Production of Sulfur Containing Kraft Lignin Products

John P. W. Inwood, Leila Pakzad, and Pedram Fatehi*

Kraft lignin is produced in great quantities in many countries, but is mainly used as an energy source. To valorize its potential end-use applications, softwood kraft lignin was modified *via* sulfuric acid and sodium sulfite treatments in this study. The modification of kraft lignin through a sulfuric acid treatment resulted in a modified lignin (SA-lignin) with a charge density of 0.8 meq/g but with a limited water solubility. The sulfonation of the kraft lignin through a sodium sulfite treatment induced a soluble sulfonated lignin (SS-lignin) with a charge density of 1.4 meq/g, which was obtained under the conditions of 90 °C, 4 h, and 0.67 Na_2SO_3/lignin molar ratio. The elemental compositions, molecular weights, and thermal and rheological properties of modified lignin samples were characterized.

Keywords: Kraft lignin; Sulfonation; Biorefining; Dispersants; Biomass; Industrial effluents

*Contact information: Department of Chemical Engineering, Lakehead University, 955 Oliver Road, Thunder Bay, Canada P7B5E1; *Corresponding author: pfatehi@lakeheadu.ca*

INTRODUCTION

Lignosulfonates are the by-products of the sulfite pulping process. They are water-soluble lignin-based products that are currently used as dispersants for various applications (Shin and Rowell 2005). Recently, the production of lignosulfonates has been declining. The number of sulfite pulping operations has been substantially reduced in many countries (Bleischwitz *et al.* 2009). Kraft is the dominant pulping process in the world. While papermaking pulp is the primary product, kraft lignin is produced as a co-product, and it is burned and used as an energy source. Otherwise, kraft lignin has limited industrial applications due to its poor reactivity and limited water solubility (Suparno *et al.* 2005; Cui *et al.* 2015).

Sulfonation is a reliable method for modifying lignocellulosic materials (Shin and Rowell 2005) including hardwood lignin (Crist *et al.* 2003) and cellulose (Syahbirin *et al.* 2012) in order to widen their end-use applications in aqueous systems. In the past, the sulfonation process was conducted under different conditions on polymers containing aromatic rings such as benzene (Zhang *et al.* 2007), toluene (Kaandorp *et al.* 1962), tert-butyl benzene (Kaandorp *et al.* 1963a), polystyrene (Kaandorp *et al.* 1963b), and poly oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene (Akovali and Ozkan 1986).

Sulfuric acid in vapor and concentrated liquid forms has been used for sulfonating polystyrene beads (Neihof 1954; Kim *et al.* 1990; Shibuya and Porter 1992), while chlorosulfonic acid is used for sulfonating wood (Theodoropoulos *et al.* 1993). However, the gaseous treatment of sulfuric acid includes dangerous operating conditions for industrial scale operations. Chlorosulfonic acid is costly because it must be used in non-aqueous based systems, which is difficult to implement commercially. Shin and Rowell (2005) used sodium sulfite in the sulfonation of *Juniperus monosperma* to create a lignocellulosic biosorbent for cadmium. Once sulfonated, modified lignin can be used as a dispersant in different media, similar to lignosulfonate produced in a sulfite pulping process

(Fatehi and Ni 2011a; Xie and Shi 2011). Such a process has potential to help kraft pulping processes gain additional revenues from a new value-added product.

Sodium sulfite treatment has been conducted on hydroxymethylated acid hydrolysis lignin to produce a lignosulfonate-based dispersant (Fatehi and Ni 2011b). The main objective of this work was to evaluate the improvement of solubility and charge density of lignin *via* introducing sulfur containing groups to kraft lignin with sulfuric acid and sodium sulfite treatments under different scenarios. Although reaction chemistries of sodium sulfite and sulfuric acid treatments of biomass were discussed in the past (Kaandorp *et al.* 1962, 1963a, 1963b; Shibuya and Porter 1992; Zhang *et al.* 2007), the impact of sulfuric acid and sodium sulfite treatments on the chemical properties (*i.e.*, charge density, molecular weight), thermal stability, and physical properties (*i.e.*, solubility and viscosity) of kraft lignin has not been reported, which is the main novelty of this work. The characteristics of the products, *i.e.*, sulfuric acid treated lignin (SA-lignin) and sodium sulfite treated lignin (SS-lignin), were evaluated with a particle charge detector, Fourier transform infrared spectrophotometry (FTIR), and thermogravimetric analysis (TGA). Based on the results, the conditions that yielded the modified lignin with the highest charge density and solubility were determined. The main novelty of this work was to provide information about the impact of two industrially attractive processes (*i.e*. sulfuric acid and sodium sulfite treatment) on the modification of lignin to produce water soluble products.

EXPERIMENTAL

Materials

Softwood kraft lignin was produced *via* LignoForce™ technology by FPInnovations and received from its laboratory located in Thunder Bay, ON, Canada. 3-(Trimethylsilyl) proionic-2,2,3,3-d acid sodium salt (TSP), poly (diallyldimethylammonium chloride) solution (PDADMAC) with a molecular weight (M_w) of 100,000 to 200,000 g/mol (20 wt.% in water) and lignosulfonate (LSSA) samples were all supplied by Sigma-Aldrich (Markham, ON, Canada). Sulfuric acid (98% purity) was provided by Fisher Scientific (Whitby, ON, Canada). Anionic polyvinyl sulfate (PVSK) with a M_w of 100,000-200,000 g/mol (98.4 wt.% esterified) was supplied by Wako Pure Chemical company (Richmond, VA, USA), and Tego@trant A100 polymer was received from Metrohm (Mississauga, ON, Canada).

Modification of Lignin

Unmodified kraft lignin (0.5 g to 1.0 g) was reacted with 1.5 g to 20 g of H_2SO_4 in round bottom glass flasks, which were vortexed at 2,900 rpm for 1 min using a Fisher Scientific Mini Vortexor (to ensure an homogenous mixture), sealed, and placed in an oil bath at a temperature of 80 °C to 160 °C for 0.5 h to 3 h. The reaction parameters were lignin/H_2SO_4 (aq) molar ratio ranging from 6.5 to 92.6, reaction times from 0.5 h to 3 h, and temperatures from 80 °C to 160 °C.

Alternatively, 0.5 g to 1.0 g of unmodified lignin was reacted with sodium sulfite (Na_2SO_3) in a multitude of conditions. The reaction parameters were the Na_2SO_3/lignin molar ratio of 0.2/0.7, reaction time of 1 h to 7 h, temperatures of 50 °C to 95 °C, and lignin concentrations of 7.4 g/L to 16.7 g/L. All reactions were conducted in a 500 mL three-neck glass flask with a magnetic stirrer at 300 rpm and assembled with a thermometer and a graham condenser in an effort to eliminate the loss of sulfonation reagents through evaporation.

After completion, both reactions were stopped via neutralization with NaOH or sulfuric acid. The reaction solution mixtures were cooled to room temperature and then placed in membrane dialysis with a molecular cut-off of 1,000 g/mol for 48 h (while changing water every 6 h) in order to separate unreacted monomers from the products. The samples collected from membrane were then dried in a 60 ºC oven overnight. The lignin treated with sulfuric acid and sodium sulfite were denoted as SA-lignin and SS-lignin, respectively.

Charge Density and Solubility

First, 1 wt.% lignin solution was prepared *via* mixing 0.5 g of dry lignin samples with 49.5 g of deionized water. After adjusting the pH to 7, the suspension was shaken for 1 h at 100 rpm and 30 °C. After mixing, the suspensions were centrifuged at 1000 rpm for 5 min at 30 °C in order to separate soluble lignin from insoluble lignin. After centrifugation, a part of the filtrate was dried at 105 °C overnight to determine its lignin concentration. By considering the mass of water (49.5 g) and the concentration of lignin in the filtrates, the mass of dissolved lignin was determined. The solubility of the lignin sample was reported as a weight percentage (wt.%) at 30 °C according to Eq.1.

$$Solubility\ (wt.\%) = \frac{mass\ of\ dissolved\ lignin}{initial\ mass\ of\ lignin} \times 100 \tag{1}$$

The other part of the filtrate was taken for a charge density analysis of soluble lignin, while precipitates were oven-dried at 60 °C for the charge density analysis of insoluble lignin. The charge density of soluble lignin samples (CDSL) was determined by direct titration, while the charge density of insoluble ones was identified by back titration. To measure the charge density of soluble samples, 1 mL 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 a PDADMAC standard solution (~0.005 M) according to Eq. 2.

$$Charge\ density\ of\ soluble\ lignin\ \left(\frac{meq}{g}\right) = \frac{Vol.titrant \times conc.titrant}{mass\ of\ lignin} \tag{2}$$

To measure the charge density of insoluble lignin samples (CDIL), approximately 0.05 g of dried insoluble lignin samples was mixed with a PVSK standard solution (~0.005 M) for 1 h at 30 °C. The concentrations 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 Eq. 3.

$$Charge\ density\ of\ insoluble\ lignin\ (\frac{meq}{g}) = \frac{(vol.PVSK\ for\ control - vol.PVSK\ for\ sample) \times conc.PVSK}{mass\ of\ lignin} \tag{3}$$

Three replicates for each sample were carried out, and the average was reported.

Elemental Analysis

The elemental analysis of lignin samples was conducted using a Vario EL Cube instrument (Langenselbold, Germany) as described in the literature (Matsushita and Yasuda 2005). The lignin samples were combusted, and the combusted gases were reduced in order to be identified by the instrument. The elemental balance of the lignin samples was developed from this combustion 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.

Thermogravimetric Analysis

Thermal behavior of the lignin samples before and after treatment was assessed by thermogravimetric 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., Kingstown, RI, USA) using N_2 (30 mL/min) with an increment rate of 10 °C/min in the temperature range of 25 °C and 800 °C (Fadeeva *et al.* 2008).

Structural Analysis

A Fourier transform infrared spectrophotometer (Milton, ON, Canada) was used to analyze the functional groups associated with the lignin samples (0.5 g oven-dried) before and after treatment.

Molecular Weight Analysis

In this set of experiments, 100 mg of dried lignin samples were suspended in 4.0 mL of acetic anhydride/pyridine 1:1 (V:V) solution stirring for 30 min at 25 °C and 300 rpm, and then kept in the dark for 24 h. The resulting solution was added to an excess (50 mL) of cold water and centrifuged/washed three times. The solvent was then removed from the samples by a freeze dryer. The acetylated samples were dissolved in 10 mL of tetrahydrofuran (THF) by stirring at 300 rpm at room temperature for 30 min and then filtered with a PTFE filter (13 mm diameter and 0.2 µm pore size). The filtered samples were used for a molecular weight analysis. The molecular weight analysis of the samples was determined using a gel permeation chromatography system, Malvern (Montreal, QC, Canada) GPCmax VE2001 Module + Viscotek TDA305 with multi-detectors (UV, RI, viscometer, low angle, and right angle laser detectors). The organic columns PolyAnalytic PAS106M, PAS103, and PAS102.5 were used for a molecular weight analysis, and HPLC-grade tetrahydrofuran (THF) was used as solvent and eluent. The flow rate was set at 1.0 mL/min.

RESULTS AND DISCUSSION

Treatment with Sulfuric Acid

Figure 1 illustrates the charge density of soluble lignin (CDSL) and insoluble lignin (CDIL) as well as the solubility of the sulfuric acid treated lignin (SA-lignin) as a function of H_2SO_4/lignin molar ratio. By increasing the molar ratio of sulfuric acid to lignin, the CDSL was slightly reduced, while CDIL remained almost constant. These charged groups originate from sulfonate and sulfate groups attached to aromatic and aliphatic parts of lignin during sulfuric acid treatment (Zhang *et al.* 2014a). In another study, increasing the acid/lignin ratio (from 6.5 to 13) caused the sulfonated group attached to novolac-lignin and novolac-hydroxymethylated lignin to increase (Cerfontain *et al.* 1985). Figure 1 also shows that the solubility of SA-lignin was between 6 and 8 wt.%. The chemical modification of lignin with sulfuric acid is a balance between the addition of charged groups to lignin (to the α position on aliphatic chain or to the phenolic hydroxide group on the ring) and condensation (*i.e.*, polymerization of lignin) in the α position on the aliphatic chain of lignin (Shimada *et al.* 1997; Yasuda *et al.*1999; Zoumpoulakis and Simitzis 2001). The lignin source and structure play important roles in the accessibility of these sites for the modification and condensation (Shimada *et al.* 1997; Yasuda *et al.*1999; Zoumpoulakis and Simitzis 2001). In contrast to a previous report (Cerfontain *et al.* 1985), condensation was dominant in that it reduced the solubility of kraft lignin when acid concentration increased.

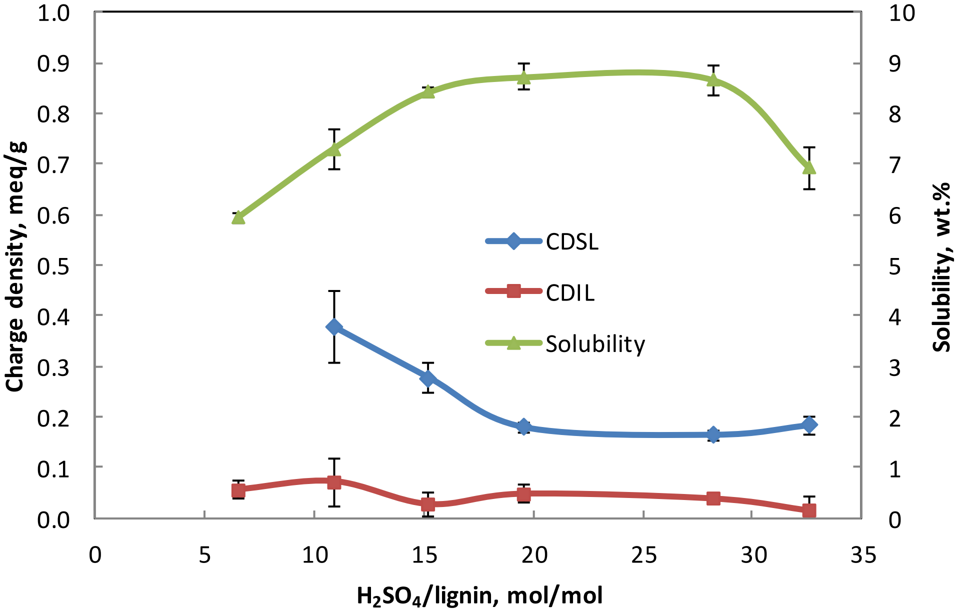


Fig. 1. Charge density of soluble lignin (CDSL), charge density of insoluble lignin (CDIL), and solubility of the SA-lignin as a function of H_2SO_4/lignin molar ratio. Experiments were conducted at 140 °C and 1 h

Figure 2 presents the charge density of the soluble lignin (CDSL) and the insoluble lignin (CDIL) as well as the solubility of the sulfuric acid treated lignin (SA-lignin) as a function of reaction temperature. As temperature increased, the CDSL decreased from 0.7 meq/g to 0.2 meq/g. This reduction is attributed to the condensation reaction, as the energy needed for condensation is less than lignin modification (Zoumpoulakis and Simitzis 2001). However, the effect of reaction temperature on the charge density of insoluble lignin was insignificant.

Figure 3 shows the impact of time on CDSL, CDIL, and the solubility of SA-lignin. By extending the reaction time, the CDSL decreased from 0.5 meq/g to 0.2 meq/g. As stated earlier, the increased time will provide conditions for the production of a more stable product, which in this case is the self-condensed guaiacyl product.

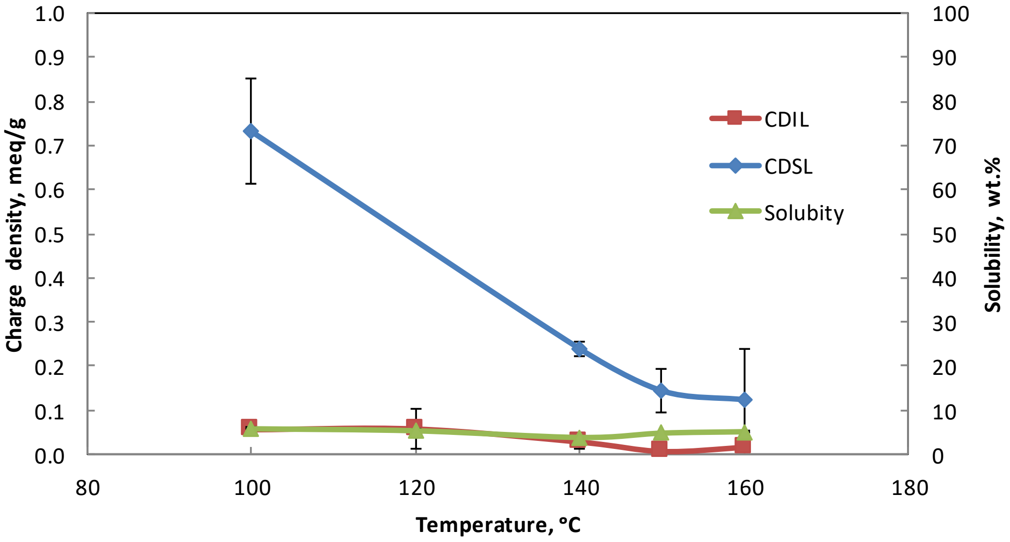


Fig. 2. Charge density of soluble lignin (CDSL), charge density of insoluble lignin (CDIL), and solubility of SA-lignin as a function of temperature. Experiments were conducted at a 6.5 molar ratio of H_2SO_4/lignin and 1 h.

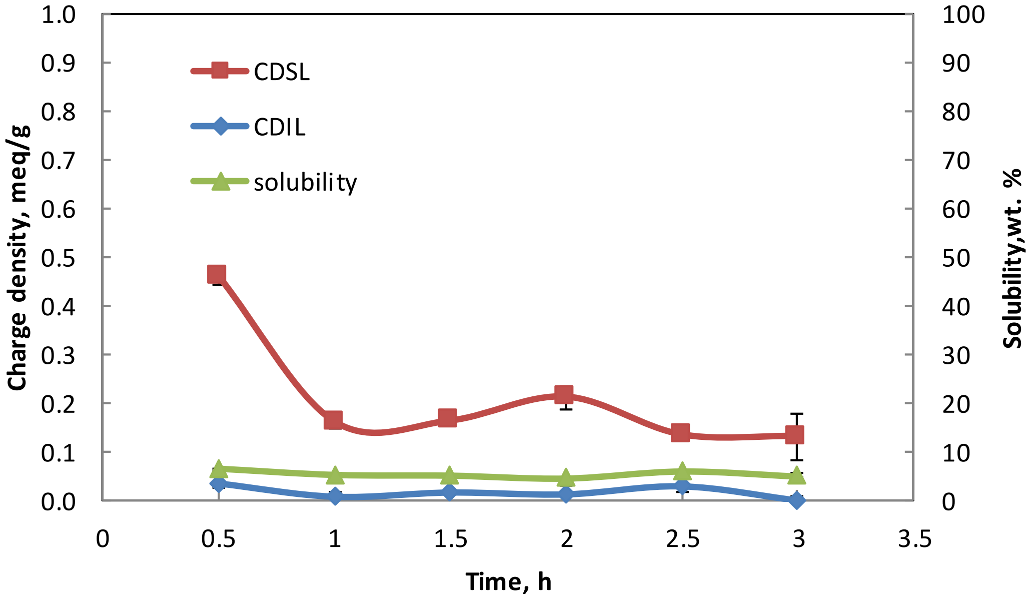


Fig. 3. Charge density of soluble lignin (CDSL), charge density of insoluble lignin (CDIL), and solubility of SA-lignin as a function of time. Experiments were conducted at a 6.5 molar ratio of H_2SO_4/lignin and 140 °C.

The results in Figs. 1 through 3 show that a product with a small CDSL (ranging from 0.2 meq/g to 0.8 meq/g) was produced through the modification 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. It has been suggested that the intramolecular condensation protects the reactive site of the guaiacyl lignin (Shimada *et al.* 1997). There is a proposed similar protection for the reactive site of the self-condensed guaiacyl products against sulfonation. The self-condensed guaiacyl product may prevent the grafting of lignin through steric hindrance and therefore inhibit the modification reaction. In this case, the condensation at the α position of aliphatic chain could eliminate the occurrence of other reactions at the α position (Yasuda *et al.* 1999).

Based on the results above, the optimum conditions for the SA-lignin was the temperature of 100 °C, reaction time of 0.5 h, and H_2SO_4/lignin molar ratio of 15.2 mol/mol, which generated SA-lignin with the charge density of 0.8 meq/g.

Modification through Sodium Sulfite Treatment

Figure 4 shows the CDSL, CDIL, and the solubility of SS-lignin as a function of the Na_2SO_3/lignin ratio. The CDSL of SS-lignin was independent of the Na_2SO_3/lignin molar ratio. The solubility of 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. Syahbirin *et al.* (2012) showed that the fluidity 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 was probably the maximum for the modification reaction of lignin.

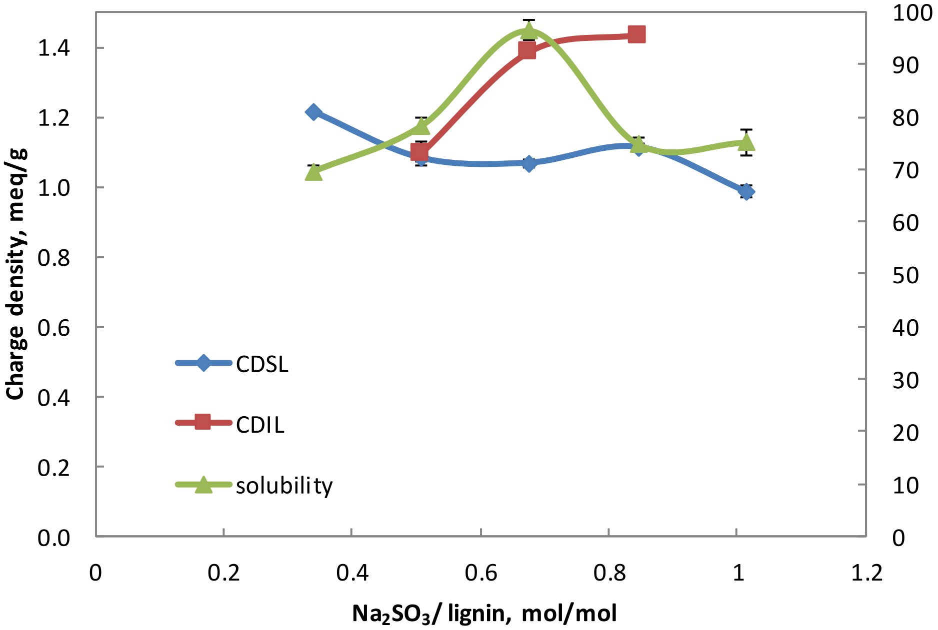


Fig. 4. The charge density of soluble lignin (CDSL), charge density of insoluble lignin (CDIL), and solubility of SS-lignin as a function of Na_2SO_3/lignin molar ratio. Experimental conditions were 95 °C, 2 h with a lignin concentration of 11.11 g/L.

Figure 5 shows the impact of temperature on the CDSL, CDIL, and solubility of the SS-lignin product. There was 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 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 a temperature greater than 80 °C, the condensation of the guaiacyl subunit became more prominent. The self-condensation of guaiacyl is favored at higher reaction temperatures (Theodoropulos *et al.* 1993). As stated previously, the condensation could occur in acidic conditions by the sulfuric acid reagent; condensation also occurs in alkaline conditions (Gierer *et al.* 1964; Yu *et al.* 2013).

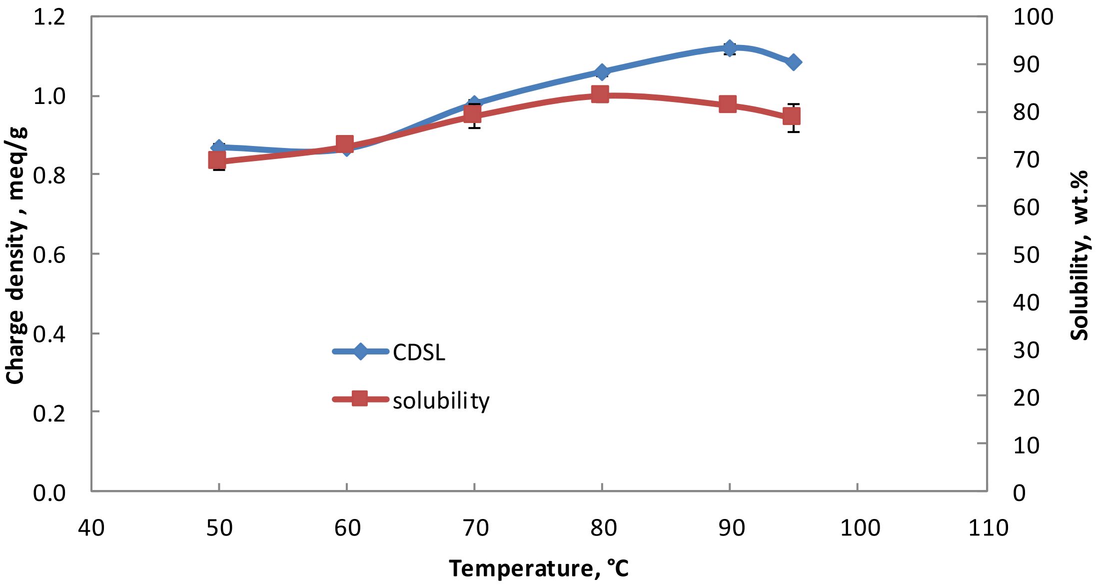


Fig. 5. The charge density of soluble lignin (CDSL) and solubility of SS- lignin as a function of temperature. Experimental conditions were Na_2SO_3/lignin molar ratio 0.50, 2 h, and lignin concentration of 11.11 g/L.

Figure 6 shows that the impact of time on the CDSL, CDIL, and solubility of SS-lignin. Reaction times varied from 1 h to 4 h, and the CDSL and CDIL of SS-lignin increased from 0.9 meq/g to 1.2 meq/g 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, as the solubility of the SS-lignin was high, an insufficient amount of insoluble SS-lignin remained for further analysis.

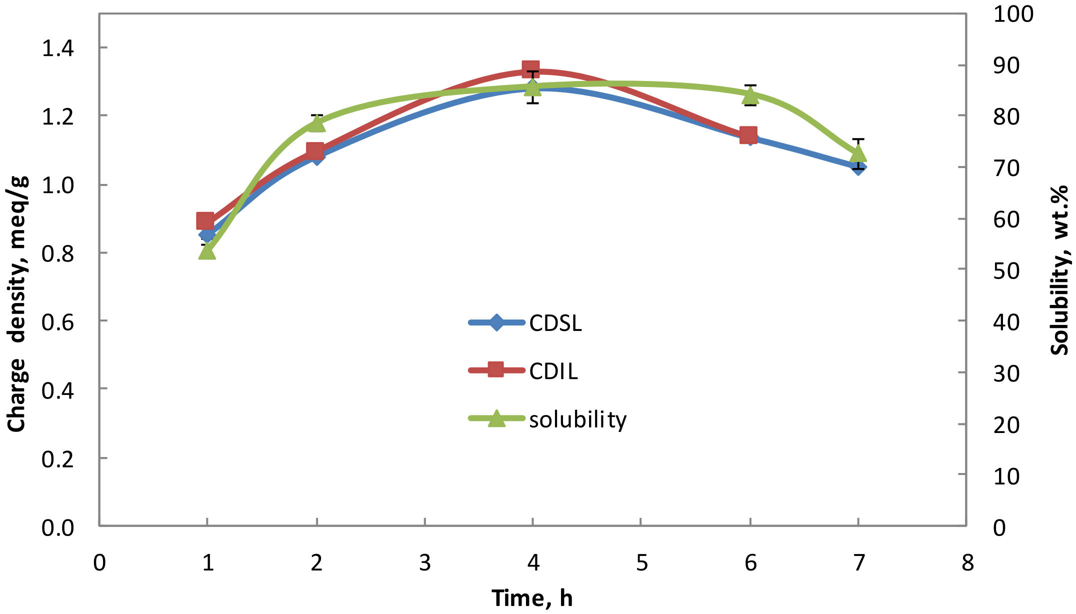


Fig. 6. Charge density of soluble lignin (CDSL), charge density of insoluble lignin (CDIL), and solubility of SS-lignin as a function of time. Experimental conditions were Na_2SO_3/lignin molar ratio of 0.50, 95 °C and lignin concentration of 11.11 g/L.

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. The decrease in solubility after 4 h of reaction may be attributed to condensation in alkaline conditions (Gierer *et al.* 1964; Yu *et al.* 2013). In short, the solubility of SS-lignin increased as reaction time extended, and it reached a plateau of 85% between 2 h to 6 h of reaction.

The optimum conditions for SS-lignin were the Na_2SO_3/lignin molar ratio of 0.67 mol/mol, reaction temperatures of 90 °C, reaction time of 4 h, and lignin concentration of 11.11 g/L, which generated SS-lignin with the charge density of 1.4 meq/g.

Characterization of Modified Lignin

The properties of modified lignin (SA-lignin and SS-lignin) prepared under the optimized conditions are shown and compared with the properties of kraft lignin used in this study and in the literature in Table 1. Unmodified kraft lignin had a M_w value of 9,700 g/mol and a M_n value of 2,100 g/mol, which are similar to those previously reported (Gierer and Petterson 1977; Meister 2002; Guerra *et al.* 2006). The molecular weight of lignin in *Pseudotsuga menziesii*, *Abies concolor*, and *E. globulus* were 38,000 g/mol, 52,000 g/mol, and 32,000 g/mol, respectively (Gierer and Petterson 1977). The M_w and M_n of softwood kraft lignin recovered by LignoTech from black liquor were reported to be 8,900 g/mol to 11,119 g/mol and 200 g/mol to 2,755 g/mol, respectively (Meister 2002). In another report, the M_w and M_n of softwood kraft lignin were 3,503 g/mol to 13,109 g/mol and 163 g/mol to 847 g/mol, respectively (Luque *et al.* 1994). As shown in Table 1, the M_w of SA-lignin was not measured due to its poor solubility. However, the M_w of SS-lignin was 8,300 g/mol, which was similar to that of unmodified kraft lignin.

Table 1. Properties of Lignin in this Study and Others

Lignin	M_w (g/mol)	M_n, (g/mol)	M_w/M_n	Elemental Analysis (wt.%)					Charge Density (meq/g)	Reference
				C	H	N	O	S		
Kraft Lignin	9679	2141	4.52	63.9	5.97	0.06	30.60	6.09	0 ± 0.03	PS[1]
SA Lignin	ND[3]	ND[3]	ND[3]	46.79	3.46	0.03	39.31	8.25	0.752 ± 0.02	PS[1]
SS Lignin	8284	2020	4.43	58.63	5.41	0.04	32.62	3.22	1.01 ± 0.02	PS[1]
Biomass Lignin	NR[2]	NR	NR	47.65	14.30	2.92	19.60	0.08	NR	Meister 2002
Softwood Ligno-sulfonate	8,900-11,119	200-2755	NR	NR	NR	NR	NR	NR	NR	Luque *et al.* 1994
Hardwood Ligno-sulfonate	5,000-15,00	NR	NR	NR	NR	NR	NR	NR	NR	Gierer *et al.* 1964

[1]PS: Present work, [2]NR: Not reported, [3]ND: Not detected
Note: All samples in this study were created under optimum conditions

Biomass lignin contained 47.7% carbon, 14.3% hydrogen, and 19.6% nitrogen (Baumberger *et al*. 2007). The results revealed that SA-lignin had a similar carbon content to unmodified biomass lignin (47%) (Baumberger *et al.* 2007). In the case of SS-lignin, the amount of carbon dropped from 63.9% in kraft lignin to 58.6%. The sulfur content of unmodified kraft lignin was 6.09%. The sulfur content of the sulfuric acid treated lignin samples (SA-lignin) was 8.25%. The sulfur content in SS-lignin was reported to be 3.22%. The decrease in the sulfur content of sulfonated lignin (compared with unmodified kraft lignin) may be an indication of impurities within the unmodified kraft lignin, as kraft lignin was washed with sulfuric acid prior to use in LignoForce™ technology (Helander *et al*. 2013). The elemental analysis of lignin samples helped identify the chemical formulas for modified lignin samples.

The chemical formula of softwood kraft lignin was determined to be $C_9H_{10.09}O_{3.23}S_{0.53}$. The derived chemical formulas of SA-lignin and SS-lignin were $C_9H_{7.98}O_{5.67}S_{0.59}$ and $C_9H_{9.96}O_{3.76}S_{0.19}$, respectively. Generally, the amounts of sulfur and oxygen in modified lignin were increased with respect to unmodified lignin, and it was more pronounced for the sulfuric acid treated sample.

FTIR Analysis

Figure 7 presents the spectra of kraft lignin, SA-lignin, and SS-lignin. For all three samples, there was a broad signal at 3,400 cm^{-1}, representing the hydroxyl group. For all three lignin samples, the aromatic skeletal vibrations were present in the range of 1,400 cm^{-1} to 1,600 cm^{-1} (Peak *et al.* 1999; Maria *et al.* 2002; Kouisni *et al.* 2012). Also, the peak at 1,371 cm^{-1} belonged to the C-H stretch in methyl groups. This is mirrored by the peak at 835 cm^{-1}, which was attributed to aromatic C-H bending (Peak *et al.* 1999; Maria *et al.* 2002; Kouisni *et al.* 2012). The peak at 618 cm^{-1} was absent in both kraft lignin and SA-lignin, but it was present in SS-lignin (Peak *et al.* 1999; Maria *et al.* 2002; Kouisni *et al.* 2012). Thus, these samples contained less sulfur. This conclusion is verified by the low charge density shown in Table 1.

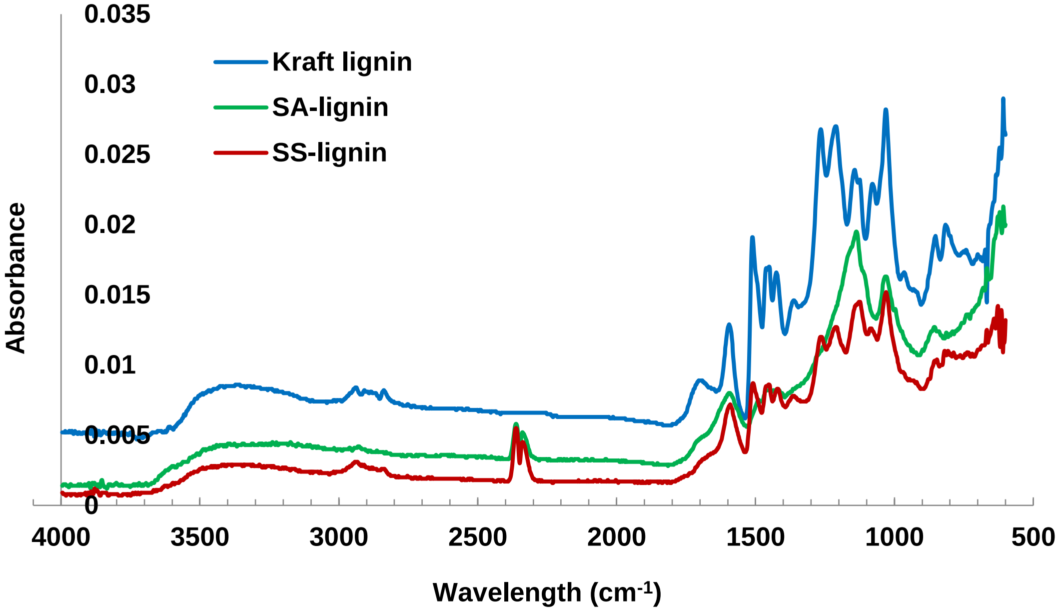
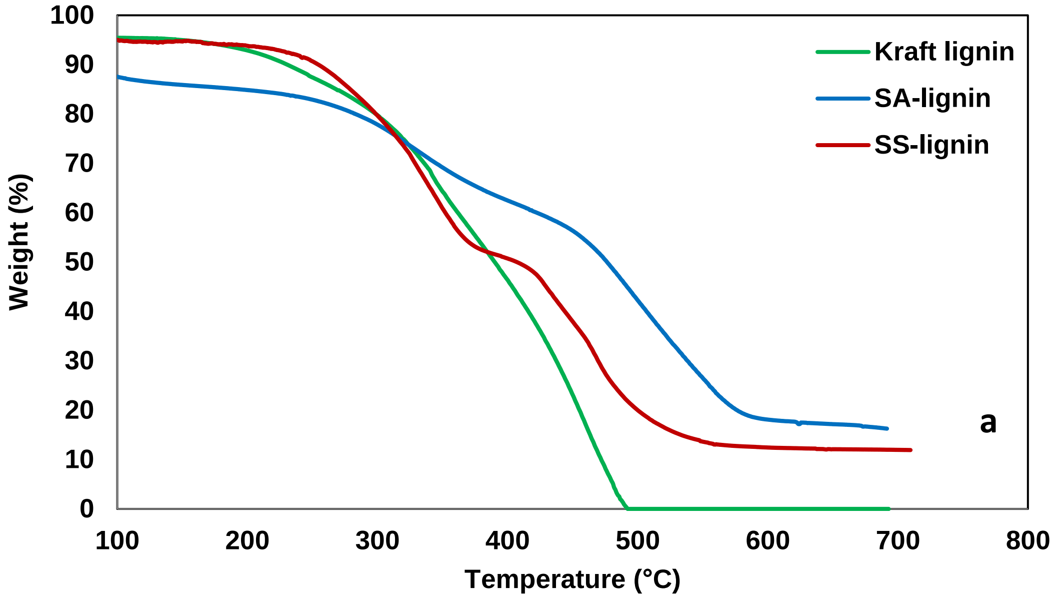


Fig. 7. FTIR spectra of unmodified and modified lignin under optimized conditions

TGA Analysis

Figure 8 presents the thermogravimetric analysis of lignin samples. As shown in Fig. 8a, kraft lignin was incinerated completely at a temperature of 500 °C, while the SA-lignin exhibited thermal resistance at this temperature. The results also showed that 17% and 9% of SA-lignin and SS-lignin remained at 750 °C, respectively.



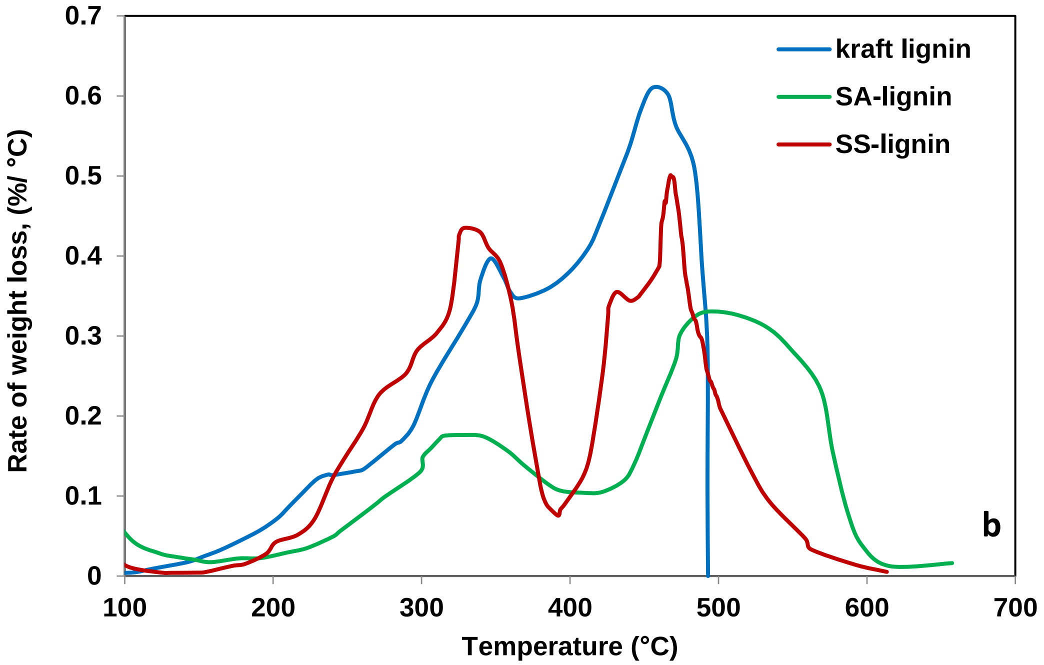


Fig. 8. (a) Weight loss of unmodified and modified lignin; (b) weight loss rate of unmodified and modified lignin. Experiments were conducted in N_2 at 30 mL/ min heated at 10 °C/min.

Lignin had a higher combustion temperature compared to other lignocellulosic materials, which was due to the interlinkages of lignin (Xu *et al.* 2006). However, hemicellulose and cellulose contain less significant structural linkages and decompose at a range of 220 °C to 300 °C and 300 °C to 340 °C, respectively (Xu *et al.* 2006). The modified lignin samples showed greater resistance to decomposition compared with kraft lignin, which may be due to increased intermolecular bonding caused by condensation. The molecular weight of SS-lignin was larger than the molecular weight of unmodified kraft lignin; thus the increase in thermal resistance for SS-lignin could result from the increased intermolecular linkages.

Figure 8b presents the weight loss rate of unmodified kraft lignin, SA-lignin, and SS-lignin as a function of temperature. There was a noticeable increase at approximately 300 °C to 350 °C in all three samples, with SS-lignin representing the highest. However, the peak at 450 °C belongs to the kraft lignin. The peaks at 350 °C and 450 °C could be due to the decomposition of condensed structures (Yang *et al.* 2004). Lignocellulosic complexes in coconut fibers lost 65% of their weight at 390 °C (Zhang *et al.* 2014b). Compared with unmodified kraft lignin, the rate of decomposition in SS- and SA-lignin decreased, which could be due to condensation and increased intramolecular bonding (Mothe and de Mirand 2009).

Solubility of SS-Lignin

The increase in solubility across a wide pH range allows a wider range of potential end-use applications. In other words, lignin should be soluble if used as a chemical agent for aqueous systems. Figure 9 shows the solubility of lignin samples in 1 wt.% solution as a function of pH. The data showed that unmodified kraft lignin was soluble under alkaline conditions. At a pH lower than 10, the solubility was dramatically reduced to zero. SS-lignin was soluble under both alkaline and neutral solutions.

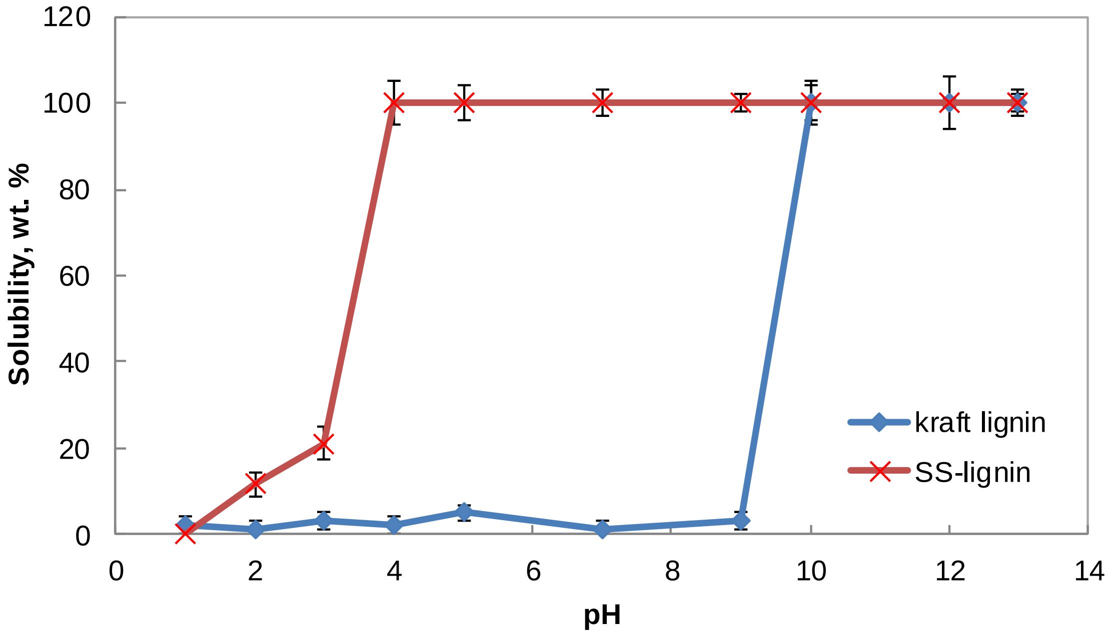


Fig. 9. Impact of pH on solubility of lignin samples. The analysis was conducted at room temperature and pressure.

The solubility of lignin samples is shown as a function of lignin concentration in Fig. 10. The solubility capacity provides the maximum amount of lignin that can be soluble in water (*i.e.*, saturation), which will affect its end-use applications as a dispersant. A higher concentration than its saturation solubility will not improve its dispersion or flocculation affinity. Lignosulfonate supplied from Sigma Aldrich (LSSA) had a high solubility of 515 g/L. The SS-lignin produced in this study had a lower solubility than LSSA. LSSA had a charge density of 1.52 meq/g, which was higher than the charge density of SS-lignin. The molecular weight of LSSA was 1458 g/mol, which was lower than that of the SS-lignin. For organic molecules, a lower MW results in higher solubility (Lv *et al.* 2013). In this work, no purification was conducted on commercial lignosulfonate prior to analysis. Commercial lignosulfonate often contains sugars and other impurities that are soluble in water, and this may affect the overall solubility performance of commercial lignosulfonate (Xie and Shi 2011).

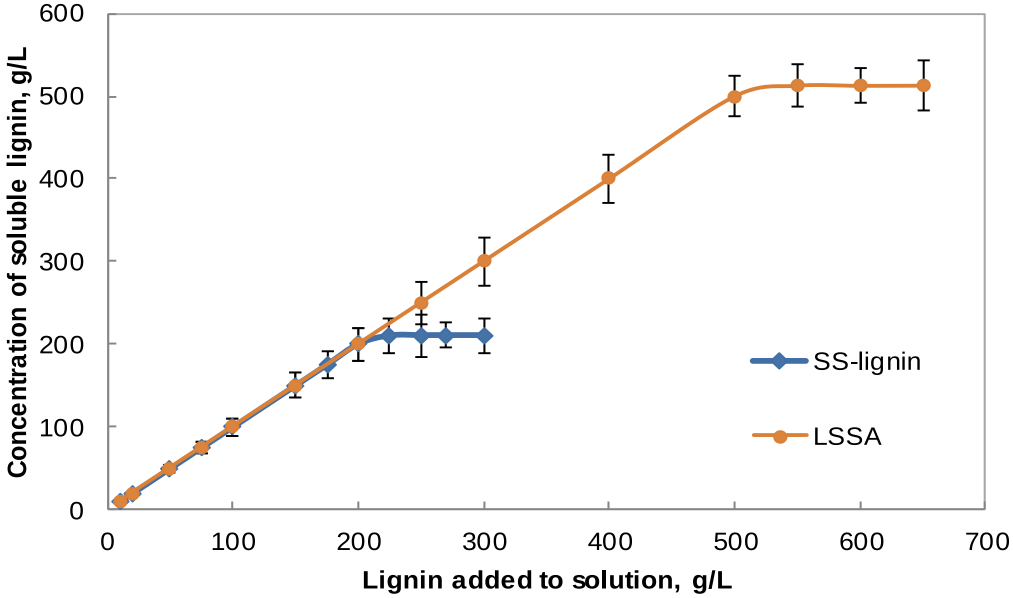


Fig. 10. Concentration of soluble lignin as a function of lignin samples added to water at pH 7. The analysis was conducted at room temperature and pressure.

Viscosity Analysis

The dynamic viscosity of the synthesized lignin samples was analyzed and drawn in Fig. 11. SS-lignin required 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 increasing the viscosity significantly.

The LSSA sample exhibited a similar, but less intense, pattern with an increase in viscosity to 0.5 PaS at 450 g/L and 1.76 PaS at 500 g/L. The lower solubility (Fig. 10) and higher viscosity (Fig. 11) of the lignin sample synthesized in this study than those of commercial lignosulfonates might be due to the impurities of lignosulfonates (water soluble compounds such as sugars), as stated earlier.

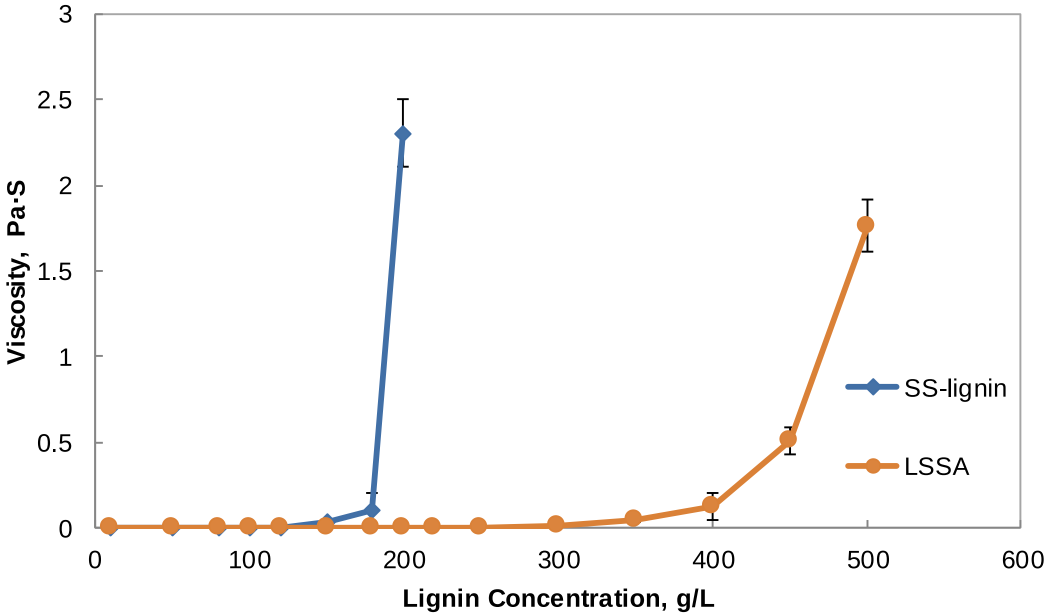


Fig. 11. Dynamic viscosity of SS-lignin as a function of lignin concentration. The analysis was conducted at 25 °C.

Although the results in Figs. 10 and 11 showed inferior performance of SS-lignin to commercial lignosulfonates, the dosage of dispersants used in industry is less than 10 g/L (He and Fatehi 2015; Oveissi *et al.* 2016). At this low concentration, comparable results were obtained for SS-lignin and a commercial lignosulfonate, which implies that SS-lignin can replace lignosulfonate to be used as a dispersant. Therefore, modified kraft lignin can function similar to lignosulfonate as can be obtained from the sulfite pulping process.

CONCLUSIONS

1. The modification of kraft lignin through sulfuric acid treatment resulted in a charge density of 0.75 meq/g and a solubility of 8%, which was obtained under the conditions of 100 °C, 0.5 h, and 15.2 H_2SO_4/lignin molar ratio.
2. The sulfonation of kraft lignin through sodium sulfite treatment 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 h, and 0.67 Na_2SO_3/lignin molar ratio.
3. Charge density and conductometric analyses confirmed the charge densities of SA- and SS-lignin were 0.8 meq/g and 1.4 meq/g, respectively. GPC analysis demonstrated that the molecular weight of the SS-lignin was 8,300 g/mol, while that of unmodified kraft lignin was 9,700 g/mol. FTIR analysis confirmed that the modification occurred qualitatively as documented by the peaks at 1040 cm^{-1}, 1110 cm^{-1}, and 618 cm^{-1}. The TGA analysis confirmed that 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.

4. The modified lignin exhibited an improved solubility across the pH range studied when compared with unmodified kraft lignin. SS-lignin had inferior viscosity results to commercial lignosulfonates, but it may still be used as a dispersant.

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