

## Effect of Chemical Structure on Pyrolysis Behavior of Alcell Mild Acidolysis Lignin

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In this study, two purified mild acidolysis lignins (MAL) extracted from triploid poplar, *i.e.*, Alcell MAL and Alkali MAL, were compared. Some properties, including elemental contents, higher heating value (HHV), functional hydroxyl group compositions, and molecular weights, were tested to characterize the structure of these two MALs. The releasing laws of gases and the distribution of products were also investigated through the use of thermogravimetric Fourier transform infrared (TG-FTIR) and pyrolysis-gas chromatography combined with mass spectrometry (Py-GC/MS). The results showed that both MALs had pyrolytic advantages, largely because of their unique chemical structures. However, although the species of volatiles from Alkali MAL were similar to those from Alcell MAL, the releasing temperature range for Alcell MAL was relatively narrow and the volatiles from it were concentrated. Among the fast pyrolytic products, phenols were the most abundant. The yield of 2,6-dimethoxy-4-(2-propenyl)phenol, which was the dominant product, was 25.66% for Alcell MAL and 20.77% for Alkali MAL, respectively. Overall, pyrolytic products from Alcell MAL were more enriched.

*Keywords:* Alcell MAL; Quantitative  $^{31}\text{P}$ -NMR; TG-FTIR; Py-GC/MS

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### INTRODUCTION

Although the Alcell pulping process is environmentally friendly, research to date indicates that the lignin-rich pulping black liquor could still be more effectively utilized. Because of its high phenolic hydroxyl content, Alcell purified mild acidolysis lignin is considered to have higher chemical activity and can be converted into bio-chemicals and bio-fuels (Gosselink *et al.* 2004). Earlier studies on the potential of recycling Alcell lignin emphasized chemical degradation, such as converting Alcell lignin into useful chemicals and fuels by using HZSM-5 catalyst (Thring *et al.* 2000). With the development of pyrolysis technology (Bridgwater *et al.* 1999; Bridgwater *et al.* 2000; Luo *et al.* 2004; Ragauskas *et al.* 2014), research on the utilization and conversion of Alcell lignin shifted its focus primarily to thermal degradation. For example, studies using optimized instruments (*e.g.*, fixed-bed, thermogravimetric analyzer) to investigate the pyrolysis kinetic of Alcell lignin have found that the activation energy of Alcell lignin varies from 80 to 158 kJ/mol, with maximum distribution at approximately 118 to 125 kJ/mol (Ferdous *et al.* 2002; Jiang *et al.* 2010a).

More recently, pyrolysis-gas chromatography combined with mass spectrometry (Py-GC/MS) has enabled researchers to identify pyrolytic products qualitatively and quantitatively. Using Py-GC/MS, various pyrolytic products (more than 50 kinds in the range from 400 to 800 °C) from Alcell lignin have been obtained (Jiang *et al.* 2010b).

However, this method does not monitor the reaction process online, such as the releasing characteristics of the volatiles.

Thermogravimetric Fourier transform infrared (TG-FTIR) analysis could well meet these demands by responding quickly to the signals of products (Bassilakis *et al.* 2001). Using TG-FTIR to contrast the characteristic bands of lignin and its products, the probable pyrolysis mechanism of lignin has been established. Lignin undergoes three consecutive stages including the evaporation of water, the formation of volatiles, and the release of gases (Liu *et al.* 2008). The catalytic effect of additives on lignin pyrolysis and gasification *via* TG-FTIR has also been investigated (Guo *et al.* 2012). Hence, TG-FTIR is now an effective and convenient method to follow the pyrolysis reactions of lignin.

The purpose of this study was to investigate the effect of chemical structure on Alcell MAL pyrolysis using TG-FTIR and Py-GC/MS, compared with Alkali MAL. The goal is to measure the release of four small molecular gases and the distribution of pyrolytic products. It is hoped that these findings will strengthen the research basis for more effective utilization and conversion of Alcell lignin.

## EXPERIMENTAL

### Materials

#### *Sample preparation*

The raw material used in this study was triploid poplar (*Populus tomentosa* Carr.), provided by Tiger Forest and Paper (Hunan Province, China). Two types of lignin, Alcell MAL and Alkali MAL, were prepared in the lab. Alcell MAL was developed under pulping conditions of 60% (v/v) ethanol solution and a solid:liquid ratio of 1:10 at 205 °C for 2.5 h. Alkali MAL was developed with 18% alkali (calculated as Na<sub>2</sub>O, wt%) and a solid:liquid ratio of 1:4 at 165 °C for 1 h.

The method used to purify the two lignins was mild acidolysis, which comes from the enzymatically acidolyzed method (Wu and Argyropoulos 2003; Lou and Wu 2008). Dilute acid solution was added to the black liquor to adjust the pH to 2.0, and then the precipitated lignin was centrifuged at 5000 rpm. The obtained lignin was washed three times with acidified deionized water (pH =2.0), then dried in a vacuum oven at room temperature for at least 48 h.

Impure lignin was suspended in acidic dioxane/water (9:1, v/v, pH=2.0) and was refluxed at 87 °C under nitrogen for 2 h. The resulting mixture solution was filtered, and the lignin solution was collected. The solid residue was washed with fresh dioxane/water (9:1, v/v) until the filtrate was clear. The total filtrated solutions were neutralized with sodium bicarbonate, then rotary evaporated at 30 °C to be thickened until a syrup-like solution formed. This thickened solution was carefully dropped into a large quantity of acidified deionized water. The precipitated lignin was then isolated by centrifugation, washed, and freeze-dried. The obtained lignin was finally washed with HPLC grade hexane and dried in a vacuum oven at room temperature.

### Methods

#### *Analytical methods*

The carbon, hydrogen, and nitrogen content in the samples were analyzed using a Vario-EL CUBE elemental analyzer (ELEMENTAR, Germany). The oxygen content was determined by the difference. The higher heating value (HHV) of the samples was tested

by a WZR-1T-CII microcomputer calorimeter (Changsha Bentley Instrument Co., Ltd., China). Quantitative  $^{31}\text{P}$ -NMR experiments (Argyropoulos 1994; 1995; Faix *et al.* 1994; Spyros and Dais 2009) were performed on a Bruker 400 MHz spectrometer (Germany). The lignin samples were dissolved in pyridine- $d_5$ / $\text{CDCl}_3$  (1.6:1, v/v) acting as the solvent. The cholesterol was used as the internal standard and 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxapholane (TMDP) as the phosphorylating agents (Granata and Argyropoulos 1995). The reaction was carried out for 2 h. Gel permeation chromatography (GPC) of the samples was carried out on an Alliance GPCV 2000 instrument (Waters Corp., USA) with a Waters Styragel HT3 column at 35 °C. The acetylated samples were dissolved in tetrahydrofuran. A series of polystyrene samples served as standards, and the flow velocity of samples was 0.5 mL/min.

#### *TG-FTIR method*

Fundamental tests were carried out on a Jupiter Thermo Gravimetric Analyzer (TGA) STA 449 F3 (Netzsch, Germany) coupled with a Fourier transform infrared spectrometer Tensor 27 (Bruker, Germany) by using a pipe. The experiments were done on the TGA at a heating rate of 20 °C/min within the temperature range of 50 to 1000 °C. High purity nitrogen was used as carrier gas with a flow rate of 20 mL/min and carbon dioxide was used as the gasifying agent with a flow rate of 40 mL/min throughout the pyrolysis process. The sample weight was required to be less than 10 mg. The volatiles released from pyrolysis would be swept quickly into the FTIR gas cell by pure nitrogen. Moreover, the FTIR gas cell and the pipe were already preheated to 150 °C before each experiment. The spectrum scope was located in the range 4000 to 667  $\text{cm}^{-1}$ , and the resolution factor was set at 4  $\text{cm}^{-1}$ .

#### *Py-GC/MS method*

The Py-GC/MS tests were performed using a CDS 5000 pyrolyser (CDS Analytical, USA). The sample was placed in the center of the inductive coil with an isothermal setting of 400 °C and a heating rate of 10 °C/ms. The pyrolysis reaction was held for 15 s, and helium was used as the carrier gas.

A QP2010-GC gas chromatograph (Shimadzu, Japan) with a split ratio of 50:1 was used for compound separation. The injector, detector, and interface temperatures were set at 250 °C. The carrier velocity was 40 cm/s. The temperature program began at 50 °C, with a heating rate of 8 °C /min to 250 °C for 5 min. A HP-5MS column (30 m, 0.25 mm inner diameter, 0.25  $\mu\text{m}$  film thickness) was selected as the separation column. The mass spectrometer was set at an ionizing voltage of 70 eV, and the mass range from  $m/z$  30 to 400 was scanned with a speed of 1.0 s/decade. Data processing was performed using Perkin Elmer NIST Spec Version 5 software (USA).

## RESULTS AND DISCUSSION

### Properties of Lignin Samples

#### *Element contents and HHV*

The results of elemental analysis and higher heating value (HHV) of the two lignins are displayed in Table 1. Owing to the same biomass resource, the elemental compositions were similar. The only clear difference was the higher carbon content in Alcell MAL. The difference mainly benefits from the different delignification processes

in different pulping methods. The higher carbon content presumably results in its higher HHV, which is a main factor in energy and resource utilization of biomass. Because of higher carbon content and lower oxygen content, lignin has higher HHV than any other biomass resources. Through calculation, the following empirical formulae were obtained:  $[C_{10}H_{11.07}O_{3.13}N_{0.02}]_n$  for Alcell MAL and  $[C_{10}H_{11.69}O_{3.51}N_{0.01}]_n$  for Alkali MAL.

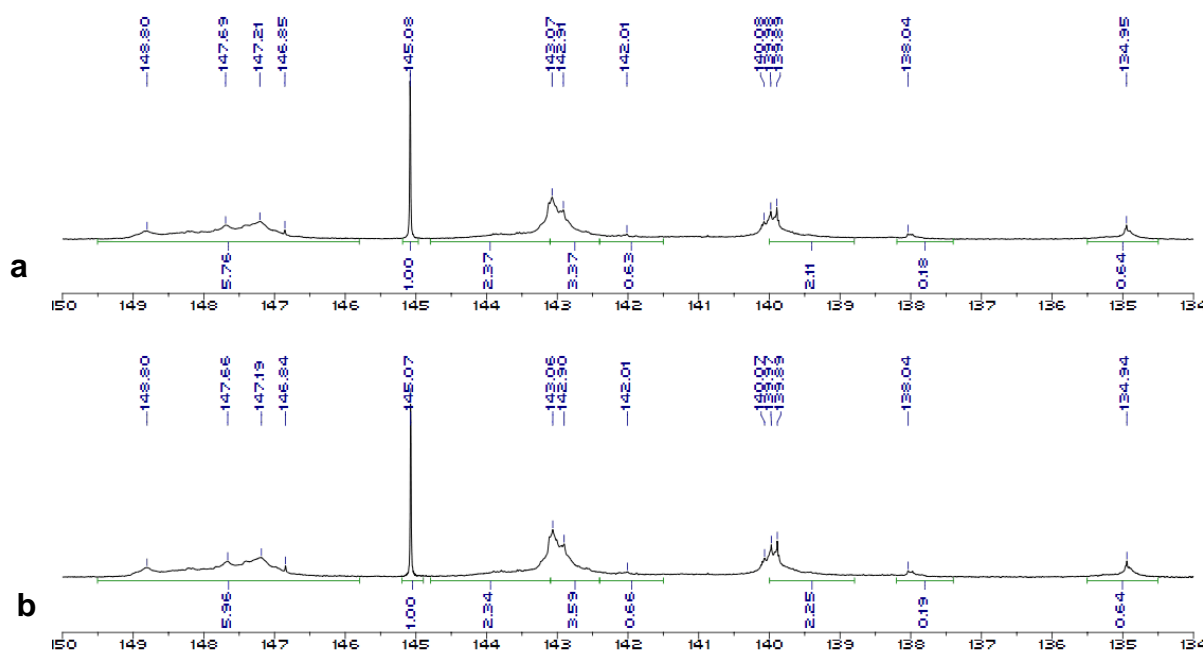
**Table 1.** Elemental Analysis and Higher Heating Value of Alcell and Alkali MALs

Sample	Elemental Contents (%)				H/C	O/C	HHV (MJ/kg)
	C	H	O <sup>a</sup>	N			
Alcell MAL	66.12	6.10	27.62	0.16	1.11	0.31	23.76
Alkali MAL	63.82	6.22	29.85	0.11	1.17	0.35	22.98

<sup>a</sup> Oxygen content was determined by difference.

#### Functional hydroxyl group composition

The quantitative <sup>31</sup>P-NMR spectra of the two samples are shown in Fig. 1, and the contents of corresponding hydroxyl groups are listed in Table 2. Through chemical shift values, different hydroxyl groups could be identified in quantitative <sup>31</sup>P-NMR spectra (Jiang *et al.* 1995; Marques *et al.* 2008). Clearly, it can be seen that the aliphatic hydroxyl group was the dominant hydroxyl type in the two MALs. In uncondensed phenolic hydroxyl groups, the amount of syringyl hydroxyl group is highest, followed by guaiacyl hydroxyl group, and finally p-hydroxyphenyl hydroxyl group. The laws are coincident with a previous study on lignin types in poplar (Franke *et al.* 2000). The content of total condensed and uncondensed phenolic hydroxyl groups was 2.217 mmol/g in Alcell MAL and 2.319 mmol/g in Alkali MAL.



**Fig. 1.** Quantitative <sup>31</sup>P-NMR spectra of (a) Alcell MAL and (b) Alkali MAL

The compositions of all types of hydroxyl groups (except carboxylic hydroxyl groups) were lower in Alcell than in Alkali MAL. This is because the reactive oxygen radicals generated from lignin degradation in the Alcell pulping process are easier to be shielded than those in soda pulping process. Though the total hydroxyl group content is slightly lower in Alcell than in Alkali MAL, it is higher than that in other reported lignins (Yang *et al.* 2011; Li *et al.* 2014). With high chemical activity, Alcell MAL and Alkali MAL could be further converted and utilized.

**Table 2.** Hydroxyl Content of Alcell and Alkali MALs Determined by Quantitative  $^{31}\text{P}$ -NMR

Chemical shift (ppm)	Hydroxyl type	Hydroxyl content (mmol/g)	
		Alcell MAL	Alkali MAL
149.5-145.8	Aliphatic hydroxyl	1.475	1.530
144.8-143.1 142.4-141.5	Condensed phenolic hydroxyl	0.768	0.770
143.1-142.4	Syringyl hydroxyl	0.863	0.922
140.0-138.8	Guaiacyl hydroxyl	0.540	0.578
138.2-137.4	P-hydroxyphenyl hydroxyl	0.046	0.049
135.5-134.5	Carboxylic hydroxyl	0.164	0.164
	<b>Total</b>	<b>3.856</b>	<b>4.013</b>

#### Molecular weight distribution

The molecular weight distribution of the two MALs are provided in Table 3, in which polydispersity (DPn) was calculated by Mw/Mn. Although their molecular weights were similar, three kinds of molecular weight of Alcell MAL were higher. This results from the different degradation levels of lignin in different pulping methods. And clearly, with the effect of NaOH, lignin is easier to degrade than with ethanol. The DPn of both MALs were large, indicating a poor uniformity and a wide range of molecular weights. According to the molecular weights and the results provided in Table 1, the empirical formulae could be further determined. They are  $\text{C}_{505.87}\text{H}_{560.00}\text{O}_{158.34}\text{N}_{1.01}$  for Alcell MAL and  $\text{C}_{421.67}\text{H}_{492.93}\text{O}_{148.01}\text{N}_{0.42}$  for Alkali MAL.

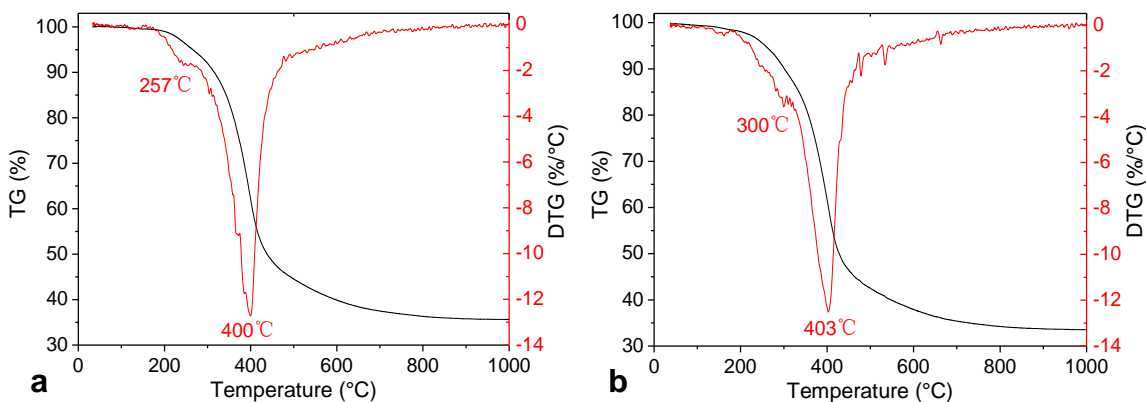
**Table 3.** Molecular Weights of Alcell and Alkali MALs

Sample	Mn	Mw	Mz	DPn
Alcell MAL	3684	9178	22675	2.49
Alkali MAL	3290	7927	21007	2.41

#### Thermogravimetric Analysis

The thermogravimetry (TG) and differential thermogravimetry (DTG) traces for the two MALs are shown in Fig. 2. The thermogravimetric characteristics are very similar. Because of high purity, only one thermal degradation stage occurred in the DTG traces. The pyrolysis peak temperatures are 400 °C for Alcell and 403 °C for Alkali MAL. At low temperature, two vibrational peaks at 257 and 300 °C, respectively, can be observed. The peak may be attributed to the loss of gaseous products (Jakab *et al.* 1995)

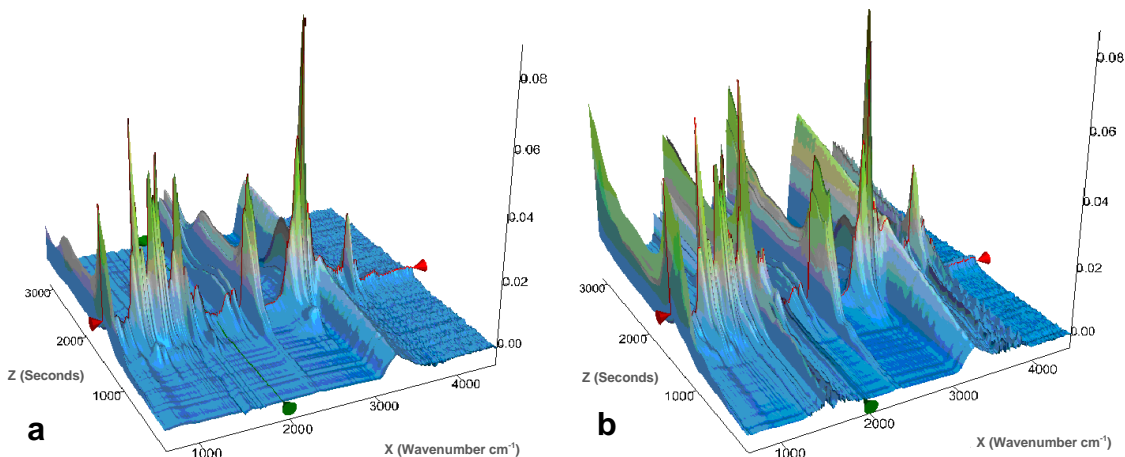
or the molecular perturbations when glass transitions in the thermal degradation. There is no ash in lignin samples, so the obtained solid residue is considered as the fixed carbon. The volatiles and fixed carbon of Alcell and Alkali MAL are 64.36% and 35.64%, and 66.44% and 33.56%, respectively. Because the temperature of the maximum rate of decomposition is about 400 °C, it was the measure chosen through which to investigate the temperature dependence of product distribution.



**Fig. 2.** TG and DTG traces of (a) Alcell MAL and (b) Alkali MAL

### Volatile Properties

As shown in the 3D infrared spectra, main volatile products could be recognized clearly. They included H<sub>2</sub>O, hydroxyl compounds, carbonyl compounds, CH<sub>4</sub>, hydrocarbon compounds, CO<sub>2</sub>, CO, and phenyl compounds. Release time of these volatile products ranged from approximately 1000 s to 2000 s. Maximum release times of two MALs were the same, at 1462 s. The volatiles from Alcell MAL were relatively concentrated, so they are more conducive to use.



**Fig. 3.** Typical 3D infrared spectra from (a) Alcell MAL and (b) Alkali MAL pyrolysis

The releasing laws with temperature of four small molecule gaseous products (CO, CO<sub>2</sub>, H<sub>2</sub>O, and CH<sub>4</sub>) are shown in Fig. 4. Except for the different law of CO<sub>2</sub> at high temperatures (above 800 °C), the release of the other three volatiles were substantially the same. Except for CH<sub>4</sub>, the absorbance of volatiles was higher from Alkali than from Alcell MAL. It is likely that the higher amount of CO, CO<sub>2</sub>, and H<sub>2</sub>O released from Alkali MAL was because absorbance was based on the quality of the

material. In addition, Alkali MAL contains richer groups of C=O and O—H, consistent with the earlier characterization. The amount of CH<sub>4</sub> from Alcell lignin was slightly higher than that from Alkali MAL. The opposite phenomenon was probably contributed by the slightly abundant side chain groups in Alcell MAL. By comparing the amount of these four products, one result can be drawn. In the thermogravimetric process, the amount of CH<sub>4</sub> was the highest, followed by CO<sub>2</sub>, H<sub>2</sub>O, and finally CO.

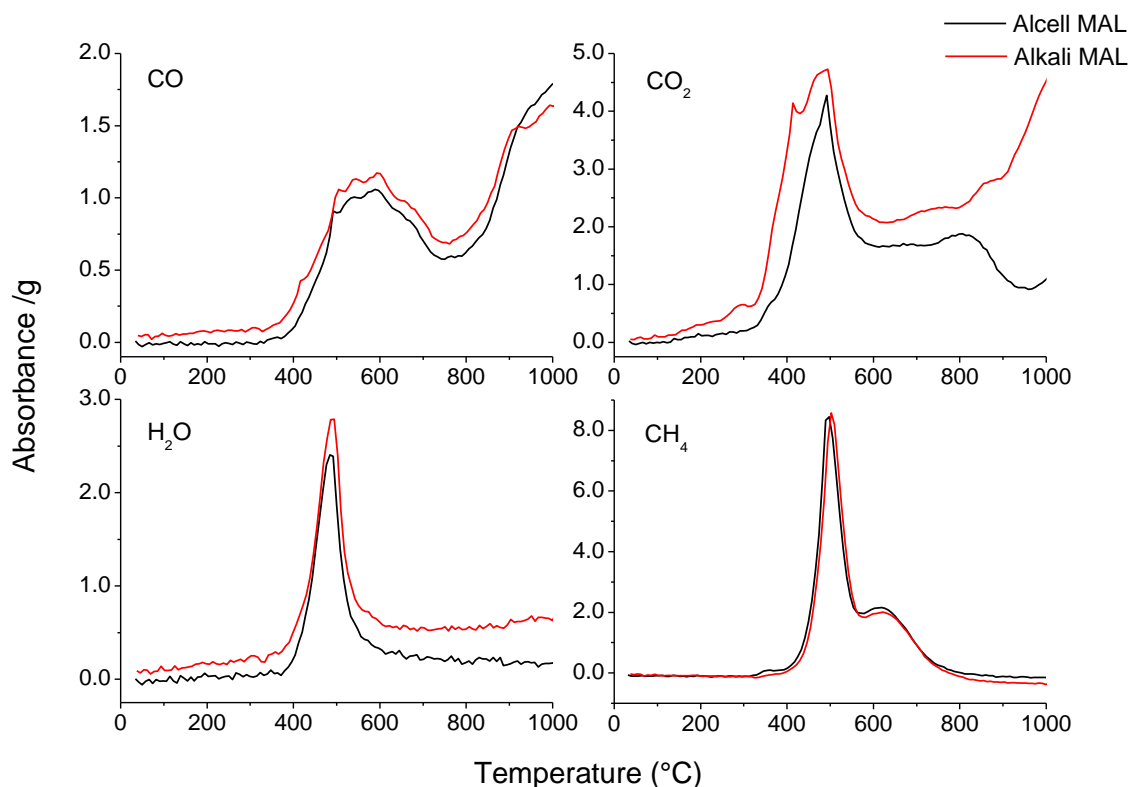


Fig. 4. Releasing laws of small molecular gaseous products from Alcell and Alkali MALs

### Fast Pyrolysis Characteristics

The pyrolytic products from Alcell MAL and Alkali MAL at 400 °C are listed in Table 4. On the basis of nature, all compounds were classified into three groups: phenols, aldehydes & ketones, and other phenyl compounds, with phenols further split into p-hydroxyphenyl, guaiacyl, and syringyl phenols. The total amount of each group is also provided.

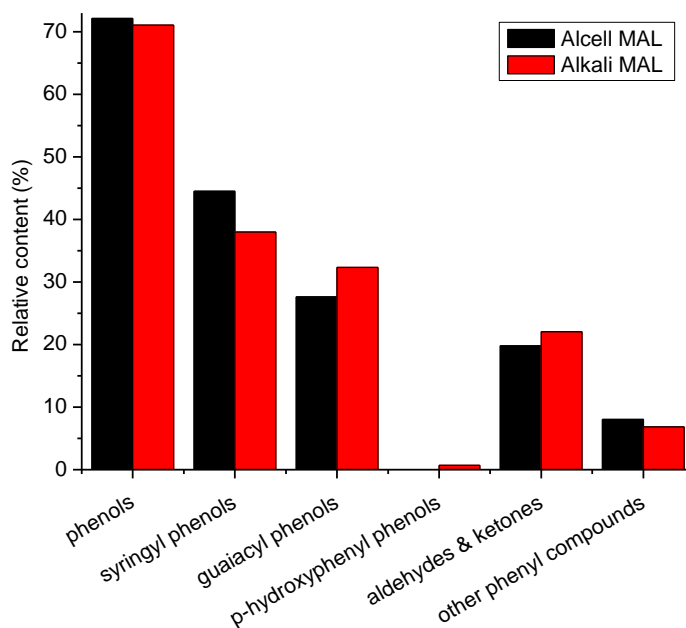
As shown in Table 4, 23 vs. 28 decomposition compounds were identified in Alcell vs. Alkali MAL, while their respective total yield of phenolic compounds was 72.14% vs. 71.09%. Among this yield, syringyl phenols formed the largest proportion, followed by guaiacyl phenols, with p-hydroxyphenyl phenols the smallest. Those were consistent with the results of quantitative <sup>31</sup>P-NMR. For Alkali MAL, the yield of syringyl phenols was lower than that of Alcell MAL, while the kinds and amount of guaiacyl phenols were higher; the only p-hydroxyphenyl phenol identified was 4-(1-propenyl)phenol. Collectively, this indicates that Alkali MAL degrades more easily than Alcell MAL. In other words, it was difficult to further enrich the products from Alkali MAL at 400 °C. Products also included 20% aldehydes and ketones. The formation of those products resulted from the rich carbonyl group in lignin, or the dehydrogenation of

hydroxyl group in fast pyrolysis process. This may also explain the large generation of CO<sub>2</sub>, CO, and other carbonyl compounds in TG-FTIR.

**Table 4.** Analysis of Pyrolytic Products from Alcell and Alkali MALs at 400 °C

Groups	Library/ID	Area Pct (%)		
		Alcell MAL	Alkali MAL	
P-hydroxyphenyl phenols (1)	Phenol, 4-(1-propenyl)-	—	0.71	
	1,2-Benzenediol	—	1.37	
	Phenol, 2-methoxy-	—	0.62	
	Phenol, 2-methoxy-4-methyl-	0.76	0.82	
	Phenol, 4-ethyl-2-methoxy-	4.51	0.38	
	Phenol, 2-Methoxy-4-vinyl	—	5.06	
	Eugenol	1.12	0.97	
	Phenol, 2-methoxy-4-(1-propenyl)-, (Z)-	1.02	1.02	
	Guaiacyl phenols (14)	Phenol, 2-methoxy-4-(1-propenyl)-, (E)-	7.84	6.68
		Phenol, 2-methoxy-4-propyl-	1.47	3.03
		Vanillin	1.32	1.71
		Benzoic acid, 4-hydroxy-3-methoxy-	4.05	3.91
		Ethanone,1-(4-hydroxy-3-methoxyphenyl)-	3.46	3.76
		2-Propanone,1-(4-hydroxy-3-methoxyphenyl)-	2.07	2.40
	3-Methoxy-4-hydroxycinnama alcohol	—	0.63	
	Total	27.63	32.36	
Syringyl phenols (5)	Phenol, 2,6-dimethoxy-	2.53	2.87	
	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	25.66	20.77	
	3,5-Dimethoxy-4-hydroxycinnamaldehyde	5.43	3.47	
	Benzaldehyde,4-hydroxy-3,5-dimethoxy-	6.73	6.49	
	Ethanone,1-(4-hydroxy-3,5-dimethoxyphenyl)-	4.15	4.41	
	Total	44.51	38.01	
Aldehydes & ketones (7)	Benzaldehyde,2-methyl-	1.23	1.07	
	Propanal,2-methyl-3-phenyl-	3.96	4.03	
	4-Methyl-2,5-dimethoxybenzaldehyde	8.57	9.15	
	4-Ethoxy-3-anisaldehyde	—	1.22	
	4-Ethoxy-2,5-dimethoxybenzaldehyde	1.11	—	
	1-Butanone,1-(2,4,6-trihydroxy-3-methylphenyl)-	4.94	4.74	
	4'-Phenylpropiophenone	—	1.85	
	Total	19.81	22.06	
Other phenyl compounds (3)	2,4,6-Trimethylbenzyl alcohol	0.92	—	
	Benzene, 1,2,3-trimethoxy-5-methyl-	3.66	3.57	
	4-Propyl-1,1'-diphenyl	3.46	3.26	
	Total	8.04	6.83	



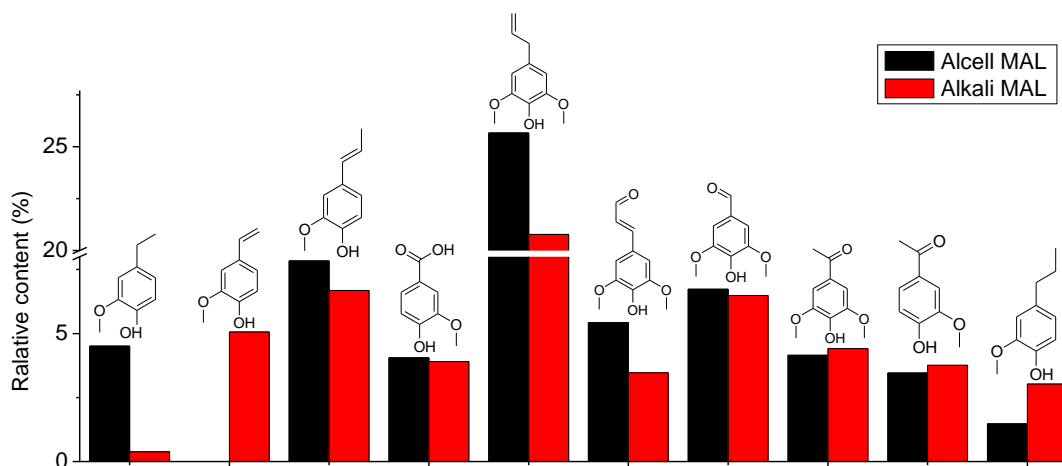


**Fig. 5.** Comparison of relative content of different groups at 400 °C

Figure 6 compares 10 abundant phenolic products. For both MALs, 2,6-dimethoxy-4-(2-propenyl)phenol was the main product, and its yield was much higher than any other products.

The yield of 2,6-dimethoxy-4-(2-propenyl)phenol, (E)-2-methoxy-4-(1-propenyl)phenol, 3,5-dimethoxy-4-hydroxycinnamaldehyde, and 4-ethyl-2-methoxyphenol from Alcell MAL was significantly higher than those from Alkali MAL. In contrast, the yield of 2-methoxy-4-vinylphenol and 2-methoxy-4-propylphenol were significantly lower than those from Alkali MAL.

Similar types of major products, but different yields, indicate that the molecular structures of two MALs were similar, but the content of functional groups and linkages were different.



**Fig. 6.** Comparison of 10 abundant phenolic products at 400 °C

## CONCLUSIONS

1. The carbon content was higher in Alcell MAL than in Alkali MAL, while the oxygen content was lower. Thus, the high heating value (HHV) of Alcell MAL was higher. Because of different degradation processes, Alcell MAL had a lower active hydroxyl group composition and a higher molecular weight than Alkali MAL.
2. The thermogravimetric characteristics of the two MALs were similar, with maximum weight loss peaking at about 400 °C. The peak in Alcell MAL at low temperature occurred earlier than in Alkali MAL. Although the kinds of volatile products both released were similar, Alcell MAL exhibited certain advantages in which the releasing was in a relatively narrow temperature range and the volatiles were concentrated.
3. The species and contents of fast pyrolytic products at 400 °C differed between the two MALs. The pyrolytic products were both relatively concentrated, and there was more syringyl structure retained in Alcell MAL pyrolytic products. Phenols occupied the maximum proportion of the pyrolytic products, and the relative content was 72.14% for Alcell MAL and 71.09% for Alkali MAL. 2,6-Dimethoxy-4-(2-propenyl)phenol composed the dominant phenolic pyrolytic products.

## ACKNOWLEDGMENTS

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## REFERENCES CITED

- Argyropoulos, D. S. (1994). "Quantitative phosphorus-31 NMR analysis of lignins, a new tool for the lignin chemist," *Journal of Wood Chemistry and Technology* 14(1), 45-63. DOI: 10.1080/02773819408003085
- Argyropoulos, D. S. (1995). "<sup>31</sup>P NMR in wood chemistry: A review of recent progress," *Research on Chemical Intermediates* 21(3-5), 373-395. DOI: 10.1007/BF03052265
- Bassilakis, R., Carangelo, R. M., and Wojtowicz, M. A. (2001). "TG-FTIR analysis of biomass pyrolysis," *Fuel* 80(12), 1765-1786. DOI: 10.1016/S0016-2361(01)00061-8
- Bridgwater, A. V., Meier, D., and Radlein, D. (1999). "An overview of fast pyrolysis of biomass," *Organic Geochemistry* 30(12), 1479-1493. DOI: 10.1016/S0146-6380(99)00120-5
- Bridgwater, A. V., and Peacocke, G. (2000). "Fast pyrolysis processes for biomass," *Renewable and Sustainable Energy Reviews* 4(1), 1-73. DOI: 10.1016/S1364-0321(99)00007-6
- Faix, O., Argyropoulos, D. S., Robert, D., and Neirinck, V. (1994). "Determination of hydroxyl groups in lignins evaluation of <sup>1</sup>H-, <sup>13</sup>C-, <sup>31</sup>P-NMR, FTIR and wet chemical methods," *Holzforschung* 48(5), 387-394. DOI: 10.1515/hfsg.1994.48.5.387

- Ferdous, D., Dalai, A. K., Bej, S. K., and Thring, R. W. (2002). "Pyrolysis of lignins: Experimental and kinetics studies," *Energy & Fuels* 16(6), 1405-1412. DOI: 10.1021/ef0200323
- Franke, R., McMichael, C. M., Meyer, K., Shirley, A. M., Cusumano, J. C., and Chapple, C. (2000). "Modified lignin in tobacco and poplar plants over-expressing the Arabidopsis gene encoding ferulate 5-hydroxylase," *The Plant Journal* 22(3), 223-234. DOI: 10.1046/j.1365-313x.2000.00727.x
- Gosselink, R., Abächerli, A., Semke, H., Malherbe, R., Käuper, P., Nadif, A., and Van Dam, J. (2004). "Analytical protocols for characterisation of sulphur-free lignin," *Industrial Crops and Products* 19(3), 271-281. DOI: 10.1016/j.indcrop.2003.10.008
- Granata, A., and Argyropoulos, D. S. (1995). "2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, a reagent for the accurate determination of the uncondensed and condensed phenolic moieties in lignins," *Journal of Agricultural and Food Chemistry* 43(6), 1538-1544. DOI: 10.1021/jf00054a023
- Guo, D., Wu, S., Liu, B., Yin, X., and Yang, Q. (2012). "Catalytic effects of NaOH and Na<sub>2</sub>CO<sub>3</sub> additives on alkali lignin pyrolysis and gasification," *Applied Energy* 95, 22-30. DOI: 10.1016/j.apenergy.2012.01.042
- Jakab, E., Faix, O., Till, F., and Székely, T. (1995). "Thermogravimetry/mass spectrometry study of six lignins within the scope of an international round robin test," *Journal of Analytical and Applied Pyrolysis* 35(2), 167-179. DOI: 10.1016/0165-2370(95)00907-7
- Jiang, Z. H., Argyropoulos, D. S., and Granata, A. (1995). "Correlation analysis of <sup>31</sup>P NMR chemical shifts with substituent effects of phenols," *Magnetic Resonance in Chemistry* 33(5), 375-382. DOI: 10.1002/mrc.1260330509
- Jiang, G., Nowakowski, D. J., and Bridgwater, A. V. (2010a). "A systematic study of the kinetics of lignin pyrolysis," *Thermochimica Acta* 498(1), 61-66. DOI: 10.1016/j.tca.2009.10.003
- Jiang, G., Nowakowski, D. J., and Bridgwater, A. V. (2010b). "Effect of the temperature on the composition of lignin pyrolysis products," *Energy & Fuels* 24(8), 4470-4475. DOI: 10.1021/ef100363c
- Li, X., and Wu, S. (2014). "Chemical structure and pyrolysis characteristics of the soda-alkali lignin fractions," *BioResources* 9(4), 6277-6289. DOI: 10.15376/biores.9.4.6277-6289
- Liu, Q., Wang, S., Zheng, Y., Luo, Z., and Cen, K. (2008). "Mechanism study of wood lignin pyrolysis by using TG-FTIR analysis," *Journal of Analytical and Applied Pyrolysis* 82(1), 170-177. DOI: 10.1016/j.jaap.2008.03.007
- Lou, R., and Wu, S. (2008). "Pyrolysis characteristics of rice straw EMAL," *Cellulose Chemistry and Technology* 42(7-8), 371-380.
- Luo, Z., Wang, S., Liao, Y., Zhou, J., Gu, Y., and Cen, K. (2004). "Research on biomass fast pyrolysis for liquid fuel," *Biomass and Bioenergy* 26(5), 455-462. DOI: 10.1016/j.biombioe.2003.04.001
- Marques, G., Gutiérrez, A., and Del Río, J. C. (2008). "Chemical composition of lignin and lipids from tagasaste (*Chamaecytisus proliferus* spp. *palmensis*)," *Industrial Crops and Products* 28(1), 29-36. DOI: 10.1016/j.indcrop.2007.12.007
- Ragauskas, A. J., Beckham, G. T., Biddy, M. J., Chandra, R., Chen, F., Davis, M. F., Davison, B. H., Dixon, R. A., Gilna, P., Keller, M., et al. (2014). "Lignin valorization: Improving lignin processing in the biorefinery," *Science* 344(6185). DOI: 10.1126/science.1246843

- Spyros, A., and Dais, P. (2009). “<sup>31</sup>P NMR spectroscopy in food analysis,” *Progress in Nuclear Magnetic Resonance Spectroscopy* 54(3-4), 195-207. DOI: 10.1016/j.pnmrs.2008.09.002
- Thring, R. W., Katikaneni, S. P., and Bakhshi, N. N. (2000). “The production of gasoline range hydrocarbons from Alcell® lignin using HZSM-5 catalyst,” *Fuel Processing Technology* 62(1), 17-30. DOI: 10.1016/S0378-3820(99)00061-2
- Wu, S., and Argyropoulos, D. S. (2003). “An improved method for isolating lignin in high yield and purity,” *Journal of Pulp and Paper Science* 29(7), 235-240. WOS:000185031700005
- Yang, Q., Wu, S., Lou, R., and Lv, G. (2011). “Structural characterization of lignin from wheat straw,” *Wood Science and Technology* 45(3), 419-431. DOI: 10.1007/s00226-010-0339-1

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