °C (Barton, 1983), the value for the hydroxymethylated guaiacyl subunit was 16.68 $(cal/cm^3)^{1/2}$. Considering the δ value of water, i.e. 22.31 $(cal/cm^3)^{1/2}$ and the δ values of modified lignin, it can be understood that hydroxymethylation of kraft lignin theoretically increased the solubility of the samples. These results were confirmed through the increase in the solubility of H-lignin (55 wt.%) compared to that of kraft lignin (0 wt.%) at pH 7. P-lignin had an δ value of 16.00 $(cal/cm^3)^{1/2}$, which was larger than that of kraft lignin (15.04 $(cal/cm^3)^{1/2}$) and smaller than that of H-lignin 16.68$(cal/cm^3)^{1/2}$. As such, a lower solubility than 55% is expected for P-lignin. The solubility of P-lignin was determined to be approximately 5%, and this poor solubility is not solely related to the phenolation reaction, but the reason for this phenomenon is unknown This study found no evidence of condensation, usually caused by acidic condition of phenolation (Xie and Shi, 2011; Yasuda and Terashima, 1982; Yasuda et al., 1981; Yasuda et al., 1980).

The solubility parameter can be used as a valuable tool to predict solubility of modified lignin samples. However, this theoretical calculation showed to be inaccurate when applied to organic materials with both non-polar and highly polar groups, thus can no longer determine the solubility of sulphonated lignin in water (Quesada-Medina et al., 2010; Schuerch, 1952).

Table 3.3 Molar Vaporization Energy and Molar Volume at 25°C for unmodified, hydroxymethylated and phenolated lignin (guaiacyl type)

Group (or atom)	Group (or atom) number	Δe_i(cal/mol)	ΔV_i (cm^3/mol)
Guaiacyl			
OH	2	7120	10
CH	1	820	-1
CH2	1	1180	16.1
CH3	1	1125	33.5
C=	1	1030	-5.5
O	2	800	3.8
Phenyl (tri-substituted)	1	7630	33.4
ΔV^O			18
Total		27625	122.1
Hydroxymethylated Guaiacyl			
OH	3	7120	10
CH	1	820	-1
CH2	2	1180	16.1
CH3	1	1125	33.5
C=	1	1030	-5.5
O	2	800	3.8
Phenyl (tetra-substituted)	1	7630	14.4
ΔV^O			18
Total		35925	129.2
Phenolated Guaiacyl			
OH	3	7120	10
CH	1	820	-1
CH2	1	1180	16.1

CH3	1	1125	33.5
C=	1	1030	-5.5
O	2	800	3.8
Phenyl (tetra-substituted)	1	7630	14.4
Phenyl (di-substituted)	1	7630	52.4
ΔV^{O}			18
Total		42375	165.5

3.4. Conclusions

H-lignin exhibited a solubility of 55% and was obtained under the conditions of 80 °C, 4.0 h, 0.55 CH_2O/lignin molar ratio and lignin concentration of 10 g/L. P-lignin exhibited a solubility of 5% and was obtained under the conditions of 80 °C, 4.0 h, 14.55 phenol/lignin molar ratio with a 60% sulfuric acid, which was followed by a dilution to 300 ml and boiling for another 2 h.

GPC analysis demonstrated that the molecular weight of H-lignin (45,220 g/mol) was greater than the molecular weight of kraft lignin (25,100 g/mol). The increase in molecular weight was attributed to the polymerization of formaldehyde and lignin The molecular weight of P-lignin was determined to be smaller than kraft lignin, with a molecular weight determined (by UV spectrophotometer detector of GPC) to be 4,155 g/mol and 9,679 g/mol, respectively. The decrease in molecular weight is associated with hydrolysis underneath acidic conditions.

FTIR analysis confirmed that the hydroxymethylation and phenolation occurred as documented by the peaks at 1371, 1240 and 830 cm^{-1}. The elemental analysis revealed that the increases in carbon and hydrogen content were indicative of the grafting of formaldehyde and phenol for H-lignin and P-lignin, respectively. The TGA analysis evaluated the thermal behavior of the lignin samples. Unmodified lignin exhibited a large peak at 450 °C, and was completely consumed at 500 °C, while H-lignin had a less significant peak at 460 °C, and was resistant to thermal degradation. In the same vein, P-lignin had a smaller peak at 550 °C and was exhibited the greatest thermal resistance.

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Chapter 4: Sulfonation via sulfuric acid

Abstract

In this work, the sulfonation of softwood unmodified kraft lignin, hydroxymethylated lignin (H-lignin) and phenolated lignin (P-lignin) was investigated through sulfuric acid treatment conducted under different conditions of H_2SO_4/lignin molar ratio, reaction temperature and time. The results showed that self-condensation of the guaiacyl phenyl propane subunits of lignin presented a barrier to the sulfonation of unmodified lignin implying that pretreatment of lignin was necessary prior to sulfonation. The results also showed that the phenolation of kraft lignin, in opposition to hydroxymethylation, prior to sulfonation was very efficient in improving the water solubility of kraft lignin and in inducing a high anionic charge density. The sulfonation was confirmed through use of FTIR and ^{13}C analysis. The maximum efficiency was obtained via phenolation under the condition of 6 ml of phenol per gram of lignin for 4 h at 80 °C reacting in a 90 ml of 60% H_2SO_4, which was followed by a dilution to 1500 ml of water and boiling for 2 h. This was followed by sulfonation under the conditions of 120 °C, 1.5 h, 6.5 molar ratio of H_2SO_4/lignin, which resulted in sulphonated P-lignin with the charge density of 3.12 meq/g and a solubility of 96.9%.

4.1. Introduction

Lignin is the second most abundant natural occurring biopolymer, preceding cellulose and provides an excellent source of inexpensive readily available reactant to create dispersants. It was stated that softwood consists of 41% cellulose, 30% lignin and 27% hemicellulose, and hardwood is composed of 46% cellulose, 22% lignin and 24% hemicellulose on average (Baeza and Freer, 2001).

Sulfonation is a reliable method for modifying lignocellulosic materials (Shin and Rowell, 2005) including Eucalyptus lignin (Syahbirin et al., 2012) and cellulose (Zhang et al., 2007) in order to create polyelectrolyte water soluble products. The sulfonation of woody materials is commonly conducted through the sodium sulfite treatment under acidic conditions in industrial scales (i.e. sulfite pulping).

In the past, sulfonation reaction was conducted under different conditions on polymers containing aromatic rings or woody materials using a multitude of sulfonation agents including concentrated sulfuric acid for sulfonation of benzene (Kaandorp et al., 1962), toluene (Kaandorp et al., 1963a), tert-butyl benzene (Kaandorp et al., 1963b), polystyrene (Akovali and Ozkan), (polyoxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene)(Shibuya and Porter, 1992) ; sulphuric acid (in vapor form) for the sulfonation of mono-dispersed cross-linked polystyrene beads (Kim et al., 1990), concentrated sulfuric acid on a macronet polystyrene backbone utilizing a catalyst (Neihof, 1954; Theodoropoulos et al., 1993) and chlorosulfonic acid on liquid wood (Xie and Shi, 2011).Alternatively, silver and mercury ions were used as potential catalysts for the sulfonation of polystyrene (Coughlin et al., 2013). However, the application of silver and mercury for this purpose is not recommended for industrial scale operations, due to their toxicity and price. Furthermore, the gaseous treatment of sulfuric acid presents a dangerous operating condition for industrial scale operations; also chlorosulfonic acid is costly as it must be performed in a solvent, which is difficult for industrial scale operations.

Lignocellulosic materials, such as cellulose and lignin, may require pretreatment to allow for an efficient sulfonation. Without any modification on the structure of the phenyl propene subunits, the α position of these phenylpropene subunits is a position at which sulfonation occurs easily (Heden et al., 1936; Holmberg and Svensk, 1935). Hydroxymethylation increases the bonding sites on lignin, hence it helps improve the occurrence of sulfonation on the newly added methoxyl group associated with the aromatic ring (Alonso et al., 2005). The phenolation of lignin, which also reacts at α position, would add two other sites at *ortho* position and allow for a total of three sites for sulfonation (instead of one on unmodified lignin). In other words, phenolation allows for a potential threefold degree of sulfonation.

One study on the sulfomethylation reaction of lignin was carried out, which showed an increased sulfur content at the ortho position on the guaiacyl phenylpropene subunit for use as a dispersant for industrial applications (Rober, 1987), such as in ore refining processes(Sarkanen and Ludwig, 1971) This reaction is usually conducted in two steps of hydroxymethylation followed by sulfonation (Matsushita and Yasuda 2005). Alternatively, the sulfomethylation can be conducted in one-step, i.e. hydroxymethylation through the addition of formaldehyde, and sulfonation via using sodium sulfite simultaneously (Yu et al., 2013).

Sulfonation introduced additional properties to materials, for example phenol/formaldehyde resins derived from lignin has shown to have improved ion exchange capacity for metals (Zoumpoulakis and Simitzis, 2001) and sulfonated juniper wood exhibited an increased absorption of cadmium (Shin and Rowell, 2005). In the past, lignosulfonates prepared from acid hydrolysis lignin, which was then phenolated followed by one of three treatments: sulfomethylation, aryl sulfonation or hydroxymethylation preceded by sodium sulfite sulfonation, showed greater dispersability than the commercially available lignosulfates derived from sulfite puling for gypsum paste (Matsushita and Yasuda, 2005).

It was also claimed that phenolation and hydroxymethylation were more effective than reduction, oxidation and hydrolysis for lignin (Hu et al., 2011). The phenolation and hydroxymethylation reactions increased the reaction sites, and was capable of increasing the reactivity of lignin (Alonso et al., 2005; Gosselink et al., 2004).

In this chapter, the sulfonation of kraft lignin was conducted with sulfuric acid under different scenarios. Alternatively, the hydroxymethylated lignin (H-lignin) and phenolated lignin (P-lignin) produced in chapter 3 was sulphonated with sulfuric acid. The characteristics of the products were evaluated by using a particle charge detector, conductometric titrator, NMR, and FTIR and TGA. The solubility of lignin after modification was also assessed. Based on the results, the conditions that yielded a sulfonated lignin derivative with the highest charge density and solubility were determined.

4.2.Experimental

4.2.1 Raw materials

In this work, washed and dried softwood kraft lignin was supplied by FPInnovations from its pilot facilities in Thunder Bay, ON. Liquefied phenol (>89% purity), formaldehyde solution (30%), sulphuric acid (98% purity) and poly (diallyldimethylammonium chloride) solution (PDADMAC) with a molecular weight (MW) of 100,000-200,000 (20 wt.% in water) were all purchased from Sigma-Aldrich, (with the exception of sulfuric acid purchased from ACP Chemicals in Montreal, Canada), and used as received. Anionic polyvinyl sulfate (PVSK) with a MW of 100,000-200,000 (98.4 wt.% esterified) was provided by Wako Pure Chem. Ltd. Japan. Tego@trant A100 was supplied from Metrohm Inc for sulfonated group analysis.

4.2.2 Pretreatments of lignin

The hydroxymethylation of softwood kraft lignin was performed with adding 25g of dried kraft lignin in a three- neck glass flask. After lignin addition, 5 ml of formaldehyde (37%) was added to the glass flask and volume of the solution was increased to 250 ml with distilled water. The pH of the solution was increased to 10 (using 2.5 M NaOH) and the system was attached to a graham condenser, under constant stirring at 100 rpm. The solution was stirred and heated at a temperature of 80 °C for 4 h. The resulting products were neutralized by sodium hydroxide and then underwent membrane dialysis with the MW cut off of 1,000 Da for two days, while changing the water every 2 h for the first 6 h and then once a day for 2 days for purification. The purified solution was then dried at 60°C in an oven so that dried modified lignin was obtained. Subsequently, 3 g of kraft lignin was added to a three necked flask with 18 ml of liquefied phenol and 90 ml of 60% w/w $H_2SO_{4(aq)}$ solutions as a catalyst. The system was charged with a stir bar, graham condenser and a thermometer. The reaction was then stirred and heated at 80 °C for 4 h. The phenolated lignin solution was then quenched with distilled water (to create a volume of 1500 ml that was boiled for another 2 h; and underwent filtration using a 45 nm nylon filter.

4.2.3 Sulfonation of lignin

Unmodified and modified (pretreated) lignin samples (0.5-1.0g) were reacted with 1.5 – 20 g 98% H_2SO_4 in a glass vials, vortexed at 2900 rpm for 1 minute using a using Fisher Scientific Mini Vortexor (to ensure homogenous mixture), sealed and placed in an oil bath at a temperature of 80-160 °C for 0.5-3h. The reaction parameters were lignin/$H_2SO_{4(aq)}$ molar ratio of (6.5-92.6), reaction time (0.5 - 3h) and temperature (80°C- 160°C). Upon removing samples from the oil bath, the sulfonation reaction was stopped through neutralizing with NaOH (2.5 M). The solutions were cooled to room temperature and unreacted sulfuric acid was separated by dialysis membranes with a molecular weight cutoff of 1000, while changing the water every 2 h for the first 6 h and then once a day for 2 days.

4.2.4. Charge density and solubility analyses

At first, 1 wt.% solution of modified lignin samples was prepared by adding the lignin samples to deionized distilled water (pH 7) and room temperature. The solution was shaken for 1 h at 100 rpm at 30 °C. After shaking, the solutions were centrifuged at 1000 rpm for 5 min in order to separate soluble and insoluble lignin from the solution. The solution part was taken for charge density analysis of soluble lignin, while precipitates were dried in an oven at 60 °C for charge density analysis of insoluble lignin. The charge density of soluble lignin samples were determined by direct titration, while the charge density of insoluble ones was identified by back titration. To measure the charge of soluble samples, 1 to 2 ml of lignin sample solutions were added to the cell of a particle charge detector, Mutek PCD-04 titrator (Herrsching, Germany) and titrated against PDADMAC standard solution (~0.005M). The volume of PDADMAC solution titrated against the samples was considered for measuring the charge density using Equation 3.1 in chapter 3. To measure the charge density of insoluble lignin samples, about 0.05 g of dried insoluble lignin samples were mixed with PVSK standard solution (~0.005M) for 1 h at 30 °C. Then, the concentration of PVSK solutions before and after mixing with lignin samples were determined by titrating with PDADMAC standard solution and the charge density of insoluble lignin was determined using Equation 3.2 in chapter 3.

4.2.5. Analysis on degree of sulfonation

A conductometric titration was considered to determine the number of moles of sulphonated group attached to lignin before and after sulfonation. In this method, a 1% wt. solution of samples was prepared with distilled water and was shaken in a Boekel Scientific water bath operating at a temperature of 30 °C and 100 rpm, for 1 h. Then, the solution was titrated against Tego@trant A100 using a Metrohm 905 Titrando.(Canada), and finally the sulfonation degree was calculated based on equation 3.

Equation 3

$$\left(\frac{\;}{\;}\right)$$

$$\frac{\;}{\;}$$

4.2.6. Elemental analysis

The elemental analysis of dried unmodified lignin, and sulfonation lignin samples was conducted using a Vario EL Cube instrument (Germany) as dictated in the literature (Fadeeva et al., 2008). Lignin samples were weighed and loaded in an integrated carousel, and flushed with carrier gas

(He). The combustion of the lignin samples was carried out, and the combusted gases were reduced in order to be identified by the instrument. The elemental analysis helped investigate the theoretical formula of lignin before and after treatment by considering the weight percentage and atomic weight of each element.

4.2.7. Thermo-gravimetric analysis

Thermal performance of unmodified and modified lignin samples were assessed using a thermo-gravimeteric analysis (TGA). The lignin samples were first dried at 105 °C and subsequently heated with a thermo-gravimetric analyzer (TGA)-i1000 series (instrument Specialist Inc.) using N_2 (30ml/min) with an increment rate of 10 °C/min in the temperature range of 25 °C and 800 °C (Zhang et al., 2011).

4.2.8. Structural analysis

The (^{13}C and ^{31}P) NMR analysis of unmodified and modified lignin samples was conducted on the lignin samples to determine the structure of lignin before and after sulfonation using a Varian Unity Inova 500. The samples were prepared according to the procedure stated in the literature (Ben and Ragauskas, 2011). Alternatively, Fourier Transform Infrared Spectrophotometer (FTIR) and Tensor 37 (Bruker,Canada) was taken into account for analyzing the functional groups associated with unmodified and modified lignin.

4.3. Results and discussion

4.3.1 Sulfonation of softwood Kraft lignin

Figure 4.1 illustrates the CDSL, CDIL, and the solubility of sulfuric acid treated lignin (SA-lignin) as a function of H_2SO_4 /lignin molar ratio. The results in Figure 1 depicts that by increasing the mole ratio of sulfuric acid to lignin CDSL, CDIL, and solubility of SA-lignin were reduced. In contrast, it was reported that by increasing the acid/lignin ratio (6.5 to 13), increased the amount of ion-exchange capacity due to an increase in sulphonated group was attached to novolac-lignin and novolac-hydroxymethylated lignin in ion exchange resin production (Zoumpoulakis and Simitzis, 2001). As novolac is the product of a 1:1 ratio of phenol-formaldehyde, and the structural differences can cause lead to alternate sulfonation ratios, as seen for H-lignin and P-lignin.

As stated in chapter 2, guaiacyl is the predominant form of phenyl propane in softwood (Erickson et al., 1973). As the condensation and the sulfonation occur simultaneously in our experimental analysis, the product with a greater stability will dominate. The self-condensed guaiacyl provides the product of greater stability, and thus was the main product of this process (Shimada et al., 1997).

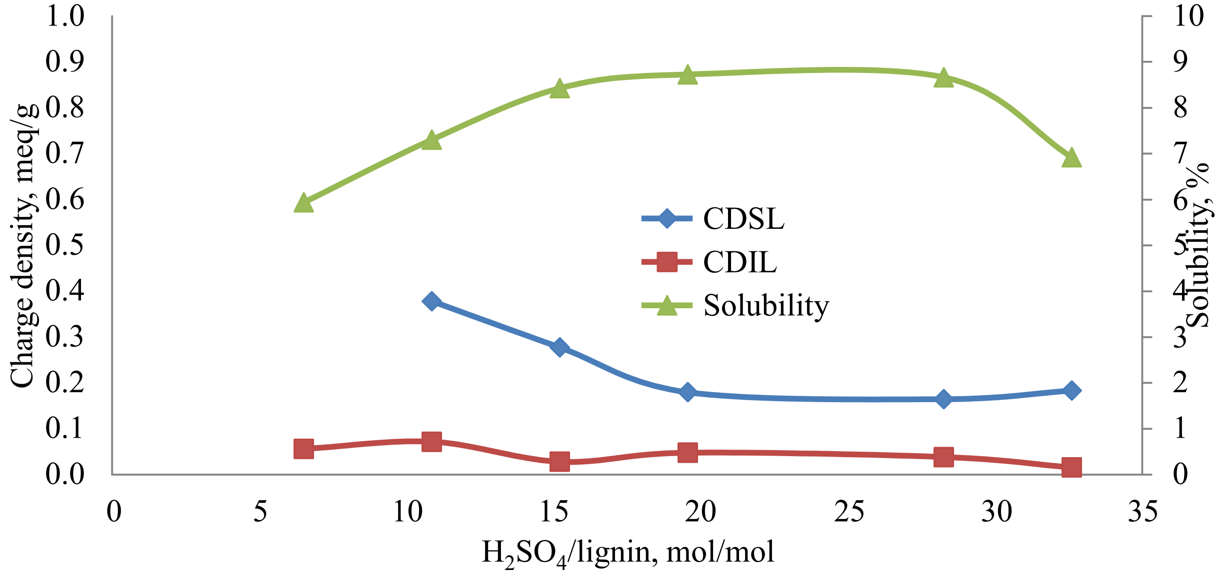

Figure 4.1. Charge density of soluble lignin (CDSL), charge density of insoluble lignin (CDIL), and solubility of the SA-lignin as a function of H_2SO_4/lignin molar ratio. Ratio optimizations were done at a temperature of 140 °C and 1 h.

Figure 4.2 presents the CDSL, CDIL, and solubility of lignin as a function of reaction temperature. It is apparent that, as temperature increased, the CDSL decreased from 0.7 meq/g to 0.2 meq/g. The thermal energy needed for condensation to become prominent lends credence towards the less reactive guaiacyl self-condensation product, as stated elsewhere (Shimada et al. 1997).

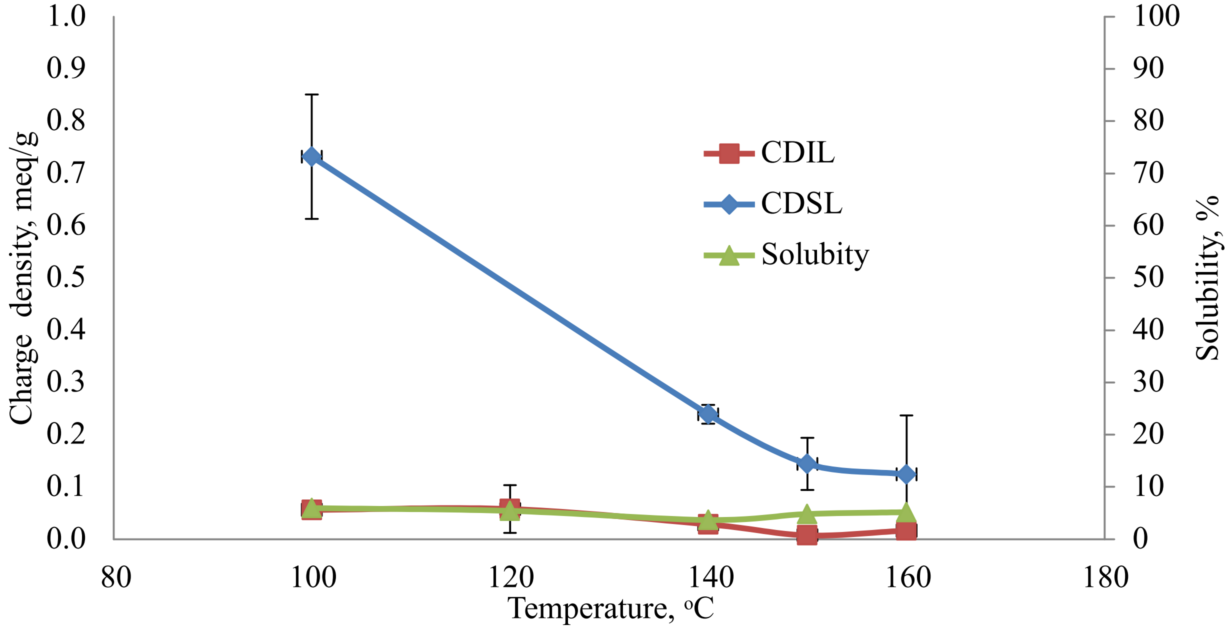

Figure 4.2. Charge density of soluble lignin (CDSL), charge density of insoluble lignin (CDIL) and solubility of SA-lignin as a function of temperature. Experiments were conducted at a 6.5 molar ratio of H_2SO_4/lignin and 1 h.

Figure 4.3 shows the impact of time on CDSL, CDIL, and solubility of lignin. It is also observable that, by extending the reaction time, the CDSL and solubility decreased from 0.5 meq/g to 0.2 meq/g and from 6 wt.% to 0 wt.%, respectively. As stated earlier, the increased time will provide conditions for the production of a more stable product, in this case the self-condensed guaiacyl product.

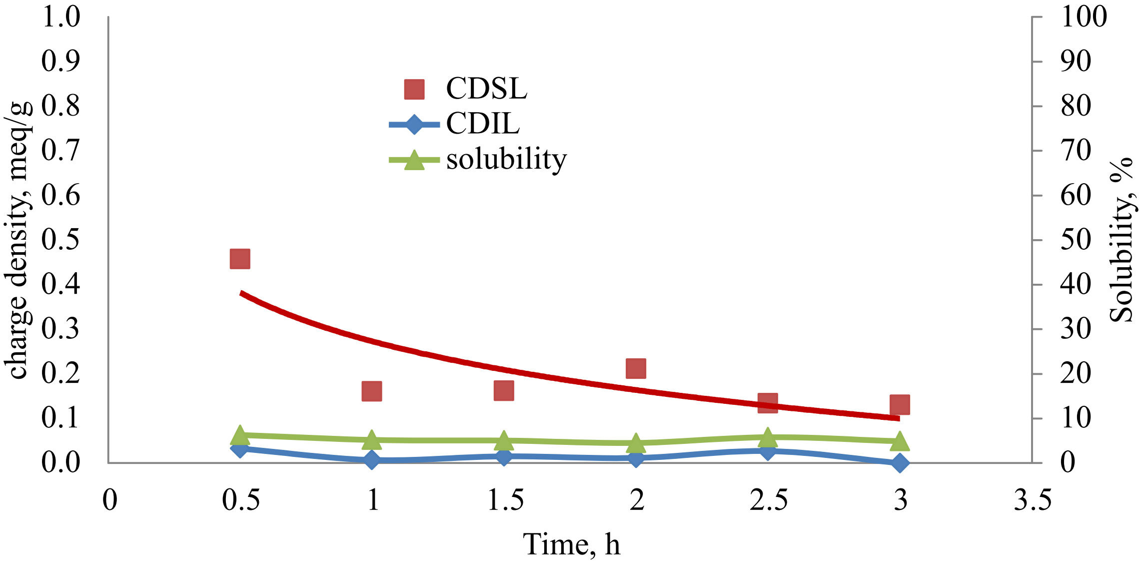

Figure 4.3. Charge density of soluble lignin (CDSL), charge density of insoluble lignin (CDIL), and solubility of SA-lignin as a function of time. Experiments were conducted at a 6.5 molar ratio of H_2SO_4/lignin and 140 °C.

The results in Figure 4.1-4.3 shows that a product with a small CDSL (ranging 0.2 to 0.8 meq/g) was produced through the direct sulfonation of kraft lignin with concentrated H_2SO_4. Furthermore, the solubility of the SA-lignin remained under 8 wt.%. The CDIL appeared to be very marginal as well. In the literature, it was claimed that the intramolecular condensation protects the reactive site of the guaiacyl lignin (Yasuda et al., 1999). We propose a similar protection for the reactive site of the self-condensed guaiacyl products against sulfonation. The self-condensed guaiacyl product may prevent sulfonation through steric hindrance and therefore inhibit sulfonation reaction. However, the sulfonation would occur at the α position as previously stated (Heden et al., 1936; Holmberg and Svensk, 1935). Therefore, the condensation at the β position of aliphatic chain could sterically hinder sulfonation from occurring at the α position.

4.3.2 Sulfonation of hydroxymethylated softwood Kraft lignin (H-lignin)

Figure 4.4 shows the CDSL, CDIL, and solubility of SAH-lignin as a function of sulfuric acid/lignin molar ratio. As seen in Figure 4.4, a maximum value of 0.4 meq/g was achieved for CDSL, while solubility and CDIL marginal. Furthermore, CDSL, CDIL and solubility exhibit no significant changes as the H2SO4/lignin molar ratio is increased.

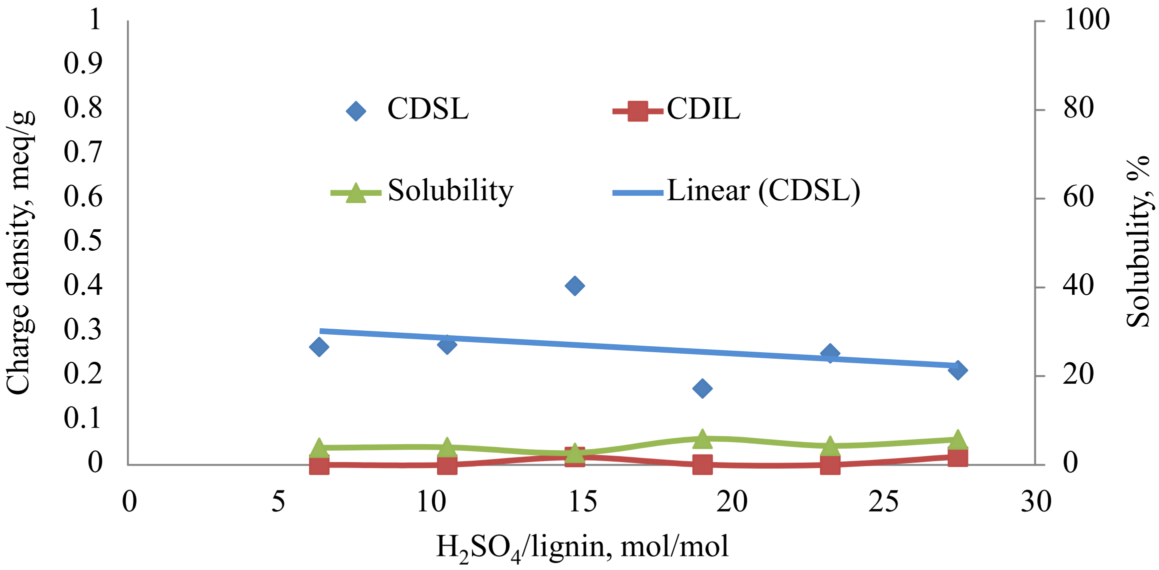

Figure 4.4. Charge density of soluble lignin (CDSL), charge density of insoluble (CDIL) and solubility of the SAH- lignin as a function of H_2SO_4/H-lignin molar ratio. Experiments conducted at 140 °C and 1 h**.**

Figure 4.5 exhibits the CDSL, CDIL, and solubility of sulphonated H-lignin as a function of time of sulfonation reaction. It is evident that CDSL, CDIL, and solubility remained at low at all times tested. CDIL was negligible and CDSL did not exceed 0.27 meq/g, regardless the reaction time.

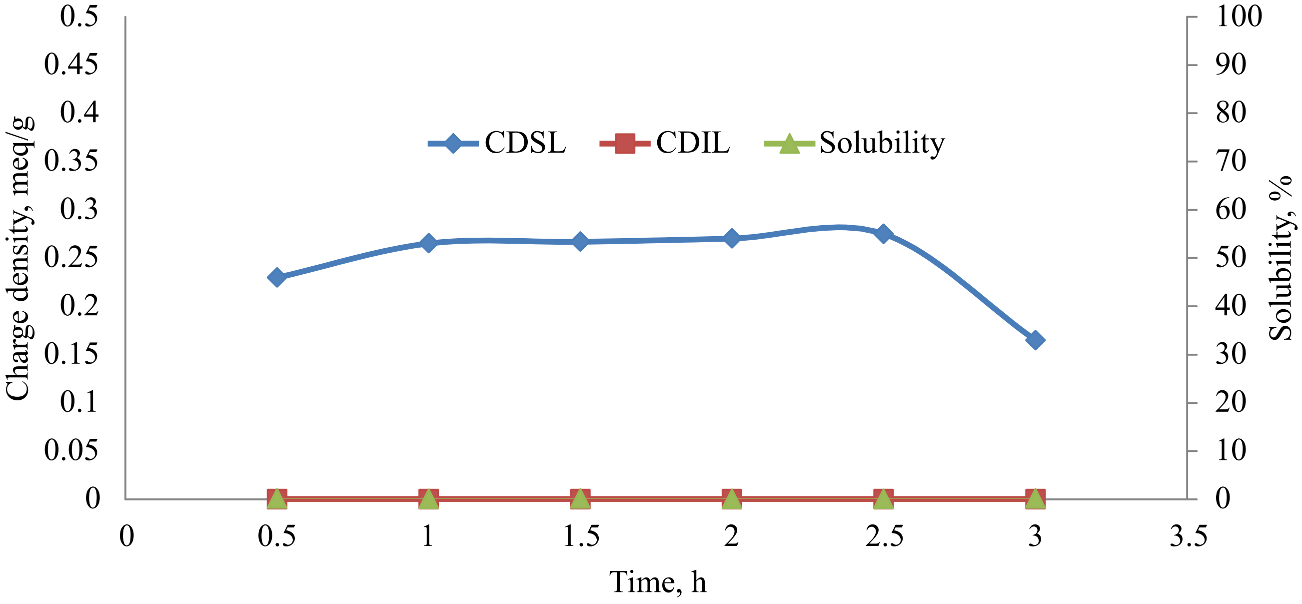

Figure 4.5. Charge density of soluble lignin (CDSL), charge density of insoluble lignin (CDIL), and solubility of the sulphonated H- lignin as a function of time. Experiments conducted at a 6.33 molar ratio of H_2SO_4/H-lignin and 140 °C.

Figure 4.6 presents the CDSL, CDIL and solubility of SAH-lignin as a function of temperature of sulfonation. Evidently, with an increase in temperature from 80 to 140 °C, the CDSL decreased from a value of 0.43 meq/g to 0.26 meq/g. The solubility and the CDIL remained negligible over the evaluated reaction temperature. This confirms the literature results that condensation reactions rely heavily on temperature and increase with time (Xie and Shi, 2011).

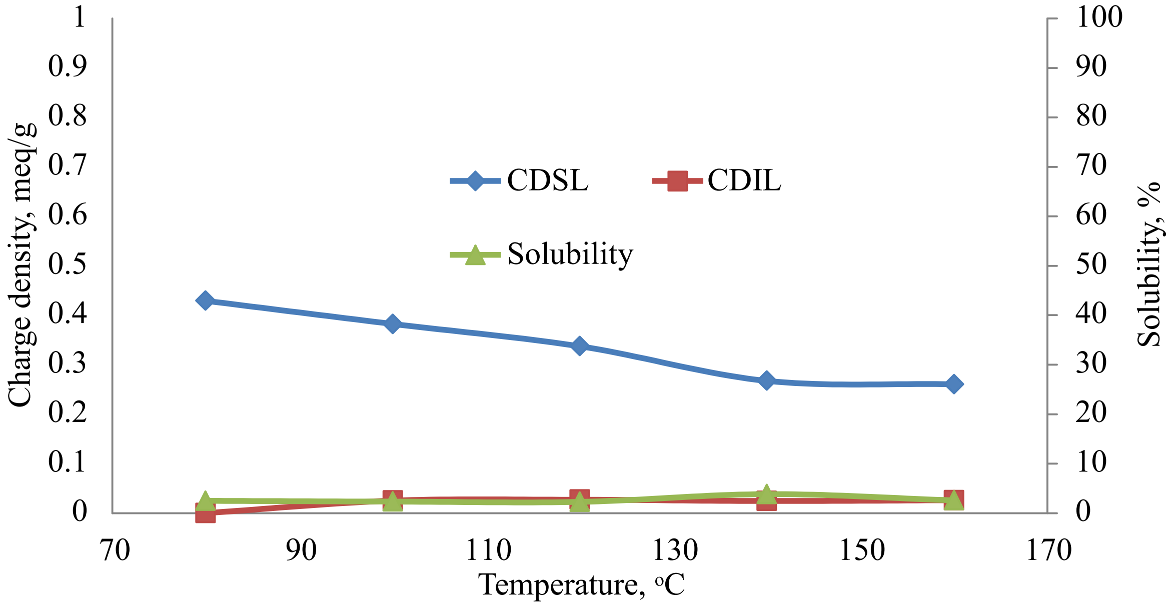

Figure 4.6. Charge density of soluble lignin (CDSL), charge density of insoluble lignin (CDIL), and solubility of the SAH-lignin as a function of time. Experiments conducted at a 6.33 molar ratio of H_2SO_4/H-lignin and 1 h.

However, H-lignin has an initial charge density of 1.2 meq/g and a solubility of 55% prior to sulfonation. Therefore, it can be concluded that the SAH-lignin had a detrimental effect on charge density and solubility, as the charge density and solubility of the H-lignin significantly dropped after sulfonation. In this respect, self-condensation of lignin under strong acidic conditions might be the main reason for such results, as described earlier (Matsushita et al., 2004).

4.3.3 Sulfonation of phenolated softwood kraft lignin

Figure 4.7 shows the CDSL, CDIL, and solubility of SAP-lignin versus H_2SO_4/lignin molar ratio. As discussed in the previous chapter, P-lignin has no charge density and insoluble in neutral water. However, through sulfonation of P-lignin, these lignin samples exhibited an anionic charge density. It is apparent that the maximum CDSL (3 meq/g) and solubility (100%) were obtained at the acid/lignin molar ratio of 12.6 to 29.4 (Figure 7), and by further increasing the ratio, the CDSL and solubility decreased. Sulfonation is clearly the dominant reaction at a low acid/lignin molar ratio and condensation became more prevalent at a higher molar ratio. The CDIL of SAP-lignin was minimal (0.5 meq/g). It should be noted that, at the low H_2SO_4/lignin molar ratios, CDIL was not presented in Figure 7 as the solubility of the products was greater than 90%, which left insufficient amount of sample for testing.

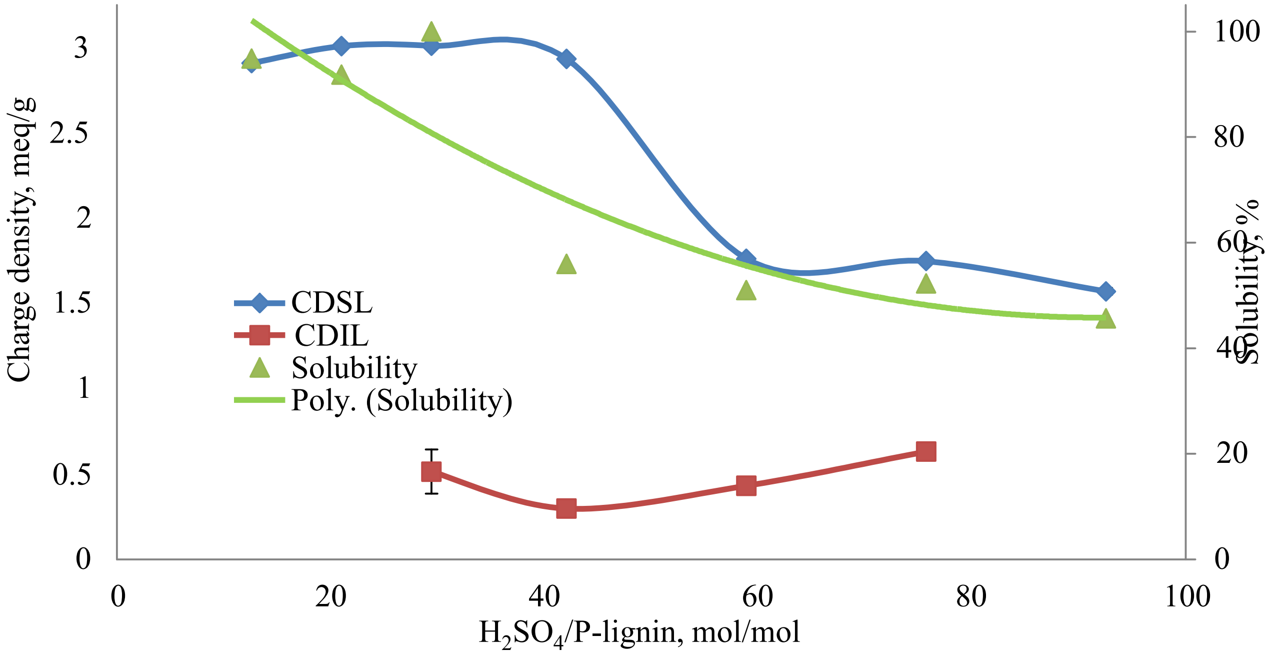

Figure 4.7. Charge density of soluble lignin (CDSL), charge density of insoluble lignin (CDIL), and solubility of the SAP- lignin as a function of H_2SO_4/lignin molar ratio. Experiments conducted at 140 °C and 1 h.

Figure 4.8 shows the CDSL, CDIL, and solubility of SAP-lignin as a function of reaction time. Clearly, temperature had a significant impact on both CDSL and the solubility of the SAP-lignin. The maximum CDSL value and solubility of 3.4 meq/g and 100% were achieved at 120-130 °C. Generally, the decrease in solubility and CDSL were most probably ascribed to the condensation of lignin at serve acidic conditions, as elaborated earlier.

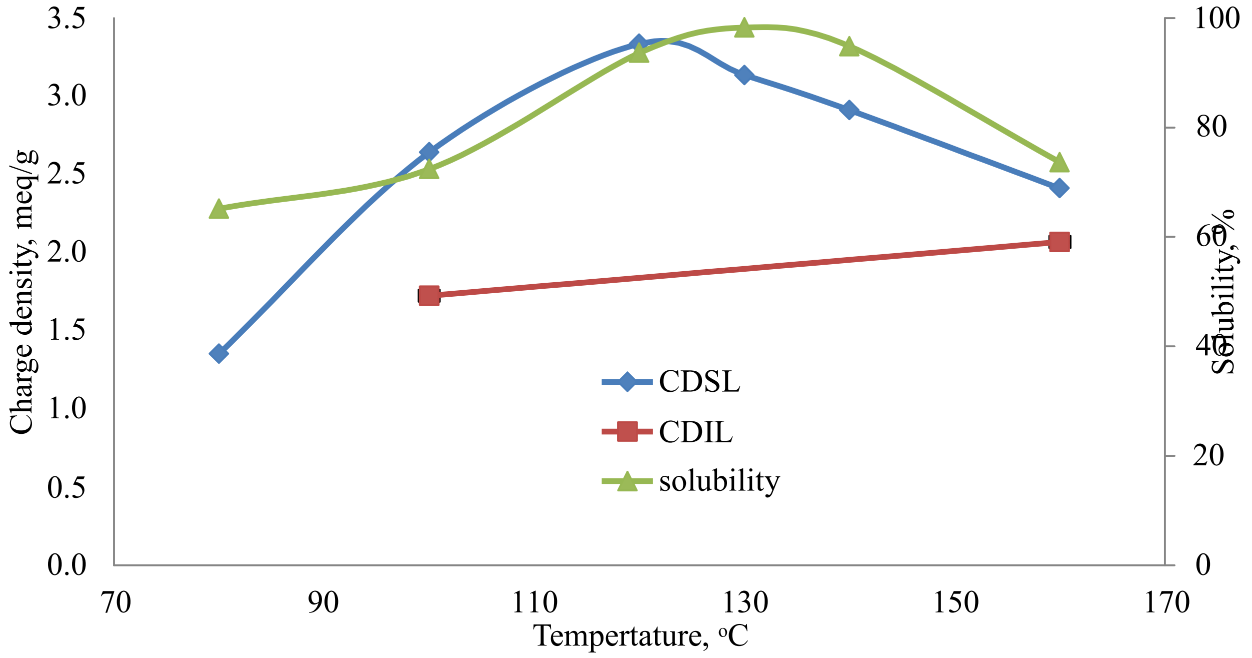

Figure 4.8. Charge density of soluble lignin (CDSL), charge density of insoluble lignin (CDIL) and solubility of the SAP- lignin as a function of temperature. Experiments conducted at a 12.6 H_2SO_4/P-lignin molar ratio and 1 h.

Figure 4.9 shows the c and solubility of SAP-lignin as a function of time of the reaction. It is observable that, the maximum charge density and solubility were obtained after 1-1.5 h of reaction, and further time extension reduced the charge density and solubility. The extended reaction time favors the condensation reaction, as previously discussed (Xie and Shi, 2011).

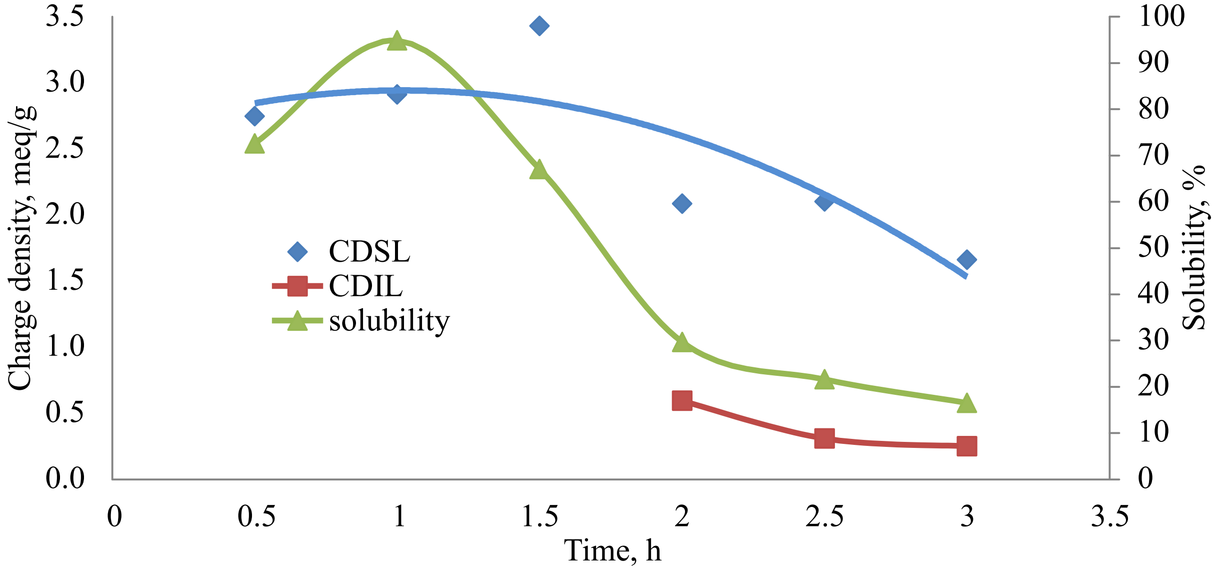

Figure 4.9. Charge density of soluble lignin (CDSL), charge density of insoluble lignin (CDIL), and solubility of SAP-lignin as a function of reaction time of sulfonation. Experiments conducted at a 12.6 H_2SO_4/P-lignin molar ratio and 140 °C.

A comparison between the results presented in Figures 4.6-49 reveals that the phenolation of lignin was an effective pretreatment to generate lignin with a high charge density and solubility. In fact, sulfonated P-lignin yielded a product with a soluble charge density of 3.1 meq/g and a solubility of 97 wt.% under the optimal conditions of 1.48×10^{-4} molar ratio of H_2SO_4/P-lignin, 1.5 h and 120°C. The high charge density may be due to the extra reaction sites available on the phenolic ring attached to the α position on the phenylpropene subunits of P-lignin. With the α position already occupied by phenol on P-lignin, sulfonation-n at the same point is unlikely. However, sulfonation on the aromatic ring of lignin and phenol, which is attached to P-lignin, at the three unoccupied *ortho* positions is possible under strongly acidic conditions. Furthermore, the addition of the phenol group provided an additional barrier to condensation and perhaps made the self-condensation of guaiacyl lignin less possible through steric hindrance.

4.3.4 Characterization of Sulfonated lignins

In one study, the molecular weight (MW) of lignin generated from milled softwood was 10,700 g/mol (Meister, 2002). Another study reported that softwood lignosulfonate had an average molecular weight of 36,000 – 61,000 g/mol. However, hardwood Kraft lignin was reported to be in the range of 5,000 to 15,000 g/mol (Luque et al., 1994). The M_W and Mn of softwood kraft lignin recovered by Lignotech from black liquor were reported to be 8,900-11,119 g/mol and 200 to 2755 g/mol, respectively (Baumberger et al., 2007). In another report, the M_W and Mn of softwood kraft lignin were 3,503-13,109 g/mol of and 163-847 g/mol, respectively (Helander et al., 2013). This study determined that unmodified kraft lignin had a MW of 25100 and a MN of 10681, which is higher than reported values and will be attributed to different tree species and /or processing conditions. The properties of sulphonated lignin prepared in this work are shown in Table 4.1. The optimum conditions for the SA-lignin, SAH-lignin and SAP-lignin were the temperatures of 100, 80 and 120 °C; reaction time of 0.5, 1.0 and 1.5 h; and H_2SO_4/lignin molar ratio of 15.2, 6.3, and 12.6 mol/mol, respectively. As can be seen, the MW of SA lignin, SAH-lignin and SAP-lignin were not detected, due to solubility issues on tetrahydrofuran after acetylation and as such Mn was detected as well.

In the past, the elemental analysis of softwood kraft lignin was reported to have 64.88% carbon, 6.3% hydrogen and 1.7 % sulfur (Helander et al., 2013). In another study, softwood kraft lignin contained a 61.26% carbon, 5.9% hydrogen and 8.7% sulfur (Helander et al., 2013). Alternatively, biomass lignin contained 47% carbon, 14.3% hydrogen, and 19.6% nitrogen (Lv et al., 2013).

Our results revealed that SA, SAH and SAP-lignin had similar carbon content (47%), which is similar to the carbon content of biomass lignin reported by Lv et al. (2013). The sulfonation degree of lignin can be measured by the change in both sulfur and oxygen contents of lignin, as sulphonated group would contribute to the overall oxygen and sulfur content of modified lignin. The sulfur content of the sulfuric acid treated lignin samples presented in this study were 8.25%, 7.73% and 7.55%, for SA, SAH and SAP lignin, respectively. SA had a higher amount of sulfur than the SAH and SAP, which is due to the presence of sulfuric acid after treatment in samples and condensation of lignin using sulfuric as a catalyst would increase the overall molecular weight and polymerization of the lower molecular weight lignin (which has been shown to have a high amount of sulfur (Helander et al., 2013)).

Through the evaluation of the elemental analysis, a proposed chemical formula can be derived. To allow for ease of comparison, a basis of 10 units of carbon will be used. The chemical formula of softwood kraft lignin was determined to be $C_9H_{8.545}O_{2.994}S_{0.075}$. Modified kraft softwood lignin species, H-lignin and P-lignin were determined to have a chemical formula of

$C_9H_{10.289}O_{4.047}S_{0.242}$ and $C_9H_{9.973}O_{3.652}S_{0.335}$.The derived chemical formula of SA-lignin, SAH-lignin and SAP-lignin were: $C_9H_{7.931}O_{5.676}S_{0.594}$, $C_9H_{7.954}O_{6.908}S_{0.557}$ and $C_9H_{8.771}O_{6.915}S_{0.614}$ and respectively. It can be seen that both sulfur and oxygen are larger in the sulfuric acid treated lignin samples, when compared to the kraft, H and P-lignin. Further analysis of theses formulae are not feasible due to inaccuracies.

The results in Table 4.1 depicted consistency between the charge density and sulfonation analyses. The sulfonation amount of of SAP-lignin was determined to be 2.71 meq/g, which is close to the charge density of SAP-lignin of 3.12 meq/g. Therefore, it can be concluded that almost all of the three reaction sites available on aromatic rings for sulfonation were utilized by the sulphonated group. On a contrary, SA-lignin and SAH-lignin possessed insignificant amount of sulphonated group and charge density.

Table 4.1: Properties of lignin studied in the work and reported in literature. All samples were created under optimum conditions for charge density and solubility.

Lignin	Mw, Da	Mn, Da.	Mw/ Mn	CHNOS					Charge density, meq/g	SO_3^- group, meq/g	Reference
				C%	H%	N%	O%	S%			
SA lignin	ND[3] ND[4]	ND[3] ND[4]	ND[3] ND[4]	58.63	5.41	0.04	32.62	3.22	1.01 ±0.02	0.99 ±0.01	PS[1]
SAH-lignin	ND[3] ND[4]	ND[3] ND[4]	ND[3] ND[4]	59.45	5.53	0.04	32.18	2.15	1.22 ±0.01	1.01 ±0.01	PS
SAP-lignin	ND[3] ND[4]	ND[3] ND[4]	ND[3] ND[4]	59.92	5.69	0.05	29.79	2.71	1.24 ±0.01	1.02 ±0.04	PS
Softwood kraft lignin	3,503-13,109	163-847	NR	64.88	6.3	0.1	NR	1.69	NR[2]	NR	(Helander et al., 2013)
Softwood kraft lignin	NR	NR	NR	61.26	5.89	0.1	NR	8.69-	NS	NR	(Helander et al., 2013)
Biomass Lignin	NR	NR	NR	47.65	4.30	2.92	19.60	0.08	NR	NR	(Lv et al., 2013)
Softwood lignosulfonate	8,900-11,119	200-2755	NR	NR	NR	NR	NR	NR	NR	NR	(Baumberger et al., 2007)
Softwood lignosulfonate	36,000-61,000	NR	NR	NR	NR	NR	NR	NR	NR	NR	(Luque et al., 1994)
Hardwood lignosulfonate	5,000-15,00	NR	NR	NR	NR	NR	NR	NR	NR	NR	(Luque et al., 1994)
Kraft lignin	9679[3] 25100[4]	2141[3] 10681[4]	4.52[3] 2.35[4]	63.9	5.97	0.06	30.60	6.09	0 ± 0.03	0 ± 0.04	PS

[1]PS: Present work, [2]NR: Not reported, [3]UV determined, [4]Light scattering results, [5]ND: Not detected

4.3.5 FTIR analysis

Figure 4.10 presents the spectra of SA lignin, SAH- and SAP-lignin samples, while the assignments to the peaks as listed in Table 4.2. At 2350-2370 cm^{-1}, a large negative peak is observed and is caused by the lack of carbon dioxide in the tested sample when compared to the background signal (atmospheric air). Comparing the lack of negative absorbance of the other sulfonated samples could denote that some carbon dioxide was detected on the lignin sample, through contact with atmosphere. It can be seen that there exists a broad signal around 3400 cm^{-1}, which denotes to the hydroxyl group. In lignin samples, the aromatic skeletal vibrations are present, which was located through the 1400 – 1600 cm^{-1} range. Also, the peak at 1371 cm^{-1} belongs to the C-H stretch in methyl groups. This peak was significantly reduced in the sulfonated P-lignin, and not observable in the sulfonated kraft and H-lignin. This is mirrored by the peak at 835 cm^{-1}, which was attributed to aromatic C-H bending. More importantly, the signals at 1040, 1110 and 618 cm^{-1} are associated with the sulfate group attached to the phenolated kraft lignin,. The peak at 618 cm^{-1} is absent in both the SA- lignin and SAH-lignin. It can be concluded from the peak analysis that these samples contained less sulfur, if any. This conclusion is verified by the low charge density and sulfonation analyses described in Table 4.1.

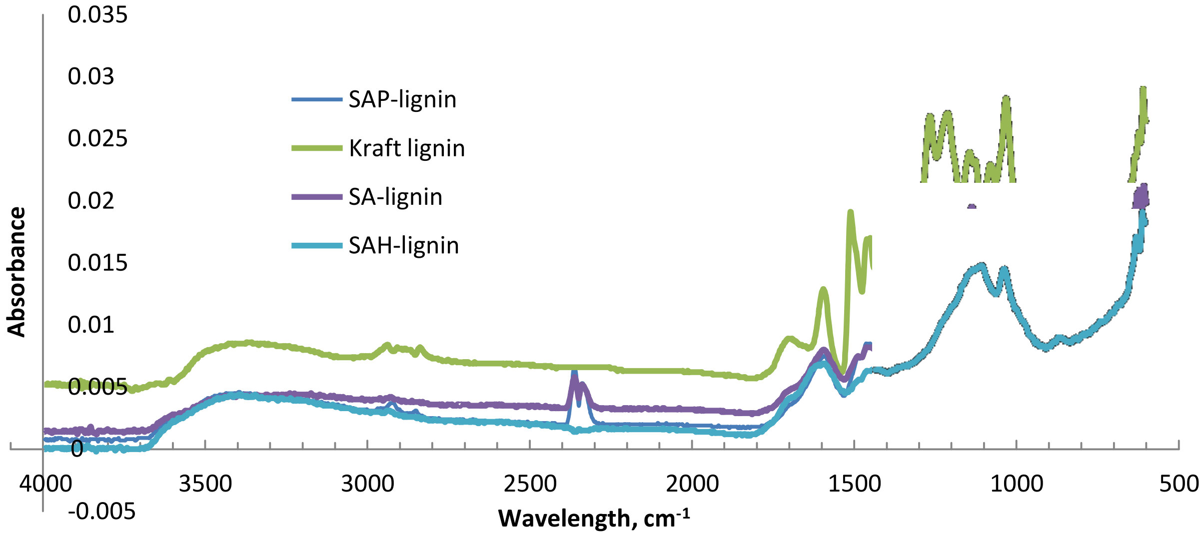

Figure 4.10. FTIR spectra of softwood kraft lignin, SA-lignin, SAH and SA P lignin for samples produced under optimized conditions.

Table 4.2. FTIR spectrum assignments (Maria et al., 2002; Peak et al., 1999; Xu et al., 2006)

Wave number (cm^{-1})	**Assignment**
3429	OH stretching
2945	CH stretching of methyl or methane group
1732, 1726	C=O stretch in unconjugated ketone and carboxyl groups
1660, 1653	C=O stretch in conjugated ketone
1606, 1507, 1434	Aromatic skeletal vibrations
1460	Aromatic methyl group vibrations
1374	Aliphatic C-H stretch in methyl
1328	Syringyl ring C-O stretching
1242	Aromatic C-O stretching
1165	C-O stretch in ester groups
1135	Aromatic C-H in plane deformation in syringyl
1110	Sulfate group
1043	Aromatic C-H in plane deformation in guaiacyl
1040	C-S elongation
855, 844	Aromatic C-H out of plane bending
618	Sulfate

4.3.6 TGA analysis

As sees in Figure 4.11, kraft lignin incinerated completely at a temperature of 500 °C, while the SA-lignin, SAH-lignin and SAP-lignin all exhibited thermal resistance at this temperature. The results also showed that 17%, 28% and 41 % of SA-lignin, SAH-lignin and SAP-lignin remained with incinerating at 750 °C, respectively. It was noted that lignin had a higher combustion temperature compared to other lignocellusoic materials, which was due to the inter linkage of lignin.(Yang et al., 2004). As the sulfonated lignin samples show resistance to decomposition when compared to kraft lignin, an increase in the intermolecular bonding may be the reason and can be attributed to condensation.

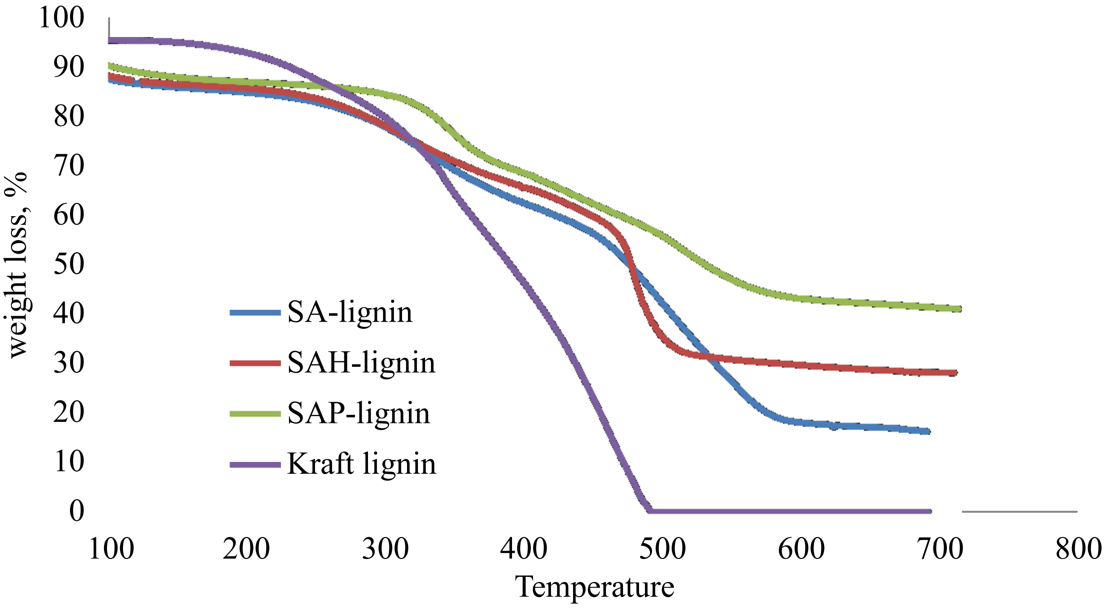

Figure 4.11. Weight loss of kraft lignin, SA-lignin, SAH and SAP-lignin at optimized conditions. Experiments conducted in N_2 at 30 ml/min heated at 10 °C/min.

Figure 4.12 presents the weight loss rate of unmodified kraft lignin, SA-lignin, SAH-lignin and SAP-lignin as a function of temperature. It can be seen that a noticeable increase occurred at approximately 300 to 350 °C in all samples, with kraft lignin representing the highest. The peaks at 350 °C and 450 °C could be due to the decomposition of condensed structures (Zhang et al., 2014). The SAH-lignin exhibited the greatest change (decomposition) at approximately 490 °C, while SA-lignin and SAP-lignin had two peaks of decompositions at 300-350 °C and 500 °C. Compared with unmodified kraft lignin, the rate of decomposition in SA-lignin and SAP-lignin decreased, which could be due to the condensation and the increase in intramolecular bonds (Lv et al., 2013). Furthermore, it was stated in the literature that lignocellulosic complexes in coconut fibers lost 65% of their weight at 390 °C(Mothe and de Mirand, 2009).

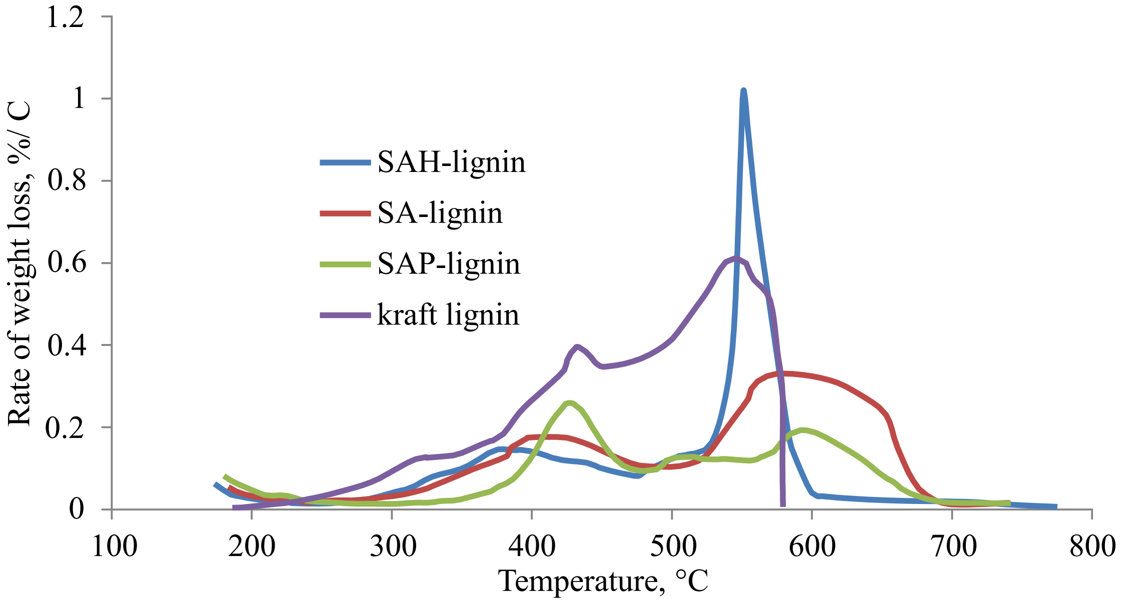

Figure 4.12. Weight loss rate of kraft lignin, SA-lignin, SAH and SAP-lignin at optimized conditions. Experiments conducted in N_2 at 30 ml/ min heated at 10 °C/min.

4.3.7. Proposed sulfonation mechanism

The sulfonation mechanism of unmodified, H-lignin and P-lignin are shown in Figure 4.13-4.15.

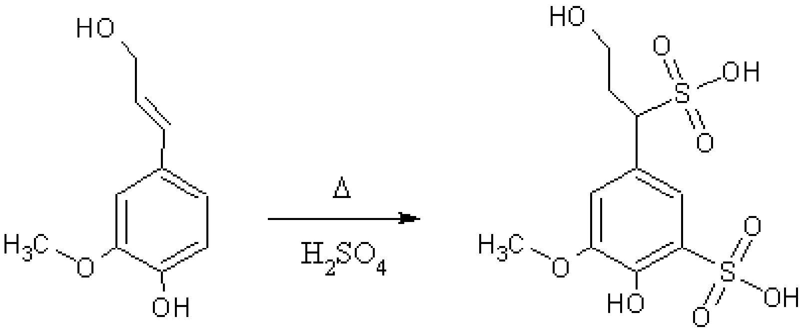

Figure 4.13. Proposed mechanism for synthesis of SA-lignin

Both the α position in kraft lignin (Heden et al., 1936; Holmberg and Svensk, 1935) and the aromatic ortho position (relative to the hydroxide group) should react with this strong sulfonation agent (Cerfontain et al., 1985).

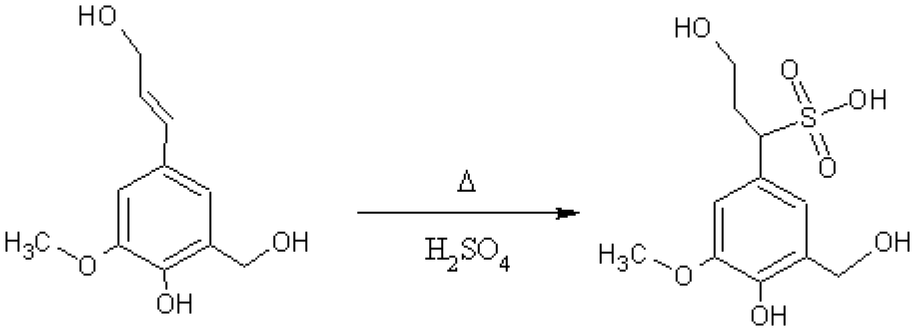

Figure 4.14. Proposed mechanism for synthesis of SAH-lignin

As the ortho position, relative to the hydroxide, is already occupied with the methoxy group from the hydroxymethylation of lignin the only available site for sulfonation of the α-position (Heden et al., 1936; Holmberg and Svensk, 1935) and aromatic substitution is unlikely.

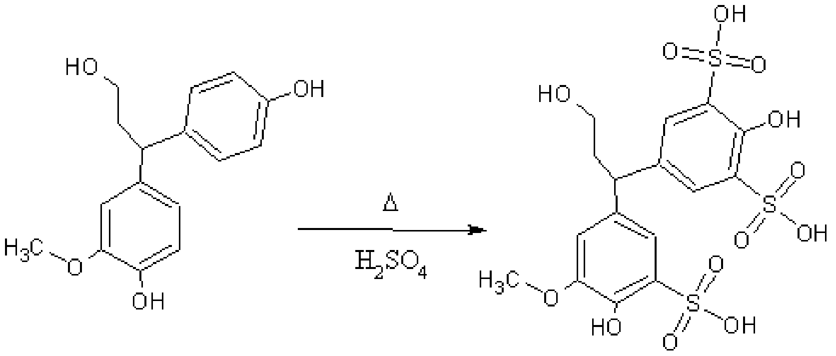

Figure 4.15. Proposed mechanism for synthesis of SAP-lignin.

The sulfonation of P-lignin can react at all three ortho sites, relative to the hydroxide, as the reactive α-position (Heden et al., 1936; Holmberg and Svensk, 1935) reacted with the phenol already. Aromatic substitution would occur due to the harsh sulfonation agent.

4.4. Conclusions

The sulfonation of kraft lignin resulted in 0.752 meq/g and a solubility of 8%, which was obtained under the conditions of 100 °C, 0.5h and 2.24 × 10^{-4} H_2SO_4/lignin molar ratio. The sulfonation of H-lignin resulted in a product with the charge density of 0.46 meq/g and solubility of 9%, which was obtained under the conditions of 80 °C, 1 h and 3.34 × 10^{-4} H_2SO_4/H-lignin molar ratio. The sulfonation of P-lignin resulted in a product with the charge density of 3.12 meq/g and solubility of 100%, which was obtained under the conditions of 120 °C, 1.5 h and a 1.48 × 10^{-4} H_2SO_4/P-lignin molar ratio.

FTIR analysis confirmed that the sulfonation occurred qualitatively as documented by the peaks at1040, 1110 and 618 cm^{-1}.

Charge density and conductometric analyses confirmed the charge densities of SA, SAH, and SAP were 0.752, 0.455 and 3.11 meq, respectively, and the sulfonation degrees of 0.21, 0.16 and 2.71 meq/g, respectively.

The elemental analysis revealed that SA- lignin had higher sulfur content (but a lower oxygen) than both SAH and SAP lignin. The TGA analysis determined the thermal behavior of the lignin samples. Unmodified lignin exhibited a large peak at 450 °C, and was completely consumed at 500 °C, while SA-lignin had a peak at 500 °C, and was resistant to thermal degradation .The TGA analysis of SAH- and SAP-lignin showed a dramatic peak at 500 °C and 550 °C, respectively.

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Chapter 5: Sulfonation via sodium sulfite

Abstract

In this work, the sulfonation of unmodified, hydroxymethylated lignin (H-lignin) and phenolated lignin (P-lignin) was investigated by sodium sulfite treatment underneath various conditions of Na_2SO_3/lignin ratios, lignin concentrations, reaction temperatures and times. Generally, the self-condensation of the guaiacyl phenyl propane subunits of lignin presented a barrier to sodium sulfite treatment. The sulfonation of kraft, H-lignin and P-lignin exhibited an increased anionic charge density and solubility. The sulfonation was confirmed by FTIR and ^{13}C- NMR analysis. The reaction conditions of kraft lignin were optimized at 90 °C, 4 h, 0.67 molar ratio of Na_2SO_3/lignin and lignin concentration of 11.11 g/L. The hydroxymethylation of kraft lignin was conducted under the conditions of 10 g/L lignin concentration, formaldehyde/lignin molar ratio of 0.4 mol/mol at 80 °C for 4 h. The sulfonation of H-lignin was performed at 95 °C, 3 h, a 0.49 Na_2SO_3/lignin molar ratio and 11.11g/L H-lignin concentration. The phenolation of kraft lignin was obtained under the conditions of 7.27 phenol/lignin molar ratio for 4 h at 80 °C reacting in a 90 ml of 60% H_2SO_4 solution, followed by a dilution to 1500 ml with distilled water and boiling for 2 h. The sulfonation of P-lignin was performed under the conditions of 90 ^{O}C, 7 h, 0.49 molar ratio of Na_2SO_3/P-lignin and lignin concentration of 11.11 g/L for SS-lignin. The results showed that a maximum charge density of 1.0, 1.2 and 1.2 meq/g were obtained for sodium sulfite kraft lignin (SS-lignin), sodium sulfite H-lignin (SSH-lignin) and sodium sulfite P-lignin (SSP-lignin), respectively. The solubility of the synthesized SS-lignin, SSH-lignin, and SSP-lignin were 100%, 100% and 96.9%, respectively. The molecular weights of the SS-lignin, SSH-lignin and SSP-lignin were determined to be 31161, 37161 and 27010 g/mol, respectively. Thermogravimetric analysis revealed that SS-lignin, SSH-lignin and SSP-lignin exhibited thermal resistance, when compared to kraft softwood lignin.

5.1. Introduction

Annually, 170 billion metric tons of lignocellulosic materials are produced and used in many applications (Klass, 1998). Cellulose is primarily used in paper production, and hemicellulose provides an excellent platform chemical for producing value added chemicals or ethanol (Carvalheiro et al., 2008). Lignin provides an excellent source of materials for sulfonation. An increase of the amount of sulfur content has been correlated with an increase in the dispersing properties of lignin (Lou et al., 2013).

Kraft lignin is completely soluble in alkaline conditions, however low solubility at neutral pH presents a barrier to its application in aqueous systems (Helander et al., 2013). In addition, the neutral surface charge density of kraft lignin leads to its marginal interaction with charged polymers and particles in solutions (Coughlin et al., 2013). As is well known, flocculants and dispersants interact with components in solutions via charge and hydrophobic interactions. Therefore, kraft lignin should be chemically modified in order to 1) improve its water solubility and 2) charge density so that it can be used as a flocculants or dispersant.

Sulfonation is a reliable method for modifying lignocellulosic materials (Shin & Rowell, 2005) including lignin derived from hardwood (Eucalyptus) (Syahbirin et al., 2012) and cellulose (Zhang et al., 2007) in order to create polyelectrolyte water soluble products. In the past, the sulfonation of lignin increased its ion exchange capacity for metals in phenol/formaledhyde resins production (Zoumpoulakis and Simitzis, 2001). In another study, sodium sulfite was used in the sulfonation of *Juniperus monosperma* to create a lignocellulosic biosorbent for cadmium (Shin & Rowell, 2005). The use of sodium sulfite provides an alternative to sulfuric acid treatment for sulfonation of lignin. However, condensation could hinder sulfonation reaction, as it takes place in sulfite pulping processes (Shimada et al., 1997) or under alkaline conditions (Gierer et al., 1964; Gierer & Petterson, 1977).

It was also claimed that phenolation and hydroxymethylation were more effective to improve the reactivity of lignin than reduction, oxidation and hydrolysis (Hu et al., 2011). The phenolation and hydroxymethylation reactions increased the reaction sites, and were capable of increasing the reactivity of lignin (Alonso et al., 2005; Gosselink et al., 2004).

In the literature, the sodium sulfite treatment was conducted on hydroxymethylated acid hydrolysis lignin in order to produce a lignosulfonate-based dispersant (Matsushita & Yasuda, 2005). In this research, the sulfur content of the generated dispersant was higher than that was commercially available. In one study, the sulfomethylation of sodium lignosulfonate was conducted in one-step, where hydroxymethylation (through the addition of formaldehyde) and sulfonation (via using sodium sulfite as the sulfonation agent) were conducted simultaneously (Yu et al., 2013).

In this chapter, the sulfonation of kraft lignin was conducted with a sodium sulfite treatment under different scenarios. Alternatively, the hydroxymethylated lignin (H-lignin) and phenolated lignin (P-lignin) produced in chapter 3 was sulphonated with sodium sulfite. The characteristics of the products were evaluated by using a particle charge detector, conductometric titrator, NMR, and FTIR and TGA. The solubility of lignin after modification was also assessed. Based on the results, the conditions that yielded a sulfonated lignin with the highest charge density and solubility were determined.

5.2. Experimental

5.2.1 Raw materials

In this work, washed and dried softwood kraft lignin was supplied by FPInnovations from its pilot scale facilities in Thunder Bay, ON. Liquefied phenol (>89% purity), formaldehyde solution (30%), and poly (diallyldimethylammonium chloride) solution (PDADMAC) with a molecular weight (MW) of 100,000-200,000 g/mol (20 wt.% in water) were all purchased from Sigma-Aldrich and used as received. Sulphuric acid (98% purity) was purchased from ACP, Montreal and used as received. Anionic polyvinyl sulfate (PVSK) with a MW of 100,000-200,000 g/mol (98.4 wt.% esterified) was provided by Wako Pure Chem. Ltd. Japan. Tego@trant A100 was used for analysis, which was supplied by Metrohm Inc, Canada.

5.2.2 Pretreatments of lignin

The hydroxymethylation of softwood kraft lignin was performed through the addition of 25g of dried kraft lignin to a 500 ml three neck flask, with 5 ml of formaldehyde (37%) and distilled with 250 ml of water (Pang et al., 2008). The pH of the reaction was increased to 10 (using 2.5 M NaOH) and the system was charged with a graham condenser, stir bar and a thermometer. The solution was stirred and heated at a temperature of 80 °C for 4 h. The resulting products were neutralized by sulphuric acid and then underwent membrane dialysis with the MW cut off of 1,000 Da for two days, while changing water every 2 h for the first 6 h and then once a day for 2 days. The purified solution was then dried at 60 °C in an oven so that dried H-lignin was obtained. In the phenolation of kraft lignin, 3 g of kraft lignin was added to a 500 ml three-neck flask with 18 ml of liquefied phenol, and 90 ml of 60 wt.%H_2SO_4 solution was added to the medium. The system was charged with a stir bar, graham condenser and a thermometer. The reaction was then stirred at 300 rpm and heated at 80 °C for 4 h. The P-lignin solution was then quenched with distilled water to create a solution of 1500 ml and boiled for another 2 h; and underwent filtration using a 45 nm nylon filter (Ma et al., 2011).

5.2.3 Sulfonated lignin

In this study, 0.5- 1.0 g of unmodified and H- and P lignin samples were reacted with Na_2SO_3 in a multitude of conditions. The reaction parameters were Na_2SO_3/ lignin ratio (0.2-0.7 m/m), reaction time (1-7 h), temperature (50-95 °C) and lignin concentration of 7.4-16.7 g/L. All reactions were conducted in a 500 ml three neck flask, with a magnetic stirrer set at 300 rpm, assembled with a thermometer and a graham condenser in an effort to eliminate the loss of sulfonation reagents through evaporation. Once the desired reactants were added, the solution was adjusted to a pH $\approx$ 10 with NaOH solution (.5 M) and heated to the appropriate temperature. Following the reaction, the products were removed from the reaction vessel, washed with distilled water and allowed to cool to room temperature. The solutions were then neutralized with a 0.4 M H_2SO_4 solution, and unreacted Na_2SO_3 and other contaminants were separated by dialysis membranes with a molecular weight cutoff of 1000, while changing water every 2 h for the first 6 h and then once a day for 2 days.

5.2.4. Charge density and solubility of unmodified and H- and P-lignin

At first, 1 wt.% solution of lignin samples was prepared by adding the lignin samples to deionized distilled water (pH 7) and room temperature. The solution was shaken for 1 h at 100 rpm at 30 °C. After shaking, the solutions were centrifuged at 1000 rpm for 5 min in order to separate soluble and insoluble lignin from the solution. The filtrate was taken for charge density analysis of soluble lignin, while precipitates were dried in an oven at 60 °C for charge density analysis of insoluble lignin. The charge density of soluble lignin samples (CDSL) was determined by the direct titration, while the charge density of insoluble ones was identified by the back titration. To measure the charge density of soluble samples, 1 to 2 ml of lignin sample solutions was added to the cell of a particle charge detector, Mutek PCD-04 titrator (Herrsching, Germany) and titrated against PDADMAC standard solution (~0.005M). These values were then used to calculate charge density using Equation 3.1 in Chapter 3. To measure the charge density of insoluble lignin samples (CDIL), about 0.05 g of dried insoluble lignin samples were mixed with PVSK standard solution (~0.005M) for 1 h at 30 °C. Then, the concentration of PVSK solutions before and after mixing with lignin samples were determined by the titrator using the PDADMAC standard solution, and the charge density of insoluble lignin was determined using Equation 3.2 in Chapter 3.

All tests were conducted on optimized sulfonated lignin species. The optimum conditions for the SS-lignin, SSH-lignin and SSP-lignin were at the temperatures of 90, 95 and 90 °C; reaction time of 4, 3 and 7 h; Na_2SO_3/lignin molar ratio of 0.67, 0.49 and 0.49; and a reaction concentration of 11.11 g/L for both lignin and H-lignin, and a P-lignin concentration of 5.56 g/L.

5.2.5. Sulfonation degree analysis

A condumentric titration was considered to determine the number of moles of sulphonated group attached to lignin before and after sulfonation. In this method, a 1 wt.% solution of lignin was prepared with distilled water and shaken in a water bath operating at a temperature of 30 °C and 100 rpm for 1 h. Then, the solution was titrated against Tego@trant A100 by Metrohm 905 Titrando.(Canada), and finally the sulfonation degree was calculated based on equation 3.

Equation 3

(——)

5.2.6. Elemental analysis

The elemental analysis of lignin samples was conducted using a Vario EL Cube instrument (Germany) as dictated in the literature (Fadeeva et al., 2008). Lignin samples were purified by dialysis membranes with a molecular weight cutoff of 1000, while changing water every 2 h for the first 6 h and then once a day for 2 days. Purified lignin samples were weighed and loaded in an integrated carousel, and flushed with carrier gas (He). The combustion of the lignin samples was carried out, and the combusted gases were reduced in order to be identified by the instrument. The elemental balance of the lignin samples can be developed from this data. The elemental analysis helped investigate the theoretical formula of lignin before and after treatment by considering the weight percentage and atomic weight of each element.

5.2.7. Thermo-gravimetric analysis

Thermal behavior of the lignin before and after treatment was assessed using a thermo-gravimetreic analysis (TGA). The lignin samples were first dried at 105 °C and subsequently heated by a thermo-gravimetric analyzer (TGA)-i1000 series (instrument Specialist Inc.) using N_2 (30ml/min) with an increment rate of 10 °C/min in the temperature range of 25 °C and 800 °C (Zhang et al., 2011).

5.2.8. Structural analysis

NMR analysis (^{13}C and ^{31}P) of lignin samples was conducted to determine the structure of lignin before and after sulfonation using a Varian Unity Inova 500. The samples were prepared according to the procedure reported elsewhere (Ben & Ragauskas, 2011). Alternatively, FTIR, using Tensor 37 Fourier Transform Infrared Spectrophotometer (Bruker,Canada) was taken into account for analyzing the functional groups associated with lignin before and after treatment.

5.3. Results and discussion

5.3.1 Sulfonation of softwood Kraft lignin

Figure 5.1 shows the CDSL, CDIL and the solubility of SS-lignin as a function of Na_2SO_3/lignin ratio. It is observable that the CDSL of SS-lignin was independent of Na_2SO_3/lignin molar ratio. The solubility of the SS-lignin is the ratio dependent as solubility peaks to 97% at a molar ratio of 0.67, which is equivalent to a mass ratio of Na_2SO_3/lignin of 0.3. It was claimed in the literature that the fluidity of of cement paste increased with sodium lignosulfonate at the Na_2SO_3/lignin mass ratio of 0.3, which indirectly implied that Na_2SO_3/lignin ratio is important in the modification reaction (Yu et al., 2013).

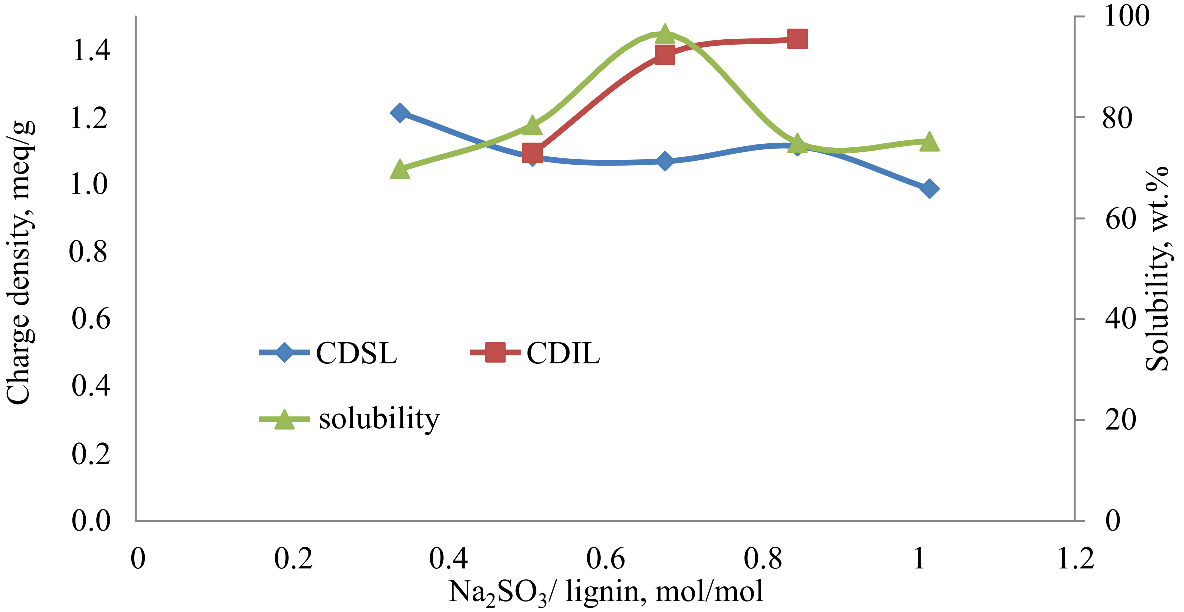

Figure 5.1. The charge density of soluble lignin (CDSL), insoluble lignin (CDIL) and solubility of SS-lignin as a function of Na_2SO_3/lignin molar ratio. Experimental conditions: 95°C,2 h with a lignin concentration of 11.11g/L.

Figure 5.2 shows the impact of temperature on the CDSL, CDIL, and solubility of SS-lignin product. The results depicted that there is a correlation between the reaction temperature and both the solubility and the CDSL with the lowest recorded CDSL of 0.87 meq/g presented at the lower temperature of 50°C. The solubility of the SS-lignin gradually improved from 70% at 50 °C to the highest (83 wt.%) at 80 °C. At temperatures greater than 80 °C, condensation of the guaiacyl subunit became a more prominent. The self-condensation of guaiacyl has been shown to favor higher reaction temperature conditions (Xie & Shi, 2011). In chapter 3, it was reported that condensation could occurr underneath acidic conditions by the sulphuric acid reagent. It was also reported that condensation could occur underneath alkaline conditions (Gierer et al., 1964; Gierer & Petterson, 1977).

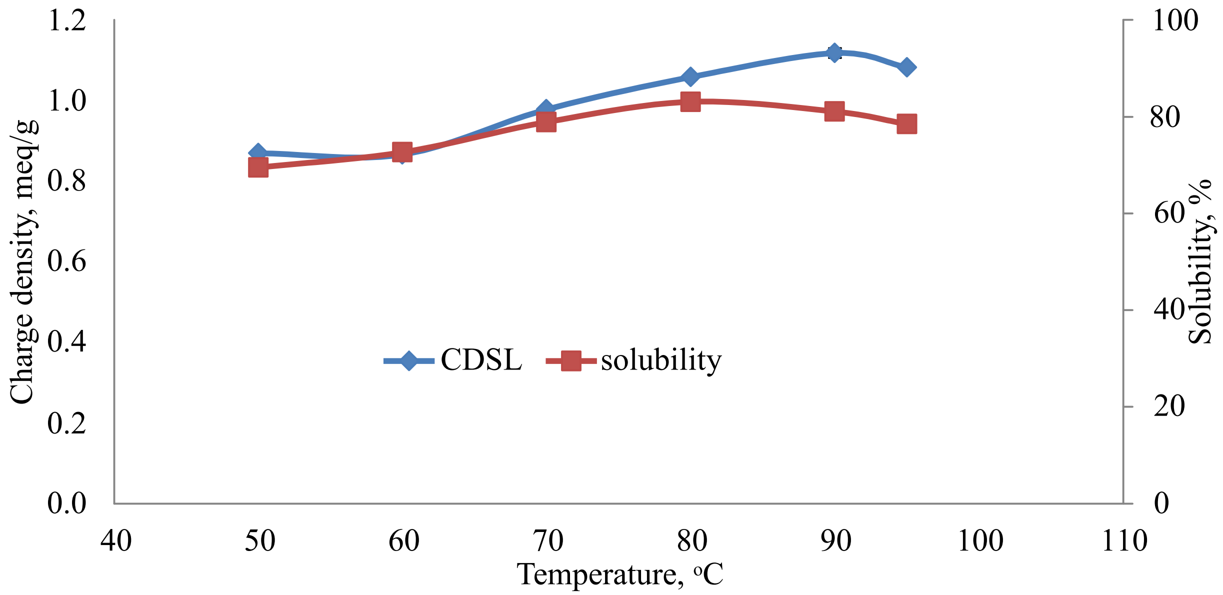

Figure 5.2. The charge density of soluble lignin (CDSL) and solubility of SS- lignin as a function of temperature. Experimental conditions: Na_2SO_3/lignin molar ratio 0.50, 2 h and lignin concentration of 11.11 g/L.

Figure 5.3 shows that impact of time on the CDSL, CDIL and solubility of SS-lignin. With reaction times varied from 1 to 4 h, the CDSL and CDIL of SS-lignin increased from 0.9 meq/g to 1.2 and 1.3 meq/g, respectively. Prolonging the reaction time appeared to have a detrimental effect on the CDSL and CDIL of SS-lignin, as the charge density dropped to 1.1 meq/g for both CDSL and CDIL. It should be noted that, although the solubility of the SS-lignin was high, a sufficient amount of insoluble SS-lignin remained for further analysis. In the literature, the fluidity of sulfonated lignosulfonate, as a concrete superplasticizer, reached a maximum at a reaction time of 4 h, which indirectly implies that the sulfonation reaction is time dependent(Yu et al., 2013).The decrease in solubility after 4 h of reaction may be attributed to condensation under alkaline condition (Gierer et al., 1964; Gierer & Petterson, 1977). In short, solubility of SS-lignin increased as reaction time extended, and reached a plateau of 85% between 2 to 6 h of reaction.

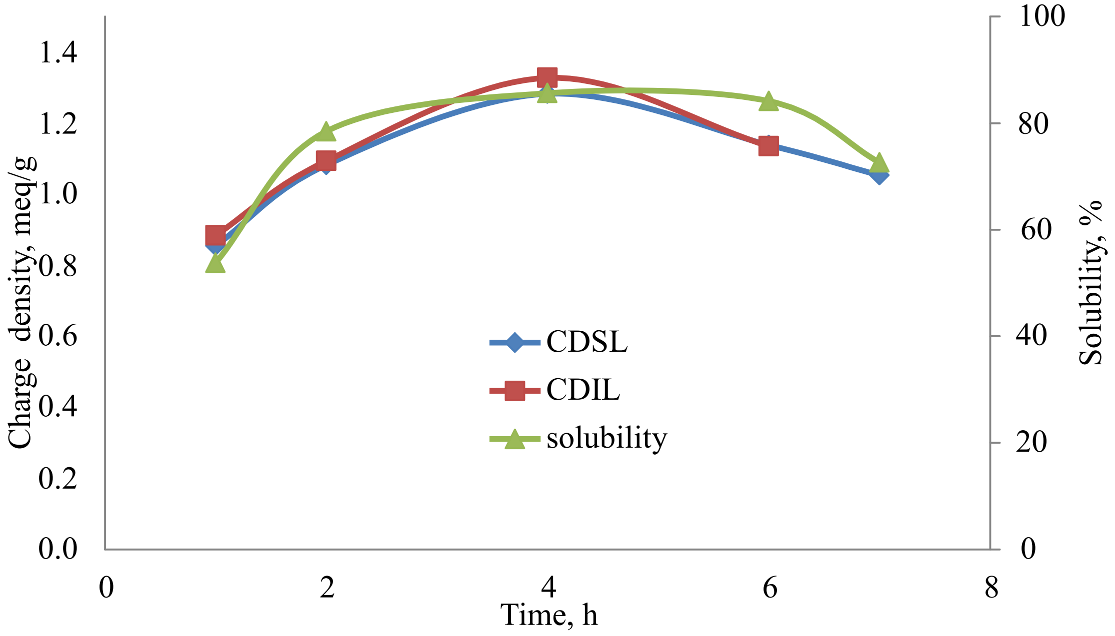

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Figure 5.3. Charge density of soluble lignin (CDSL), charge density of insoluble lignin (CDIL) and solubility of SS-lignin as a function of time. Experimental conditions: Na_2SO_3/lignin molar ratio of 0.50, 95 °C and lignin concentration of 11.11 g/L.

Figure 5.4 presents the correlation between lignin concentration and the charge density and solubility of SS-lignin. The results depicted that solubility had a peak at 80 wt.% when lignin concentration was between 10 and 15 g/l. Lignin concentration have severe implication on the scale up process, and could pose difficulties for industrial scale operations. In the case of spent black liquor, the lignin content is known to be 33.3 mg/g and 30.7 mg/g for mixed softwood and hardwood, respectively (Gebremeskel & Aldaeus, 2013). As such, the lignin from spent liquor would have to be diluted by a factor of 3 (as shown in Figure 4) to provide an optimized reaction concentration, as SS-lignin had a high solubility at the concentration of 11.1 mg/g.

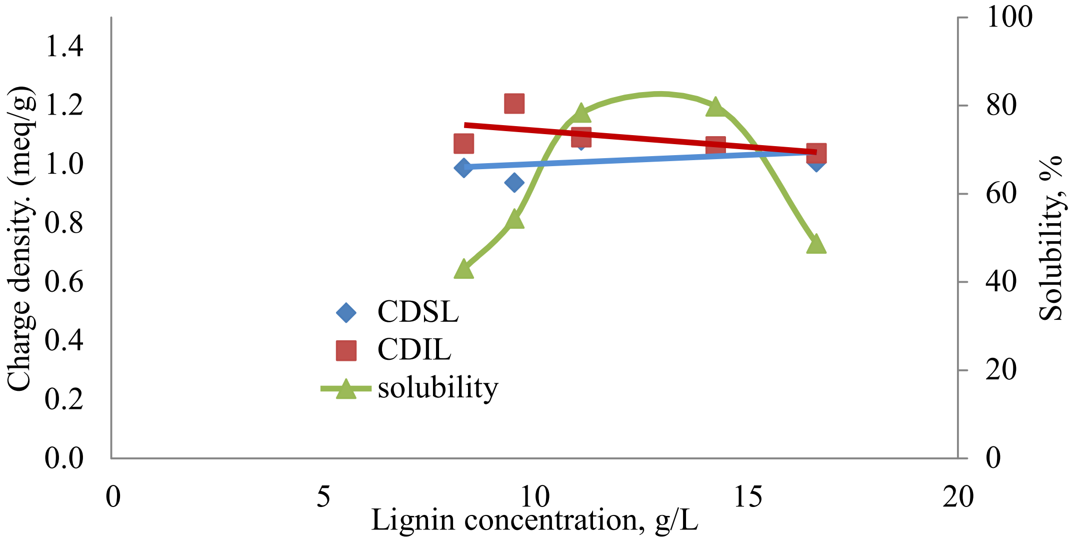

Figure 5.4. Charge density of soluble lignin (CDSL), charge density of insoluble lignin (CDIL) and solubility of SS-lignin as a function of the concentration of lignin. Experimental conditions: Na_2SO_3/lignin, a molar ratio 0.50 mol/mol, 95 °C and 2 h.

5.3.2. Sulfonation of Hydroxymethylated (H-lignin) via sodium sulfite treatment

Figure 5.5 shows the CDSL and the solubility of SSH- lignin as a function of the Na_2SO_3/H-lignin molar ratio. It is seen that the solubility increased from 75% to a maximum of 95.6 % at the Na_2SO_3/H-lignin molar ratio of 0.33. A decrease in solubility is noted as the sulfonation agent molar ratio was increased to 0.82 mol/mol. Condensation has been found to occur in alkaline conditions, and elemental sulfur within the solution acts as an inhibiting agent (Gierer et al., 1964; Gierer & Petterson, 1977). This was observed in the literature (Matsushita et al., 2009; Matsushita et al., 2004a; Matsushita et al., 2004b) to sterically hinder, through polymerization, the reactive sites for sulfonation. The charge density decreased from an initial charge density of 1.6 meq/g to 1.3 meq/g once the ratio increased from 0.67 to 1.2 Na_2SO_3/H-lignin. Comparing Figures 1 and 5, it is understood that the optimized ratio for H-lignin is higher than that for unmodified lignin and has been reported in the literature (Yu et al., 2013). This decrease may be due to the presence of hydroxymethyl group on phenyl propene group being sulfonated at lower Na_2SO_3/H-lignin ratio, and condensation occurring at higher increase.

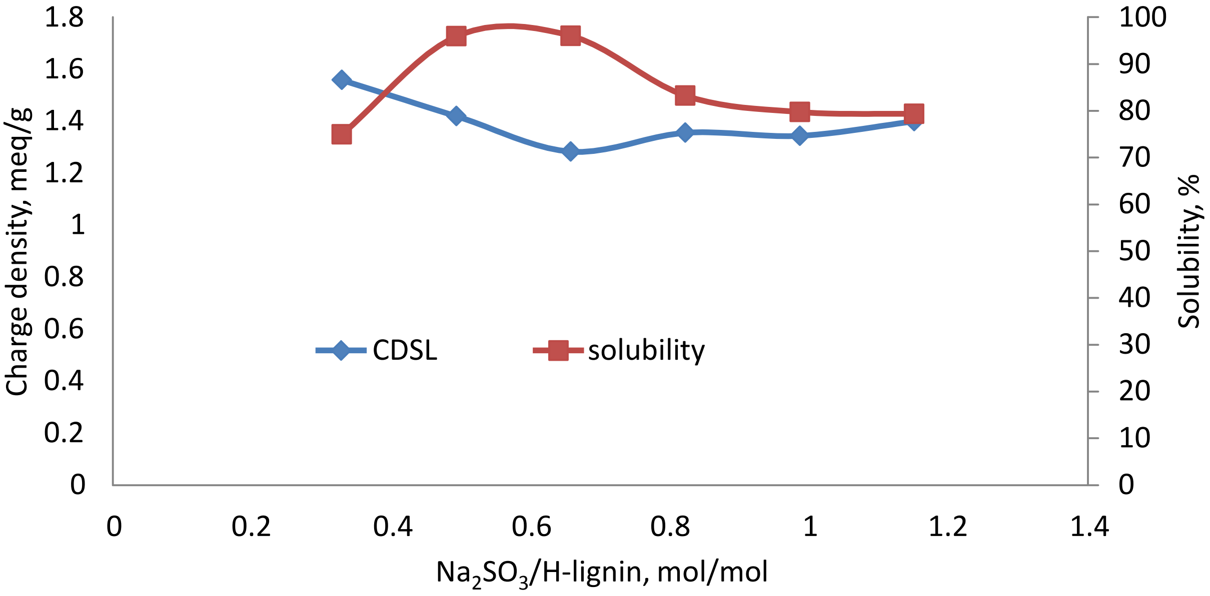

Figure 5.5. Charge density of soluble lignin (CDSL) and solubility of SSH-lignin as a function of Na_2SO_3/H-lignin molar ratio. Experimental conditions: 95 °C, 2 h and a lignin concenration of 11.1 g/L

Figure 5.6 illustrates the impact of time on the CDSL and solubility of H- lignin. The CDSL increased from 1.08 and 1.6 meq/g as time of reaction extended from 1 h to 5 h. At shorter reaction times, the SSH- lignin exhibited an increased solubility to 97% after 3 h of reaction. However, extending the reaction time led to a drop in solubility. As stated earlier, an increased reaction time favors condensation over sulfonation (Xie & Shi, 2011), which has been stated earlier to occur in alkaline conditions (Gierer et al., 1964; Gierer & Petterson, 1977).

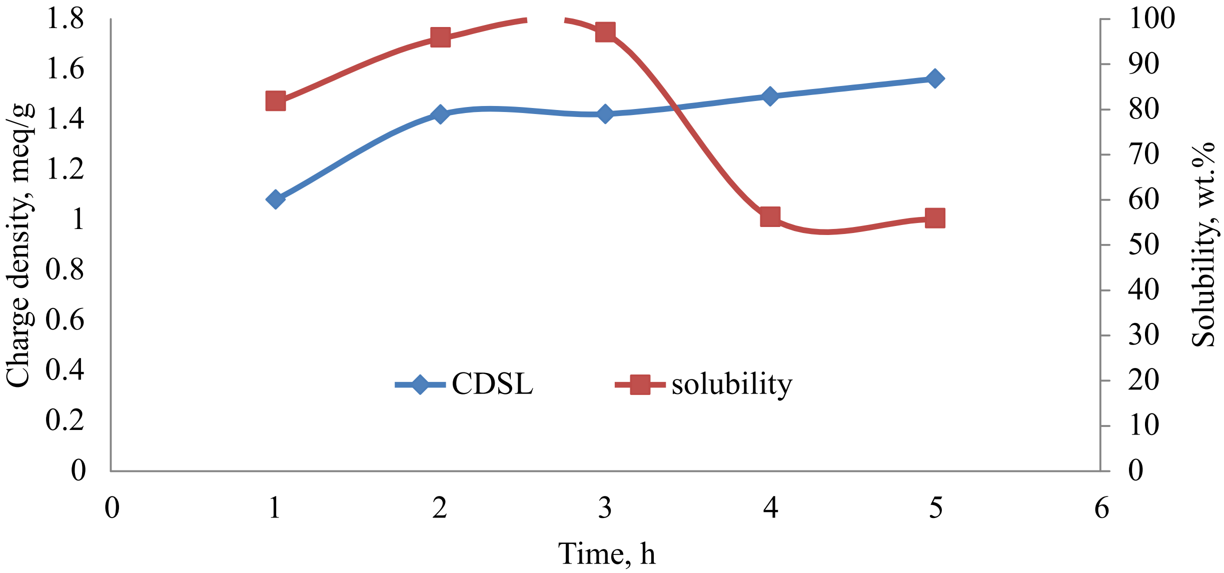

Figure 5.6. Charge density of soluble lignin (CDSL) and solubility of SSH-lignin as a function of reaction time. Experimental conditions: Na_2SO_3/H-lignin molar ratio of 0.37 mol/mol, 95 °C and a H-lignin concentration of 11.1 g/L.

Figure 5.7 presents the influence of temperature on the CDSL and solubility of H-lignin via sodium sulfite treatment. Through the examination of solubility and CDSL, a temperature of 95 °C was the optimum with the highest charge density of 1.4 meq/g and solubility of 96 wt.%. The optimized temperature for the sulfomethylation of sodium lignosulfonate was 95 °C in the literature (Yu et al., 2013) yielding a product with the greatest fluidity. However, a lower temperature of 85 °C was reported as optimum for the sulfonation of woody biomass (Xie & Shi, 2011).

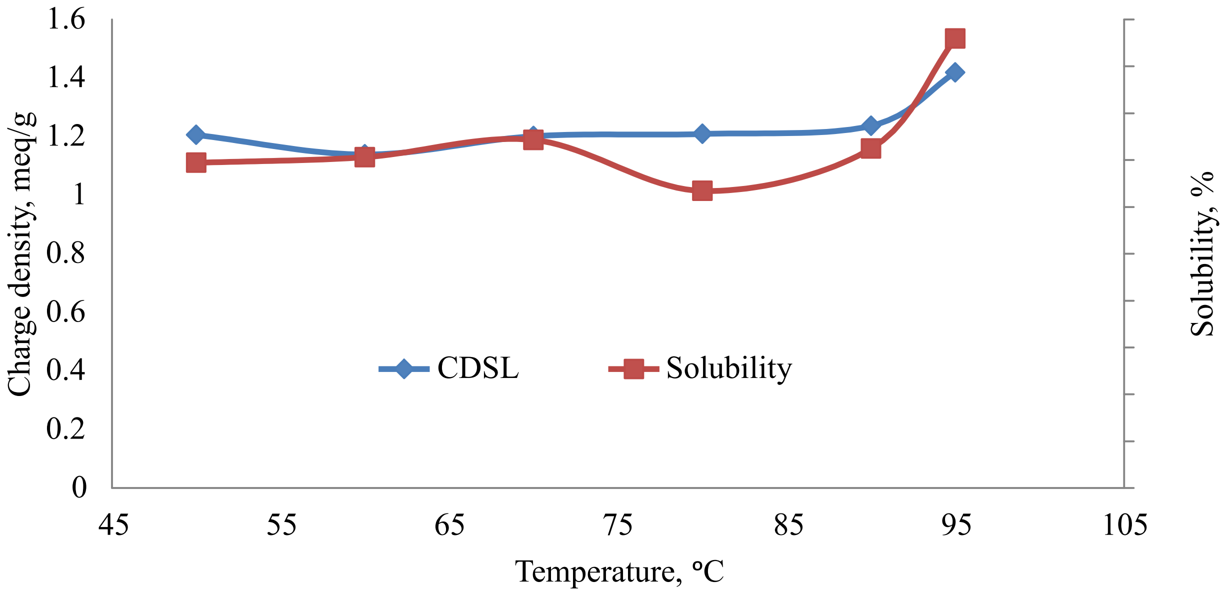

Figure 5.7. Charge density of soluble lignin (CDSL) and solubility of SSH-lignin as a function of reaction temperature. Experimental conditions: Na_2SO_3/H-lignin molar ratio of 0.37, 2 h and a H-lignin concentration of 11.1 g/L.

Figure 5.8 reflects the impact of lignin concentration on the CDSL and solubility of SSH-lignin. It is noted that the sulfonation of H-lignin is concentration independent. As CDSL is independent, an increase in the H-lignin concentration can be increased beyond the 11.11 g/L, and would facilitate the industrial application of lignin, respectively (Gebremeskel & Aldaeus, 2013). This is in contrast to results presented in Figure 3, where the CDSL and solubility of SS-lignin was dependent of lignin concentration. These results imply that there was a limitation on the sodium sulfite treatment of H-lignin and the maximum charge density was 1.4 meq/g.

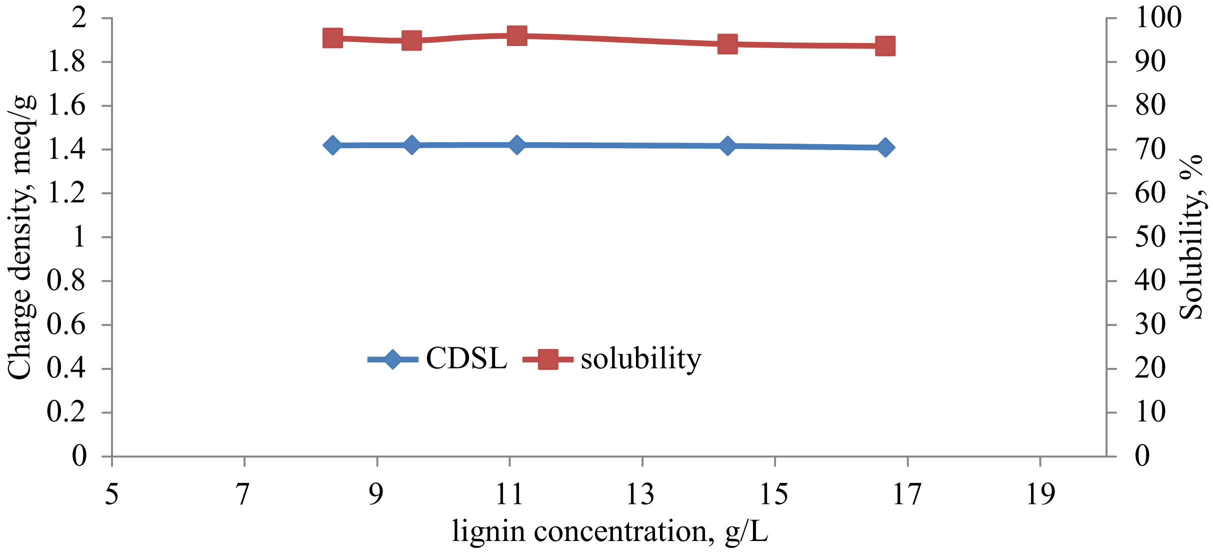

Figure 5.8. Charge density of soluble lignin (CDSL) and solubility of SSH-lignin as a function of lignin concentration. Experimental conditions: Na_2SO_3/H-lignin molar ratio of 0.37, 2 h, and 95 °C.

5.3.3. Sulfonation of Phenolated (P-lignin) via sodium sulfite treatment

Figure 5.9 presents the effect of Na_2SO_3/P-lignin molar ratio on the CDSL and solubility of SSP-lignin. Evidently, increasing the molar ratio of Na_2SO_3/P-lignin resulted in a greater solubility, but a smaller charge density. The decrease in the solubility could be related to the condensation of lignin underneath alkaline conditions (Gierer et al., 1964; Gierer & Petterson, 1977). Since the initial solubility of P-lignin was reduced, when compared to kraft lignin (as seen in Chapter 3), a greater amount of sulfonation is expected to achieve a similar solubility as SS-lignin. The results indicate that a molar ratio of 0.49 Na_2SO_3/P-lignin produced a SSP-lignin with the highest CDSL value of 1.3 meq/g and solubility of 69 wt.%. A lower molar ratio of 0.33 Na_2SO_3/P-lignin allowed for a CDSL of near-equivalent magnitude when evaluated in Figure 9, however the produced SSP-lignin exhibited a lower solubility of 57 wt.%. It has been determined that dispersants exhibit efficiency with an increase in sulfonation degree (Plank et al., 2009), and a molar ratio of 0.49 exhibits the greatest amount of sulfonation degree through the evaluation charge density. This was also reported in another report in which 30% of Na_2SO_3/sodium lignosulfonate provided the best results (i.e. highest fluidity for cement paste) (Yu et al., 2013).

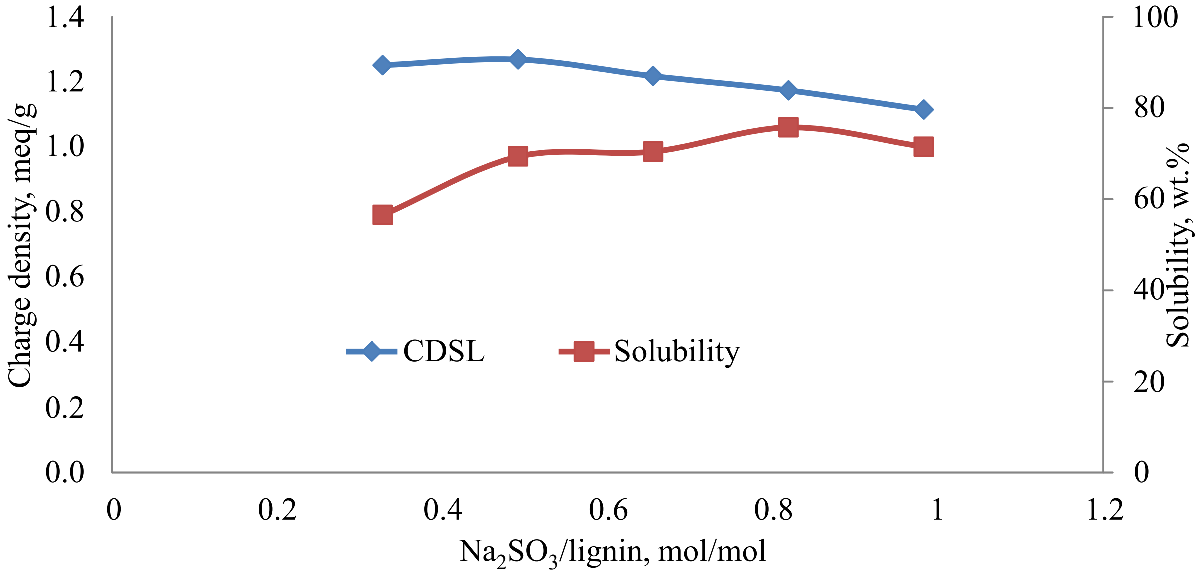

Figure 5.9. Charge density of soluble lignin (CDSL) and solubility of SSP-lignin as a function of Na_2SO_3/P-lignin molar ratio. Experimental conditions: 95 °C, 2 h, and P-lignin concentration of 5.56 g/L.

Figure 5.10 presents the effect of time of reaction on the CDSL and solubility of SSP-lignin. The results showed that, by extending the time of reaction, the CDSL and solubility of SSP-lignin was improved, which is in contrary to the results reported on SS-lignin and SSH-lignin, as well as that reported in the literature for lignosulfonate (Yu et al., 2013). It could be interpreted that the sulfonation was improved by the extension of time, but the degree of sulfonation on soluble lignin was not increased. At a reaction time of 3 h to 4 h the solubility reached a plateau at of 73%.

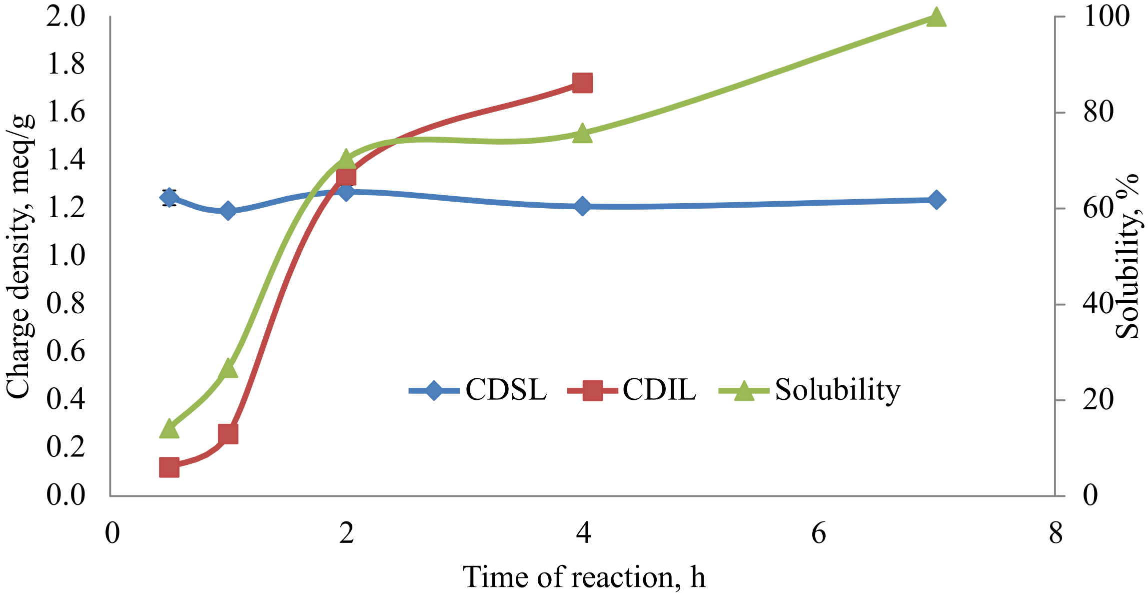

Figure 5.10. Charge density of soluble lignin (CDSL), charge density of insoluble lignin (CDIL) and solubility of SSP-lignin as a function of time. Experimental conditions: Na_2SO_3/P-lignin molar ratio of 0.37 mol/mol, 95 °C and P-lignin concentration of 5.56 g/L

Figure 5.11 exhibited the influence of reaction temperature on the CDSL, CDIL and solubility of SSP-lignin. As the temperature is increased from 50 °C to 95 °C, the solubility, CDSL and CDIL of SSP-lignin was improved. As the CDSL and CDIL were increased via sulfonation, an increase in dispersive ability was predicted by previous studies (Plank et al., 2009).

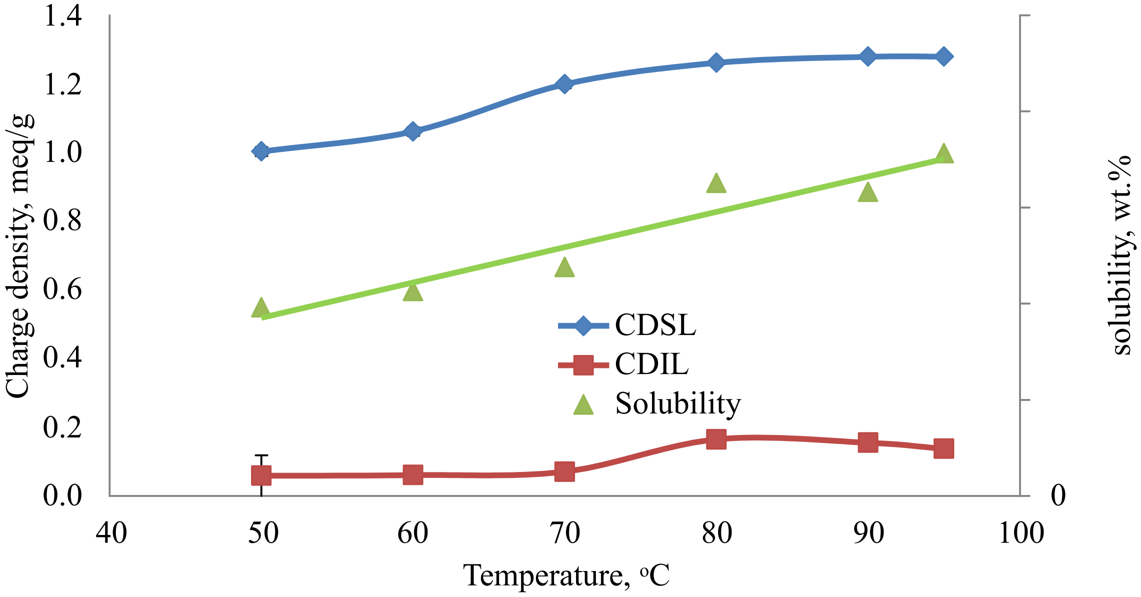

Figure 5.11. Charge density of soluble lignin (CDSL), charge density of insoluble lignin (CDIL) and solubility of SSP-lignin as a function of temperature. Experimental conditions: Na_2SO_3/P-lignin molar ratio of 0.37 mol/mol, 2 h and P-lignin concentration of 5.56 g/L.

The impact of lignin concentration on the CDSL and solubility of SSP-lignin were described in Figure 5.12. Apparently, the charge density was independent of lignin concentration, but the solubility reached plateau of 70 wt.% at 5.5 g/l lignin concentration.. It is inferred from these results that by increasing the lignin concentration, the no change in charge density and solubility could be achieved. From this analysis, a P-lignin concentration of 5.5 g/L yielded the greatest CDSL and solubility.

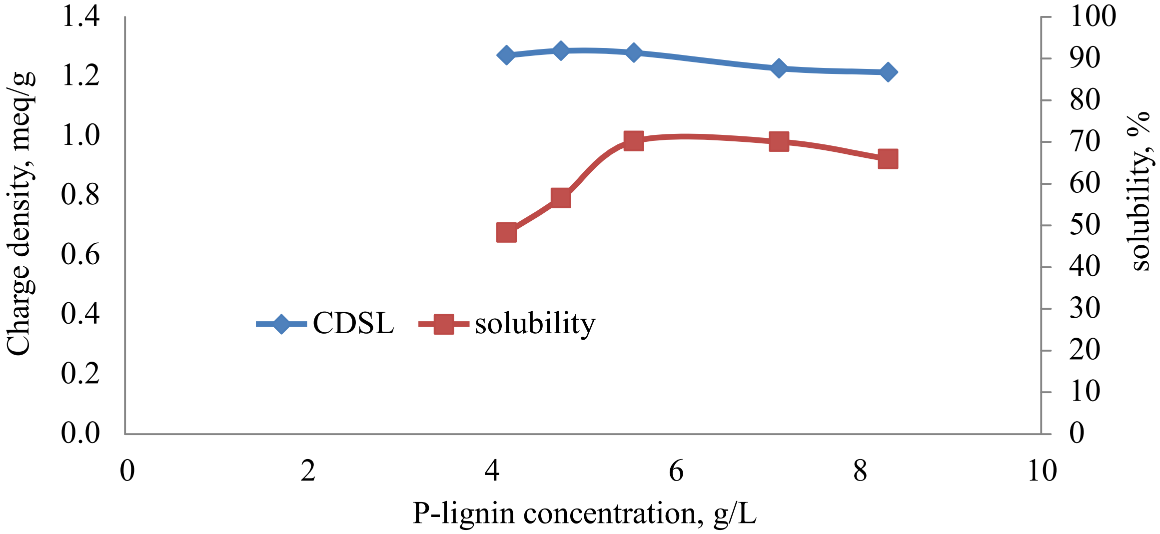

Figure 5.12. Charge density of soluble lignin (CDSL) and solubility of SSP-lignin as a function of P-lignin concentration. Experimental conditions: Na_2SO_3/P-lignin molar ratio of 0.37, 95 C and 2 h.

5.3.4 Characterization of Sulfonated lignins

The properties of sulphonated lignin (SS-lignin, SSH-lignin and SSP-lignin), prepared under the optimized conditions of: Na_2SO_3/lignin molar ratio of 0.67, 0.49 and 0.49 mol/mol; reaction temperatures of 90, 95 and 90 °C; reaction time of 4, 3 and 7 h; and a reactant concentration of 11.11, 11.11 and 5.55 g/L, for lignin, H-lignin, and P-lignin, respectively, are shown in Table 5.1. As can be seen, the MW of SS-lignin, SSH-lignin and SSP-lignin were 31161, 37160 and 27010 g/mol, respectively. Our study determined that unmodified kraft lignin had a M_W of 25100 g/mol and a M_n of 10681 g/mol, which is higher than reported values in the literature and can be attributed to the mixture of separate tree species. The molecular weight of lignin present in different tree species is varied, as *Pseudotsuga menziesii, Abies concolor* and *E. Globulus* contain lignin with a molecular weight of 38000, 52000 and 32000 g/mol, respectively (Guerra et al., 2006). In one study, the molecular weight (M_W) of lignin generated from milled softwood was 10,700 g/mol (Meister, 2002). Another study found that softwood lignosulfonates had an average molecular weight of 36,000 – 61,000 g/mol. However, the hardwood kraft lignin was reported to be in the range of 5,000 to 15,000 g/mol (Luque et al., 1994) while in another study, the Mw and Mn of hardwood kraft lignin were reported to be in the range of 8,900-11,119 g/mol and 200 to 2755 g/mol, respectively.(Baumberger et al., 2007). In the same vein, the M_W and Mn of softwood kraft lignin were 3,503-13,109 g/mol and 163-847 g/mol, respectively (Helander et al., 2013). Included in Table 1 are the results on the molecular weight analysis of SS-lignin, SSH-lignin and SSP-lignin. As seen, the Mn of was 13266, 28367 and 23693 g/mol, respectively. The SS- and SSH-lignin molecular weight was marginally larger than unmodified kraft lignin, which may imply that the sodium sulfite treatment slightly accelerated the condensation (chain extension) reaction under alkaline conditions (Gierer et al., 1964; Gierer & Petterson, 1977). The presence of sulfur in the solution has shown to have an inhibiting effect on alkaline condensation of lignin (Gierer & Petterson, 1977), The molecular weight of SS-, SSH- and SSP- lignin (31161, 37160 and 27010 Da, respectively) were larger than the unmodified kraft lignin's molecular weight (5100 Da), which indicates slight condensation of lignin. Prior to sulfonation, the molecular weight of H-lignin was significantly larger, 45420 g/mol (as seen in Chapter 3), and decreases dramatically after sulfonated to SSH-lignin. This decrease in molecular weight can be attributed to hydrolysis, which have been observed in the literature in alkaline solution (Mao et al., 2012; Nenkova et al., 2011). While condensation underneath alkaline conditions occurs (Gierer et al., 1964; Gierer & Petterson, 1977), the hydrolysis of H-lignin is the dominant reaction. With the influx of sulfur, in the form of sulfate ions, condensation is inhibited. The molecular weight of P-lignin increased during sulfonation as it was smaller than kraft lignin prior to sulfonation, and slightly greater than kraft lignin. Thus for the sulfonation of P-lignin, condensation presents itself as the dominant reaction over hydrolysis. The increase in molecular weight is beneficial as a dispersant, as higher molecular weighted lignosulfonate apply a larger steric force which increases the efficiency of dispersants (Matsushita & Yasuda, 2005).

The elemental compositions of the lignin samples are also included in Table 5.1. In the past, the elemental analysis of softwood kraft lignin was reported to have 64.88% carbon, 6.3% hydrogen and 1.7 % sulfur (Helander et al., 2013). The same study examined the permeate of softwood kraft lignin solution at pH 9, it was passed through a 1000 Da filter, to find that the lignin contain in the permeate contained a 61.26% carbon, 5.9% hydrogen and 8.7% sulfur (Helander et al., 2013). Alternatively, biomass lignin contained 47% carbon, 14.3% hydrogen, and 19.6% nitrogen (Lv et al., 2013). In the present work, it is noted that the amount of carbon dropped from 63.9% in kraft lignin, to 58.6, 59.5 and 59.9% in SS-, SSH- and SSP-lignin, respectively. A decrease in hydrogen content of lignin samples is also noted. However, with the small decrease of hydrogen for the sulfonated lignin, the amount of hydrogen is still comparable to softwood kraft lignin value of 5.9% (Helander et al., 2013).

In the past, the sulfonation degree was determined by the percentage of sulfur present in lignin (Matsushita & Yasuda, 2005) and in the sulfur content of commercial lignosulfonate was 6%. In this study, sulfuric acid lignin was modified through hydroxymethylation, which was followed by sulfonation and the lignin had a sulfur content of 5.4 -11.4%. Other studies have determined that the amount of sulfur in kraft lignin is 1.69-8.69% (Helander et al., 2013). The sulfur content in our current study was reported to be 3.22, 2.15 and 2.71%, respectively, for SS-, SSH- and SSP-lignin. The decreased amount of sulfur (compared to unmodified kraft lignin) may be indicative of impurities within the unmodified kraft lignin, as kraft lignin was acid-washed with sulfuric acid prior to use.

The elemental analysis helped determine the chemical structure of the lignin samples. To allow for ease of comparison, a basis of 9 units of carbon was used in the structure. The chemical formula of softwood kraft lignin (unmodified lignin) was found to be $C_9H_{8.55}O_{2.99}S_{0.08}$. The chemical formula of SS-lignin, SSH-lignin and SSP-lignin were $C_9H_{9.90}O_{3.76}S_{0.19}$, $C_9H_{9.98}O_{3.66}S_{0.12}$ and $C_9H_{10.18}O_{3.35}S_{0.15,}$ respectively. It is generally seen that the amounts of sulfur and oxygen were increased with respect to unmodified lignin.

Table 5.1. Properties of lignin studied in this work and reported in the literature. All samples were created under optimum conditions as explained in section 5.3.4.

Lignin	Mw, Da	Mn, Da.	Mw/ Mn	CHNOS					Charge density, meq/g	SO_3^- group, meq/g	Reference
				C%	H%	N%	O%	S%			
SS lignin	8284[3] 31161[4]	2141[3] 13260[4]	4.43[3] 1.55[4]	58.63	5.41	0.04	32.62	3.22	1.01 ±0.02	0.99 ±0.01	PS[1]
SSH-lignin	8243[3] 37161[4]	2001[3] 28367[4]	4.53[3] 1.31[4]	59.45	5.53	0.04	32.18	2.15	1.22 ±0.01	1.01 ±0.01	PS
SSP-lignin	4061[3] 27010[4]	1273[3] 23693[4]	3.19[3] 1.14[4]	59.92	5.69	0.05	29.79	2.71	1.24 ±0.01	1.02 ±0.04	PS
Softwood kraft lignin	3,503-13,109	163-847	NR	64.88	6.3	0.1	NR	1.69	NR[2]	NR	(Helander et al., 2013)
Softwood kraft lignin	NR	NR	NR	61.26	5.89	0.1	NR	8.69	NS	NR	(Helander et al., 2013)
Biomass Lignin	NR	NR	NR	47.65	4.30	2.92	19.60	0.08	NR	NR	(Lv et al., 2013)
Softwood lignosulfonate	8,900-11,119	200-2755	NR	NR	NR	NR	NR	NR	NR	NR	(Baumberger et al., 2007)
Softwood lignosulfonate	36,000-61,000	NR	NR	NR	NR	NR	NR	NR	NR	NR	(Luque et al., 1994)
Hardwood lignosulfonate	5,000-15,00	NR	NR	NR	NR	NR	NR	NR	NR	NR	(Luque et al., 1994)
Kraft lignin	9679[3] 25100[4]	2141[3] 10681[4]	4.52[3] 2.35[4]	63.9	5.97	0.06	30.60	6.09	0 ± 0.03	0±0.04	PS

[1]PS: Present work, [2]NR: Not reported. [3]UV determined, [4]Light scattering results

The conductometric analysis indicated a sulfonated group of 1.01, 1.22 and 1.24 meq/g for SS-lignin, SSH-lignin and SSP-lignin, respectively. It can be concluded that the developed charge density on kraft lignin via sodium sulfite sulfonation is solely due the attached sulphonated group to the lignin backbone, as the charge density and conductometric analyses showed very close results. Past studies have claimed that the unmodified lignin would be easily sulfonated at the α position of the phenyl propene units (Heden et al., 1936; Holmberg & Svensk, 1935), and we propose that a similar sulfonation occurred on lignin. SSH-lignin has a charge density of 1.22 meq/g and sulfonate content of 1.0 meq/g. the sulfonataed group can be attached to the α position (Heden et al., 1936; Holmberg & Svensk, 1935) or at the reactive hydroxymethyl group (Matsushita & Yasuda, 2005). In 2005, it was stated that the addition of hydroxymethyl groups to the aromatic ring could result in a greater sulfonated product (Matsushita & Yasuda, 2005). It was also noted that the addition of formaldehyde would react with lignin at the unsubstituted positions on the phenyl propene units and form a network comprised of with terfunctional junctions (Zoumpoulakis & Simitzis, 2001). Phenolation has also been shown to occur at the reactive α position in the literature (Yasuda et al., 1998) and would interfere with the sulfonation at the stated reaction position. SSP-lignin has a charge density of 1.24 meq/g, with the sulphonated group of 1.02 meq/g. The results on SS-, SSH- and SSP-lignin analysis would imply that the sulfonation of kraft, H- and P-lignin would yield the same results. H-lignin and P-lignin possessed an initial charge density of 1.2 meq/g and 0.0 meq/g, respectively, with a solubility of 55% and 6%, respectively. The sulfonation of H-lignin yielded an SSH-lignin with a similar charge density, but with the solubility of 100%. SSP-lignin exhibited 100% solubility with a similar charge density. Therefore, it can be concluded that the sulfonation with sodium sulfite yielded soluble lignin with a similar charge density and solubility, regardless of pre-treatment process.

5.3.5 FTIR analysis

Figure 5.13 presents the spectra of kraft lignin, SS-lignin, SSH-lignin and SSP-lignin samples, while the assignments to the peaks listed in Table 5.2. It can be seen that there exists a broad signal around 3400 cm^{-1}, which denotes to the hydroxyl group, but is less intense for SSH-lignin. In all four lignin samples, the aromatic skeletal vibrations are present and are located at 1400 – 1600 cm^{-1} range. It is also noted that the peak at 1371 cm^{-1}, which can be attributed to C-H stretch in methyl groups is significantly reduced in the SSH-lignin, and unobservable in the SS- a SSH-lignin. The peak at 835 cm^{-1} attributing to the aromatic C-H bending is not present in SS- and SSH-lignin lignin. More importantly, the signals at 1040, 1110 and 618 cm^{-1}, which are associated with the sulfonate group attached to the phenolated kraft lignin are clear in the spectra. The peak at 618 cm^{-1} is present in all modified lignin samples, and not observed in kraft lignin. This provides further indication that sulfur is incorporated into sodium sulfite lignin samples.

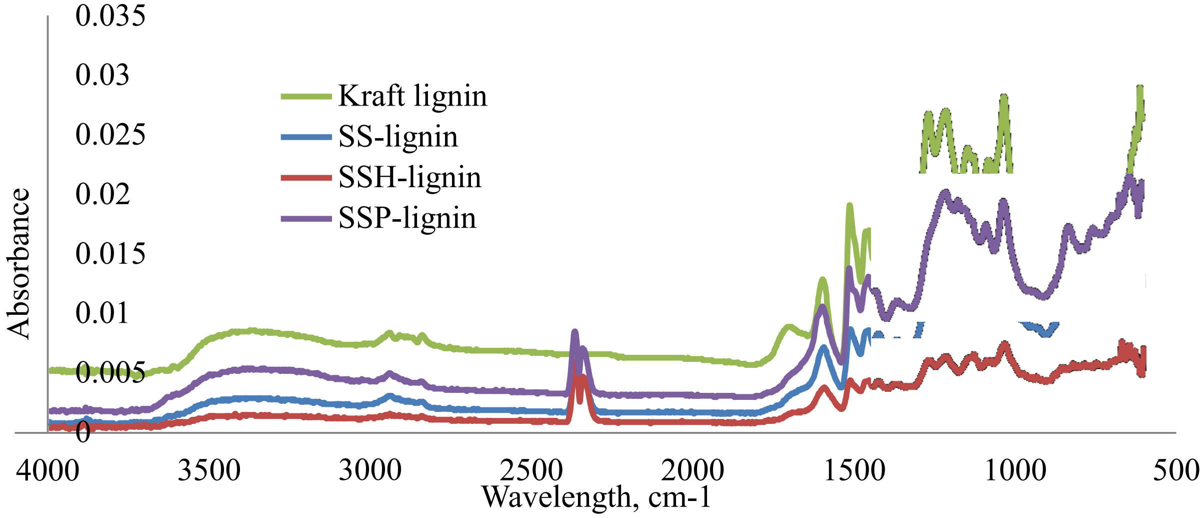

Figure 5.13. FTIR result of kraft lignin, and SS-lignin, SSH-lignin, SSP-lignin.

Table 5.2. FTIR spectra assignment (Maria et al., 2002; Peak et al., 1999; Xu et al., 2006)

Wave number (cm^{-1})	**Assignment**
3429	OH stretching
2945	CH stretching of methyl or methane group
1732, 1726	C=O stretch in unconjugated ketone and carboxyl groups
1660, 1653	C=O stretch in conjugated ketone
1606, 1507, 1434	Aromatic skeletal vibrations
1460	Aromatic methyl group vibrations
1374	Aliphatic C-H stretch in methyl
1328	Syringyl ring C-O stretching
1242	Aromatic C-O stretching
1165	C-O stretch in ester groups
1135	Aromatic C-H in plane deformation in syringyl
1110	Sulfate group
1043	Aromatic C-H in plane deformation in guaiacyl
1040	C-S elongation
855, 844	Aromatic C-H out of plane bending
618	Sulfate

5.3.6 TGA Analysis

Figure 5.14 presents the TGA analysis of the samples. It is seen that kraft lignin incinerated completely at a temperature of less than 500 °C, while the SS-lignin, SSH-lignin and SSP-lignin exhibited thermal resistance. The ash remained (9%, 11% and 17 % for SS-lignin, SSH-lignin and SSP-lignin, respectively) after heating to temperatures greater than 700 °C shows this resistance clearly. It was also noted that, due to the interlinkages of lignin, it will have a higher combustion temperature compared to other lignocellulosic materials. Hemicellulose and cellulose contain less significant structural linkages and decompose at a range of 220-300 °C and 300-340 °C, respectively (Yang et al., 2004). As the molecular weight of SS, SSH and SSP-lignin were larger than the molecular weight of unmodified kraft lignin, the increase in thermal resistance is a result of the increase in intermolecular linkages. As an increase in thermal resistance was noted in lignin, versus cellulose and hemicellulose, due to increased intramolecular linkages, a similar increase in intramolecular is the contributing cause to the increase in thermal resistance exhibited by SS, SSH and SSP-lignin.

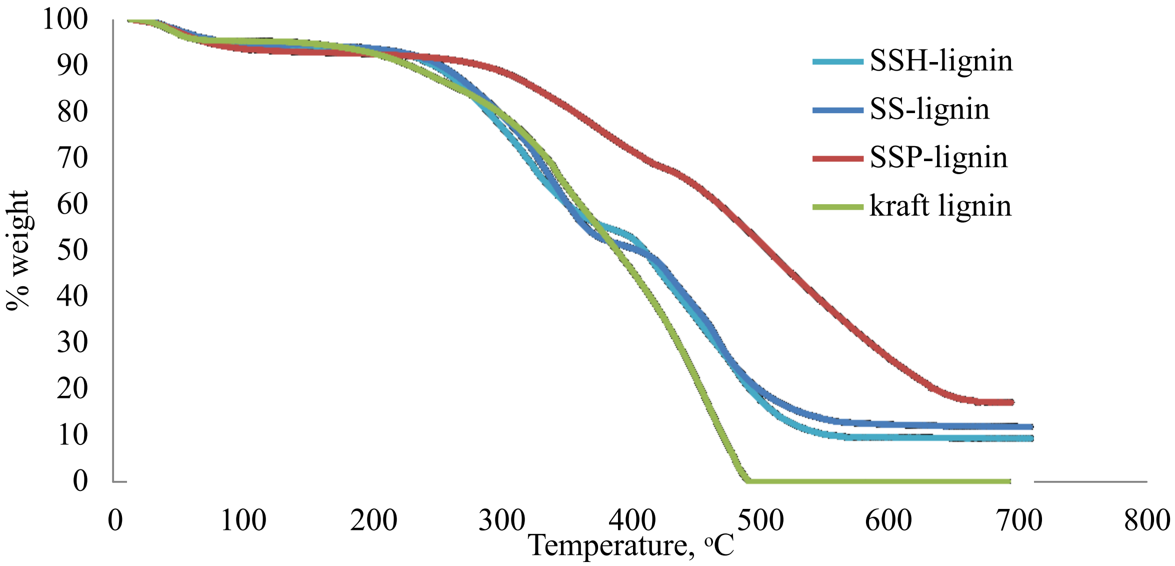

Figure 5.14. Weight loss of kraft lignin, and SS-lignin, SSH- and SSP-lignin. Experiments conducted in N_2 at 30 ml/min heated at 10 °C/min.

Figure 5.15 presents weight loss rate of kraft lignin, SS-, SSH- and SSP-lignin. It can be seen that a noticeable increase occurred at approximately 300 to 350 °C in all samples, with kraft lignin representing the highest. Of the two major peaks exhibited, the largest of these being represented at 450-500 °C, and the maximum occurring approximately around 350 °C. The smaller of these peaks, at 350 °C shows that the SSH- and SSP-lignin exhibited a less drastic drop in loss of weight, which may be due the increased intramolecular linkages which accompany phenolation and hydroxymethylation (Ma et al., 2011). However, as seen in Figure 14 the sulfonated lignin samples did not decompose and this was noted in the literature to be due to slow pyrolysis (Lv et al., 2013). The results also depicted that the modified samples all had two major peaks of decompositions, one at a temperature range of 250-238 °C, and another mainly in the range of 400-600 °C.

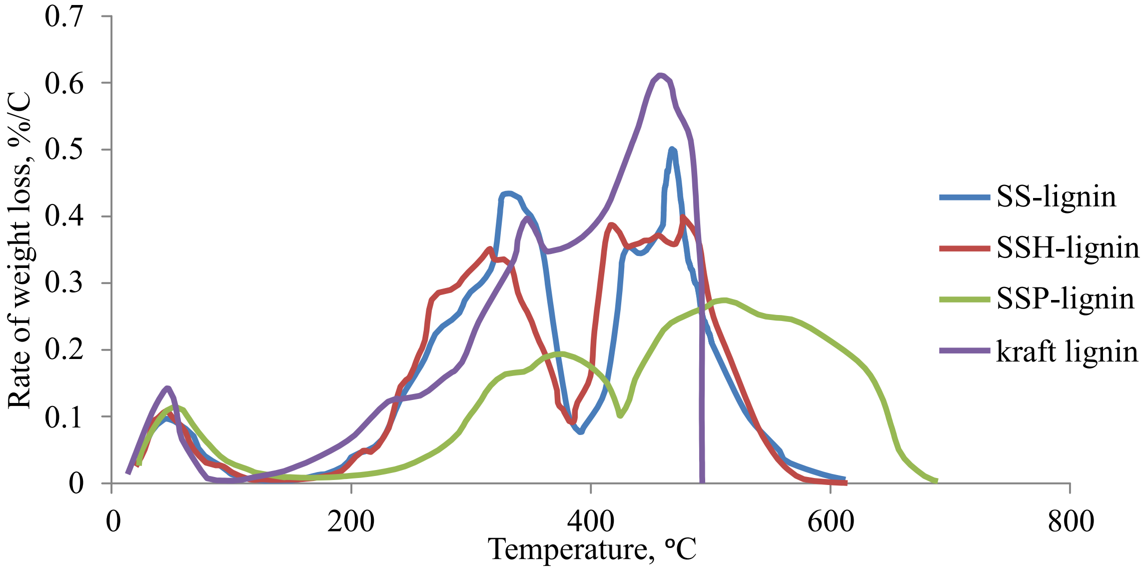

Figure 5.15. Weight loss rate of kraft lignin, SS-lignin, SSH-lignin and SSP-lignin. Experiments conducted in N_2 at 30ml/ min heated at 10°C/min.

5.3.7.Proposed sulfonation mechanism

The sulfonation mechanisms of unmodified lignin, H-lignin and P-lignin are shown in Figure 5.16-5.18.

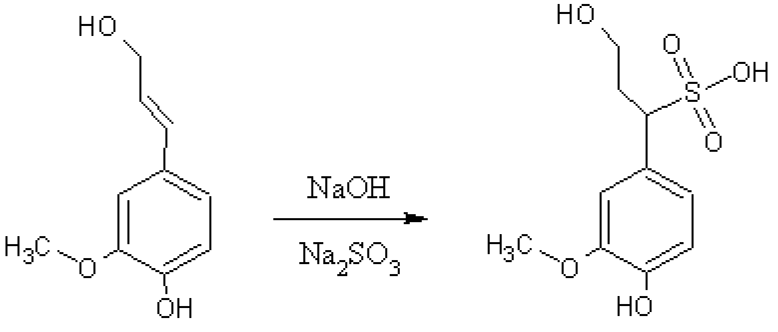

Figure 5.16. Proposed mechanism for synthesis of SS-lignin

The sulfite ion in sodium sulfite solution would be expected to react with the α-position in kraft lignin (Heden et al., 1936; Holmberg & Svensk, 1935), as seen in Figure 5.16. The sulfite group is not expected to react at the ortho position (relative to the hydroxide group) as stronger conditions are needed for aromatic substitution (Cerfontain et al., 1985).

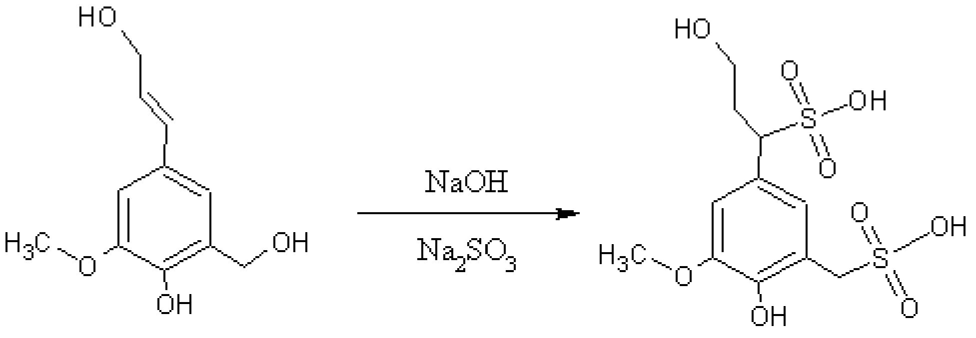

Figure 5.17. Proposed mechanism for synthesis of SSH-lignin

The sulfite group would be expected to react with the α-position (Heden et al., 1936; Holmberg & Svensk, 1935) on SSH-lignin, and at the reactive methoxy group attached through hydroxymethylation (Matsushita & Yasuda, 2005). However, the results may suggest that the sulphonated group was not attached to the aromatic ring as explained in section 5.3.5.

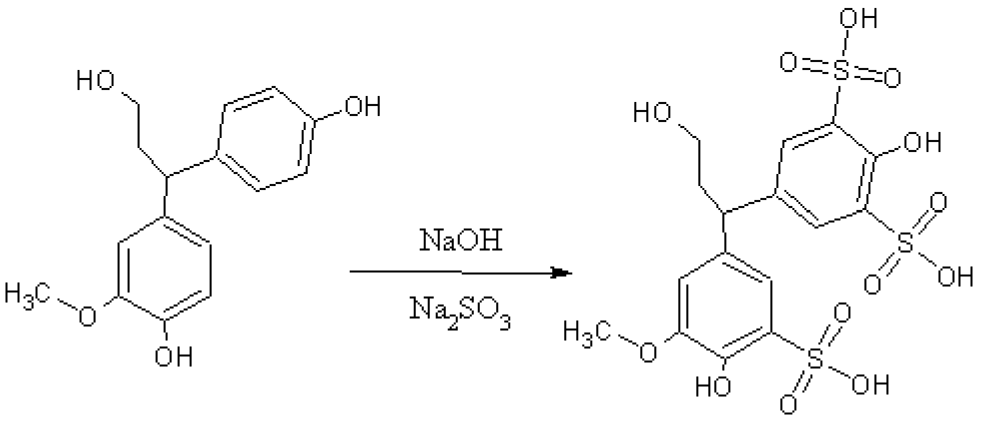

Figure 5.18. Proposed mechanism for synthesis of SSP-lignin

The sulfonation of P-lignin presents difficulties with determination of the reactive sites for sulfite group as the reactive α-position (Heden et al., 1936; Holmberg & Svensk, 1935) reacted with the phenol already. Aromatic substitution usually requires harsher conditions and this could explain why the long reaction time of 7 h was needed. The discussion in section 5.3.5 elaborated that the efficiency of this reaction was limited, similar to unmodified and H-lignin treatments.

5.4 Conclusions

The sulfonation of kraft lignin resulted in the charge density of 1.0 meq/g and a solubility of 100%, which was obtained under the conditions of 90 °C, 4.0 h and 0.67 Na_2SO_3/lignin molar ratio. The sulfonation of H-lignin resulted in a product with the charge density of 1.2 meq/g and solubility of 100%, which was obtained under the conditions of 95 °C, 3 h and 0.5 Na_2SO_3/H-lignin molar ratio. The sulfonation of P-lignin resulted in a product with the charge density of 1.2 meq/g and solubility of 100%, which was obtained under the conditions of 90 °C, 7 h and a 0.5 Na_2SO_3/P-lignin molar ratio.

GPC analysis demonstrated that the molecular weight of the SS-lignin, SSH and SSP lignin were 31161, 37161, 27010 g/mol and the molecular weight of kraft lignin was 25100 g/mol. Competing reaction of hydrolysis and alkaline condensation were most probably the cause of these changes.

FTIR analysis confirmed that the sulfonation occurred qualitatively as documented by the peaks at1040, 1110 and 618 cm^{-1}.

Charge density and conductometric analyses confirmed the charge densities of SS-, SSH-, and SSP-lignin were 1.01, 1.2 and 1.2 meq, and the sulfonation contents of 0.99, 1.01 and 1.02 meq/g, respectively.

The elemental analysis revealed that sulfur content was not indicative of an increase in charge for the SS-, SSH- and SSP-lignin, when compared to kraft lignin probably due to contamination of samples. The TGA analysis evaluated the thermal behavior of the lignin samples. Unmodified lignin exhibited a large peak at 450 °C, and was completely consumed at 500 °C, while SS-lignin had a peak at 460 °C, and was resistant to thermal degradation. The TGA analysis of SSH- and SSP-lignin showed a dramatic peak at 440 °C and 540 °C, respectively.

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Chapter 6: Various applications of sulfonated lignin

Abstract

In this work, sulfonated kraft lignin (SS-lignin), sulphonated and hydroxymethylated lignin (SSH-lignin) and sulfonated phenolated lignin (SAP and SSP-lignin) were considered for further analysis. SS-lignin was prepared with a 0.67 mol/mol ratio of Na_2SO_3/lignin, lignin concentration of 11.11 g/L, and reaction temperature of 90 °C and time of 4 h. SSH-lignin was prepared with a 0.67 mol/mol ratio of Na_2SO_3/lignin, lignin concentration of 11.11 g/L, and reaction temperature of 95 °C and time of 3 h. SSP-lignin was prepared under the conditions 0.49 mol/mol ratio of Na_2SO_3/P-lignin, of 90 °C, lignin concentration of 11.11 g/L and 7 h of reaction . Unmodified and H-lignin, which were treated with sulfuric acid (SA-, and SAH-lignin), were not selected for analysis as they were water insoluble. SAP-lignin was also prepared via reacting P-lignin with sulfuric acid at the reaction temperature of 120 °C; time of 1.5 h; and H_2SO_4/lignin ratio of 6.5 mol/mol. The solubility properties of SS-, SSH-, SSP-, and SAP-lignin were investigated in this chapter. Also, the adsorption of these lignin samples on cement admixture and their application in cement as superplasticizer were assessed. The results showed that sulfonated lignin samples were ineffective as cement superplasticizer, but initial results showed that it could be a good dispersant for kaolinite. The lignin samples had a high adsorption level on cement particles, and their adsorption was higher on precipitated calcium carbonate than kaolinite The sulfonated lignins were also found to be effective flocculants for the cationic dye ethyl violet, but less so for basic blue 3 dye.

6.1. Introduction

The need for readily available, cheap and environmentally friendly value-added chemicals is high Canada. Lignin can be used in the production of value-added chemicals. However, only 2% of lignin was being used for the creation of value-added products as of 2005 (Kubo and Kalda, 2005). Lignin can be used as a platform chemical for the development of dispersants, adsorbents and flocculants.

Various lignin species were modified and used as dispersants in cement admixture. The modification of lignin tended to increase the workability, reduce the water requirement and durability of cement. In one study, lignin was modified through the sulfonation, oxidation and hydroxymethylation, and then utilized as a superplasticizer for cement(Ouyang et al., 2009). . In one study, an twofold increase in the adsorption of lignin on cement was noted through the sulfomethylation of calcium lignosulfonate (Pang et al., 2008). The oxidation and hydroxymethylation of calcium lignosulfonate improved the adsorption amount of lignin on cement particles by a factor of 20 when compared to the sulfomethylated calcium lignosulfonate. Generally, there is a correlation between rheological properties (i.e. fluidity) and the sulfur content of a dispersant (Matsushita and Yasuda, 2005). The water requirement of cement admixture was reduced in another study through the addition of sulfonated non-wood lignin to the cement admixture (Li et al., 2011). In another study, wheat straw lignin, produced via ethanol pulping and underwent hydroxymethylation and sulfonation with Na_2SO_3 in a formaldehyde solution. It was determined that sulfonated lignin allowed for 14.9% less water usage at a higher compressive strength when compared to commercially available lignosulfonates (Li et al., 2011). Alternatively, sulfonation was conducted on non-lignin chemical compounds (i.e. phenolic resins) and the product was then used for improving the workability of cement (Hsu et al., 2000). It was stated that the addition of sulfonated phenolic resin to cement, the fluidity of the cement was increased (e.g. the slump test results was improved from 0 cm to 25 cm). This same study also found that the molecular weight of the sulfonated phenolic resin affected the workability and compressive strength, and 3×10^4 g/mol was deemed to be the optimum molecular weight. However, it is not clear if sulfonated softwood kraft lignin can be used as a dispersant for cement.

Lignin was also modified and used as an adsorbent in various studies. A study in 1992 evaluated the effect of sodium lignosulfonate on the adsorption of sodium dodecyl sulfate onto mineral surface, such as calcite and barite (Sadowski, 1992). It was shown that sodium lignosulfonate had a greater anionic charge density than did sodium dodecyl sulfate, which competed for adsorbing on the surface of barite. With this competition for a limited amount of surface, the total amount of adsorbed sodium dodecyl sulfate was reduced. In another study, kraft lignin was used as an adsorbent of Ni and V in the oil industry (Pérez et al., 2006). Other studies found that lignin and other woody materials were able to adsorb a greater amount of metals cations once sulfonated (Farag, 1995; He et al., 2014; Liang et al., 2013; Winardi et al., 2014; Yasuda and Asano, 2000; Zoumpoulakis and Simitzis, 2001).

Fillers have are used in composites and papermaking to reduce the cost of the product and to improve the properties. However, a major problem of fillers is their compatibility with other components of composites and papermaking. Previously, various lignin species were adsorbed on activated carbon, calcium carbonate, and calcium oxide; and the products were reported to be used as modified fillers in various applications such as papermaking and composites(Fatehi et al., 2013a; Fatehi et al., 2010). However, it is unclear if the sulfonated softwood kraft lignin can be used for serving for this purpose.

Flocculants have been used in the past to remove hazardous or undesirable compounds from various solutions. Commercially available flocculants include alum, ferric or synthetic organic flocculants (Li et al., 2008). Alum presents has a low solubility and thus there is residual alum after adding to water, which should be treated (Banks et al., 2006). This is a health concern for human being, as aluminum has been linked with Alzheimer's (Gonzalez-Dominguez et al., 2014). Other flocculants (e.g. ferric compounds) leave unfavorable color or taste in the water (Li et al., 2008) or converted into toxic or carcinogenic monomers (Shih et al., 2001). Lignin presents itself as an interesting compound to be converted to a flocculants as it degrades naturally into non-toxic monomers (You et al., 2009) and shows great potential due to its large and complex polyphenolic structure (Doherty et al., 2011). In 1975, lignosulfonate was used as a flocculant in the separation of insoluble compounds, such as talc ($Mg_3Si_4O_{10}(OH)_3$) and other phyllosilicates from molybdenum concentrates (Hiscox et al., 1975). Cationically modified lignin was investigated as a flocculent for anionic dye to simulate waste (Zhang et al., 2013). In this respect, it was noted that the molecular weight and charge density of flocculants presents a major role on its performance (Ahvazi et al., 2011). However, it is unknown if the sulfonated softwood kraft lignin can be used as flocculants for wastewater systems.

In this study, the solubility of synthesized sulfonated lignin samples (SS-, SSH-, SSP-, and SAP-lignin) was investigated under different scenarios; and their applications as a cement superplasticizer, as adsorbent and a flocculent for dye solutions were evaluated a. Furthermore, their adsorption performance on some fillers, such as calcium carbonate and kaolinite, was investigate to produce modified fillers.

6.2. Experimental

6.2.1. Raw Materials

In this work, washed and dried softwood kraft lignin (and a lignosulfonate solution) was supplied by FPInnovations from its pilot facilities in Thunder Bay, ON. Ethyl violet, calcium carbonate, kaolinite, sodium sulfite and lignosulfonate were all purchased from Sigma-Aldrich and used as received. Also, sodium sulfite treated kraft lignin (SS-lignin), SSH-lignin and SSP-lignin were used as raw materials in this chapter. SS-lignin was prepared with a 0.67 molar ratio of Na_2SO_3/lignin, lignin concentration of 11.11 g/L, and reaction temperature of 90 °C and time of 4 h. SSH-lignin was prepared with a 0.67 molar ratio of Na_2SO_3/lignin, lignin concentration of 11.11 g/L, and reaction temperature of 95 °C and time of 3 h. SSP-lignin was prepared under the conditions 0.49 molar ratio of Na_2SO_3/P-lignin, of 90 °C, 7 h and lignin concentration of 11.11 g/L for SS-lignin. SAP-lignin was also prepared via reacting P-lignin with sulfuric acid at the reaction temperature of 120 °C; time of 1.5 h; and H_2SO_4/lignin molar ratio of 6.5 mol/mol. The optimization processes were all discussed in previous chapters.

6.2.2. Solubility determination at different pHs

At first, 5 wt.% solution of lignin samples was prepared by adding the sulfonated lignins to deionized distilled water (pH 7), adjusted to different pH values and room temperature. These solutions were adjusted to different pH values through the addition of 2.5 M NaOH solution, or 0.4 M H_2SO_4 solution. Then, the solution concentration was adjusted to 1 wt.% , and the samples were shaken for 1 h at 100 rpm at 30 °C. After shaking, the solutions were vacuum filtered through a dried and pre-weighed filter and the precipitates were dried at 100 °C overnight. The solubility of lignin was determined according to equation 6.1:

Equation 6.1

6.2.3. Solubility determination at different concentrations

Different concentrations of lignin samples were prepared in 20 ml glass vials. A small stir bar was placed in the lignin solutions and the solutions were stirred at 600 rpm for 10 min. or until no precipitate remained. Once stirred, lignin solutions were filtered through a pre-weighed dried filter paper, which was dried at 105 °C overnight and subsequently the filters weighed. The solubility was verified by determining the amount of sulfonated lignin samples in the supernatants through the use of a UV spectroscopy, Thermo Scientific Genesys 10S UV-Vis, at 205 and 280 nm. The absorbance was compared to calibration standards to determine the concentration of sulfonated lignin in solutions.

6.2.4. Viscosity determination

Various concentrations of lignin samples were placed in 20 ml glass vials. A small stir bar was placed in the vials and the solutions were stirred at 600 rpm for 10 min or until no precipitate remained. Then, 6.7g of the lignin solution was added into a Brookfield Viscometer DV-II+ Pro, which is temperature controlled by a VWR Temperature Controller, and viscosity of the solution was determined with a temperature of 25 °C and 5 to 50 rpm.

6.2.5. Cement and kaolinite fluidity analysis

In this set of experiments, different dosages of lignin samples were added to 90 g (180 ml for kaolinite solution) water and the solution was stirred until all lignin was dissolved. 300g of cement or kaolinite was added into a mixing bowl, the lignin solution was added to cement or kaolinite and the mixture was stirred for 6 min. The fluidity of the mixture was determined by the method stablished in an earlier study using a cone (60 mm tall, 36 mm top diameter, and 60 mm bottom diameter) (Li et al., 2012). The flow value was determined from the average of two perpendicular reading of diameter of the spread cement or kaolinite paste, and is shown in Equation 6.2.The flow value increases as the final diameter becomes larger based on the addition of a dispersant.

Equation 6.2.

6.2.6. Adsorption of lignin on cement, kaolinite or PCC

In this set of experiment, 1g of cement, kaolinite or precipitated calcium carbonate (PCC) was added into 20 ml of lignin solution of varying concentrations (0- 40 g/L) and the mixtures were shaken in a water bath for 24 h, at 100 rpm at 30 °C (Pang et al., 2008). After shaking, the samples were centrifuged using a Thermo Scientific Sorvall ST 16 Centrifuge at 4000 rpm for 5 min, after which a clear supernatant was observed. The concentration of lignin remaining in solutions was measured by UV spectroscopy using a Thermo Scientific Genesys 10S UV-Vis at 205 and 280 nm. The standard solution of lignin in distilled water, adjusted to pH 10, was used for calibration. The adsorption amount was calculated by the difference in the concentrations of lignin in the supernatant before and after the adsorption test.

6.2.7. Charge density analysis of dye samples

At first, 1 wt.% solution of the cationic dyes was prepared by adding the dyes to deionized distilled water (pH 7) and room temperature. The charge densities of the cationic dyes were determined by a direct titration. To measure the charge density of soluble samples, 1 to 2 ml of the dye solution were added to the cell of a particle charge detector, Mutek PCD-04 titrator (Herrsching, Germany) and titrated against PDADMAC standard solution (~0.005M). The volume of PDADMAC solution titrated against the samples was considered for measuring the charge density using Equation 3.1. in Chapter 3.

6.2.8. Dye flocculant analysis

In this set of experiments, 0.1 wt.% standard solution of both dyes (basis blue 3 and ethyl violet) and a 0.3wt.% solution of the sulfonated lignin samples were prepared. The dye solutions were further diluted by a factor of 10, and 20 ml of the diluted samples was added to 50 ml of centrifugal tubes. Different amounts of the lignin solutions were added to the prepared ethyl violet and basic blue 3 solution. Afterward, the mixtures were shaken in a water bath at 30 °C for 10 minutes at 100 rpm. After shaking, the samples were centrifuged using a Thermo Scientific Sorvall ST 16 Centrifuge at 2500 rpm for 10 min. The absorbance of the supernatant was measured at 595 nm for ethyl violet and 654 nm for basic blue 3 by Thermo Scientific Genesys 10S UV-Vis. The effectiveness of the lignin samples as flocculants was evaluated at different ethyl violet concentrations before and after mixing. Calibration standards for ethyl violet and basic blue 3 were created and a standard curve was utilized to determine the amount the concentration of the dyes after the treatment with lignin samples.

6.2.9 pH effect on dye removal

In this set experiments, 0.1 wt.% of ethyl violet dye solution and 0.3 wt.% of lignin sample solutions were prepared. Basic blue dye was not selected for this analysis as lignin samples were ineffective in removing it. The dye solutions were further diluted by a factor of 10, and 20 ml of the diluted samples was added to 50 ml of centrifugal tubes. Their individual pH was adjusted to 3, 5, 7, 9 and 11 using either 2.5 NaOH or 2.4 M H_2SO_4 solutions. Optimum amount of lignin solutions (based on Table 6.4) were added to the ethyl violet dye solution. SS-, SSH-, SSP-, and SAP-lignin concentrations were 0.087, 0.170, 0.468, and 0.087 g/l in the dye solution, respectively. Afterward, the mixtures were shaken in a water bath at 30 °C for 10 min. at 100 rpm. After shaking, the samples were centrifuged using a Thermo Scientific Sorvall ST 16

Centrifuge at 2500 rpm for 10 min. The absorbance of the supernatants was measured at 595 nm using a Thermo Scientific Genesys 10S UV-Vis. Calibration standards for ethyl violet were created and a standard curve was utilized to determine the concentration of the dyes after the treatment with lignin samples, which helped determine dye removal.

6.3. Results and Discussion

6.3.1 Solubility of lignin samples

The charge density and MW of lignin samples that were generated in previous chapters are listed in Table 6.1.

Table 6.1. Physical properties of sulfonated lignin samples

Sulfonated lignin	Charge Density (meq/g)	Molecular weight, (g/mol)	
		Malls	UV
Softwood kraft lignin	0	25100	9679
SS-lignin	1.01	31161	8284
SSH-lignin	1.22	37161	8243
SSP-lignin	1.24	27010	4061
SAP-lignin	3.11	NR*	4155
LSSA	1.52	NR	1458

*NR: Not reported

Figure 6.1 shows the solubility (1 wt.%) of lignin samples as a function of pH. It is inferred from the Figure that unmodified kraft lignin was soluble under alkaline conditions. As the pH is lower than 10, the solubility is dramatically reduced to zero. H-lignin exhibited 55% solubility at pH 7. In contrast, P-lignin exhibits diminished solubility in alkaline conditions and requires a pH greater than 12 for a complete solubility.

Of the sulfonated lignin samples, SSH- and SAP- lignin samples exhibit complete solubility over all pH ranges. SSH-lignin has a large amount of polar groups as it contains methoxy and the sulfonated groups, they both affect the solubility of lignin and would aid in maintaining a high solubility. The high solubility of SAP-lignin can be attributed to its high charge density granted from the increased amount of sulfonated group on lignin. Also, the addition of hydroxide from phenolation may contribute to the high solubility of SAP-lignin. The smaller MW of SAP-lignin than SSP-lignin (Table 6.1) may be the reason for its higher solubility. SS-lignin was soluble under both alkaline and neutral solutions with decreasing solubility. The MW of SS-lignin was larger than that of SSP lignin, whereas SS-lignin had a smaller charge density (Table 6.1). Both of these factors contribute to its lower solubility compared to SSP-lignin.

The increase in solubility across a wide pH range allows a greater end use application. In other words, lignin should be soluble if used in water soluble application, and its high solubility over a wide pH range helps this.

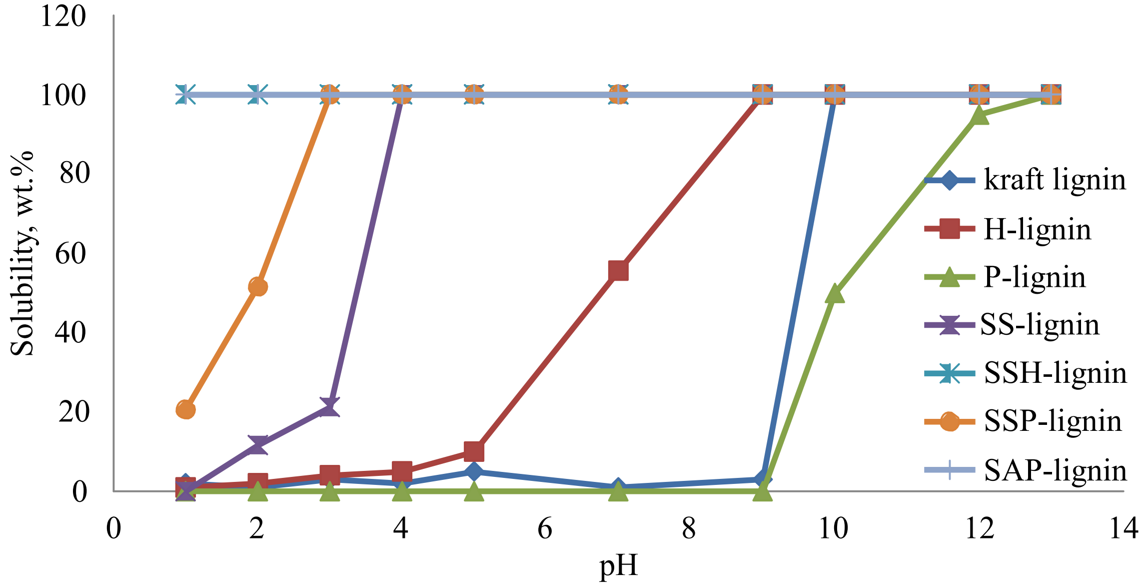

Figure 6.1. Impact of pH on solubility of lignin samples. Analysis was conducted at room temperature and pressure.

The solubility of lignin samples is shown as a function of lignin concentration in Figure 6.2. The solubility capacity provides the maximum amount of lignin that can be soluble in water, which will affect its application in end use product. For example, it can be used as a dispersant if it is soluble. Thus, a higher concentration than its saturation solubility will not improve its dispersion or flocculation affinity. It is shown in Figure 6.2 that lignosulfonates from Sigma and FPInnovations (LSSA and LSFP) exhibited greater solubility than the sulfonated lignin samples synthesized in this study. Lignosulfonate supplied from FPInnovations (LSFP) exhibited the greatest solubility with a maximum of 551 g/l, and lignosulfonate supplied from Sigma Aldrich (LSSA) had the second highest solubility of 515 g/l. The solubility of the produced lignin samples were very similar, which may be attributed to the close molecular weight of the samples. The sulfonated lignin in this study had a lower solubility than the commercially available lignosulfonate, LSSA. LSSA was determined to have a charge density of 1.52 meq/g, which was lower than the charge density of SAP-lignin, but higher than the other sulfonated lignin evaluated in this study. The molecular weight of LSSA was determined to be 1458 g/mol which is smaller than that of the sulfonated lignin in this study. For organic molecules, the lower the MW, the higher the solubility would be (Zumdahl and Zumdahl, 2007). Another reason for the higher solubility of commercial lignosulfonates is their high impurities, such as sugars (Fatehi and Ni, 2011).

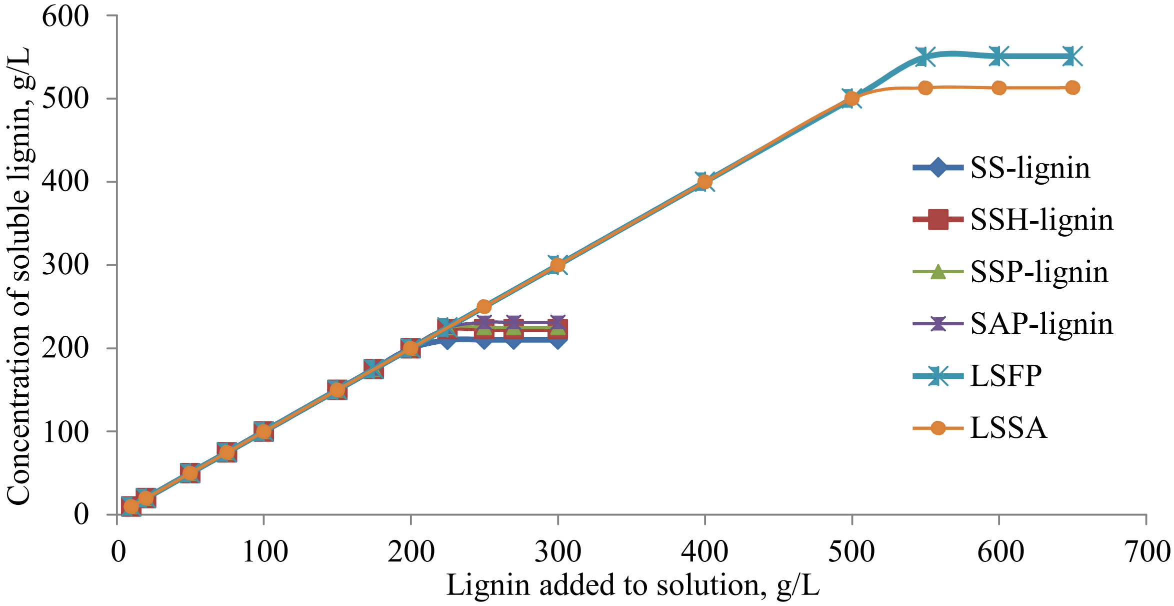

Figure 6.2. Concentration of soluble lignin as a function of lignin samples added to water at pH 7. Analysis conducted at room temperature and pressure.

6.3.2. Viscosity analysis

The dynamic viscosity of the synthesized lignin samples were analyzed and drawn in Figure 6.3. It is noted that SS-lignin requires the lowest concentration in water to dramatically increase the viscosity of water, as the viscosity increased to a 2.4 PaS at the concentration of 200 g/L. However, the commercial lignosulfonates can attain a far greater concentration prior to viscosity increases significantly. LSFP-sample was able to reach a concentration of 400 g/L before the viscosity increased to 0.78 PaS, which steeply rose to 4.36 PaS at a concentration 500 g/L. LSSA sample exhibited a similar, but less intense, pattern with an increase in viscosity to 0.5 PaS at

450g/L and 1.76 PaS at 500g/L. The lower solubility (Figure 6.2) and higher viscosity (Figure 6.3) of the lignin samples synthesized in this study than commercial lignosulfonates could be due to the impurities of lignosulfonates (water soluble compounds such as sugars). These results could indirectly imply that the MW of synthesized lignin was higher was less than those of commercial lignosulfonates. This was verified with the low MW of LSSA, as seen in Table 6.1.

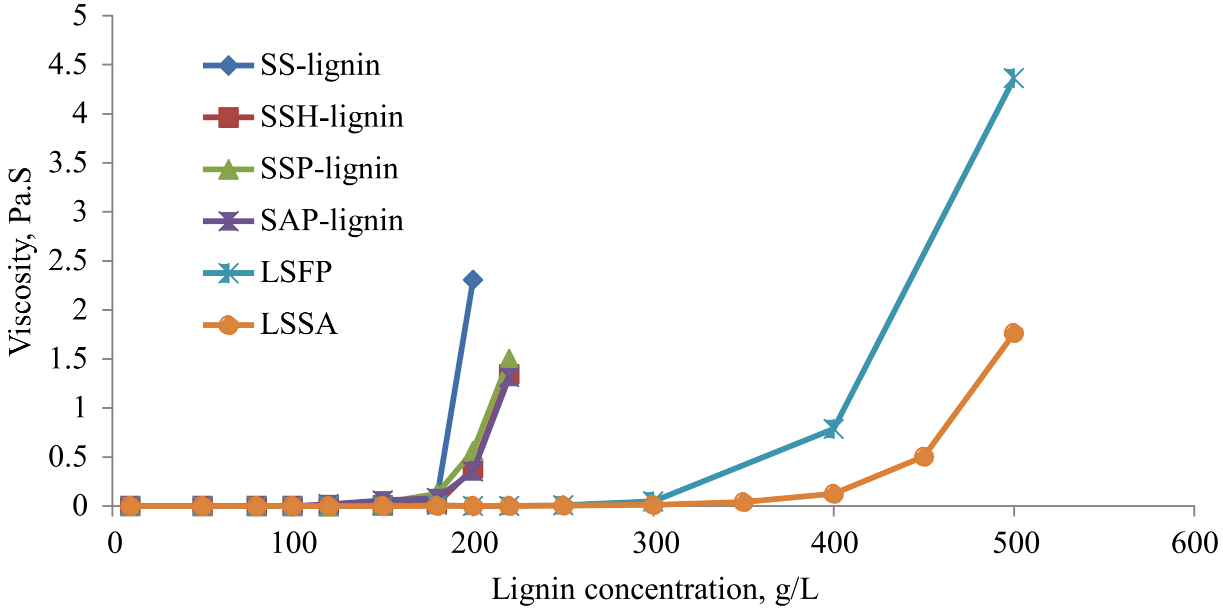

Figure 6.3. Dynamic viscosity of SS-, SSH-, SSP- and SAP-lignin as function of lignin concentration. LSSA and LSFP samples were used as reference. Analysis conducted at 25 °C.

6.3.3. Cement fluidity analysis

Figure 6.4 shows the impact of lignin samples on the fluidity of cement. The lignin samples (SS-, SSH-, SSP-, and SAP-lignin) exhibit little effect on the fluidity of cement. The increase in sulfur has been noted to increase the adsorption on cement (Dong et al., 2013) and with higher adsorptions, a greater amount of the lignosulfonates are needed in the mixture (Flatt et al., 1998). Due to limited quantity of sulfonated lignin produced in this study, this test could not be performed. However, LSFP and LSSA samples increased the cement fluidity from 55 mm to 215 mm by adding 1% lignin in the cement mixture.

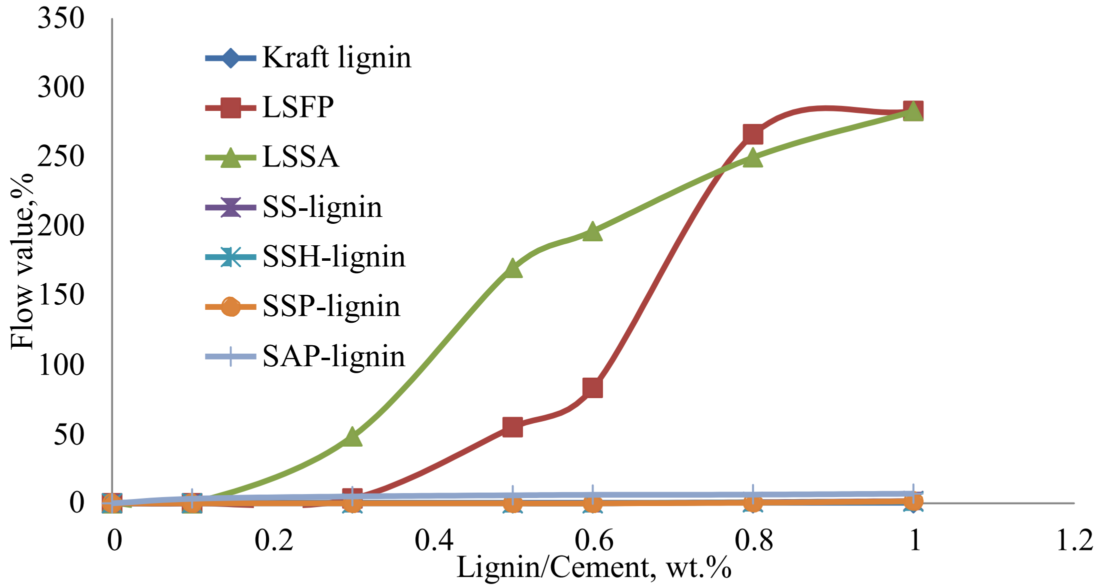

Figure 6.4. Cement fluidity spread values as a function of lignin/cement ratio in the mixture.

The impact of the SSP- and SAP-lignin (the most soluble lignin samples in Figure 6.1) on the fluidity of kaolinite was assessed at a concentration of 0.5 g/g sulfonated lignin/kaolinite ratio, and results are shown in Table 6.2. The kaolinite suspension without lignin exhibited no flow values (Li et al., 2012). By adding either of the sulfonated lignin samples (SSP and SAP-lignin), the kaolinite paste could be so spread on the plate that no results could be obtained on the flow test It is inferred from these results that lignin samples could be used to disperse kaolinite, but further analysis is needed to obtain an optimum dosage of lignin to obtain a desired flow value.

Table 6.2. Fluidity of kaolinite via adding SSP- and SAP- lignin

Lignin added to kaolinite paste	Lignin/kaolinite wt. %	Flow Value
No lignin present	0	0
SSP-lignin	0.5	Undeterminable
SAP-lignin	0.5	Undeterminable

6.3.4. Adsorption performance of lignin samples

In the literature, lignosulfonate was used as superplasticizer for cement mixtures (Ouyang et al., 2009). In an effort to understand the lack of dispersive performance of the synthesized lignin samples, their adsorption performance on cement was investigated (Hsu et al., 2000; Li et al., 2012). Figure 6.5 shows the adsorption behavior of kraft lignin on cement particles. Generally, the adsorption of lignocelluloses will reach plateau on adsorbents, which is the saturation level of adsorption on adsorbents. However, the results in Figure 6.5 exhibits that, within the scope of this study, the adsorption did not reach saturation, and a higher dosage of lignin samples is required to saturate cement.

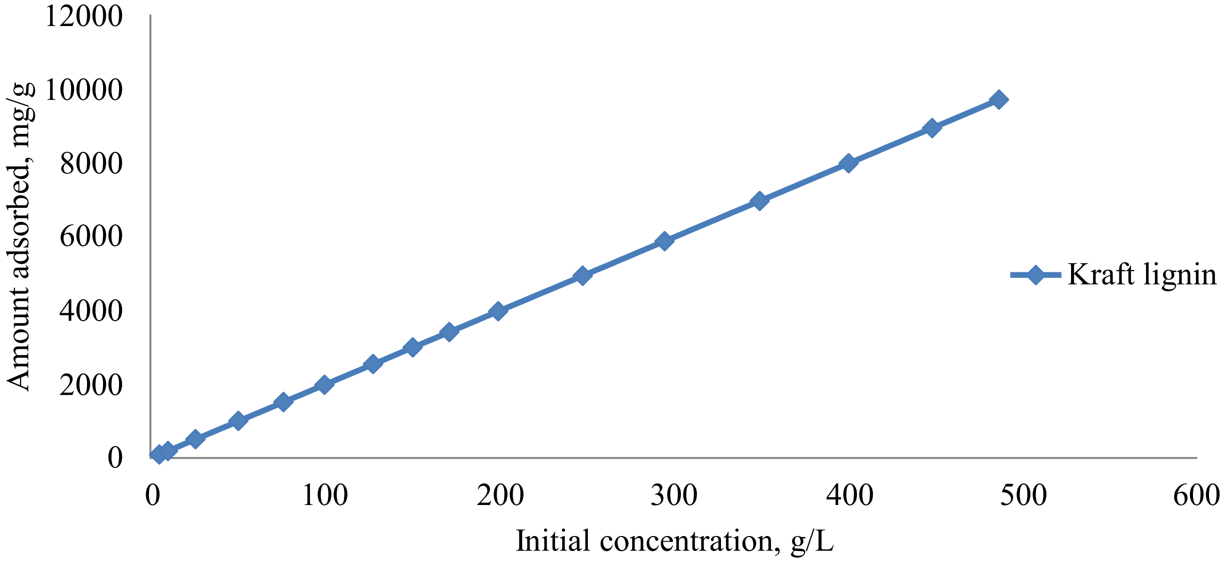

Figure 6.5. The adsorption performance of kraft lignin on cement particles. Experiments conducted at 30 °C, 24 h and 100 rpm.

In the past, an increase in the sulfur content of lignin was reported to improve its adsorption tendency on cement (Dong et al., 2013; Dos Santos et al., 2012; Fourest and Volesky, 1996; Gaballah and G., 1998; Liang et al., 2013). This is because an increase in sulfur content of lignin (a highly polar group), increase its tendency to develop bonding with adsorbent containing oxidized groups. Portland cement contains oxidized metals, such as SiO_2, Al_2O_3, Fe_2SO_3, CaO and MgO (Ali et al., 2008). Therefore, by increasing the sulfur content of lignin, its adsorption capacity is increased. Figure 6.6 shows the adsorption performance of lignin samples on cement particles. It is seen that lignin samples were all adsorbed on cement particles within the scope of this study.

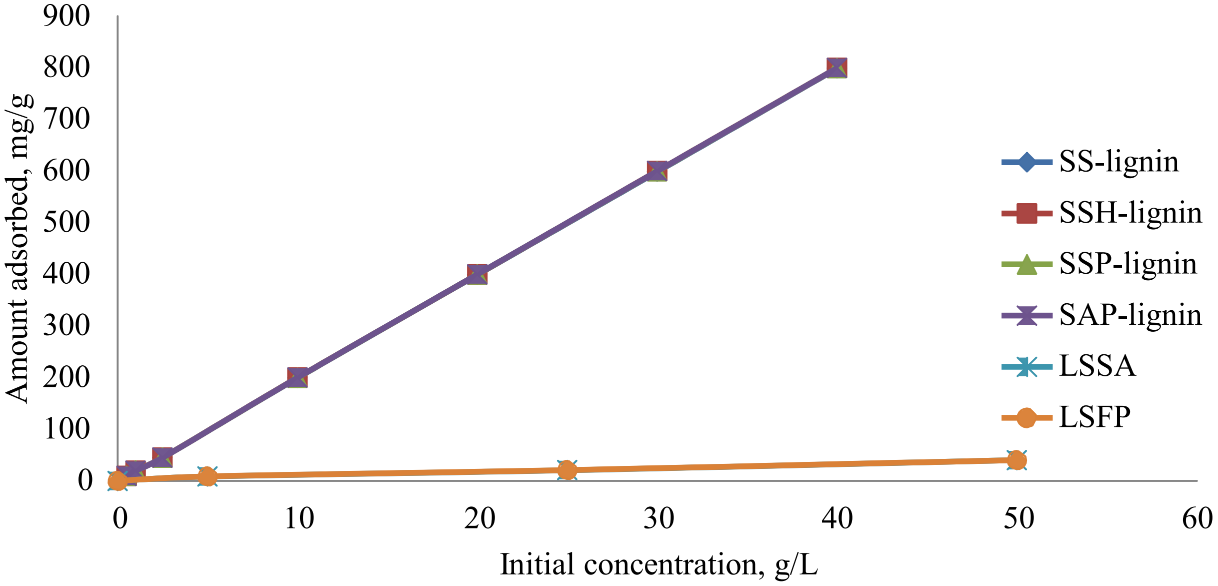

Figure 6.6. The adsorption performance of lignin samples on cement particles. Experiments conducted at 30°C, 24 h and 100 rpm.

Generally, to have a dispersive properties, the surface charge density of particles in suspension should be modified, which will occur upon a significant adsorption of adsorbate on adsorbent. However, Figure 6.5 shows that this did not occur. Alternatively, some unadsorbed dispersants (i.e. lignin samples) should be available in the suspension in order to introduce repulsion between particles in the suspension in order to improve the fluidity of suspension (i.e. cement in Figure 6.4). However, the results in Figures6.5 and 6.6 reject this phenomenon as all of added lignin samples were adsorbed on cement particles.

6.3.5. Production of modified fillers via adsorption

The adsorption of lignin samples were evaluated on kaolinite as shown in Figure 6.7. It is observable that kraft lignin did not adsorb on kaolinite, but did the sulfonated lignin samples. The SS-lignin presented the lowest adsorption, which had the lowest sulfonation degree (Chapter 5) (Farag, 1995). Other sulfonated lignin samples had close adsorption performance on kaolinite, and furthermore the low adsorption of samples on kaolinite further supports its fluidity results presented in Table 6.2. Increasing the sulfur content and molecular weight of lignin were reported to improve the adsorption of lignin (Matsushita and Yasuda, 2005) and this is mirrored by our results, as the sulfonation degree increased the adsorption in Figure 6.7. The increase in molecular weight increases the adsorption level of the sulfonated lignin (compare as the results in SSP-lignin and SAP-linin in Figure 6.7 and Table 6.1).

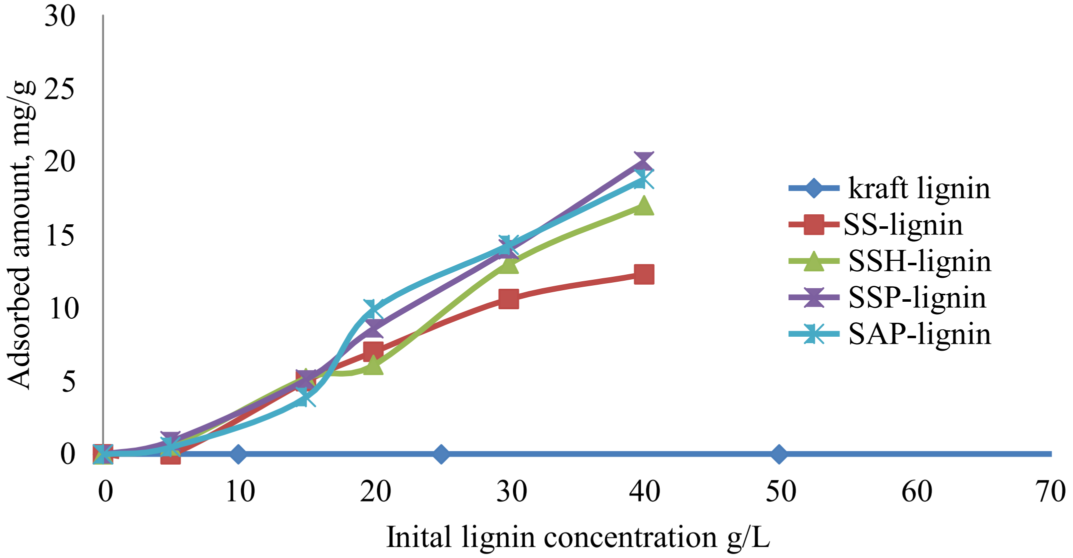

Figure 6.7. Adsorption of lignin samples on kaolinite. Experiments were performed under the conditions of 30 °C, 24 h and 100 rpm.

The adsorption performance of the sulfonated lignin samples on calcium carbonate was depicted in Figure 6.8. It is observable that kraft lignin and SS-lignin had the lowest adsorption on calcium carbonate, and SAP- and SSP- lignin had the highest adsorption capacities. In the literature, increased charge density was noted to improve the adsorption capacity of lignocellulosic materials on calcium carbonate (Fatehi et al., 2013b). This is verified by this study, as the SAP-lignin exhibits the greatest charge density and the greatest adsorption affinity. SSP-lignin represents the second highest absorbent, but has a similar charge density to SSH-lignin (which has a much lower adsorption). The difference can be accounted for by the increase in phenolic groups, as phenols were seen to adsorb to a variety of substances (i.e. have a high adsorption capacity) (Ahmaruzzaman, 2008). Increases in molecular weight were associated with an increase in adsorption capacity (Matsushita and Yasuda, 2005).

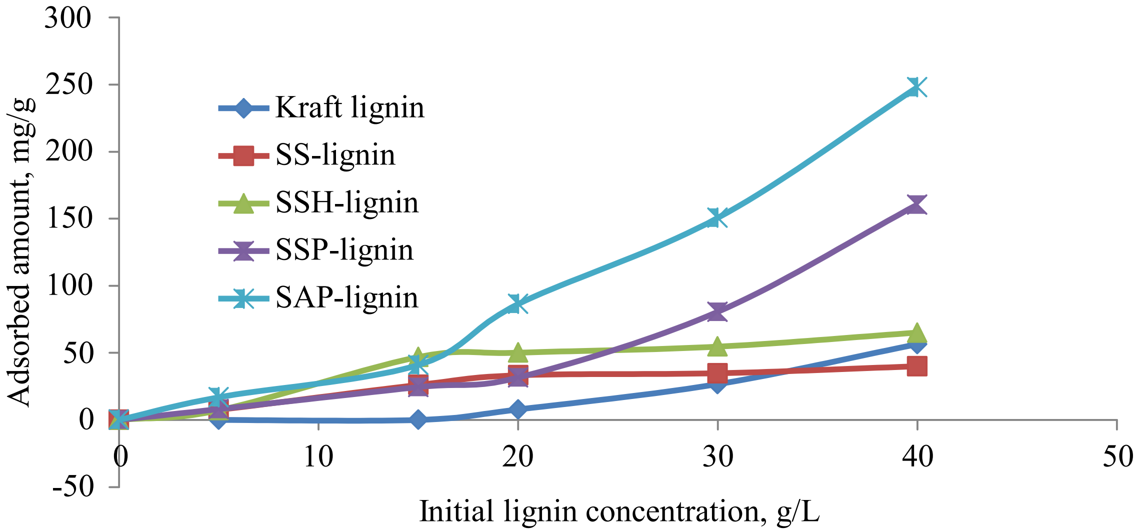

Figure 6.8. Adsorption performance of kraft, SS-, SSH-, SSP- and SAP-lignin on PCC. Experiments were conducted under the conditions of 30 °C, 24 h and 100 rpm.

Generally, charge density, MW, hydrophilicity and molecular structure of organic materials as well as the properties of adsorbents affect their adsorption performance on adsorbents. As lignin samples had different charge densities, MWs, and cement, kaolinite and PCC are physicochemically different, it is difficult to distinguish the main reason for altered adsorption performance of lignin samples on cement, kaolinite and PCC. However, the results showed that modified lignin samples had better adsorption than unmodified lignin, and the highest adsorption was achieved for SAP- and SSP-lignin samples. The surface properties of adsorbents will be different via adsorption, which depends on the properties of the adsorbed lignin samples. The modified PCC and kaolinite can potentially be used as fillers in composites or papermaking (e.g. container board).

6.3.6. Flocculation analysis

The lignin samples synthesized in this study were evaluated as flocculants. In this set of experiments, ethyl violet was chosen as a model wastewater solution, which represents the wastewater of textile industry. Ethyl violet and basic blue are cationic dye species, and as such would interact with the anionic sulfonated lignin samples (i.e. SS-, SSH-, SSP-, and SAP-lignin), form complexes that would eventually precipitates. Their respective charge density and molecular weight are shown in Table 6.3.

Table 6.3. Properties of the cationic dyes used in this study

Cationic Dye	Charge density, meq/g	Molecular weight (g/mol)
Ethyl violet	2.57	492.14
Basic Blue 3	2.29	359.19

Figure 6.9 shows the impact of lignin samples on ethyl violet dye removal. It is generally noted that , there was an optimum dosage for lignin addition in removing dye. If the dosage of lignin samples was higher than optimum, the excess amount of lignin samples produced overcharged complexes, which repelled each other and thus the precipitates were not removed from the dye solution. This is a typical behavior of flocculants in solutions. It is also noted that the lowest and highest negatively charged sulfonated lignin samples removed a similar amount of dye, (69% and 72%, respectively) with a similar lignin concentration in solutions, which implies that the charge density was not the only factor in determining the flocculation performance of lignin samples. SSH- and SSP-lignin samples required a higher dosage for effectively removing dye, and these lignin samples have a similar charge density of 1.21 and 1.24 meq, respectively. Further studies must be performed to relate the removal performance of ethyl violet dye to the properties of these sulfonated lignin samples.

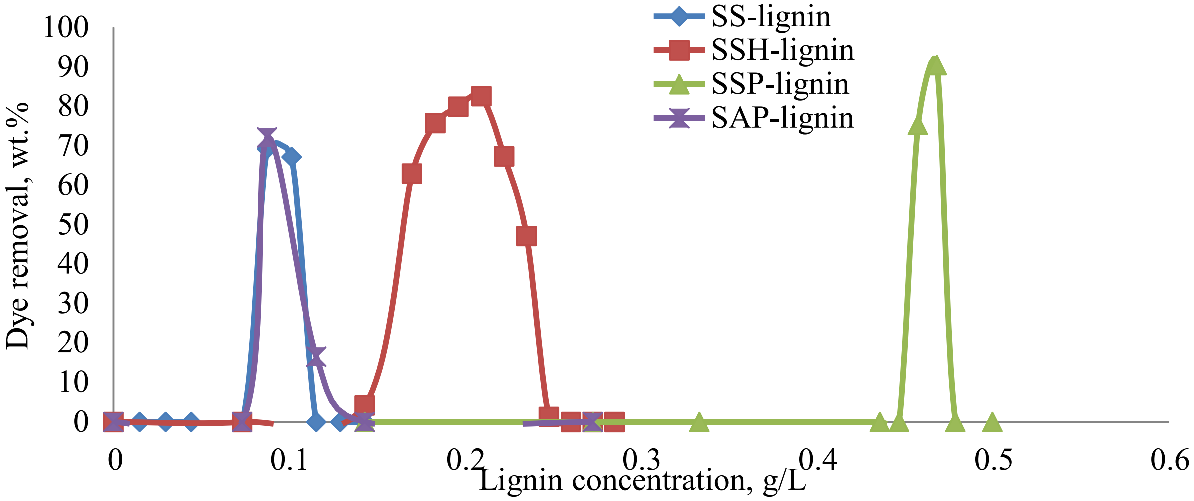

Figure 6.9. Impact of the concentration of lignin samples on the removal of ethyl violet dye from 1 g/l solution. Experiments were conducted under the conditions of 30 °C, 10 min and 100 rpm.

Figure 6.10 presents the impact of synthesized sulfonated lignin samples in removing basic blue dye from its solution. It was found that the sulfonated lignin removed only small amounts of dye from the solution (i.e. less than 10%), although the charge density of basic blue dye is similar to that of ethyl violet (Table 6.3) it is unclear why the performance of lignin samples in dye removal is different. However, the altered structures of these dye samples could be a contributing factor in lignin efficiency as a flocculant. Therefore, further studies are necessary to understand the mechanism behind this behavior.

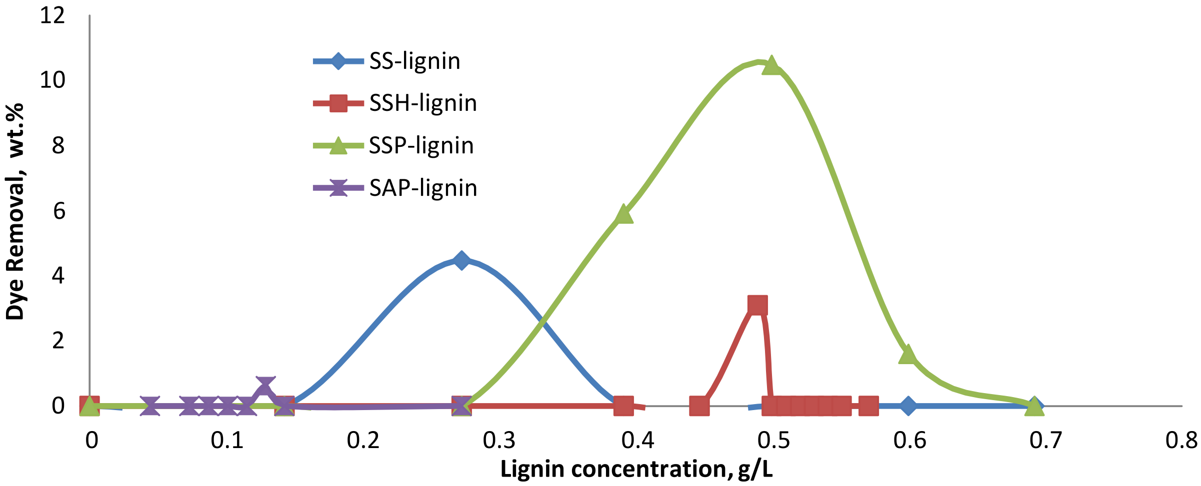

Figure 6.10. Impact of the concentration of lignin samples on the removal of basic blue 3 dye from its 1g/L solution. Experiments were conducted under the conditions of 30°C, 10 m and 100 rpm.

Table 6.4 lists the overall performance of lignin samples on dye removal. The charge density, molecular structure, and molecular weight of flocculants are crucial factors that affect their performance. (Guibal and Roussy, 2007). As the MW of lignin samples were reported to be in the same range, the impact of molecular structure and charge density should play major roles. By considering the similar charge densities of lignin samples (Table 6.1), but their different flocculation performance (Table 6.4), it can be indirectly inferred that the structure of lignin samples or dye samples played a major role. This is might be due space constrains or the extent of hydrophobicity/hydrophobicity of lignin samples or dye samples that affect their interaction performance. Further studies are required to prove this. However, the results imply that SS- and SAP-lignin samples were the best in removing dye samples even though a higher dye removal was obtained via having a higher concentration of SSP and SSH-lignin samples in solutions.

Table 6.4. The overall removal of dye from solution via applying lignin samples

Samples	Lignin/ dye (g/g)	Ethyl violet removal (wt.%)	Lignin/dye (g/g)	Basic blue removal (wt.%)
SS-lignin	2.77	69.15	67.06	4.47
SSH-lignin	6.91	82.58	193.98	3.09
SSP-lignin	17.08	90.44	57.25	10.48
SAP-lignin	2.77	72.10	220.05	0.61

The effects of pH on the flocculation efficiency of the lignin samples are shown n Figure 6.10.. It was found that SAP-lignin could remove a significant amount of ethyl violet dye over a wide range pH (3 to 9). As pH increases the cationic dye would be complexes with increasing amount of hydroxides and thus the efficiency of an anionic flocculants would drop. This shielding effect was noted in acidic conditions for cationic dye in the past (Shen et al., 2006) and we propose a similar mechanism for anionic dye in this study. The high efficiency of SAP-lignin is due to its high charge density, but the reason for the behavior of other dye is unknown and needs further studies. However ,the results clear shows that this behavior is not related to the charge density or MW of lignin samples, as explained earlier.

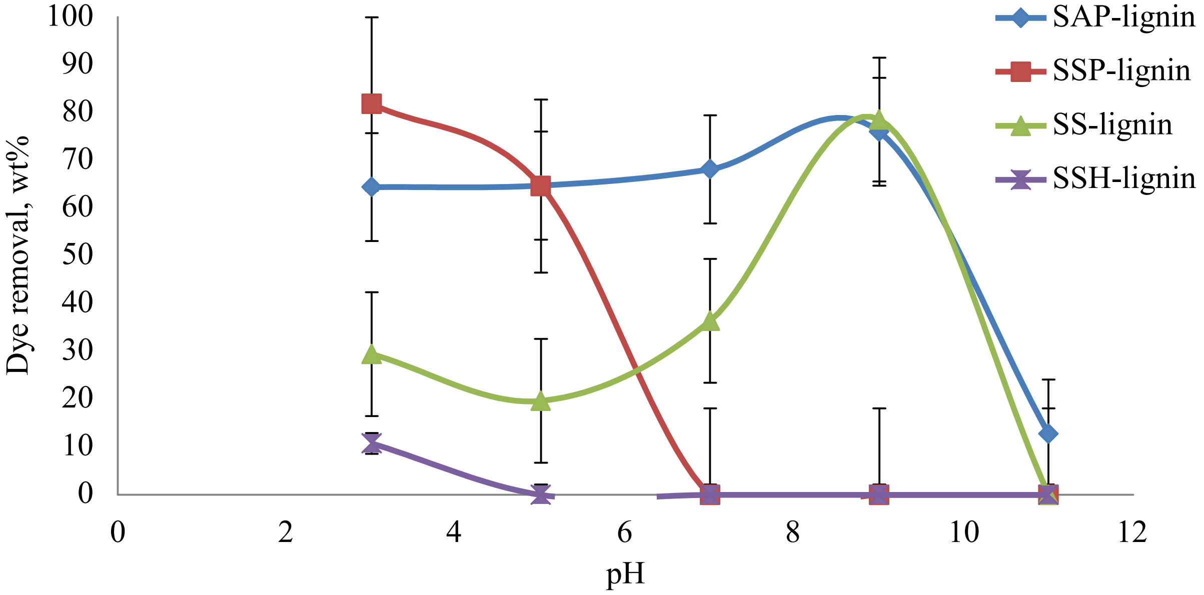

Figure 6.11. The impact of pH on the removal of ethyl violet dye from 1g/L solution. .SS-, SSH-, SSP-, and SAP-lignin concentrations were 0.087,0.170, 0.468, and 0.087 g/l in the dye solution, respectively. Experiments were conducted under the conditions of 30°C, 10 min and 100 rpm.

*

6.4. Conclusions

It can be concluded that SSP-lignin, and SAP-lignin were soluble across the tested pH range, but SS-lignin and SSH-lignin became insoluble at a pH lower than 3 and 1, respectively. It was determined that the solubility of the synthesized sulfonated lignins was lower than commercially and industrially available lignosulfonates. Due to high adsorption of unmodified and sulfonated lignin samples, the fluidity of cement admixture was not affected by the lignin samples. However, the sulfonated lignin holds promise as a dispersant for kaolinite suspension. The sulfonated lignin samples adsorbed considerably on kaolinite and precipitated calcium carbonate, which modified the surface of these fillers (modified fillers were produced for composite and papermaking). Furthermore the adsorption of lignin samples on PCC was higher than that on kaolinite. SS-, SSH-, SSP-, and SAP-lignin were successfully used as a flocculent for dye removal and they could remove 69.15, 82.58, 90.44 and 72.10 % of ethyl violet from its solution, respectively. However, the lignin samples were inefficient in removing basic blue 3 dye from its solution. The results also showed that pH has a major role in the efficiency of lignin samples for dye removal, but SAP-lignin was fairly effective in a wide pH range of 3 and 9. However, further studies are needed to understand the main mechanism behind fluidity, adsorption and flocculation performance of these lignin samples.

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Chapter 7: Conclusions and recommendations

7.1. Conclusions

In this study, washed and dried softwood kraft lignin was phenolated and hydroxymethylated in order to improve its reactivity toward sulfonation.

Hydroxymethylation was found to improve both charge density and solubility, while phenolation did not increase the charge density and solubility of kraft lignin.

Unmodified (SS-), hydroxymethylated (SSH-), and phenolated (SSP-) softwood kraft lignin were sulfonated via treating with sodium sulfite in order to produce water soluble sulfonated lignin samples. The results showed that sulfonation created soluble products with an anionic charge density in order of increasing magnitude: unmodified kraft lignin, H- lignin, and P-lignin.

The sulfonation of softwood kraft lignin, H-lignin, and P-lignin via sulfuric acid treatment did not result water soluble lignin, and the main reason was lignin condensation under strong acidic conditions. However, SAP-lignin had the greatest charge density of the current study.

The sulfonated kraft lignin had inferior fluidity results compared with commercial lignosulfonates. The sulfonated lignins exhibited an improved solubility across the pH range when compared with unmodified kraft lignin.

The addition of the sulfonated lignin samples to cement exhibited no marked improvement compared to unmodified kraft lignin in terms of fluidity. The fluidity of kaolinite mixture was significantly improved via adding SSP and SAP lignin to it. The sulfonated lignins generally exhibited a greater adsorption than unmodified kraft lignin on calcium carbonate and kaolinite, which implies that they could be used to produce modified fillers. Furthermore, the sulfonated lignin samples were found to be effective in flocculating dye solution, which implies that the lignin samples could be used as flocculants for textile industry.

7.2. Recommendations

In an effort to understand the structural differences between softwood kraft lignin, SS-, SSH-, SSP-, and SAP lignin, nuclear magnetic resonance spectroscopy of the samples should be undertaken. Structural elucidation of kraft, H-lignin and P-lignin before and after the reactions could reveal the reaction mechanism of the sulfonated lignins. The molecular weight analyses of all samples should be considered as future work, as it is determining factor in charactering the properties of lignin-based products.

Other sulfonation procedures, such as sulfomethylation using different chemicals should be investigated and the properties of the products should be assessed and compared with those of the products of this study and of commercial lignosulfonate in order to formulate a process for producing sulphonated lignin with desired properties.

The application of lignin-based products in cement admixture should be conducted in depth. Basically, the reaction mechanics of sulfonation should be adjusted so that the lignin-based products can be dispersants for cement admixture. This can be conducted by relating the properties of lignin and its performance in cement. After adjusting this, the impact of lignin-based dispersants on the strength properties of cement should be studied.

The adsorption properties of sulphonated lignin on fillers should be studied in more details and under different scenarios in order to produce modified fillers with desired properties. In this case, the desired properties should be an indicator of the extent of lignin adsorption on fillers. Also, the desorption of the already adsorbed lignin from the fillers should be investigated. The application of sulphonated lignin as a flocculent should be investigated in more details and under various environments. This will provide guidelines for generating lignin-based flocculants for wastewater of different industries. As our results were promising, more focus should be on this application.

Another avenue of research could be a comparison between the performance of sulfonated hardwood and softwood kraft lignin in various applications. The difference in phenyl propene ratio’s and molecular weight may produce sulfonated lignin with different properties.

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