

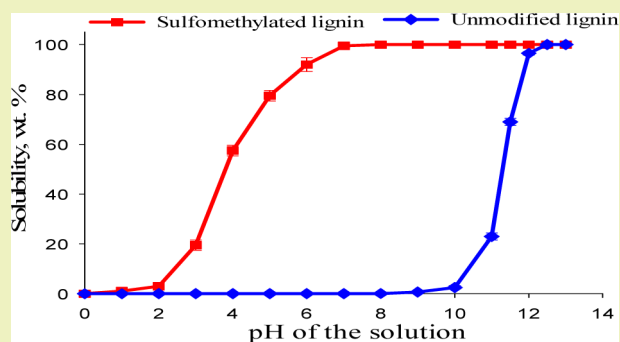
Production of Water-Soluble Hardwood Kraft Lignin via Sulfomethylation Using Formaldehyde and Sodium Sulfite

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ABSTRACT: Kraft lignin can be extracted from black liquor (i.e., spent liquor) of a kraft pulping process to produce value-added chemicals, but its limited water solubility hampers its end-use applications. The main objective of this study was to investigate the sulfomethylation of kraft lignin to produce water-soluble kraft lignin with an anionic charge density. In this work, hardwood kraft lignin was modified with formaldehyde and sodium sulfite under alkali conditions. The optimum conditions for sulfomethylation were 0.5 M NaOH_(aq), 0.9 mol/mol sodium hydroxymethyl sulfonate/lignin at 100 °C for 3 h, and 20 g/L lignin concentration. The resulting lignin had a charge density of -1.60 mequiv/g and sulfonate group content of 1.48 mmol/g. The molecular weight, structure, thermal behavior, and elemental analyses of the product were also assessed. The modified lignin was used as a cement dispersant, and the dispersibility of cement was increased from 60 to 155 mm by adding 1.2 wt % of sulfomethylated lignin to cement. Unmodified lignin did not change the dispersibility of cement.

KEYWORDS: Kraft lignin, Sulfomethylation, Sodium sulfite, TGA, Charge density, FTIR, Solubility



INTRODUCTION

Lignin is the most abundant renewable resource after cellulose. In chemical pulping processes, around 100 million tons of lignin is produced annually.¹ However, the majority of kraft lignin is incinerated in the recovery section of the kraft process for energy recovery. Kraft lignin can be recovered and used in the production of value-added products.² In this regard, lignosulfonate (LS), which is produced as a byproduct of the sulfite pulping process, has been used in various end-use applications such as a dye dispersant and chelating agent.³ The supply of LS is limited in the world, and sulfonated lignin from other technical lignins should be produced so that the market demand can be satisfied.

Sulfonated lignin with a high purity and quality can be produced from different lignin types and species. Studies were conducted on the preparation of water-soluble sulfonated lignin from wood and nonwood lignin via sulfonation⁴ and sulfomethylation.⁵ In one study, sulfomethylated lignin (SML) was prepared by treating wheat straw lignin with formaldehyde and sodium sulfite.⁶ Yasuda and co-workers⁷ converted acid-hydrolyzed pinewood lignin model compound (cresol) to water-soluble sulfonated lignin via sulfonation using sodium sulfite. Lignin has also been extracted from birch wood and converted to a water-soluble product via sulfonation with sodium sulfite under alkaline conditions.⁸ However, the production of water-soluble sulfonated hardwood kraft lignin has not been attempted in the past and is the first objective of this study.

Several applications were suggested for sulfonated lignin. SML obtained from treating sugar cane bagasse lignin with

sodium sulfite and formaldehyde was used as a dispersant in pesticide formulations.⁹ In another study, SML prepared from the sulfomethylation of esparto grass lignin with sodium sulfite and formaldehyde was used as a water reducer for cement admixture.¹⁰ In another study, sulfonated lignin produced from treating softwood kraft lignin with sodium sulfite was found to be effective as a corrosion inhibitor for iron-based materials.¹¹ Alternatively, lignosulfonate produced via sequential chemical modification of wood kraft lignin using aliphatic polyamine, aliphatic acyl chloride, formaldehyde, and sodium sulfite served as a surfactant for crude oil.⁴ In the past, sulfonated lignin prepared by treating low molecular weight pine (softwood) kraft lignin with sodium sulfite was used as a flocculant in water purification systems.¹²

Due to the large production of hardwood lignin in the kraft pulping process, the surplus amount of hardwood lignin could be used in the production of various value-added products. The sulfomethylation of hardwood kraft lignin offers an opportunity for producing water-soluble products. The main novelty of this work is the production of SML from hardwood kraft lignin and the application of the product as a dispersant in a cement admixture. Also, the impact of sulfomethylation on the charge density of produced SML is discussed for the first time, which is known to be an important parameter of dispersants and flocculants in polyelectrolyte systems.¹³ The charge density of lignin can be directly related to its sulfomethylated groups.¹⁴

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The present study investigates the influence of reaction parameters on the preparation of SML from hardwood kraft lignin using formaldehyde and sodium sulfite. The characteristics of SML were determined by means of Fourier transform infrared spectroscopy (FTIR), potentiometric titration, charge density, and elemental analyses, and the application of SML as a cement dispersant was investigated in this work.

EXPERIMENTAL SECTION

Materials. Mixed hardwood kraft lignin was supplied by FPInnovations from its pilot plant facilities located in Thunder Bay, ON.¹⁵ Commercial cement was purchased from a retailer in Thunder Bay, Canada. Commercial lignosulfonate, sodium hydroxide, formaldehyde (37 wt %), tetrahydrofuran (THF, 99.9 wt %), acetyl bromide (99 wt %), acetic acid (99.7 wt %), and sodium sulfite used in this study were obtained from Sigma-Aldrich and used as received. Sulfuric acid (98 wt %) obtained from Sigma-Aldrich was diluted to 1 M concentration prior to use. Cellulose acetate dialysis membrane (molecular weight cutoff of 1000 g/mol) was obtained from Spectrum Laboratories, Inc., USA. Polydiallyldimethylammonium chloride (PDADMAC) was obtained from Sigma-Aldrich and diluted to 0.005 M prior to use. Potassium polyvinyl sulfate (PVSK) was obtained from Wako Pure Chemical Industries Ltd., Japan, and diluted to 0.005 M prior to use.

Sulfomethylation. The sulfomethylation of kraft lignin was conducted as previously described in the sulfomethylation of alkali corn stalk lignin.⁶ A 1 g sample of hardwood kraft lignin (M_w 180 g/mol) was mixed with formaldehyde (37 wt %) and sodium sulfite under various conditions. The reaction parameters investigated were NaOH concentration (0.25–1 molar concentration), sodium hydroxymethylsulfonate/lignin ratio (0.3–1.2 mol/mol), reaction temperature (80–140 °C), reaction time (1–7 h), and lignin concentration (10–25 g/L). All the reactions were carried out in a 100 mL three-neck round-bottom glass flask under constant stirring at 150 rpm. Upon completion, the solution was cooled to room temperature and then brought up to pH 7 using 1 M sulfuric acid. Unreacted sodium hydroxide, sodium sulfite, and formaldehyde were separated from sulfonated kraft lignin by dialysis membranes, while water was changed every 12 h for 2 days. The dialyzed samples were then dried at 105 °C in an oven overnight and stored at 4 °C for further use. Based on the charge density and solubility, the modified lignin, which was generated using of 0.5 M NaOH_(aq), 0.9 mol/mol sodium hydroxymethyl sulfonate/lignin ratio at 100 °C for 3 h, and a lignin concentration of 20 g/L, was selected as the best sample for further characterization with FTIR, thermogravimetric analysis (TGA), and an elemental analyzer. Hardwood kraft lignin (1 g) was mixed with formaldehyde (0.1 M) and sodium sulfite (0.1 M) under alkali conditions (pH 12). The reaction was carried out in a 100 mL three-neck round-bottom glass flask at 100 °C for 8 h under constant stirring at 150 rpm. Samples were drawn from the flask every 1 h, and the pH of the medium was determined using a pH meter, HI 208 (HANNA Instruments). This analysis determined the impact of reaction time on the pH of the reaction medium.

Taguchi's orthogonal array was used for obtaining the maximum charge density and solubility of SML under optimized conditions.¹⁶ In this study, L16 orthogonal design with five factors (each at four levels) was used to investigate the effect of parameters on the sulfomethylation reaction.¹⁷ The conditions listed in Table 1 were selected for conducting optimization analysis using a L16 orthogonal design. In each experiment, three samples were prepared to minimize the errors. The standard deviation was determined based on the results and is shown in Figures 2–7.

Afterward, the analysis of variance model (ANOVA) with *F*-test (Fisher test) was used to identify which process parameter significantly affected the sulfomethylation reaction and which combination levels of process parameters produced a maximum response.¹⁷ The definition of sample variance is shown in eq 1:¹⁸

Table 1. Parameters Considered for Optimization of the Sulfomethylation Reaction Based on Taguchi's L16 Orthogonal Array Design

run	time (h)	temp (°C)	NaOH concentration (M)	CH ₃ NaO ₄ S/lignin ratio (mol/mol)	lignin concentration (g/L)
1	1	80	0.25	0.3	10
2	1	100	0.5	0.6	15
3	1	120	0.75	0.9	20
4	1	140	1	1.2	25
5	2	80	0.5	0.9	25
6	2	100	0.25	1.2	20
7	2	120	1	0.3	15
8	2	140	0.75	0.6	10
9	3	80	0.75	1.2	15
10	3	100	1	0.9	10
11	3	120	0.25	0.6	25
12	3	140	0.5	0.3	20
13	4	80	1	0.6	20
14	4	100	0.75	0.3	25
15	4	120	0.5	1.2	10
16	4	140	0.25	0.9	15

$$S^2 = \frac{1}{n-1} \sum (y_i - \bar{y})^2 \quad (1)$$

where $\sum (y_i - \bar{y})^2$ refers to the sum of squared (SS) deviation from the mean, $1/(n-1)$ refers to degrees of freedom (df), and S^2 refers to mean squares (MS).

F-test refers to the significance of variance or factor, which is quantified by eq 2:¹⁸

$$F = \frac{MS_F}{MS_E} \quad (2)$$

where MS_F is a mean square of the factor and MS_E is a mean square of the error. According to the *F*-test, if the variance caused by the factor (MS_F) is higher than the variance caused by the error (MS_E), the factor will have a significant effect on the response; thus, the higher the *F*-test, the higher the significance effect of the factor would be.¹⁸

Solubility. Solubility Determination. To measure the solubility of lignin samples, 0.2 g of unmodified lignin (UL) or SML was suspended in 20 mL of deionized water by stirring at 100 rpm for 2 h at 30 °C in a water bath shaker.¹⁹ The samples were centrifuged at 1000 rpm for 5 min, and the supernatant was dried overnight in a 60 °C oven. As lignin produced via LignoForce technology has different structures and molecular weights,¹⁵ the sulfomethylation of lignin may not be able to solubilize all lignin segments. Therefore, reporting the solubility in wt % directly shows how much of the original lignin segments were solubilized. The solubility of lignin in the supernatants was determined according to eq 3.

$$\text{water solubility (wt \%)} = \frac{\text{mass of dissolved lignin}}{\text{initial mass of lignin}} \times 100 \quad (3)$$

Solubility versus pH. To measure the solubility of lignin samples at different pH values, 0.2 g of unmodified and SML samples was suspended in 20 mL of deionized water at different pH values ranging from 1 to 12. These samples were incubated in a water bath shaker for 2 h at 30 °C and 100 rpm. The solubility of these samples was determined according to eq 3.

Solubility versus Concentration. To measure the solubility of lignin samples at different concentrations, the SML sample was mixed with deionized water and was incubated in a water bath shaker at 100 rpm, pH 7, for 2 h at 30 °C, and its solubility was measured according to the procedure stated above and eq 3.

Charge Density and FTIR Analyses. To measure the charge density of the lignin samples, SML and commercial lignosulfonate were initially dried at 105 °C overnight to remove moisture. A 0.2 g

sample of lignin was dissolved in 20 mL of deionized water and incubated for 1 h at 30 °C in a water bath shaker at 150 rpm. After the incubation, the samples were centrifuged at 1000 rpm for 10 min, and supernatants were collected for the charge density analysis with a particle charge detector (Mutek, PCD 04, Germany) and titrated against a PDADMAC standard solution (0.005 M).

To measure the charge density of cement particles, 0.2 g of cement was added into 20 mL of the PVSK standard solution (0.005 M) and incubated for 2 h at 30 °C in a water bath shaker at 150 rpm. Simultaneously, a control sample (20 mL PVSK solution) without cement particles was also incubated under the same conditions. After the incubation, the samples were centrifuged at 1000 rpm for 10 min and the collected supernatants were titrated against a PDADMAC standard solution (0.005 M). The differences between the blank and test samples were used to calculate the charge density of cement particles according to the procedure established previously.²⁰

The FTIR analysis was conducted on unmodified and SML samples. The samples were dried in a 105 °C oven overnight, and 0.05 g of the sample was then used for structural characterization using FTIR (Bruker Tensor 37, Germany, ATR accessory). The spectra were recorded in transmittance mode in the range of 500 and 4000 cm⁻¹ with a 4 cm⁻¹ resolution, and 32 scans per sample were conducted.

ζ-Potential Analysis. In this experiment, 0.2 g of cement was added to 20 mL of 10 g/L SML concentration and incubated in a water bath shaker at 30 °C for 2 h at 150 rpm. Simultaneously, to measure the ζ-potential of cement particles in the absence of SML, a 0.2 g of cement was added to 20 mL of distilled water and incubated under the same conditions as described above. After the incubation, the ζ-potential of the samples was analyzed using a compact automatic zetameter (Laval Laboratories Inc.).²¹ All the measurements were carried out at room temperature with constant electric field (8.4 V/cm). Before and after each measurement, the microelectrophoresis cell was washed with deionized water to prevent any contamination.

Sulfonate Group Analysis. The aqueous potentiometric titration method was used to measure the sulfonate group attached to unmodified and SML samples using an automatic potentiometer, Metrohm, 905 Titradot, Switzerland. In this experiment, a 1 g sample was added to 100 mL of distilled water and the pH of the solution was adjusted to 7.0 using 1 M H₂SO₄. The solutions were then titrated against a cationic polymer, TEGO trant A 100, in order to determine the number of sulfonate groups. The degree of substitution was calculated based on eq 4:²²

$$\text{degree of substitution} = \frac{M \times A}{1 - 0.117 \times A} \quad (4)$$

in which *A* is total sulfonate group content (mmol/g), 0.117 (g/mmol) is the net increase in mass for each sodium sulfomethyl group attached to lignin, and *M* is mass of the basic unit of lignin (0.188 g/mmol for a C₉ unit of lignin).²³

Molecular Weight Analysis. A 0.1 g sample of air-dried UL was dissolved in 4 mL of acetic anhydride/pyridine 1/1 (v/v) solution and was stirred for 30 min at 300 rpm at 25 °C. The solution was left for 24 h in the absence of light, and then the solution was poured in an excess (50 mL) of ice water and centrifuged/washed three times. The solvent was then removed from the sample using a freeze-dryer. The acetylated UL was dissolved in 10 mL of THF at 300 rpm for 30 min at room temperature and filtered with a polytetrafluoroethylene filter (13 mm diameter and 0.2 μm pore size). The collected filtrate samples were used for molecular weight analysis. For determining the molecular weight of SML and commercial lignosulfonate, a 0.05 g of sample was air-dried and then dissolved in 10 mL of a 0.1 M NaNO₃ solution and filtered with a nylon 0.2 μm filter (13 mm diameter). The filtered samples were used for molecular weight analysis.

The molecular weight analysis of the samples was carried out using size exclusion chromatography (Malvern GPCmax VE2001 Module + Viscotek TDA305 with RI and viscometer detectors). For UL measurements, the organic columns of PolyAnalytic PAS106M, PAS103, and PAS102.5 were used, and high-performance liquid chromatography grade THF was used as solvent and eluent. The flow rate was set at 1.0 mL/min. For SML and commercial lignosulfonate

measurements, the columns of PolyAnalytic PAA206 and PAA203 were used, and 0.1 M NaNO₃ solution was used as solvent and eluent. The flow rate was set at 0.70 mL/min. The column temperature was set at 35 °C for both systems. Polystyrene polymers were used as standards for the organic system and the poly(ethylene oxide) for the aqueous system.

Elemental Analysis. The elemental analysis of lignin samples was performed using a Elementar Vario EL Cube elemental analyzer by a combustion analysis method. The samples were first dried in a 105 °C oven overnight in order to remove any moisture. Approximately, 2 mg of unmodified and SML samples was weighed in silver vessels and loaded in the integrated carousel of the elemental analyzer. Furthermore, the samples were automatically transferred into a combustion tube and burned at 1200 °C. Afterward, the combustion gases were reduced and analyzed for carbon, hydrogen, nitrogen, and oxygen content of the samples.²⁴

Thermogravimetric Analysis. The thermal analysis of sulfomethylated and unmodified lignin samples was conducted using a thermogravimetric analyzer (i-1000 series, Instrument Specialist Inc.). The samples were dried in an oven at 105 °C overnight, and 8 mg of unmodified and SML samples was used for this analysis. The analysis was carried out under nitrogen at a steady flow rate of 35 mL/min. Each sample was heated from room temperature to 800 °C at a rate of 10 °C/min.

Cement Fluidity. The fluidity of cement paste was determined according to the Chinese National Standard of GB 8077-2000. A 300 g sample of cement, 120 g water, and 3 g sulfomethylated or unmodified lignin was added into a paste blender and stirred for 4 min. The paste was then rapidly poured into the truncated flow cone mold (base diameter of 60 mm, top diameter of 35 mm, and height of 60 mm) on a glass plate. Once the cone was lifted, the cement paste collapsed and spread. The maximum diameter of the spread, *d*₁, and the diameter perpendicular to it, *d*₂, were measured. The mean value, (*d*₁ + *d*₂)/2, was considered as the fluidity of cement paste.²⁵ Three replicates for each sample were carried out, and the average was reported. Similarly, the cement fluidity of commercial lignosulfonate was also measured using the same method described above, and its result was compared with that of sulfomethylated kraft lignin.

RESULTS AND DISCUSSION

Reaction Scheme of Sulfomethylation of Lignin. The synthesis of the sulfonated kraft lignin is shown in Figure 1. In

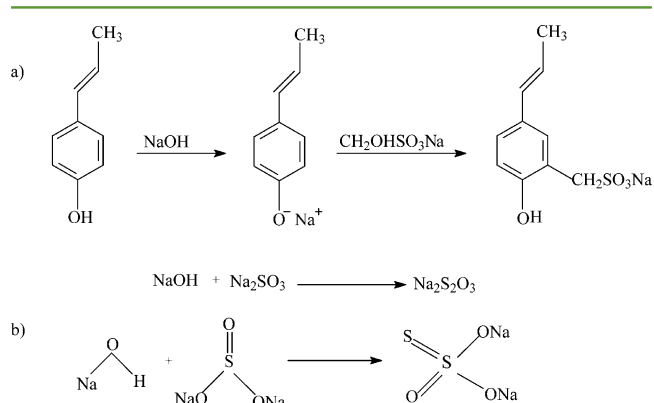


Figure 1. (a) Sulfomethylation of lignin and (b) undesired sodium thiosulfate production.

this reaction, formaldehyde provides a methyl group and sodium sulfite provides a sulfonated group for sulfomethylation. This reaction proceeds through electrophilic substitution. Under alkali conditions, the phenolic groups in lignin are converted to active electrophiles and the sodium sulfonate methyl derivative is formed by the nucleophilic addition of the sodium sulfite anion. There are possible competing side

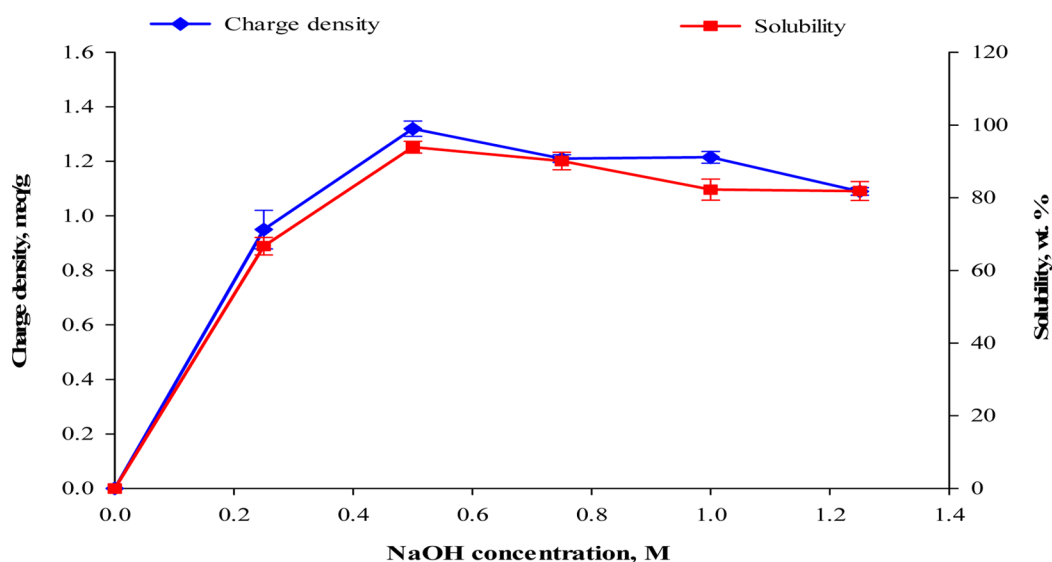


Figure 2. Effect of NaOH concentration on the charge density and solubility of sulfomethylated kraft lignin under the conditions of 20 g/L lignin concentration, 0.2 mol/mol sodium hydroxymethyl sulfonate/lignin ratio, and 90 °C for 2 h.

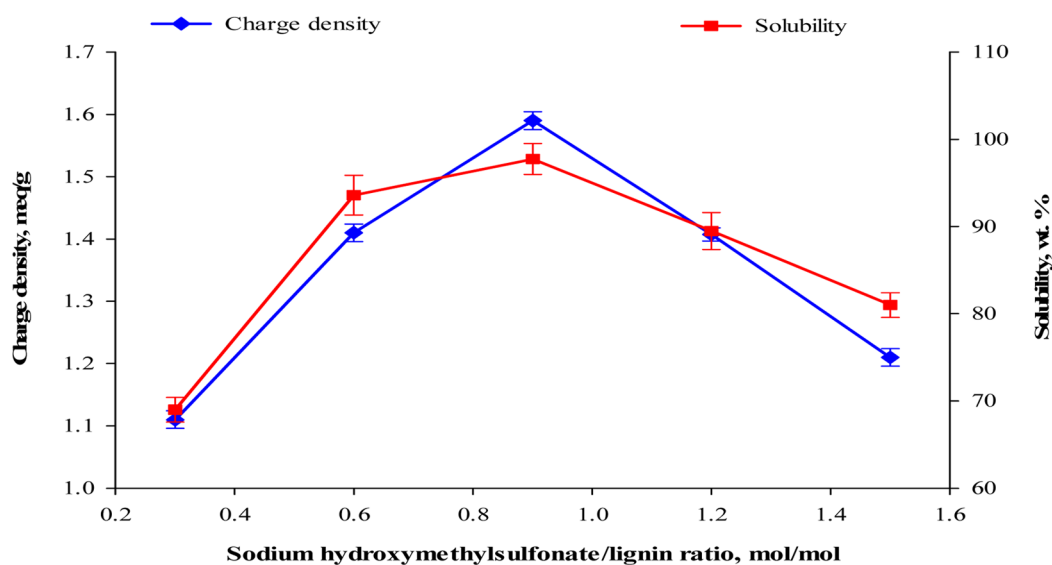


Figure 3. Effect of mole ratio of sodium hydroxymethyl sulfonate/lignin on the charge density and solubility of sulfomethylated kraft lignin under the conditions of 0.5 M NaOH concentration, 20 g/L lignin concentration, and 100 °C for 3 h.

reactions, including the production of sodium thiosulfate, which lowers the overall yield of the SML as shown in Figure 1.²⁶

It is noted that the charge density of modified lignin is directly related to its sulfomethylated group content. As the sulfomethylation reaction only affects the sulfomethylated groups attached to lignin, the change in the charge density of modified lignin is directly related to the change in the sulfomethylated group of lignin. The charge density is a parameter commonly used for analyzing the performance of a dispersant, thus the charge density was selected as one of the parameters for assessing the properties of SML.

Effect of NaOH Concentration. The sulfonation of alkali lignin is influenced by pH,⁶ and Figure 2 presents the impact of NaOH on the charge density and the solubility of SML. As is observable, a maximum charge density of 1.3 mequiv/g and solubility of 93 wt % were obtained at 0.5 M NaOH concentration. The increases in charge density and solubility were due to the impact of NaOH on the progress of

sulfomethylation reaction (as shown in Figure 1a). The progress in the sulfomethylation of lignin is closely related to the ability of nucleophilic substitution of the hydroxyl group with a sulfonate group under alkaline conditions. Thus, the concentration of NaOH in solutions should be sufficient to promote the sulfomethylation process. Below 0.5 M NaOH_(aq), alkaline concentration was not sufficient for the reaction, and NaOH concentration that was higher than 0.5 M provided a suitable alkali environment for the undesired side reaction to progress. In the past, lignin obtained from the stem of a cotton plant showed an increase in solubility from 1% (unmodified lignin) to 89% due to sulfomethylation using sodium sulfite and formaldehyde at pH 8, which was the optimum pH in the pH range studied.²⁵

Effect of Sodium Hydroxymethyl Sulfonate/Lignin Mole Ratio. Figure 3 shows the impact of sodium hydroxymethyl sulfonate/lignin mole ratio on the charge density and solubility of SML. The maximum charge density

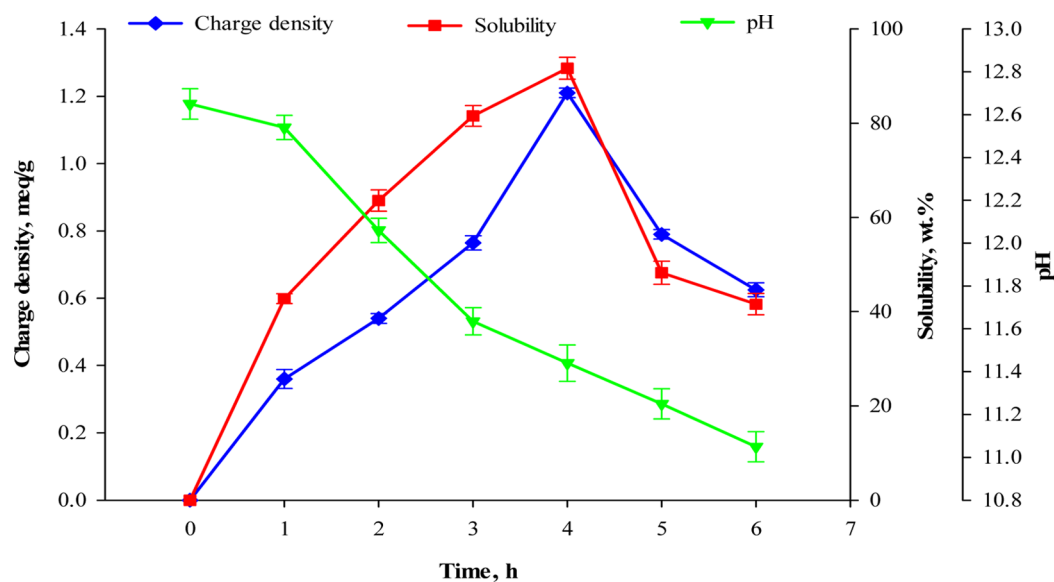


Figure 4. Effect of time on the charge density and solubility of sulfomethylated kraft lignin and the pH of reaction medium, which was conducted under the conditions of 0.5 M NaOH concentration, 0.9 mol/mol sodium hydroxymethyl sulfonate/lignin ratio, 100 °C, and 20 g/L lignin concentration.

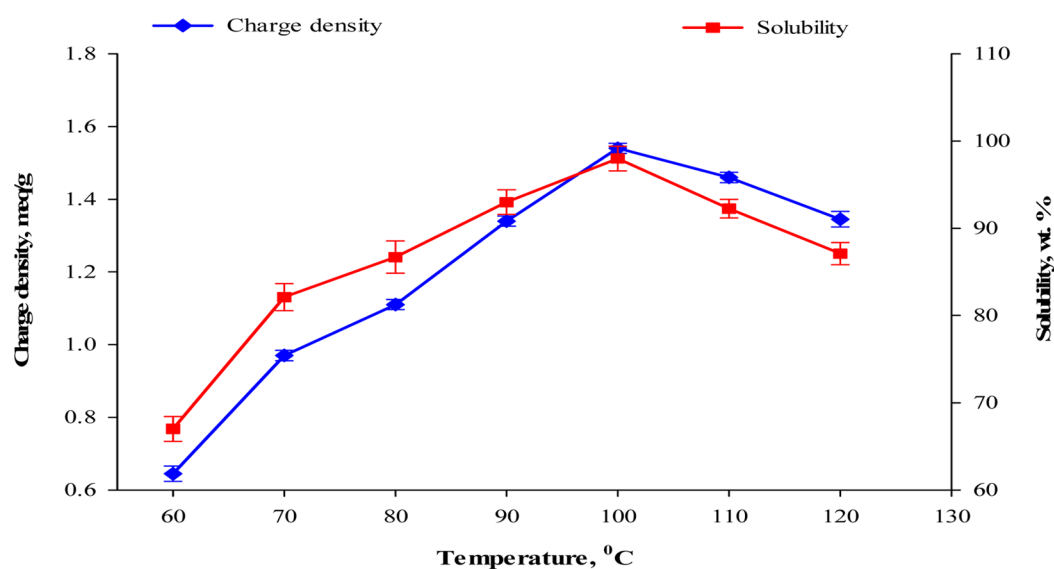


Figure 5. Effect of temperature on the charge density and solubility of sulfomethylated kraft lignin under the conditions of 0.5 M NaOH concentration, 0.2 mol/mol sodium hydroxymethyl sulfonate/lignin, 20 g/L lignin concentration, and 3 h reaction time.

and solubility of lignin were 1.6 mequiv/g and 100 wt %, respectively, which was obtained at a 0.9 mol/mol sodium hydroxymethyl sulfonate/lignin ratio. In the hydroxymethyl sulfonate/lignin range of 0.2 and 0.9 mol/mol, the increase in the charge density and solubility of lignin is due to the increase in the amount of sodium hydroxymethyl sulfonate in the solution, which improved the amount of sulfonate groups attached. The decreases in the charge density and solubility are probably due to undesirable side reactions as explained in previous sections. In the past, the molar ratio of 0.6 sodium hydroxymethyl sulfonate/lignin was found to be optimum for producing a dispersant for gypsum.²⁷ In another report on the sulfomethylation of alkali lignin from corn stalk, the maximum sulfonate group content of 1.29 mmol/g, which is directly related to its maximum charge density, was obtained at 1:1 weight ratio of lignin to sodium sulfite.⁶ In the previous work,

only two process parameters (time and sodium sulfite/lignin ratio) were optimized to produce SML. In the current study, more process parameters were included for optimizing the sulfomethylation reaction. The inclusion of more process parameters and the alteration in lignin sources were probably the reasons for different results reported in this work and the previous study.

Effect of Time. The impact of reaction time on pH, charge density, and solubility of SML are represented in Figure 4. The maximum charge density of 1.54 mequiv/g and solubility of 98 wt % were obtained at 3 h. When time was extended from 0 to 3 h, there was an increase in charge density and solubility. However, further prolonging the time of reaction had a negative effect on the charge density of lignin, which could be due to the progress in the efficiency of side reaction (Figure 1). In addition, as the reaction progressed, a decrease in pH from 12.7

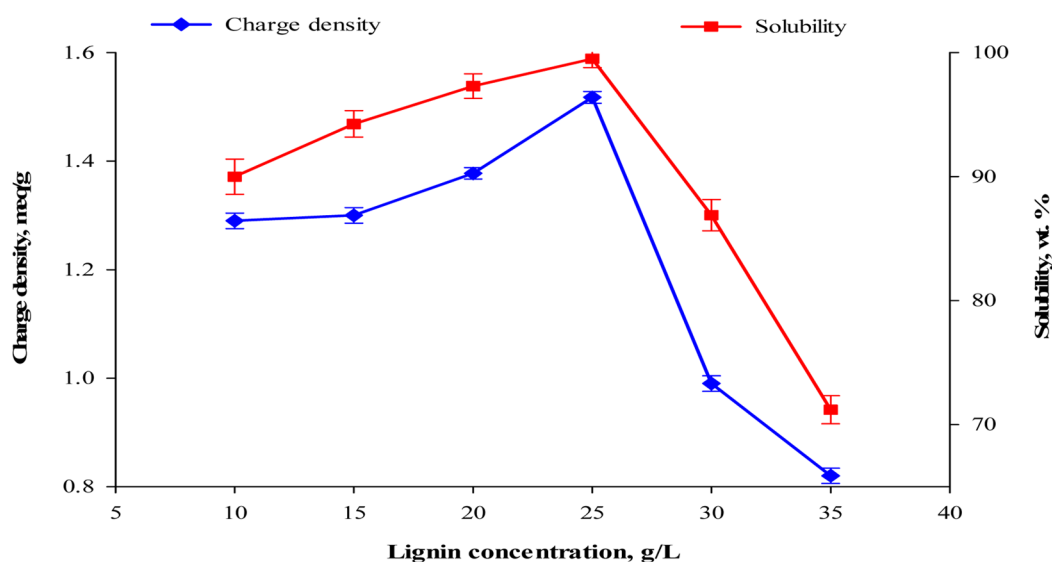


Figure 6. Effect of concentration of lignin on the charge density and solubility of sulfomethylated kraft lignin under conditions of 0.5 M NaOH concentration, 0.9 mol/mol sodium hydroxymethyl sulfonate/lignin ratio, and 100 °C for 3 h.

Table 2. Optimization of Parameters That Impact the Sulfomethylation Reaction of Lignin

factor	sum of squared deviations		mean square		F-test	
	charge density (mequiv/g)	solubility (wt %)	charge density (mequiv/g)	solubility (wt %)	charge density (mequiv/g)	solubility (wt %)
time (h)	0.98	1988.25	0.33	662.75	32.80	70.38
temp (°C)	0.03	28.25	0.007	9.42	0.73	0.70
NaOH concentration (g/L)	0.02	40.25	0.006	13.42	0.65	1.42
sodium hydroxymethylsulfonate/lignin (mol/mol)	0.16	156.25	0.053	52.08	5.37	5.53
lignin concentration (g/L)	0.03	42.75	0.01	14.25	1.53	1.51

to 11.2 was observed due to the consumption of NaOH.²⁸ In previous reports, as the reaction time extended from 2 to 5 h during the sulfomethylation of alkali lignin from corn stalk, the charge density of lignin was increased from 0.2 to 0.7 meq/g, and further extension of time had no effect on the reaction.⁶ Yu and co-workers have also reported the oxidation and sulfomethylation of sodium lignosulfonate and found that extending the reaction time to 3 h resulted in an increase in the sulfomethylation degree from 0.65 to 1.45 mmol/g; thus it can be inferred that its charge density was most probably increased via extending time to 3 h.²⁹ Similar results were also reported on the sulfonation of esparto grass lignin using sodium sulfite, in which a maximum sulfonation degree of 1.24 mmol/g was obtained in 4 h of reaction.¹⁰

Effect of Temperature. The changes in charge density and solubility of the SML as a function of temperature are presented in Figure 5. When the reaction temperature was increased from 80 to 100 °C, the charge density and solubility of kraft lignin increased to 1.55 mequiv/g and 100 wt % solubility, respectively. Pang and co-workers³⁰ have reported the sulfomethylation of calcium lignosulfonate, in which the maximum sulfonation degree of 1.23 mmol/g was obtained at 90 °C. The initial increase in the charge density and solubility is due to more frequent collisions between the reactants at a higher temperature.²⁹ Similar results were reported by Li and co-workers on the sulfonation of wheat straw hydroxymethyl ethanol lignin with sodium sulfite, in which increased temperature from 60 to 80 °C led to an increase of the sulfonate group content from 0 to 1.22 mmol/g.³¹ Further

increase in temperature decreased the charge density and solubility, possibly due to formation of undesirable products (sodium thiosulfate) at high temperatures.²⁹ The formation of this product was reported in the treatment of softwood kraft lignin with formaldehyde and sodium sulfite. A decrease in sulfonation degree from 1.45 to 1.05 mmol/g was accompanied by an increase in the production of sodium thiosulfate when the temperature was increased from 100 to 150 °C.³⁰ Therefore, it may be inferred that the production of undesirable products was most probably the reason for a decrease in the charge density of SML in this work.

Effect of Lignin Concentration. The effect of lignin concentration on the charge density and solubility of SML is plotted in Figure 6. The maximum charge density of 1.6 meq/g and solubility of 98.8 wt % were obtained at 20 g/L lignin concentration. The reason for an increase in the charge density and solubility is that lignin is a complex molecule and has very few reaction sites to react with reagents. Thus, with the increase in the lignin concentration, the frequent and effective collisions between the reaction sites and chemicals probably increased, which improved the sulfomethylation reaction.³² However, further analysis is needed to identify the exact reason for this behavior, which is out of the scope of this study. Further increase in the concentration decreased the charge density and solubility, which could be due to the limitation of stirring the solution with a magnetic bar (i.e., mechanical constrains) in the reaction setup of this study. A similar trend was reported on the production of surface-active agents from beechwood lignin that was obtained from an organosolv pulping process, in which the

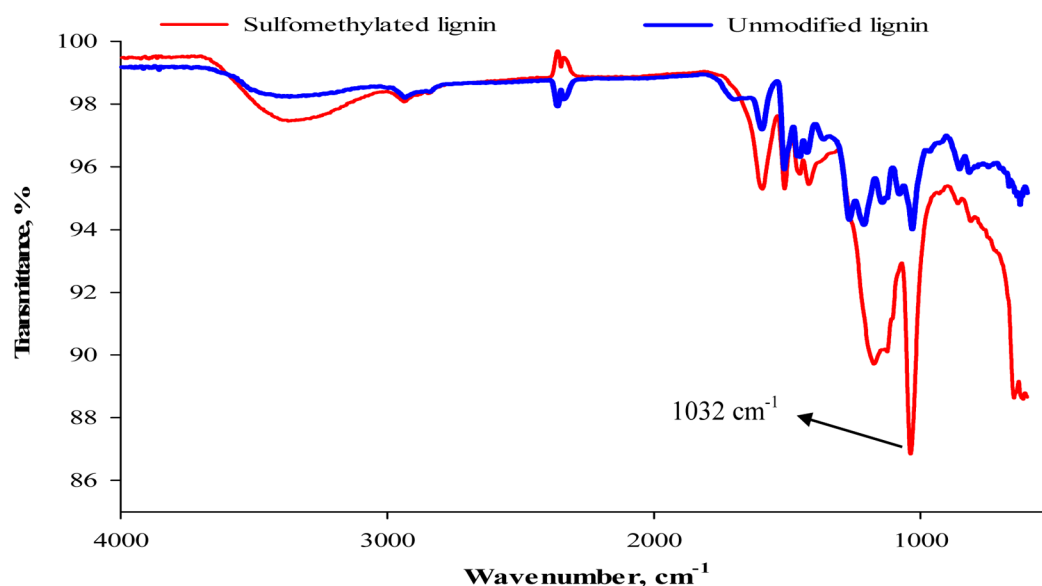


Figure 7. FTIR spectra of unmodified and sulfomethylated kraft lignin produced under conditions of 0.5 M NaOH_(aq), 0.9 mol/mol sodium hydroxymethyl sulfonate/lignin ratio, 100 °C, 3 h, and 20 g/L lignin concentration.

Table 3. Properties of unmodified and sulfomethylated lignin

sample	elemental analysis					sulfonated group (mmol/g)	degree of substitution	M_w (g/mol)	cement fluidity (mm)
	C (wt %)	H (wt %)	O (wt %)	N (wt %)	S (wt %)				
unmodified lignin	64.76 ± 0.02	5.78 ± 0.5	26.67 ± 0.8	0.03 ± 0.002	1.05 ± 0.7	0.03 ± 0.004	0.005	22,746 ± 124	60 ± 2
SML	53.76 ± 0.02	4.94 ± 0.5	33.81 ± 0.8	0.04 ± 0.002	3.21 ± 0.6	1.48 ± 0.02	0.33	53,360 ± 316	155 ± 4

initial increase in lignin concentration increased the solubility to 90%, and further increase caused a decrease in solubility.^{33,34}

Orthogonal Design Analysis. The purpose of the orthogonal design is to investigate which process parameter significantly affects the charge density and solubility of SML.³³ Table 2 lists the sum of squared deviation (SS), mean squares (MS), and *F*-test (*F*). When *F*-test is large, the variation in the process parameter has a significant effect on the results.³⁴ Based on the results in Table 2, time has the maximum effect (*F*-test value of 32.80) and NaOH concentration (*F*-test value of 0.65) has the minimum effect on the charge density of the SML. Similarly, time has the maximum effect (*F*-test value of 70.38) and temperature has the minimum effect (*F*-test value of 0.7) on the solubility of the SML. These results indicate that the reaction time was the most influential factor for the charge density and solubility of SML. Furthermore, based on the ANOVA analysis, the optimal processing conditions for obtaining the maximum charge density and solubility were 0.5 M NaOH concentration, 0.9 mol/mol sodium hydroxymethylsulfonate/lignin ratio, temperature of 100 °C, time of 3 h, and lignin concentration of 20 g/L, which is consistent with the optimized conditions obtained in Figures 2–6.

FTIR Analysis. The FTIR spectra of unmodified and SMLs are presented in Figure 7. The strong and broad band around 3431 cm⁻¹ is characteristic of the OH or phenolic groups.³⁵ The peaks at 2361 and 2336 cm⁻¹ are associated with C–H stretching of methyl or methylene groups. The increase in absorption peaks at 1593 and 1510 cm⁻¹ is attributed to the aromatic functionality in lignin and benzene ring skeletal vibration.²⁸ The increase in absorption peaks at 1460 and 1423

cm⁻¹ corresponds to C–H bending and C–H stretching of methylene groups.⁹ The peak at 1200 cm⁻¹ can be attributed to C=O stretching of the guaiacyl unit and to C–O and C=O stretching of the aromatic ring.³⁶ The absorption peak at 1036 cm⁻¹ on SML is attributed to sulfonate groups, which was not present in unmodified lignin and confirmed the grafting of sulfonate groups to the lignin in the sulfomethylation reaction.⁹ In the previous work, the sulfonate group attached to lignin was confirmed by the increase in the absorption peak at 1040 cm⁻¹ in the FTIR spectrum of sulfomethylated sodium lignosulfonate.⁹

Properties of Sulfomethylated Lignin. The SML with the highest charge density and solubility, which was produced under the conditions of 0.5 M NaOH concentration, 0.9 mol/mol ratio of sodium hydroxymethyl sulfonate/lignin ratio, 100 °C, 3 h, and 20 g/L lignin concentration, was selected for further analysis. Table 3 shows the properties of unmodified and SMLs. The number of sulfonate groups in kraft lignin was increased from 0.03 on unmodified lignin to 1.48 on SML, which corresponds to a degree of substitution (DS) of 0.005 and 0.33 for unmodified and SML, respectively. The degree of substitution for unmodified lignin corresponds to the sulfonate group that is already attached to lignin or present in the kraft lignin as impurities (as kraft lignin was separated from black liquor via sulfuric acid treatment in the process of kraft lignin isolation).³⁷ In the past, the degree of substitution of the sulfonate group was increased from 0.02 to 0.18 by reacting sugar cane bagasse lignin with sodium sulfite under the conditions of 5% NaOH, 37 wt % of formaldehyde, 1.2 g of sodium sulfite, and 95 °C for 150 min.³⁸

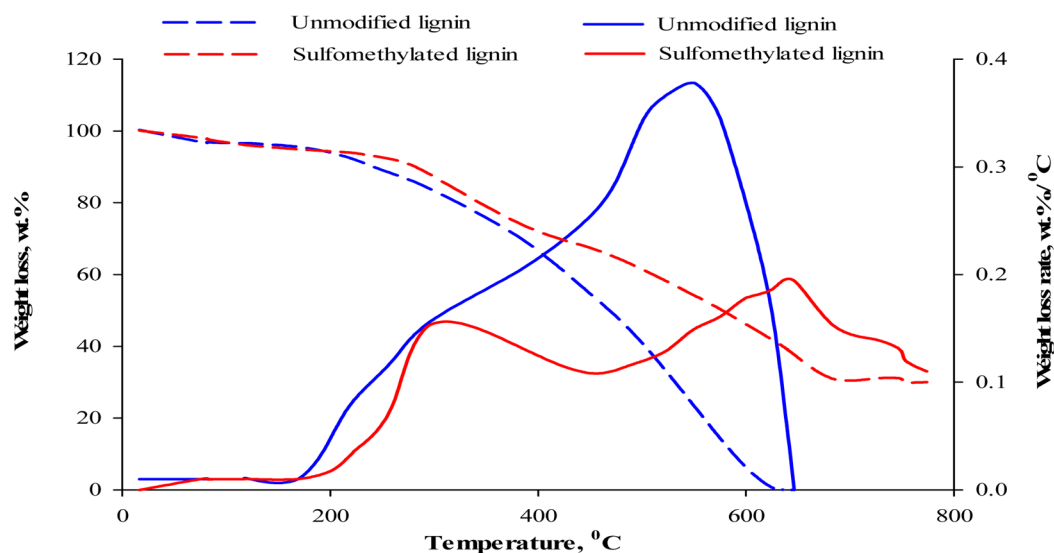


Figure 8. Weight loss (solid line) and weight loss rate (dashed line) of unmodified and SML produced under the conditions of 0.5 M NaOH_(aq), 0.9 mol/mol sodium hydroxymethyl sulfonate/lignin ratio, 100 °C, 3 h, and 20 g/L lignin concentration at 35 mL/min nitrogen flow rate.

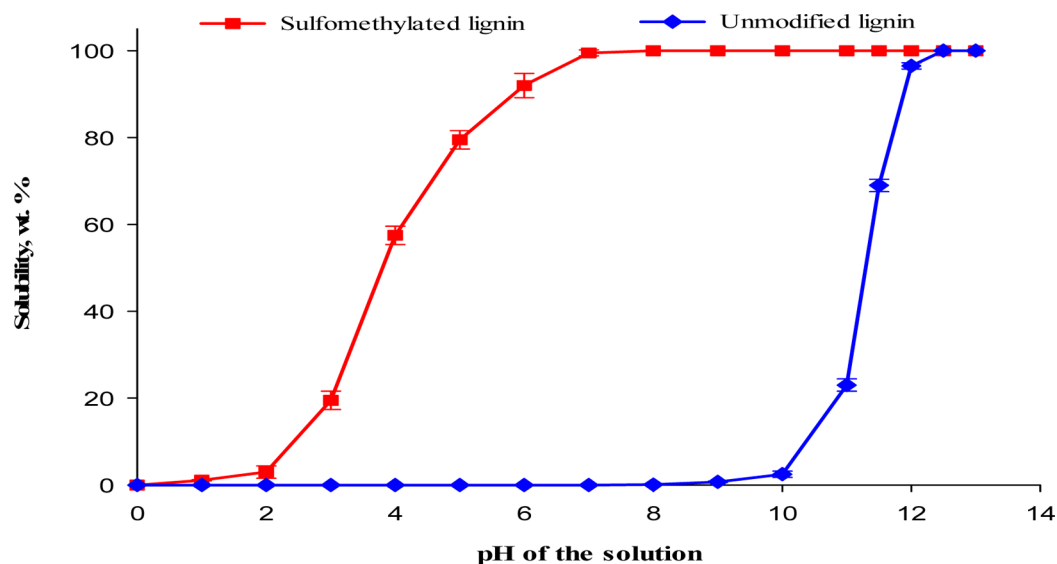


Figure 9. Effect of pH on the solubility of unmodified and SML under conditions of 10 g/L lignin concentration, 30 °C, 2 h.

The results from the molecular weight analysis for unmodified and sulfomethylated kraft lignin samples are provided in Table 3. The SML (53 360 g/mol) had a molecular weight higher than that of unmodified lignin (22 746 g/mol). This increase in molecular weight is due to the replacement of hydroxyl groups with sulfomethyl groups in SML.¹⁹ Previously, the oxidation and sulfomethylation of liginosulfonate with FeSO₄, formaldehyde, and sodium sulfite showed an increase in molecular weight (20 650 g/mol for modified lignin compared to 2378 g/mol for unmodified lignin).²⁸ In another report, the molecular weight of wheat straw kraft lignin was increased from 1900 to 55 700 g/mol via grafting with sodium sulfite.²⁴ As the lignin sources are different in the present study and previous reports,^{23,29} the structure and molecular weight of produced lignin as outcomes of pulping processes will be different. It is also possible that the lignin segment condensed under alkaline conditions, and this increased the molecular weight of lignin.

The elemental analysis of unmodified lignin and sulfomethylated kraft lignin is also provided in Table 3. The sulfur and

oxygen contents of lignin were increased, and the hydrogen content decreased in the modified lignin compared with unmodified lignin, which confirmed the sulfomethylation of kraft lignin.²⁵ Similar results were reported by Matsushita and co-workers on the sulfomethylation of acid-hydrolyzed pine wood lignin with sodium hydroxymethyl sulfonate.²⁷ The sulfomethylation of wheat straw alkali lignin with sodium sulfite showed an increase in sulfonate group content from 0 to 1.48 mmol/g.¹⁹ Based on the results tabulated in Table 3, the chemical formulas of unmodified and SML were C₉H_{9.65}O_{2.78}S_{0.05} and C₉H_{9.92}O_{4.23}S_{0.20}, respectively (nitrogen was omitted due to its trace amount).

Thermogravimetric Analysis. Figure 8 shows the results of TGA analysis for unmodified and SML samples. At a temperature less than 300 °C, the unmodified lignin decomposed faster than SML. The increase in the thermal stability of lignin is an advantage for its end-use applications as a dispersant and flocculant.⁶ This increase is due to the introduction of sulfomethylated groups in the modified lignin

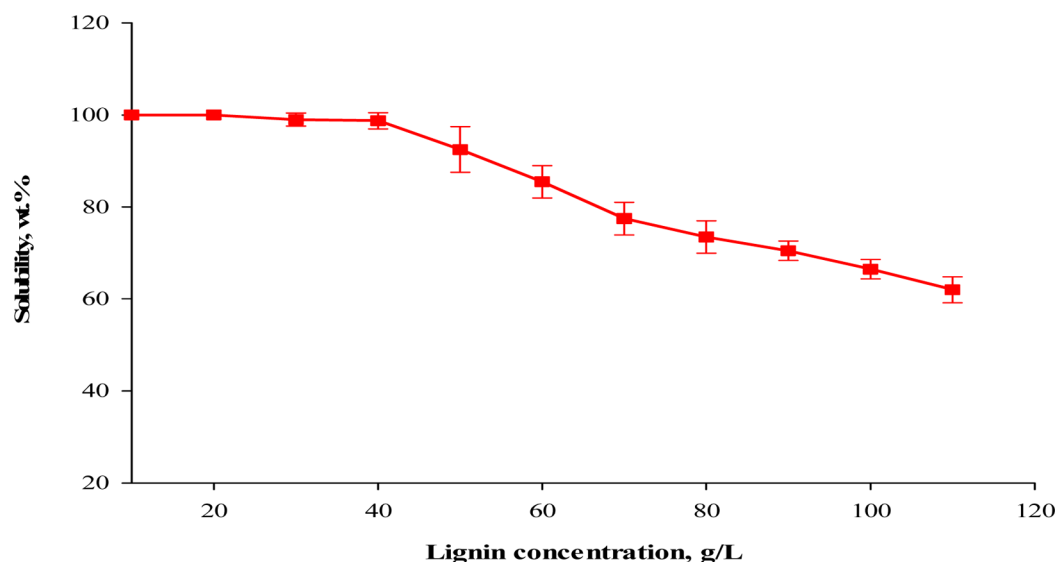


Figure 10. Effect of SML concentration on its solubility under the conditions of pH 7, 30 °C, and 2 h.

during sulfomethylation.³⁹ The unmodified lignin decomposed continuously above 200 °C and was completely degraded at 650 °C. In the case of SML, the degradation began at 250 °C and there was only 70% weight loss at 650 °C. This is due to the introduction of methyl and sulfonate groups in sulfomethylation. It was reported that methyl groups will be decomposed mostly between 700 and 800 °C.⁴⁰ The TGA analysis clearly confirmed that the introduction of sulfonate and methyl groups into lignin increased its thermal stability when compared to unmodified lignin.

Impact of pH and Concentration on the Solubility of Lignin. As pH influences the solubility of lignin, its end-use applications will also be affected. Therefore, it is crucial to investigate the impact of pH on the solubility of SML. The dependency of the lignin solubility on the pH is shown in Figure 9. The unmodified and SML are soluble at a high pH; however, decreasing the pH to 10 led to its insolubility.⁴¹ The SML became insoluble at pH 6, and its solubility was dramatically reduced at pH 3. The pK_a of the sulfonic acid group is 2.8. Thus, the sulfonate group is in its protonated form below pH 2.8, and this decreased the solubility of lignin. Above pH 2.8, the sulfonate group deprotonates, which improves the hydrophilicity and thus the water solubility of lignin.⁴² The high solubility of SML is due to the introduction of sulfonate groups via sulfomethylation, as discussed earlier.

The effects of concentration of SML on its solubility under a neutral condition are presented in Figure 10. It can be understood that, with the increase in the concentration of lignin from 10 to 40 g/L, SML exhibited 100 wt % solubility. Lignin reached the saturation concentration of 40 g/L in an aqueous solution (pH 7) in this experiment.⁴² At a concentration that was greater than 40 g/L, SML probably developed hydrogen bonding (and self-assembly), which limited its solubility.⁴³

Effect of Sulfomethylated Lignin on Cement Fluidity. In order to improve the durability of a fresh cement admixture, additives such as lignosulfonates are usually mixed with cement admixtures.⁴⁴ These additives improve the workability and fluidity of the cement admixture. In this study, SML produced under optimal conditions was tested as an additive to improve the fluidity of the cement admixture.⁴⁵ The results of cement fluidity analysis are also shown in Table 3. In the presence of

SML, cement fluidity was found to increase to 155 mm compared to cement fluidity in the absence of lignin (60 mm). However, unmodified lignin did not show any increase in cement fluidity (60 mm). This behavior is due to the introduction of a sulfonate group to the lignin via sulfomethylation and its water-soluble nature.²³ The SML with an anionic charge density (−1.6 meq/g) adsorbs strongly to the cement particles that have a positive charge density (+0.13 meq/g). Considering the charge densities of SML and cement as well as the dosage of SML in cement suspension (1.2 wt %), we estimated that the overall charges of the cement suspension were changed to −1.79 meq/g, which implies that strong anionic charges are introduced to the suspension and strong electrostatic repulsion force is created between the cement particles, and thereby the dispersibility of cement particles was improved. Furthermore, the ζ -potentials of cement suspensions before and after adding SML were 3.25 and −8.2 mV, respectively, which confirm a significant change in the sign and increased value of overall electrostatic charges of the suspension. In the previous work,¹⁵ SML had a sulfonate group content (−1.5 mmol/g) similar to that of the present work, but the SML of the previous work had a molecular weight (9688 g/mol) lower than that of this work. A comparison may suggest that SML with a similar sulfonate degree, but a lower molecular weight, would be more effective at dispersing cement particles. In the past, sulfonated lignin prepared by treating wheat straw alkali lignin with sodium sulfite showed a cement fluidity of 216 mm compared to that (65 mm) of unmodified lignin.²⁰ Furthermore, the fluidity of a cement paste that contained SML was compared with that of a commercial lignosulfonate (215 mm). The higher fluidity of cement paste with commercial lignosulfonate (compared to that with SML) is due to its low molecular weight (9243 g/mol) and a higher charge density (−1.8 meq/g) compared to those of SML. This analysis may suggest that SML with a higher charge density but lower molecular weight should be produced to have a more efficient cement fluidity.

CONCLUSIONS

Sulfomethylated hardwood kraft lignin was successfully prepared in an aqueous medium by using sodium sulfite and

formaldehyde under alkali conditions. The experimental design results showed that the optimal conditions for sulfomethylation were 0.5 M of NaOH_(aq), 0.9 mol/mol of sodium hydroxymethyl sulfonate/lignin ratio, 100 °C, and 3 h reaction time with a lignin concentration of 20 g/L. The sulfomethylated lignin had -1.6 meq/g charge density and 1.48 mmol/g of sulfonate group, while unmodified lignin had negligible charge density and 0.03 mmol/g of sulfonate group. Molecular weight analysis confirmed that the molecular weight of lignin increased via sulfomethylation from 22 746 to 53 360 g/mol. Solubility analysis confirmed the high solubility (40 g/L) of SML at neutral pH, whereas unmodified lignin was insoluble at pH 7. The solubility was pH-dependent in that kraft lignin was insoluble at pH below 10, but SML was insoluble at pH below 3. The FTIR analysis also confirmed the structural changes, while TGA analysis showed an increase in the thermal stability of lignin via sulfomethylation. Also, the fluidity of cement was improved to 155 mm by adding SML, while that of cement was improved to 60 mm by adding unmodified lignin.

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Notes

The authors declare no competing financial interest.

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