THE SOLUBILITY OF LIGNIN FROM BAGASSE IN A 1,4-BUTANEDIOL/WATER SYSTEM

Qiang Wang,[a,b] Kefu Chen,[a] Jun Li,[a,]* Guihua Yang,[b] Shanshan Liu,[c] and Jun Xu [a]

The solubility of lignin from bagasse in a 1,4-butanediol/water mixed solution was investigated and explained by the solubility parameter (δ-value). To explore the lignin solubility, enzymatic hydrolysis/mild acidolysis lignin (EMAL) isolated from bagasse was used as the starting material to prepare lignin solution by ultrasonic treatment. The lignin content in solution was determined by UV-vis spectroscopy at a wavelength of 280 nm. The results showed that 240 minutes of ultrasonic treatment was needed to achieve lignin dissolution equilibrium in the 1,4-butanediol/water mixture. Maximum lignin solubility (14.6 g/L) occurred at a concentration of 80% (v/v). The δ-value of lignin (14.0 (cal/cm^3)$^{1/2}$) was calculated based on the atomic and functional groups present in the phenylpropane unit. The δ-values of the 1,4-butanediol/water showed a decrease from 22.31 to 11.09 (cal/cm^3)$^{1/2}$ as the concentration of 1,4-butanediol increased. The maximum lignin solubility predicted by the δ-value should occur at a concentration of 80% (v/v), which agreed with the experimental result.

Keywords: Bagasse; Lignin; Solubility; 1,4-butanediol

*Contact information: a: State Key Lab of Pulp and Paper Engineering, South China University of Technology, Guangdong Public Laboratory of Paper Technology and Equipment, Guangzhou, China; b: Key Lab of Paper Science and Technology of Ministry of Education, Shangdong Polytechnic University, Jinan, China; c: Institute of Chemical Industry of Forest Products, Chinese Academy of Forestry, Nanjing, China.; * Corresponding author: wangqiang8303@163.co m*

INTRODUCTION

Nowadays, the biorefinery concept is gaining more and more interest throughout the world (Lee et al. 2006; Ragauskas et al. 2006). This concept includes the separation of lignocellulosic materials for value-added products. Three main compounds (cellulose, hemicelluloses, and lignin) constitute lignocellulose, and any one of these purified compounds can have valuable applications. For instance, cellulose can be converted through enzymol-yisis to produce ethanol (Keshwani et al. 2009; Gnansounou et al. 2010), hemicellulose can be used as tabletting material or for preventing blood coagulation (Xu et al. 2006), and lignin can be used in the production of polyurethanes or biocomposites. A large number of processes that focus on a bio-refinery have been reported. These approaches include the steam explosion/ ethanol process, the SPORL process (Zhu et al. 2010), and the ethanol/ ultrafiltration process (Liu et al. 2011).

Lignin, being one of the most abundant families of polymers, is an enormous renewable resource and has captured the attention of technologist and entrepreneurs (Suhas et al. 2007). However, a conventional pulping process using strong alkali or sodium sulfide to cleave the protolignin into black liquor (an effluent from the pulping process that is rich in lignin and chemicals). During this procedure, the structure and properties of lignin are changed, and the utilization is limited, so it can only be used for low-added value applications and the production of energy (Chakar et al. 2004). Fortunately, the solvent used for organosolv pulping can separate lignin in better quality, including such attributes as a high purity, an absence of sulphur contaminants, and a less condensed molecular structure. As a consequence, such lignin has a wide potential usage. A number of processes involving organic solvents have been investigated, using solvents such as ethanol, acetone, dioxane, and methanol. The use of some of these solvents in a pulping process has even achieved commercial or pre-commercial scale (Yawalata et al. 2004).

The high-boiling solvent (HBS) 1,4-butanediol, which was employed in this work, is a newly developed aqueous solvent system that can be used as a delignification agent for raw materials (Kishimoto et al. 2001, 2002). The remarkable characteristic of this solvent is its high boiling temperature (228^{o}C), which translates into lower pressure during pulping. The cleavage of the intra- and inter-polymeric interactions between the different biopolymers that constitute plant materials can occur during HBS pulping within a temperature range between 170 and 220^{o}C.

The solubility of lignin in the solvent system has direct importance for HBS pulping, which can be used to estimate the finishing point of pulping as a fundamental parameter. However, there are few reports on this issue. In this study, the enzymatic hydrolysis/mild acidolysis lignin (EMAL) of bagasse was used as raw material, and the solubility of lignin in the HBS-water was investigated. The objective was to determine the solubility of lignin in HBS-water, as interpreted by means of the solubility parameter theory.

EXPERIMENTAL

Material

EMAL of bagasse was used as the starting material. The procedure for isolation followed a two-step method (Argyropoulos et al. 2002). The first stage used a mild enzymatic treatment on ball-milling bagasse meal, which was extracted by benzene-ethanol for 8h; then a mild acidolytic step was carried out (the dioxane:water ratio was 85:15; hydrochloric acid concentration was 0.05mol/L) for 2h. The lignin can be obtained after rotary evaporated, precipitated and freeze drying.

Apparatus and Chemicals

A UV-vis spectrophotometer (HACH DR5000, equipped with a 1 cm path length flow cell, resolution: 1nm) was used for the absorption analysis. An ultrasonic bath was used to assist in dissolving lignin.

^{31}P-NMR spectra were recorded with a Bruker DRX-400 FT-NMR spectrometer in chloroform-d with cholesterol as an internal standard. The chemicals used for NMR detection were purchased from Sigma-Aldrich.

All chemicals used in the experiments were from commercial sources.

Working Method

The lignin solubility in 1,4-butanediol/water was determined by UV-vis spectroscopy at 280 nm. The coefficient of absorbance (*B)* as shown in Eq. 1 was obtained by measuring the absorbance of EMAL using UV-vis spectra as described in previous literature (Pasquini et al. 2005),

$$S = \frac{A_{280}}{B} \tag{1}$$

where *S* is the solubility of lignin in solvent (g/L), A_{280} is the absorbance at wavelength of 280nm, *B* is the coefficient of absorbance.

RESULTS AND DISCUSSION

UV-vis Absorbance of EMAL of Bagasse in HBS

It is well known that the characteristic absorbance of lignin varies when using different solvents. In this study 1,4-butanediol was used as a reference for all UV-vis detection. The spectra of EMAL and the response plot for lignin concentration are shown in Fig. 1.

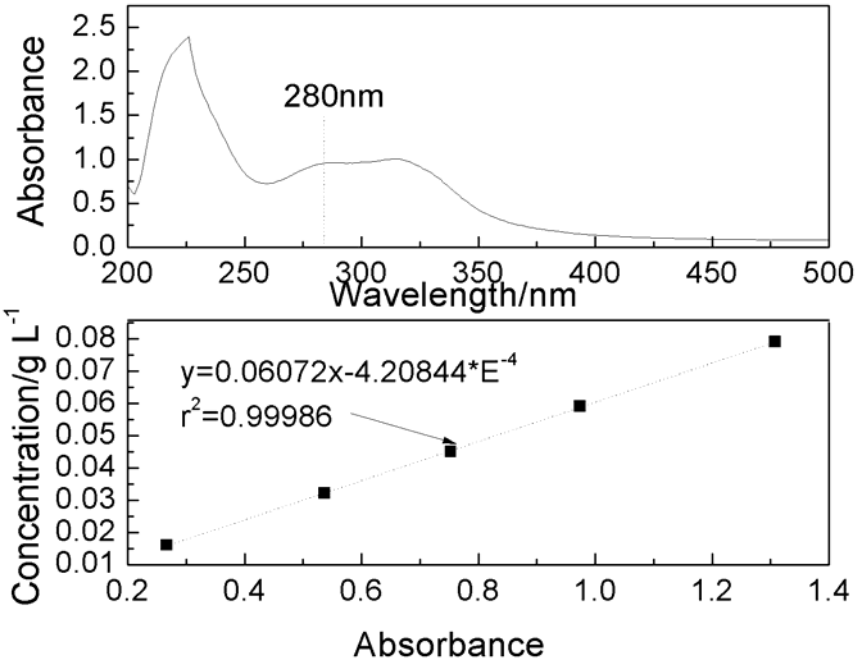

Fig. 1. UV-vis spectra of EMAL and response plot for lignin concentration determination. The lower figure was obtained at a wavelength of 280 nm.

As can be seen in Fig. 1, the UV-vis absorbance of EMAL has a characteristic absorption peak from 280 nm to 320 nm, which agrees with the literature (Chen et al.

2006). The absorbance response plot for lignin determination was carried out by varying lignin concentration in 1,4-butanediol. Obviously, there was a linear relationship between UV-vis absorbance at 280 nm and the content of lignin introduced, within the range 0.3 to 1.3.

Time for Determination

The procedure of lignin dissolving into a 1,4-butanediol/water is an equilibrium process of a solid dissolved into liquor, which requires a certain time to reach using ultrasonic promotion at room temperature. The lignin solubility in 1,4-butanediol/ water depended on the time, as shown in Fig. 2.

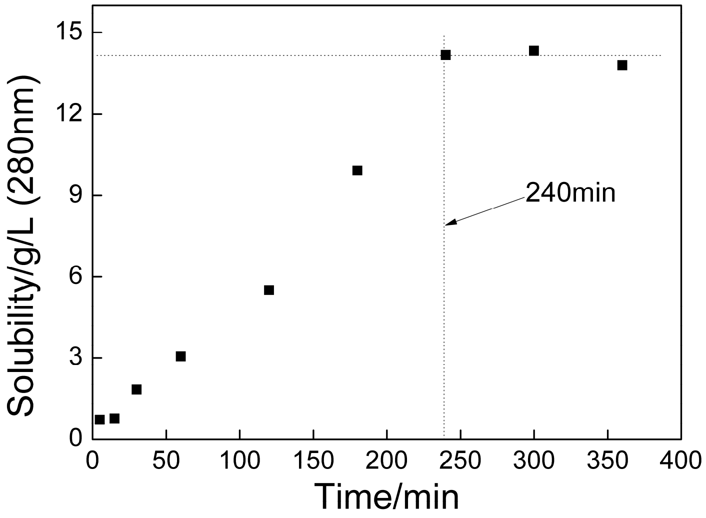

Fig. 2. Absorbance at 280nm versus time

During the ultrasonic treatment process, the contents of the vial co-existed as solid (lignin) and liquor (1,4-butanediol/water dissolve with lignin); therefore, the lignin content in solvent can be considered the lignin solubility at a specific condition. As can be seen in Fig. 2, the solubility of lignin increased from 0 to 240 minutes. If the time after immersion was increased to 360 minutes, the absorbance remained constant. Based on this conclusion, 240 minutes was the amount of time selected for the lignin solubility measurements.

Determination of Lignin Solubility

Solubility determination was carried out by weighing an excess amount of lignin (100mg) and adding it to 5mL of solvent mixture, where the 1,4-butanediol concentration was varied from 20% to 90% (v/v) . The vials were then sealed and put into an ultrasonic bath for 240 minutes. After that, the solubility of each sample was determined according to Eq. 1, and the results are presented in Fig. 3.

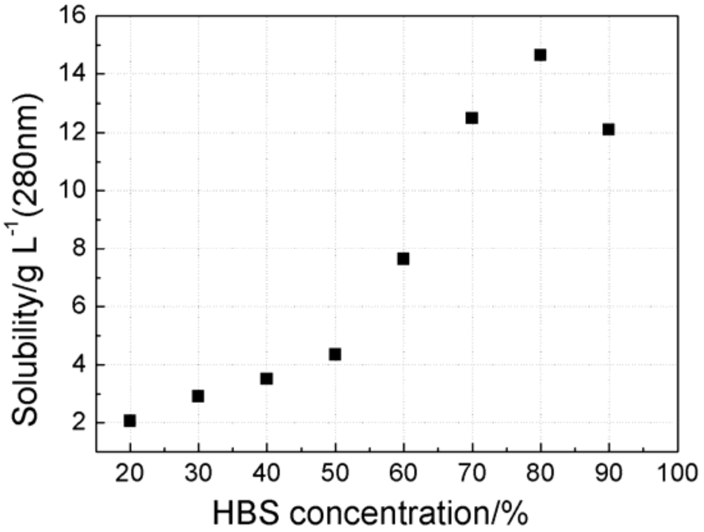

Fig. 3. Lignin solubility versus 1,4-butanediol concentration at 25°C

It can be seen that the solubility of lignin was highly dependent on the 1,4-butanediol concentration and showed an increasing trend. At the beginning, the solubility was only 2 g/L; then the value doubled when the 1,4-butanediol concentration reached 50%. When the 1,4-butanediol concentration further increased to 80%, the solubility rapidly increased to about 15 g/L, which is about 7 times the solubility of the 20% 1,4-butanediol sample. However, when the 1,4-butanediol concentration was increased to 90%, the solubility lowered. This agrees with what the literature reports, i.e., the higher solvent concentration would affect the lignin solubility (Ni et al. 1995).

Solubility Parameter Theory

As reported by Schuerch (1952), the solubility of the mixture was affected by the solvent, which can be explained by the solubility parameter theory (δ-value) (Hildebrand et al. 1936). This theory is used for non-polar and slightly polar systems and considers their hydrogen bonding capacity (Balogh et al. 1992). According to Schuerch (1952) the ability of a solvent to dissolve a solute is a function of the cohesive energy density and hydrogen bonding capacity of the solvent. A good solvent for a certain solute, such as lignin, has a Hildebrand's solubility parameter value close to that of lignin. When different solvents have the same value, the ability to dissolve lignin increases with increase in their capacity to form hydrogen bonds. Therefore, the δ-value of the lignin and those of the solvent mixtures were determined to explain the diversity of solubility results that were observed in the experiment.

The δ-value of lignin

Lignin, which is a network polymer, can be dissolved into solvent. Several methods for estimating the δ-value of polymer were proposed. One of them was based on the contribution of atomic and functional groups when the structure of the repeating unit of the polymer is known (Ni et al. 1995). The repeating unit in lignin is called the phenylpropane unit. The estimated equation is as follows,

$$E = \sum \Delta e_i \qquad (2)$$

$$V = \sum \Delta v_i \qquad (3)$$

where the Δe_i and Δv_i are the additive atomic and functional group contributions for the energy of vaporization (E) and molar volume (V), respectively, of a phenylpropane unit. Data concerning the atomic and functional group contributions to E and V are listed in Table 1. The δ-value is then calculated by the following equation:

$$\delta=(E/V)^{1/2} \qquad (4)$$

Table 1. Solubility Parameter of Typical Step Phenylpropane Units of Lignin

Atom or group	Unit G		Unit H		Unit S	
	Δe_i (cal/mol)	Δv_i (cm^3/mol)	Δe_i (cal/mol)	Δv_i (cm^3/mol)	Δe_i (cal/mol)	Δv_i (cm^3/mol)
OH	7120	10.0	2×7120	2×10.0	7120	10.0
CH_2	1180	16.1	1180	16.1	1180	16.1
C=	1030	-5.5			1030	-5.5
CH	820	-1.0	2×820	2×(-1.0)	820	-1.0
Phenyl	Trisubstituted 7630	33.4	Tetrasubstitued 7630	14.4	p 7630	52.4
CH_3	1125	33.5	2×1125	2×33.5		
O	2×800	2×3.8	3×800	3×3.8	2×800	2×3.8
Δv_i*		18		18		18
Total	20505	112.1	29340	144.9	19380	97.2

*Correction factor for divergence in the *v* value (Ni et al. 1995)

To calculate the δ-value of the lignin present in EMAL from bagasse, the structural elements and functional groups of this lignin need to be known. The lignin is made up of three types of repeating phenylpropane units: guaiacyl (G), syringyl (S), and p-hydroxyphenyl (H) (Ni et al. 1995). Typical structures for these G-, S-, and H-type phenylpropane units are shown in Fig. 4. As shown in Table 1, the calculation of the δ-value for the G, S, and H units yielded values of 13.52 $(cal/cm^3)^{1/2}$, 14.23 $(cal/cm^3)^{1/2}$, and 14.12 $(cal/cm^3)^{1/2}$, respectively.

The ^{31}P-NMR analysis of the EMAL was carried out to determine the ratio of the three types of lignin repeating units. As shown in Fig. 5, the p-hydroxyl moiety showed the highest content, followed by guaiacyl. In EMAL from bagasse, the syringyl unit showed the lowest content, which agrees with the literature (Sun et al. 1999). The molar ratio of lignin type G, H, and S contained in bagasse was G (140-138.8 ppm), H (138.2-137.4 ppm), and S (143.1-142.38 ppm) = 2.65:5.07:1. Therefore, the average solubility parameter for the lignin was determined to be 14.0$(cal/cm^3)^{1/2}$, which is accordance with previous reports that ALCELL lignin (13.7 $(cal/cm^3)^{1/2}$) and hydrolyzed almond shell lignin (14.60$(cal/cm^3)^{1/2}$) (Quesada et al. 2010; Ni et al 1995) .

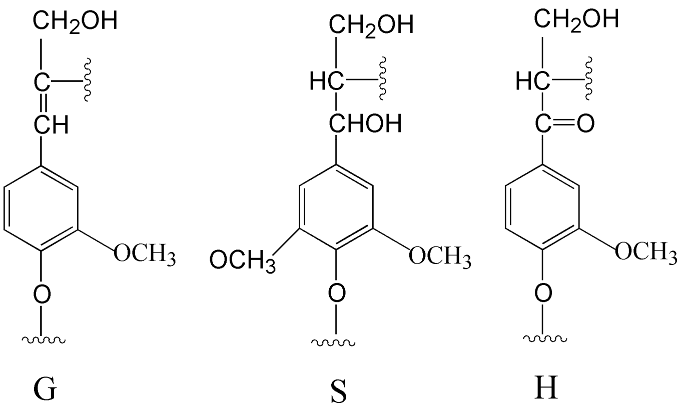

Fig. 4. The repeating units of EMAL from bagasse

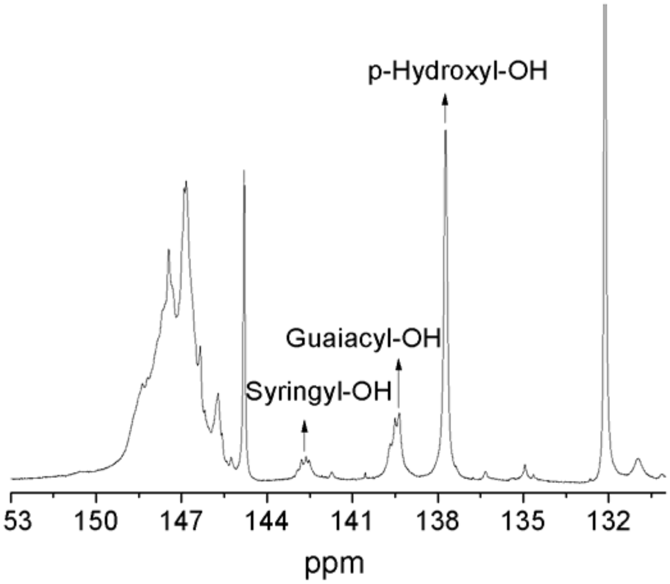

Fig. 5. ^{31}P-NMR spectrograms of EMAL of bagasse

The δ-value for HBS solvent mixture

According to Schuerch (1952), the δ-value for low molecular weight liquids can be calculated as,

$$\delta=[(\Delta H-RT)\rho/M_w]^{1/2} \tag{5}$$

where ΔH is the vaporization heat in cal/mol, T is the normal boiling point in K, ρ is the density in g/cm^3, and M_w is the molecular weight in g/mol.

The data required concerning vaporization heat, normal boiling point, and density were obtained from Perry et al. (1984) and Invensys Simsci ProII (version 8.3). The results obtained for the calculation of the δ-value of the 1,4-butanediol/water are listed in

Table 2. As can be seen, the δ-value of mixture decreased as the 1,4-butanediol concentration increased.

Table 2. Solubility Parameters of 1,4-butanediol/water

Concentration(%)	0	20	30	40	50	60	70	80	90	100
$\triangle H^*$(cal/mol)	9723	10684.8	11085.9	11559.0	12140.6	12880.9	13864.9	15218.3	17049.8	18325.4
T(K)	373.15	425.7	435.8	444.4	452.4	460.3	468.5	477.4	487.8	501.2
ρ^* (g/cm^3)	0.997	1.003	1.005	1.007	1.010	1.012	1.015	1.016	1.018	1.020
M_w(g/mol)	18.000	21.516	23.815	26.652	30.238	34.917	41.277	50.425	64.705	90.122
δ(cal/cm^3)$^{1/2}$	22.31	18.25	17.75	17.24	16.73	16.20	15.66	15.06	14.30	11.09

*Obtained at 25°C and 1atm.

Based on the δ-value theory, lignin has maximum solubility when the δ-value of 1,4-butanediol/water is close to its own (14.0(cal/cm^3)$^{1/2}$). According to data from Table 2, one can expect that the mixture above 70% 1,4-butanediol concentration should result in the highest solubility, followed by the lower values of 1,4-butanediol concentration. Actually, the predictions of the solubility parameter theory agreed with the experimental results very well. This is also supported by our previous study, which indicated that higher 1,4-butanediol concentration would lead to higher delignification (Wang et al. 2011). The exception was in the case of 90% 1,4-butanediol, for which the solubility was lower than in 70% and 80% 1,4-butanediol. This may caused by the decreased of hydrogen-bonding capacity of the solvent (Quesada et al. 2010).

CONCLUSIONS

1. Enzymatic hydrolysis/mild acidolysis lignin (EMAL) from bagasse was selected to determine the solubility of lignin in 1,4-butanediol/water. The maximum lignin solubility was exhibited at the 1,4-butanediol concentration of 80% (v/v).
2. The solubility parameter theory (δ-value) can explain the relationship between solvent concentration and lignin solubility successfully. The δ-value of EMAL of bagasse was 14.0 (cal/cm^3)$^{1/2}$, which is close to the HBS concentration of 80% (v/v).
3. Higher concentrations of 1,4-butanediol concentration will lower lignin solubility.

ACKNOWLEDGEMENTS

This work was financially supported by "973" special fund of China (Grant No.: 2010CB732205), the Pulp & Paper Engineering State Key Laboratory, South China University of Technology (Grant No.: 2007ZD01).

REFERENCES CITED

Argyropoulos, D. S., Sun, Y., and Palus, E. (2002). "Isolation of residual kraft lignin in high yield and purity," *Journal of Pulp and Paper Science* 28(2), 50-54.

Balogh, D., Curvelo, A., De Groote, R. (1992). "Solvent effects on organosolv lignin from Pinus caribaea hondurensis," *Holzforschung* 46 (4), 343-348.

Chakar, F. S., and Ragauskas, A. J. (2004). "Review of current and future softwood kraft lignin process chemistry," *Industrial Crops and Products* 20, 131-141.

Chen, Y. P., Chen, R. Q., Chen, X. S., Yang, X. X., Wu, G. Y., and Chen, Y. T. (2006). "Spectra and structural analysis of high boiling solvent lignin from bagasse," *Spectroscopy and Spectral Analysis* 26(10), 1880-1883.

Gnansounou, E., and Dauriat, A. (2010). "Techno-economic analysis of lignocellulosic ethanol: A review," *Bioresource Technology* 101(13), 4980-4991.

Hildebrand, J. H., and Scott, R. L. (1936). *The Solubility of Nonelectrolytes*, Reinhold, New York.

Keshwani, D. R., and Cheng, J. J. (2009). "Switchgrass for bioethanol and other value-added applications: A review," *Bioresource Technology* 100(4), 1515-1523.

Kishimoto, T., and Y. Sano (2001). "Delignification mechanism during high-boiling solvent pulping Part 1. Reaction of guaiacylglycerol-beta-guaiacyl ether," *Holzforschung* 55(6), 611-616.

Kishimoto, T., and Sano, Y. (2002). "Delignification mechanism during high-boiling solvent pulping - Part 2. Homolysis of guaiacylglycerol-beta-guaiacyl ether," *Holzforschung* 56(6), 623-631.

Lee, S. Y., M. A. Hubbe, and Saka, S. (2006). "Prospects for biodiesel as a byproduct of pulping- a review," *BioResources* 1(1), 150-171.

Liu, Z. H., Fatehi, P., Jahan, M. S., and Ni, Y. H. (2011). "Separation of lignocellulosic materials by combined processes of pre-hydrolysis and ethanol extraction," *Bioresource Technology* 102(2), 1264-1269.

Ni, Y., and Hu, Q. (1995). "Alcell lignin solubility in ethanol-water mixtures," *Journal of Applied Polymer Science* 57(12), 1441-1446.

Pasquini, D., Pimenta, M. T. B., Ferreira, L. H., and Curvelo, A. A. S. (2005). "Extraction of lignin from sugar cane bagasse and *Pinus taeda* wood chips using ethanol-water mixtures and carbon dioxide at high pressures," *The Journal of Supercritical fluids* 36(1), 31-39.

Perry, R. H., D. W. Green, Maloney, J. O. (1984). *Perry's Chemical Engineers' Handbook*, McGraw-Hill, New York.

Quesada-Medina, J., López-cremades, F. J., and Olivares-carrillo, P. (2010). "Organosolv extraction of lignin from hydrolyzed almond shells and application of the δ-value theory," *Bioresource Technology* 101, 8252-8260.

Ragauskas, A. J., Williams, C. K., Davison, B. H., Britovsek, G., Cairney, J., Eckert, C. A., Jr, W. J. F., Hallett, J. P., Leak, D. J., Liotta, C. L., Mielenz, J. R., Murphy, R., Templer, R., and Tschaplinski, T. (2006). "The path forward for biofuels," *Science* 311(5760), 484-489.

Schuerch, C. (1952). "The solvent properties of liquids and their relation to the solubility, swelling, isolation and fractionation of lignin," *Journal of the American Chemical Society* 74(20), 5061-5067.

Suhas, Carrot, P. J. M., and Ribeiro-Carrott, M. M. L. (2007). "Lignin - from natural adsorbent to activated carbon: A review," *Bioresource Technology* 98(12), 2301-2312.

Sun, R. C., Fang, J. M., Goodwin, A., Lawther, J. M., and Bolton, A. J. (1999). "Fractionation and characterization of ball\milled and enzyme lignins from abaca fibre," *Journal of the Science of Food and Agriculture* 79(8), 1091-1098.

Xu, F., Sun, J. X., Liu, C.F., and Sun, R. C. (2006). "Comparative study of alkali- and acidic organic solvent-soluble hemicellulosic polysaccharides from sugarcane bagasse," *Carbohydrate Research* 341(2), 253-261.

Wang, Q., Chen, K. F., Liu, S. S., Li, J., and Xu, J. (2011) "Kinetics of bagasse delignification by using high boiling solvent," *BioResources* 6(3), 2366-2374.

Yawalata, D., and L. Paszner (2004). "Anionic effect in high concentration alcohol organosolv pulping," *Holzforschung* 58(1), 1-6.

Zhu, W., J. Y. Zhu, Gleisner, R., and Pan, X. J. (2010). "On energy consumption for size-reduction and yields from subsequent enzymatic saccharification of pretreated lodgepole pine," *Bioresource Technology* 101(8), 2782-2792.

Article submitted: May 7, 2011; Peer review completed: June 18, 2011; Revised version received and accepted: June 21, 2011; Published: June 24, 2011.