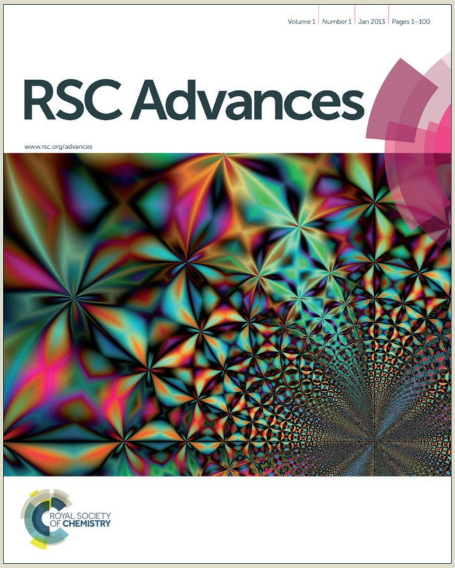
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Preparation of sulfomethylated softwood kraft lignin as a dispersant for cement admixture

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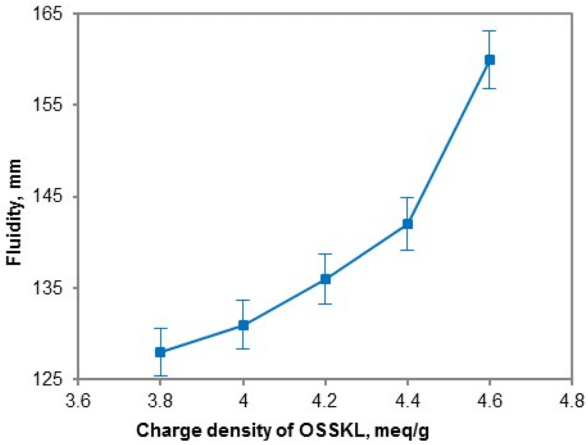
Graphic Abstract



Abstract

Kraft lignin is currently combusted in kraft pulping process. However, it can be modified to produce value-added products. The modification of kraft lignin using a combination of oxidation and sulfomethylation was studied in this work in order to produce sulfomethylated lignin. The oxidized lignin with a carboxylate group of 1.95 meq/g was obtained under the optimal oxidation conditions of 100 ºC and 1 h of treatment with 20 wt.% nitric acid concentration. The sulfomethylated lignin with a sulfonation degree of 2.05 meq/g was obtained under the optimal sulfomethylation conditions of 100 ºC, 3 h treatment, formaldehyde to lignin molar ratio of 1/1, sodium metabisulfite to lignin molar ratio of 0.5/1, and 4.0 wt.% sodium hydroxide concentration. The sulfomethylated lignin with a higher charge density adsorbed more on cement particles and improved the fluidity of a cement paste more effectively than did commercial lignosulfonates. Adding 0.5 wt.% of sulfomethylated lignin to the cement paste increased the fluidity of the paste from 65 mm to 200 mm, while the addition of 0.4 wt.% of unmodified kraft

lignin to the paste resulted in 70 mm fluidity.

Keywords: sulfomethylation, oxidation, kraft lignin, dispersant, green chemical

1. Introduction

Kraft lignin (KL) is produced in the kraft pulping process via acidification of black liquor. It constitutes about 85% of the total lignin production of the world.[1] In the kraft process, the hydroxide and hydrosulfide anions react with lignin, causing lignin to become heavily fragmented into different molecular weights and insoluble in water at neutral pH. Compared with native lignin, kraft lignin has an increased amount of phenolic hydroxyl groups due to the extensive cleavage of β-aryl ether bonds that occur during kraft pulping.[2,3]

Lignosulfonate is mainly produced via a sulfite pulping process in the world. It is a water soluble by-product and has a sulfonate group (i.e. a charged group) on its structure, which facilitates its use in various applications including paper coating, binder, dispersant in oil drilling and coal-water slurry and cement admixture.[4-8] However, 1) the production of lignosulfonate is limited in the world, and 2) lignosulfonate has a limited sulfonate group (i.e. charge density). On the other hand, KL is vastly produced in the world, and it can be extracted from black liquor via commercial processes,[9] but it is mainly used for supplying energy.[10-11] Compared with lignosulfonate of a sulfite process, kraft lignin is water insoluble and lacks sulfonate groups. By increasing its water solubility, the end-use applications of kraft lignin can be broadened.

The solubility of KL can be improved by means of chemical modifications.[3] Sulfonation was proposed as a useful method to improve the water solubility of KL.[12-14] The sulfonation can be conducted under acidic conditions. However, KL may form condensed structures that impair its reactivity under acidic conditions.[15] To prevent the condensation, the sulfonation reaction of lignin was carried out at a high pressure and high temperature, but this would result in high equipment and operating costs.[16] The sulfonation of KL under alkaline conditions was not also very effective.[16] To improve the reactivity of KL (i.e. prohibiting condensation), methylation, phenolation and oxidation were proposed in the past.[17,18] Alternatively, KL can be oxidized using nitric acid, permanganate, chlorine, chlorine dioxide or hypochlorite under mild conditions, which may partially break the side chain of KL.[14] By oxidizing KL, methoxyl and phenolic hydroxyl groups on the aromatic rings of KL are most likely removed, which decreases the steric hindrance of the oxidized lignin and this leads to increased reactivity between the methylene sulfonic group and the oxidized lignin during the subsequent sulfomethylation reaction.[19-21] The oxidation of KL with nitric acid has the advantages including 1) it produces few by-products, 2) nitric acid can be recycled,[22] and 3) the amount of carboxylate groups on KL is increased, which renders KL more hydrophilic and anionically charged. The first objective of this study was to oxidize KL with nitric acid in order to improve the reactivity of KL prior to sulfomethylation and to sulfomethylate the oxidized lignin.

Once modified, KL can be used in many applications including emulsifying agents/emulsion stabilizers, sequestering agents, pesticide dispersants, dye/cement dispersants, additives in alkaline cleaning formulations, flocculants, and as extenders for phenolic adhesives.[23] Water reducers (also known as plasticizers) are extensively used in the construction industry to increase the fluidity of concrete, or reducing the water content of cement pastes.[24] These dispersants function by generating electrostatic repulsion, steric hindrance, or a lubrication layer among cement particles when added to a concrete admixture, improving the workability of the concrete.[19] The water reducing rate of commercial water reducing agents is under 12%, while the water reducing rate of superplasticizers, e.g. naphthaline dispersant is over 12%.[25] The second objective of this work was to assess the performance of sulfomethylated lignin as a dispersant for a cement admixture. Also, it is important to understand how the properties of sulfomethylated lignin affect its performance as a dispersant for the cement admixture, which was the third objective of this study.

In this work, the production of sulfonated kraft lignin was assessed in a laboratory scale, and the performance of the product as a dispersant for a cement admixture was assessed. The sulfomethylation process investigated in this work can be commercialized, but more detailed analyses will be required prior to commercialization. An industrially produced softwood KL was oxidized by means of nitric acid treatment in order to improve its reactivity, and hence its subsequent sulfomethylation. The properties and the effectiveness of sulfomethylated SKL as a dispersant for the cement admixture were assessed. The main novelty of this work was the production of sulfomethylated SKL as a dispersant for the cement admixture. Also, the impact of the charge density of sulfomethylated KL on the fluidity of the cement admixture was studied for the first time in this work.

2. Methodology

2.1. Materials

Softwood kraft lignin (SKL) was produced by LignoForce^{TM} technology of FPInnovations that is located in Thunder Bay, ON, Canada.[9] The cement used was hydraulic cement for general use, type 10, packaged by Target products Ltd, Canada. Nitric acid solution (65 wt.%) was acquired from CALEDON laboratory chemicals, Canada. Commercial lignosulfonic acid sodium salt (LASS) with the sulfonation degree of 1.68 meq/g, sodium hydroxide, sodium metabisulfite ($Na_2S_2O_5$), polydimethyl diallyl ammonium chloride (PDADMAC), and formaldehyde (CH_2O) with the concentration of 37 wt.% were all purchased from Sigma-Aldrich (Canada). 1,3-didecyl-2-methylimidazolium chloride (DDMICI) was obtained from Metrohm Ltd (Switzerland). Also, commercial sodium lignosulfonate (SLS) with the sulfonation degree of 1.57 meq/g was obtained from a local company.

2.2. Oxidation and sulfomethylation of SKL

A 5 g sample of SKL was added into a 500 mL three-neck round bottom glass flask. The oxidation reaction was conducted at different temperatures (60 ºC, 70 ºC, 80 ºC, 90 ºC, and 100 ºC) and time intervals (0.5 h, 1 h, 2 h, 3 h, and 4 h) and concentrations of nitric acid (10-30 wt.%) at 500 rpm. After the reaction, the reaction medium was cooled to ambient temperature and the pH was adjusted to 7 using a 4M $NaOH_{(aq)}$ or $HCl_{(aq)}$ solution. The oxidized SKL (OSKL) was dialyzed with a membrane dialysis (molecular weight cut off of 1000 g/mol) for 24 h, while exchanging water every 12 h, and then dried in an oven overnight at 105 °C. After oxidation; sodium hydroxide, formaldehyde, and sodium metabisulfite were added to the oxidized lignin solution and the sulfomethylation reaction was conducted under different molar ratios of CH_2O to lignin (0.4-1.2 mol/mol) and $Na_2S_2O_5$ to lignin (0.3-0.7 mol/mol), temperatures (60 ºC, 70 ºC, 80 ºC, 90 ºC, and 100 ºC) and time intervals (0.5 h, 1 h, 2 h, 3 h, and 4 h). After sulfomethylation, the sulfomethylated lignin (OSSKL) sample was neutralized as stated above. The OSSKL was dialyzed with a membrane dialysis (molecular weight cut off of 1000 g/mol) for 24 h, while exchanging water every 12 h, and then dried in an oven overnight at 105 °C.

Alternatively, a sample was produced under the oxidation conditions of 100 ºC and 1 h of treatment with 20 wt.% nitric acid concentration, and then this sample was sulfomethylated under the conditions of 100 ºC, 3 h treatment, formaldehyde to lignin molar ratio of 1/1, sodium metabisulfite to lignin molar ratio of 0.5/1, and 4.0 wt.% sodium hydroxide concentration to produce OSSKL, but no dialysis was used during the production of this sample, and it was donated as NOSSKL.

2.3. Box-Behnken experimental design

The Box-Behnken design (BBD) was employed as a statistical tool to investigate the impact of process parameters on the properties of OSKL and OSSKL.[26] The current study with several variables using the one-variable-at-a-time approach revealed the importance of the oxidation temperature and time, and the concentration of nitric acid on the OSKL, and the impact of the CH_2O and $Na_2S_2O_5$, temperature and time on the properties of OSSKL.

2.4. Charge density analysis

The charge density of lignin samples was measured using a Mütek particle charge detector (PCD-04). In this experiment, 0.5 mL or 1 mL of a 1 wt.% lignin solution and 10 mL of deionized water was added to the PCD titrator cell.[27] The titrations were then performed using a standard solution of PDADMAC. The specific charge density of the sample was calculated using equation 1:

$$q = \frac{v \cdot c}{w} \qquad (1)$$

where q is specific charge density (meq/g); c is the concentration of titrant (mol/L, but reported as eq/L since 1 mol of PDADMAC contains 1 eq charge density); v is volume of titrant used for titrating samples (mL); and w is dried weight of samples added to the container of the titrator (g).

2.5. Functional group analyses

The sulfonate and carboxylate groups of OSKL and OSSKL were measured using an automatic potentiometric titrator (905-Titrando, Metrohm, Switzerland). The sulfonate and carboxylate groups were measured using the aqueous potentiometric titration method at different pH values (sulfonic group at pH 7 and carboxylic group at pH 10) using a DDMICI standard solution as a titrating solution. The sulfonate and carboxylate group contents were calculated according to equations 2 and 3:[28,29]

$$SD = \frac{E_1 \times D}{S} \qquad (2)$$

$$C = \frac{(E_2 - E_1) \times D}{S} \qquad (3)$$

where SD is the sulfonate group degree (meq/g), C is the carboxylate group degree (meq/g); D is the concentration of DDMICI standard solution (mol/L, but reported as eq/L as 1 mol of DDMICI contains 1 eq charge density); E_1 is the consumed volume of DDMICI standard solution (mL), E_2 is the consumed volume of DDMICI standard solution (mL); and S is the dried weight (g) of lignin samples used in this analysis.

2.6. Molecular weight analysis of SKL, OSKL, OSSKL, LASS, and SLS

The molecular weight analysis of OSKL, OSSKL, LASS and SLS were performed by Gel Permeation Chromatography (GPC) (Viscotek GPCmax, Malvern, UK). A 100 mg sample of air dried SKL was initially suspended in 4.0 mL of acetic anhydride/pyridine 1:1 (V:V) solution and stirred for 30 min at 300 rpm and 25 °C, and then kept in a dark place at 25 °C for 24 h. The solution was then poured into an excess (50 mL) of ice water and centrifuged/washed 3 times. The solvent was removed from sample via freeze drying. For SKL analysis, the acetylated SKL were initially dissolved in tetrahydrofuran (THF) at a 5 g/L concentration. The solutions were filtered with 0.2 μm filter (13 mm diameter). The filtered solutions were used for molecular weight analyses. For OSKL and OSSKL analysis, a 50 mg sample of air dried lignin was dissolved in 10 mL of 0.1 mol/L $NaNO_3$ solution and filtered with a nylon 0.2 μm filter (13 mm diameter). The filtered solutions were used for molecular weight analysis. The eluent of the organic system was THF and that of aqueous system was a 0.1 mol/L sodium nitrate solution, but both had 0.7 mL/min flow rate in the GPC. Polystyrene polymers were used as standards for the organic system and the polyethylene oxide for the aqueous system for the calibration of the GPC.

2.7. FTIR analysis

Fourier Transform Infrared (FTIR) analysis of SKL, OSKL and OSSKL were carried out at room temperature using a TENSOR 37 FTIR Spectrophotometer (Bruker, Germany) equipped with a Universal Attenuated Total Reflectance (ATR) sampling (ZnSe cell) and diamond window (about 1.5 mm of diameter). The samples were placed directly onto the ATR crystal using the micrometer pressure clamp. The spectra of samples were recorded at a resolution of 4 cm^{-1} in the range of 600 cm^{-1} to 4000 cm^{-1} collecting 32 scans per sample.[23,30]

2.8. ^{1}H-NMR analysis

The OSKL and OSSKL were analyzed with ^{1}H-NMR analysis. 40-50 mg of dried OSKL and OSSKL were dissolved in D_2O at 80-100 mg/mL concentration. The solution was stirred at 200 rpm for 30 min to fully dissolve. The NMR spectra of these samples were recorded using an INOVA-500 MHz instrument (Varian, USA) with a 45° pulse and relaxation delay time of 1.0 s.

2.9. Adsorption of lignin on cement particles

To make a cement admixture, it is more practical to add cement particles to lignin solutions rather than to prepare a cement admixture and subsequently to add lignin particles. To be consistent with the fluidity analysis, the adsorption analysis was conducted via adding cement particles to lignin solutions. In this set of experiment, an OSSKL, LASS or SLS aqueous solution

(10 mL) with a given concentration (0.1~0.7 g/L) was prepared in a glass tube, and then 0.6 g of cement was added to it in order to make a 50/3 mass ratio of modified lignin/cement. The mixture was then stirred at 150 rpm for 120 min at 30 °C, and then centrifuged for 10 min at 3000 rpm (Sorvall ST16). The concentration of supernatant was determined using a UV/vis spectrophotometer (Genesys 10S UV-Vis) with a calibration curve developed previously for lignin samples at 280 nm. The adsorption of modified lignin on the surface of the cement particles (n^S) was calculated as according the equation 4:[31]

$$n^s = \frac{V(C_0 - C)}{m} \qquad (4)$$

Where C_0 and C are the concentrations of modified lignin in the solution before and after treating with cement (mg/mL), V is the initial volume of the modified lignin solution (L), and m is the weight of cement (g).

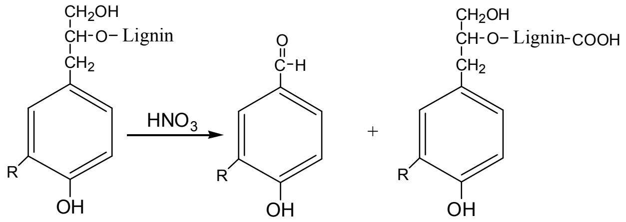
2.10. Fluidity of cement paste

The fluidity of cement paste was determined according to the method described previously:[31] A different amounts of lignin samples were dissolved in 105 g of water, which was added to the 300 g of cement and the mixture was placed into a commercial paste blender and stirred for 4 min (140 ± 5 rpm for 2 min, and 285 ± 10 rpm for 2 min). Subsequently, the paste was rapidly poured into the truncated flow cone mold (base diameter of 6 ± 0.05 cm, top diameter of 3.6 ± 0.05 cm, and height of 6 ± 0.05 cm) on a steel plate. Once the cone was lifted, the cement paste collapsed and spread. The paste was allowed to flow on the plate for 30 seconds. The maximum diameter (d_1) of the spread and the diameter (d_2) perpendicular to it were measured. The average value, $(d_1 + d_2)/2$, was reported as the fluidity of the cement paste. Three replicates for each sample were carried out and the average was reported.

3. Results and Discussion

3.1. Oxidation of SKL

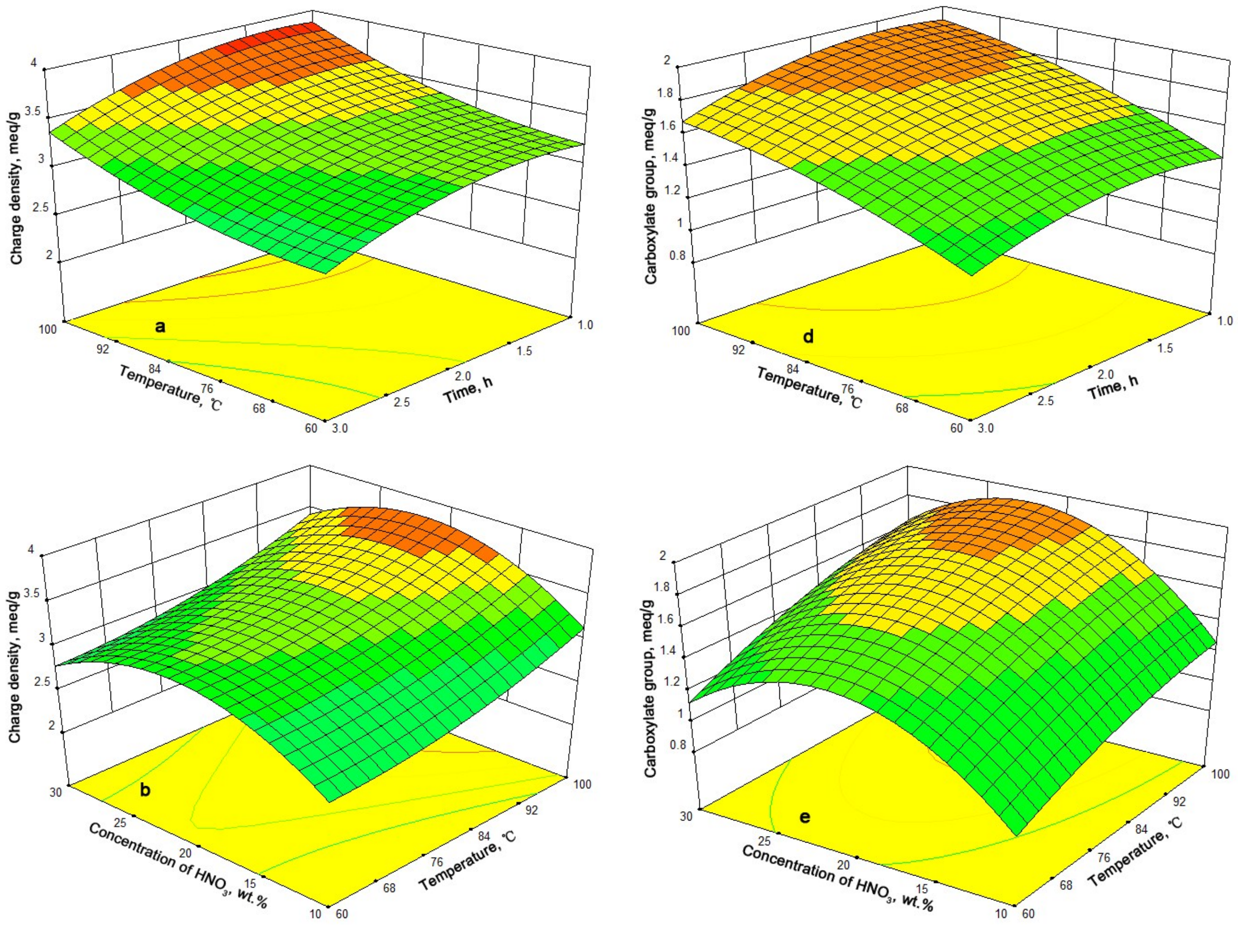
The oxidation reaction of SKL is shown in Scheme 1.



Scheme 1. The oxidation scheme of SKL (R is H or OCH_3)[14,21]

The oxidation reaction of kraft lignin produces 4-hydroxy-3-methoxybenzaldehyde (vanillin) and a variety of low molecular weight compounds that contain carboxylate group. The oxidation of SKL should increase its reactivity for sulfomethylation.[14,21]

The impact of reaction parameters on the charge density and carboxylate group of OSKL is shown in Figure 1. The analysis showed that the charge density and carboxylate group of the OSKL were dependent on all tested parameters and the effect of process parameters were interrelated.



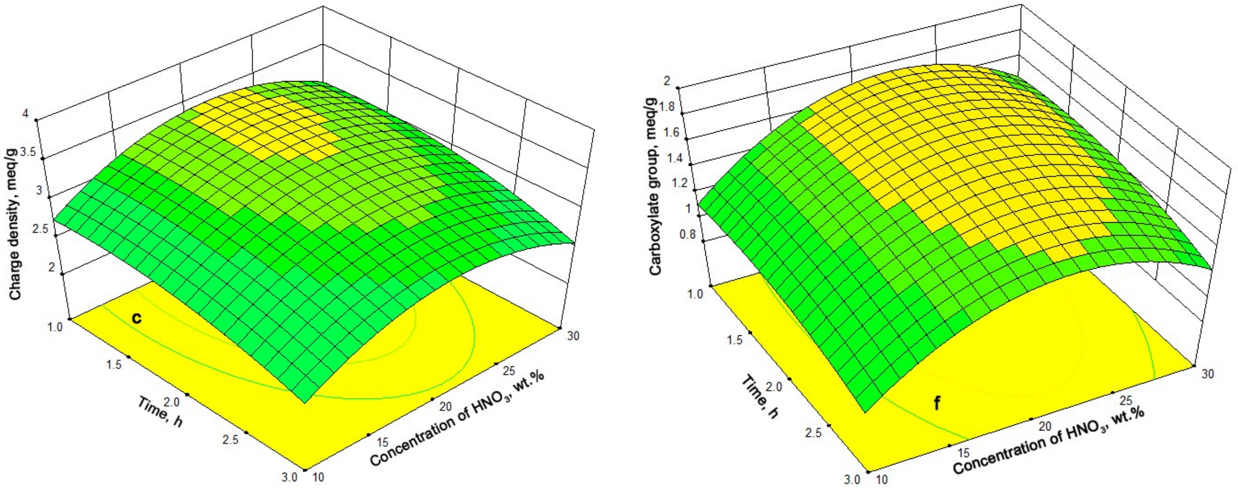
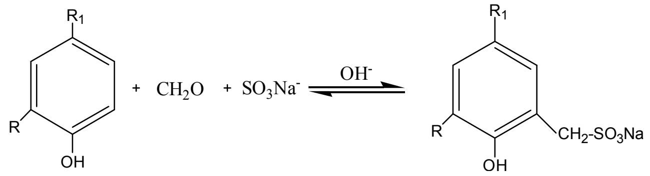


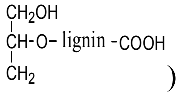
Figure 1. Impact of oxidation process parameters on the charge density and carboxylate group of OSKL.

The results showed that the charge density and carboxylate group of OSKL were increased with a temperature increase (Figure 1a, 1d and 1e). The oxidation of lignin is an endothermic process and with an increase in temperature, the number of carboxylate groups will increase on lignin.[32] This behavior may be due to the fact that at a higher temperature, the reactivity of lignin increases and this enhances the rate of lignin depolymerization.[33,34] Figure 1 also illustrates that the charge density and carboxylate group of OSKL were increased to a certain value and then decreased with the time extension and with the nitric acid concentration increase. This may be attributed to the fact that a longer time and excess nitric acid dealkylated the lignin extensively. Based on this analysis, the maximum charge density and carboxylate group can be estimated to be 3.9 meq/g and 1.95 meq/g for OSKL, respectively, which could be obtained under the conditions of 100 °C, time of 75 min, and a nitric acid concentration of 22.2 wt.%. Experimentally, OSKL was produced under the conditions of 100 °C, time of 1 h, and a nitric acid concentration of 20 wt.%, and this sample had the charge density and carboxylate group of 3.87 meq/g and 1.95 meq/g, respectively.

3.2. Sulfomethylation of OSKL

The sulfomethylation reaction scheme of OSKL is shown in Scheme 2.

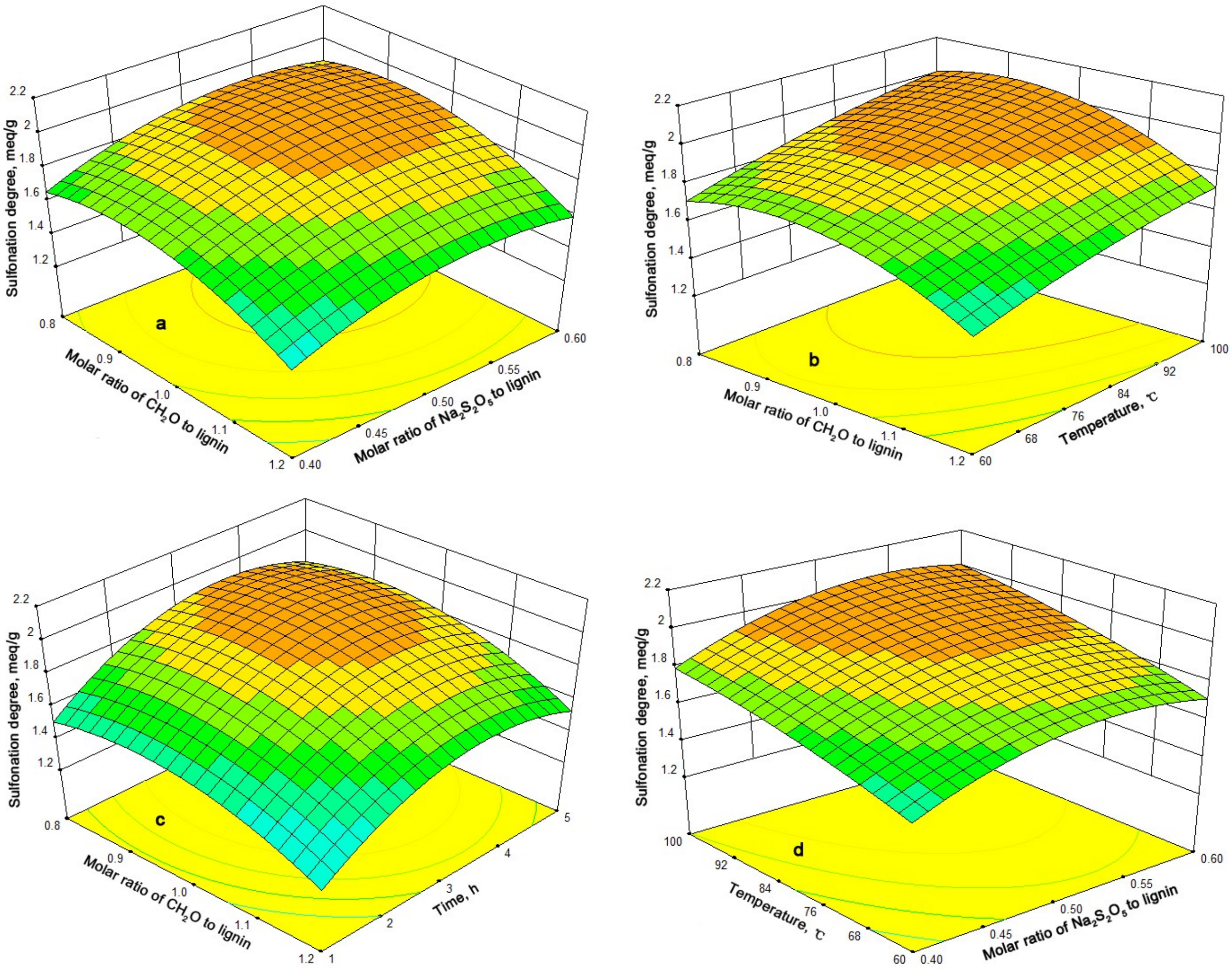


Scheme 2. The sulfomethylation scheme of OSKL (R is H or OCH_3, R_1 is  $\overset{O}{\overset{\|}{C}}\text{-}H$ or  $\begin{array}{l} CH_2OH \\ | \\ CH\text{-}O\text{-}\ lignin\ \text{-}COOH \\ | \\ CH_2 \end{array}$)[14]

It is observable that the reaction occurs with equal moles of alkali metal sulfite salt and phenolic units under alkaline conditions. Repeating reactive units of lignin should have a hydroxyl group on its aromatic ring.[14] Formaldehyde is known to react with phenolic compounds at the *ortho* positions to the hydroxyl group in alkaline media. Hydroxymethyl groups introduced in lignin are favorable for the further sulfonation.[16,35]

3.3. Impact of the reaction conditions of sulfomethylation on the sulfonation degree

The impact of sulfomethylation process parameters on the sulfonation degree of OSSKL were shown in Figure 2.



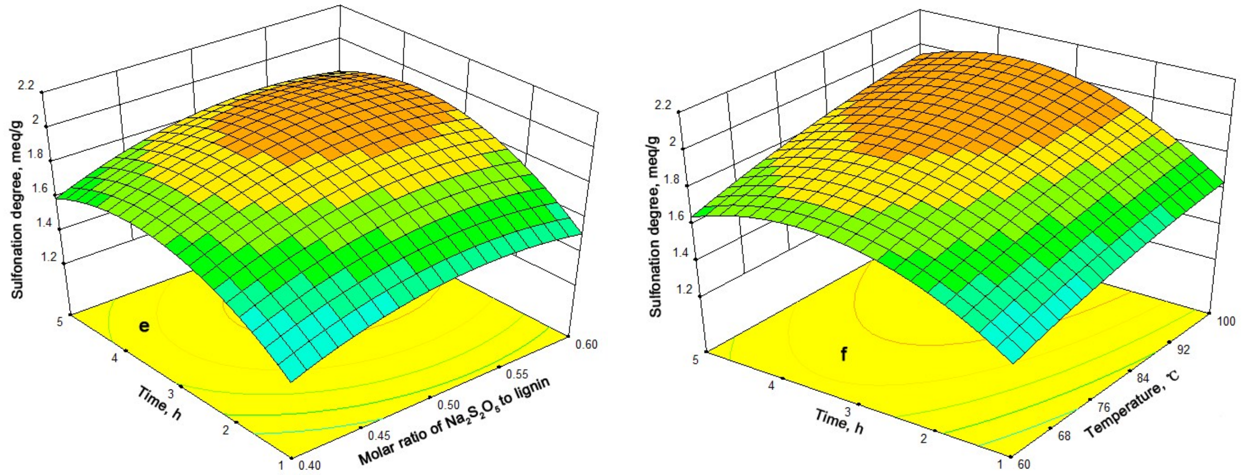


Figure 2. Impact of sulfomethylation process parameters on the sulfonation degree of OSSKL.

It is observable in Figure 2 that the degree of sulfonation was increased to a certain value and then decreased with the increment in the molar ratios of HCHO and $Na_2S_2O_5$ to lignin. By increasing the amount of HCHO, the number of hydroxymethyl group formed on the OSKL is increased, which leads to more sulfonic group attachment on OSKL during sulfomethylation. However, an excessive dosage (1<molar ratio of HCHO to lignin) of formaldehyde hampered the reaction. This could be due to the fact that superfluous formaldehyde leads to the condensation of lignin units, which prevents sulfonate group from reacting with lignin, leading to a decrease in the degree of sulfonation.[16,19] In this case, an excessive amount of $Na_2S_2O_5$ leads to a decrease in sulfonation degree. Furthermore, the number of sulfonate group was increased by an increase in temperature, and the number of sulfonate group reached a maximum after 3 h. In the past, it was observed that 3 h reaction time at 95 ºC was sufficient in producing sulfomethylated lignin.[36] Therefore, the maximum estimated sulfonation degree was 2.03 meq/g for OSSKL, which could be achieved under the conditions of 97.1 ºC, 3.2 h using a 0.97/1 HCHO to lignin and 0.48/1 $Na_2S_2O_5$ to lignin molar ratios. Experimentally, the sulfonated degree of OSSKL was 2.05 meq/g, which was produced under the conditions of 100 ºC for 3 h using a 1/1 HCHO to lignin and 0.5/1 $Na_2S_2O_5$ to lignin molar ratio.

3.4. Molecular weight analysis of lignins

The weight averaged molecular weight (M_w), numerical average molecular weight (M_n), and polydispersity (M_w/M_n) of SKL, OSKL, OSSKL, LASS, and SLS are shown in Table 1.

Table 1. Molecular Weight of SKL, OSKL, OSSKL, LASS, and SLS Analyzed by GPC

Sample	M_w, g/mol	M_n, g/mol	M_w/M_n

SKL	16,770	5,457	3.07
OSKL	13,845	7,500	1.85
OSSKL	18,299	14,979	1.22
LASS	16,426	9,328	1.76
SLS	15,478	5,342	2.90

As seen in Table 1, the overall M_w and M_n of OSKL and OSSKL were slightly different from those of SKL, but the polydispersity was dramatically reduced by oxidation and sulfomethylation, and the polydispersity of OSSKL was less than that of LASS and SLS. This implies that the molecular weight distribution of OSKL and OSSKL were improved and lignin became more homogenous by the oxidation and sulfomethylation processes. This could be due to the fact that the oxidation affected the structure of SKL (most likely due to the partial decomposition of the SKL) resulting in lignin (OSSKL) with a similar structure and molecular weight after oxidation. The molecular weight of OSSKL increased via sulfomethylation and was higher than that of LASS and SLS, which could be due to the addition of methylene sulfonate group to OSKL and the condensation of OSKL with formaldehyde.[37]

3.5. FTIR analysis of SKL, OSKL, and OSSKL

The IR spectra of SKL, OSKL, and OSSKL are shown in Figure 3. As seen, the peak at 1597 cm^{-1} can be attributed to the aromatic groups present in lignin. The characteristic peak from the phenyl rings vibration appears at 1510 cm^{-1}, but OSKL have no obvious peak at 1510 cm^{-1}. The strong and broad band at around 3370 cm^{-1} is the characteristic of the OH group or phenolic compounds.[38] The adsorption band at around 1,226 cm^{-1} was assigned for C=O deformation.[39] This indicates the presence of carboxylic group (–COOH) on the OSKL. The peak at 1250 cm^{-1}, which is assigned to guaiacyl ring with C–O stretching vibration, is weaker in OSKL than in SKL, indicating the decomposition of the phenyl rings by oxidation. The absorption peak of OSSKL at 1193 cm^{-1} is from the asymmetry stretching vibration of the sulfur-oxygen bond (O=S=O), but at 1119 cm^{-1} and 1044 cm^{-1} are the symmetry stretching vibration of (O=S=O) bond.[40,41] The peak at 1376 cm^{-1} of OSSKL is associated with C-H deformation and C-H in-plane deformation of methylene group ($–CH_2$).[42] This indicates the presence of methylene sulfonic group ($–CH_2SO_3^-$) on the OSSKL.

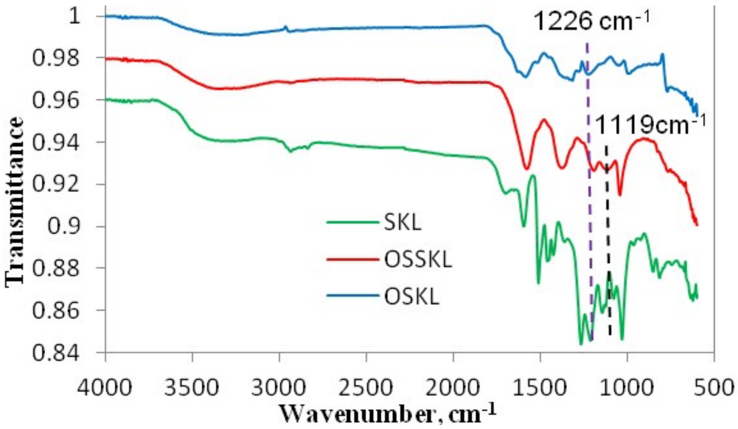


Figure 3. FTIR spectra of SKL, OSKL and OSSKL

3.6 ^{1}H-NMR analysis of OSKL and OSSKL

The ^{1}H-NMR spectra of OSKL and OSSKL are shown in Figure 4. As can be seen, the peak at 8.2 ppm can be assigned to the hydrogen of phenolic hydroxyl, the peak at 6.3-7.7 ppm is attributed to the hydrogen of aromatic ring. The peak at 3.5-4.0 ppm corresponds to the hydrogen of methoxyl groups. The peak at 2.4-2.6 ppm was associated with the proton of methylene.[43]

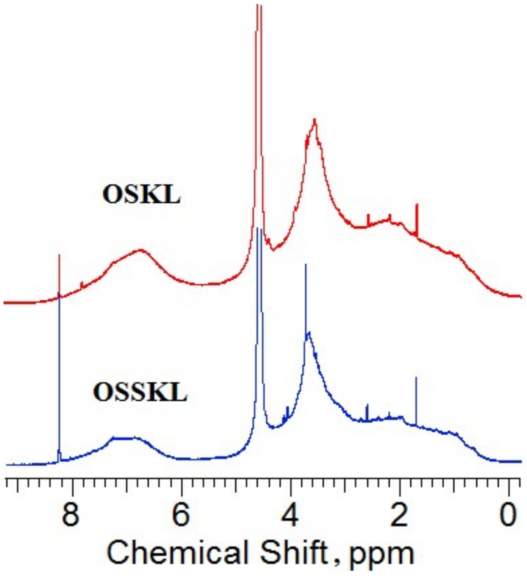


Figure 4. ^{1}H-NMR spectra of OSKL and OSSKL

3.7. Adsorption analysis of OSSKL

The effect of the charge density of OSSKL on the adsorption of OSSKL on the surface of cement particles (n^S) is shown in Figure 5.

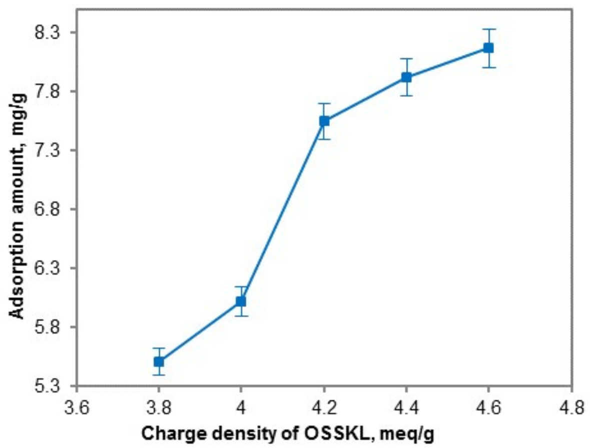


Figure 5. Effect of charge density on adsorption amount on cement particles; conditions were 0.6 g of cement, 10 mL of modified lignin aqueous solution, and the mixture was stirred at 150 rpm for 120 min at 30 °C.

By increasing the charge density of OSSKL, its adsorption amount on the surface of cement particles was increased. Methylene sulfonate group provides a negative charge density on lignin, which is the main driving force for the adsorption of OSSKL on the surface of cement particles by electrostatic attraction. This phenomenon was observed by others in the past.[16,23] Adsorption isotherms of OSSKL, LASS and SLS are shown in Figure 6.

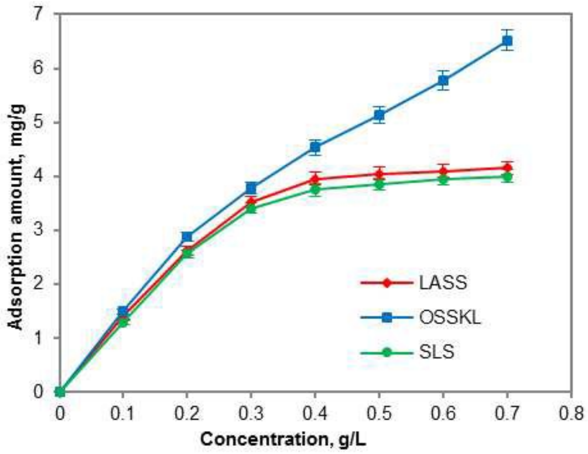


Figure 6. Adsorption isotherms of OSSKL, LASS and SLS; conditions were 0.6 g cement, 10 mL of modified lignin aqueous solution, the mixture was stirred at 150 rpm for 120 min at 30 °C.

The OSSKL was adsorbed more than the other lignins on the surface of cement particles. The sulfonation degree of the OSSKL (2.04 meq/g) was higher than that of LASS (1.68 meq/g) and SLS (1.57 meq/g). The negatively charged sulfonate group on the OSSKL than on LASS and

SLS introduced larger attractive force between adsorbents (i.e. lignin) and cement particles.[15] It should be stated that the adsorption of lignin on cement was generally 0.5 mg/g less when cement admixture was initially prepared and lignin solutions were subsequently added to the admixture.

3.7. Effect of charge density of lignin on fluidity of cement paste

The effect of sulfonation degree on the fluidity of cement paste is shown in Figure 7. The results showed that the higher the charge density of OSSKL, the higher the fluidity of cement paste could be achieved. Both of higher adsorption amount on the surface of cement particles and increased negative charges (sulfonate group) in the cement paste admixture can improve the electrostatic repulsion among cement particles and consequently the fluidity of cement paste (i.e. dispersion of superplasticizer).[19,31]

Figure 7. Effect of charge density of OSSKL on the fluidity of cement paste, conditions were 0.9 g of OSSKL dissolved in 105 g of water, 300 g of cement.

The effect of dosage of different lignin samples on the fluidity of cement paste is shown in Figure 8.

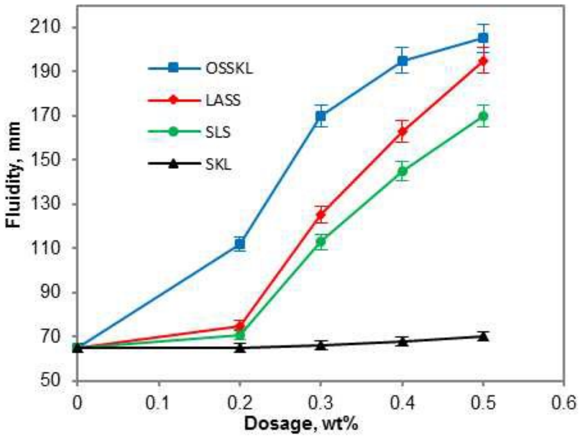


Figure 8. Effect of dosage of different lignin products on the fluidity of cement paste, conditions were 0.35/1 weight ratio of water to cement, 300 g of cement.

The fluidity of OSSKL was higher than that of LASS, SLS and SKL. When the dosage of lignin was 0.4%, the fluidity of OSSKL, LASS, SLS, and SKL was 200 mm, 165 mm, 145 mm, and 70 mm, respectively. This could be due to the higher sulfonation degree of OSSKL than that of LASS, SLS and SKL. This result indicates that OSSKL acted as a strong dispersant in the cement paste and OSSKL can be used as a superplasticizer.[19] In another set of experiments, NOSSKL (OSSKL without dialysis) was used as a dispersant and the fluidity of cement was 114 mm at 0.4 wt.%, which is lower than that of OSSKL. A comparison between the results of OSSKL and NOSSKL indicated that the by-product of oxidation and sulfomethylation reduced the dispersion efficiency of OSSKL, as NOSSKL was produced without dialysis. Therefore, further purification would be needed to improve the dispersion efficiency of sulfonated lignin. Comparing with sulfite pulping, the sulfomethylation of kraft lignin is more complicated, but the results revealed that sulfonated products with better performance can be produced from kraft lignin.

4. Conclusions

The charge density and carboxylate group content of OSKL were 3.87 meq/g and 1.95 meq/g, respectively, under these conditions of 100 °C, 1 h, and 20 wt.% nitric acid concentration. The suitable conditions for the sulfomethylation of OSKL were 100 ºC and 3 h of treatment with 1/1 HCHO to lignin and 0.5/1 $Na_2S_2O_5$ to lignin molar ratio. Under these conditions, the degree of sulfonation of OSSKL was 2.05 meq/g. The sulfonation had a marginal effect on the molecular weight, however, the polydispersity index of lignin decreased significantly after sulfomethylation.

The adsorption amount of OSSKL on the surface of cement particles was higher than that of other lignin products and the fluidity of OSSKL was higher than that of LASS, SLS and SKL.

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Supplementary Data

The raw data for charge density, carboxylate and sulfonate group and molecular weight analyses is available on supplementary data of this manuscript. This material is available free of charge via the Internet at http://pubs.rsc.org.

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