Application of Solubility Parameter Theory to Organosolv Extraction of Lignin from Enzymatically Hydrolyzed Cornstalks

Yueyuan Ye,[a,]* Yunquan Liu,[a] and Jie Chang [b,]*

The Hildebrand solubility parameter (δ-value) was applied to explain the effect of organic solvent concentration on lignin removal during organosolv extraction of lignin from enzymatically hydrolyzed cornstalks under atmospheric pressure and low temperature (≤ 75 °C) without additional catalyst. The δ-value of lignin, calculated using the group-contribution method, was 13.70 $(\text{cal/cm}^3)^{1/2}$. The proximity of the δ-value between organic solvent-water and lignin explained the delignification capacity of the organic solvent-water. The concentration of organic solvent in the aqueous mixture that led to the highest delignification (*i.e.*, 34.5%, 41.8%, and 53.7% delignification for ethanol-water, 1,4-dioxane-water, and tetrahydrofuran-water, respectively) was around 65 to 75% vol., which was in keeping with the prediction by the solubility parameter theory.

Keywords: Organosolv extraction; Biorefining; Solubility parameter; Enzymatically hydrolyzed cornstalk

*Contact information: a: College of Energy, Xiamen University, Xiamen, Fujian, 361005, China; b: State Key Laboratory of Pulp & Paper Engineering, School of Chemistry and Chemical Engineering, South China University of Technology, 381 Wushan Road, Tianhe District, Guangzhou 510641, People's Republic of China; *Corresponding authors: yyye@xmu.edu.cn; changjie@scut.edu.cn*

INTRODUCTION

Lignin is the second most abundant natural polymer on Earth. In recent years, there has been an increasing trend for using lignin as a raw material for value-added products (Zakzeski *et al.* 2010). The extraction of lignin from lignocellulosic biomass has been studied for over 100 years. Although traditional chemical and semi-chemical pulping processes have successfully separated lignin from lignocellulosic biomass, they produce degraded lignin with impurities and large amounts of highly polluting waste water (particularly those using sulfur compounds in China) (Zakzeski *et al.* 2010). With growing environmental concerns, recent investigations have focused on both the use of unconventional raw materials (*e.g.*, agricultural and forest residues) and the development of more efficient lignin extraction processes, such as organosolv processes (Ferraz *et al.* 2000; Pan *et al.* 2006; Stockburger *et al.* 1993).

A number of processes involving organic solvents that allow lignocellulosic biomass, including both conventional and alternative raw materials such as agricultural and forest residues to be efficiently delignified, have been reported. Typical organosolv processes use low-boiling point organic solvents (Klein *et al.* 2010; Lehnen *et al.* 2002) (*e.g.*, acetone, methanol, ethanol, formic acid, and 1,4-dioxane), which can be easily recovered by distillation. Because of the inevitable moisture in raw materials, organic solvents thereupon are mixed together with water to form a mixed solvent medium. Usually, organosolv delignification is favored by the addition of acids as catalysts and is performed under high pressure and high temperatures of about 180 °C or even 210 °C (McDonough 1993; Pan *et al.* 2006). The degree of delignification obtained and the selectivity of lignin extraction process depends on the operating conditions applied, particularly regarding the type of organic solvent employed, and the concentration of the organic solvent in the water mixture (Jiménez *et al.* 2001; Vazquez *et al.* 1997).

Although great efforts have been made to optimize the organosolv extraction process (Akgul and Kirci 2009; Kim and Pan 2010; Li *et al.* 2007), little work has been done to study the solubility relationship between mixed solvent systems and lignin.

In this work, the δ-value of lignin was calculated using the group-contribution method (Fedors 1974). The organosolv extraction of lignin was studied using ethanol-water, 1,4-dioxane-water, and tetrahydrofuran-water from a solid lignin-rich industrial waste (*i.e.*, residue of enzymatically hydrolyzed cornstalks). The extraction was performed under atmospheric conditions, at low temperature (≤ 75 °C), and with no added catalysts. The main variables affecting the extraction process (extraction temperature, organic solvent concentration, and cooking time) were studied. The relationship between the Hildebrand solubility parameter (in this work the δ-value is identified as the Hildebrand solubility parameter) of the mixed solvent systems and lignin and the amount of delignification was interpreted by means of the δ-value analysis.

EXPERIMENTAL

Materials

Enzymatically hydrolyzed corn stalks, a residue from a lignocellulosic ethanol (EtOH) production process, were supplied by COFCO Limited (the biggest food company in China). Before organosolv extraction, the solid residue was milled to 40-mesh. The composition of the residue was as follows (expressed as % weight on a dry basis): lignin, 60.9 (55.0 Klason lignin plus 5.9 acid soluble lignin); ash, 8.03; moisture, 7.3; and holocellulose, 22.4; which were determined by TAPPI standards: T 13 wd-74, T 222 om-02, T 211 om-07, T 12 wd-82, and T 9 wd-75, respectively.

EtOH, 1,4-dioxane, and tetrahydrofuran (THF) as analytical reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. and used without any treatment.

Methods

Organosolv Extraction Process

Organosolv extraction processing of enzymatically hydrolyzed corn stalks was performed in a 100-mL flask equipped with a reflux condenser. Enzymatically hydrolyzed corn stalk particles (5 g) and 40 mL of organic solvent-water medium were loaded into the flask. After introducing cool water to the reflux condenser, the flask was then put into a water bath at a set temperature. Extraction temperature, time, and organic solvent concentration were varied within the ranges of 35 to 75 °C, 10 to 120 min, and 15 to 95% (v/v), respectively, while the ratio of extraction medium to solid was set constant at 8 (mL medium/g solid).

At the end of organosolv delignification, the solid and liquid phases were separated by filtration, and the solid was washed with 50 mL of the same organosolv medium used for lignin extraction. The solid obtained was then dried in an oven at 105

± 3 °C and weighed. The liquid phase and wash liquid were mixed together and kept in 250-mL bottles in the refrigerator.

The parameter delignification (expressed as % dry weight) was defined to monitor the organosolv process. The delignification was determined based on the difference between the amount of Klason lignin contained in the initial material and that present in the extracted solid residue. The Klason lignin content of the solid materials was determined two or three times, and the error in its determination was ± 2.87%.

Calculation of solubility parameter

The total solubility parameter, or δ-value, is defined as the square root of the cohesive energy density. The equation is expressed as,

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

where E is the energy of vaporization at zero pressure and V is the molar volume. The δ-value of organic solvent water mixtures were calculated by the empirical method (Barton 1975) which can be described with the following equation:

$$\delta_{\mathrm{m}} = \sum_{\mathrm{i}=1}^{\mathrm{n}} \varphi_{\mathrm{i}}\delta_{\mathrm{i}} = \varphi_1\delta_1 + \varphi_2\delta_2 + \ldots \tag{2}$$

where δ_{m} is the δ-value of the organic solvent-water extraction medium, φ_{i} is the volume fraction of the i^{th} solvent, and δ_{i} is the δ-value of i^{th} solvent.

However, because of the polydispersity and undefined composition of lignin, the direct calculation of its energy of vaporization and molar volume is considerably difficult. Thus, the indirect method should be employed. The group-contribution method, a simple method for estimating the δ-value proposed by Fedors (1974), is based on the assumption that the atomic and the functional groups increments could be summed over the known structure of the substance (including simple molecular solvents as well as high molecular weight polymers) to obtain estimates for δ-value. The sums can be expressed as follows,

$$E = \sum \Delta e_i \tag{3}$$

$$V = \sum \Delta v_i \tag{4}$$

where Δe_{i} and Δv_{i} are the additive atomic or group contributions to the energy of vaporization and molar volume, respectively. Considering that the T_{g} of lignin is greater than 25 °C, a divergence of V occurred, which can be taken into account by introducing a small correction factor (Fedors 1974), which is,

$$\Delta v_{\mathbf{0}} = 4n, n < 3 \tag{5}$$

or

$$\Delta v_{\mathbf{0}} = 2n, n \geq 3 \tag{6}$$

where n is the number of main chain skeletal atoms in the smallest repeating unit of the polymer. In the case of the lignin in this work, the smallest repeating unit in lignin polymer is the phenylpropane unit, which contains nine skeletal atoms.

RESULTS AND DISCUSSION

Solubility Parameters for Lignin and Extraction Medium

The δ-value for lignin

To calculate the δ-value of extracted lignin, the structural elements and functional groups of the lignin need to be determined. From the published scientific literature, it is well known that the repeating unit in the lignin molecule is the generic phenylpropane unit, which includes guaiacyl (G), syringyl (S), and *p*-hydroxyphenyl (H). Therefore, the lignin in this work is assumed to be composed of these three repeating units. These repeating units are displayed in Fig. S1 (see Appendix). The δ-values of the three types of units were then calculated, as shown in Table S1.

The δ-values of the repeating units of G, S, and H were calculated to be 14.70, 12.83, and 14.05 $(\mathrm{cal/cm^3})^{1/2}$, respectively. According to the group-contribution method, the δ-value of lignin is between 12.83 and 14.70 $(\mathrm{cal/cm^3})^{1/2}$; the real value depends on the ratio of the G, S, and H units in lignin. In this work, the ratio of G, S, and H units in cornstalk lignin was 40%, 50%, and 10% (see Table S3), respectively, determined according to the conventional nitrobenzene oxidation method (Buranova and Mazza 2008). Thus, the δ-value of the extracted lignin was approximated to be 13.70 $(\mathrm{cal/cm^3})^{1/2}$ based on this ratio of lignin units. This calculated δ-value is near to the lignin solubility parameter reported in the literature, which generally ranges from 12 to 15.5 $(\mathrm{cal/cm^3})^{1/2}$ (Hansen 2007; Ni and Hu 1995; Schuerch 1952; Thielemans and Wool 2005).

The δ-value of organic solvent-water solutions

The calculated results of the δ-value of organic solvent-water solutions are summarized in Table S2. The δ-values of pure water, EtOH, 1,4-dioxane, and THF are 23.4, 12.9, 9.9, and 9.5 $(\mathrm{cal/cm^3})^{1/2}$, respectively (Hansen 2007). The δ-value of the mixed solvent medium increases as the amount of water is continually increased. It should be noted that the δ-value of 1,4-dioxane-water and THF-water mixtures are generally lower than that of the EtOH-water mixture series at the same volume level.

Delignification of the Organosolv Extraction

Influence of extraction solvent composition

In this part of the investigation, an extraction temperature of 55 °C and an extraction time of 120 min were chosen to study the influence of organic solvent concentration in the medium on lignin extraction. The results are demonstrated in Fig. 1.

All solvent-water mixtures that had an organic solvent content lower than 35% vol. in the extraction media resulted in low delignification (< 10%). When the water content decreased to 25% vol., the delignification increased to the maximum; when the water content was below the value of 25% vol., the delignification decreased for EtOH-water and THF-water remained almost unchanged for 1,4-dioxane-water. It can be seen that the mix solvent with concentration with 65 to 75% vol. of organic solvent resulted in the highest delignification. For the three solvent-water systems, the highest delignification was 34.5% for EtOH-water, 41.8% for 1,4-dioxane-water, and 53.7% for

THF-water, respectively. From Fig. 1, it is apparent that the THF-water media had a stronger ability to extract lignin than either EtOH- and 1,4-dioxane-water media.

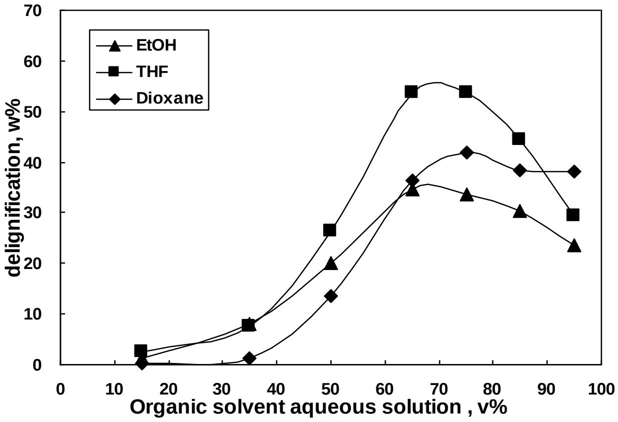

Fig. 1. Effect of organic solvent concentration on the organosolv extraction process (extraction temperature = 55 °C, extraction time = 120 min, and liquid-to-solid ratio = 8 (mL medium/g solid)

In view of these results and the purpose of maximum delignification, a 75% vol. organic solvent concentration in organosolv medium was selected to study the influence of extraction time and extraction temperature on the lignin removal process.

Influence of extraction time.

Figure 2 shows the evolution of delignification with extraction time. From the plots in Fig. 2, it was observed that delignification was almost unchanged (< 5%) in investigated extraction time for THF-, EtOH-, and 1,4-dioxane-water series. This indicated that extraction time had little influence on delignification for all solvents applied.

Regardless of the extraction time, the THF-water series always yielded higher degrees of delignification than EtOH- or 1,4-dioxane-water series. This illustrated that THF-water solution had a stronger ability to solubilize lignin than EtOH- or 1,4-dioxane-water solution from the solid residue, which will be explained later (see the Solubility Theory Application section).

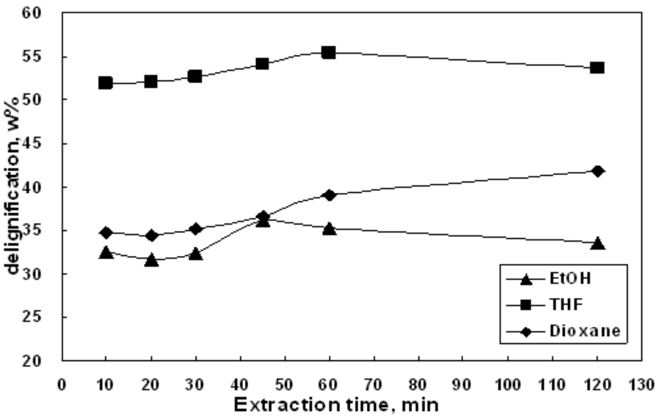

Fig. 2. Effect of extraction time on the organosolv extraction process (extraction temperature = 55 °C and liquid-to-solid ratio = 8 (mL medium/g solid))

Influence of extraction temperature

The influence of the extraction temperature on organosolv delignification is presented in Fig. 3. In the case of EtOH-water solution, delignification increased as the temperature increased up to 55 °C (33.8%); afterwards, the degree of delignification remained constant at higher extraction temperatures. In the case of 1,4-dioxane-water solution, delignification increased (from 34% to 42%) as the extraction temperature increased (from 35 to 75 °C). However, in the case of THF-water solution, it is interesting that delignification remained constant over the temperature range examined. Results in Fig. 3 indicate that extraction temperature had little influence on the amount of delignification for the solvent-water mixtures studied.

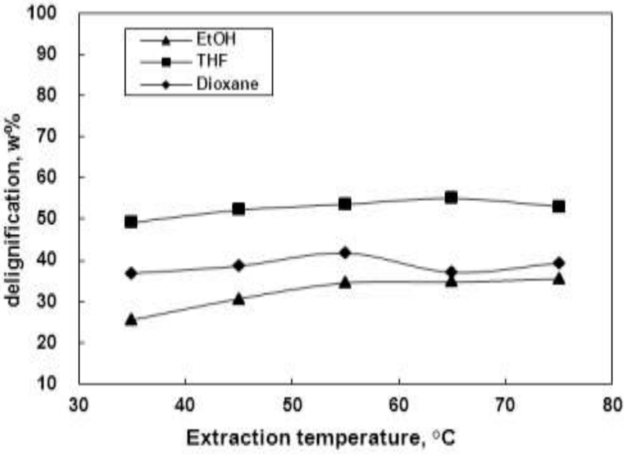

Fig. 3. Effect of extraction temperature on the organosolv extraction process (extraction time = 120 min and liquid-to-solid ratio = 8 (mL medium/g solid))

Solubility Theory Application

Solubility parameter theory has found general application in the field of polymer-solvent interactions. Using this theory, predictions of the solubility of polymers in a solvent can be made. According to this theory (Hansen 2007; Hildebrand and Scott 1950), the solubility of a polymer in a solvent or solvent system will depend on the condition that their solubility parameters (δ-value) are very near to one another, which can be expressed as follows:

$$| \delta_{\text{solute}} - \delta_{\text{solvent}} | \leq 2\ (\text{cal/cm}^3)^{1/2} \quad (7)$$

Thus, during organosolv extraction of enzymatic hydrolyzed residue, maximum delignification should occur when the δ-value of organic solvent-water medium is close to that of the lignin.

All solvent-water mixtures that had an organic solvent content lower than 35% vol. in the extraction media resulted in low delignification (< 10%). With the water content decreased to 25% vol., the delignification increased to the maximum; when the water content was below the value of 25% vol., the delignification decreased for EtOH-water and THF-water but remained almost unchanged for 1,4-dioxane-water. It can be seen that the mix solvent with concentration with 65 to 75% vol. of organic solvent resulted in the highest delignification. For the three solvent-water systems, the highest delignification was 34.5% for EtOH-water, 41.8% for 1,4-dioxane-water, and 53.7% for

THF-water, respectively. From Fig. 1, it is apparent that the THF-water media had a stronger ability to extract lignin than either EtOH- and 1,4-dioxane-water media.

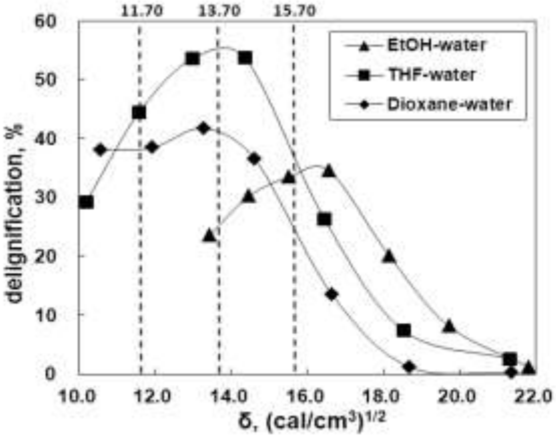

Fig. 4. Effect of δ-value of the extraction medium on organosolv delignification

The extraction conditions, extraction time, and extraction temperature investigated in this work had little effect on delignification. Also, all experiments were carried out at atmospheric conditions and without any delignification catalyst. Taking all these items into consideration, it can be concluded that organosolv delignification is strongly dependent on the organic solvent concentration in the solvent-water mixture.

Based on solubility parameter theory, lignin will come up to maximum solubility at the point where the δ-value of the extracted lignin and the δ-value of the mixed solvent are almost equal, otherwise poor dissolution of lignin in the mixed solvent occurred. According to Table S2, comparing the δ-value of lignin with the mixed aqueous solvents, one would expect that for the EtOH series, concentration of 85 to 95% EtOH, and for the 1,4-dioxane or the THF series, concentration between 65 and 75% organic solvent, would lead to the greatest degree of delignification. For all organic solvent-water systems, the delignification capacity of the mixed solvents, predicted by the solubility parameter theory, agreed with the experimental results obtained.

However, for the EtOH series, the greatest delignification capacity was obtained with the EtOH concentration of 75%, where the extraction medium δ-value differs from the lignin δ-value of about 2 $(cal/cm^3)^{1/2}$ (Fig. 4). It is more interesting that the delignification in 65% EtOH was almost equal to that of 75% EtOH, even though the δ-value of 65% EtOH is 16.58 $(cal/cm^3)^{1/2}$, which is about 3 $(cal/cm^3)^{1/2}$ units higher than the calculated δ-value of the extracted lignin. This can be explained by the fact that EtOH can form intermolecular H-bonds and that the H-bonding capacity only changes slightly as an increasing amount of EtOH is added to the water, which lead to high association of alcohol molecules and lower solvation power than expected (Schuerch 1952). Additionally, lignin contains hydrophilic groups, such as -OH and -CO-, and hydrophobic groups, such as aromatic rings. A good solvent for lignin demands hydrophilic and hydrophobic interaction. Hydrophobic interactions play an important role in organic solvent-water mixtures (Katayama and Ozutsumi 2008). Of the three solvent-water systems investigated in this study, the THF-water system led to the largest hydrophobicity because it contains largest hydrophobic function (Takamukua *et al.* 2003), which caused the most disruption of the H-bonded network of water. Thus, the solubility of EtOH-water is lower than that of 1,4-dioxane-water and THF-water and resulted in the lowest degree of delignification of the organic solvent-water systems examined in this work.

CONCLUSIONS

1. The solubility parameter of lignin was calculated by the group-contribution method. The δ-values of lignin and the G, S, and H units were 13.70 and 14.70, 12.83, and 14.05 $(cal/cm^3)^{1/2}$, respectively.
2. It was found that extraction time and temperature had little influence on the delignification of enzymatically hydrolyzed cornstalks in our study. Solvent mixtures with 65 to 75% vol. organic solvent resulted in the highest levels of delignification.
3. The experimental results revealed that the closer the δ-values of the organosolv mixed solvent approached that of lignin, the greater solubility of lignin was observed, thus leading to a greater degree of delignification.

ACKNOWLEDGMENTS

We are grateful for the financial support from the Natural Science Foundation of China (NSFC; Grant No. 21306156) and the 973 R&D Program (Grant No. 2012CB215306). The authors are also grateful for the kind support from the Committee of the 4th International Conference on Biorefinery towards Bioenergy (ICBB 2013) in Xiamen, China.

REFERENCES CITED

Akgul, M., and Kirci, H. (2009). "An environmentally friendly organosolv (ethanol-water) pulping of poplar wood," *J. Environ. Biol.* 30(5), 735-740.

Barton, A. F. M. (1975). "Solubility parameters," *Chem. Rev*. 75(6), 731-752.

Buranov, A. U., and Mazza, G. (2008). "Lignin in straw of herbaceous crops," *Ind. Crops Prod.* 28(3), 237-259.

Fedors, R. F. (1974) "A method for estimating both the solubility parameters and molar volumes of liquids," *Polym. Eng. Sci.* 14(2), 147-154.

Ferraz, A., Rodríguez, J., Freer, J., and Baeza, J. (2000). "Formic acid/acetone-organosolv pulping of white-rotted *Pinus radiata* softwood," *J. Chem. Technol. Biotechnol.* 75(12), 1190-1196.

Hansen, C. M. (2007). *Hansen Solubility Parameters: A User's Handbook*, 2nd Ed., CRC Press, Boca Raton, FL.

Hildebrand, J. H., and Scott, R. L. (1950). *The Solubility of Nonelectrolytes,* 3rd Ed., Reinhold, New York.

Jiménez, L., Pérez, I., García, J. C., and Rodríguez, A. (2001). "Influence of process variables in the ethanol pulping of olive tree trimmings," *Bioresour. Technol.* 78(1), 63-69.

Katayama, M., and Ozutsumi, K. (2008). "The number of water-water hydrogen bonds in water-tetrahydrofuran and water-acetone binary mixtures determined by means of X-ray scattering," *J. Solution Chem.* 37(6), 841-856.

Kim, D. E., and Pan, X. J. (2010). "Preliminary study on converting hybrid poplar to high-value chemicals and lignin using organosolv ethanol process," *Ind. Eng. Chem. Res.* 49(23), 12156-12163.

Klein, A. P., Beach, E. S., Emerson, J. W., and Zimmerman, J. B. (2010). "Accelerated solvent extraction of lignin from *Aleurites moluccana* (candlenut) nutshells," *J. Agric. Food Chem.* 58(18), 10045-10048.

Lehnen, R., Saake, B., and Nimz, H. H. (2002). "Impact of pulping conditions on FORMACELL aspen: Investigation of methoxyl and ester groups, carbohydrates, molar mass and glass transition temperatures," *Holzforschung* 56(5), 498-506.

Li, K. C., Xu, Y. J., and Zhang, M. Y. (2007). "Lignin precipitation on the pulp fibers in the ethanol-based organosolv pulping," *Colloids Surf. A:* 301(1-3), 255-263.

McDonough, T. J. (1993). "The chemistry of organosolv delignification," *TAPPI J.* 76(8), 186-193.

Ni, Y., and Hu, Q. (1995). "Alcell lignin solubility in ethanol-water mixtures," *J. Appl. Polym. Sci.* 57(12), 1441-1446.

Pan, X. J., Kadla, J. F., Ehara, K., Gilkes, N., and Saddler, J. N. (2006). "Organosolv ethanol lignin from hybrid poplar as a radical scavenger: Relationship between lignin structure, extraction conditions, and antioxidant activity," *J. Agric. Food Chem.* 54(16), 5806-5813.

Schuerch, C. (1952). "The solvent properties of liquids and their relation to the solubility, swelling, isolation and fractionation of lignin," *J. Am. Chem. Soc.* 74(20), 5061-5067.

Stockburger, P. (1993). "An overview of near commercial and commercial solvent based pulping process," *TAPPI J.* 76(6), 71-74.

Takamukua, T., Nakamizoa, A., Tabataa, M., Yoshidab, K., Yamaguchib, T., and Otomo, T. (2003). "Large-angle X-ray scattering, small-angle neutron scattering, and NMR relaxation studies on mixing states of 1,4-dioxane-water, 1,3-dioxane-water, and tetrahydrofuran-water mixtures," *J. Mol. Liq.* 103-104(3), 143-159.

Thielemans, W., and Wool, R. P. (2005). "Lignin esters for use in unsaturated thermosets: Lignin modification and solubility modeling," *Biomacromol.* 6(4), 1895-1905.

Vazquez, G., Antorrena, G., Gonzalez, J., Freire, S., and López, S. (1997). "Acetosolv pulping of pine wood. Kinetic modelling of lignin solubilization and condensation," *Bioresour. Technol.* 59(2-3), 121-127.

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," *Chem. Rev.* 110(6), 3552-3599.

Article submitted: January 14, 2014; Peer review completed: March 19, 2014; Revised version received and accepted: April 9, 2014; Published: April 23, 2014.

APPENDIX

Table S1. δ-value Calculation of the Three Typical Repeating Units

Atom or group	**$\triangle e_i$ (cal/mol)**	**$\triangle \upsilon_i$ (cm^3/mol)**
G (Guaiacyl structure)		
C=×4	4120	-22.0
CH=×2	2060	27.0
CH	820	-1.0
CH2	1180	16.1
CH3	1125	33.5
CO	4150	10.8
O×2	1600	7.6
OH	7120	10.0
conjugated double bonds×3	1200	-6.6
6-membered ring	250	16
△υ0		18
total	23625	109.4
δ(cal/cm^3)$^{1/2}$		14.70
S (Syringyl structure)		
C=×4	4120	-22.0
CH=×2	2060	27.0
CH×2	1640	-2.0
CH2	1180	16.1
CH3×2	2250	67.0
O×3	2400	11.4
OH	7120	10.0
conjugated double bonds×3	1200	-6.6
6-membered ring	250	16
△υ0		18
total	22220	134.9
δ(cal/cm^3)$^{1/2}$		12.83
H (p-Hydroxyphenyl structure)		
C=×3	3090	-16.5
CH=×5	5150	67.5
CH2	1180	16.1
OH	7120	10.0
OH	5220	13.0
conjugated double bonds×3	1200	-6.6
6-membered ring	250	16
△υ0		18
total	23210	117.5
δ(cal/cm^3)$^{1/2}$		14.05

Table S2. δ-value Calculation of the Organic Solvent-water Solutions

C_{Org}[a], %v	δ_{E+W}[b], (cal/cm^3)$^{1/2}$	δ_{THF+W}[c], (cal/cm^3)$^{1/2}$	$\delta_{dioxane+W}$[d], (cal/cm^3)$^{1/2}$
100	12.9	9.5	9.9
95	13.4	10.2	10.6
85	14.5	11.6	11.9
75	15.5	13.0	13.3
65	16.6	14.4	14.6
50	18.2	16.5	16.7
35	19.7	18.5	18.7
15	21.8	21.3	21.4
0	23.4	23.4	23.4

a, C_{Org}, concentration of organic solvent; b, δ_{E+W}, the δ value of EtOH and water mixtures; c, δ_{THF+W}, the δ value of THF and water mixtures; d, $\delta_{dioxane+W}$, the δ value of dioxane and water mixtures.

Table S3. The G/S/H Ratio of the Extracted Lignin (wt %, based on lignin)

Lignin	Vanillin	Syringaldehyde	p-Hydroxy-benzaldehyde	G/S/H	Yield
$L_{65\%E+W}$	6.73	8.79	1.71	3.9/5.1/1	17.23
$L_{65\%dioxine+W}$	6.92	8.36	1.82	3.8/4.6/1	17.10
$L_{65\%THF+W}$	6.85	8.33	1.69	4.1/4.9/1	16.87
$L_{75\%E+W}$	7.15	8.53	1.70	4.2/5.0/1	17.38
$L_{50\%E+W}$	6.48	8.49	1.65	3.9/5.1/1	16.62

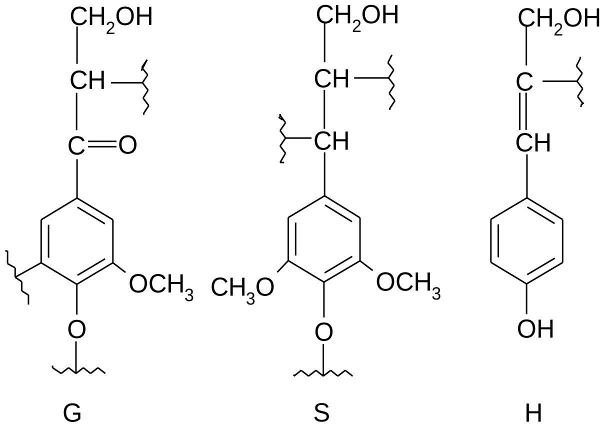

Fig. S1. The three typical repeating units, the building blocks of lignin. G, guaiacyl structure; S, syringyl structure; H, the p-hydroxyphenyl structure