Characterization of Bio-oils from Alkaline Pretreatment and Hydrothermal Liquefaction (APHL) of Cypress

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Four bio-oils obtained from the hydrothermal liquefaction (at 280 °C for 0 min) of untreated and pretreated cypresses were subjected to several types of chemical analyses to compare their structural features and chemical constituents. Pretreatments were carried out with alkali at 90 °C for 0.5, 1, and 2 h. The bio-oils were further divided into water-soluble oil, diethyl ether-soluble oil, and diethyl ether-insoluble oil fractions. Alkaline pretreatment had a significant effect on the contents of different components in the bio-oils. The diethyl ether-insoluble oil fraction was made up of intermediate-sized macromolecular fragments of lignin decomposed during the hydrothermal liquefaction process. The G_6 resonance, β-5, β-β', and β-O-4' peaks (which were present in the spectra of milled-wood lignin) almost disappeared from the spectra of the diethyl ether-insoluble oil fractions obtained *via* hydrothermal liquefaction of pretreated and untreated cypresses. At the same time, the intensities of the peaks corresponding to methoxy groups, G_2, and G_5 resonances were reduced. Long-duration alkaline pretreatment created a strong, highly water-soluble oil fraction with a wide molecular weight distribution.

Keywords: Pretreatment; Liquefaction; Bio-oil; Characterization

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INTRODUCTION

Hydrothermal liquefaction, which can break biomass down into small, soluble molecular fragments, is a relatively low-temperature process compared to pyrolysis. In addition, hydrothermal liquefaction of biomass has high de-oxygenation ability and there is no need to dry the biomass used. The effective use of biomass is very important with respect to both economic and ecological sustainability (Tekin *et al.* 2013). There have been a number of studies aimed at developing new biomass liquefaction processes to increase the bio-oil yield. Processes involving an acid-chlorite pretreatment, followed by liquefaction of biomass in hot, compressed water and sub- or supercritical ethanol, have been investigated (Liu *et al.* 2011a,b). Results showed that mild pretreatments were more effective in increasing the bio-oil yield and decreasing the optimum temperature. Wen *et al.* (2013) indicated that ultrasonic pretreatment destroyed the crystalline structure of cellulose and increased the conversion of cellulose during the liquefaction process. Further, it has been demonstrated that various pretreatment processes affect the chemical composition of the resulting bio-oil.

Bio-oil is a complex mixture of more than 400 different oxygenated hydrocarbons, such as acids, ketones, esters, ethers, phenols, and furans. These hydrocarbons can be used as substitutes for diesel oil or gasoline in the automotive power industry or to produce valuable chemical products after separation and purification

processes (Wang *et al.* 2013). Gas chromatography-mass spectrometry (GC-MS) is a testing method that can separate and identify the components of organic mixtures. Many researchers have evaluated the compositions of bio-oil by GC-MS (Duan *et al.* 2013; Wang *et al.* 2013). However, GC-MS cannot be used to separate and identify those components that cannot be gasified at the tested temperatures. Despite much effort, complete chemical characterization of bio-oil has not been accomplished due to the complexity and sheer number of the components in it.

During a typical liquefaction process, biomass is decomposed into large molecular fragments that eventually break down into smaller, oily-compound molecules. Liquefied biomass therefore contains some large molecules, depending on the process conditions. Many studies have dealt with the analysis of the hydrothermal liquefaction products in bio-oils. However, no known study has focused on the large molecules present in bio-oils.

In this study, bio-oil obtained from alkaline pretreatment and hydrothermal liquefaction was separated into different fractions. The various fractions were evaluated by Fourier transform infrared (FT-IR), GC-MS, gel permeation chromatography (GPC), and nuclear magnetic resonance (NMR). The objectives of this study were to investigate the effects of alkaline pretreatment on the characteristics of the resulting bio-oil and to determine the reaction mechanism by which the hydrothermal liquefaction of biomass occurs.

EXPERIMENTAL

Materials

The bio-oil sample used in this study was obtained from the hydrothermal liquefaction (at 280 °C for 0 min) of both alkaline-pretreated and untreated cypress (wood). In the alkaline pretreatments, cypress (150.0 g) was incubated with 5% (w/v) aqueous sodium hydroxide solution at a solid-to-liquid ratio of 1:6 (w/v) at 90 °C for 0.5, 1, and 2 h. All chemicals were chromatographically pure or of analytical grade and were used as purchased, without further purification. In a typical liquefaction run, the reactor was loaded with 10 g of cypress and 100 mL of water. After the reaction was completed, the bio-oil was separated into three fractions. The reaction mixtures were separated by filtration though filter paper under a vacuum, and 200 mL of de-ionized water was used to wash the solid products. After removal of the water from the wash solution under reduced pressure in a rotary evaporator, the solid was designated as water-soluble oil (WSO). The water-insoluble fractions were washed with acetone until the solvent became colorless. After the acetone was removed, the acetone-soluble oil was designated as heavy oil. The acetone-insoluble fraction was dried and designated as solid residue. The heavy oil was dissolved with dichloromethane (10 mL), and then washed with diethyl ether (90 mL). The diethyl ether insoluble oil was dried at 60 °C for 24 h and designated as DEIO. The diethyl ether soluble oil (DESO) was obtained by removing the diethyl ether in a rotary evaporator.

Characterization

The bio-oil mixture was washed with diethyl ether and dichloromethane mixtures (90:10, v/v) and the diethyl ether-soluble fraction of the bio-oil was analyzed by GC-MS.

Both the quantitative and qualitative analyses of the samples were performed using an Agilent 7890A/5978 (Santa Clara, CA) apparatus equipped with an HP-5 capillary column. The GC temperature was set to 40 °C for 2 min and then increased to 300 °C at a heating rate of 5 °C/min. The carrier gas (He) flow rate was 1 mL/min, and the injection size was 0.1 μL. The FT-IR, GPC, and NMR analyses of the products were performed as previously described (Liu *et al.* 2014).

RESULTS AND DISCUSSION

GC-MS Analysis

GC-MS analysis was carried out to determine the compounds present in the bio-oils. Bio-oil is a very complex mixture, and more than 200 compounds were detected (see Table 1).

Table 1. Compounds Identified in Bio-Oils from the Hydrothermal Liquefaction of Un-Pretreated and Pretreated Cyprus

Compound	Compound Content (%)			
	None	0.5 h	1 h	2 h
Phenol	7.1	6.2	2.4	2.7
Phenol, 2-methoxy-	-	1.8	1.8	1.6
3,4-Dihydroxyacetophenone	-	1.2	2.5	1.3
1,3-Bis (trimethylsiloxy) benzene	1.7	2.7	1.9	2.6
Vanillin	7.3	9.4	7.2	-
Phenol, 2-methoxy-4-(1-propenyl)-	-	-	-	1.6
Phenol, 2-methoxy-4-(1-propenyl)-, (E)-	2.5	3.1	3.3	3.4
Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	-	1.7	1.5	2.2
4-Amino-2,3-xylenol	6.5	-	11.9	-
6-Amino-2,4-dimethylphenol	-	13.2	-	16.2
Phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-]	19.9	13.3	12.8	14. 3
Total phenolic compounds	45.0	52.6	45.3	31.6
Ethylbenzene	-	-	7. 1	-
p-Xylene	-	-	11.5	-
Benzaldehyde	16.4	9.9	6.6	7.2
p-Benzoquinone, 2-methyl-	-	1.2	4.1	-
4-Isopropylbenzenethiol, S-methyl-	3.8	2.6	6.5	3.8
9H-Fluorene, 2-methyl	-	1.2	-	1.7
Diphenylamine	5. 1	3.1	3.9	5. 1
Total benzene ramifications	20.2	18.0	32.6	12.7
2,5-Furandicarboxaldehyde	5.2	4.7	3.1	5.2
2-Furancarboxaldehyde, 5-(hydroxymethyl)-	-	4. 2	-	4.8
Total furan derivatives	5.2	8.9	3.1	10.0
1,2-Cyclopentanedione, 3-methyl-	-	3.6	4.2	3.8
2-Cyclohexen-1-one, 4-(1-methylethyl)-	-	-	1.8	-
Total ketones	-	3.6	6.0	3.8
1,2-Benzenedicarboxylic acid, butyl 2-methylpropyl ester	4.2	2.6	1.5	1.2
4-Ethylbenzoic acid, ethyl ester	-	2.8	-	2.9
Total esters	4.2	5.4	1.5	4.1

"-": not detected, or peak area less than 1% of total area

The assignment of peaks was conducted *via* computer matching of the mass spectra with data from the NIST 2005 library. The possible names of all compounds accounting for more than 1.0% of the total area identified in this fraction are listed in Table 1.

As shown in Table 1, phenolic compounds (45.0%) were the primary components identified in the bio-oil produced from the liquefaction of untreated cypress, followed by benzene derivatives (20.2%), furan derivatives (5.2%), and esters (4.2%). Table 1 also shows that alkaline pretreatment had a significant effect on the intensities of different components' peaks in the bio-oil spectra. It can be stated that the formation of phenolic compounds and furan derivatives was enhanced by alkaline pretreatment for 0.5 h. The relative concentration of phenolic compounds and furan derivatives in the bio-oil increased from 45.0 and 5.2% to 52.6 and 8.9%, respectively, following the 0.5-h alkaline pretreatment. Compared to the untreated cypress-derived bio-oil, the bio-oil produced from the liquefaction-pretreated cypresses had low total ketones contents (3.6%, 6.0%, and 3.8% following 0.5, 1.0, and 1.5-h pretreatment periods, respectively). Two examples of the ketones detected are 3-methyl-1,2-cyclopentanedione and 4-(1-methylethyl)-2-cyclohexen-1-one. There was not enough evidence to prove that the formation of ketones could be solely attributed to the degradation of cellulose. Small functional groups cracked from lignin monomers could also be a source of ketones (Huang *et al.* 2013).

Generally, the bio-oil resulting from the hydrothermal liquefaction of biomass includes a wide range of compounds, and it is very difficult to produce a specific compound in high concentration without using only a single biomass component (*i.e.*, cellulose, hemicelluloses, or lignin) (Brunner 2009; Tekin *et al.* 2013). The phenolic and benzene derivatives in the bio-oils originated primarily from the degradation of lignin *via* fission of aryl ether linkages (Huang *et al.* 2013). The furan derivatives formed primarily from the holocellulose component of the cypress (Xu and Etcheverry 2008). Some esters were produced from the hydrothermal liquefaction of cypress, which could be due to esterification reactions between acidic and phenolic compounds. In this study, alkaline pretreatment significantly changed the chemical constituents of the bio-oil. One rational explanation is that the alkaline pretreatment changed the components and structure of the cypress wood itself.

FT-IR Characterization

Biomass-based liquefaction bio-oil contains some macromolecular fragments that cannot be gasified under GC-MS conditions. The chemical structures present in the WSO and DEIO fractions were also tested by FT-IR. The FT-IR spectra of the DEIO and WSO fractions are shown in Fig. 1. The FT-IR spectra of the four DEIO and four WSO fractions obtained from the hydrothermal liquefaction processes (of both untreated and pretreated cypresses) were quite similar, indicating that they contained similar functional groups. The compounds in the heavy oil originated primarily from the degradation of lignin. Therefore, the DEIO fraction contained the intermediate-sized macromolecular fragments of decomposed lignin from the hydrothermal liquefaction process. As can be seen in the DEIO fraction spectra in Fig. 1, the relative intensities of the bands corresponding to aromatic skeleton vibrations, at wavenumbers of 1597, 1508, 1456, and 1424 cm^{-1}, are present in all four spectra (Sun *et al.* 2011). This reveals that the majority of the lignin fragments were macromolecular and that the 'core' of the lignin structure did not change significantly during the hydrothermal liquefaction treatment under the

given conditions. A strong band at 1695 cm^{-1} in the four DEIO fraction spectra is attributed to unconjugated ketones (Sun *et al.* 2004). According to the FT-IR spectra of cypress MWL, the band at 1139 cm^{-1} is attributed to the relative absorbance intensity of ether (C-O-C) bonds (Liu *et al.* 2014). The band originally present at 1139 cm^{-1} shifted towards a lower wave number of 1119 cm^{-1}, indicating the presence of new ether in the DEIO fraction. A weak absorption at 1360 cm^{-1} corresponds to C-H deformations. The relative absorbance intensity of aliphatic C-OH groups, at 1028 cm^{-1}, is greater than that of ether (C-O-C) bonds, at 1119 cm^{-1}. The band at 859 cm^{-1} represents aromatic C-H deformations. As shown in Fig. 1-WSO, the weak signal at 1725 cm^{-1} is consistent with the stretching vibrations of C=O groups, which could indicate the presence of acids, esters, or ketones. In addition, an absorbance peak at 1595 cm^{-1} typically represents the stretching vibrations of C=C groups in alkenes or aromatics (Li *et al.* 2008). The peaks at 1728, 1205, 1123, and 1089 cm^{-1} indicate the presence of phenols, alcohols, esters, and ethers, respectively, subject to O-H deformation vibration and C-O stretching (Qian *et al.* 2007). The peaks at 886 and 807 cm^{-1} indicate the existence of some substituted phenolic and aromatic groups (Wu *et al.* 2009). The medium-intensity peaks located at 1515 and 1429 cm^{-1} are due to aromatic skeletal stretching, which may be a result of phenols or aromatics degraded from lignin.

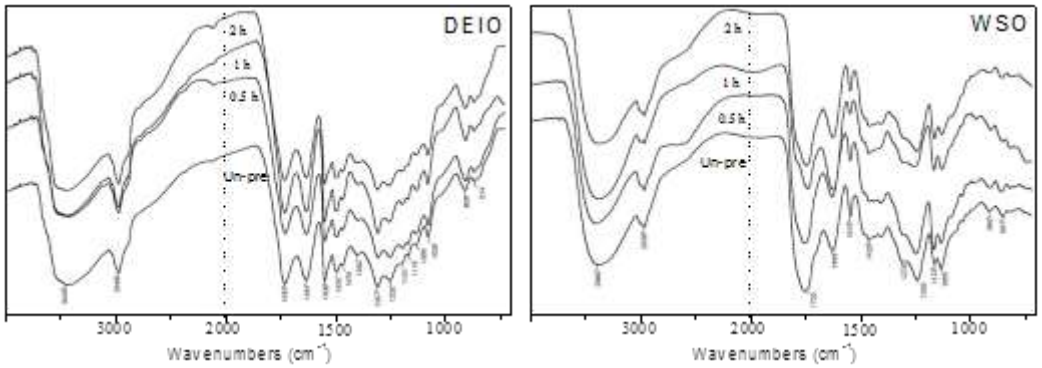

Fig. 1. FT-IR spectra of DEIO and WSO fractions obtained from the hydrothermal liquefaction of untreated and pretreated cypress

Molecular Weight Distribution

Table 2. Weight-average (M_w) and Number-average (M_n) Molecular Weights and Polydispersity Indices (M_w/M_n) of the DEIO and WSO Fractions Obtained from the Hydrothermal Liquefaction of Untreated and Pretreated Cypresses

Samples	M_w (g/mol)	M_n (g/mol)	M_w/M_n
DEIO-untreated	1405	985	1.4
DEIO-0.5 h	1648	1081	1.5
DEIO-1 h	1829	1152	1.6
DEIO-2 h	1782	1116	1.6
WSO-untreated	314	205	1.5
WSO-0.5 h	275	193	1.4
WSO-1 h	301	214	1.4
WSO-2 h	1132	228	4.9

Table 2 shows the weight-average (M_w) and number-average (M_n) molecular weights and polydispersity indices (M_w/M_n) of each fraction tested. The DESO fraction from the untreated cypress liquefaction run had a M_w of 1405 g/mol, which increased to 1648 (0.5 h), 1829 (1 h), and 1782 (2 h) g/mol when the cypress was pretreated with alkali for various durations. The increase of the DEIO fraction M_w following alkaline pretreatment may be because the pretreatment improved the digestibility of the cypress wood during the hydrothermal liquefaction process. The similarly low polydispersity index observed in all the DEIO fractions (M_w/M_n ranging from 1.5 to 1.6) indicated a relatively narrow weight distribution. It should be noted that the results of the WSO fraction testing were different than those of the DEIO fraction. Alkaline pretreatment for 2 h resulted in a major increase in M_w, from 314 to 1132 g/mol, and led to a wide molecular weight distribution. The polydispersity index increased from 1.5 to 4.9. Long-duration alkaline pretreatment yielded high WSO fragmentation and a wide molecular weight distribution. Alkaline pretreatment was believed to break down intermolecular ester bonds that cross-link lignin and hemicelluloses (LCC), as a significant amount of hemicelluloses were solubilized during the alkaline pretreatment process (Sun and Cheng 2012; Zhang *et al.* 2009). Therefore, the longer pretreatment time resulted in more separation of LCC and delignification of larger WSO fragmentation.

HSQC ^{13}C-^{1}H Correlation NMR Analysis

The structure of the polysaccharide fractions can be better interpreted based on NMR results. The HSQC NMR spectra of the DEIO fractions obtained from hydrothermal liquefaction of pretreated (0.5 h) and untreated cypresses were examined to obtain more information regarding the structure of the bio-oil. According to FT-IR analysis results, the DEIO fraction primarily contained lignin fragments. For comparative purposes, the HSQC NMR spectra of the cypress MWL and DEIO fractions are shown in Fig. 2. The NMR spectra of the MWL from the pretreated (0.5 h) and untreated cypresses were similar because the pretreatment cannot break down the main functional groups present in the fractions. The cross-signals from the MWL and DEIO fractions were assigned by comparing them with values reported in literature (Li *et al.* 2012; Xiao *et al.* 2012). Because the MWL fraction spectrum shows relatively complete and strong signals, the signal interpretation focused largely on MWL.

In the side region of the MWL fractions, the cross-signals of the β-O-4' substructures (A) and the methoxy groups (δ_C/δ_H 55.1, 3.6 ppm; -OMe) were the most prominent. The corresponding C_α-H_α and C_γ-H_γ β-O-4' substructures (A) were observed at δ_C/δ_H values of 71.0 to 72.4 (4.4 to 4.9 ppm) and 60.1 (3.2 to 3.8 ppm), respectively, whereas the corresponding C_β-H_β structures were observed at a δ_C/δ_H value of 83.8 (4.2 ppm) for substructures linked to G units. Strong signals for resinol substructures (B) were observed with C_α-H_α, C_β-H_β, and double C_γ-H_γ correlations at δ_C/δ_H values of 83.9 (4.8 ppm), 53.6 (3.2 ppm), and 71.1 (3.6 to 4.2 ppm), respectively. Phenyl coumaran substructures (C) were also found with C_α-H_α, C_β-H_β, and C_γ-H_γ correlations at δ_C/δ_H values of 86.4 (5.5 ppm), 53.4 (3.5 ppm), and 63.1 (3.6 ppm), respectively. The main cross-signals in the aromatic region of the HSQC spectrum corresponded mainly to the substituted benzene rings of the lignin units. Strong signals corresponding to G units were observed at δ_C/δ_H values of 110.5 (7.0 ppm) for C_2-H_2, 119.1 (6.8 ppm) for C_6-H_6, and 114.5 (6.6 ppm) for C_5-H_5.

Comparing the HSQC NMR spectra of DEIO and MWL fractions, the most significant changes were that the β-5, β-β', and β-O-4' signals disappeared from the spectra of the DEIO fractions obtained from the hydrothermal liquefaction of pretreated (0.5 h) and untreated cypresses. Moreover, the intensities of the methoxy groups' peaks were reduced. Simultaneously, the aromatic lignin region displayed a noticeable reduction in the relative intensities of the G_2 and G_5 resonances. The G_6 resonance almost disappeared from the HSQC NMR spectra of the DEIO fractions as compared to the MWL fractions' spectra. The disappearance of the β-5, β-β', β-O-4', and G_6 peaks indicated that those units degraded and re-polymerized during the hydrothermal liquefaction process.

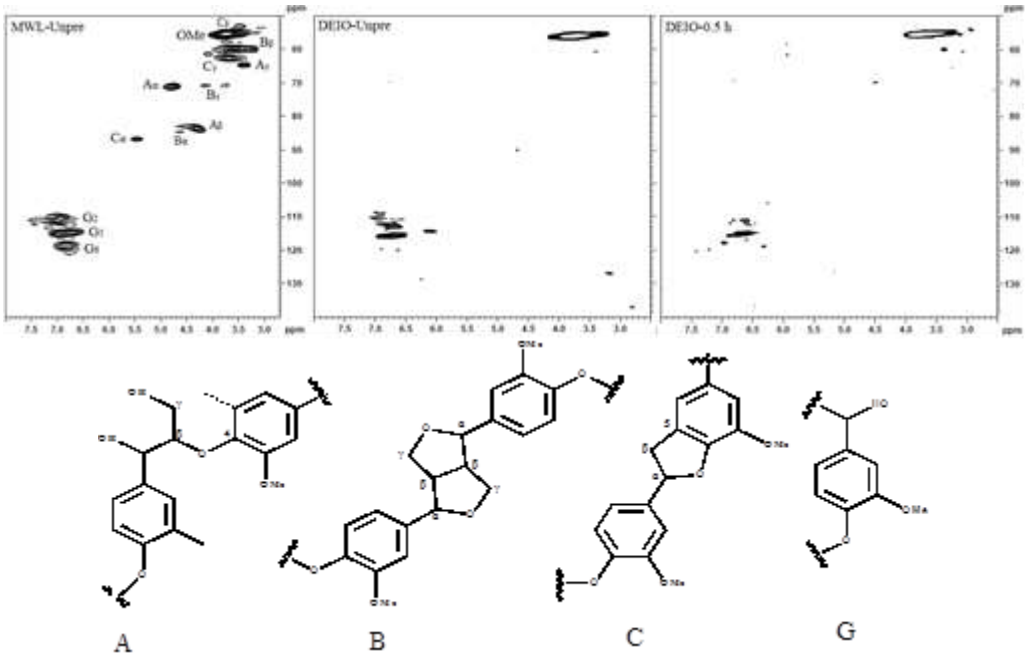

Fig. 2. HSQC spectra of MWL and DEIO fractions produced from the hydrothermal liquefaction of untreated and pretreated (0.5 h) cypress

Investigation of Presumed APHL Mechanism

To identify the mechanism of the alkaline pretreatment and hydrothermal liquefaction of cypress, a simple reaction model of the reaction process is shown in Fig. 3. Hydrothermal liquefaction of biomass degrades cellulose, hemicelluloses, and lignin into products of various molecular structures. For instance, the WSO fraction obtained from the hydrothermal liquefaction of cypress formed primarily from the decomposition of cellulose and hemicelluloses, whereas the heavy oil (including DESO and DEIO fractions) fraction primarily came from the degradation of lignin *via* fission of ether linkages (*e.g.*, β-O-4' and α-O-4') and condensed linkages (*e.g.*, 5-5' and β-5). According to GPC analysis, the molecular weight distributions of the WSO and DEIO fractions were quite variable, ranging from 100 to 10000 g/mol and 300 to 5000 g/mol, respectively. Results showed that bio-oil contains macromolecules such as oligosaccharides in the WSO, DEIO, and heavy oil fractions. The biomass liquefaction products were separated into three main groups of components by separation and dissolution, macromolecule hydrolysis/alkylation/dealkylation, and monomer decomposition. Alkaline pretreatment

affected the yields and types of compounds in the bio-oil resulting from the hydrothermal liquefaction of cypress. The alkaline pretreatment changed the main chemical components, physical structure, and thermochemical characteristics of the cypress wood itself. However, there was no evidence to establish that the changes in chemical structure had an impact on the hydrothermal liquefaction process.

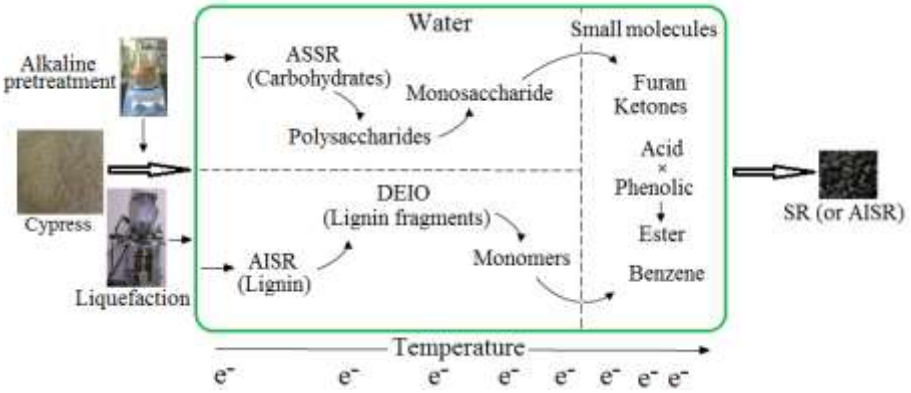

Fig. 3. Proposed mechanism for the hydrothermal liquefaction of cypress

CONCLUSIONS

1. Diethyl ether-insoluble oils consisted mostly of lignin fragments. Alkaline pretreatment had a significant effect on the peak intensity of different components in the bio-oil spectra.
2. The most significant changes observed were that the G_6 resonance and β-5, β-β', and β-O-4' peaks nearly disappeared from the spectra of the diethyl ether-insoluble oil fraction obtained from the hydrothermal liquefaction of pretreated and un-pretreated cypress. Furthermore, the intensity of the methoxy groups' and the G_2 and G_5 resonances' peaks were reduced.
3. Bio-oil may contain macromolecules, such as oligosaccharides, in the water-soluble, oil-soluble, and diethyl ether-insoluble oil fractions. Long-duration alkaline pretreatment yielded highly water-soluble oil fragmentation and a wide molecular weight distribution.

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REFERENCES CITED

Brunner, G. (2009). "Near critical and supercritical water. Part I. Hydrolytic and hydrothermal processes," *J. Supercrit. Fluid.* 47(3), 373-381.

Duan, P., Xu, Y., and Bai, X. (2013). "Upgrading of crude duckweed bio-oil in subcritical water," *Energ. Fuel.* 27(8), 4729-4738.

Hu, F., and Ragauskas, A. (2012). "Pretreatment and lignocellulosic chemistry," *Bioenerg. Res.* 5(4), 1043-1066.

Huang, H. J, Yuan, X. Z, Zeng, G., Liu, Y., Li, H., Yin, J., and Wang, X. (2013). "Thermochemical liquefaction of rice husk for bio-oil production with sub- and supercritical ethanol as solvent," *J. Anal. Appl. Pyrol.* 102(7), 60-67.

Huang, H. J., Yuan, X. Z., Zhu, H., Li, H., Liu, Y., Wang, X., and Zeng, G. (2013). "Comparative studies of thermochemical liquefaction characteristics of microalgae, lignocellulosic biomass and sewage sludge," *Energy* 56(11), 52-60.

Li, J., Wu, L., and Yang, Z. (2008). "Analysis and upgrading of bio-petroleum from biomass by direct deoxy-liquefaction," *J. Anal. Appl. Pyrol.* 81(2), 199-204.

Li, M. F., Sun, S. N., Xu, F., and Sun, R. C. (2012). "Mild acetosolv process to fractionate bamboo for the biorefinery: Structural and antioxidant properties of the dissolved lignin," *J. Agr. Food Chem.* 60(7), 1703-1712.

Liu, H. M., Feng, B., and Sun, R. C. (2011a). "Acid-chlorite pretreatment and liquefaction of cornstalk in hot-compressed water for bio-oil production," *J. Agr. Food Chem.* 59(19), 10524-10531.

Liu, H. M., Feng, B., and Sun, R. C. (2011b). "Enhanced bio-oil yield from liquefaction of cornstalk in sub- and super-critical ethanol by acid-chlorite pretreatment," *Ind. Eng. Chem. Res.* 50(19), 10928-10935.

Liu, H. M., and Liu, Y. L. (2014). "Characterization of milled solid residue from cypress liquefaction in sub- and super ethanol," *Bioresour. Technol.* 151, 424-427.

Peterson, A. A., Vogel, P. F., Lachance, R. P., Fröling, M., Antal, M. J., and Tester, J. W. (2008). "Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies," *Energ. Environ. Sci.* 1(1), 32-65.

Qian, Y., Zuo, C., Tan, J., and He, J. (2007). "Structural analysis of bio-oils from sub- and supercritical water liquefaction of woody biomass," *Energy* 32(3), 196-202.

Sun, J. X., Xu, F., Sun, X. F., Sun, R. C., and Wu, S. B. (2004). "Comparative study of lignins from ultrasonic irradiated sugar-cane bagasse," *Polym. Int.* 53(11), 1711-1721.

Sun, R. C., Lu, Q., and Sun, X. F. (2001). "Physico-chemical and thermal characterization of lignins from *Caligonum monogoliacum* and *Tamarix* spp," *Polym. Degrad. Stabil.* 72(2), 229-238.

Sun, Y., and Cheng, J. (2012). "Hydrolysis of lignocellulosic materials for ethanol production: A review," *Bioresour. Technol.* 83(1), 1-11.

Tekin, K., Karagöz, S., and Bektaş, S. (2013). "Hydrothermal conversion of woody biomass with disodium octaborate tetrahydrate and boric acid," *Ind. Crops Prod.* 49(8), 334-340.

Wang, S., Wang, Q., Jiang, X., Han, X., and Ji, H. (2013). "Compositional analysis of bio-oil derived from pyrolysis of seaweed," *Energ. Convers. Manage.* 68(4), 273-280.

Wu, L., Guo, S., Wang, C., and Yang, Z. (2009). "Production of alkanes (C_7-C_{29}) from different part of poplar tree via direct deoxy-liquefaction," *Bioresour. Technol.* 100(6), 2069-2076.

Xiao, L. P., Shi, Z. J., Xu, F., and Sun, R. C. (2012). "Characterization of MWLs from *Tamarix ramosissima* isolated before and after hydrothermal treatment by spectroscopical and wet chemical methods," *Holzforschung* 66(3), 295-302.

Xu, C. B., and Etcheverry, T. (2008). "Hydro-liquefaction of woody biomass in sub- and super-critical ethanol with iron-based catalysts," *Fuel* 87(3), 335-345.

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