Microwave-assisted Liquefaction of Rape Straw for the Production of Bio-oils

Xing-Yan Huang,[a,b,#] Feng Li,[b,#] Jiu-Long Xie,[a,b,*] Cornelis F. De Hoop,[a,*]
Chung-Yun Hse,[c] Jin-Qiu Qi,[b] and Hui Xiao [b]

The acid-catalyzed liquefaction of rape straw in methanol using microwave energy was examined. Conversion yield and energy consumption were evaluated to profile the microwave-assisted liquefaction process. Chemical components of the bio-oils from various liquefaction conditions were identified. A higher reaction temperature was found to be beneficial to obtain higher energy consumption efficiency as heated by microwaves. Fourier transform infrared spectroscopy of the bio-oils indicated that hydroxyl groups underwent oxidation with increasing liquefaction temperature and/or prolonged reaction time; methanol esterification of oxidation products was also observed during the liquefaction process. The GC-MS chromatograms indicated that the further decomposition of C5 and C6 sugars resulted in a remarkable reduction of hydroxyl group products and an apparent increase in levulinic ester; furan derivatives and succinic acid derivatives were increased as well. The chemical reactions in liquefaction for the production of bio-oils mainly included decomposition of hemicelluloses, cellulose, and lignin; the oxidation reactions of the hydroxyl groups and methanol esterification were also presented. Comprehensively, a high content of hydroxyl group products was obtained at a moderate liquefaction condition (140 °C/15 min), and a high yield of levulinic ester products was acquired in severe reaction conditions (180 °C/15 min), regardless of energy consumption efficiency.

Keywords: Microwave; Liquefaction; Rape straw; Bio-oils

*Contact information: a: School of Renewable Natural Resources, Louisiana State University Agricultural Center, Baton Rouge, Louisiana 70803, USA; b: College of Forestry, Sichuan Agricultural University, Chengdu, Sichuan 611130, PRC; c: Southern Research Station, USDA Forest Service, Pineville, Louisiana 71360, USA; [#]Xing-Yan Huang and Feng Li are co-first authors; *Corresponding authors: jxie6@lsu.edu; cdehoop@lsu.edu*

INTRODUCTION

Alternative fuel and chemicals derived from lignocellulosic biomass, such as agro-waste, have attracted the attention of researchers worldwide because of the continuing depletion of fossil fuel (Larabi *et al*. 2013). As an agro-waste from the edible oil industry, large quantities of rape straws are produced annually, particularly in China (Wang 2007). Rape straw has great potential in the production of value-added products, such as composites (Huang *et al*. 2016), bioethanol (Lewandowska *et al.* 2016), and stock-feed (Ke *et al.* 2011).

Several studies have investigated the conversion of lignocellulosic biomass into heavy liquid oil *via* pyrolysis and direct liquefaction (Chang *et al*. 2012; Tarves *et al*. 2016). The advantage of direct liquefaction is that the reaction occurs at a relatively low temperature and consumes less energy than pyrolysis (Doassans-Carrère *et al*. 2014).

The liquefying agent is vital to the efficient liquefaction of lignocellulosic biomass. Solvents such as glycerol, water, and alcohol have been used to liquefy lignocellulosic biomass (Xie *et al.* 2016a). Alcohol remarkably enhances biomass liquefaction because it dissolves carbohydrates and lignin (Xu *et al*. 2012, 2016). Due to its low boiling point, methanol can be easily recovered from bio-oil by rotary evaporation.

Microwave heating has been successfully applied in the liquefaction of lignocellulosic biomass (Xie *et al.* 2016a; Zhou *et al.* 2016). Microwave irradiation offers the advantage of extremely rapid heating throughout the volume of the reaction mixture because it penetrates and produces a volumetrically distributed heat source (Bren *et al*. 2008). Parameters such as liquefaction temperature and reaction time on the liquefaction conversion yield have been extensively studied in previous investigation (Xie *et al*. 2014a,b). Despite the high conversion yield of microwave liquefaction, the energy consumption efficiency during this process and the quality of the liquefied products with respect to various liquefaction parameters have not yet been investigated thoroughly.

Bio-oil obtained from liquefaction of lignocellulosic biomass is a versatile chemical source for the production of polyurethane foam (Xie *et al.* 2014b). Furthermore, methyl levulinate has been successfully prepared from liquefaction bio-oil (Feng *et al*. 2015). Several analytical techniques can be used to characterize bio-oil components. Gas chromatography coupled with mass spectrometry (GC-MS) is the most frequently used method to analyze the chemical components of bio-oils (Villadsen *et al.* 2012), due to its versatility, as well as the availability of a large library of mass spectra for compound identification. The characterization of chemical components of bio-oils with respect to reaction condition provides insights to the changes of bio-oils during liquefaction.

In this work, chemical components and structures of the bio-oils obtained from different liquefaction reactions were analyzed by Fourier transform infrared spectroscopy (FT-IR) and GC-MS. The specific objective of this study is aimed to optimize the microwave liquefaction of rape straw from the point of high conversion yield and low energy consumption and to evaluate their changes in bio-oil with respect to the liquefaction condition. The results in this study will provide an efficient pathway in preparation of bio-oils from lignocellulosic biomass via microwave liquefaction.

EXPERIMENTAL

Materials

The rape straw collected in Sichuan Province, China, was ground into 20- to 40-mesh and oven-dried at 105 °C until it reached a constant weight. The chemical compositions of rape straw were as follows: α-cellulose (36.72%), hemicelluloses (32.67%), Klason lignin (13.66%), alcohol-toluene extractives (4.46%), and ash content (8.27%). The holocellulose, α-cellulose, lignin content, alcohol-toluene extractives, and ash content were determined according to ASTM standards D 1104-56 (1971), D 1103-60 (1971), D 1106-96 (1996), D 1107-96 (1996), and D 1102-84 (2001), respectively. The hemicellulose content was established as reported by Zhang *et al.* (2012). All chemicals, including sulfuric acid (H_2SO_4) and methanol, were purchased from commercial sources and used without further purification.

Methods

Microwave-assisted liquefaction

The liquefaction of rape straw was performed in a Milestone MEGA laboratory microwave oven (Shelton, CT, USA) equipped with an ATC-400FO automatic fiber optic temperature control system (Fig. 1). A typical run was carried out with 2 g of rape straw, 12 g of methanol, and 0.36 g of sulfuric acid. The mixed reactants were sealed in 100 mL Teflon reaction vessels with a magnetic stirring bar. The output power of the microwave energy was auto-adjusted based on the temperature feedback from the sensor under the maximum power of 700 W. The sealed vessels were subjected to microwave irradiation. The reaction temperature was increased from room temperature to the desired temperature (*i.e.*, 140 °C, 160 °C, and 180 °C) within 5 min and then maintained for 0 to 10 min. An ice bath was applied to quench the finished reaction. After cooling, the liquefied products were dissolved in 150 mL of methanol under constant stirring for 4 h and filtered through Whatman No. 4 filter paper to separate the liquid and the solid residue. The liquid portion was evaporated at 65 °C under vacuum to remove the methanol. The gaseous products were vented because the yield of gaseous products was negligible. The residue remaining on the filter paper was oven-dried for determining the conversion yield by Eq. 1.

$$\text{Conversion yield (\%)} = \left(1-\frac{\text{weight of residue}}{\text{weight of raw rape straw}}\right)\times 100 \qquad (1)$$

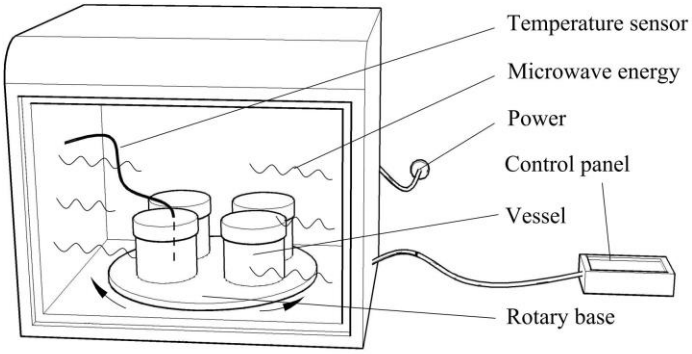

Fig. 1. Diagram of microwave-assisted liquefaction reaction system

The unit energy consumption is defined as the energy needed to convert one gram of rape straw into bio-oils. The energy requirement was calculated as the average microwave power multiplied by time. The average microwave power during the whole process was read on the electric control panel of the system. The energy consumption for each reaction was calculated as the total energy requirement for this reaction divided by the weight of the rape straws liquefied.

Characterization of bio-oils

The chemical structures of the bio-oils from different liquefaction conditions were performed using a Nicolet Nexus 670 FT-IR equipped with a Thermo Nicolet Golden Gate MK II Single Reflection ATR accessory (Madison, WI, USA). A droplet of the bio-oil was covered flatwise on the detection window. Each sample was analyzed in the range of resolution from 400 to 4000 cm^{-1} with a spectral resolution of 4 cm^{-1}, and a total of 32 scans were collected.

The general profiles for the bio-oils were gained using electron-ionization-mass spectrometry (EI-MS). The products were analyzed on a mass spectrometer (Agilent 5975C VL MSD, Santa Clara, CA, USA), and the products were separated into their components using a gas chromatograph (Agilent 7890A) equipped with a fused capillary column (DP-5, L = 30 m, i.d. 0.32 mm, film thickness 0.25 µm) with 5% phenyl and 95% dimethylpoly-siloxane as the stationary phase. The carrier gas was helium at a flow rate of 1.8 mL/min. The conditions for the detection were as follows: the injection mode had a split rate of 35; the column was held at 50 °C for 2 min and then heated to 250 °C at the rate of 10 °C/min; and the injector temperature was 250 °C. The identification of the components was confirmed using total ion chromatograms, as well as fragmentation patterns.

RESULTS AND DISCUSSION

Liquefaction Reaction

The effect of liquefaction temperature on the conversion yield of rape straw at five reaction times is depicted in Fig. 2. To investigate the efficiency of the microwave with respect to temperature, the catalyst content was maintained at 3% of the weight of methanol. Liquefaction was initiated at the beginning of the process. The conversion yield increased dramatically as the liquefaction temperature increased from 140 °C to 180 °C. The increase in conversion yield during the initial period at low temperature (140 °C and 160 °C) was mainly due to the rapid degradation of the easily accessible rape straw cell wall components, such as lignin, hemicelluloses, and amorphous cellulose (Zhang *et al*. 2012).

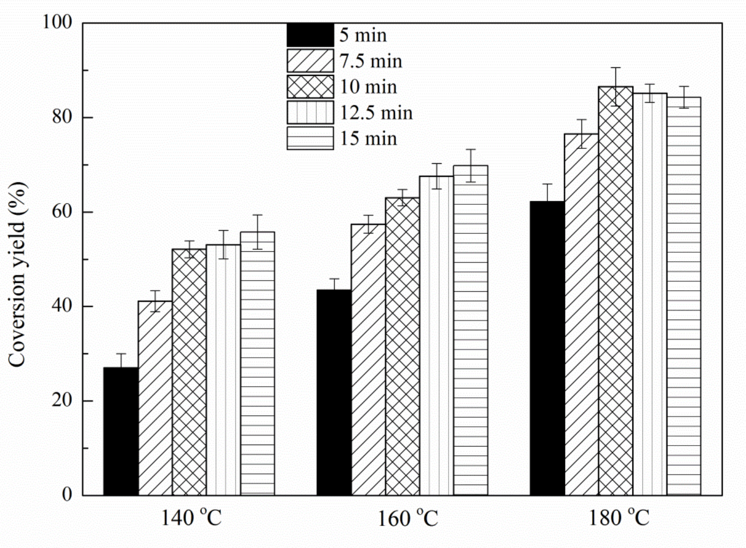

Fig. 2. Conversion yield with respect to liquefaction temperature and time (Other conditions: methanol/rape straw, 6/1; sulfuric acid, 3%)

The conversion yield greatly increased with increasing liquefaction time, especially from 5 to 10 min. After 10 min, the conversion yield slightly decreased, and the color of the liquefied residue changed from grey to dark-brawn, and even black at 15 min. It was difficult for the solvent to penetrate into the crystalline region of the cellulose, which slowed the reaction and decreased the conversion yield. Moreover, severe conditions (high temperature and/or long time) could induce the recondensation of the already liquefied lignin and hemicellulose fragments (Xie *et al*. 2016a). Additionally, side reactions of the decomposed cellulose may yield insoluble substances (Girisuta *et al*. 2006). Furthermore, the silica and silicates in the ashes may inhibit further liquefaction of the crop residues and cellulose (Xiao *et al*. 2013). Therefore, the resistance of cellulose, ash, and the recondensed fragments contributed to the decrease in conversion yield with long periods of microwave irradiation. Because recondensation took place after a prolonged reaction time, the energy consumed at that period may have been wasted. Therefore, energy consumption analysis was essential to avoid energy waste and to ensure the high quality of the end product.

Energy Efficiency Evaluation

Though the maximum conversion yield of 86.54% was observed at 180 °C for 10 min, this did not mean that the reaction reduced energy consumption. As shown in Fig. 3, higher liquefaction temperature resulted in lower energy consumption, except for the comparison between 160 °C/15 min and 180 °C/15 min. Microwave pretreatment opens water pathways in woody material, dramatically increasing its permeability and accelerating moisture migration in wood (Panthapulakkal and Sain 2013). Microwaves induce heat at the molecular level by direct conversion of electromagnetic energy into heat, resulting in a fast heating rate (Sobhy and Chaouki 2010). Therefore, the energy consumption of microwave-assisted liquefaction would be lower than from conventional heating. As compared with conventional liquefaction, microwave-assisted liquefaction could save more than 85% energy consumption (Xie *et al.* 2016b). Hence, it is safe to state that the microwave-assisted liquefaction is a time and energy saving method to convert renewable biomass into bio-oil.

Additionally, high pressure induced by high temperature in the sealed reaction system also enhances the conversion yield (Zhang *et al*. 2012). Consequently, high liquefaction temperature resulted in higher conversion yield and required lower energy consumption during the liquefaction regardless of liquefaction time.

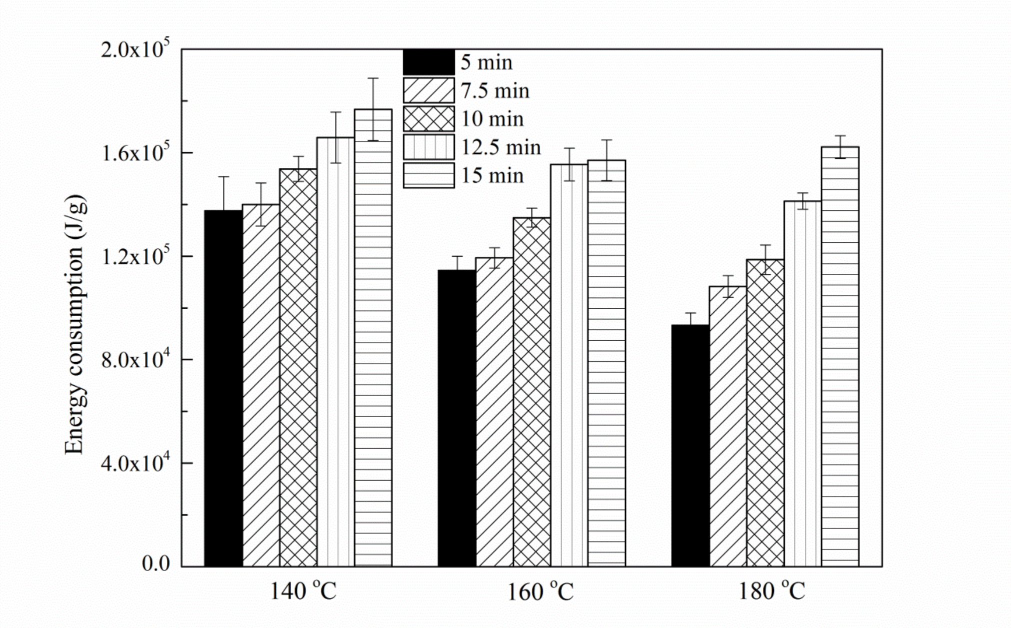

Fig. 3. Energy consumption as a function of liquefaction temperature and time (Other conditions: methanol/rape straw, 6/1; sulfuric acid, 3%)

The energy consumption of the 180 °C/15 min reaction was higher than that of the 160 °C/15 min reaction. This result suggests that recondensation took place at 180 °C/15 min, which decreased the extent of liquefaction. Because the excess energy was consumed in recondensation rather than decomposition, the energy was wasted. Therefore, the energy consumption evaluation of the liquefaction process could have also been used as an indicator of the occurrence of recondensation.

FT-IR Spectra

Figure 4 presents the FTIR spectra of the bio-oils from different liquefaction conditions. The broad band at around 3330 cm^{-1} was related to the characteristic stretching vibration of hydroxyl groups (Sain and Panthapulakkal 2006), indicating that all bio-oils contained a remarkable amount of hydroxyl groups. The absorption peaks at 1710 to 1740 cm^{-1} corresponded to carbonyl or ester groups (Neto *et al*. 2013). As shown in the Fig. 4, the intensity at 1740 cm^{-1} in the bio-oils spectra increased from 160 °C/15 min to 180 °C/15 min, which could have been caused by oxidation and methanol esterification with increasing temperature, because the oxidation of hydroxyl groups could have formed the carbonyl groups (Celikbag and Via 2016). Methanol esterification reaction may have also occurred during liquefaction (Xu *et al*. 2016), which could have increased the intensity of carbonyl groups. The extremely strong intensity at 1740 cm^{-1} from the 140 °C/15 min reaction was attributed to the rapid decomposition of hemicelluloses into C5 sugars with high content of hydroxyl groups. The intensified peak at 1409 cm^{-1} from 140 °C/15 min to 180 °C/15 min, which arose from the plane deviational vibration of hydroxyl group in carboxylic groups, further evidenced the oxidation reactions during liquefaction (Zhang *et al*. 2007).

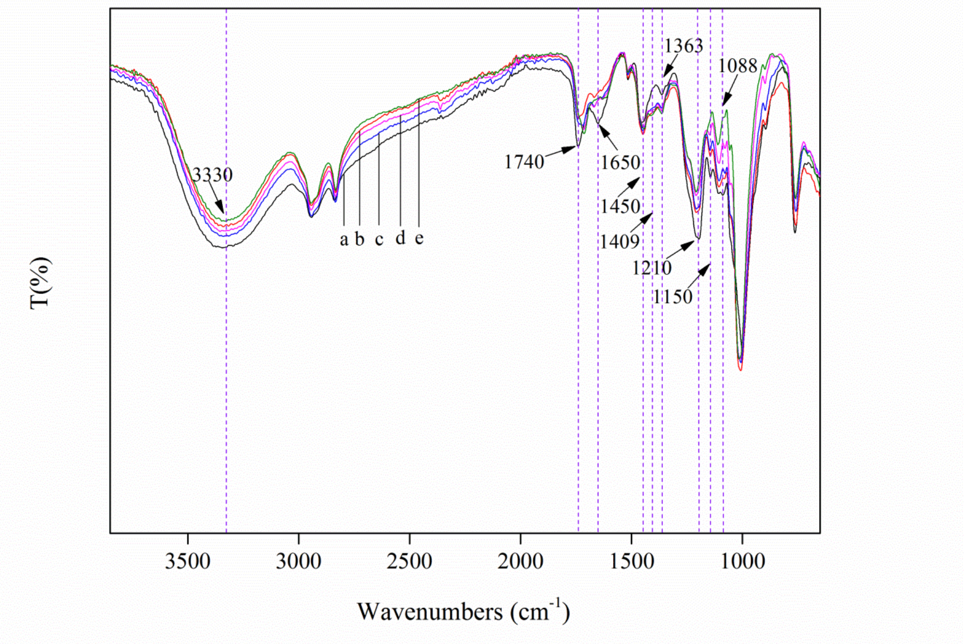

Fig. 4. FT-IR transmittances of bio-oils from different treatments: (a) 140 °C/15 min; (b) 160 °C/15 min; (c) 180 °C/7.5 min; (d) 180 °C/10 min; (e) 180 °C/15 min

The characteristic peaks of aromatic ring at 1650 and 1450 cm^{-1} and benzene ring at 1363 cm^{-1} and 1210 cm^{-1} tended to be weaker with extended liquefaction, indicating that the decomposed lignin at the initial liquefaction stage underwent recondensation (Zhang *et al*. 2011; Zheng *et al*. 2011). The intensity of 1210 cm^{-1} decreased as the liquefaction proceeded, demonstrating that the lignin derivatives participated in a cross-link reaction. The absorbance at 1150 cm^{-1} was due to the ether bond in cellulose (Salehian *et al*. 2013), which was weakened with prolonging reaction times and increasing liquefaction temperatures, suggesting that the cellulose participated in recondensation. The intensity peak at 1088 cm^{-1} corresponding to the stretching vibration of C-O from polysaccharide gradually decreased as liquefaction proceeded (Zheng *et al*. 2011). This result was confirmed by the GC-MS analysis of bio-oils as discussed below.

GC-MS Analysis

The chemical components of the bio-oils obtained from the 140 °C/15 min, 160 °C/15 min, 180 °C/7.5 min, 180 °C/10 min, and 180 °C/15 min reactions are shown in Tables 1 and 2. Bio-oils were mainly composed of C5 and C6 sugars, esters, furan derivatives, carbonyl compounds, and aliphatic hydrocarbons.

Table 1. Main Components of Bio-Oils (by area/%) from Different Treatments

Treatment	C5 Sugars	C6 Sugars	Aromatics	α-D-ribopyranoside, methyl	Esters	Levulinate Ester
140 °C/15 min	46.30	14.43	4.52	33.11	15.18	0.50
160 °C/15 min	28.25	19.74	7.20	15.38	18.47	2.69
180 °C/7.5 min	19.97	17.84	7.22	8.67	21.79	6.53
180 °C/10 min	11.11	14.17	8.48	3.05	31.74	14.65
180 °C/15 min	7.19	7.17	8.35	1.50	43.27	21.71

As shown in Fig. 5, GC-MS chromatograms are divided approximately into four zones within the retention time. The impurities mainly consisted of furfural, acetic acid, and ethanol, *etc*. The carbonyl compounds in the bio-oils were primarily composed of esters, sulfuric acid derivative, furan derivatives, aliphatic hydrocarbons, succinic acid derivatives, and a small amount of C6 sugars, and aromatics. C5 sugars, C6 sugars, and aromatics were derived from hemicelluloses, cellulose, and lignin *via* liquefaction, respectively. Glycosidic bonds and dominant linkages between cellulose and hemicelluloses underwent methanolysis under acidic condition, resulting in the release of C5 and C6 derivatives. Similarly, aromatics derivatives were released through cleaving the linkages of β-O-4, 4-O-5, and dibenzodioxocin units (Xu *et al.* 2012; Xu *et al.* 2016). The presence of C5, C6 sugars, and aromatics in bio-oils demonstrated the decomposition of hemicelluloses, cellulose, and lignin.

The total amount of C5, C6 sugars, and the aromatic derivatives remarkably decreased from 65.25% to 22.71% (area %) from 140 °C/15 min to 180 °C/15 min (Table 1). Ten types of C5 sugars derivatives, such as methyl 2-O-methyl-β-d-xylopyranoside, methyl α-D-rhamnopyranoside, methyl α-D-ribopyranoside, *etc.*, were identified, accounting for 46.30% at 140 °C/15 min. This was remarkably reduced to 7.19% (area %) as the liquefaction temperature increased to 180 °C. This result suggested that the decomposition rate of the C5 sugars outweighed their generation. As shown in Table 1, the C5 sugar derivatives of methyl α-D-ribopyranoside was about 33.11% at 140 °C/15 min, which declined to 1.5% at 180 °C/15 min (area %). Its isomeric form of methyl β-D-ribopyranoside was also detected. The reduction of methyl α-D-ribopyranoside made a primary contribution to decreasing of C5 sugars. Eight kinds of C6 sugars derivatives, such as levoglucosenone, D-allose, and 3-Methylmannoside were detected. The total content of C6 sugar derivatives increased from 14.43 (140 °C/15 min) to 19.74 (160 °C/15 min), then decreased to 7.17% (area %) with increasing temperature to 180 °C (Table 1). This result indicated that the decomposition of cellulose mainly took place at the reaction condition of 140 °C/15 min, and that the decomposition outweighed its recondensation before 160 °C for 15 min.

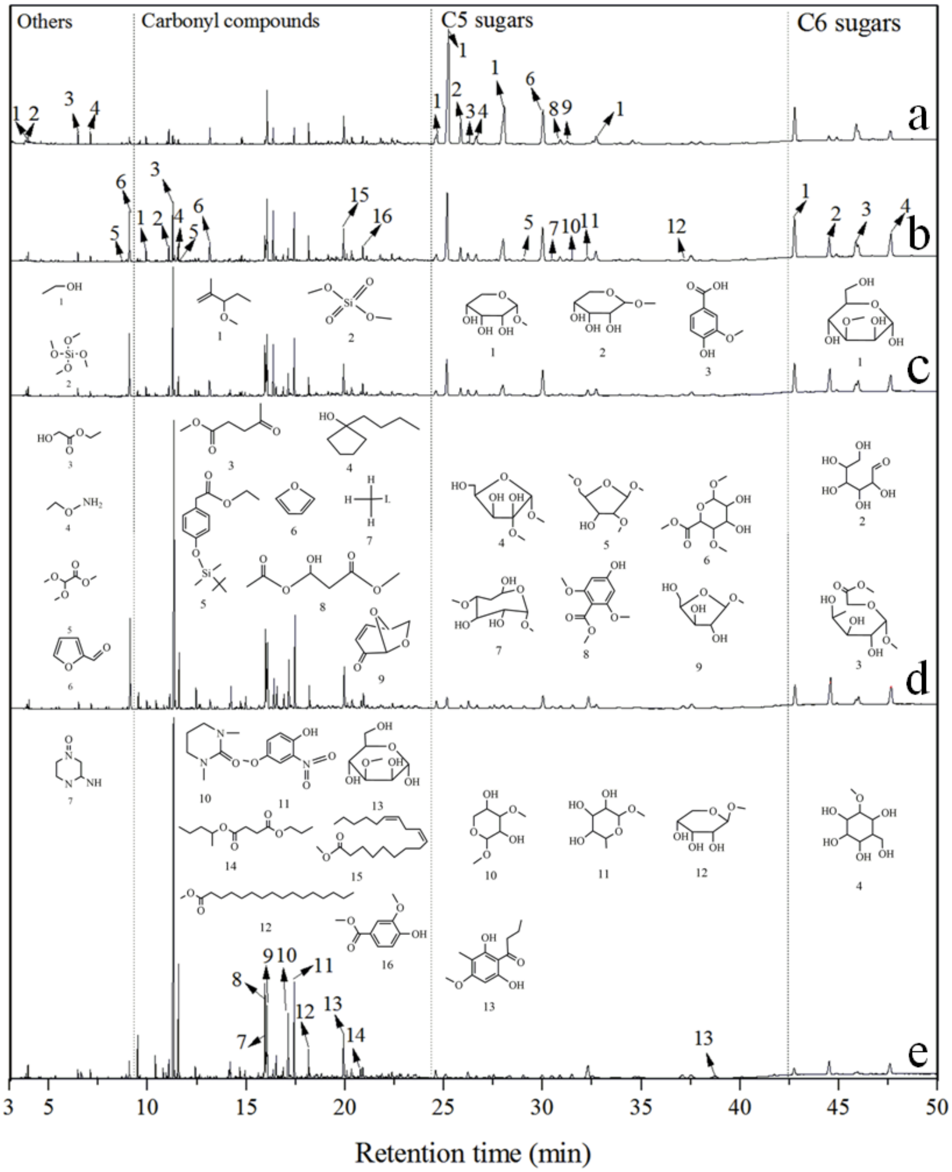

Fig. 5. GC-MS chromatograms of bio-oils from different treatments: (a) 140 °C/15 min; (b) 160 °C/15 min; (c) 180 °C/7.5 min; (d) 180 °C/10 min; (e) 180 °C/15 min

The aromatic derivatives, such as benzoic acid 4-hydroxy-3-methoxy- methyl ester, 2-fluorobenzoic acid, 3,5-difluorophenyl ester, aspidinol, *etc.*, were randomly distributed on the chromatograms (Table 2). The content of the aromatic derivatives generally increased from 4.52% at 140 °C/15 min to 8.48 % (area %) at 180 °C/10 min, and then slightly decreased to 8.35% at 180 °C/15 min (Table 1). The increase of aromatic derivatives revealed the decomposition of lignin, while the slight reduction in aromatics content was probably due to recondensation. For the preparation of polyurethane foams, the hydroxyl group of bio-oils is a key index for quality control and the formulation determination. The content of the hydroxyl group was mainly attributable to the amount of the C5, C6, and aromatics and their derivatives because each of those components can provide 2-5 hydroxyl groups. The GC-MS demonstrated that the content of C5, C6, and aromatics were remarkably decreased by exceeding the reaction time, which led to the possible decline of hydroxyl substances. Therefore, severe liquefaction reaction conditions should be avoided if the bio-oils will be used in the production for preparation of polyurethane foam.

The ester content in bio-oils remarkably increased from 15.18 (140 °C/15 min) to 43.27% (180 °C/15 min) (Table 1), which was primarily attributed to the increase of pentanoic acid, 4-oxo-, methyl ester (a type esterification product of levulinic acid with methanol). This levulinate is an important chemical with numerous potential applications, such as a fuel additive used to improve petroleum stability, low-temperature fluidity, and flash point (Girisuta *et al*. 2006). Hence, in this case, to obtain a high yield of levulinate ester, the liquefaction should be subjected to a severe reaction condition.

Other oxygenated by-products, such as furfural, methyl 2-furoate, furan, and succinic acid derivatives, increased as the liquefaction processed (Table 2). The furan derivatives that dehydrated from xylose originated from further decomposition of hemicelluloses (Dias *et al*. 2005). The further decomposition of cellulose and hemicelluloses may also have generated organic acids, such as acetic acid (Kabyemela *et al*. 1999; Zou *et al*. 2011). The organic acids were esterified with methanol under acidic conditions, resulting in the increase of esters. Hence, it was speculated that the severe liquefaction caused the further decomposition of C5 and C6 sugars. Furthermore, dimethyl sulfate was also detected, which implied that sulfuric acid was involved in esterification.

Table 2. Components of Bio-Oils from Different Treatments#

Peak	Chemical	Area (%)*				
		a	b	c	d	e
1	Ethanol	0.32	0.16	0.17	0.14	0.16
2	Tetramethyl silicate	0.13	0.07	0.07	0.07	0.08
3	Undecane	0.10	0.08	0.06	0.05	0.07
4	o-Ethylhydroxylamine	0.63	0.43	0.40	0.29	0.40
5	Butanoic acid, 3-methyl-2-[(phenylmethoxy)imino]-, trimethylsilyl ester	0.64	0.24	0.25	0.22	0.37
6	Acetic acid, dimethoxy-, methyles	0.15	0.16	0.16	0.17	-
7	3-Aminopyrazine 1-oxide	0.36	2.29	3.23	3.77	0.95
8	Cyclopropanecarboxylic acid, 2-methyl-2-methoxy, methyl ester	0.07	0.15	0.29	0.65	1.70
9	Cyclotrisiloxane, hexamethyl-	0.05	0.05	0.07	0.08	0.11
10	Furfural	0.44	0.51	0.53	0.4	0.10
11	3-Methoxy-3-methyl-1-pentene	-	0.08	0.15	0.37	0.95
12	Cyclopropanecarboxylic acid, 2-methyl-2-methoxy, methyl ester	-	0.03	0.07	0.16	0.45

13	Acrolein,dimethyl acetal	0.06	0.07	0.10	0.14	0.37
14	2-Butenedioic acid (E)-, dimethyl	0.20	0.08	0.09	0.09	0.14
15	Sulfuric acid, dimethyl ester	0.90	0.76	0.59	0.68	0.93
16	Pentanoic acid, 4-oxo-, methyl ester	0.50	2.69	6.53	14.7	21.7
17	Methyl 2-furoate	0.30	0.34	0.40	0.41	0.37
18	Butanedioic acid, dimethyl ester	0.32	0.84	0.99	2.28	4.72
19	4-Hydroxyphenylacetic acid, ethyl	0.06	0.06	0.06	0.06	0.09
20	Succinic acid, heptyl 2-propyl ester	-	0.06	0.10	0.13	0.16
21	1H-Imidazole, 2-methyl-	0.08	0.07	0.06	-	-
22	Cyclopentasiloxane, decamethyl-	0.05	0.06	0.08	0.12	0.16
23	2(5H)-Furanone, 5-methyl-	-	0.06	0.12	0.23	0.22
24	Succinic acid, heptyl 3-methylbut-2-yl ester	-	0.04	0.06	0.07	0.11
25	1,3-Dioxolane-4,5-dimethanol, 2,2-	-	0.04	0.08	0.09	0.14
26	Furan	1.16	1.64	1.57	0.74	0.21
27	5H-Imidazole-4-carboxylic acid, 5-3-dodecyl ester	-	0.16	0.33	1.03	0.81
28	Phenol, 2-methoxy-	-	0.04	0.05	0.05	0.07
29	1-Pentanethiol, 4-methyl-l-	-	0.17	0.24	0.36	0.54
30	2,4(1H,3H)-Pyrimidinedione, dihydro-	0.40	0.30	0.27	0.12	0.11
31	1-(2-Thienyl)-1-propanone	0.13	0.23	0.33	0.61	0.43
32	Methane, iodo-	0.26	1.33	2.83	3.79	4.63
33	Levoglucosenone	0.41	1.10	1.72	1.78	1.13
34	3-Acetoxy-3-hydroxypropionic acid, methyl ester	3.02	3.13	3.31	2.96	3.46
35	Methyl tetradecanoate	0.12	0.17	0.22	-	-
36	Pentanedioic acid, 2-oxo-, dimethyl ester	-	-	-	-	0.31
37	5-Amino-3H-[1,2,3]triazole-4-carbo	1.03	2.55	2.75	1.39	0.49
38	Glycolaldehyde dimethyl acetal	0.10	0.47	0.90	1.43	1.54
39	Succinic acid, ethyl 2-(2-methoxyethyl)heptyl ester	-	-	0.06	0.10	0.18
40	2-Fluorobenzoic acid, 3,5-difluorophenyl ester	0.13	0.35	0.51	0.72	0.57
41	1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone	0.08	0.66	1.27	2.28	3.11
42	Phenol, 4-methoxy-2-nitro-	0.96	2.33	2.96	4.22	4.28
43	Isopropylimidazole-2-thione	-	0.07	0.08	0.13	0.14
44	Hexadecanoic acid, methyl ester	1.13	1.12	0.93	0.92	1.21
45	2H-Pyran-2-one, 4-hydroxy-6-methyl	-	0.09	0.11	0.20	0.28
46	Methyl-2,4-di-O-methyl-α-D-glucopyranoside	0.25	0.41	0.37	0.26	0.11
47	Citric acid, trimethyl ester	1.92	2.15	2.80	2.94	3.16
48	Octadecanoic acid, methyl ester	0.43	0.48	0.41	0.47	0.61
49	9-Octadecenoic acid, methyl ester(E)-	0.66	0.81	0.85	0.90	0.87
50	9,12-Octadecadienoic acid (Z,Z)-,methyl ester	0.66	1.12	1.08	1.16	0.88
51	Methyl 2-O-methyl-β-D-xylopyranoside	0.31	0.42	0.34	0.25	0.19

52	Methyl-α-D-rhamnopyranoside	0.65	0.73	0.65	0.42	0.36
53	Benzoic acid, 4-hydroxy-3-methoxy-, methyl ester	0.67	0.71	0.59	0.55	0.63
54	α-D-ribopyranoside, methyl	1.5	1.08	0.98	0.89	0.92
55	α-D-ribopyranoside, methyl	21.84	9.39	5.00	1.48	0.58
56	2H-Pyran-3,4,5-triol, tetrahydro-2-methoxy-6-methyl-	3.41	1.72	1.06	0.39	-
57	2,4'-Dihydroxy-3'-methoxyacetophenone	0.41	1.15	1.05	1.06	0.91
58	α-D-lyxofuranoside, methyl	1.55	1.11	0.9	0.46	0.31
59	α-D-Ribopyranoside, methyl	9.77	4.91	2.69	0.68	-
60	α-D-xylofuranoside, methyl 2,5-di-O-methyl	-	0.27	0.31	0.42	0.47
61	Methyl(methyl 4-O-methyl-α-D-mannopyranoside)uronate	7.44	6.41	5.09	2.26	0.7
62	Methyl-4-O-methyl-α-D-glucopyranoside	-	0.19	0.27	0.43	0.55
63	Benzoic acid, 4-hydroxy-3,5-dimethoxy-, hydrazide	1.00	0.73	0.51	0.45	0.50
64	α-D-xylofuranoside, methyl	0.56	0.38	0.26	-	-
65	Methyl 3-O-methyl-β-D-xylopyranoside	-	0.21	0.31	0.52	0.6
66	α-D-glucopyranoside, methyl	0.64	0.94	1.32	2.17	2.23
67	Methyl(methyl 4-O-methyl-α-D-mannopyranoside)uronate	2.04	2.08	1.68	0.82	-
68	β-D-ribopyranoside methyl	-	0.32	0.44	0.74	0.83
69	Aspidinol	0.65	1.59	1.24	1.15	0.93
70	3-Methylmannoside	6.69	7.01	5.68	3.30	1.04
71	D-Allose	0.93	3.07	4.55	4.30	2.07
72	Propanoic acid, 3-methoxy-, methyl ester	0.63	0.45	0.37	0.26	0.19
73	α-D-galactopyranosiduronic acid, methyl, methyl ester	3.84	3.08	1.52	0.70	0.24
74	α-D-galactopyranoside, methy	2.31	4.88	3.73	3.40	2.03

*Area percent is based on the total ion current
#(a) 140 °C/15 min; (b) 160 °C/15 min; (c) 180 °C/7.5 min; (d) 180 °C/10 min; (e) 180 °C/15 min

CONCLUSIONS

1. The conversion yield remarkably increased with increasing liquefaction temperature and prolonging reaction time; whereas, it decreased at 180 °C/10 min.
2. Higher liquefaction temperature was beneficial to obtaining higher energy consumption efficiency as heated by microwave irradiation. The recondensation reactions at severe liquefaction conditions may have led to energy waste.
3. The FT-IR spectra suggested that oxidation reactions of hydroxyl groups and methanol esterification occurred during liquefaction. GC-MS demonstrated the decomposition of hemicelluloses, cellulose, and lignin during liquefaction; the further decomposition of C5 and C6 sugars caused the reduction of hydroxyl groups and the increase of levulinate ester in bio-oils.
4. The main chemical components of bio-oils were directly related to liquefaction

conditions. Moderate liquefaction conditions could result in a high content of hydroxyl group products, while severe reaction conditions could produce a high yield of levulinic ester products, regardless of energy consumption efficiency.

ACKNOWLEDGMENTS

This work is funded by the USDA Forest Service 2015 Wood Innovations Funding Opportunity program, Agreement 15-DG-11083150-054. The authors also appreciate the financial support from China Scholarship Council.

REFERENCES CITED

ASTM D 1104-56 (1971). “Standard test method for holocellulose in wood,” ASTM International, West Conshohocken, USA.

ASTM D 1103-60 (1971). “Standard test method for alpha-cellulose in wood,” ASTM International, West Conshohocken, USA.

ASTM D 1106-96 (1996). “Standard test method for acid-insoluble lignin in wood,” ASTM International, West Conshohocken, USA.

ASTM D 1107-96 (1996). “Standard test method for ethanol-toluene solubility of wood,” ASTM International, West Conshohocken, USA.

ASTM D 1102-84 (2001). “Standard test method for ash solubility of wood,” ASTM International, West Conshohocken, USA.

Bren, U., Kržan, A., and Mavri, J. (2008). “Microwave catalysis through rotationally hot reactive species,” *The Journal of Physical Chemistry A* 112(2), 166-171. DOI: 10.1021/jp709766c

Celikbag, Y., and Via, B. K. (2016). “Characterization of residue and bio-oil produced by liquefaction of loblolly pine at different reaction times,” *Forest Product Journal* 66(1/2), 29-36. DOI: 10.13073/FPJ-D-14-00110

Chang, C. C., Wu, S. R., Lin, C. C., Wan, H. P., and Lee, H. T. (2012). “Fast pyrolysis of biomass in pyrolysis gas: Fraction of pyrolysis vapors using a spray of bio-oil,” *Energy & Fuels* 26(5), 2962-2967. DOI: 10.1021/ef201858h

Dias, A. S., Pillinger, M., and Valente, A. A. (2005). “Dehydration of xylose into furfural over micro-mesoporous sulfonic acid,” *Journal of Catalysis* 229(2), 414-423. DOI: 10.1016/j.jcat.2004.11.016

Doassans-Carrère, N., Ferrasse, J. H., Boutin, O., Mauviel, G., and Lédé, J. (2014). “Comparative study of biomass fast pyrolysis and direct liquefaction for bio-oils production: Products and characterizations,” *Energy & Fuels* 28(8), 5103-5111. DOI: 10.1021/ef500641c

Feng, J. F., Jiang, J. C., Xu, J. M., Yang, Z. Z., Wang, K., and Guan, Q. (2015). “Preparation of methyl levulinate from fractionation of direct liquefied bamboo biomass,” *Applied Energy* 154, 520-527. DOI: 10.1016/j.apenergy.2015.04.115

Girisuta, B., Janssen, L. P. B. M., and Heeres, H. J. (2006). “A kinetic study on the decomposition of 5-hydroxymethylfurfural into levulinic acid,” *Green Chemistry* 8, 701-709. DOI: 10.1039/b518176c

Huang, L. L., Xia, P., Liu, Y.M., Fu, Y., Jiang, Y. Y., Liu, S. Q., and Wang, X. L. (2016). “Production of biodegradable board using rape straw and analysis of mechanical properties," *BioResources* 11(1), 772-785. DOI: 10.15376/biores.11.1.772-785

Kabyemela, B. M., Adschiri, T., Malaluan, B. M., and Arai, K. (1999). "Glucose and fructose decomposition in subcritical and supercritical water: detailed reaction pathway, mechanisms, and kinetics," *Industrial & Engineering Chemistry Research* 38(8), 2888-2895. DOI: 10.1021/ie9806390

Ke, L. X., Wu, Q., and Zhang, D. Q. (2011). "Bioconversion of rape straw into a nutritionally enriched substrate by *Ganoderma lucidum* and yeast," *African Journal of Biotechnology* 10(29), 5648-5653. DOI: 10.5897/ajb10.2353

Larabi, C., al Maksoud, W., Szeto, K. C., Roubaud, A., Castelli, P., Santini, C. C., and Walter, J. J. (2013)."Thermal decomposition of lignocellulosic biomass in the presence of acid catalysts," *Bioresource Technology* 148, 255-260. DOI: 10.1016/j.biortech.2013.08.070

Lewandowska, M., Szymańska, K., Kordala, N., Dabrowska, A., Bednarski, W., and Juszczuk, A. (2016). "Evaluation of *Mucor indicus* and *Saccharomyces cerevisiae* capability to ferment hydrolysates of rape straw and *Miscanthus giganteus* as affected by the pretreatment method," *Bioresource Technology* 212, 262-270. DOI: 10.1016/j.biortech.2016.04.063

Neto, W. P. F., Silvério, H. A., Oliveira, N., and Pasquini, D. (2013). "Extraction and characterization of cellulose nanocrystals from agro-industrial residue-soy bulls," *Industrial Crops and Products* 42, 480-488. DOI: 10.1016/j.indcrop.2012.06.041

Panthapulakkal, S., and Sain, M. J. (2013). "Investigation of structural changes of alkaline-extracted wood using X-ray microtomography and X-ray diffraction: A comparison of microwave versus conventional method of extraction," *Journal of Wood Chemistry and Technology* 33(2), 92-102. DOI: 10.1080/02773813.2012.751427

Sain, M., and Panthapulakkal, S. (2006). "Bioprocess preparation of wheat straw fibers and their characterization," *Industrial Crops and Products* 23(1), 1-8. DOI: 10.1016/j.indcrop.2005.01.006

Salehian, P., Karimi, K., Zilouei, H., and Jeihanipour, A. (2013). "Improvement of biogas production from pine wood by alkali pretreatment," *Fuel* 106, 484-489. DOI: 10.1016/j.fuel.2012.12.092

Sobhy, A., and Chaouki. J. (2010). "Microwave-assisted biorefinery," *Chemical Engineering Transactions* 19, 25-30. DOI: 10.3303/cet1019005

Tarves, P. C., Mullen, C. A., and Boateng, A. A. (2016). "Effects of various reactive gas atmospheres on the properties of bio-oils produced using microwave pyrolysis," *ACS Sustainable Chemistry & Engineering* 4(3), 930-936. DOI: 10.1021/acssuschemeng.5b01016

Villadsen, S. R., Dithmer, L., Forsberg, R., Becker, J., Rudolf, A., Iversen, S. B., Iversen, B. B., and Glasius, M. (2012). "Development and application of chemical analysis methods for investigation of bio-oils and aqueous phase from hydrothermal liquefaction of biomass," *Energy & Fuels* 20(11), 6988-6998. DOI: 10.1021/ef300954e

Wang, H. Z. (2007). "Strategy for rapeseed industry development based on the analysis of rapeseed production and demand in China," *Chinese Journal of Oil Crop Sciences* 29(1), 101-105. (in Chinese)

Xiao, W. H., Niu, W. J., Yi, F., Liu, X., and Han, L. J. (2013). "Influence of crop residue types on microwave-assisted liquefaction performance and products," *Energy & Fuels* 27(6), 3204-3208. DOI: 10.1021/ef4003457

Xie, J. L., Hse, C. Y., Shupe, T. F., and Hu, T. X. (2016a). "Influence of solvent type on microwave-assisted liquefaction of bamboo," *European Journal of Wood and Wood Products* 74 (2), 249-254. DOI: 10.1007/s00107-016-1009-2

Xie, J. L., Hse, C. Y., Shupe, T. F., Pan, H., and Hu, T. X. (2016b). "Extraction and characterization of holocellulose fibers by microwave-assisted selective liquefaction of bamboo," *Journal of Applied Polymer Science* 133 (18). DOI: 10.1002/app.43394Xie, J. L., Hse, C. Y., Shupe, T. F., Qi, J. Q., and Pan, H. (2014a). "Liquefaction behaviors of bamboo residues in a glycerol-based solvent using microwave energy," *Journal of Applied Polymer* 131(6), DOI: 10.1002/app.40207

Xie, J. L., Qi, J. Q., Hse, C. Y., and Shupe, T. F. (2014b). "Effect of lignin derivatives in the bio-polyols from microwave liquefied bamboo on the properties of polyurethane foams," *BioResources* 9(1), 578-588. DOI: 10.15376/biores.9.1.578-588

Xu, J. M., Jiang, J. C., Hse, C. Y., and Shupe, T. F. (2012). "Renewable chemical feedstocks from integrated liquefaction processing of lignocellulosic materials using microwave energy," *Green Chemistry* 14, 2821-2830. DOI: 10.1039/c2gc35805k

Xu, J. M., Xie, X. F., Wang, J. X., and Jiang, J. C. (2016). "Directional liquefaction coupling fractionation of lignocellulosic biomass for platform chemicals," *Green Chemistry* 18, 3124-3138. DOI: 10.1039/C5GC03070F

Zhang, H. R., Pang, H., Shi, J. Z., Fu, T. Z., and Liao, B. (2012). "Investigation of liquefied wood residues based on cellulose, hemicellulose, and lignin," *Journal of Applied Polymer Science* 123(2), 850-856. DOI: 10.1002/app.34521

Zhang, H. R., Ding, F., Luo, C. R., Xiong, L., and Chen, X. D. (2011). "Liquefaction and characterization of acid hydrolysis residue of corncob in polyhydric alcohols," *Industrial Crops and Products* 39, 47-51. DOI: 10.1016/j.indcrop.2012.02.010

Zhang, T., Zhou, Y. J., Liu, D. H., and Petrus, L. (2007). "Qualitative analysis of products forms during the acid catalyzed liquefaction of bagasse in ethylene glycol," *Bioresource Technology* 98, 1454-1459. DOI: 10.1016/j.biortech.2006.03.029

Zheng, Z. F., Pan, H., Huang, Y. B., Hse, C. Y., Zhang, X. L., and Feng, H. (2011). "Rapid liquefaction of wood in polyhydric alcohols under microwave heating and its liquefied products for preparation of rigid polyurethane foam," *The Open Materials Science Journal* 5, 1-8. DOI: 10.2174/1874088X01105010001

Zhou, M. C., Eberhardt, T. L., Xin, P. P., Hse, C. Y., and Pan, H. (2016). "Liquefaction of torrefied wood using microwave irradiation," *Energy & Fuels* 30(7), 5862-5869. DOI: 10.1021/acs.energyfuels.6b01004

Zou, X. W., Qin, T. F., Wang, Y., and Huang, L. H. (2011). "Mechanisms and product specialties of alcoholysis processes of polar components," *Energy & Fuels* 25(8), 3786-3792. DOI: 10.1021/ef200726w

Article submitted: October 28, 2016; Peer review completed: December 29, 2016; Revised version received and accepted: January 20, 2017; Published: January 30, 2017.
DOI: 10.15376/biores.12.1.1968-1981