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1 Modification of lignin with dodecyl glycidyl ether and chlorosulfonic acid

2 for preparation of anionic surfactant

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Abstract Lignin was modified through incorporation of lipophilic and hydrophilic groups 13 for the preparation of surfactant. In this case, alkaline lignin reacted with dodecyl glycidyl 14 ether in the presence of dimethyl benzyl amine to incorporate lipophilic long alkyl chains, 15 and then sulfonated with chlorosulfonic acid for the introduction of hydrophilic 16 sulfonic acid group. Results showed that the reaction between dodecyl glycidyl ether and 17 carboxy group in lignin was the predominant reaction at 95 °C-110 °C. It was found that 18 the surface tension of the synthesized lignin surfactant solution was lower than that of 19 commercial surfactant sodium dodecylbenzenesulphonate when concentration was below 20 0.4 %, indicating that the surfactant prepared from alkaline lignin had a good surface 21 activity. A lowest critical micelle concentration of 0.50 g L^{-1} and the corresponding surface 22 tension at 29.17 mN/m were achieved when the surfactant was derived from the lignin 23 24 grafted with dodecyl glycidyl ether at 110 °C. The anionic lignin surfactants prepared in 25 this study is a promising feedstock as detergents or to enhance oil recovery.

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28 1. Introduction

29 The use of sustainable resources for energy and advanced eco-friendly material has drawn much attention due to the increased consumption of fossil resources associated with 30 energy crisis and climate change.^{1, 2} Lignocellulose, mainly composed of cellulose, 31 hemicellulose and lignin, is a promising and renewable resource for biofuel, chemicals, 32 and biomaterials without competition with human's food.³ There are some conundrums of 33 the development of bio-ethanol for making biomass-to-biofuels economic⁴, but it has great 34 potential economic benefits to develop new materials and chemicals derived from 35 lignocellulose. After cellulose and hemicelluloses, lignin is the third most abundant 36 biopolymer from biomass and considered as the most abundant aromatic renewable 37 38 resource. Lignin mainly consists of *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units derived from three major monolignols, namely, p-coumaryl alcohol, coniferyl 39 alcohol, and sinapyl alcohol. These units are connected by various inter-unit linkages (e.g., 40 β -O-4', β -5', β - β ', 5-5', 5-O-4', and β -1', etc.) through an enzyme-initiated dehydrogenative 41 polymerization ^{5, 6} Lignin can be isolated from wood, annual plants (such as wheat straw) 42 and agricultural residues (such as corncobs) by different processes.^{7, 8} However, lignin is 43 44 considered as low-value and underutilized by-product from pulping and bio-refinery industries. Most of lignin fraction resulted from these processes is burned as fuel, and only 45 a small portion of lignin is converted to commercial products. The effective utilization of 46 47 lignin to produce value-added products through chemical modification will make the biomass industry economically feasible with respect to the replacement of chemicals and 48 49 materials derived from fossil sources. Lignin is an excellent candidate for chemical 50 reactions due to its highly functional characteristics (rich in phenolic and aliphatic hydroxyl groups) for the development of new chemicals. 51 Surfactants are extremely important chemicals, and numberless types of surfactants 52

52 Surfactants are extremely important chemicals, and numberless types of surfactants 53 are used for a myriad of applications, thus the development of lignin surfactant has a good 54 industrial prospect. Lignin itself is not very useful as a surfactant because of the nature 55 character of lignin, for example, the complex macromolecular structure, the large 56 molecular weight, the low hydrophilicity and lipophilicity.^{9, 10} To work effectively, most

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57	surfactant require water soluble and oil soluble characteristics. Lignin must be changed
58	into the fraction which has the hydrophilic or amphiphilic property. To date, the
59	introduction of hydrophilic groups into lignin by sulfonation ^{11, 12} , carboxylation ^{13, 14} , and
60	Mannich reaction ¹⁵ has been investigated by many researchers. However, these methods
61	can only enhance hydrophilicity but to lipophilicity of lignin, and the surface activity of
62	these lignin surfactants is not satisfactory. In fact, a good lignin surfactant requires water
63	soluble and oil soluble characteristics by the incorporation of both lipophilic and
64	hydrophilic groups. Morrow et al. ¹⁶ have described a method of producing surfactants for
65	enhancing oil recovery from lignin by two reactions of lignin, i.e., alkylation with
66	different alkyl halides at phenolic sites, sufficient oxidation to break the lignin into smaller
67	polymeric and monomeric units, and sulfonation to increase their water solubility. Naae et
68	<i>al.</i> ¹⁷ reduced lignin in the presence of CO and H ₂ , the resulted products were alkoxylated
69	with α -olefin epoxide introducing a long alkyl chian, and these compounds were changed
70	into oil soluble lignin surfactant by sulfonation, sulfation and alkoxysulfation. Zeng et al.
71	¹⁸ have reported that hydrophilic sulfonic group and lipophilic adbietic group were
72	introduced into the molecular structure of Kraft lignin, and the rosin-modified
73	lignosulfonate lowed the surface tension of a 10 g L^{-1} aqueous solution to 49.3 mN/m.
74	The aim of the present study was to prepare lignin surfactant by simultaneous
75	incorporation of lipophilic and hydrophilic groups into lignin. Alkaline lignin was
76	modified with dodecyl glycidyl ether in the presence of dimethyl benzyl amine as a
77	catalyst, and then was converted into anionic surfantant by sulfonation with
78	chlorosulfonic acid. The structure of lignin after reaction with dodecyl glycidyl ether was
79	examined by FT-IR, GPC, ³¹ P-NMR and ¹³ C-NMR, and the surface activity of the lignin
80	surfactant was investigated through determining the surface tension of the aqueous
81	solution.

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83 2. Experimental

84 2.1. Materials

Alkaline lignin (AL) from corncob was obtained from Shandong Longlive
Bio-technology Co., Ltd, China. Laurylalcohol, epichlorohydrin (ECH), tetrabutyl

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ammonium bromide (TBAB), N,N-dimthylbenzylamine (BDMA), sodium dodecyl 87

benzene sulfonate (SDBS) and dimethyl sulfoxide (DMSO) were purchased from 88

Sinopharm Chemical Reagent Beijing Co., Ltd, China. Chlorosulfonic acid (99%) was 89

provided by Xiya reagent (Chengdu, China). 90

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2.2. Preparation of dodecyl glycidyl ether (DGE)

To a vigorously stirred mixture containing 37.2 g (0.2 mol) of laurylalcohol, 200 mL 92 of toluene, 50.0 g of 48% aqueous sodium hydroxide solution and 3.2 g (0.01 mol) of 93 TBAB, 37.0 g (0.4 mol) of ECH were added dropwise for 15 min at ambient temperature, 94 and the reaction was run for 6 h at 50 °C. When the resulting solution was cooled to room 95 temperature, the organic layer was separated and washed 4 times with distilled water (200 96 mL, 60 °C). Then the organic layer was evaporated at 60 °C under reduced pressure to 97 obtain DGE. The epoxy value of DGE was 0.33 mol epoxy / 100 g DGE, determined 98 according to the method described by Hou.¹⁹ 99

2.3. Reaction of AL with DGE 100

A 250 mL round-bottom flask containing 8.0 g lignin, 1.8 g BDMA, 8.0 g DGE and 101 160 mL DMSO was heated for 5.0 h at various temperatures (95-110 °C). The reaction 102 was guenched by adding 20 mL of 2.0 M HCl under stirring for 30 min at room 103 temperature. The solvent was removed by rotary evaporation, and the residue was washed 104 with distilled water and petroleum ether for several times, and then dried overnight at 105 60 °C to give grafted lignin, named as DGE-AL. 106

2.4. Sulfonation of DGE-AL 107

The sulfonation of DGE-AL was conducted according to the procedure in a previous 108 report with minor modifications.¹¹ A total of 2.0 g chlorosulfonic acid in 20 mL anhydrous 109 dichloromethane (CH₂Cl₂) was added dropwise into 1.0 g of DGE-AL in 10 mL 110

dichloromethane. The mixture was mechanically stirred for 2 h in an ice bath. Next, 30 111 mL of 2 M NaOH was added and the mixture was stirred for 1 h in an ice bath, and then it 112 was adjusted with 1 M HCl to pH 8.0. The resulting mixture was dialyzed with a cellulose 113 tube (cut off Mw-3000) against water and lyophilized to yield sulfonated DGE-AL, named 114 as SD-AL. 115

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2.5. Sample characterization 117 FT-IR spectra were recorded in a Thermo Scientific Nicolet iN10 FT-IR Microscope 118 (Thermo Nicolet Corporation, Madison, WI, USA) equipped with a liquid nitrogen cooled 119 MCT detector. The spectra were collected in the range of 4000-650 cm^{-1} at 4 cm^{-1} 120 resolution. NMR spectra were recorded on a Bruker AVIII 400 MHz spectrometer at 25 °C. 121 For ¹³C-NMR spectra, 80 mg samples were dissolved in 1 mL of DMSO- d_6 . The sample 122 was modified following the procedure below for ³¹P-NMR determination. Approximate 30 123 mg of oven-dried sample was dissolved in pyridine/chloroform (1.6:1, v/v) in a small vial 124 and stirred continuously. N-hydroxyl naphthalimide was used as internal standard, and 125 chromium acetylacetonate as the relaxation reagent. Then, 126 2-chlorl-4,4,5,5-tetramethyl-1,3,2-dioxa-phosphalane (TMDP) was used for 127 phosphitylation of hydroxyl groups. The molecular weight of the sample was determined 128

by gel permeation chromatography (GPC). The lignin sample was dissolved in

tetrahydrofuran (2 mg/mL), and then the solution was analyzed on a high performance

131 liquid chromatography system (Agilent 1200 series, Agilent technologies, USA) with a

DAD detector. The molecular weights were calibrated via monodisperse polystyrene
standards. The sulfur content of the lignin surfactant was examined by elemental analysis
using a Vario EL III Elemental analyzer instrument (Elementar, Germany) according to a
previous report.²⁰

136 **2.6. Measurement of surface tension**

An automatic surface tensiometer (JK99B, Shanghai Zhongchen Digital Technic Apparatus Co., Ltd) was used to measure the surface tension of the surfactant solution at different concentrations at room temperature (18 °C). Deionized water (surface tension 74.950 mN/m) was employed for reference, and commercial surfactant SDBS was used as a control. Critical micelle concentration (CMC) values of lignin surfactants were identified from the plot of the surface tension versus the surfactant concentration of water solution.

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3. Results and discussion 146

3.1. Synthesis and characterization of DGE-AL 147

148	Typically, Lewis bases are used to accelerate the reaction between epoxides and the
149	hydroxyls of phenols, alcohols and carboxyl. ²¹ In this study, BDMA was chosen as a
150	catalyst of the reaction between DGE and lignin, and DGE was introduced into lignin
151	through lignin hydroxyl-epoxide reaction (see Scheme 1). Because of the low
152	hydrophilicity and lipophilicity, lignin had a low solubility in neutral water and most of
153	organic solvents. For a homogeneous reaction between lignin and DGE, DMSO was
154	employed as a solvent for the reaction system. In order to avoid self-polymerization of
155	DGE in the presence of tertiary amine ²² , the reaction temperature was set at 95, 100 and
156	110 °C. After reaction, hydrochloric acid was used to deactivate the remnant DGE, and the
157	inactivated DGE and DGE homopolymer were washed off with petroleum ether. As seen
158	from Table 1, the DGE-AL yields were as high as 62.68-65.25%, and the molecular
159	weights of the products derived from the reaction conducted at 95, 100, and 110 °C were
160	1300, 1410, and 2050 g mol ⁻¹ , respectively.
161 162	Table 1 The yields, weight average (M_w) and number average (M_n) molecular weight of

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the products from the reaction of DGE with alkaline lignin

Samples ^a	Yield (%) ^b	$M_{\rm w}$ (g mol ⁻¹)	$M_{\rm n} ({\rm g \ mol}^{-1})$	$M_{ m w}/M_{ m n}$	
DGE-AL 1	65.25	2050	720	2.85	
DGE-AL 2	64.31	1410	600	2.37	
DGE-AL 3	62.68	1300	580	2.23	
AL	-	850	540	1.59	

^a AL, raw material alkaline lignin; DGE-AL 1, DGE-AL 2 and DGE-AL 3 were obtained 164 by the reaction of DGE with lignin in the presence of BDMA at 110, 100 and 95 °C for 5 h, 165 166 respectively.

^b the yield of DGE-AL was based on the total weight of reactant. 167



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Scheme 1 The reaction of DGE with lignin in the presence of BDMA.

³¹P-NMR technique has been widely applied in classification and quantitative 172 determination of several different classes of hydroxyl groups in the native and modified 173 lignin.²³⁻²⁵ In this study, phosphitylating agent TMDP was utilized to obtain the qualitative 174 and quantitative information about hydroxyl groups in lignin before and after graft. The 175 ³¹P-NMR spectra of the samples are illustrated in Figure 1 and the contents of different 176 hydroxyl groups are listed in Table 2. For DGE-AL 1 and DGE-AL 3, the content of total 177 OH was lower than that of AL, indicating the successful introduction of DGE into lignin 178 in the presence of BDMA. As compared to DGE-AL 3, the dramatic reduction of the 179 carboxylic OH content in DGE-AL 1 suggested that the reaction between epoxide and 180 carboxyl was the predominant reaction when reaction temperature increased from 95 °C to 181 182 110 °C. This can be explained by the mechanism of glycidyl ether reactions with alcohols, phenols and carboxylic acids in the presence of tertiary amine as a catalyst. 183



From Equation 1, a zwitterion (Z) was formed by the interaction between tertiary amine and epoxide which acted as an efficient catalyst due to its high basicity.²¹ Because of the relatively high acidity of carboxyl in lignin, the reaction between carboxyl and glycidyl ether occurred first. As see from Fig. 1, the chemical shifts of 150.0-145.4 ppm, 144.5-137.0 ppm, and 136.0-133.6 ppm are assigned to aliphatic, phenolic, and carboxylic

acid OH, respectively.²⁶ With respect to the reaction mechanism of hydroxyl-glycidyl 190 ether reactions, the following hypothesis was made: some new hydroxyl groups were 191 derived from the open-ring reaction of epoxy group of DGE. Accordingly, three new kinds 192 of signals were assigned at the chemical shifts of aliphatic OH, derived from the reactions 193 of DGE with aliphatic, phenolic, and carboxylic acid OH in lignin. This was supported by 194 195 the presence of three new peaks (147.9-147.4, 147.1-146.8, and 146.6-145.8 ppm) in the spectra of DGE-AL 1 and DGE-AL 3, which correspond to the chemical shifts of aliphatic 196 OH. From Fig. 1, the signals at 146.6-145.8 ppm varied more noticeably as compared to 197 those at 147.9-147.4 ppm and 147.1-146.8 ppm probably due to the large reduction of the 198 content of carboxylic OH in DGE-AL 1 as compared to DGE-AL 3 (Table 2). The signals 199 at 146.6-145.8 ppm were probably due to the hydroxyls derived from carboxyl-glycidyl 200 ether reaction, whereas the absorptions at 147.9-147.4 ppm and 147.1-146.8 ppm probably 201 correspond to the hydroxyl groups derived from the alcohol and phenol-glycidyl ether 202 reactions, respectively. 203

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Table 2 Quantification of hydroxyl content of alkaline lignin before and after reaction with
 DGE by quantitative ³¹P-NMR method

		- 1					
	Hydroxyl content (mmol g ⁻¹ of lignin)						
Samples ^a	Aliphatic	Syringyl	Guaiacyl	<i>p</i> -Hydroxy	Carbox	Total	Total
	OH	OH	OH	phenyl OH	ylic OH	phenol	OH
						OH	
AL	2.26	0.84	1.67	1.02	2.24	1.52	8.03
DGE-AL 1	2.77	0.64	1.16	0.55	0.39	1.04	5.51
DGE-AL 3	2.70	0.78	1.32	0.40	0.88	1.20	6.27

^a AL, DGE-AL 1 and DGE-AL 3 corresponding to the lignin samples in Table 1.

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Fig. 3 shows the ¹³C-NMR spectra of AL and DGE-AL. In the aliphatic region, five 226 well-defined peaks were observed at 14.0, 25.6, 28.7, 29.0 and 31.3 ppm in DGE-AL 227 spectra, and these peaks are assigned to the methyl carbon and methylene carbon of 228 dodecyl chains. Generally, the ¹³C-NMR chemical shift of the carbon atoms bonded to 229 oxygen (CH₂O, C-O-C, C-O-C=O) in glycerol ether or glycerides are assigned at the 230 bands of 60.0-70.0 ppm.²³⁻²⁹ As expected, the additional peaks at 60.0-72.7 ppm attributed 231 to the carbon atoms in glycerol ethers cross-linked structure (see Scheme 1, I, II, III) were 232 observed in DGE-AL spectra. Because of the complexity of the ring-opening reaction of 233 epoxy compound as well as the complicated structure of lignin macromolecule,³⁰ no effort 234 was made to assign these peaks. It was concluded that the expected compounds were 235 formed in the reaction of lignin and DGE under the catalysis of dimethylbenzylamine. 236

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243 3.2. Preparation and characterization of SD-AL

Surfactants are amphiphilic materials containing both a polar long-chain hydrocarbon 244 "tail" and polar, usually ionic, "head" groups. Because of the lack of hydrophilic groups, 245 only the introduction of long alkyl chain into lignin cannot make lignin became a good 246 surfactant. In this case, lignin achieved both hydrophilic and hydrophobic characteristics 247 248 which were different from those of commercial surfactants. AL grafted with DGE under different temperatures were sulfonated with chlorosulfonic acid, and then neutralized with 249 sodium hydroxide, yielding anionic surfactant SD-AL. The FT-IR spectra of SD-AL are 250 shown in Fig. 2. For the spectra of SD-AL, the intensity of the bands at 2924 and 2853 251 cm⁻¹ correspond to methyl and methylene vibration, respectively. The new absorptions at 252 1073 and 1040 cm⁻¹ correspond to the symmetric and asymmetric stretching vibrations of 253 S–O bond, respectively.³¹ The appearance of a strong peak at 1217 cm⁻¹ is indicative of 254 the S=O stretch of the sulfatesalt as well as the sulfonic acid,³² indicating the existence of 255 SO₃ groups in SD-AL. As compared to DGE-AL, the intensity of the peak at 1120 cm⁻¹ 256 corresponding to C-O-C stretching vibration in SD-AL became weak, indicating the 257 partial hydrolysis of ester groups during the preparation of SD-AL. 258

The effect of hydrolysis of ester groups during the preparation of SD-AL was 259 investigated through examining the content of the dichloromethane-insoluble components 260 of DGE-AL after treatment with 2 M NaOH for 1 h in an ice bath. Briefly, 1g of DGE-AL 261 was added to 30 mL of 2 M NaOH and the solution was stirred for 1h in an ice bath. After 262 263 the reaction, DGE-AL was regenerated by precipitation through adjusting the resulting solution to pH=2 with 30% acetic acid. The result showed that the contents of 264 dichloromethane-insoluble components were 29.71%, 27.72 % and 26.43% of the weight 265 of regenerated DGE-AL 1, DGE-AL 2 and DGE-AL 3, respectively. This indicated that 266 some de-alkylation of DGE-AL occurred during the preparation of SD-AL. The 267 generation of dichloromethane-insoluble components should be due to the hydrolysis of 268 the ester groups in DGE-AL. Thus, optimization of the neutral condition for sulfonic acid 269 270 group should be conducted in a future study. 271

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274	surfactant samples						
	Samples ^a	Samples ^a Elemental analysis (%)		Yield (%) ^b	CMC (g L ⁻¹)	Surface tension of CMC (mN/m)	
		S	С	Н	_		
	AL	-	63.00	5.60	-	-	-
	SD-AL 1	7.14	45.00	5.21	78.2	0.50	29.17
	SD-AL 2	7.27	46.15	5.96	77.8	0.55	29.65
	SD-AL 3	7.81	46.23	5.91	78.5	0.58	30.21
	SDBS	-	-	-	-	0.97	30.50

273	Table 3 Elemental analysis, yield, CMC and surface tension of water at CMC of all
274	autostant samplas

^a SDBS, commercial surfactant sodium dodecyl benzene sulfonate; SD-AL 1, SD-AL 2
and SD-AL 3 derived from the sulfonation of DGE-AL 1 DGE-AL 2, and DGE-AL 3 at
the same condition, respectively.

^b the yield of SD-AL was based on the weight of DGE-AL.

-, no measurement.

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281 3.3. Characteristics of SD-AL as a surfactant

Fig. 4 shows the isotherms of the surface tension of aqueous solution plotted against concentrations of SD-AL as compared to commercial surfactant SDBS. By the addition of

lignin surfactant, the surface tension of water decreased with the increase of the

concentration. For SD-AL 1, SD-AL 2, and SD-AL 3, the surface tension was lower than

that of SDBS when the concentration of aqueous surfactant solution was below 0.4 %.

287 After sulfurization under the same conditions, the lignin surfactant derived from the

reaction of lignin with DGE at a high temperature had a low surface tension at equivalent

concentration of aqueous solution. It was consistent with the result reported by Košíková

et al., in which the higher amount of alkylhalide was used to modify the prehydrolysis

lignin, the lower surface tension was observed.³³



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Fig. 4 Isotherms of surface tension of water plotted against concentration of SD-AL surfactant and SDBS.

Generally, the concentration of surfactant influences the physical and chemical 297 properties of surfactant solution. CMC is considered to be a fundamental property of 298 surfactants. A number of interfacial phenomena such as detergency can take place due to 299 the presence of micelles in solutions. In addition, other phenomena such as the surface 300 tension reduction is not directly influenced by the formation of micelles.³⁴ Therefore, 301 CMC and the corresponding surface tension are important indicators to measure the 302 surface activity of surfactants SD-AL. As seen from the data listed in Table 3, the CMC of 303 SD-AL decreased with the increase of reaction temperature between DGE and lignin, a 304 lowest CMC (0.50 g L^{-1}) and the corresponding surface tension (29.17 mN/m) were 305 306 achieved when the surfactant derived from the lignin grafted with DGE under 110 °C. This was because under a similar content of sulfur, surfactant derived from the lignin grafted 307 with DGE under high temperature has a high lipophilicity than that prepared under low 308 temperature. The CMC and surface tension at the corresponding CMC of all surfactants 309 derived from lignin were lower than the CMC (0.97 g L^{-1}) and the corresponding surface 310

311	tension (30.50 mN/m) of the commercial surfactant SDBS, indicating that SD-AL
312	surfactants had a good surface activity. Furthermore, the lignin surfactant prepared showed
313	a good ability to reduce the surface tension of aqueous solution, comparable to those of
314	the products prepared previously. In Košíková B's work, ³³ a series of lignin-based surface
315	active agents derived from alkylation of beechwood prehydrolysis lignin with
316	laurybromide decreased the surface tension of aqueous solution to 30-40 mN/m at the
317	concentration of 1 g L ⁻¹ . Homma <i>et al.</i> ³⁵ reported that nonionic polymeric surfactants
318	derived from the modification of acetic acid lignin with polyethylene glycol
319	diglycidylethers lowed the surface tension of aqueous solution to 36 mN/m at the
320	corresponding CMC (50g L^{-1}). The results of the present study suggested that lignin
321	surfactants with high surface activity was prepared by modification of lignin with DGE
322	and chlorosulfonic acid.

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324 4. Conclusion

A long alkyl chain was successfully introduced into lignin by the reaction between 325 lignin and DGE in the presence of BDMA as a catalyst. The reaction between DGE and 326 carboxy group was the predominant reaction at 95 °C-110 °C. The surface tension of the 327 lignin surfactant solution was lower than that of commercial surfactant sodium 328 dodecylbenzenesulphonate when the concentration of surfactant solution was below 0.4 %, 329 indicating that the surfactants prepared from modified alkaline lignin had a good surface 330 activity. A lowest CMC (0.50 g L^{-1}) and the corresponding surface tension (29.17 mN/m) 331 were achieved when the surfactant was derived from the lignin grafted with DGE at 110 332 °C. The anionic lignin surfactants prepared in this study could be utilized as detergents or 333 to enhance oil recovery. 334

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337 Acknowledgements

- 338 We express our gratitude for the financial support from Beijing Forestry University Young
- 339 Scientist Fund (BLX2012025), the National Natural Science Foundation of China
- 340 (3110103902), the Major State Basic Research Projects of China (973-2010CB732204),
- and the Open Foundation of the State Key Laboratory of Pulp and Paper Engineering
- 342 (201261).

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