Available online at www.sciencedirect.com
SciVerse ScienceDirect
APCBEE Procedia 3 (2012) 53 – 59
Procedia APCBEE
www.elsevier.com/locate/procedia

ICCCP 2012: 5-6 May 2012, Kuala Lumpur, Malaysia

# Hydrogenation of Alkali Lignin Catalyzed by Pd/C

Ye Jie-wang[a,]*, Fang Gui-zhen[b], Jin Chun-de[a]

[a] *National Engineering & Technology Research Center of Wood－based Resources Comprehensive Utilization, ZheJiang A & F University，Lin’ an 311300, China*
[b] *Key Laboratory of Bio-based Material Science and Technology, Northeast Forestry University, Harbin, 150040, China*

## Abstract

Hydrogenation of alkali lignin was carried out in the presence of Pd/C catalyst at hydrogen pressure 1~5 MPa. Catalytic activity of Pd/C catalyst was investigated according to the structure changes of alkali lignin, which were characterized by UV and $^1$H-NMR spectroscopy. The measurement of average molecular weight undertook by gel permeation chromatography (GPC). Changes on function groups of alkali lignin were analyzed through chemical methods. Results show that total hydroxyl, phenolic hydroxyl and alcoholic hydroxyl increase 64.23%, 37.10% and 89.67%, respectively, while carbonyl and carboxyl decrease separately 43.50% and 53.41%. No significant differences of the total acidic groups and the phenyl structure were found after reaction. GPC analysis shows the weight average molecular weight ($M_w$) and number average molecular weight ($M_n$) are both decreased, and the polydispersity of alkali lignin is increased The active function groups of alkali lignin are increased obviously, and reactive activity of alkali lignin is enhanced as a result. The present results demonstrate Pd/C catalyst shows an excellent catalytic activity on reductive reaction of alkali lignin and hydrogen.

*Keywords:* Pd/C Catalyst, Alkali Lignin, Hydrogenation, Activation

Lignin is a three-dimensional amorphous biopolymer composed of phenylpropanoid units linked together by ether and carbon-carbon bonds. Depending on the tree species, lignin constitutes 15-35 % of the wood. It is formed between the fibre cells and acts, besides other functions, as a cementic material thus imparting rigidity to the wood structure. It is considered to be one of the most promising future organic resources not only because it is renewable, but also is second only to cellulose in abundance among the naturally occurring

---

* Corresponding author. Tel.: +086-571-63732790; fax: +086-571-63732790
*E-mail address*: yjw0418@zafu.edu.cn

doi:10.1016/j.apcbee.2012.06.045

polymers [1]. Despite many attempts in the past to utilize lignin, the only major commercial application of technical lignin today is in the form of lignosulphonate, which are water-soluble. These modified lignins are primarily employed as agents for binding, dispersion and emulsion stabilization in a variety of industries [2]. Although most attempts to utilize lignin were made in the phenol formaldehyde resin field, some work has been conducted into its use in the production of polyurethane [3, 4]. However, there are few researches on enhancing the reactive groups in recent studies. Some reports refer to this aspect, such as oxidant degradation, hydrogenolysis at high temperature and pressure[5], ammoxidation[6], activation with strong alkali solution[7], electrochemistrical hydrogenation[8], electrochemistry oxidation degradation[9], etc. These methods can partly change the chemical structure of alkali lignin, and the reactivity has improved to some extent. For certain reasons and localizations, they can't meet the performance demand of products, or aren't appropriate to industrialize. These researches haven't achieved good results for the low reactivity of lignin, especially the alkali lignin, which containing high methoxyl groups, lower alcoholic hydroxyl groups, a great number of guaiacyl and a few syringyl.

The present work focused on improving the reactivity of alkali lignin through reductive reaction of alkali lignin and hydrogen catalyzing by Pd/C catalyst. Pd/C catalyst is widely used in various kinds of industries for its high activity, excellent selectivity, mild reaction conditions, few dosage, long service life and simple techniques. The selective deoxidization of hydroquinone dibenzyl ether catalyzed by Pd/C catalyst has been reported [10, 11].

## 1. Materials and Methods

### *1.1. Materials*

Raw alkali lignin was obtained from Shangdong Tralin Paper CO., LTD producing by alkaline pulping with wheat straw. The raw alkali lignin was purified with a mixture of 1.2-dichloroethane and alcohol (2:1 by volume), followed by precipitating with ether and washing with ether and petroleum ether for several times, then the refined alkali lignin was prepared under drying in vacuum. All catalysts were prepared by using $PdCl_2$ as the palladium donor at a constant Pd-loading of 5-wt % according to the literature [12]. Granular active carbons with a particle size of 0.45mm to 0.9mm were produced by coco shell at Tangshan Jianxin Activated Carbon CO., LTD, $PdCl_2$ and other reagents are analytically pure (AR).

### *1.2. Methods*

Alkali lignin was dissolved by 0.1 mol/L of NaOH solution before loading. The experiments were carried out in a 100mL micro-autoclave at 350-450K with a hydrogen pressure 1-5 MPa. After reaction, the alkali lignin was precipitated by 1 mol/L of HCl at pH 2, filtrating, and washed with distilled water until neutral. All the functional groups were determined according to the previous literature [13].

UV analysis was acquired on TU-1800PC at a scanning wavelength between 200 nm to 400nm. Alkali lignin was dissolved with a mixture of dioxane and water (9:1 by volume). 2ml of the obtained solution was diluted to 50ml with a buffer solution of pH 6, using as reference. The absorption value was determined at the same determination condition, using 0.2N of NaOH solution as diluent.

Alkali lignin samples were acetylated before used, and then dissolving with dimethyl sulfoxide (deuterated) before $^1$H-NMR and GPC analysis.$^1$H-NMR analysis was carried out with a JeolFX-90Q NMR spectrometer at the scanning frequency of 89.55 MHZ using tetramethylsilane (TMS) as internal standard. GPC analysis was obtained on JASCO-BORWIN GPC equipped with JASCO UV-1575 detector, using polystyrene (PS) as reference sample, tetrahydrofuran as moving phase, at the chromatographic condition of a flow rate of

1.0mL/min,a sample size of 20μL, a column temperature of 25℃ and a column pressure of 2.9MPa.

## 2. 2. Results and Discussion

### *2.1. Physical property changes of alkali lignin*

Using 1 g alkali lignin, hydrogen pressure 4 MPa, physical changes of alkali lignin at different reaction time were observed at 390K, showing in Table 1.

Table 1. Physical changes of alkali lignin

| No. | Catalyst[a] | Reaction time/ h | Yield / % | pH[b] |
|---|---|---|---|---|
| 1[c] | | 0 | 100 | 12.79 |
| 2[d] | | 2 | 98.84 | 11.89 |
| 3 | 5% Pd/C | 1 | 86.88 | 11.13 |
| 4 | 5% Pd/C | 2 | 85.78 | 10.17 |
| 5 | 5% Pd/C | 3 | 84.33 | 10.05 |
| 6 | 5% Pd/C | 4 | 84.27 | 10.02 |
| 7 | CuO | 2 | 98.75 | 12.55 |
| 8 | Raney Ni | 2 | 90.26 | 11.76 |

a: the amount of catalysts were 5 wt%; b: when lignin was dissolved completely; c: alkali lignin material; d: in the absence of catalyst .

The physical characteristics of alkali lignin had changed little using CuO as catalyst, indicating a poor catalytic activity. Raney Ni was also applied at the same conditions. Results showed the yield and pH, when the alkali lignin was dissolved completely, were both decreased, although not obvious contrast to Pd/C.

The experimental data indicate a weight reducing of alkali lignin at the presence of Pd/C, suggesting that part of small molecules were removed and some lignin were degraded during the reaction. The pH was decreased after reaction, indicating the solubility of the alkali lignin in neutral or alkalescent solution has enhanced and the polar function groups of alkali lignin have increased or the molecular weight of alkali lignin has decreased. After the reaction, the colour of alkali lignin was shaded from grey to puce along with the prolonging of reaction time, showing the alkali lignin has been changed in the reaction.

### *2.2. Functional groups analysis of alkali lignin*

The contents of functional groups were determined to analyze chemical structural variation of alkali lignin after the reaction. Table 2 summarizes the results of changes on function groups of alkali lignin after reactions.

Table 2. Changes on function groups of alkali lignin (%)

| No. | Catalyst[a] | Time (hour ) | Total hydroxyl (%) | Phenolic hydroxyl (%) | Aliphatic hydroxyl (%) | Carbonyl (%) | Carboxyl (%) | Total acidic (%) |
|---|---|---|---|---|---|---|---|---|
| 1[b] | | 0 | 6.57 | 3.18 | 3.39 | 5.08 | 2.64 | 5.82 |
| 2[c] | | 3 | 6.62 | 3.22 | 3.40 | 5.14 | 2.57 | 5.79 |
| 3 | 5% Pd/C | 1 | 8.29 | 3.86 | 4.43 | 3.80 | 1.51 | 5.37 |
| 4 | 5% Pd/C | 2 | 9.66 | 4.11 | 5.65 | 3.43 | 1.44 | 5.55 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 5 | 5% Pd/C | 3 | 10.79 | 4.36 | 6.43 | 2.87 | 1.23 | 5.59 |
| 6 | 5% Pd/C | 4 | 10.52 | 4.17 | 6.35 | 2.64 | 1.36 | 5.53 |
| 7 | CuO | 3 | 7.32 | 3.45 | 3.87 | 4.94 | 2.42 | 5.87 |
| 8 | Raney Ni | 3 | 7.68 | 3.52 | 4.16 | 4.05 | 1.94 | 5.46 |

a: the amount of catalysts were 5 wt%; b: alkali lignin material; c: in the absence of catalyst.

Raney Ni and CuO were tested under the same conditions for 3h. Raney Ni showed better activity to improve the phenolic hydroxyl and aliphatic hydroxyl, and reduce carbonyl and carbonyl. However, the active functional groups weren't improved highly. By using Pd/C as catalyst, the total hydroxyl content of alkali lignin deoxidized at different reaction time has increased greatly, especially at the time of 3 h; the total hydroxyl content is 10.79%, increasing 64.23%. The phenolic hydroxyl and aliphatic hydroxyl groups increase 37.10% and 89.67% respectively. By contrast, the carbonyl and carboxyl decrease separately 43.50% and 53.41%, showing that some carboxyl groups had been changed into aliphatic hydroxyl groups during the reaction. The total acidic groups have little change after the reactions. These experiments indicate that Pd/C catalyst has an excellent catalytic activity on reductive reaction of alkali lignin and hydrogen, and the following analyses were based on Pd/C as catalyst.

### *2.3. UV analysis*

Comparative study on the UV spectra of activated alkali lignin and the refined alkali lignin was shown in Fig. 1. O-benzene ring shows an electron vibration in the ranges of 208nm to 215nm and 250nm to 290nm. The absorption in range of 300nm to 350nm is attributed to the conjugated vibration originated by the benzene ring conjugated with carbonyl or double band of ethylene, both of which are in the branch of alkali lignin.

Because of few coumaric acid and ferulic acid, the UV absorption spectra of lignin from wood have no absorption in range of 300-350nm, while the lignin from gramineous plants and glasses comprises many conjugated structures, such as coumaric acid, ferulic acid phenyl coumarone and stilbene, etc., which show an absorption in range of 300-350nm. The absorptions in 215nm, 250nm and 300nm appearing in Figure1 are the difference UV absorption of lignin from the gramineous plant or the glasses.

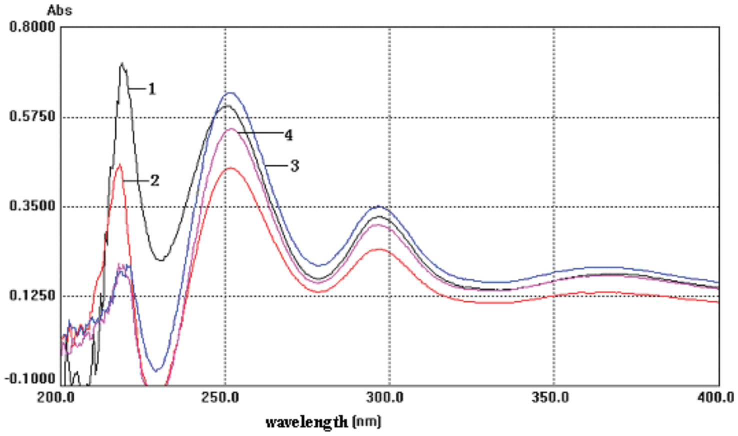

Fig. 1. UV spectra of alkali lignin

1-refined alkali lignin;2-alkali lignin deoxidized for 1 h;3- alkali lignin deoxidized for 2 h；4- alkali lignin deoxidized for 3 h

### 2.4. $^1$H-NMR analysis

$^1$H NMR spectra of the refined alkali lignin and the alkali lignin deoxidized for 2 hours are shown in Fig.2 and Fig.3 [14-16]. Benzenoid protons in p-hydroxybenzyl absorb at $\delta$=7.7ppm. H in Aromatics and side chain (in which α,β are conjugated double bonds) absorb at$\delta$=7.3ppm. The aromatic absorptions in 6.9 and 6.7 are separately attributed to guaiacyl and syringyl. The aromatic protons calculated in total have an increasing trend, suggesting a reduction of condensation and an activity enhancement of alkali lignin. Absorption in the range of 4.0-6.0ppm reverts to protons of several kinds of structures, involving β-ethenyl and benzyl. The number of protons has increased, showing the alkali lignin has been deoxidized. The absorptions in 3.2 and 3.7 are assigned to methoxyl, which has decreased 17.73%, indicating that the methoxyl has been changed into hydroxyl, causing an enhancement in the activity of alkali lignin, according with the results obtained by the chemical and spectral analysis.

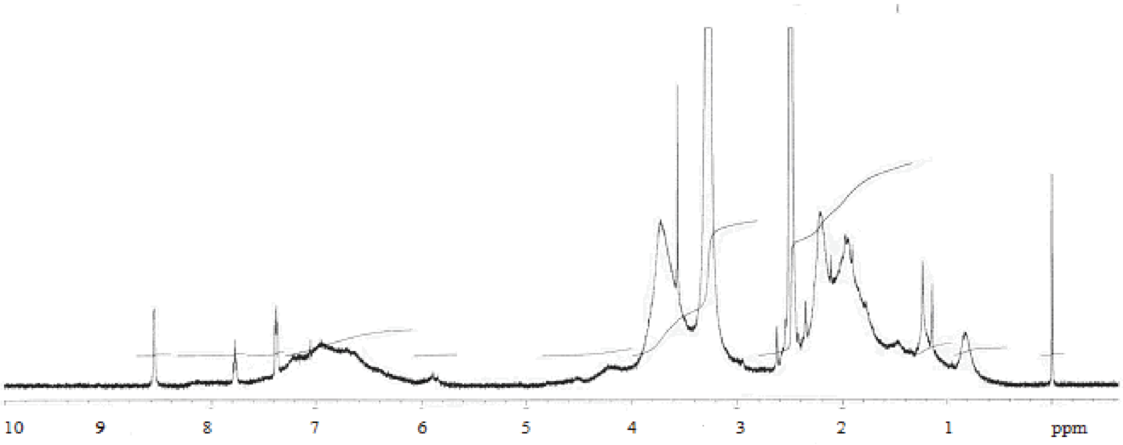

Fig. 2. $^1$H NMR spectra of refined alkali lignin

Hydrogen as hydrogen donor was changed into benzene in the catalytic system. Alkali lignin and hydrogen were adsorbed on the surface of Pd, which is distributed on the surface of activated carbon. At the catalysis of Pd, catalytic hydrogenation of alkali lignin may be taken place, that is, carboxyl may be deoxidized to aliphatic hydroxyl. At the same time, catalytic hydrogenolysis of alkali lignin also can be occurred, causing degradation of ether bond, such as methyl-aryl ether, increase of phenolic hydroxyl, decrease of methoxyl. The reaction mechanism should be confirmed in future research.

### 2.5. GPC analysis

Weight average molecular weight ($M_w$) and number average molecular weight ($M_n$) were both decreased (Table 3), and the $M_n$ was decreased more, causing the increasing of polydispersity index, from 1.92 to 2.68. In macromolecule with polydispersity, the lower molecular weight has more contribution to $M_n$, and the larger has more contribution to $M_w$ [17]. Therefore, alkali lignin was depolymerized to large numbers of small molecules during hydrogenation. Links between structure cells of alkali lignin were broken, and more phenolic hydroxyls were formed as a result.

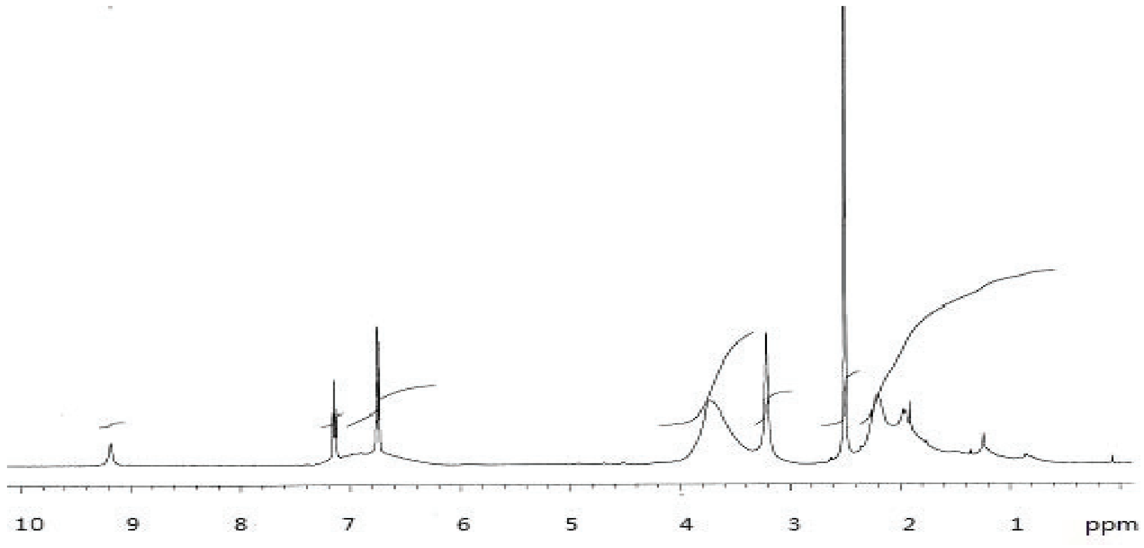

Fig. 3. $^{1}$H NMR spectra of alkali lignin deoxidized for3 h

Table 3. Comparison on average molecular weight of alkali lignin

| | $M_n$ | $M_w$ | $D=M_W/M_N$ |
|---|---|---|---|
| Refined alkali lignin | 8758 | 16849 | 1.92 |
| Activated alkali lignin | 5196 | 13943 | 2.68 |

## Acknowledgements

The financial support by the National Natural Science Foundation of China (Grant No. 30471363) and the Youth Innovation Team Foundation of Zhejiang A&F University (2009RC03) is gratefully acknowledged.

## References

[1] Pandey M P, Kim C S. Lignin Depolymerization and Conversion: A Review of Thermochemical Methods. *Chem. Eng. Technol*, 2011, 34(1): 29-41.

[2] Stewart D. Lignin as a base material for materials applications: Chemistry, application and economics. *Industrial Crops and Products*, 2008, 27(2):2202-207.

[3] Liu Z M, Yu F, Fang G Z ,et al. Performance characterization of rigid polyurethane foam with refined alkali lignin and modified alkali lignin. *Journal of Forestry Research*, 2009, 20(2);161-164.

[4] Thring R W, VanderLaan M N and Griffin S L. Polyurethanes from Alcell® lignin. *Biomass and Bioenergy*. 1997, 13 (3).125-132.

[5] Carlo B, Maurizio D A. Degradation and recovery of fine chemicals through singlet oxygen treatment of lignin. *Industrial Crops and Products*, 2004, 20: 243-259.

[6] Xue J W, Lee Z Z,Tai D S. Study on Oxidative Ammonolysis Reaction of Alkali Lignin. *Journal of Cellulose Science and Technology*. 2000, 8(3):22-27.

[7] Sun R. C, Fang J. M, Goodwin A. Physical chemical and structural charaterization of alkali lignin from abca fiber. *Wood chemistry and technology*,1998,18(3):313-331.

[8] Zhang J N, Zhang X Y, Xie D M, et al. Effect of Technological Factors on Electrochemical Hydrogenation of Lignin. *The Canadian Journal of Chemical Engineering*. 2002, 80(4):1-5.

[9] Kovalenko E I, Popova O V, Aleksandrov A A, et al. Electrochemical modification of lignins. *Russian Journal of Electrochemistry,* 2000, 36 (7): 706-711.

[10] Li L, Pang Q J, The selective reduction of p-dibenzoxy benzene. *WCJPS*, 1996, 11(4): 234-236.

[11] Coleman R S, Shan J A. Chmoselective Cleavage of Benzyl Ethers, Esters and Carbamates in the Presence of other Easily Reducible Groups. *Synthesis*, 1999: 1399-1405.

[12] Albers P, Burmeistera R, Seibold K, et al. Investigations of Palladium Catalysts on Different Carbon Supports, *Journal of Catalysis* , 1999, 181(1):145–154.

[13] Liu G S, Functional analysis of lignin. *Northeast Forestry University Press*, 1996, 29-172.

[14] Fai X O, Argyropoulos D S, Robert D, *ed al*. Determination of hydroxyl groups in lignins evaluation of $^{1}$H-, $^{13}$C-, $^{31}$P-NMR, FTIR and wet chemical methods[J] . *Holzforschung*, 1994, 48(5);387-394.

[15] Kim Y S, Newman R H. Solid state $^{13}$C-NMR study of wood degraded by the Brown Rot Fungus Gloeophyllum trabeum. *Holzforchung*, 1995, 49(2):109-114.

[16] Wu S B, Zan H Y. Changes in physico-chemical characteristics and structures of wheat straw soda lignin after modification. *Journal of South China University of Technology*, 1998, 26(11):96-104.

[17] Li J, Fu S Y. Determination on molecular weight and distribution of alkali lignin by aqueous GPC. *Journal of Cellulose Science and Technology*, 1998, 6(1):63-66.