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CHARACTERIZATION OF LIGNINS FROM THE BLACK LIGUOR OF AUSTRALIAN EUCALYPTUS KRAFT PULPING

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ABSTRACT

Lignin samples were separated from the black liquor of Australian eucalyptus kraft pulping by ethanol-acid precipitation or acid precipitation. Elemental analysis, FT-IR, and ^{1}H NMR were conducted to compare their structural characteristics. The thermal behaviors were studied by TGA and heating value was examined with oxygen bomb calorimeter. The obtained C_9 expanded formulas for acid-extraction lignin and ethanol-acid-extraction lignin were $C_9H_{9.52}O_{2.96}$ and $C_9H_{9.58}O_{3.18}$, respectively. According to FT-IR and 1H NMR analyses, the two lignins were similar to hardwood lignin of type GS. However, the acid-extraction lignin showed a high proportion of syringyl (S) unit. TG results showed that degradation process of the two lignins was similar, but their degradation temperatures were different. The weight loss rate reached its maximum value of 8.49 wt% / °C and 4.39 wt% / °C for ethanol-acid-extraction lignin and acid-extraction lignin, whose temperature of maximum weight loss was 371°C and 356°C respectively. Results of oxygen bomb calorimeter tested showed the incendiary heat of ethanol-acid-extraction lignin was higher than that of acid-extraction lignin.

KEYWORDS: Black liquor, lignin, FT-IR, ^{1}H NMR, TGA, incendiary heat.

INTRODUCTION

Lignin, the second most abundant terrestrial polymer after cellulose, is produced by plants at annual quantity of 150 billion tons (Hu et al. 2018). It has a complicated chemical structure that includes three major units: p-coumaryl, coniferyl, and sinapyl alcohols (Naron et al. 2017, Xiong et al. 2017). Currently, lignin plays a critical role in biomass utilization, for example, to produce adhesives, coatings, and fine chemicals, to replace petrochemical resources for fuel, polymers and

low-molecular-weight chemical products. Consequently, lignin has been a promising renewable resource for the production of aromatic chemicals and biofuel.

Lignin can be obtained from the black liquor which is a significant water pollution source coming from the Pulp & Paper industry. The total lignin quantity in the pulping black liquor is estimated about 50 million tons per year. However, only 2% lignin from the Pulp & Paper industry is commercially utilized (Cheng and Brewer 2017). Therefore, how to efficiently make use of the lignin extraction from black liquor is of great significance for solving the problem of environmental pollution.

The detail characterization of lignin to unveil its chemical properties is a critical step for its utilization. Therefore, it is of significance to make clear the characterization of lignin from black liquor. Many researchers have been studied the physico-chemical properties and structure of lignin in a number of investigations by various methods. Yuan et al. (2009) studied the physico-chemical properties of degraded lignins from the black liquor of KP-AQ pulping. Hu et al. (2013) used thermogravimetric-Fourier transform infrared spectroscopy to study the structure of lignin from black liquor. Zhu et al. (2015) studied the molecular properties and carbohydrate content of lignins precipitated from black liquor. Li et al. (2017) investigated the structure and combustion characteristics of lignin from bagasse soda pulping black liquor. Zhang et al. (2017) researched the relationship between the structural changes and pyrolysis behavior of wheat straw lignin from the black liquor.

In this study, the technical lignins were separated from the black liquor of Australian eucalyptus kraft pulping by ethanol-acid or acid precipitation. The structural characteristics of the two types of lignins (ethanol-acid-extraction lignin and acid-extraction lignin) were identified by means of elemental analysis, FTIR, and 1H NMR spectroscopy. The thermal behaviors of the lignins were examined by TGA. The incendiary heat of the lignins was determined by oxygen bomb calorimeter.

MATERIAL AND METHODS

Materials

Papermaking black liquor, which was prepared by kraft pulping from Australian eucalyptus, was obtained from Huatai Paper Mill (Anqing, Anhui, China). The original characteristics of the black liquor are shown in Tab. 1. All reagents were purchased from Hefei Bao Tim Electronics Co., Ltd. (Hefei, Anhui, China).

Tab. 1: Initial characteristics of black liquor.

Property	Value
Total solids content (%)	18.33
Lignin content (%) of dry solids	22.84
Organic/inorganic ratio	1.50
pH	14
Density ($g \cdot cm^{-3}$)	1.08
Silicon dioxide content ($g \cdot L^{-1}$)	0.96
Sulfidity (%)	20-22
Effective alkali ($g \cdot L^{-1}$)	10-12

Elemental analysis (%)	
Carbon	26.38
Hydrogen	3.14
Oxygen	-
Nitrogen	0.07
Sulfur	1.03

Lignin extracted from black liquor

In this study, lignin was extracted from the black liquor with acid or ethanol-acid on laboratory scale according to the method adapted from Garcia et al. (2009) and Hermiati et al. (2017) by some modifications. In acid-extraction method, 98% sulphuric acid was added into 100 ml of the black liquor and stirred at 60°C until pH = 3. While in ethanol-acid-extraction method, 100mL of the black liquor was firstly treated with 100 ml of absolute ethanol to precipitate sugars. After separating the sugar precipitates, the addition of sulphuric acid (98% wt) into the black liquor was continued up to pH = 3. Lignin suspensions in acid solution obtained from both methods were kept for 8 hours to complete the precipitation.

(a) black liquor *(b) acid-extraction lignin* *(c) ethanol-acid-extraction lignin*

Fig. 1: Lignin extracted from black liquor.

Then the lignin precipitates were separated from their solution by vacuum filtration, washed sufficiently and subsequently freeze-dried as crude lignin. Photos of the acid-extraction lignin and ethanol-acid-extraction lignin are shown in Fig.1.

Elemental analysis

Elemental composition including the C, H, N, and S contents were determined with a Vario EL Cube analyser. The O content was calculated by subtracting 100 with the total of C, H, N, and S.

Fourier-transform infrared analysis (FTIR)

FTIR spectra of lignins were recorded in KBr discs on a Nicolei 6670 FT-IR spectrophotometer (Bruker Company) with a resolution of 2 cm^{-1}, from 4000 to 400 cm^{-1}.

Nuclear magnetic resonance analysis (NMR)

In this set of experiments, the samples were acetylated firstly according to Hu (2013). The precipitated lignin samples (300 mg) were acetylated with 15 ml of pyridine acetic anhydride solution (Ac_2O/pyridine, 1:1, v/v) at room temperature for 72h. After 72 h, 250 ml diethyl ether was added to precipitate the lignins. The lignins were washed with diethyl ether until the lignins were odorless (pyridine odor of lignin was removed). The acetylated lignins were dried

in a desiccators over P_2O_5 and ^1H NMR spectra were recorded with 15 mg acetylated lignins dissolved in 1 ml of DMSO-d_6 using a Agilent DD2 spectrometer at 600 MHz.

Thermogravimetric analysis (TGA)

The thermal behaviors of the acid-extraction lignin and the ethanol-acid-extraction lignin samples were studied using thermogravimetric curves (TG) and the derivative thermogravimetric curves (DTG) obtained by a Netzsch 209 TGA instrument. The experiment was performed at a heating rate of 20°C·min^{-1} within the temperature range from 30°C to 800°C, using purity nitrogen as carrier gas with a flow rate of 20 ml·min^{-1}.

Incendiary heat

The incendiary heat of the acid-extraction lignin and the ethanol-acid-extraction lignin were determined according to calorimeter method by using oxygen bomb calorimeter (BH-IIS). Benzoic acid was used as the combustion adjuvant in determining the incendiary heat of the two lignins.

RESULTS AND DISCUSSION

Elemental analysis

The elemental composition of the acid-extraction lignin and ethanol-acid-extraction lignin are presented in Tab. 2.

Tab. 2: Elemental analysis of acid-extraction lignin and ethanol-acid-extraction lignin.

Sample	C (%)	H (%)	N (%)	S (%)	O (%)
Acid-extraction lignin	61.69	5.44	0.17	5.59	27.11
Ethanol-acid-extraction lignin	62.55	5.55	0.15	2.20	29.55

For the both lignins, the content of carbon (acid-extraction lignin 61.69% and ethanol-acid-extraction lignin 62.55%) was predominant over the other main elements. It can be found that sulfur content in ethanol-acid-extraction lignin was lower than that from acid-extraction lignin, while carbon, hydrogen, nitrogen and oxygen contents were relatively the same. Considering sulfur, which could convert into harmful substances such as SO_2 (Liu et al. 2017). Therefore, the low sulphur content of ethanol-acid-extraction lignin will no doubt help to reduce the emission of SO_2 from combustion and reduce environmental pollution. According to an empirical formula based on the elemental composition of lignin, which the number of carbon atoms was assumed to be equal to 9 (Hermiati et al. 2017), the molecular formula for acid-extraction lignin and ethanol-acid-extraction lignin were $C_9H_{9.52}O_{2.96}$ and $C_9H_{9.58}O_{3.18}$, respectively.

FT- IR spectra

The FT-IR analysis of acid-extraction lignin and ethanol-acid-extraction lignin are shown in Fig. 2. The bands accordance with what is usually reported in literature (Robert et al. 1984, Risanto et al. 2014, Zhao et al. 2009, Wang et al. 2015, Boeriu et al. 2004, Gordobil et al. 2016) are listed in Tab. 3.

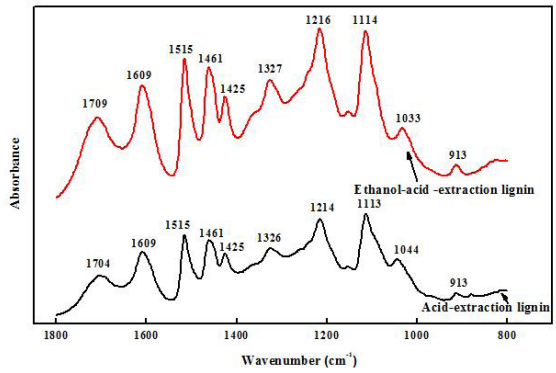

Fig. 2: FT-IR spectra of acid-extraction lignin and ethanol-acid-extraction lignin.

Tab. 3: FT-IR absorption bands of acid-extraction lignin and ethanol-acid-extraction lignin.

Band location (cm^{-1})		Band (cm^{-1})	Assignment
Acid-extraction lignin	Ethanol-acid-extraction lignin		
1704	1709	1712-1702	C=O stretching in unconjugated ketone, and aldehyde groups
1609	1609	1610-1590	Aromatic skeletal vibrations plus C=O stretching
1515	1515	1515-1505	Aromatic skeletal vibrations
1461	1461	1470-1460	C-H deformations (asymmetric in -CH3 and -CH2-)
1425	1425	1430-1425	Aromatic skeletal vibrations combined with C-H in-plane deformations
1326	1327	1325	syringyl ring brething with C=O stretching
1214	1216	1216-1211	guaiacyl ring brething with C=O stretching
1113	1114	1115	Ar-CH in -plane deformation (syringil)
1044	1033	1044-1030	C=O(H) and C=O(C) (first order aliphatic OH and ether)

From Fig. 2, it can be known that the two-lignin fractions have rather similar FT-IR spectra, typical of hardwood lignin. This indicated that the "core" of the lignin does not change dramatically during the process of lignin extracting from black liquor. The bands at 1712-1702 cm^{-1} are assigned to the unconjugated ketones and aldehyde groups. Both of the two lignins had apparent characteristics bands for the aromatic skeletal vibrations at 1609, 1515, 1425 cm^{-1}. C-H deformations can be found at 1470-1460 cm^{-1}. The band at 1325 cm^{-1} is associated with the C=O stretching of syringyl structure in lignin molecules. Peaks at 1216-1211 cm^{-1} are assigned to the guaiacyl structure in lignin molecules. The C-H stretch assigned to syringyl rings is presented at 1115 cm^{-1}. The peaks at 1044-1030 cm^{-1} are related to C=O stretching of primary alcohols. Bands at 915-910 cm^{-1} are attributed to aromatic C-H out of plane bending.

The characteristics of S/G ratios in lignin (Yuan et al. 2009) become visible in the spectra, which the bands at 1326/1327 and 1113/1114 cm^{-1} are associated with syringyl structures in lignin molecules, while the bands at 1214/1216 cm^{-1} are associated with guaiacyl units in lignin molecules

(Fig. 2). The intensity ratios of 1326 (1327) cm^{-1}/1214 (1216) cm^{-1} and 1113 (1114) cm^{-1}/1214 (1216) cm^{-1} were higher in acid-extraction lignin than in ethanol-acid-extraction lignin. This indicates that acid-extraction lignin have a relatively higher content of S units than ethanol-acid-extraction lignin (Faix 1991).

^{1}H NMR spectra

The ^{1}H NMR spectra of acid-extraction lignin and ethanol-acid-extraction lignin are presented in Fig. 3. Tab. 4 shows the hydrogen signal integrations subdivided into different structural regions (Yan et al. 2009, Li et al. 2017).

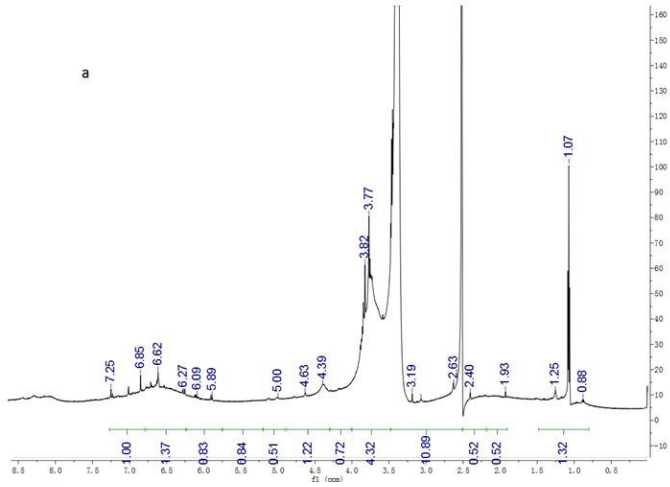

Fig. 3a: ^{1}H NMR spectra of the precipitated acid-extraction lignin.

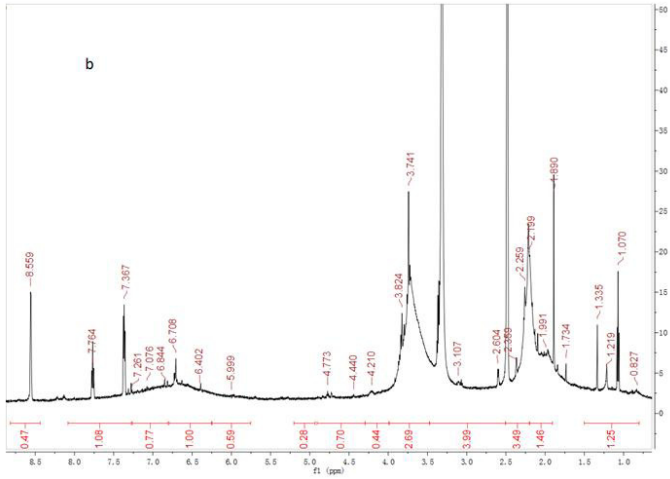

Fig. 3b: ^{1}H NMR spectra of the precipitated ethanol-acid-extraction lignin.

Tab. 4: 1H NMR signal integrations and assignments.

Peak (ppm)	Assigment
7.25-6.80	Aromatic H in guaiacyl units
6.80-6.25	Aromatic H in syringyl units
6.25-5.75	H_α of β-O-4 and β-1 structures
5.20-4.90	H of xylan residue
4.90-4.30	H_α and H_β of β-O-4 structures
4.30-4.00	Hγ in β-O-4, β-β, β-5 and β-1 structures
4.00-3.48	H in -OCH3
3.48-2.50	H_β in β-β structures
2.50	H in DMSO-d6
2.22-1.60	H of aliphstic acetates
1.60-0.80	H in aromatic

In the ^{1}H NMR spectra, the signal at 2.50 arises from DMSO d_6. The signals at 7.25-6.80 ppm are belong to the aromatic protons in G unit while the signals at 6.80-6.25 ppm are due to the S unit. In this study, the S/G ratio was determined according to the literature based on the peaks in the regions 6.25-6.80 and 6.80-7.25 ppm (Qin 2001). The S/G ratios of acid-extraction lignin and ethanol-acid-extraction lignin were 1.37:1 and 1.30:1, respectively. This indicates that the structure of acid-extraction lignin contains more amounts of S unit than that in ethanol-acid-extraction lignin. The results by 1H NMR spectra are in accordance with those by FT-IR presented above. The signals of methoxyl protons (-OCH_3) are strong at 4.00-3.48 ppm. The signals originated from H_α, H_β and H_γ of β-O-4, respectively, at 4.30-4.90 and 4.00-4.30 ppm were weak. The shoulder at 5.00 ppm, which is visible in the spectrum of acid-extraction lignin, while disappeared in ethanol-acid-extraction lignin, arises from the protons of xylan residual. This shows that the ethanol-acid-extraction lignin could separate lignin and hemicelluloses completely.

TG analysis

Fig. 4 presented the TG-DTG curves analysis of acid-extraction lignin and ethanol-acid-extraction lignin. As shown in Fig. 4, the thermal degradation process of acid-extraction lignin and ethanol-acid-extraction lignin included three steps: the first step from 30°C to 200°C, the second step from 200°C to 500°C and the third step from 500°C to 800°C.

The characteristic of the three-steps degradation of acid-extraction lignin and ethanol-acid-extraction lignin was similar with the pyrolysis process from Klason lignin (Ma et al. 2016). In the first step, the mass loss of acid-extraction lignin and ethanol-acid-extraction lignin was, respectively, about 3.62% and 3.86%. This was mainly due to removal of absorbed water from the samples and volatilization of low molecular weight organics (Brebu et al. 2013). In the second step, as shown in the DTG curves, the maximum mass loss rate (4.39 wt %/°C) of acid-extraction lignin was at 356°C. The thermal decomposition rate of ethanol-acid-extraction lignin was higher than that of acid-extraction lignin and the maximum mass loss rate (8.49 wt %/°C) was attained at 371°C. The different structure of acid-extraction lignin and ethanol-acid-extraction lignin may result in this result. Compared with acid-extraction lignin, ethanol-acid-extraction lignin is highly enriched in G units (as confirmed by FT-IR and ^{1}H NMR spectra), which was

confirmed to be more thermally stable (Zhao et al. 2014). Therefore, ethanol-acid-extraction lignin has more structure stable lignin, and it may result in the increasing of the maximum decomposition rate. In the third step, the mass loss was only 11.04% for acid-extraction lignin and 10.33% for ethanol-acid-extraction lignin. Char from the main components was the main product in this stage instead of bio-oil (Wang et al. 2014). The mass fraction of ethanol-acid-extraction lignin residue was 41.67% that was higher than acid-extraction lignin (36.29%). Because the content of carbon elementary the ethanol-acid-extraction lignin (62.55%) was higher than acid-extraction lignin (61.69%).

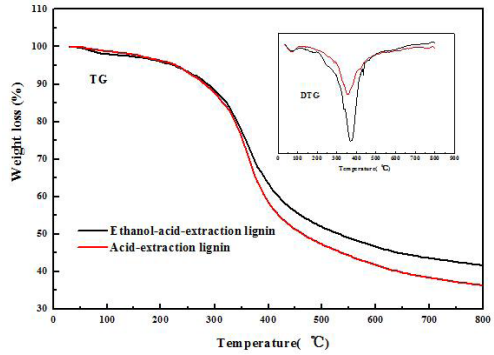

Fig. 4: TG and DTG curves of acid-extraction lignin and ethanol-acid-extraction lignin.

Incendiary heat

The energy content of fuel is determined by its heat of combustion. The incendiary heat of acid-extraction lignin and ethanol-acid-extraction lignin determined by oxygen bomb calorimeter was 21591 J/g and 22237 J/g, respectively. This property depends on the material constituents, especially closely related to the carbon, hydrogen, and oxygen element. In ethanol-acid-extraction lignin, the carbon, hydrogen, and oxygen contents were all higher than that of acid-extraction lignin (Tab. 2). Another reason is that the method of ethanol-acid-extraction lignin might be more complete purification of lignin from the black liquor than that of acid-extraction lignin. Consequently, ethanol-acid-extraction lignin is more suitable to be a source of fuel than acid-extraction lignin.

CONCLUSIONS

In this study, lignin obtained from the black liquor of Australian *eucalyptus* kraft pulping through two different methods: ethanol-acid precipitation and acid precipitation. Both of ethanol-acid-extraction lignin and acid-extraction lignin were similar to hardwood lignin of type GS. Nevertheless, the chemical composition and structure of the two lignins were somewhat different. The acid-extraction lignin showed a strong predominance of S units, as evidenced by both FT-IR and ^{1}H NMR analyses. The average per C9 unit formula for acid-extraction lignin and ethanol-acid-extraction lignin were $C_9H_{9.52}O_{2.96}$ and $C_9H_{9.58}O_{3.18}$, respectively. TG curve indicates that degradation process of acid-extraction lignin and ethanol-acid-extraction lignin is similar, which is consist of drying stage, fast degradation stage and slow degradation stage, but their degradation temperatures are different. The weight loss rate reached its maximum value of 8.49 wt %/°C at the temperature of 371°C for ethanol-acid-extraction lignin, which was higher than that for acid-extraction lignin. According to the oxygen bomb calorimeter

tested, the incendiary heat of ethanol-acid-extraction lignin (22237 J/g) was higher than that of acid-extraction lignin (21591 J/g). Therefore, the ethanol-acid-extraction lignin was a potential source of fuel.

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