Fuel properties of bio-oil/bio-diesel mixture characterized by TG, FTIR and ¹H NMR

Jiang Xiaoxiang*, Naoko Ellis**, and Zhong Zhaoping*,†

*Thermoenergy Engineering Research Institute, Southeast University, Nanjing 210096, Jiangsu Province, P. R. China
**Chemical and Biological Engineering, University of British Columbia, 2360 East Mall, Vancouver, V6T 1Z3, Canada*
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Abstract−There has been an increasing interest in alternative fuels made from biomass which is abundant and renewable. Bio-oil and bio-diesel seem to be such promising liquid fuels. Bio-oil produced by fast pyrolysis of biomass is highly viscous, acidic, and has high water content. To overcome these problems as a fuel, a method of emulsifying bio-oil with bio-diesel was performed in the previous paper, and a stable mixture of bio-oil and bio-diesel was successfully prepared. In this paper, several properties of the mixture are discussed by using TG, FTIR and ¹H NMR. The results show us that, compared with crude bio-oil, some properties of bio-oil/bio-diesel mixture such as water content, acid number, viscosity are much improved. The thermal decomposition of the mixture under air/nitrogen is shown using a thermogravimetric analyzer (TGA). Further information about the functional groups is exhibited through Fourier Transform infrared spectrometer (FTIR) and nuclear magnetic spectroscopy (NMR).

Key words: Bio-oil, Bio-diesel, Mixture, FTIR, TG, ¹H NMR

INTRODUCTION

Although fossil fuels such as coal, petroleum and natural gas play a dominant role in the world energy consumption, there's an increasing concern with the environmental issues resulting from the excessive use of fossil fuels. The development of renewable energy sources is of increasing importance. Bio-oil and bio-diesel seem to be such promising liquid fuels.

Bio-oil is the liquid product of fast pyrolysis of biomass. The advantage of bio-oil lies not only as a greenhouse gas neutral energy source, but also as an opportunity to reduce reliance on fossil fuels and to support sustainable forest development. But it is a complex mixture of hundreds of oxygenated organic compounds; this may be due to the depolymerization of the three blocks of biomass. The intricate composition makes bio-oil unstable. To overcome these disadvantages, several physical and chemical bio-oil upgrading technologies, such as catalytic cracking [1-5], hydro-treatment [6-9], blending bio-oils with organic solvents [10-12], emulsification with petroleum diesel [13-15] and steam reforming [16-18], have been tested at a bench scale. Additionally, emulsification of bio-oil with diesel fuel is shown to be an economical and viable fuel choice in diesel engines without the need for much modification [13,15].

Bio-diesel is defined as the mono-alkyl ester derivatives of long chain fatty acids, produced from oil crops, waste cooking oil, or animal fat via a relative simple transesterification process. Bio-diesel is also a renewable fuel. It is environmentally innocuous, safe to handle, and has a relatively high flash point. The characteristics, such as heating value, density, viscosity are comparable to #2 diesel from petroleum. Bio-diesel presents a very promising project of functioning as alternative fuels to fossil diesel. The properties of bio-diesel can be compared favorably with the characteristics required for internal combustion engine fuels [19,20].

In the previous paper, we reported on a successful production of bio-oil and bio-diesel mixture [21]. One of the motivations for this process is to separate the mixture from the high molecular weight compounds in the bio-oil such as pyrolytic lignin, which are undesirable as fuel, yet a promising source for high-value chemicals [22]. The resulting mixtures are characterized based on the mixture stability and fuel properties. It is shown that the mixture's characteristics, such as heating value, density, viscosity, are comparable to #2 diesel from petroleum. In this paper, some other properties of the mixture are discussed by using TG, FTIR and ¹H NMR.

EXPERIMENTAL SECTION

The bio-oil produced from fast pyrolysis of softwood residue was supplied from VTT, Finland. Octanol was used as the emulsifier. All the measurements were made under the following optimal conditions: the initial ratio of bio-oil to bio-diesel of 4 : 6 by volume; the octanol content of 4% by volume; the stirring intensity at 1,200 rpm, the mixing time of 15 min; and the emulsifying temperature at 30 °C. In the previous study [21], the stability of the emulsification was characterized by a parameter S defined as the volume of bio-oil dissolved in a unit volume of bio-diesel. After mixing for 15 min, mixtures were placed in a 100 ml graduated cylinders where S values were recorded against time. For the mixture, quick separation could be observed, and the stratification stopped in about 8 hrs. The upper layer is the mixture of bio-oil and bio-diesel, while the bottom layer is bio-oil rich phase, which contains the higher molecular weight compounds such as pyrolytic lignin. The properties of the upper layer (bio-diesel rich phase) were then characterized. All analysis was repeated at least three times in order to obtain the average. Further details on the mixture preparation are given elsewhere [21].

The water content and the acid number of the emulsion were de-

†To whom correspondence should be addressed.
E-mail: zzhong@seu.edu.cn

termined by Metrohm 794 Basic Titrino. The viscosity of the sample was measured by Advanced Rheometer 2000. Shear rate was 100 l/s, measuring temperature was 25 ℃. The average molecular weight was measured by gel permeation chromatography (GPC). RI was used as a detector. Tetrahydrofuran (THF) was used as a solvent at a flow rate of 0.5 ml/min. The functional groups of the samples were measured by IR spectra. The attenuated total reflectance (ATR) method was used with a Varian FTIR 3100 spectrometer to record the spectra. The samples were applied as a film to the zinc selenide crystal. Thermo-gravimetric Analysis (TGA) was performed on a simultaneous TGA/DSC, SDT Q600, TA instrument. Samples of 15-20 mg were heated from RT to 600 at a constant heating rate of 5, 10 and 20 ℃/min under nitrogen/air, with a flow rate of 30 ml/min. ^{1}HNMR spectra of bio-oil/bio-diesel mixture were recorded as follows: The samples were run using AVANCE Bruker AV 400 Spectrometer with 5 mm BBO probe. Acetone-d_6 was used as the solvent. All the experiments were done at 40 ℃. The spectra were obtained using a 90° pulse angle. The spectra width was 6793 Hz and the acquisition time was 3.1 sec. The frequency for ^{1}HNMR was 400.19 MHz.

RESULTS AND DISCUSSION

1. Ultimate Analysis

Ultimate analysis of bio-oil, bio-diesel and mixture (40 vol% bio-oil) is shown in Table 1. We can see that the bio-oil contains approximately 50% oxygen, which is much lower in bio-diesel (9.71%). The high oxygen content makes bio-oil unstable. The high heating values of bio-oil, bio-diesel and the mixture are 15.275 kJ kg^{-1}, 41.431 kJ kg^{-1} and 35.761 kJ kg^{-1}, respectively.

2. Properties of Bio-oil, Bio-diesel and Top Emulsion Phase

Table 2 shows the results of properties of the bio-oil, bio-diesel, and the top bio-diesel rich phase, with the numbers representing the average of three times repeated analysis. From Table 2, we can

see that the viscosity and density of the upper layer, that is the bio-diesel rich phase, are very similar with those of bio-diesel. The viscosity of bio-diesel rich phase is decreased remarkably compared with bio-oil. Owing to certain acid compounds of bio-oil mixing with biodiesel, the acid value of the upper layer increases from the original bio-diesel. From the lower water content of the top layer compared to the original bio-oil, it is confirmed that the water content remains with the pyrolytic lignin rich layer. This makes it ideal for the use of the top layer as fuel.

3. Combustion Properties

To have a better understanding of the mixture's combustion and decomposition characteristics, the thermal degradation behavior of the mixture was investigated. The typical TG and DTG curves of mixture under air and nitrogen are shown in Fig. 1, the heating rate is 20 ℃/min.

Comparing the two TG curves under different gaseous environment, we can see they perfectly match each other before 140 ℃, only some slight difference can be found around 150 ℃, and after that, the two curves look similar again. From the DTG curve under air, it was indicated the thermal degradation of the mixture registered as a broad peak, the mass loss rate before the peak was slower than that after the peak. At the first stage below 150 ℃, some compounds with low boiling point evaporated. Because of the thermal instability of the mixture, when the temperature went up to 150 ℃, the compounds with high boiling point evaporated and cracked. And at last some cellular coke remained.

The DTG curve under nitrogen at a heating rate of 20 ℃/min registered as two peaks: the first peak around 150 ℃ was broad, while the other was sharp. The difference of the DTG curves under different gaseous environment was around 150 ℃. The mass loss
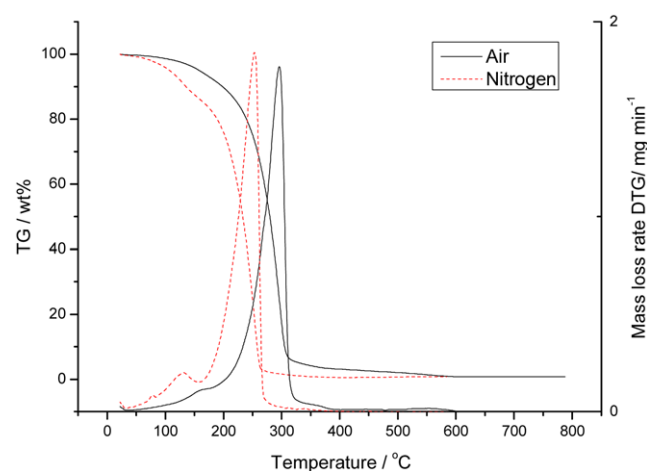
Table 1. Typical composition and energy content of bio-oil, bio-diesel and mixture (initial 40 vol% bio-oil)

| | Elemental analysis (wt%) | | | | HHV* |
	C	H	O	N	(MJ/kg)
Bio-oil	39.96	7.74	52.19	0.11	15.275
Bio-diesel	77.54	11.75	9.71	1.00	41.431
Mixture	66.48	11.89	21.50	0.13	35.761

The heating values were calculated from elemental analysis date by Equation

$$HHV(MJ/kg) = \left[338.2 \times \%C + 1442.8 \times \left(\%H - \frac{\%O}{8} \right) \right] \times 0.001 \quad (1)$$

Fig. 1. TG and DTG curves of the mixture under air/nitrogen.

Table 2. Properties of bio-oil, bio-diesel and bio-diesel rich phase

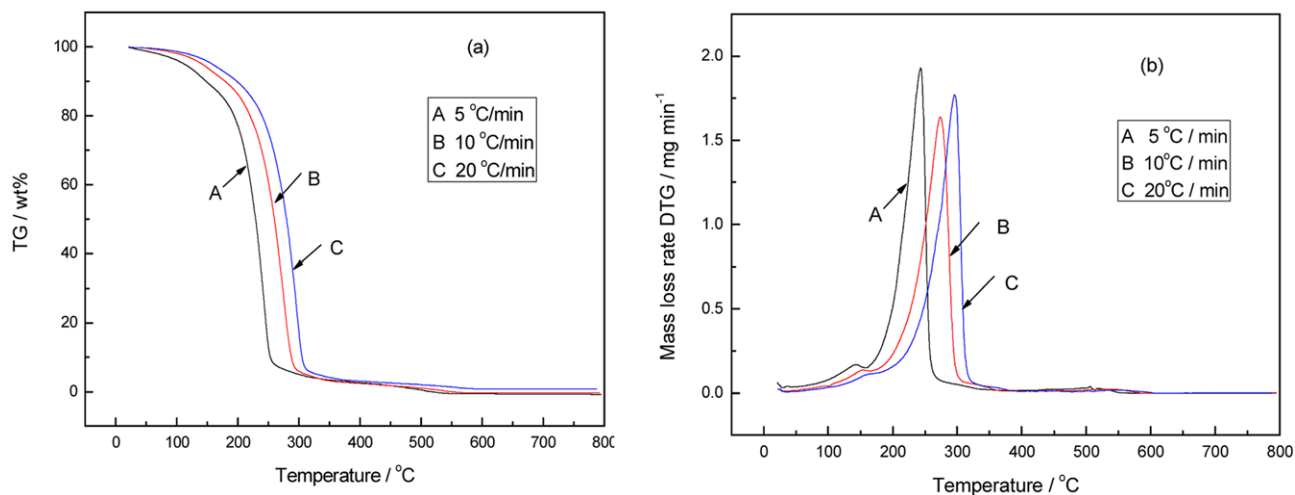| Method (initial v% of bio-oil)	Products	Viscosity (T=25) (*10^{-3} Pa·s)	Density (g/cm^3)	Acid value (mgKOH/g)	Volume ratio of upper and bottom layer	Average molecular weight (Mw)	Water content (wt%)
Raw materials	Bio-oil	67.39	1.200	79.23	/	421	28.0538
	Bio-diesel	6.590	0.881	0.55	/	280	0.1607
40 v%bio-oil	Mixture	4.665	0.895	14.01	73:27	311	0.4558

Fig. 2. TG (a) and DTG (b) curves of the mixture at heating rate of A 5 ℃/min, B 10 ℃/min, C 20 ℃/min in air.

rate here was faster than that under air, the reasons being maybe the existence of oxygen, and that the cracking actions were restrained and some oxidation reactions occurred.

Typical TG curves of the mixture decomposed at 5, 10 and 15 ℃/min under air are shown in Fig. 2(a). The heating rate is a crucial factor affecting the decomposition results. The higher heating rate may decrease the distribution of the heat in the mixture molecules and make the decomposition start at higher temperature. Thus, the shape of the TG curves, the initial decomposition temperature and the temperature for a given weight loss are increasing with the increasing heating rates.

Fig. 2(b) is the DTG curve of the mixture at different heating rate in air. It shows a transition in the peak temperature of 243-296 ℃. The peak temperature was also increased with the higher heating rate.

4. Functional Groups Analysis

Fig. 3 shows the IR spectra of bio-oil, bio-diesel and the mixture.

4-1. Bio-diesel

Since the bio-diesel is mainly mono-alkyl ester, the intense C=O stretching band of methyl ester appears at 1,743 cm^{-1}. The aliphatic hydrogen at 2,929 cm^{-1} and 2,856 cm^{-1} indicated the main components of bio-diesel are long carbon chain. The medium C-O

bands at 1,252, 1,200 and 1,175 cm^{-1} are also expected in Fig. 3 (a), (b), (c). The absorbance at 3,010 cm^{-1} indicated the C=C bond association, while absorbance at 1,376 cm^{-1} indicated the -CH$_3$ bond.

4-2. Bio-oil

We found the intense O-H stretching band at 3,390 cm^{-1}, which means that bio-oil contains some alcohol, phenol chemicals. We also found the intense C-H stretching band at 2,912 cm^{-1}, that is, during the pyrolysis processing, hydrocarbon alkyl was one of the products. Besides, the C=O stretching band at 1,677 cm^{-1} indicated the existence of ketone and phenol compounds of the product. The C-C stretching band at 1,478 cm^{-1} tells us that some high polymers decomposed into the small ones like hydrocarbon alkyl and methyl ketone. The aromatic C-H in-plane plus C-O in primary stretching band at 1,044 cm^{-1} showed the appearance of arone chemicals. The stretching band around 600-900 cm^{-1} illuminated the existence of C-H out-of-plane and the recombination of aromatic rings.

4-3. Mixture

Due to the dominant volume percent of bio-diesel in the mixture, the spectra look similar to bio-diesel. However, because of the entry of bio-oil into the mixture, there's some difference between the spectra of bio-diesel and mixture. The intense stretching band of O-H at 3,380 cm^{-1} (Fig. 3(c)) indicated there's plenty of water in bio-oil, but the signal was not clear enough in the spectra of mixture (Fig. 3(a)), which confirmed the low water content of mixture.

Besides, the other absorbance peaks also show us the existence of ethanol, phenol, ether, ester and aromatic hydrocarbon compounds.

5. ^{1}H NMR Analysis

The ^{1}H NMR spectra of the mixture samples are shown in Fig. 4. The integral values of selected regions of the spectra on a quantitative percentage basis are presented in Table 3. The prominent region of the spectra, from 0.5-1.5 ppm, represents aliphatic protons that are attached to carbon atoms. The mass percent about 55% of the mixture indicates the high aliphatic content, which may due to the dominant percentage and the aliphatic chain of bio-diesel in the mixture. Next region from 1.5-3.0 ppm represents the protons bonded to the carbon atoms of acetylenic, benzylic, allylic, ester, acid and carbonyl compounds that are present in the mixture. The next ^{1}H NMR spectra region between 3.0 and 4.5 ppm contains about 9%
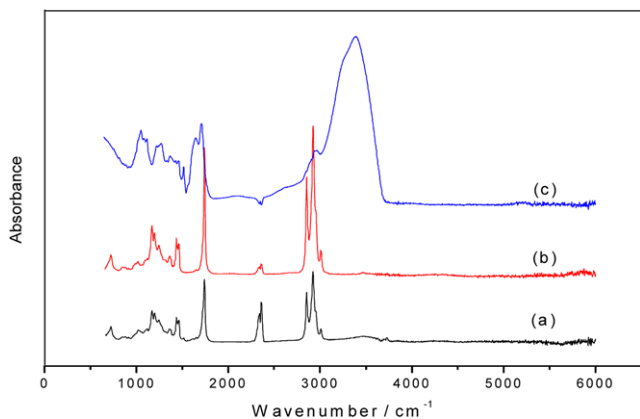

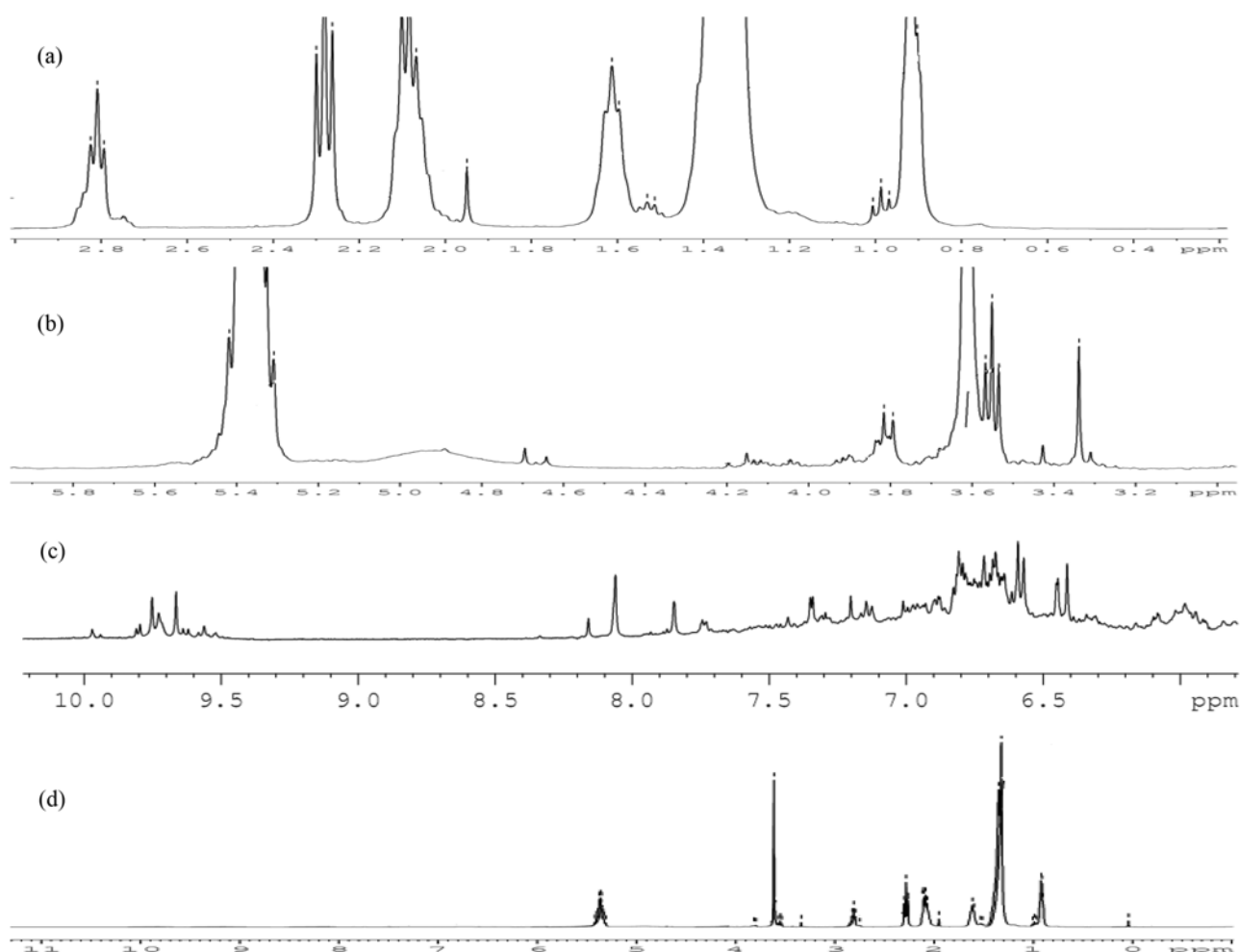**Fig. 3. FTIR spectra of (a) mixture, (b) bio-diesel and (c) bio-oil.**

Fig. 4. ¹H NMR spectra of the mixture (a) 0.5-3.0 ppm; (b) 3.0-6.0 ppm; (c) 6.0-10.0 ppm; (d) 0.0-10.0 ppm.

Table 3. Distribution of H in the mixture determined by ¹HNMR

Chemical shifts (ppm)	Type of H	Distribution of H as % of total H in
0.5-1.5	C_3H_6, RCH_3, R_2CH_3, R_3CH	54.691%
1.5-3.0	CC-**H**, Ar-C-**H**, C=CC**H**₃, **H**-C-COOR, **H**-C-COOH, **H**-C-C=O	24.643%
3.0-4.5	**H**-C-OH, **H**-COR, RCOO-C-**H**	9.206%
4.5-6.0	C=C-**H**	8.903%
6.0-8.5	Ar-**H**	1.458%
9.5-10.0	R-(**H**-)C=O	0.235%

of protons in bio-oil/bio-diesel mixture. The spectra of this region represent protons attached to carbon atoms of alcohol, ether of ester. We detected the proton bonded to carbon atoms of vinylic in the region from 4.5 to 6.0 ppm. However, some aromatic ether (i.e., lignin derived methoxy-phenols) should occur in this region, but we just found very weak peaks in the spectra. As we know, bio-oil contains large amount of pyrolytic lignin. Little detection of it shows us that the mixture doesn't have many pyrolytic lignin, which re-

mains in the bio-oil rich phase (bottom layer). The region of the spectrum (6.0-8.5 ppm) contains about 1.5% protons in the mixture. It represents aromatic proton atoms. The protons between 9.5-10.0 ppm are most likely due to the presence of aldehydic compounds.

CONCLUSION

The higher water content, thermal instability and the other drawbacks stunt the development of bio-oil. The mixture of bio-oil and bio-diesel seems to be a promising transportation fuel. The typical physical properties are encouraging. Compared to bio-oil, the properties are much more improved as follows: (1) Viscosity ($\times 10^{-3}$ Pa·s): bio-oil-67.39; mixture-4.665. (2) Acid number (mgKOH/g): bio-oil-79.23; mixture-14.01. (3) Water content (wt%): bio-oil-28.0538; mixture-0.4558.

Comparing the two TG curves under different gaseous environment, we can see they perfectly match each other before 140 °C, only some slight difference can be found around 150 °C, and after that, the two curves look similar again.

The shape of the TG curves, the initial decomposition temperature and the temperature for a given weight loss are increasing with the increasing heating rates.

The IR spectra of the mixture look similar to bio-diesel. Due to the entry of bio-oil into the mixture, there's some difference between the spectra of bio-diesel and mixture. All in all, the mixture is still a complicated mixture, which almost contains every kind of chemical. ^{1}H NMR spectra have shown some reactions among the active protons bonded to different carbon atoms.

ACKNOWLEDGEMENT

NOMENCLATURE

HHV : high heating value, calculated by the formula on Table 1
LHV : low heating value
TGA : thermal gravimetric analysis
FTIR : fourier transform infrared spectrometer
NMR : nuclear magnetic spectroscopy
GPC : gel permeation chromatography

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