

Fractionation and characterization of bio-oil from microwave-assisted pyrolysis of corn stover

Changyan Yang¹, Bo Zhang^{1,2}, Johannes Moen¹, Kevin Hennessy¹, Yuhuan Liu^{1,3}, Xiangyang Lin^{1,4}, Yiqin Wan^{1,3}, Hanwu Lei⁵, Paul Chen¹, Roger Ruan^{1,3,*}

(1. Center for Biorefining, Department of Bioproducts and Biosystems Engineering, University of Minnesota, 1390 Eckles Avenue, Saint Paul, MN 55108, USA; 2. Department of Natural Resources and Environmental Design, North Carolina A&T State University, Greensboro, North Carolina, USA; 3. School of Life Sciences, Nanchang University, Nanchang, Jiangxi 330047, China; 4. College of Biological Science and Technology, Fuzhou University, Fuzhou 350108, China; 5. Bioproducts, Sciences and Engineering Laboratory (BSEL), Department of Biological Systems Engineering, Washington State University, Richland, WA 99354, USA)

Abstract: Bio-oil from thermochemical conversion of biomass is a complex mixture of polar and non-polar compounds, and cannot be used directly as a combustion engine fuel due to its low heating value, high viscosity, chemical instability, and incomplete volatility. Mixed-solvent extraction was developed to fractionate bio-oils from microwave-assisted pyrolysis of corn stover to produce light oil (a mixture of light and inflammable fuel oil components from bio-oil) with low viscosity and low combustion residue, and high value chemicals. Different fractions from bio-oil were characterized using GC/MS and TG, and a major chemical (hydroxy-butanedioic acid diethyl ester) was separated.

Keywords: fractionation, characterization, pyrolysis, bio-oil, corn stover

DOI: 10.3965/j.issn.1934-6344.2010.03.0-0

Citation: Changyan Yang, Bo Zhang, Johannes Moen, Kevin Hennessy, Liu Yuhuan, Lin Xiangyang, et al. Fractionation and characterization of bio-oil from microwave-assisted pyrolysis of corn stover. *Int J Agric & Biol Eng*, 2010; 3(3): —.

1 Introduction

Mounting concerns over decline in fossil oil reserve and rise in energy demand and cost has prompted

enormous interests in renewable energy from biomass^[1]. Pyrolysis is one of the most promising alternatives under development today to convert biomass into useful products and energy^[2].

Received date: 2010-03-12 **Accepted date:** 2010-07-27

Biographies: **Changyan Yang**, Research Associate, renewable energy, Email: yang1207@umn.edu; **Bo Zhang**, Research Associate, renewable energy, Email: bzhang@ncat.edu; **Johannes Moen**, Graduate Student, renewable energy, Email: johannes_moen@yahoo.com; **Kevin Hennessy**, Graduate Student, renewable energy, Email: henne196@tc.umn.edu; **Yuhuan Liu**, PhD, Assistant Professor, biomass refining, food science; MOE Biomass Engineering Center and State Key Lab of Food Science and Technology, Nanchang University, 235 East Nanjing Road, Nanchang, Jiangxi, China 330047. Email: liuyuhuan@ncu.edu.cn; **Xiangyang Lin**, PhD, Professor, Bioresource utilization and processing, Biocatalysis and Biotransformation, Email: xiangyanglin@fzu.edu.cn; **Yiqin Wan**, PhD Candidate, Assistant Professor, renewable energy, bioresource utilization and processing, food engineering; Nanchang University, Jiangxi Province, China, 330047, Email: msyqwan@yahoo.com.cn; **Hanwu Lei**, PhD, Assistant Professor, renewable energy, bioresource utilization and

processing, food engineering; Bioproducts, Sciences and Engineering Laboratory (BSEL), Dept. Biological Systems Engineering, Washington State University, 1710 University Drive, Richland, WA 99354, Email: hlei@tricity.wsu.edu; **Paul Chen**, PhD, Program Director, Major: Food Science, Research Interests: renewable energy, biorefining, food science, food engineering, Center for Biorefining, Dept. BioProducts & BioSystems Engineering, University of Minnesota, 1390 Eckles Ave, St. Paul, MN 55108, Email: chenx088@umn.edu;

Corresponding author: **Roger Ruan**, PhD, Professor, Yangtze Scholar Distinguished Guest Professor at Nanchang University, Director at Center for Biorefining, and Professor at University of Minnesota. Food science and nutrition, food engineering, renewable energy, biorefining, bioprocessing, and value-added process development; Dept. BioProducts & BioSystems Engineering, Dept. of Food Science and Nutrition, University of Minnesota, 1390 Eckles Ave, St. Paul, MN 55108, Tel: 612-625-1710; Fax: 612-624-3005, Email: ruanx001@umn.edu

Microwave pyrolysis is one of the many ways of converting biomass into higher value products such as oils, gases, charcoal and chemicals. The conversions of corn stover^[3] and sewage sludge^[4-6] are among the recent studies in the fields of microwave pyrolysis and bioenergy. Increased process yield, environmental compatibility, savings in process time and low requirements for space and capital equipment are among the advantages reported about microwave processing of materials^[7].

In conventional pyrolysis system, large sized particles are difficult to agitate and process in the fluid bed, as they tend to settle to the bottom of the bed where heat transfer and speed of thermal processing are reduced. This has a negative effect on the efficiency of production of bio-oil, which is increased when the particle size is reduced. Very fine feedstock grinding is required by conventional pyrolysis. Pyrolysis oil and char yields were found to be largely dependent of particle size^[8]. Fine particles increase overall heat transfer, but require substantial amount of energy and effort for size reduction, pre-processing and sizing of biomass feed material. Thermochemical conversion reactions can take place rapidly in large-sized biomass materials by using microwave irradiation^[9]. Very fine feedstock grinding required by conventional pyrolysis is not necessary for microwave pyrolysis process, resulting in substantial energy savings. Oils from microwave pyrolysis of sewage sludge is reported to contain no harmful compounds such as heavy polycyclic aromatic hydrocarbons (PAHs), which was the case for oils from conventional pyrolysis of the same feedstock^[5].

Bio-oil is the major product stream from biomass pyrolysis. However, crude pyrolytic bio-oil can not be used in an engine due to its low heating value, high viscosity, chemical instability, incomplete volatility and solid sediment^[10]. Many methods for upgrading bio-oil to a usable liquid fuel, such as emulsification^[10-12], hydrotreating^[10,13-14], and catalytic cracking^[14-15], have been studied and need to be further improved.

Bio-oil separation by solvent extraction, as reported in the literature^[10,16], is a simple method for refining bio-oil. Many studies focus on the separation of chemicals from

bio-oil or the analysis of bio-oil fractions using a multi-step extraction method^[16].

Bio-oil fractionation through mixed-solvent extraction, a method of combining light oil (a mixture of light and inflammable fuel oil components from bio-oil) separation and chemicals production, is an innovative and much economical method for refining crude pyrolytic liquid and producing substitute fuels for petroleum-based fuels. Herein, we reported a two-step fractionation process that is to extract light oil and chemicals from crude bio-oil.

2 Materials and methods

2.1 Materials

Corn stover pellets were provided by Agricultural Utilization Research Institute, Waseca, Minnesota.

2.2 Process and apparatus

Bio-oil was produced from microwave-assisted pyrolysis of corn stover. Corn stover pellets (approximately 5 mm in diameter × 2 cm in length) were first dried in air. The pyrolysis was then carried out in a microwave cavity oven by placing 250.0 g of corn stover pellets in a 1-L quartz flask which in turn was placed inside the microwave cavity. The oven was purged with nitrogen gas at a flow rate 200 mL/min for two minutes before microwave treatment to create an oxygen-starved environment. A constant power of 800 W at 2,450 MHz was supplied to the microwave oven. Heating of the corn stover lasted about 40 min, which is thought to be sufficient for complete pyrolysis based on the preliminary experiments. The temperature of the sample during the experiments was monitored immediately after microwave heating was terminated using a K-type thermocouple. The final mean temperature of the pyrolysis in our experiments ranged from 450°C to 650°C. The volatile pyrolyzates were condensed after passing through a water-cooled condenser (at 5-10°C), and then collected in a bottle as crude bio-oil and weighed.

2.2.1 Fractionation of bio-oil

The process used for bio-oil separation is presented in Figure 1. Two hundred milliliters of bio-oil was first mixed with water (according to 1:1, V/V) at 40°C in high-speed mixer, and then emulsified and separated. This operation was performed in order to separate the top

emulsion phase containing alkenes and low molecular lignin and precipitate the heavy oil of the bottom layer. The emulsion phase (light oil rich) was further extracted with a mix-solvent containing pentane and furans (1:1 V/V). The solvent in the extracted phase was then evaporated at 40°C under vacuum and then recycled. The remaining material was then weighed.

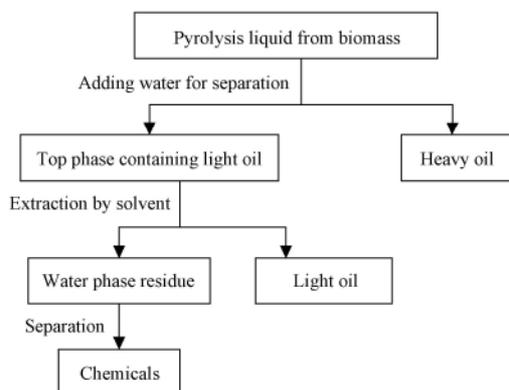


Figure 1 Fractionation scheme of bio-oil for light oil and chemicals

2.2.2 Elemental analysis

A CE-440 elemental analyzer (EAI Exeter Analytical Inc., North Chelmsford, Massachusetts) was used to determine the weight fraction of carbon, hydrogen and nitrogen, and oxygen of the bio-oil fractions (The weight fraction of oxygen was calculated by difference). The heating value of bio-oil fraction was calculated from Friedl's equation^[17] based on the elemental analysis.

2.2.3 GC-MS analysis

Chemical compositions of the light oil were determined using an HP 6890 GC/MS with a DB-5 capillary column. The GC was programmed at 40°C for half an hour minute and then increased at 10°C/min to 300°C and finally held with an isothermal for ten minutes. The injector temperature was 300°C and the injection size was 1 μ L. The flow rate of the carrier gas (helium) was 0.6 mL/min. The ion source temperature was 230°C for the mass selective detector. The compounds were identified by comparing our spectral data with the NIST Mass Spectral library.

2.2.4 Thermogravimetric analysis

A TG/DTA microbalance (TG/DTA 6300, Perkin Elmer, Waltham, Massachusetts) was used for the thermogravimetric tests. The samples were heated from

room temperature to 550°C under an air flow rate of 20 mL/min at 20°C/min. Samples of 3-4 mg were used.

3 Results and discussion

3.1 Fractionation of bio-oil

Biomass pyrolysis assisted by microwave heating could produce 40%-60% of liquid products, depending on the types of biomass, pyrolysis condition, and catalysts etc. Bio-oil yield from microwave-assisted pyrolysis of corn stover was about 40%-50% of corn stover (dry base), as shown in Table 1.

Table 1 Product yields from microwave-assisted pyrolysis of corn stover at different temperatures

Experimental number	Final temperature /°C	Gas /%	Char /%	Bio-oil /%	Heavy oil /%
A1	450-500	23.9	26.9	49.2	9.6
A2	500-550	28.8	23.6	47.6	10.4
A3	550-600	35.0	21.8	43.2	9.8
A4	600-650	50.2	18.1	31.7	6.7

Before fractionation, bio-oil sample was mixed at the volume ratio of 1:1. After stirred for ten minutes at 40°C, bio-oil was separated into two phases. The upper phase is a relatively stable, light emulsion containing water soluble chemicals and light oily components, and was subjected to the second extraction in the next step. The bottom phase is a large molecule oily mixture characterized by high viscosity and water insolubles, and is named as heavy oil. The heavy oil yield from our experiments was about 10%-20% of bio-oil from corn stover pyrolysis assisted by microwave heating. The yields of different products including heavy oil from microwave-assisted pyrolysis of corn stover at different temperatures are shown in Table 1.

After evaluating a number of solvent extractions, a mix-solvent containing pentane and furans (1:1 v/v) was the most effective extraction mixed solvent for separate light oil and chemicals from the crude bio-oil. As it is well known, the extraction yield is influenced by temperature, pressure, inorganic salts, phase ratio, extraction times, etc. We chose ambient temperature and pressure condition for economical and operational considerations. In order to optimize the yield of light oil, the effects of inorganic salts including NaCl, CaCl₂ and

ZnCl₂, and number of extraction were investigated. The results are shown in Figure 2.

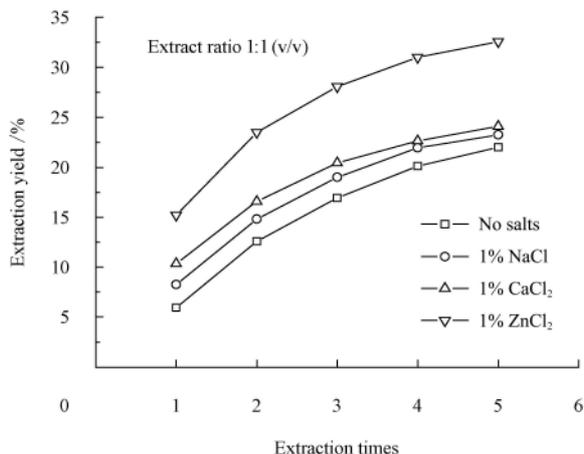


Figure 2 Light oil extraction yield vs. number of extraction

The yield of light oil increases from 5% to 22% with an increase in the number of extraction, and tends to level off after four to five times of extraction. Different salts have different effects on the yield of light oil. Interestingly, ZnCl₂ promoted higher yield of light oil than NaCl and CaCl₂. This suggests a stronger salting-out effect^[18] of ZnCl₂ on the extraction of light oil from bio-oil emulsion phase. The extraction yield of light oil with a three-stage extraction (three times of extraction) could be up to 28% if 1% ZnCl₂ is added. Therefore, the total yield of light oil and heavy oil acquired from microwave-assisted pyrolysis of corn stover are about 10%-15% and 5%-12%, respectively. Figure 3 shows a picture of light oil and heavy oil

separated from bio-oil.

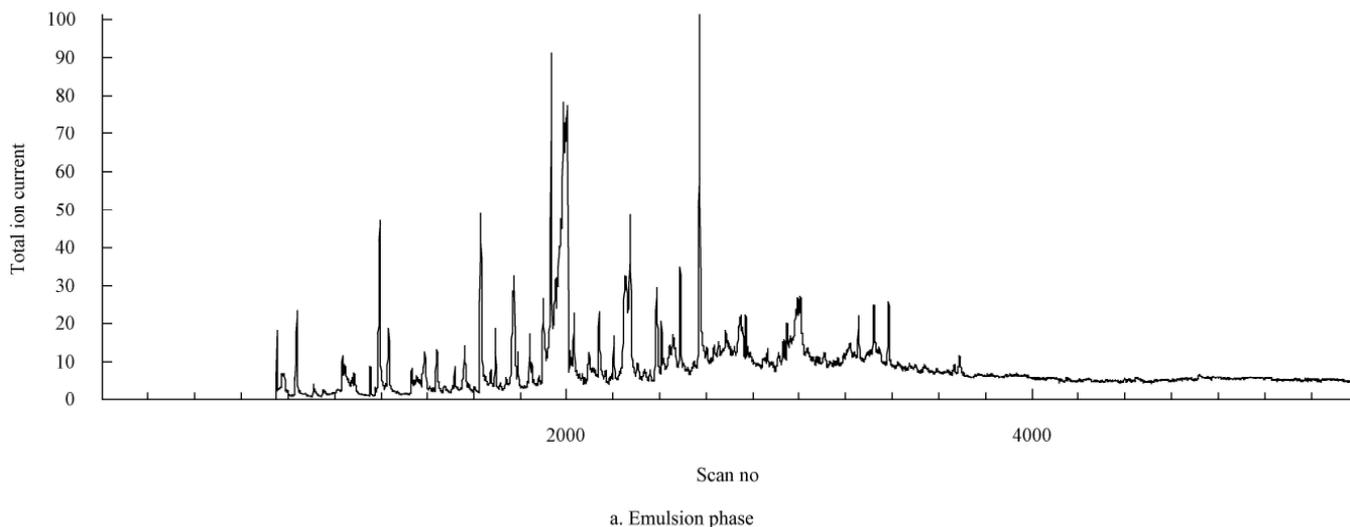


Figure 3 Picture of light oil, heavy oil and bio-oil from left to right

3.2 GC/MS characterization of bio-oil fractions

To further understand the bio-oil fractionation, GC/MS analysis was carried out to determine the composition of fractions from bio-oil by extraction. The bio-oil samples were prepared from the pyrolysis of corn stover assisted by microwave heating at 500-550°C and with 1% ZnCl₂. Figure 4 shows the total ion chromatograms (TIC) spectra of light oil, water fraction residue extracted from the emulsion phase. The results of the composition of different fractional products were shown in Table 2.

Heavy oil is mainly composed of high molecular weight phenols with different methoxy, and ethoxy groups etc, and not shown here.



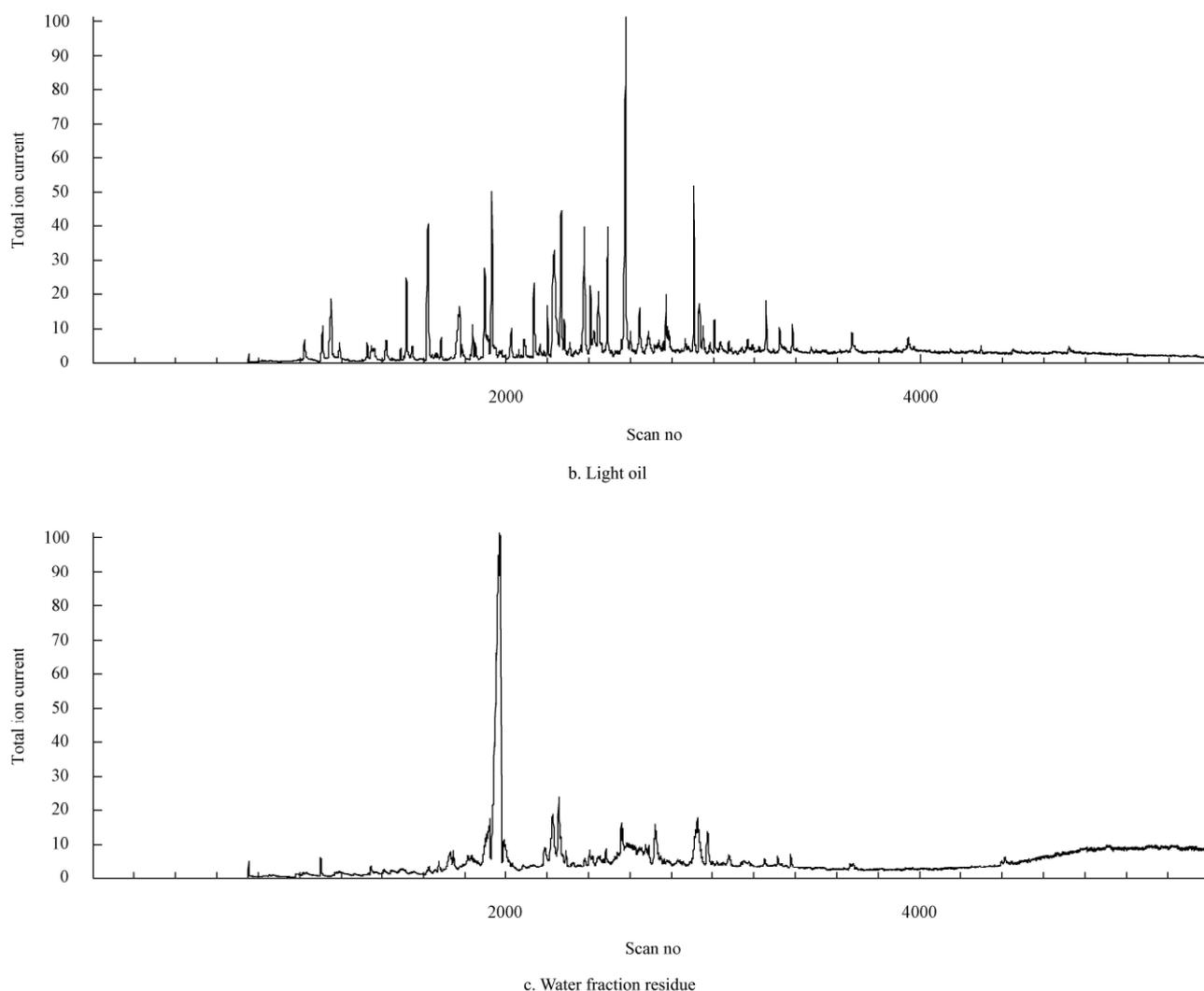


Figure 4 TIC spectra of bio-oil emulsion phase, light oil and water fraction residue

Table 2 Chemical composition of different fractions separated from bio-oil

Number	Retention time /min	Tentative compound name	Formula	Bio-oil emulsion phase/Area%	Water residue /Area%	Light oil /Area%
1	6.83	3-Methyl-2-butenic acid, allyl ester	C ₈ H ₁₂ O ₂	0.841		1.297
2	7.41	Ethane, 1,1,1-trimethoxy-	C ₅ H ₁₂ O ₃	1.072	1.122	1.357
3	7.70	Furfuryl hexanoate	C ₁₁ H ₁₆ O ₃	2.001		3.214
4	7.96	Acetic acid, 5-acetoxy-4-nitrotetrahydropyran-3-yl ester	C ₉ H ₁₃ NO ₇	0.467		0.722
5	8.85	Cyclopentane, 1,1'-ethylidenebis-	C ₁₂ H ₂₂	0.356		0.653
6	8.97	1,6-Anhydro-2,3-dideoxy-.beta.-D-threo-hexopyranose	C ₆ H ₁₀ O ₃	0.216	0.382	
7	8.98	Furan, 2-ethyl-5-methyl-	C ₇ H ₁₀ O	0.734		1.343
8	9.46	Hexanoic acid, 1-cyclopentylethyl	C ₁₃ H ₂₄ O ₂	1.049	1.123	0.913
9	9.93	Hexadecanoic acid, 3-hydroxy-, methyl ester	C ₁₇ H ₃₄ O ₃	0.153		0.294
10	10.11	2-Furanethanol, 4-methoxy-(S)-	C ₇ H ₁₀ O ₃	1.172		2.315
11	10.29	Furfuryl glycidyl ether	C ₈ H ₁₀ O ₃	0.454		0.554
12	10.81	Phenol	C ₆ H ₆ O	4.018		5.579
13	10.83	d-Glucose, 2,3,4,6-tetra-O-methyl-	C ₁₀ H ₂₀ O ₆	0.344	0.739	
14	11.15	Furan, tetrahydro-2,5-dimethoxy-	C ₆ H ₁₂ O ₃	0.241	0.485	
15	11.23	Butanoic acid, 2,3-dihydroxypropyl ester	C ₇ H ₁₄ O ₄	0.426		0.558
16	11.83	1,2-Cyclopentanedione, 3-methyl-	C ₆ H ₈ O ₂	3.142	3.213	3.607
17	12.24	Phenol, 3-methyl-	C ₇ H ₈ O	1.007		1.015
18	12.33	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	C ₇ H ₁₀ O ₂	0.419		0.474
19	12.64	Phenol, 4-methyl-	C ₇ H ₈ O	2.137		4.086

Number	Retention time /min	Tentative compound name	Formula	Bio-oil emulsion phase/Area%	Water residue /Area%	Light oil /Area%
20	12.77	Furan, tetrahydro-2-(methoxymethyl)-	C ₆ H ₁₂ O ₂	1.986	2.263	
21	12.87	Mequinol	C ₇ H ₈ O ₂	4.683	4.836	4.923
22	13.12	Butanedioic acid, hydroxy-, diethyl ester, (ñ)-	C ₈ H ₁₄ O ₅	21.373	46.241	
23	13.29	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	C ₇ H ₁₀ O ₂	0.774	0.876	0.704
24	13.5	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	C ₇ H ₁₀ O ₂	1.346	1.123	1.388
25	13.91	Phenol, 2,5-dimethyl-	C ₈ H ₁₀ O	0.783		0.844
26	14.21	Phenol, 4-ethyl-	C ₈ H ₁₀ O	1.201		1.958
27	14.42	Phenol, 3-methoxy-2-methyl-	C ₈ H ₁₀ O ₂	0.464		0.611
28	14.56	2-Nonenal	C ₉ H ₁₆ O	1.831	3.787	
29	14.66	1,4-Benzenediol, 2,5-dimethyl-	C ₈ H ₁₀ O ₂	0.731		1.042
30	14.87	Hydroquinone	C ₆ H ₆ O ₂	4.435		7.673
31	15.03	1,4:3,6-Dianhydro- α -D-glucopyranose	C ₆ H ₈ O ₄	2.823	6.813	
32	15.09	Benzofuran, 2,3-dihydro-	C ₈ H ₈ O	2.801		4.563
33	15.2	2-n-Heptylfuran	C ₁₁ H ₁₈ O	0.612		1.008
34	15.38	Phenol, 2-ethyl-4-methyl-	C ₉ H ₁₂ O	0.338		0.473
35	15.84	4-Methoxybenzene-1,2-diol	C ₇ H ₈ O ₃	2.115		4.724
36	16.04	Phenol, 4-ethyl-2-methoxy-	C ₉ H ₁₂ O ₂	0.786		1.357
37	16.16	1,4-benzenediol, diacetate	C ₁₀ H ₁₀ O ₄	0.538		1.281
38	16.29	3,5-Dihydroxytoluene	C ₇ H ₈ O ₂	1.127		2.397
39	16.59	2-Cyclohexen-1-one, 3-methyl-6-(1-methylethylidene)-	C ₁₀ H ₁₄ O	1.240		3.014
40	17.17	Biphenyl	C ₁₂ H ₁₀	6.583		12.31
41	17.62	2,3-Dimethylhydroquinone	C ₈ H ₁₀ O ₂	1.267		1.663
42	17.91	Benzaldehyde, 3-hydroxy-4-methoxy-	C ₈ H ₈ O ₃	1.011		1.496
43	18.13	1,3-Di-O-acetyl- α - β -D-ribofuranose	C ₉ H ₁₄ O ₇	0.218	3.398	
44	18.24	1,3-Benzenediol, 4-ethyl-	C ₈ H ₁₀ O ₂	0.400		0.993
45	18.47	Benzenemethanol, 3,4-dimethoxy-	C ₉ H ₁₂ O ₃	1.781		2.867
46	19.09	1,2-Benzenediol, 4-(1,1-dimethylethyl)-	C ₁₀ H ₁₄ O ₂	0.520		0.566
47	19.37	Phenol, 2,4,6-tris(1-methylethyl)-	C ₁₅ H ₂₄ O	0.380		3.206
48	19.49	1,6-anhydro- β -D-glucopyranose (levoglucosan)	C ₆ H ₁₀ O ₅	3.835	8.297	
49	19.53	Benzene, 1,2,3-trimethoxy-5-methyl-	C ₁₀ H ₁₄ O ₃	0.520		1.837
50	19.67	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	C ₁₀ H ₁₂ O ₃	0.383		0.752
51	19.82	D-Mannoheptulose	C ₇ H ₁₄ O ₇	1.232	3.987	
52	19.88	Phenol, 2-ethoxy-4-(2-propenyl)-	C ₁₁ H ₁₄ O ₂	0.167		0.34
53	20.03	Benzenemethanol, 2-(phenylmethyl)-	C ₁₄ H ₁₄ O	0.586		0.83
54	20.23	Benzenepropanoic acid, 4-hydroxy-, methyl ester	C ₁₀ H ₁₂ O ₃	0.365		0.582
55	21.11	2,5-Dimethoxy-4-ethylbenzaldehyde	C ₁₁ H ₁₄ O ₃	0.621		0.637
56	21.7	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	C ₁₁ H ₁₄ O ₃	0.586		1.17
57	22.13	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	C ₁₀ H ₁₂ O ₄	1.123		0.981
58	22.54	Desaspidinol	C ₁₁ H ₁₄ O ₄	0.936		0.799
59	23.15	4'-Phenylpropiophenone	C ₁₅ H ₁₄ O	0.117		0.234
60	24.46	n-Hexadecanoic acid	C ₁₆ H ₃₂ O ₂	0.216		0.979
61	24.52	2H-1-Benzopyran-2-one, 3,5,7-trihydroxy-	C ₉ H ₆ O ₅	0.663	1.868	
62	26.27	Linoleic acid ethyl ester	C ₂₀ H ₃₆ O ₂	0.563		1.276
63	28.63	Hexanedioic acid, bis(2-ethylhexyl) ester	C ₂₂ H ₄₂ O ₄	0.101		0.187
64	31.47	Phenol, 4,4'-methylenebis, [2,6-dimethoxy-	C ₁₇ H ₂₀ O ₆	0.128		0.371

Light oil can be considered as a mixture of several macro-families. These macro-families may include polycyclic aromatic hydrocarbons (PAHs), phenols, esters, furan derivatives, aliphatic hydrocarbons, some acids, benzenemethanol, etc. Polycyclic aromatic hydrocarbons are about 12% of the total oil, which mainly contains

biphenyl. Phenols presented in the light oil are about 46%, which are made up of phenol, diphenols, methyl phenols, ethyl phenols, and methoxy phenols. As four main phenols, hydroquinone, phenol, 4-methoxybenzene-1,2-diol and 4-methylphenol represented 7.7%, 5.6%, 4.7% and 4.1% of the light oil, respectively. The esters

presented in the oil are about 5%, which mainly contain hexadecanoic acid ester, linoleic acid ethyl ester, benzenepropanoic acid ester and butanoic acid ester. Furan derivatives represented about 13%, which are mostly composed of 2-furanethanol, dihydrobenzofuran, heptyl furan and methyl furan. Aliphatic hydrocarbons presented in the oil are mainly composed of 1,1'-ethylidenebis- cyclopentane. Acids presented in the light oil are long chain acids with an aliphatic group, for example, n-hexadecanoic acid.

The water fraction residue of the emulsion phase extracted by mix-solvent extraction mainly contains hydroxy-butanedioic acid diethyl ester and a lot of anhydrosugars such as levoglucosan, glucopyranose, and ribopyranose, etc. After separation of bio-oil emulsion phase, the percent of hydroxy-butanedioic acid diethyl ester in water is over 46%, suggesting that the mixed solvent has very high selectivity, and could be used to purify special chemical from bio-oils.

3.3 Thermal gravimetric analysis of bio-oil fractions

This light oil fraction separated from bio-oil emulsion phase has a lighter color and lower density than the heavy oil, and burns easily. Its higher heating value is about 21-24 MJ/kg. To further characterize combustion of light oil, a set of experiments of light oil combustion in air was tested with a thermal gravimeter. The comparison of evaporation and combustion for light oil, heavy oil and gasoline is shown in Figure 5. The results show that almost no carbon residue was left after light oil combustion, but heavy oil combustion results in over 25% carbon residue. The temperature of thermal weight

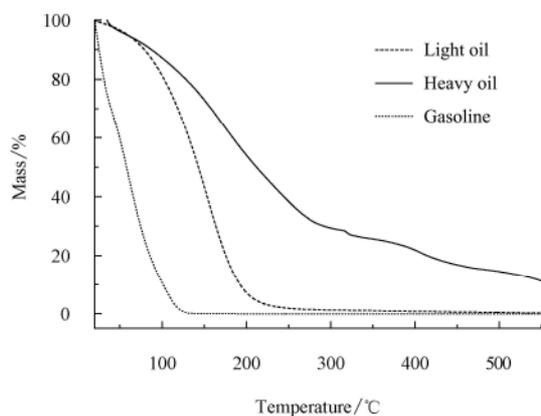


Figure 5 TG comparison of light oil, heavy oil with gasoline at 20 mL/min (air), 20°C/min

loss in air at heating rate of 20°C/min is 30-120°C for gasoline, 100-200°C for light oil and 100-300°C for heavy oil, suggesting that light oil can be used as a clean alternative fuel.

4 Conclusions

The two-step fractionation procedure is an effective method to separate bio-oil to light oil, heavy oil, and chemicals. The light oil, with no combustion residue and a much lower temperature of evaporation and combustion, is a good alternative fuel for engines. Hydroxy-butanedioic acid diethyl ester in water was found to be the major chemical in the water fraction, suggesting that the mixed solvent used has very high selectivity.

Acknowledgements

This work was supported by University of Minnesota IREE and Center for Biorefining and China Ministry of Education PCSIRT Program (IRT0540), Hubei Provincial Department of Education of China (No.Q200715004) and Hubei Provincial Natural Science Foundation of China (No.2007ABA253).

[References]

- [1] Demirbas A. Biomass resource facilities and biomass conversion processing for fuels and chemicals. *Energy Conversion and Management*, 2001; 42: 1357–1378.
- [2] Klass D L. *Biomass for renewable energy, fuels and chemicals*. San Diego, US, Academic press. 1998.
- [3] *Microwave Pyrolysis of Biomass*. Michigan: St Joseph. 2006.
- [4] Menéndez J A, Domínguez A, Inguanzo M, Pis J J. Microwave pyrolysis of sewage sludge: analysis of the gas fraction. *Journal of Analytical and Applied Pyrolysis*, 2004; 71(2): 657–667.
- [5] Domínguez A, Menéndez J A, Inguanzo M, Pis J J. Investigations into the characteristics of oils produced from microwave pyrolysis of sewage sludge. *Fuel Processing Technology*, 2005; 86(9): 1007–1020.
- [6] Domínguez A, Menéndez J A, Inguanzo M, Pís J J. Production of bio-fuels by high temperature pyrolysis of sewage sludge using conventional and microwave heating. *Bioresource Technology*, 2006; 97(10): 1185–1193.
- [7] National Research Council (U.S.). Commission on Engineering and Technical Systems. Committee on Microwave Processing of Materials: *An Emerging Industrial*

- Technology. Microwave Processing of Materials*. Washington, D.C.: National Academy Press. 1994.
- [8] Czernik S, Bridgwater A V. Overview of applications of biomass fast pyrolysis oil. *Energy & Fuels*, 2004; 18(2): 590–598.
- [9] Lei H, Ren S, Julson J. The effects of reaction temperature and time and particle size of corn stover on microwave pyrolysis. *Energy & Fuels*, 2009; 23: 3254–3261.
- [10] Czernik S, Bridgwater A V. Overview of application of biomass fast pyrolysis oil. *Energy & Fuels*, 2004; 18: 580–598.
- [11] Chiamonti D, Bonini M, Fratini E, Tondi G, Gartner K, Bridgwater A V, et al. Development of emulsion from biomass pyrolysis liquid and diesel and their use in engines – Part 1: emulsion production. *Biomass and Bioenergy*, 2003; 25: 85–89.
- [12] Chiamonti D, Bonini M, Fratini E, Tondi G, Gartner K, Bridgwater A V, et al. Development of emulsion from biomass pyrolysis liquid and diesel and their use in engines – Part 2: Tests in diesel engines. *Biomass and Bioenergy*, 2003; 25: 101–111.
- [13] Bridgwater A V. Production of high-grade fuels and chemicals from catalytic pyrolysis of biomass. *Catalysis Today*, 1996; 29: 285–295.
- [14] Bridgwater A V. Catalysis in thermal biomass conversion. *Applied Catalysis. A, General*, 1994; 116: 5–47.
- [15] Williams P T, Horne P A. Characterization of oils from the fluidized bed pyrolysis of biomass with zeolite catalyst upgrading. *Biomass Bioenergy*, 1994; 7: 223–226.
- [16] Mohan D, Pittman C U, Steele P H. Pyrolysis of wood/biomass for bio-oil: A critical review. *Energy & Fuels*, 2006; 20: 848–889.
- [17] Friedl A, Padouvas E, Rotter H. Prediction of heating values of biomass fuel from elemental composition. *Analytica Chimica Acta*, 2005; 544(1-2): 191–198.
- [18] Guan G F, Xu C, Wan H, Yao H Q. Salting-out effect on complexation extraction of monocarboxylic acids. *Journal of Chemical Engineering of Chinese Universities*, 2006; 20(4): 657–660.