Characterization of lignin extracted from eucalyptus wood chip by organosolv and organosolv subsequent alkaline precipitation processes

Thepparat Klamrassamee[1,2], Navadol Laosiripojana[1,2], Dylan Cronin[3], Lalehvash Moghaddam[3], William O. S. Doherty[3,*]

[1]*The Joint Graduate School of Energy and Environment, King Mongkut's University of Technology, Bangkok, Thailand*
[2]*Centre for Energy Technology and Environment, Ministry of Education, Thailand*
[3]*Centre for Tropical Crops and Biocommodities, Queensland University of Technology, Brisbane, Australia*

Abstract:
The present work studied the characteristics of lignin extracted from eucalyptus wood chip by organosolv (as called organosolv lignin; OL), and organosolv subsequent alkaline precipitation (as called organosolv lignin subsequent alkaline precipitation; OLA). It is noted that lignin from soda process (as called soda lignin; SL) was also characterized for comparison. In detail, OL was fractionated using ternary mixture of methyl isobutyl ketone (MIBK): methanol: water in the presence with 0.008 M of H_2SO_4 acid promoters at 180°C for 60 min. Then, it was characterized by Klason lignin, elemental analysis, thermal gravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), and Fourier transform-Infrared spectroscopy (FT-IR) to determinate the physico-chemical properties and structural features. When compared with OLA, the result of FT-IR proved the OL structure not changed when OL was treated with alkaline precipitation. Moreover; organosolv subsequent alkaline precipitation could remove the contaminations content of OL (i.e. sugar, sulfur, MIBK) due to their association between lignin and contaminations.

Keywords: *Organosolv; precipitation; lignin; association; and contamination*

**Corresponding author. Tel.: +61 7 31381245, Fax: +61 7 3138 4132*
E-mail address: w.doherty@qut.edu.au

1. Introduction

Lignin is an aromatic polymer found in the lignocellulosic biomass which is typically deposited in nearly all vascular plants and provides rigidity and strength to their cell walls. They are traditionally considered to be dehydrogenative polymers from three monolignols: p-coumaryl alcohol (H), coniferyl alcohol (G), and sinapyl alcohol (S) (Corma et al., 2007; Zakzeski et al., 2010). The major inter unit linkages within the lignin macromolecule is the ether linkage β-O-4, consisting of more than half of the linkage structures of lignin. It is different ratios, linked together by various types of ether, aryl and carbon-carbon bonds such as 4-*O*-5, β-β, β-1, β-5, dibenzodioxocin and 5-5 (Berlyn, 1972; Glasser et al., 1983). The lignin separation process from lignocellulosic biomasses highly influences the final structure, purity and corresponding properties (Ibarra et al., 2005). Typically, lignin separation methods are defined as belonging to one of two main categories, depending on the presence or absence of sulfur. Sulfur lignins (Kraft and lignosulfonates lignins), are primarily produced by pulp and paper industries and are mainly concerned with the isolation of lignin from cellulose. Sodium hydroxide (NaOH) and sodium sulfide (Na_2S) are utilized in Kraft process, whereas aqueous sulfur dioxide (SO_2), calcium, sodium, magnesium, and ammonia are used in sulfite process. Sulfur-free lignins can be classified into one of two main categories, lignins prepared via solvent pulping (e.g. organosolv lignin), and those from alkaline pulping (e.g. soda lignin) (Laurichesse & Avérous, 2014) . In this work, organosolv process using ternary mixture of methyl isobutyl ketone (MIBK): methanol: water in the presence with 0.008 M of H_2SO_4 acid promoters was applied to fractionated lignin from eucalyptus wood chip, then the alkaline precipitation was sequentially applied to remove the contaminations (i.e. sugar, sulfur, MIBK) after organosolv process. The extracted lignins were compared by several characterization techniques.

2. Material and methods

Eucalyptus chips was fractionated containing 16.7% w/v biomass with ternary mixture of MIBK:methanol:water in the presence with the homogeneous (0.008 M of H_2SO_4 acid promoters);

detailed information on this OL isolation process has been published previously (Klamrassamee et al., 2013). For OLA, OL was weighed approximately 20 g in a 600 ml beaker, then 2 M NaOH was drop wise in beaker until complete dissolution and the mixture was left at 35°C (using water bath) for 30 min. The mixture is filtered; and 2 phases can be separated including (i) base insoluble lignin (solid on filter paper) and (ii) base soluble lignin (filtrate). The base insoluble lignin (BIL) was obtained by a wash until pH 7, while base soluble lignin was left at temperature room overnight. Detail procedure of OLA isolation has been described elsewhere (Mousavioun et al., 2010) . For soda lignin (SL) was extracted using 0.7 M sodium hydroxide solution from sugar cane fibre (i.e., bagasse) obtained from Mackay Sugar Mill, (Mackay, QLD, Australia). The procedure for lignin isolation has been described elsewhere (Mousavioun et al., 2010). All of lignins were characterized using; elemental analysis, Klason lignin, molecular weight, X-ray photoelectron spectroscopy (XPS) analysis, Fourier transform-Infrared spectroscopy (FT-IR), and Thermal gravimetric analysis (TGA).

3. Results and discussion

OL was extracted with ternary mixture of methyl isobutyl ketone:methanol:water (25:42:33) in the presence with the homogeneous (0.008 M of H_2SO_4 acid promoters). From this process, the yield of lignin around 15% of feedstock (or 50% of lignin substrate) can be obtained (Klamrassamee et al., 2013). From OLA, OL was operated through alkaline precipitation process for removing the contamination. This step after precipitation can be gained two fractions; base soluble lignin (obtained lignin yield around 85% of OL) and base insoluble lignin (obtained lignin yield around 15% of OL; called BIL). TGA showed that OL and OLA extracted with MIBK/methanol/water in the presence at high temperature (180°C) and long time (60 mins) produced more residues (37-41%) at 800°C compared to other using solvent lignins such as methanol-water mixture, and ethanol-water mixture) (El Hage et al. 2009; Alriols et al., 2010). This indicates that lignins at high temperature long time may contain more condensed aromatic structures, which is more thermally stable**.** It was revealed that the result of TGA analysis of OL and OLA obtained high residue solid (37-41%). In addition, the elemental analysis and XPS revealed that OL sample had small sulfur content 0.5% of weight (Table 1 and Figs. 1(a)-(b)). The content of sulfur may occur from the sulfur of eucalyptus and degradation of acid promoter (H_2SO_4). For OLA sample, no sulfur was observed indicating the efficient removal of contamination from lignin sample. In addition, as shown in Table 2, the results of the compositional analysis (sugars, Klason lignin (acid insoluble lignin; AIL), acid soluble lignin (ASL), and ash contents) of the various lignins. The sugar analysis revealed that glucan and xylan were dominant constituents of the three lignin samples, while arabian was only presented in minor quantities. The results show that the OLA sample contains significantly less sugars and ash than the OL sample, indicating the efficacy of the re-precipitation treatment as a purification process for removal of these contaminants. As a result the purity of this sample was slightly increased, to a value of 93.24%. The results clearly indicate that both the sugars and ash content of the OL sample can be significantly reduced by applying the re-precipitation treatment process.

Table 1 Elemental analysis of lignins (wt%)

Lignin sample	C	O	H	N	S
OL	60.42	31.11	5.66	0.08	0.53
OLA	59.33	32.29	5.48	0.00	0.00
SL	59.72	29.22	6.14	0.61	0.00

Table 2 Composition of lignin samples (wt%)

Lignin sample	Biochemical composition (% wt)						
	Glucan	Xylan	Arabinan	Ash	AIL	ASL	Lignin purity (% wt)
OL	0.03	0.91	0.05	0.12	92.59	0.04	92.63
TOL	0.01	0.29	0.02	0.04	93.14	0.10	93.24
SL	0.50	1.5	0.00	0.60	87.12	3.15	90.27

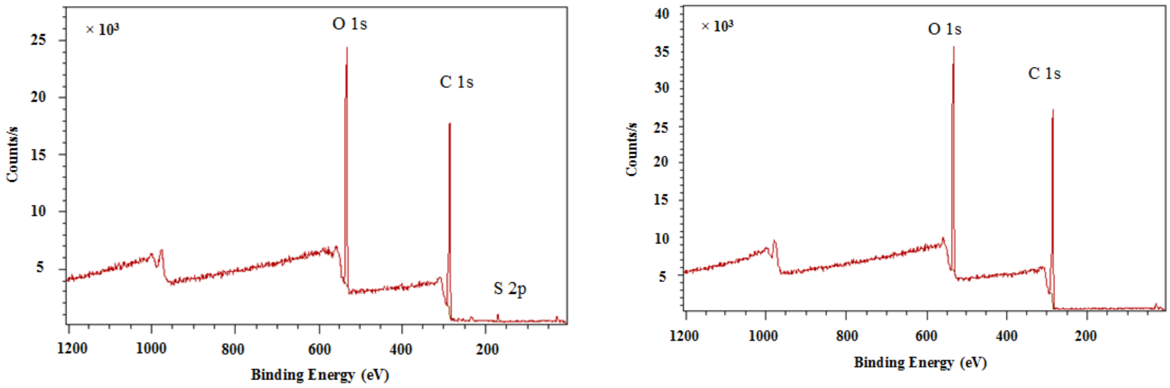

Fig. 1 (a) XPS survey scan spectrum for OL sample; (b) XPS survey scan spectrum for OLA sample.

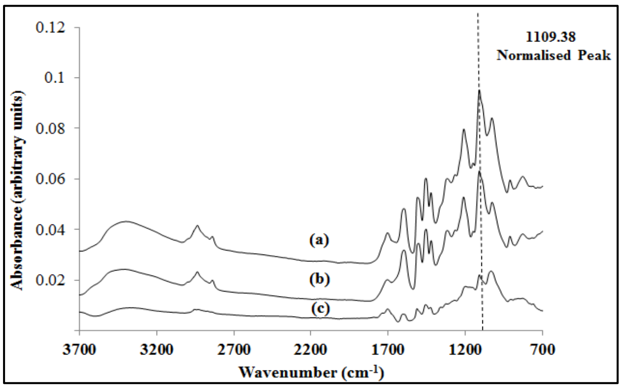

Fig. 2 FTIR spectra of lignins (a) OL sample (b) OLA sample (c) Subtracting of OL sample spectra from OLA sample (BIL).

For FT-IR analysis of all lignin samples are shown in Fig. 2. To obtain insight into the OL and OLA sample spectra, the FTIR spectra of the lignin samples, OL sample (Fig. 2(a) was subtracted from OLA sample Fig. 2(b)) to obtain the subtract spectra as shown in Fig. 2(c). Both spectra were normalized on the 1109 cm^{-1} peak before spectral subtraction because peak heights between spectra could be compared. The position of peak at 1109 cm^{-1}, it was chosen for normalizing. Fig. 2(c) was shown that the result of spectral subtraction was presented the majority of peaks for positive obtaining peaks. It was also clearly indicated that the contaminations of OL (i.e. sugars, MIBK) were associated with the bonding interactions with the OL sample. The highest three peaks (1029 cm^{-1}, 1109 cm^{-1}, and 1210 cm^{-1}) of lignin were indicated after the OL sample spectrum was subtracted from OLA sample spectrum. Moreover, four enhanced lignin peaks at 1455 cm^{-1}, 1510 cm^{-1}, 1600 cm^{-1}, and 1705 cm^{-1} are presented (Fig. 2(c)) indicating increased bond interactions between contaminations of OL (i.e. sugars, MIBK) and OL sample. In addition, all of peaks after subtraction spectra were shown that they obtained positive peaks, indicating further enhanced bonding occurring between contamination contents in OL and OL sample. In conclusion, OL treated with alkaline precipitation could remove the contamination (i.e. sugars and MIBK), the result was also confirmed with the compositions of lignins (Table 1).

4. Conclusion

Organosolv lignins (OL) were separated from woody eucalyptus with ternary mixture of methyl isobutyl ketone (MIBK), methanol, water in the presence of H_2SO_4 acid promoters (0.008 M) at high temperature (180ºC) and long residence time (60 min). OL contains high residue solid of 37% with small sulfur content of 0.5%, from which this sulfur may come from the source of eucalyptus and degradation of acid promoter (H_2SO_4). The alkaline precipitation process can be efficiently used to remove most of contaminations contents in OL (i.e. sugar, sulfur, MIBK) without the change in core structure of lignin.

Acknowledgement

The authors would to thank sincere appreciation of the Royal Golden Jubilee scholarship (RGJ) was supported Thailand Research Fund and the Joint Graduates School of Energy and Environment (JGSEE) at King Mongkut's University of Technology Thonburi (KMUTT) by providing scholarship to first author and the Queensland University of technology (QUT) for financing this project.

References

Alriols, M.G., García, A., Llano-ponte, R., and Labidi, J. 2010. Combined organosolv and ultrafiltration lignocellulosic biorefinery process. Chemical Engineering Journal 157(1): 113-120.

Berlyn, G. 1972. Lignins: Occurrence, Formation, Structure and Reactions by K. V. SARKANEN; C. H. Ludwig. American Scientist 60(4): 506-507.

Corma, A., Iborra, S., and Velty, A. 2007. Chemical Routes for the Transformation of Biomass into Chemicals. Chemical Reviews 107(6): 2411-2502.

El Hage, R., Brosse, N., Chrusciel, L., Sanchez, C., Sannigrahi, P., and Ragauskas, A. 2009. Characterization of milled wood lignin and ethanol organosolv lignin from miscanthus. Polymer Degradation and Stability 94(10): 1632-1638.

Glasser, W.G., Barnett, C.A., Muller, P.C., and Sarkanen, K.V. 1983. The chemistry of several novel bioconversion lignins. Journal of Agricultural and Food Chemistry 31(5): 921-930.

Ibarra, D., del Río, J.C., Gutiérrez, A., Rodríguez, I.M., Romero, J., Martínez, M.J., and Martínez, Á.T. 2005. Chemical characterization of residual lignins from eucalypt paper pulps. Journal of Analytical and Applied Pyrolysis 74(1-2): 116-122.

Klamrassamee, T., Champreda, V., Reunglek, V., and Laosiripojana, N. 2013. Comparison of homogeneous and heterogeneous acid promoters in single-step aqueous-organosolv fractionation of eucalyptus wood chips. Bioresour Technol 147: 276-84.

Laurichesse, S., Avérous, L. 2014. Chemical modification of lignins: Towards biobased polymers. *Progress in Polymer Science* 39(7): 1266-1290.

Mousavioun, P., Doherty, W.O.S., and George, G. 2010. Thermal stability and miscibility of poly(hydroxybutyrate) and soda lignin blends. Industrial Crops and Products 32(3): 656-661.

Zakzeski, J., Bruijnincx, P.C.A., Jongerius, A.L., and Weckhuysen, B.M. 2010. The Catalytic Valorization of Lignin for the Production of Renewable Chemicals. Chemical Reviews 110(6): 3552-3599.