

## STUDY ON THE STRUCTURAL CHANGE OF LIGNIN DURING AUTO-CATALYZED ETHANOL-WATER PULPING OF ASPEN BY $^1\text{H-NMR}$

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This study concerns the structural change of lignin during auto-catalyzed ethanol-water pulping of aspen by  $^1\text{H-NMR}$ . The results showed that the linkages of alkyl-aryl ether of lignin, such as the  $\alpha$ -ether linkages ( $\alpha\text{-O-4}$ ) and the  $\beta$ -ether linkages ( $\beta\text{-O-4}$ ), were broken and the alkyl part formed carbenium at the  $\text{C}\alpha$  and  $\text{C}\beta$  of the aliphatic branch. Meanwhile, the aryl part of ether accepted one  $\text{H}^+$  and formed phenol. Because of the electronegative effect originating from the electron cloud of phenyl, partial carbenium of  $\text{C}\beta$  was rearranged. Due to its ether or hydroxyl linkage, rearranging to  $\text{C}\beta$ , the  $\text{C}\alpha$  was changed into carbenium and formed a new  $\beta\text{-O-4}$  alkyl-aryl ether. The  $\beta\text{-O-4}$  alkyl-aryl ether was not stable and broken further. So the large molecule of lignin was disintegrated into a smaller one and dissolved into ethanol. Finally, the  $\alpha^+$  carbenium reformed  $\alpha\text{-O-4}$  linkages of ether with phenol.

*Keywords:* Auto-catalyzed; Ethanol-water; Pulping; Aspen; Lignin structure;  $^1\text{H-NMR}$ ; Mechanism of delignification

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### INTRODUCTION

Aspen resources are distributed widely in China. Aspen is a preferred raw material to produce mechanical pulp, chemi-mechanical pulp, and chemical pulp in the papermaking industry. For chemical pulping, sulfate and sulfite pulping are the main pulping processes, for which waste liquor is difficult to dispose and causes certain pollution to the environment. Organosolvent pulping often is considered to be a newer pulping method. However, the idea can be traced back to the 19<sup>th</sup> century, when the use of ethanol was proposed to remove lignin and produce pulp. Extensive research really began from the 1980 (Sahina and Young 2008; Xu 2008). Advantages of this process include less pollution discharged, recycling of the organosolvent, and environmental friendliness. Furthermore, the by-product lignin from black liquor can be purified and modified to produce valuable products, which is different from the case of sulfite or sulfate pulping, in which the lignin is fired or utilized crudely (Yong 2006; Ni and Lora 1996).

Auto-catalyzed ethanol pulping is characterized in that no chemical reagent needs to be added as a catalyst, and the organic acids released in the process of pulping act as catalysts. Furthermore, as a result of the lack of chemical additives, ethanol can be

recovered easily (Cui and Zhou 2008). So the problem of difficult-to-treat waste liquor can be solved well.

Nowadays, many researchers have systematically studied auto-catalyzed ethanol pulping of nonwood (such as reed, tobacco haulm, wheat and straw), while aspen hasn't been researched enough. In this work, the structural changes of aspen lignin in pulp and black liquor were analyzed by  $^1\text{H-NMR}$ . The reaction mechanism of auto-catalyzed ethanol-water pulping of aspen was also studied.

## **EXPERIMENTAL**

### **Materials**

Italian poplar was provided by Hunan Tiger Forest and Paper Corporation of China. The size of wood chip was 4cm to 6cm length, 2cm to 3cm width and 2mm to 4mm thickness. Ethanol was 95% (v/v) industrial product. Wood powder between 40 and 60 mesh size was obtained by grinding dry chips. The powder was stored in a jar with a ground plug.

### **Methods**

#### *Cooking process*

An electrical cooker of ZQS-1 type made in Shanxi University of Science & Technology was used. There are four stainless steel canakins (volume 1L) inside the cooker. In order to adapt to the demand of higher temperature and pressure of auto-catalyzed ethanol pulping, the water was replaced with glycerol. Cooking parameters were maximum temperature 205 °C, wood-to-liquor ratio 1:10, 150 min up to 205 °C, 120 min at 205 °C, and ethanol concentration 60%.

#### *Pulp washing*

After cooking, pulp was loaded in a hop-pocket and wrung to collect the black liquor and measure pH immediately. Then pulp was washed successively with ethanol at concentrations of 60%, 50%, 40%, and 30%, respectively. Finally, the pulp was washed with tap water of 80 °C to remove the ethanol from the pulp.

#### *Research methods for lignin structure*

Preparation of lignin in material (MWL) and lignin in pulp (PL) was according to the literature (Yong 2006; Shao et al. 2008). Lignin in black liquor (BL) was prepared as follows: First, black liquor obtained after time at maximum temperature of 0 min, 30 min, 60 min, 90 min, 120 min, and 150 min was diluted by 10 times, respectively. Second, after precipitation, the diluted black liquor was filtered to obtain BL that had been exposed to the maximum temperature for different lengths of time.

The NMR device was of INVOA superconductive type with a frequency of 400 million made in VARIAN Company of America. To get a visible signal of lignin hydroxyl structure in  $^1\text{H-NMR}$  experiment, the hydroxyl on lignin sample was acetylated by adding acetyl chloride (Crestini et al. 2009).

## RESULTS AND DISCUSSION

### $^1\text{H-NMR}$ Summarization

By means of an  $^1\text{H-NMR}$  integral curve, one can obtain the proportion of each integral area, and the percentage of protons in each area can be calculated. Then, the functional group content concerned can be speculatively combined with the elemental analysis and measuring of the methoxyl content. Based on the proton  $^1\text{H-NMR}$  chemical shift in  $^1\text{H-NMR}$  spectrum, the kinds of functional group can be confirmed (Shi and He 2003).

### $^1\text{H-NMR}$ and Analysis

After hydroxyl group acetylation, the MWL, PL, and BL were studied with the  $^1\text{H-NMR}$  analyzer, and the spectra were as follows:

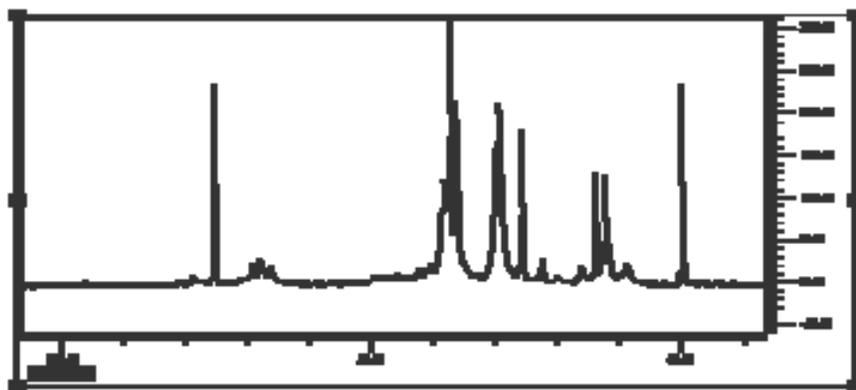


Fig. 1.  $^1\text{H-NMR}$  spectrogram of aspen MWL

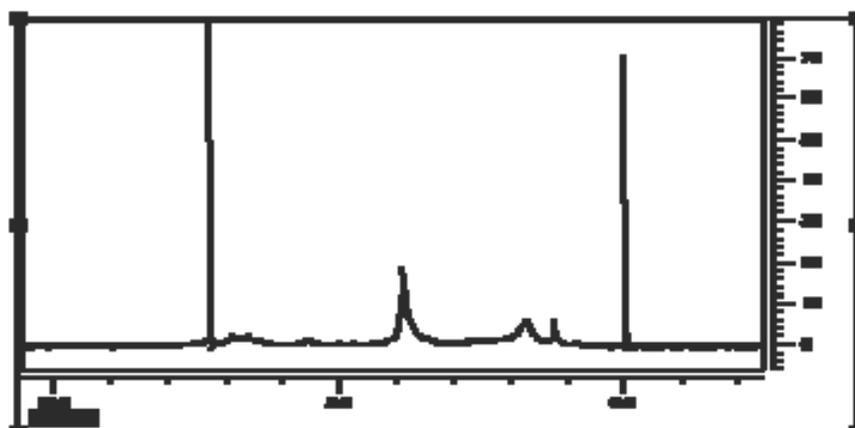


Fig. 2.  $^1\text{H-NMR}$  spectrogram of pulp PL

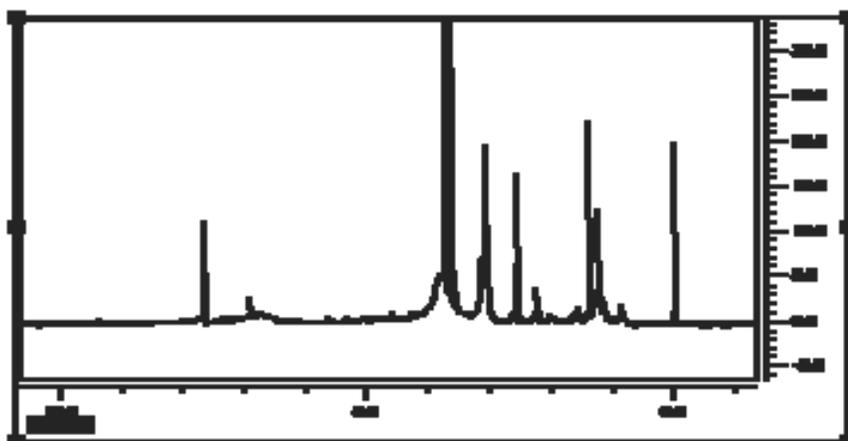


Fig. 3.  $^1\text{H-NMR}$  spectrogram of BL from black liquor

Figures 1 to 3 are  $^1\text{H-NMR}$  spectrograms of MWL from aspen material, pulp, and black liquor, respectively. According to corresponding relationship between chemical shift and proton of lignin units, the analysis was as follows:

(1) The  $^1\text{H-NMR}$  chemical shifts ( $\delta$  for short) of aspen MWL are shown in Table 1. From Table 1, it can be found that  $\delta$  values in the range 6.818 to 6.940 corresponded to the proton of guaiacyl phenyl, and  $\delta$  values of 6.618 to 6.818 were from the proton of syringyl phenyl, which shows that the lignin molecule of aspen was comprised of guaiacyl and syringyl units. According to the percentages of protons, the proportion of guaiacyl and syringyl was about 6:5, and the proportion of the hydroxyl quantity in the branch chain of lignin and phenyl hydroxyl was about 2:1.

(2) Comparing Table 1 to Table 2, it could be found that the percentage of protons of  $\beta$ -5,  $\beta$ - $\beta$ , and  $\beta$ -1 of lignin in pulp was close to that of aspen material, which shows that the C-C bond is stable and difficult to break. In Table 1, the proton percent of guaiacyl and syringyl of aspen material was 5.47 and 4.53 respectively, while in Table 2, that of pulp had declined to 1.62 and 1.13, respectively. This indicates that  $\alpha$ -O-4 and  $\beta$ -O-4 alkylaryl ethers were largely broken, so most of the guaiacyl and syringyl groups had been removed from the pulp in the course of the delignification process. This conclusion is consistent with Meshgini's research (Meshgini and Sarkanen 1989).

(3) The  $^1\text{H-NMR}$  chemical shift of BL is shown in Table 3. From Table 3, it can be found that the proton percent of guaiacyl and syringyl of BL was 4.62 and 4.37 respectively, which indicated that lignin has been largely removed from wood chip into black liquor. Most of the guaiacyl and syringyl groups in the material had been removed after the principal delignification phase and residual delignification phase. Furthermore,  $\delta$  values in the range 1.741 to 1.783 corresponded to the protons of acetyl groups on the acyclic branch, which content was much larger than that of pulp. Meanwhile, protons of aromatic acetyl groups in pulp essentially disappeared, which showed that a mass of hydroxyl on acyclic branch was dissolved into black liquor with benzene-propane units removed. This conclusion is similar to that of earlier workers (Lora and Gopal 1993; Tring and Vanerlaan 1996).

(4) Aziz and Sarkanen (1989) had proposed that the linkage of  $\alpha$ -O-4 ether was broken at the beginning of cooking, which accelerated the dissolution of lignin. Once the lignin was dissolved, cleavage and rearranging of ether linkage of  $\beta$ -O-4 would occur again. In addition, the  $\alpha$ -O-4 linkage can form again. This has been conformed in Meiyun Zhang's research (Zhang 2004).

**Table 1.** Chemical Shift of Aspen MWL  $^1\text{H-NMR}$  and Percent of Protons

Area	Shift $\delta$	Proton type	Percent of protons
1	7.263~7.674	$\text{CDCl}_3$ solvent	6.27
2	6.818~6.940	proton of guaiacyl phenyl	5.47
3	6.618~6.818	proton of syringyl phenyl	4.53
4	5.180~5.740	$\alpha$ -H in $\alpha$ -O-4 and $\beta$ -O-4	0.72
5	4.300~5.180	$\beta$ -H in $\beta$ -5 and $\beta$ - $\beta$	4.21
6	3.531~4.228	proton in $-\text{OCH}_3$	40.41
7	2.253~2.327	proton of phenolic acetyl	2.28
8	1.580~2.190	proton of acetyl on fatty propane	4.35

**Table 2.** Chemical Shift of Pulp MWL  $^1\text{H-NMR}$  and Percent of Protons

Area	Shift $\delta$	Proton type	Percent of protons
1	7.263~7.674	$\text{CDCl}_3$ solvent	4.94
2	6.818~6.940	proton of guaiacyl phenyl	1.62
3	6.618~6.818	proton of syringyl phenyl	1.13
4	5.180~5.740	$\alpha$ -H in $\alpha$ -O-4 and $\beta$ -O-4	0.42
5	4.300~5.180	$\beta$ -H in $\beta$ -5 and $\beta$ - $\beta$	2.83
6	4.150~4.300	$\text{H}_\beta$ in $\beta$ -1, $\beta$ -5, $\beta$ -O-4 and $\beta$ - $\beta$	2.64
7	3.599~3.827	proton in $-\text{OCH}_3$	47.75
8	2.251~2.350	proton of phenolic acetyl	3.06
9	1.580~2.190	proton of acetyl on fatty propane	5.20

**Table 3.** Chemical Shift of BL  $^1\text{H-NMR}$  and Percent of Protons

Area	Shift $\delta$	Proton type	Percent of protons
1	7.263~7.674	$\text{CDCl}_3$ solvent	8.94
2	6.818~6.940	proton of guaiacyl phenyl	4.62
3	6.618~6.818	proton of syringyl phenyl	4.37
4	5.320~5.700	$\alpha$ -H in $\alpha$ -O-4	1.42
5	3.705~3.949	proton in $-\text{OCH}_3$	48.46
6	1.741~1.783	proton of acetyl on fatty propane	17.95

According to the results of the  $^1\text{H-NMR}$  tests, it could be concluded that the lignin molecule changed as follows. First, the linkages of alkyl-aryl ether on lignin such as  $\alpha$ -ether linkages ( $\alpha$ -O-4) and  $\beta$ -ether linkages ( $\beta$ -O-4) were broken, and the part of alkyl formed carbenium ions at the  $\text{C}_\alpha$  and  $\text{C}_\beta$  of the aliphatic branch. Meanwhile, the aryl part of ether accepted one  $\text{H}^+$  and formed phenol, as illustrated by reactions 1 and 2 in Fig. 4. Thereafter, because of the electronegative effect originating from the electron cloud of phenyl, a portion of the carbenium of  $\text{C}_\beta$  was rearranged. Due to its ether or hydroxyl linkage rearranging to  $\text{C}_\beta$ , the  $\text{C}_\alpha$  was changed into carbenium and formed new  $\beta$ -O-4 alkyl-aryl ethers. The  $\beta$ -O-4 alkyl-aryl ether was not very stabile, so it was broken again. The bigger molecules of lignin were disintegrated into smaller molecules and



the aryl part of ether accepted one  $H^+$  and formed phenol. Thereafter, part of the carbenium of  $C_\beta$  was rearranged, and the  $C_\alpha$  was changed into carbenium to form new  $\beta$ -O-4 alkyl-aryl ethers. Finally,  $\alpha^+$  carbenium reformed  $\alpha$ -O-4 linkages of ether with phenol.

## ACKNOWLEDGEMENTS

The work was financially supported by the Natural Science fund of Liaoning Province of China (20052160).

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Article submitted: April 13, 2009; Peer review completed: May 17, 2009; Revised version received and accepted: May 29, 2009; Published June 1, 2009.