

# Selective Extraction of Bio-oil from Hydrothermal Liquefaction of *Salix psammophila* by Organic Solvents with Different Polarities through Multistep Extraction Separation

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Bio-oil obtained from hydrothermal liquefaction of *Salix psammophila* is a very complicated mixture with some highly valued chemicals. In order to separate the chemicals from bio-oil, solvent extraction using nine solvents with different polarities were investigated in detail. The bio-oil extraction yield of the nine solvents were from high to low: tetrahydrofuran > toluene > ethyl acetate > acetone > ether > methylene chloride > methanol > petroleum ether > n-hexane. Based on their extraction yield, an efficient solvent combination of n-hexane, ethyl acetate, and tetrahydrofuran was used to separate the bio-oil through multistep extraction into three parts: light oil (26.13%), mid-weight oil (54.19%), and heavy oil (19.68%). These fractions were characterized by gas chromatography-mass spectrometry, Fourier transform infrared spectroscopy, <sup>1</sup>H nuclear magnetic resonance spectroscopy, and thermogravimetric analysis. The results showed that most of the highly valued chemicals were contained in the light oil; the mid-weight oil consisted of aromatic oligomer derived from the decomposition of lignin, which could be a promising candidate for partial substitute for petroleum-asphalt binder; the heavy oil was rich in alkanes

*Keywords:* Bio-oil; Multistep solvent extraction; Hydrothermal liquefaction; Separation

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## INTRODUCTION

Bio-fuels and bio-chemicals are becoming more and more attractive and competitive as complementary to or substitutions for petroleum-based products, due to their economic and environmental benefits (Demirbas 2008). Various technologies, including pyrolysis (Beis *et al.* 2010), gasification (Aznar *et al.* 2006), and mechanical extraction with esterification (McKendry 2002), have been used to convert biomass to bio-energy and bio-chemicals. Compared with the low product yield and high energy consumption of former bio-refining technologies, hydrothermal liquefaction (HTL) is a promising third-generation method for biomass utilization (Ross *et al.* 2010).

To improve its application and industrialization, various separation methods, such as distillation (Zhang *et al.* 2013), adsorption using ion-exchange resins (Gaikar and Anasthas 2002), and micro emulsion liquid membrane separation (Wiencek and Qutubuddin 1992), have been used either to obtain useful chemicals from bio-oil or as a tool to analyze the bio-oil (Oasmaa *et al.* 2003; Guo *et al.* 2013). Solvent extraction is a highly efficient way to separate different fractions from bio-oil. In previous studies,

various organic solvents were used to extract phenols from HTL products, such as pentane (Putun *et al.* 1999), tetrahydrofuran (Li *et al.* 2013a), acetone (Zou *et al.* 2009), toluene, methanol, diethyl ether, n-hexane, and dichloromethane (Oasmaa *et al.* 2003; Garcia-Perez *et al.* 2007; Sukhbaatar *et al.* 2009; Javaid *et al.* 2010). Li *et al.* (2013b) extracted 12.7 wt% levoglucosan from bio-oil using water. However, the macromolecular oligomer of coniferyl, synapyl, and p-coumaryl alcohols hindered further separation and application of bio-oil (Kim *et al.* 2010). The use of the other techniques also has been limited as a result of the presence of large amounts of medium molecular weight compounds ( $500 < M_n < 3000$ ) in pyrolysis oil (Mahfud *et al.* 2008). These compounds are known to cause severe pore blocking of resins and membranes, resulting in a rapid drop in performance (Bridgwater *et al.* 1999). However, these sticky medium-mass molecules can be promising candidates for partial replacement for petroleum-asphalt binder (Fini *et al.* 2011). Improving the solvent extraction efficiency for the separation of medium molecular compounds (*i.e.*, oligomers) from highly valued low-molecular-weight chemicals (*i.e.*, 2-cyclopenten-1-one, 2-methyl-, phenol, 2-methoxy-, and phenol, 2,6-dimethoxy-) is important for both direct application and further separation of bio-oil.

In the present study, a novel combination of solvents was selected to sequentially extract and separate bio-oil into three fractions. These three bio-oil fractions with two additional intermediate fractions were characterized with gas chromatography-mass spectrometry (GC-MS), Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance spectroscopy (NMR), and thermogravimetric analysis (TGA).

In order to choose the appropriate solvent combination, the extraction yield and the composition of bio-oil fraction were evaluated by using nine organic solvents with different polarities (petroleum ether, n-hexane, toluene, ether, methylene chloride, tetrahydrofuran, ethyl acetate, methanol, and acetone). The main objective of the present work was to determine a facile and efficient solvent combination with multistep extraction to enhance the separation and application of bio-oil, based on the study of nine organic solvents.

## EXPERIMENTAL

### Materials

The bio-oil used in the experiments was obtained from Shanghai Fuhuan Bioenergy Co. Ltd. *Salix psammophila* (barren-ground willow) branches, which were used as the raw materials, were obtained from the sandy land of Xilinguole in Inner Mongolia, northern China. *Salix psammophila* is planted widely to prevent wind erosion and control desertification. In order to maintain a benign ecological system, the systematic cutting and curing of the shrub is necessary, producing a large amount of SP branch residues. According to a previous study (Li *et al.* 2013a), the raw material had a low content of moisture (8.9%) and ash (1.60%) and a high content of volatile matter (79.78%). The cellulose, hemicellulose, and lignin contents in volatile matter were 55.45, 18.89, and 25.89%, respectively. The pilot-scale HTL was operated at 300 °C and 13 MPa for 30 min in an air atmosphere. The bio-oil in this study was extracted from bio-crude, and bio-crude was the solid phase of the HTL product after filtering through a steel strainer with an average pore size of 0.8 μm. Nine organic solvents with different polarities (Table 1) were used to extract the bio-oil. Solvent polarity was defined as the overall solvation capability for reactants and activated complexes as well as for

molecules in the ground and excited states, and was an solvation polarizability expression of refractive index (Katritzky *et al.* 2004).

**Table 1.** Polarity of Solvents Used for Extraction

Solvent	PE	HEX	TL	Ether	DCM	THF	EAC	DMK	MeOH
Polarity	0.01	0.1	2.4	2.7	3.4	4.2	4.3	5.4	6.6
PE: petroleum ether (60-90); HEX: n-Hexane; TL: toluene; DCM: dichloromethane; THF: tetrahydrofuran; EAC: ethyl acetate; DMK: acetone; MeOH: methanol									

## Methods

### *Single solvent extraction*

Three-gram samples of bio-crudes were separately extracted using nine kinds of solvents (50 mL) with different polarities. The extraction was conducted under ultrasonic irradiation (USI) in an ice water bath for 20 min, followed by filtration with a Buchner funnel filtration system under vacuum. The organic filtrate was collected, and the filtrate's water was removed with anhydrous sodium sulfate. The organic filtrate was then evaporated under reduced pressure in a rotary evaporator to completely remove the solvent. The substance left was considered bio-oil.

The extractability of bio-oil was calculated with the following equation:

$$\text{Extractability of Bio - oil} = \frac{\text{mass of Bio - oil}}{\text{mass of Bio - crude}} \times 100\% \quad (1)$$

The extraction with each solvent was conducted as exhaustively as possible to obtain extracts 1 through 9 (*i.e.*, E1-E9). All of the experiments were conducted three times.

### *Multistep solvent extraction*

Three-gram samples of bio-crudes were extracted with 50 mL of tetrahydrofuran (THF) under USI for 20 min and then filtered. The extraction and filtration procedures were repeated twice to ensure that the extraction was as exhaustive as possible. The remnants from the filter were considered residue. The organic filtrate was evaporated to completely remove the solvent, and THF-extracted oil (TEO) was obtained. The TEO was then extracted with ethyl acetate (EAC) through the same procedure as described in the previous paragraph, in order to obtain the EAC-insoluble solid (*i.e.*, heavy oil, HO) and the EAC-extracted oil (EEO). The EEO was further extracted by n-hexane to get the n-hexane-insoluble solid (*i.e.*, mid-weight oil, MO) and the n-hexane-extracted oil (*i.e.*, light oil, LO).

### *Product analysis*

The compositions of the bio-oil extracts (E1-E9) and five fractions (LO, MO, HO, EEO, and TEO) were analyzed with an Agilent 6890/5973 GC-MS (Agilent, USA) equipped with an HP-5 MS capillary column (5% phenyl and 95% dimethylpolysiloxane, 30 mm × 0.25 mm × 0.25 μm). High purity helium was used as the carrier gas with a flow rate of 1 cm<sup>3</sup>/min<sup>-1</sup>. A total of 1 μL of bio-oil solution (0.05 g/10 mL solvent) was injected into the column.

The GC oven temperature was held at 50 °C for 2 min and then programmed to reach a temperature of 260 °C at a heating rate of 5 °C/min. The temperature of the injector and detector was set at 280 °C. Data were collected and analyzed using MSD ChemStation E.02 with Wiley mass spectra library. Semi-quantitative analyses were performed according to the peak area of each compound in each extract.

The FTIR spectra of the five bio-oil fractions were obtained from potassium bromide (KBr) pellets using a NEXUS 470 FTIR ESP spectrometer (Thermo, USA) in the wavenumber of 4000 and 400  $\text{cm}^{-1}$ .

The chemical structures of the five bio-oil fractions were also analyzed using hydrogen 1 ( $^1\text{H}$ ) NMR. The  $^1\text{H}$  NMR spectra were recorded by a VNMRS-500 MHz (Agilent, USA), using ~70 mg oil samples dissolved in 450  $\mu\text{L}$  of deuterated chloroform. The operation conditions were: pulse delay of 1 s, spectral width of 8012.8 Hz, and 65 scans. All experiments were conducted at 25 °C.

The thermal characteristics of the bio-oil samples were analysed with a Pyris 1 thermogravimetric analyser (Perkin-Elmer, USA). Bio-oil samples of about 15 mg were heated from to 600 °C at a constant heating rate of 10 °C/min and nitrogen gas flow rate of 20 mL/min.

## RESULTS AND DISCUSSION

### Single Solvent Extraction

Figure 1 shows a graphic expression of the bio-oil extraction yield variations with different solvents. It is obvious from this figure that the oil yield differed greatly with the polarity of the solvents. The highest yield (45%) of oil extraction was obtained by using THF as the extraction solvent. Toluene also had high extraction yield on bio-oil. Ethyl acetate, acetone, dichloromethane, ether, and methanol extracted nearly 30% bio-oil from the bio-crude, while n-hexane only had an extraction yield of 8.27%.

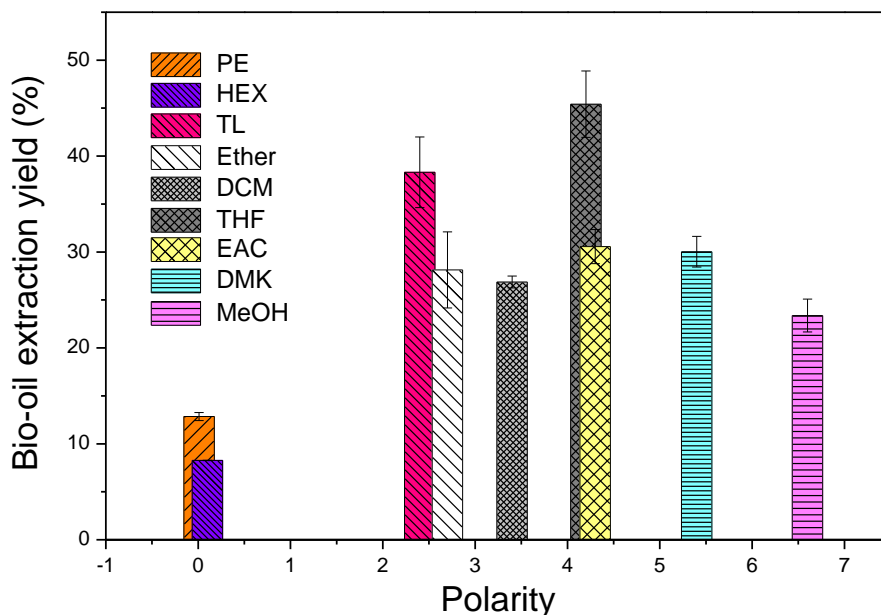


Fig. 1. Bio-oil extraction yields of solvents with different polarity

The yield of extracted bio-oil did not vary linearly with the polarity of the solvent, but fluctuated up and down, creating mountain-like peaks, indicating that the bio-oil was rich in both high and low-polarity compounds. Therefore, solvent extraction not only can be considered as an efficient way to separate highly valued chemicals with oligomer, but also as a promising method to separate different chemical families from bio-oil.

The extracted oil samples were analyzed using GC-MS. The 81 main organic compounds detected from the bio-oil obtained through solvent extraction were classified into 8 groups (*i.e.*, ketones, phenolics, alkoxyphenolics, indanones, indoles, esters, fatty acids, and alkanes). In previous studies, identification and grouping of the compounds in bio-oil was performed by GC-MS (Marsman *et al.* 2007; Sfetsas *et al.* 2011).

As can be seen from Table 2, petroleum ether (PE) was demonstrated to be an effective solvent for extracting alkanes from the bio-crude, which has also been reported in a study with bio-oil derived from stalks (Zhao *et al.* 2007). The used PE 60-90 was produced by Sinopharm Chemical Reagent Co., Ltd, and was the mixture of pentane and hexane. Compared to hexane, the higher recovery of oil extractability showed by PE (60-90) was attributed to the addition of pentane. The length range of the alkanes was from C16 to C24. Lu *et al.* (2012) suggested that the alkanes may originally exist in the biomass as waxes rather than as products from the biomass chemical conversion. Wang *et al.* (2011) also believed that the formation of alkanes in the oil can be mainly attributed to components (triglycerides and hydrocarbons) that are present in the extractives of biomass.

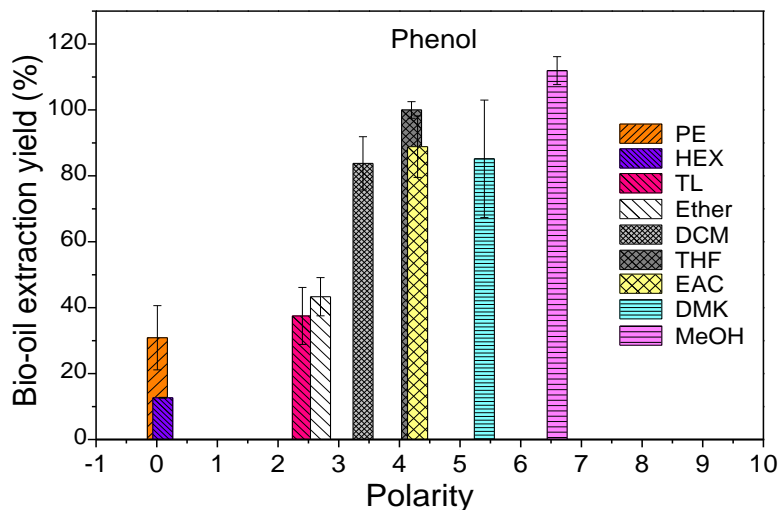
Ketones, phenolics, and alkoxyphenolics were found as the main decomposition products of the biomass HTL. According to Table 2, ketones and phenolic compounds were easier to extract by solvents with high polarity, such as THF, EAC, acetone, and methanol. Ketones and phenolics are polar compounds, and their extraction efficiency increased with increased extraction solvent polarity, which is in accordance with the principle of dissolution in a similar material structure. The multiple-point external standard method was also used with the GC-MS SIM scan mode. The quantitative analysis results of phenol and phenol, 2-methoxy- shown in Fig. 2 are similar to the results of phenolics in Table 2, which were calculated by peak area.

**Table 2.** Extraction of the Main Chemical Families with Selected Solvent

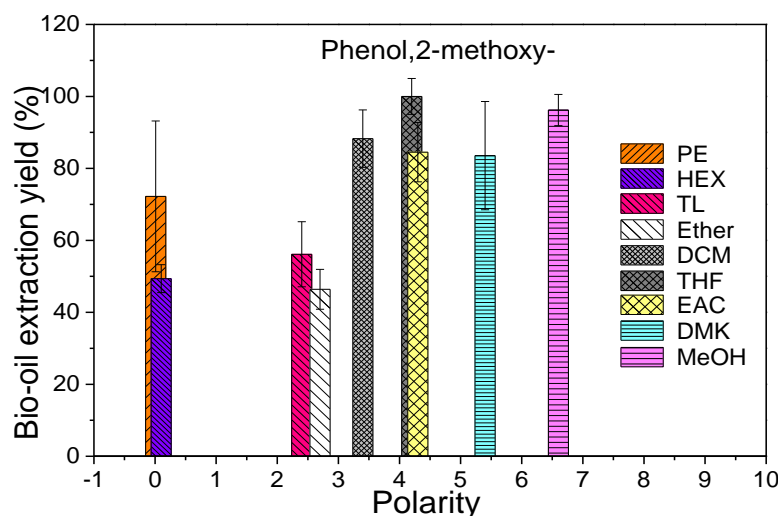
Chemical Family	Relative extraction percentage via various solvents (%)								
	PE	HEX	TL	Ether	DCM	THF	EAC	DMK	MeOH
Ketones	50.2	40.2	50.4	59.5	85.0	100.0	89.4	94.5	94.1
Phenolics	68.2	45.8	51.9	65.9	70.9	91.4	88.9	90.1	100.0
Alkoxyphenolics	80.9	67.5	72.4	59.0	83.3	100.0	90.1	99.2	89.8
Indanones	59.8	43.3	29.4	34.5	50.6	74.7	100.0	92.6	90.3
Indoles	100.0	76.9	50.3	34.2	34.2	56.2	60.1	61.9	55.7
Esters	100.0	50.0	31.0	35.1	48.0	36.2	18.3	45.4	45.7
Fatty acids	100.0	30.4	24.7	35.4	54.6	23.0	19.2	26.8	27.6
Alkanes	100.0	55.1	70.5	71.3	60.1	74.2	44.7	30.9	6.2

PE: petroleum ether (60-90); HEX: n-Hexane; TL: toluene; DCM: dichloromethane; THF: tetrahydrofuran; EAC: ethyl acetate; DMK: acetone; MeOH: methanol  
 Note: The peak areas of the main chemical families were compared after a normalizing process

However, the GC-MS results in Table 2 did not match the total bio-oil extraction yield results shown in Fig. 1. For example, toluene showed a higher extraction yield than PE, but according to the GC-MS analysis, PE actually extracted more chemicals. Other researchers (Tsai *et al.* 2007; Zhou *et al.* 2012) have also reported that there were significantly more organic compounds than detected in bio-oil. One possible explanation may be that the extracted oil samples had many substances that were not GC-amenable, which greatly affected the oil yield.



a



b

**Fig. 2.** Extraction capabilities of solvents on main chemicals of bio-oil by quantitative analysis. (a) phenol and (b) phenol,2-methoxy-

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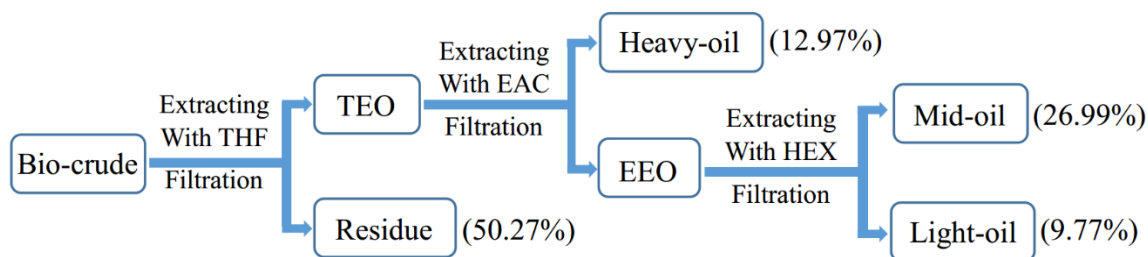
significantly more organic compounds than detected in bio-oil. One possible explanation may be that the extracted oil samples had many substances which were not GC-amenable, which greatly affected the oil yield.

Gerdes *et al.* (2002) carried out a quantitative analysis of bio-oil and found that crude bio-oil consisted of approximately 25% high molecular lignin compounds. Oasamaa *et al.* (2010) also confirmed the presence of high molecular mass lignin with a content of 20%. It was concluded that, in order to analyze the components of oil fractions, it was better to separate the bio-oil into several fractions by using several solvents with different polarities in the proper sequence.

### Multistep Extraction and Subsequent Analysis

According to the results from Fig. 1, n-hexane and THF had the lowest (8.27 %) and highest (45.41 %) bio-oil extraction rate, respectively. The fraction that was extracted by THF instead of n-hexane may have been the high molecule compounds, such as aromatic oligomers. Lu *et al.* (2012) found that the intertwisting between the alkanes and some n-hexane-insoluble species in the bio-crude could make it difficult to extract the alkanes with n-hexane. In order to decrease the effect of the intertwisting and to extract as much useful substance as possible, THF was chosen as the first extraction solvent. Ethyl acetate was chosen as an extraction solvent in the multistep extraction for its similar polarity with THF, but lower bio-oil extraction rate. The THF-extracted oil (TEO) was extracted by EAC to get the EAC-insoluble solid (*i.e.*, HO) and the EAC-extracted oil (EEO). In last position, n-hexane was used to extract from EEO, separating highly valued chemicals of n-hexane-extracted oil (*i.e.*, LO) from macromolecule oligomer of the n-hexane-insoluble solid (*i.e.*, MO). Hence the solvent combination of n-hexane, EAC, and THF was selected to sequentially extract and separate bio-oil to enhance the analysis and direct application of bio-oil.

As shown in Fig. 3, bio-crude from *Salix psammophila* was divided into light oil (12.97 %), mid-weight oil (26.99 %), heavy oil (9.77 %), and residue (50.27 %) using multistep extraction. The actual appearance of the three oil types and their solutions are shown in Fig. 4. The heavy oil looked like carbon black and was easy to grind into a fine powder. The mid-weight oil was also black, but its appearance was more like petroleum asphalt, which is tough and lustrous; it became sticky and flexible at high temperature, as does asphalt. By contrast, light oil was more like grease, and so red, soft, and sticky at room temperature. The appearances of three oil solutions were also quite different; light oil in n-hexane was light yellow, mid-weight oil was orange red, and the heavy oil in THF looked black and thick.

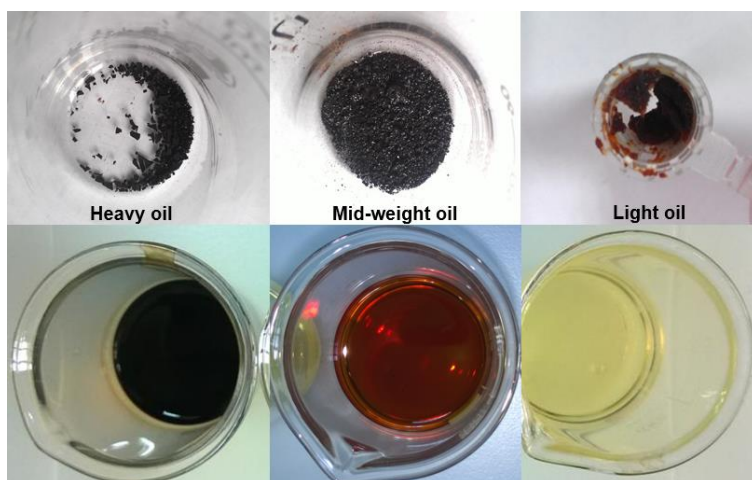


**Fig. 3.** The multistep extraction procedure and fraction proportion in bio-crude (EEO: EAC-extracted oil; TEO: THF-extracted oil)

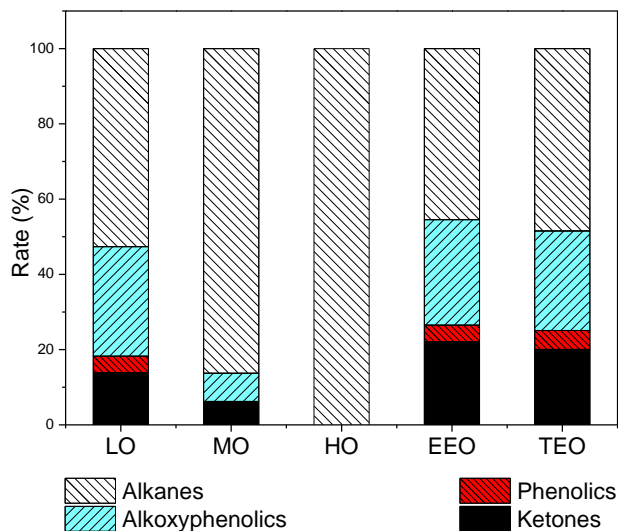
Analyses by the GC-MS, FTIR, NMR, and TG methods were conducted to investigate the chemicals and main group structure of the oil samples.

#### GC-MS analysis of bio-oil samples from multistep extraction

Through multistep extraction, five oil samples were obtained: light oil, mid-weight oil, heavy oil, EAC-extracted oil, and THF-extracted oil. All five samples were analyzed by GC-MS. Four main chemical families, to include ketones, phenolics, alkoxyphenolics, and alkanes were compared with the results of the previous GC-MS analysis to investigate the content differences. As shown in Figs. 5 and 6, most of the highly valued low-molecular-weight chemicals were contained in the light oil instead of the mid-weight oil or the heavy oil. According to the GC-MS results, there were very few highly valued low-molecular-weight chemicals in the heavy oil, and only a few ketones and alkoxyphenolics in the mid-weight oil.

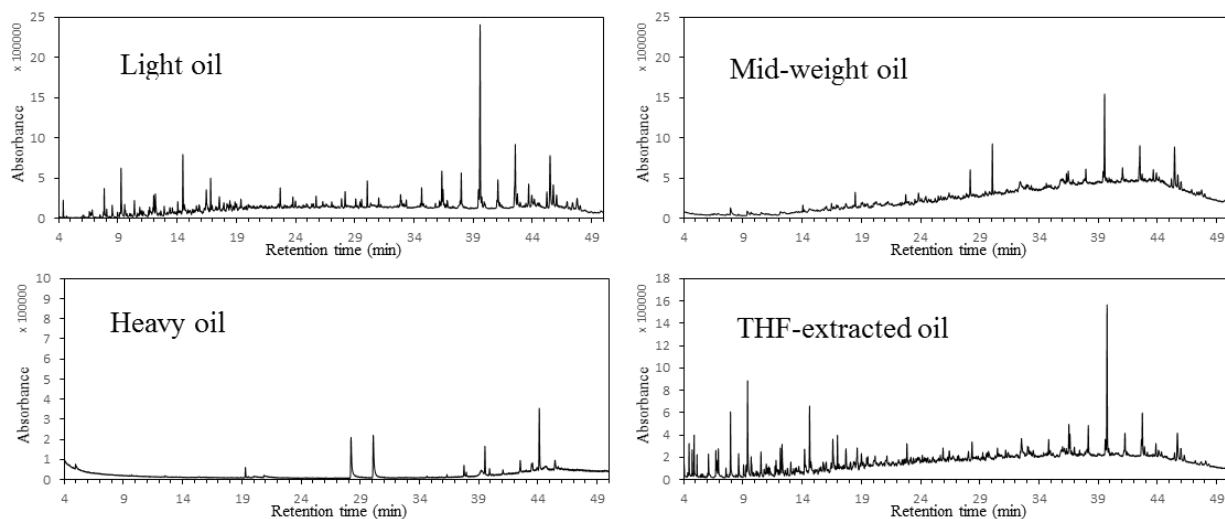


**Fig. 4.** Appearance of heavy oil, mid-weight oil, and light oil and their corresponding solutions



**Fig. 5.** Different group components detected in five oil samples (LO: Light oil; MO: Mid-weight oil; HO: Heavy oil; EEO: EAC-extracted oil; TEO: THF-extracted oil)



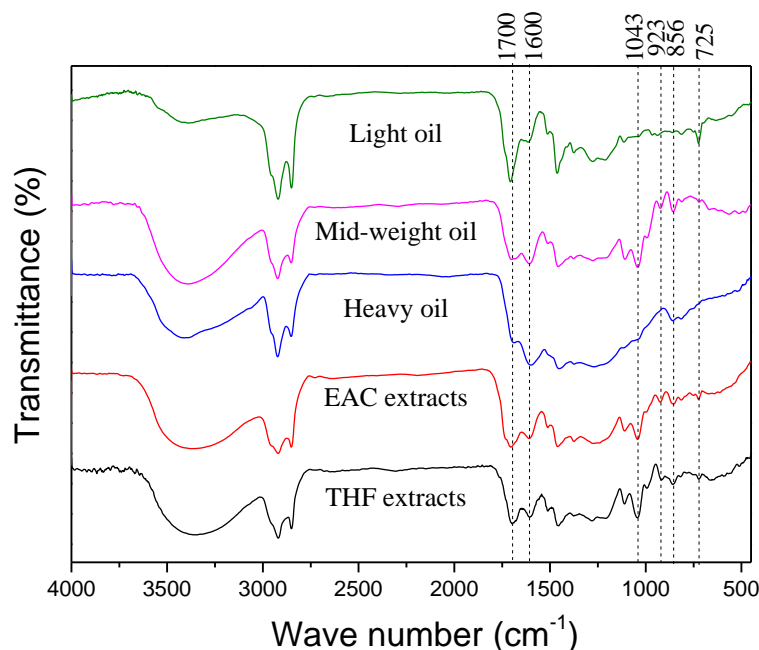


**Fig. 6.** GC-MS total ion chromatograms of bio-oil samples

*FTIR analysis of bio-oil samples from multistep extraction*

The FTIR spectra of the bio-oil samples obtained under different extraction conditions are shown in Fig. 7, and the peaks of the functional groups in the bio-oil sample are listed in Table 3.

Compared with the five spectra in Fig. 7, an interesting comparison can be found at 1600 and 1700  $\text{cm}^{-1}$ ; the peak at 1600  $\text{cm}^{-1}$  was stronger than that at 1700  $\text{cm}^{-1}$  only in the spectra of heavy oil and mid-weight oil, meaning that these two heavy fractions had more alkenes or aromatic compounds than other carbonyl compounds, such as mono-alkyl ester, ketones, aldehydes, and carboxylic acids. The low-oxygen-group characteristics of heavy oil allowed for lower acidity and greater stability.



**Fig. 7.** FTIR spectra of bio-oil fractions through multistep extraction

Another interesting comparison was found at 1043 and 1100  $\text{cm}^{-1}$ . This C–O stretching vibration was found in both EEO and TEO samples, but spectra changed in the heavy oil, mid-weight oil, and light oil fractions. Obvious peaks were found only in the spectra of the mid-weight oil, indicating that the main C–O bond structure was in the mid-weight oil. These C–O chemical bonds may come from phenolics and partial decomposed lignin.

**Table 3.** FTIR Analysis of Bio-oil Functional Groups

Frequency range ( $\text{cm}^{-1}$ )	Group	Class of compound
3350	O–H stretching	Polymeric O–H,
2923, 2848	CH, CH <sub>2</sub> stretching, C–H stretching	Alkanes
1700	C=O stretching	mono-alkyl ester, Ketones, aldehydes, carboxylic acids
1602	C=C stretching	Alkenes, Aromatic compounds
1282, 1205	C–O–C stretching	Phenol, esters, ethers
1110, 1043	C–O stretching	Phenol, esters, ethers
923, 856, 809, 723	C–H in-plane bending	Aromatic compounds

The peak at 923  $\text{cm}^{-1}$  of the C–H in-plane bending (indicating aromatic compounds) disappeared in the spectra of the heavy oil. Some detail differences in the 650 to 900  $\text{cm}^{-1}$  area showed the lack of aromatic compounds in the heavy oil.

#### *<sup>1</sup>H NMR analysis of bio-oil samples from multistep extraction*

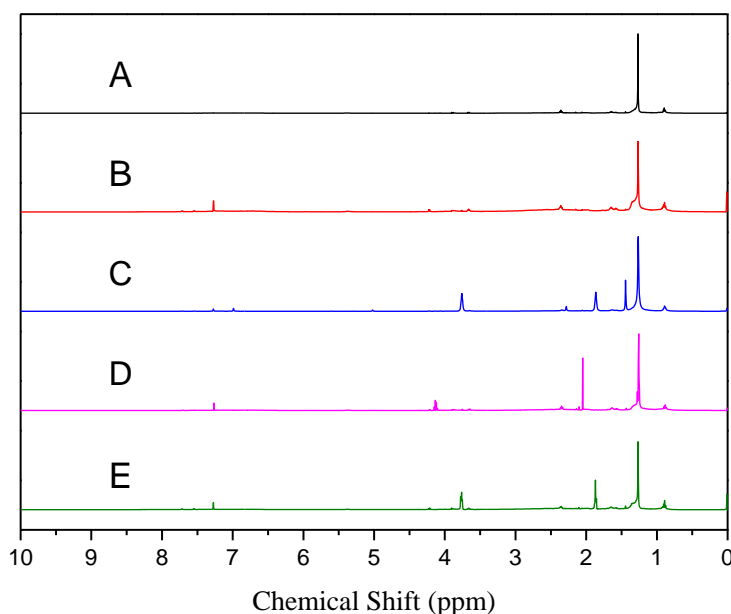
The proton NMR spectra of the five different bio-oil samples are shown in Fig. 8, and the five different bio-oil samples spectra on a quantitative percentage basis are given in Table 4. The <sup>1</sup>H NMR spectra could be divided into seven regions as illustrated in Table 4 based on the chemical shifts of specific proton types.

**Table 4.** Percentage of Hydrogen Based on <sup>1</sup>H NMR Analysis of Bio-oil Samples, Grouped according to Chemical Shift Range

Chemical shift	Type of hydrogen	*Hydrogen content w/%				
		TEO	EEO	HO	MO	LO
0-1.5	-CH <sub>3</sub> , -CH <sub>2</sub> -	35.76	44.76	58.07	41.64	58.92
1.5-2.1	-CH <sub>2</sub> -, aliphatic OH	19.42	12.98	13.95	11.54	9.57
2.1-3.1	CH <sub>3</sub> -C=O, CH <sub>3</sub> -Ar, -CH <sub>2</sub> -Ar	11.43	19.70	4.33	24.00	15.41
3.1-4.25	CH <sub>3</sub> -O-, -CH <sub>2</sub> -O-, =CH-O-	12.94	7.89	12.91	8.97	4.41
4.25-6.0	-CH-O-, ArOH, HC=C (nonconjugated)	11.81	3.48	3.54	3.38	3.46
6.0-6.8	HC=C (nonconjugated)	2.31	3.60	0.62	3.75	2.86
6.8-8.12	ArH, HC=C (conjugated)	6.33	7.59	6.58	6.71	5.38

TEO: THF-extracted oil; EEO: EAC-extracted oil; HO: Heavy oil; MO: Mid-weight oil; LO: Light oil  
\* integral area percentage of total integral area

The prominent region of the spectrum (*i.e.*, 0.5 to 1.5 ppm) represents aliphatic protons bonded to carbon atoms. Their mass percent of about 58% in the heavy oil indicated the high aliphatic content. This was consistent with the FTIR result that the heavy oil was rich in alkanes, which may be due to the dominant percentage and aliphatic chain of bio-diesel in the heavy oil. The mass percent of this region in the light oil was also considerable, due to the high extractive capability of n-hexane on alkanes.



**Fig. 8.**  $^1\text{H}$  NMR spectra of bio-oil samples. (A) Light oil, (B) Mid-weight oil, (C) Heavy oil, (D) EAC-extracted oil, and (E) THF-extracted oil

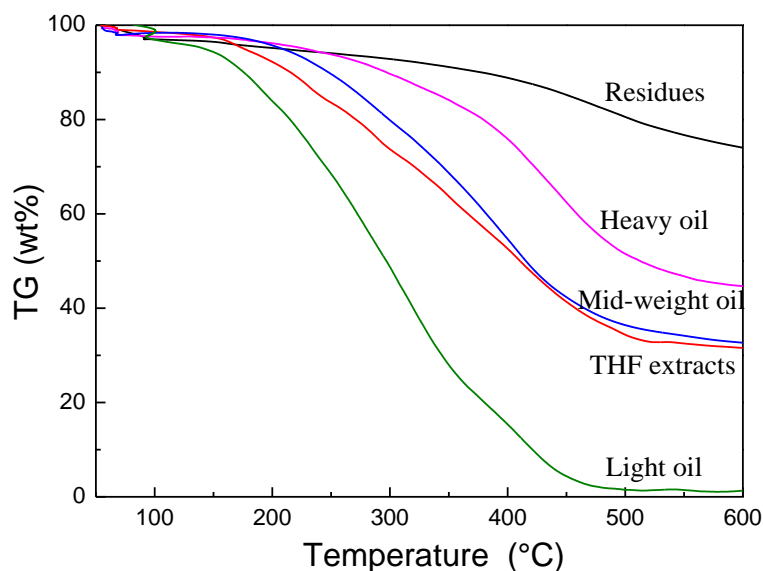
The next significant portion of the  $^1\text{H}$  spectrum was 2.1 to 3.1 ppm, representing the protons attached to the carbon atoms of acetylenic, benzylic, allylic, ester, acid, and carbonyl compounds. Results showed that the mid-weight oil contained a mass of benzylic compounds, which was also consistent with the result of the FTIR analysis that the mid-weight oil may be rich in phenolics or partially decomposed lignin.

In a previous study, Pittman *et al.* (2012) found that the 3.0 to 4.2 ppm range of the  $^1\text{H}$  spectrum was related to the methoxy content. As shown in Fig. 8, although all five samples had peaks in this region, their chemical environments were quite different, which indicated they had different  $-\text{O}-\text{C}-$  structure.

The vinyl protons on the  $\beta$ -carbon of  $\alpha$ ,  $\beta$ -unsaturated acids, aldehydes, and ketones contributed to the increase of  $^1\text{H}$  integrations between 8.12 and 6.8 ppm, a region that also includes aromatic protons.

#### *Thermogravimetric analysis of bio-oil samples from multistep extraction*

The thermal degradation characteristics of bio-oil samples are displayed in Fig. 9 in the form of thermogravimetry (TG) curves.



**Fig. 9.** TG curves of the bio-oil samples heated in nitrogen

According to the experimental procedure, the bio-crude was divided into THF extracts and residues, and the THF extracts was divided into light oil, mid-weight oil, and heavy oil through multistep extraction. The insoluble-tetrahydrofuran fraction (residues) lost weight slowly and lost only 26.4% of its total weight, which indicated that it mainly contained components like anhyrosugars, hydrochar, and high-molecular-mass molecules. The TG curve of THF extracts was a combination of the three oil fractions. The light oil lost weight quite quickly, and almost all evaporated above 500 °C; the results agreed with the GC-MS and FTIR analysis that light oil was mainly contained low-molecular-weight molecule. The mid-weight oil lost weight quicker than the THF extracts because of the light oil fraction in THF extracts. The weight loss of heavy oil was even slower and less, which means the heavy oil had more high-molecular-weight molecules.

## CONCLUSIONS

1. The bio-oil extraction yield of nine solvents with different polarities from high to low were as follows: tetrahydrofuran > toluene > ethyl acetate > acetone > ether > methylene chloride > methanol > petroleum ether > n-hexane.
2. A novel solvent combination of n-hexane, EAC, and THF was selected to sequentially extract and separate the bio-oil into three fractions of different applications, *i.e.*, light oil (26.13%), mid-weight oil (54.19%), and heavy oil (19.68%).
3. Light oil contains low-molecular-weight compounds, which can be used to extract highly valued chemicals such as phenols and cyclopentenones. Mid-weight oil was found to comprise aromatic oligomers, such that it can be a promising candidate for partial substitute for petroleum-asphalt binder. Heavy oil was found to be rich in

alkanes. The current multi-step extraction method provides a potential separation and composition analysis strategy for different types of bio-oil in the future.

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