OXIDATION AND SULFOMETHYLATION OF ALKALI-EXTRACTED LIGNIN FROM CORN STALK

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A lignosulfonate was prepared from alkali-extracted corn stalk lignin (AEL) by oxidation under mild conditions and sulfomethylation. The oxidized AEL exhibited lower molecular weight, narrower molecular weight distribution, and higher phenolic hydroxyl content than AEL, demonstrating that oxidized AEL was more reactive than those before oxidation. The content of sulfonic groups was significantly increased with the increase in sodium sulphite to AEL ratio, while the content slightly decreased when the ratio was above 1:1. During the sulfomethylation, the content of sulfonic groups increased with time and then achieved a constant level with the increase in time. The content of sulfonic groups reached 1.29 mmol/g, the maximum value, at 5 h and a sodium sulphite to AEL ratio of 1:1. The solubility of AEL was obviously improved by sulfomethylation with the increase in the content of sulfonic groups. The surface activity of AEL was improved after sulfomethylation. The sulfomethylation products exhibited good dispersibility and showed potential for use as a dye dispersant.

Keywords: Alkali extracted lignin; Oxidation; Sulfomethylation; Solubility; Surface tension; Dispersibility

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INTRODUCTION

Lignin, the most abundant natural polymer second only to cellulose, has been gradually recognized as a potential raw material for preparing high-valued products. Technical lignins, usually recovered from the pulping and paper making industry, are thought to be useful in preparing these products. Lignosulfonate, usually obtained from waste liquor of sulfite pulping, is one of the most useful lignin products. It can be used as a dye dispersant, a water reducer of cement, or a chelating agent, *etc*. However the supply of lignosulfonate in some countries is limited because sulfite pulping is seldom used. Sometimes lignosulfonate has to be prepared by sulfonation of alkali lignin.

Over the last two decades, increasing studies on sulfonation of alkali lignin have been reported. Watanabe *et al.* (1990, 1992) investigated the radical sulfonation of lignin. Yasuda and Asano (2000) synthesized a strongly acidic cation exchange resin from sulfuric acid lignin by phenolation, resinification, and sulfonation. Ouyang *et al.* (2007) prepared a concrete dispersant from alkali lignin by sulfomethylation. Therefore, it is of significance to study sulfonation of AEL to expand its application in high value products.

The sulfonation of soda lignin, however, is satisfactory due to the wide molecular weight distribution, low solubility, and poor reactivity of soda lignin.

Recently, a new type of technical lignin, named alkali-extracted lignin (AEL), has been obtained by the extraction of stalk with dilute alkali solution under mild conditions. During the production of bio-butanol, corn stalk was first treated by enzyme-catalyzed hydrolysis to isolate hemicelluloses and amorphous cellulose. The hemicelluloses and amorphous cellulose isolated from the procedure were used to produce butanol. The residue was extracted by dilute NaOH solution at approximately 120°C to dissolve lignin. Then the solution was acidified precipitate lignin (AEL). AEL exhibits a narrower molecular weight distribution and higher reactivity than soda lignin due to the mild separation conditions. AEL is thus expected to produce lignin based products.

Some chemical modification is beneficial to improve the reactivity of AEL. The molecular weight and the phenolic hydroxyl content of lignin should be adjusted to improve the reactivity of AEL. As a typical method, oxidation by oxygen of peroxide can increase the phenolic hydroxyl content. However, these procedures usually require high temperature and high pressure, and lots of byproducts are formed during the procedure. Therefore, it is desirable to conduct the oxidation under mild conditions.

Lignin in black liquor has been reported to be oxidized by Fenton reagent (the mixture of peroxide and ferrous ion) under mild conditions. Araujo *et al.* (2002) reported that Fenton reagent induced an extensive degradation of lignin (95% to 100% conversion) at a high concentration (60 mmol/L) of hydrogen peroxide. Bentivenga *et al.* (2003) treated recycled paper containing 27% lignin with Fenton reagent, and the lignin that existed in the recycled paper was extensively degraded. These studies show a Fenton reagent under mild conditions can oxidize lignin. It can be estimated that similar reactions can be adopted in the modification of technical lignins.

In this study, Fenton reagent first oxidizes AEL, and then the oxidized AEL (O-AEL) is sulfomethylated to prepare sulfomethylated AEL (S-AEL). The structural changes of AEL were investigated. The impacts of sulfomethylation on sulfonic group content, solubility, surface activity, and dispersibility were also investigated.

EXPERIMENTAL

Materials

AEL, produced from the residues of butanol production by dilute alkali extraction of corn stalk, was supplied by Songyuan Laihe Chemicals Co., Ltd, China. Lignosulfonate (LS, $\overline{Mw} \geqslant 20\times10^3$) was a commercial product of Kaishantun Chemical Pulp Plant, China. Dye red (1-amino-2-phenoxy-4-hydroxyanthraquinone, CAS No.: 7418-58-5) was supplied by Shenzhen Rainbow Dyestuff Co., Ltd, China. Other chemicals used in this study were of reagent grade. Cation exchange resin and anion exchange resin were produced by Guangdong Guanghua Science & Technology Co., Ltd, Guangzhou, China.

Oxidation of AEL

5 g of AEL, 0.5 to 2 mL of hydrogen peroxide, 0.566 g of ferrous sulphate, and 100 mL of deionized water were added into a 250 mL three-neck flask equipped with a stirrer, a thermometer, and a reflux condenser. Then the mixture was stirred at 30 to 60°C

and pH 3 to 5 for 1 h. After the reaction, the flask was cooled to room temperature. The oxidized AEL, named as O-AEL, was centrifuged, washed, and vacuum-dried.

Sulfomethylation of AEL and O-AEL

The reaction mixture of oxidized material was heated to 75°C, and the pH was adjusted to 9 with 0.1 mol/L NaOH. Subsequently, 0.5 to 1.5 mL of formaldehyde was added into the solution and then the solution was stirred for 1 h. After that, 1 to 8 g of sodium sulfite was added to the solution after the solution was heated to 90°C, and then the mixture was stirred for 1 to 8 h. After the reaction, the product was filtered by ionic and cationic exchange columns in sequence. Sulfomethylated AEL(S-AEL) was then obtained by freeze-drying. AEL was also sulfomethylated under the same condition.

Characterizations of AEL, O-AEL, and S-AEL

The molecular weight and the distribution of acetylated AEL and acetylated O-AEL were measured by Agilent 1100 gel permeation chromatography (GPC) equipped with an Agilent-25 column and a R401 differential refractory index detector. The samples were eluted with THF with the flow rate of 1 mL/min. The column temperature was 35°C. The columns were calibrated with narrowly distributed polystyrene standards.

The hydroxyl content of AEL and O-AEL were analyzed by ^{31}P-NMR spectroscopy on a Bruker DRX-400 spectrometer according to the method of Zawadzki and Ragauskas (2001). The lignin samples were derivatized with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane according to the method of Granata and Argyropoulos (1995) before ^{31}P-NMR characterization.

The phenolic hydroxyl contents of AEL and O-AEL were determined by ionization difference spectroscopy (Goldschmid 1954).

The sulfonic group content of S-AEL was determined by conductometric titration (Öster *et al.* 1988) .

Evaluation of Solubility

The solubility of AEL and S-AEL was evaluated by testing the pH of precipitation with the addition of 0.1 mol/L HCl into the sulfomethylation product. 0.1 mol/L HCl solution was dropped into the 50 g/L aqueous solution of lignin with stirring. The pH at which the solution began to precipitate was recorded with the use of a pH meter.

Measurement of Surface Tension

The surface tension of aqueous S-AEL solution was measured at 15°C and pH 5 by the Wilhelmy plate method (Boucher *et al.* 1967) with use of a DCAT21 tension meter (DataPhysics Instruments GmbH, Germany).

Evaluation of Dispersibility

7 g of dispersant, 10 g of dye red, and 5 drops of 1% EDTA (pH 8.6 to 9.2) were mixed thoroughly in 25 g of water in a 250 mL beaker. Then the pH of the dye dispersion was adjusted to 8 with 100 g/L acetic acid. Glass beads (200 g) were added into the

beaker. After being milled for 4 h, the dispersion was filtered and diluted to 1 L with deionized water.

The dispersibility of the dye dispersion was evaluated according to Test Method 146-2006, which was described in AATCC Technical Manual (2007). The filtration time was recorded to evaluate the dispersibility. Dispersant-free dye dispersion was used in the control test.

RESULTS AND DISCUSSION

Structural Characteristics of AEL and O-AEL

It has been reported that the oxidation efficiency of Fenton reagent is influenced by pH, H_2O_2 dosage, and temperature (Lin and Lo 1997). In this study, the impacts of pH, H_2O_2 dosage, and temperature on the oxidation of AEL were investigated.

The molecular weight and the molecular weight distribution of AEL and O-AEL are shown in Table 1. Obviously, O-AEL presented much lower molecular weight and narrower molecular weight distribution than AEL. The results implied that the degradation could be achieved by oxidation with Fenton reagent under mild conditions. A possible reason for the results was that the hydroxyl radical produced by Fenton reagent led to the cleavage of ether linkages in AEL.

Table 1. Molecular Weight and Molecular Weight Distribution of AEL and O-AEL

Sample	Temperature (°C)	pH	H_2O_2 (mmol/L)	$\overline{Mn}$	$\overline{Mw}$	$\overline{Mw}/\overline{Mn}$
AEL	-	-	-	3720	8870	2.38
O-AEL1	50	5	5	2990	5020	1.68
O-AEL2	50	5	10	3340	5320	1.59
O-AEL3	50	5	15	3180	5390	1.69
O-AEL4	50	5	20	3080	4950	1.61
O-AEL5	50	3	10	2990	4940	1.65
O-AEL6	30	5	10	2710	5630	2.08
O-AEL7	40	5	10	2950	5410	1.83
O-AEL8	60	5	10	3130	5250	1.68

The data of O-AEL1 through O-AEL4 in Table 1 indicated that increasing the dosage of H_2O_2 led to decreased $\overline{Mn}$ of O-AEL. This can be attributed to the increased hydroxyl radicals corresponding to the increase of H_2O_2 dosage. The $\overline{Mw}$ of O-AEL, however, slightly increased when H_2O_2 dosage was increased from 10 mmol/L to 15 mmol/L and then was significantly decreased when H_2O_2 dosage increased to 20 mmol/L. The results indicated that increased dosage (20 mmol/L) of H_2O_2 favored the degradation of high molecular weight fraction of AEL. Additionally, the data of O-AEL1 and O-AEL5 showed that the oxidation at pH 3 could degrade AEL more extensively than that at pH 5. A possible reason was that more hydroxyl radicals were produced at pH 3 than at pH 5, as was reported by Lindsey and Tarr (2000). Furthermore, the $\overline{Mw}$ of O-AEL tended to decrease when the temperature rose to 60°C from 30°C. The results implied that elevated temperature favored the degradation of high molecular weight fraction of AEL. The narrowest molecular weight distribution of O-AEL was observed when the oxidation was carried out at 50°C.

The contents of phenolic hydroxyl in AEL and O-AEL are shown in Table 2. As shown in Table 2, the content of phenolic hydroxyl in O-AEL was much higher than that in AEL. It could be deduced that quantities of aryl ether linkages in AEL were cleaved and converted to phenolic hydroxyl groups during the oxidation process.

Table 2. Phenolic Hydroxyl Content of AEL and O-AEL

Sample	Temperature (°C)	pH	H_2O_2 (mmol/L）	Phenolic hydroxyl content （mmol/g）
AEL	-	-	-	2.85
O-AEL1	50	5	5	3.14
O-AEL2	50	5	10	3.26
O-AEL3	50	5	15	3.35
O-AEL4	50	5	20	3.28
O-AEL5	50	3	10	3.29
O-AEL6	30	5	10	3.03
O-AEL7	40	5	10	3.15
O-AEL8	60	5	10	3.30

As shown in Table 2, the data of O-AEL1 through O-AEL4 also showed that the content of phenolic hydroxyl in O-AEL increased with the initial increase of addition of hydrogen peroxide and then decreased when the dosage exceeded 15 mmol/L. A possible reason is that the phenolic hydroxyl was oxidized, with the creation of carboxyl groups, at the high concentration of hydrogen peroxide. In addition, the content of phenolic hydroxyl groups in O-AEL increased with the elevation of temperature from 30°C to 60°C, demonstrating that elevating temperature favored the cleavage of aryl ether linkages during the oxidation. Additionally, the O-AEL1 and O-AEL5 had similar content of phenolic hydroxyl. The results indicated that the content of phenolic hydroxyl in O-AEL had no significant change when the pH was varied in the range of 3 to 5.

Although the content of phenolic hydroxyl groups in AEL was increased by the oxidation, the total amount of reactive hydroxyls was limited because not all the phenolic hydroxyl in AEL could contribute to the reactions. It is well known that the phenolic units in lignin can be classified into two categories, *i.e.*, the units with substituted carbon-5 and the units with unsubstituted carbon-5, as shown in Fig. 1.

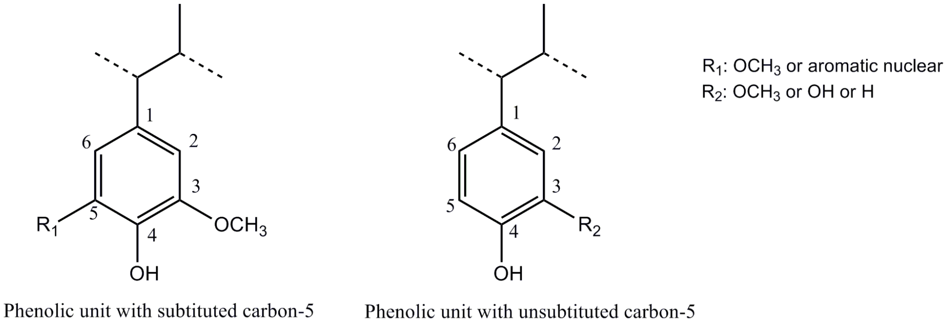


Fig. 1. Phenolic units in lignin

The sulfomethylation of lignin occurred at the unsubstituted carbon-5 sites in phenolic units of lignin. Thus, phenolic units with unsubstituted carbon-5 are necessary for sulfomethylation. The content of unsubstituted phenolic units reflects the reactivity of lignin in the sulfomethylation.

The contents of hydroxyls and carboxyl in AEL and O-AEL1 are listed in Table 3. The contents of p-hydroxyphenyl units, catechol units, and guaiacyl units summed up to 1.46 mmol/g, accounting for 49% of the phenolic hydroxyls in AEL. Conversely, the contents of p-hydroxyphenyl units, catechol units, and guaiacyl units summed up to 1.67 mmol/g, accounting for 52% of the phenolic hydroxyls in O-AEL1. It was inferred from the results that O-AEL1 was more reactive in sulfomethylation than AEL.

Table 3. Different Hydroxyls Contents of Lignin Calculated from ^{31}P-NMR Spectra

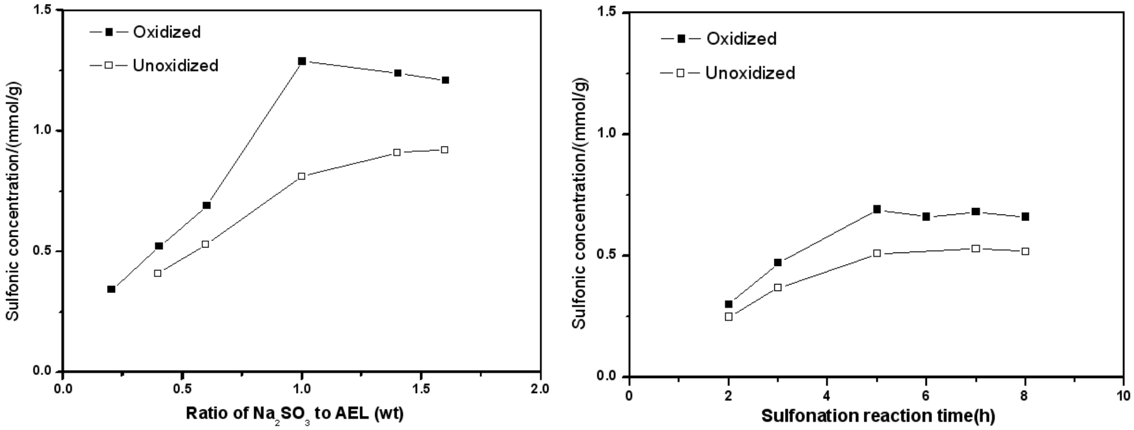
Chemical-shift range δ ^{31}P-NMR (ppm)	Assignment	Content (mmol/g)	
		AEL	O-AEL1
150.0-145.5	Aliphatic hydroxyl	1.04	0.98
137.2-144.8	Total phenolic hydroxyl	2.97	3.24
140.0-144.8	Phenolic hydroxyl in syringyl units and condensation structure	1.51	1.57
139.2-140.0	Phenolic hydroxyl in guaiacyl units	0.63	0.69
138.7-139.2	Phenolic hydroxyl in catechols units	0.21	0.10
137.0-138.7	Phenolic hydroxyl in p-hydroxyphenyl units	0.62	0.88
134.0-136.0	Carboxyl	0.68	0.79

Consequently, the decreased molecular weight and the increased content of phenolic hydroxyl in AEL had been achieved after oxidation by Fenton reagent under mild conditions. Thus, O-AEL was expected to be more reactive for further sulfomethylation.

Impact of Sulfomethylation on Sulfonic Group Content

The water solubility of lignin depends on the content of hydrophilic groups. The introduction of a sulfonic group can improve the solubility of lignin. In this paper, sulfonic groups were introduced into AEL and O-AEL by sulfomethylation. The contents of sulfonic groups in S-AEL prepared from O-AEL and AEL are shown in Fig. 2.

It is obvious that the content of sulfonic groups in S-AEL prepared from O-AEL was higher than that prepared from AEL under the same conditions. The results indicated that the oxidation made AEL more reactive in sulfomethylation. The result is in good agreement with the previous inference obtained from ^{31}P-NMR. The sulfomethylation of lignin was primarily influenced by sodium sulfite dosage and the time of sulfonation. The impacts of the sodium sulfite dosage and the time of sulfonation on the content of sulfonic group in S-AEL were investigated. The content of sulfonic group in S-AEL prepared from O-AEL was 0.34, 0.52, 0.69, 1.29, 1.26, and 1.21 mmol/g, respectively, when the weight ratio of sodium sulfite to AEL was 1:5, 2:5, 3:5, 1:1, 8:5, and 2:1, respectively, as shown in Fig. 2(a). The results indicate that increasing the sodium sulfite addition resulted in the remarkable increase in sulfonic group content at first and then a slight decrease. The content of sulfonic group reached 1.29 mmol/g with the sodium sulfite to AEL ratio of 1:1. In addition, the impact of sulfonation time on the content of sulfonic group of S-AEL is shown in Fig. 2(b). The sulfonic group content of S-AEL increased rapidly in the initial 5 h and remained constant after that. The results demonstrated that the reaction was finished at the time 5 h.



(a) **(b)**

Fig. 2. Effect of sulfomethylation on sulfonic group content

Notes: (a), oxidation conditions: pH 5, 50°C, 1 mL of H_2O_2, 0.566 g of $FeSO_4{\cdot}7H_2O$, and 1 h; hydroxymethylation conditions: pH 9, 75°C, 0.75 mL of formaldehyde, and 1 h; sulfonation conditions: 90°C, 5 h. (b), oxidation conditions: pH 5, 50°C, 1 mL of H_2O_2, 0.566 g of $FeSO_4{\cdot}7H_2O$, and 1 h; hydroxymethylation conditions: pH 9, 75°C, 0.75 mL of formaldehyde, and 1 h; sulfonation conditions : 90°C and 3:5 ratio of sodium sulfite to AEL

Solubility of S-AEL

It is widely accepted that the solubility of lignin depends on the content of hydrophilic groups in lignin and the molecular weight distribution of lignin. Generally, the solubility of alkali lignin can be improved by sulfonation or sulfomethylation. As is well known, the solubility of lignin depends on the pH of lignin solution. In this study, the solubility of lignin was evaluated by the pH of precipitation of aqueous lignin solution during the acidification procedure.

Table 4. pH of Precipitation of AEL and S-AEL

Sample	Time of sulfonation (h)	Content of sulfonic group (mmol/g)	pH of precipitation
AEL	-	0	8.0
S-AEL	2	0.30	4.0
	3	0.47	2.5
	5	0.69	2.0

Note: Other modification conditions of S-AEL were in accordance with that of note (b) in Fig. 2

The solubility of both AEL and S-AEL are shown in Table 4. The pH of precipitation of S-AEL was significantly lower than that of AEL, reducing with the increasing content of sulfonic group. The results indicated that the solubility of AEL was improved after sulfomethylation and that an increased content of sulfonic groups in S-AEL was favorable for improved solubility.

Surface Tension of Aqueous Solution of S-AEL

It was reported that increased contents of hydrophilic groups, *e.g.* hydroxyls and carboxyls, resulted in reduced surface tension of lignin solution (Matsushita *et al.* 2008). In this study, a rather hydrophilic lignin product named S-AEL was prepared by the sulfonation of AEL. The surface tension of aqueous S-AEL solution was measured to evaluate the surface activity of S-AEL.

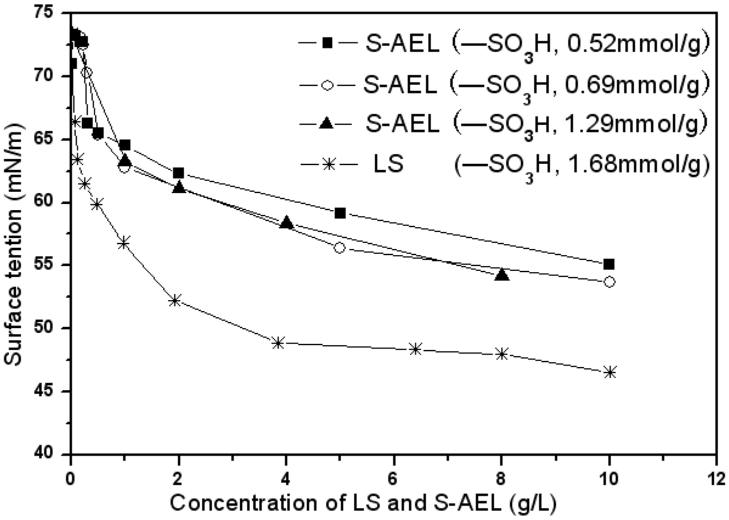


Fig. 3. Surface tension of aqueous solution of LS and S-AEL

The impact of lignin concentration on the surface tensions of aqueous solution of commercial LS and S-AEL are shown in Fig. 3. The surface tension of S-AEL significantly decreased with the increase in the concentration. The results implied that the surface activity of AEL was improved after sulfomethylation. However, the surface tension of S-AEL was higher than that of LS at the same concentration. A possible reason for the result was that the content of sulfonic groups in LS (1.68 mmol/g) was higher than that in S-AEL (0.52, 0.69, and 1.29 mmol/g). In addition, the molecular weight of lignin also might affect the surface tension of lignin solution.

Dispersibility of S-AEL

Like lignosulfonates, a class of widely-used dye dispersants, sulfonated or sulfomethylated lignin, can also be used for such purpose (Dilling and Huguenin 1999). In this study, we tried to use S-AEL as a dispersant. The dispersibility of S-AEL was compared with that of a commercial LS dye dispersant.

The dispersibility was characterized by the filtration time on the dye dispersion. The filtration time on the dispersant-free dye was measured to be 80 s, while the filtration time on the dye dispersion containing S-AEL was only 33 s. The results indicated that S-AEL presented good dispersibility. However, the filtration time on the dye dispersion containing S-AEL was slightly longer than that on the dye dispersion containing LS (31 s). The results demonstrated that S-AEL could not perform as well as a dispersant as LS did. One possible reason for the results was that the steric repulsive force of S-AEL was weaker than that of LS due to the lower molecular weight of S-AEL than that of LS. Additionally, a lower content of sulfonic groups in S-AEL than that in LS leads to a weaker electrostatic repulsion between S-AEL than that between LS. Therefore, the total repulsion between dye particles adsorbed S-AEL was weaker than that adsorbed by LS. According to AATCC Test Method 146-2006, the filtration time is divided into five classes: Class A (0 to 24 s); Class B (25 to 49 s); Class C (50 to 74 s); Class D (75 to 120 s); and Class E (>120 s). Therefore, the S-AEL, as well as LS, achieved Class B in dispersibility, though S-AEL did not exhibit as good performance as LS.

CONCLUSIONS

1. Fenton reagent, under mild conditions, oxidized AEL from corn stalk. The oxidation resulted in reduced molecular weight of AEL and a relatively narrow molecular weight distribution. The content of phenolic hydroxyl in AEL significantly increased after oxidation.
2. S-AEL was prepared from AEL by oxidation and subsequently sulfomethylation. The content of sulfonic groups was remarkably increased with the increase in the concentration of sodium sulfite. The surface activity of AEL was enhanced after oxidation and sulfomethylation. S-AEL demonstrated its potential for use as a dye dispersant due to its good dispersibility.

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