

*Research article*

## Research on upgrading of pyrolysis oil from Japanese cedar by blending with biodiesel

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**Abstract:** Bio-oil produced by the pyrolysis of biomass is a kind of alternative energy, but high viscosity and high water content make it difficult to be used in internal combustion engines. To overcome these problems, a method of blending bio-oil with biodiesel was investigated. In this study, the characteristics of the cedar bio-oil blended with biodiesel and their possible usage as a fuel were evaluated. The bio-oil was derived from Japanese cedar. The suitable mixing ratio and the optimum mixing condition were discussed. The investigation included the analysis of the elemental composition, the heating value, the density, the viscosity, the cetane index and the water content. The results proved that the mixed fuels without any additive show much improved properties on the viscosity, the water content and the oxygen content compared to the initial bio-oil. The GC-MS was used to reveal the main components and the mixing mechanism of the mixture.

**Keywords:** bio-oil; biodiesel; blended fuel; stratification; GC-MS analysis

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### 1. Introduction

Many researchers estimate that the depletion time of fossil fuel is less than 40, 70 and 200 years for oil, gas and coal, respectively, if the world continues consuming fossil fuels at the unchanged rates [1]. WEO 2006 estimated a depletion time for oil of between 39 and 43 years, 164 years for coal and 64 years for gas. Oil will be depleted earlier than the other types of fossil fuel. Many researchers believe that the peak of oil production will come before 2030 [2,3].

To alleviate the energy crisis, considerable attention has been focused on the development of

alternative fuels. Renewable biomass source is a logical choice to replace fossil fuel [4]. The liquid product from the pyrolysis of biomass, known as bio-oil, is a promising renewable energy resource which has received extensive recognition around the world for their characteristics as combustion fuels used in boilers, engines or gas turbines and resources in chemical industries. However, some problems limit its industrial utilization and recommendation. Compared with heavy petroleum fuel oil, bio-oil has several undesired properties for fuel applications such as high oxygen, high water contents, high viscosity, low heating value and high corrosiveness. Various technologies have been developed for the bio-oil upgrading, including the hydrotreating [5,6], the hydrocracking [7,8], the solvent addition [9], the steam reforming [10], and the emulsification [11,12]. However, none of these bio-oil upgrading technologies has been widely commercialized due to high cost and low biofuel efficiency [13].

This research was carried out aiming at the usage of the woody bio-oil in a diesel engine with a simple fuel upgrading. The bio-oil used in this research derived from the waste biomass, Japanese cedar, were produced in a pilot-scale gasification plant in Japan. In order to avoid usage of fossil fuel, biodiesel was chosen as the mixing material. The researches on bio-oil blended with biodiesel were seldom reported. M. Garcia-Perez et al. tested the mixtures obtained from certain conditions and showed that the solubility of bio-oil in biodiesel is not as high as previously reported [14,15]. A. Alcala et al. discussed the effect of the mixing ratio and the additive dosage to the blending result and concluded that the type and the quantity of alcohol is critical for the blend formation and stability [16]. Jiang X et al. revealed that the phenomena occurring in the mixing is the emulsification but failed to get a stable mixed fuel without additives [17,18].

In this study, partial mixing of the bio-oil and biodiesel was achieved without any additives for the purpose of producing low-cost blend fuel. Compared with the research reported by M. Garcia-Perez, the solubility of the cedar bio-oil in the biodiesel was two times higher than the mallee bio-oil or pine bio-oil in biodiesel, but a little lower than the mallee/bio-oil in the biodiesel-EtAc and half lower than the pine bio-oil in biodiesel-EtAc. The temperature was an important factor to accelerate the process of mixing without negative impacts. The stratification always happened after the blending with the upper layer having improved fuel properties. The gas chromatography-mass spectrometry (GC-MS) was used to investigate the main components and the mixing mechanism after the stratification stabilized.

## **2. Materials and experimental method**

### *2.1. Raw material*

The bio-oil was produced from the pyrolysis of Japanese cedar [19]. The pyrolysis gas produced in an updraft gasifier passed through a cooler to remove water and heavy tar and then was introduced to a centrifuge separator to recover misty light/medium tar (bio-oil). The biodiesel was produced from waste cooking oil by the transesterification method with KOH catalyst which was supplied from Best Trading.inc, Japan. The effects of the initial bio-oil/biodiesel volume ratio, the mixing time, and the mixing temperature were examined in this study.

## 2.2. Experimental facility and procedure

Initial mixtures of bio-oil and biodiesel were prepared by adding 10, 20, 30, 40, 50 and 60% (by volume) bio-oil into biodiesel and mixed with mechanical agitation. Each mixture was prepared at three temperatures of 25, 40 and 60 °C. The stirring speed was fixed at 1000 ppm, a moderate speed. The mixing time lasted at most 30 hours and the mixtures were observed every 10 minutes in the first hour and every 5 hours for the later 29 hours. All experimental conditions are listed in Table 1.

**Table 1. Mixing experimental parameters.**

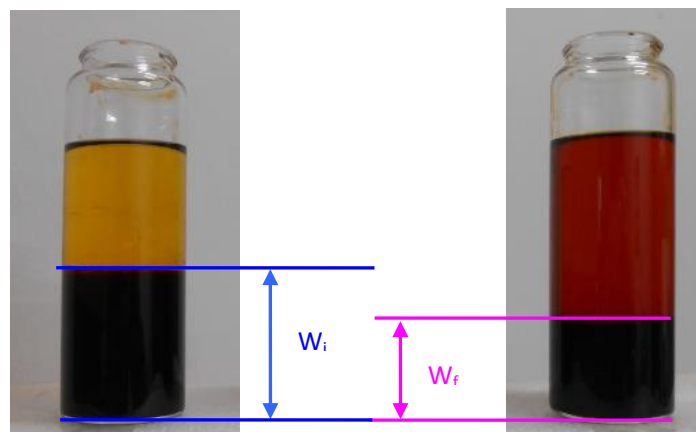
Mixing temperature	25 °C, 40 °C, 60 °C
Mixing time	10 min, 20 min, 30 min 40 min, 50 min, 1 h, 5 h, 10 h, 15 h, 20 h, 25 h, 30 h
Stirring speed	1000 ppm
Percentage of bio-oil	10%, 20%, 30%, 40%, 50%, 60%

In this research, the stratification happened inevitably when the stirring stopped. The stratification will be stabilized within 60 minutes after settled in the room temperature. The proportion of the stratification changed with the stirring time and the initial blending ratio. All mixtures after the stratification came to a steady state where the mixed liquid were stable in the room temperature for more than 3 months without appearance of any more stratification and/or precipitation. The time needed for this stabilized mixing was between 10 hours and 25 hours. After the stratification, the upper and the lower layers were separated and weighed respectively.

## 3. Result and Discussion

### 3.1. Stratification

Once the stirring stopped, a layer of darker color liquid with higher density started to settle at the bottom. The amount of the lower layer liquid after the blending always reduced compared to that before the blending. The lower layer after the blending had a higher viscosity and a darker color than the upper layer as shown in Figure 1.



**Figure 1. Mixtures before the blending (left side) and after the blending (right side).**

After settled in the room temperature for 1 hour, the stratification stabilized and the mixture came to a steady state which means that the mixed liquid was capable of stabilizing in the room temperature for more than 3 months without appearance of additional stratification and/or precipitation.

After reaching the steady state, the changed proportion (CP) of the lower layer by weight was used to evaluate the mixing result. It is defined as the following:

$$CP = (W_i - W_f) / (W_i) \times 100\%$$

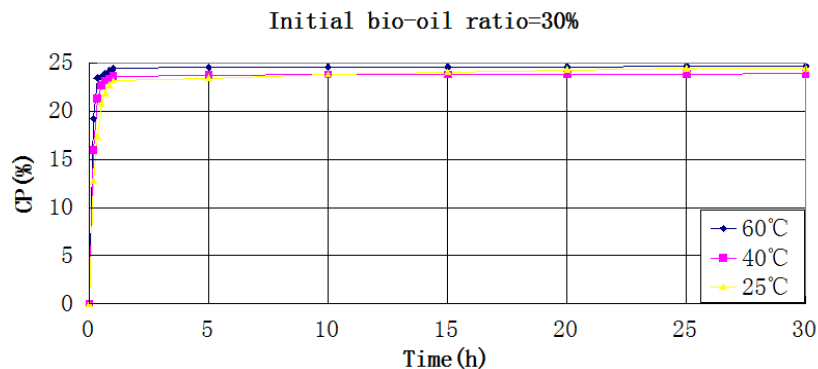
where CP: The changed proportion of the lower layer weight;

$W_i$ : Weight of the initial bio-oil (lower layer) before the blending;

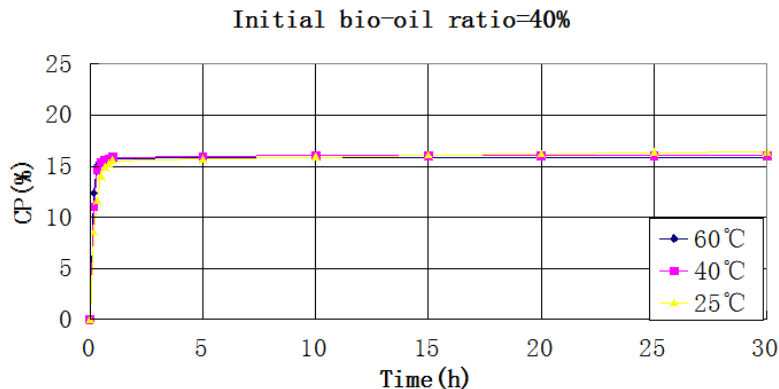
$W_f$ : Weight of the stabilized lower layer after the blending.

### 3.2. Effect of the mixing time and temperature

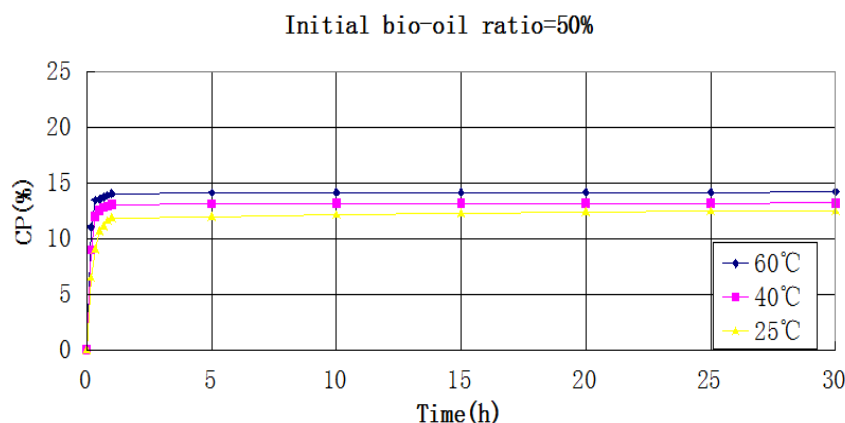
CP values were measured every ten minutes in the first hour and every five hours in the later 29 hours which is long enough for each mixtures to reach the maximum CP value. The CP values as functions of the mixing time, the initial bio-oil ratio and the mixing temperature are shown in Figures 2, 3 and 4.



**Figure 2. CP for 30% bio-oil content mixture at different mixing temperatures.**



**Figure 3. CP for 40% bio-oil content mixture at different mixing temperatures.**



**Figure 4. CP for 50% bio-oil content mixture at different mixing temperatures.**

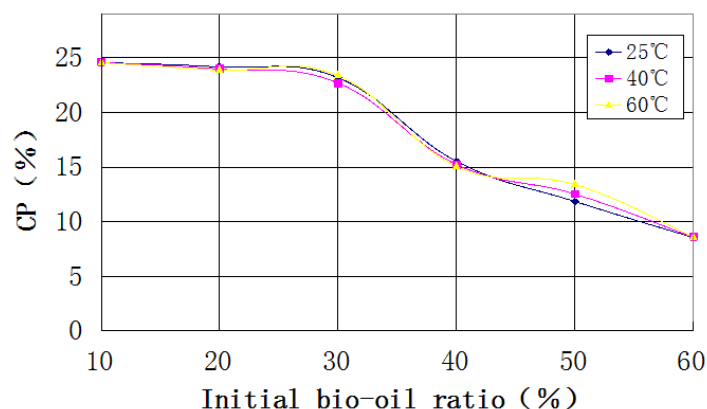
From Figures 2, 3 and 4, it can be seen that the mixing time for obtaining the maximum CP value was 25 hours at the mixing temperature of 25 °C regardless of the mixing ratio, but the mixing time needed for the maximum CP value decreased to 15 hours at the mixing temperatures of 40 and 60 °C. The major part of the mixing occurred in the first hour. For the later 20 hours, the increase of the CP value is less than 5%. By measuring every 10 minutes in the first hour, we can see that 95% of the maximum CP value was obtained in 20 minutes for the 40 and 60 °C mixtures, and 1 hour for the 25 °C mixtures. This clearly shows that the heating accelerates the mixing process but does not affect the maximum CP value so much. After separating the upper layer and the lower layer of the mixture when 95% of the maximum CP value was achieved, the stability of the two layers did not show much difference compared to mixtures which were blended for 30 hours. The separated liquids did not appear additional stratification and/or precipitation for 3 months.

The physical and chemical properties of mixtures in higher temperatures also did not show any negative changes though some researchers pointed out that bio-oil should not be heated because it tends to coagulate the droplets, causing polymerization or destabilization [20].

Figures 2, 3, and 4 also show that at the same mixing temperature condition, the mixtures with lower initial bio-oil ratio always showed higher maximum CP values than the ones with higher bio-oil ratio. This phenomenon will be discussed in the section 3.3.

### 3.3. Effect of the mixing ratio

Figure 5 shows the maximum CP value at various initial mixing ratios of bio-oil from 10% to 60%. The mixing temperature almost did not affect the curves. When the initial bio-oil mixing ratio was no more than 30%, the maximum CP values were closed to 25%, showing that the amount of bio-oil which could not be mixed into biodiesel was about 75% when the initial bio-oil mixing ratio was low. However, when the initial bio-oil mixing ratio was larger than 30%, the maximum CP value decreased gradually, and down to less than 10% when the initial bio-oil mixing ratio was 60%.



**Figure 5. The maximum CP value at different initial bio-oil mixing ratios.**

#### 3.4. Main properties of raw and mixed fuels

The following characteristics were determined in this section: elemental analysis of C, H, O, N, and S, moisture content, ash content, density, high heating value (HHV), cetane index, kinetic viscosity and chemical composition.

Ash content and elemental analysis of C, H, and N were determined by JM10 at 950 °C. Elemental analysis of O was determined by Vario micro cube at 1150 °C. Elemental analysis of S was determined by HSU-20+ICS-1100 after complete combustion. The moisture content was measured using Karl Fischer method in accordance with the standards JIS K 2275. HHV was determined in accordance with the standards JIS K 2279. The kinetic viscosity was measured by ostwald viscometer at 40 °C. The cetane index was calculate in accordance with the standards JIS K 2280-5.

Table 2 compares the main properties of the upper layer of the mixture (blend oil) with raw bio-oil and biodiesel. This table shows substantial improvement of the oil quality when bio-oil was blended with biodiesel. An interesting observation is that the initial bio-oil mixing ratio did not strongly affect the properties of the blend oils. The density of the blend oils dropped compared with bio-oil. The kinematic viscosity of the blend oils drastically decreased and there also was a big drop in the oxygen and water contents. The HHV significantly increased to about 90% of that of biodiesel.

The evaluation indicators of renewable fuels typically include cetane number/cetane index, viscosity, and HHV. Compared to biodiesel which is available for engine, the cetane index of the 1:9 upper layer mixtures was only a little low. The cetane index of 3:7 upper layer mixtures was lower than 1:9 mixtures but still more than 35. These two types of mixtures were certainly can be applied to medium-speed diesel engine. The viscosity of three types of mixture was more closed to biodiesel than to bio-oil. Lower water content ensured that the loss of HHV was not too much. The HHV of the three types were half higher than the bio-oil and only 10% lower than the biodiesel. Overall, when the bio-oil mixing ratio was up to 30%, the performance of the main characteristic of mixtures decreased but not much compared to the biodiesel. The mixtures were suitable for medium-speed diesel engine and the 1:9 ratio mixtures were even suitable in high-speed diesel engine for its cetane index was closed to 40.

**Table 2. Main characteristics of the upper layer mixture compared with raw bio-oil and biodiesel (all mixtures were made at 40 °C with 30 hours mixing).**

Bio-oil:Biodiesel	10:0	5:5	3:7	1:9	0:10
C (%)	57.5	73.9	74.4	75.1	76.6
H (%)	7.0	11.1	11.1	12.0	12.6
N (%)	0.0	0.0	0.0	0.0	0.0
O (%)	35.5	14.9	14.4	12.8	10.8
S(mg/kg)	0.0	0.0	0.0	0.0	0.0
H <sub>2</sub> O (%)	7.9	2.8	2.5	1.1	0.0
Ash (%)	0.0	0.0	0.0	0.0	0.0
Density (g/cm <sup>3</sup> )	1.14	0.94	0.90	0.87	0.87
HHV (MJ/kg)	25.4	37.1	37.3	39.6	41.2
Cetane index	-*	22.42	35.74	40.78	46.30
Kinetic viscosity (mm <sup>2</sup> /s @ 40 °C)	6.80	4.82	4.51	3.91	3.80

\*Cetane index of bio-oil was not suited to JIS K 2280-5 method for its high density.

### 3.5. Compositional analysis

The raw bio-oil obtained from woody biomass had a higher kinematic viscosity than biodiesel as shown in Table 2. The complexity of the bio-oil itself results in the difficulty to analyze and characterize. The GC-MS is the technique most widely used in the analyses of the oil composition [21].

A Rxi®-5Sil MS Column was used in the GC and helium was selected as the carrier gas. The oven heating profile was set at an increase of 4 °C /min from 40 to 300 °C, with the initial temperature and the final temperature maintained for 10 minutes. The initial injection temperature was 300 °C. The full analysis took 84 minutes.

The bio-oil contains hundreds of ingredients. The major components of the bio-oil identified by GC-MS database are shown in Table 3. The peaks of bio-oil mainly appeared in the first 45 minutes. No peak area of bio-oil was over 10%. The oxygen content should be high and hydrocarbon content is relatively low because almost every component contains oxygen element. High contents of ketone, acid and phenol reduce the energy density and stability of bio-oil. These are drawbacks for the utilization of bio-oil.

Table 4 shows the main components of biodiesel. It can be seen from Table 4 that the main components of biodiesel are long chain fatty acids. Methyl octadecene and methyl hexadecanoate dominate the main properties of biodiesel. The retention time of their peaks were mainly detected after 45 minutes.

**Table 3. Main components in bio-oil.**

Retention time (min)	Area (%)	Name
41.2	7.85	.beta.-D-Glucopyranose, 1,6-anhydro-
2.4	4.59	Acetic acid
21.6	3.89	Phenol, 2-methoxy-
22.9	3.51	Hexanal
27.0	2.68	Catechol
26.1	2.56	Creosol
2.5	2.20	2-Propanone, 1-hydroxy-
1.2	2.17	Methyl Alcohol
39.4	2.17	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-
35.5	1.99	Phenol, 2-methoxy-4-(1-propenyl)-, (Z)-
29.4	1.90	Phenol, 4-ethyl-2-methoxy-
1.4	1.67	Water
30.5	1.66	1,2-Benzenediol, 3-methyl-
1.4	1.62	Acetone
1.3	1.55	Methyl formate
32.2	1.49	Phenol, 2-methoxy-3-(2-propenyl)-
23.1	1.42	Maltol
16.6	1.39	Phenol
11.7	1.36	2(5H)-Furanone
37.8	1.28	2(3H)-Naphthalenone,4,4a,5,6,7,8-hexahydro-4a-methyl-
3.4	1.17	.+/-.-Tetrahydro-3-furanmethanol
26.6	1.14	2,6-Dimethyl-octa-2,6-dien-1-ol
19.0	1.13	2-Cyclopenten-1-one, 2,3-dimethyl-
39.7	1.12	4-Ethoxy-3-anisaldehyde
33.9	1.07	Vanillin
27.5	1.05	5-Hydroxymethyldihydrofuran-2-one
38.1	1.05	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-

**Table 4. Main components in biodiesel.**

Retention time (min)	Area (%)	Name
54.9	30.59	9-Octadecenoic acid, methyl ester, (E)-
53.8	16.98	9,12-Octadecadienoic acid (Z,Z)-, methyl ester
49.6	10.84	Hexadecanoic acid, methyl ester
55.1	8.88	Methyl stearate
58.5	2.03	cis-11-Eicosenoic acid, methyl ester
59.1	1.84	Methyl 18-methylnonadecanoate
49.7	1.63	2-Methylheptanoic acid
49.8	1.62	Pentanoic acid, 2-methyl-
63.4	1.59	Docosanoic acid, methyl ester
49.8	1.39	Tridecanoic acid, methyl ester
67.0	1.05	9-Octadecenoic acid, 1,2,3-propanetriyl ester, (E,E,E)-
49.8	0.90	Pentadecanoic acid, 14-methyl-, methyl ester



Tables 5–7 shows the main components of the blend oils at different initial bio-oil mixing ratios. Methyl octadecene and methyl hexadecanoate dominate the main properties of three kinds of blend oils. Their main ingredients were nearly the same as biodiesel, regardless of the mixing ratio. That is why the properties of the blend oils, such as the proportion of elements, the water content and the viscosity were rightly closed to biodiesel, especially closed to the properties of methyl octadecene and methyl hexadecanoate.

**Table 5. Main components in the blend oil with 1:9 (bio-oil/biodiesel) mixing ratio.**

Retention time (min)	Area (%)	Name
54.9	31.59	9-Octadecenoic acid, methyl ester, (E)-
53.9	20.78	9,12-Octadecadienoic acid (Z,Z)-, methyl ester
49.6	16.31	Hexadecanoic acid, methyl ester
55.0	10.76	Methyl stearate
58.5	2.04	cis-11-Eicosenoic acid, methyl ester
59.0	1.78	Methyl 18-methylnonadecanoate
63.4	1.16	Docosanoic acid, methyl ester
67.1	0.78	9-Octadecenoic acid, 1,2,3-propanetriyl ester, (E,E,E)-
48.8	0.66	9-Hexadecenoic acid, methyl ester, (Z)-
67.8	0.49	Tetracosanoic acid, methyl ester

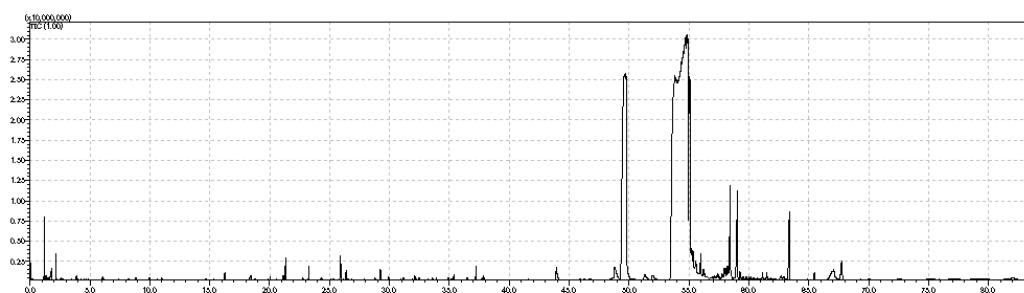
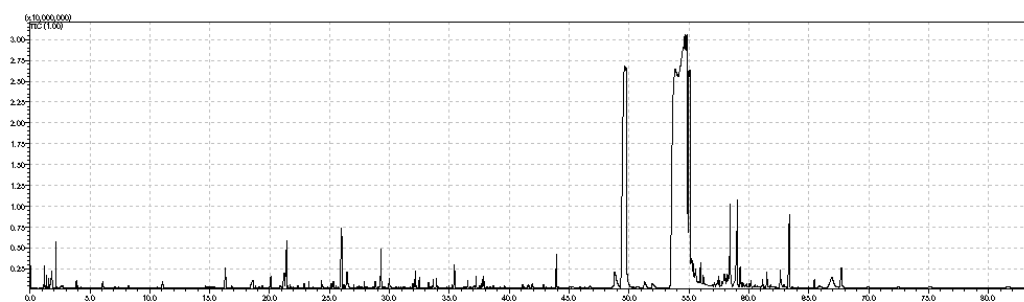
**Table 6. Main components in the blend oil with 3:7 (bio-oil/biodiesel) mixing ratio.**

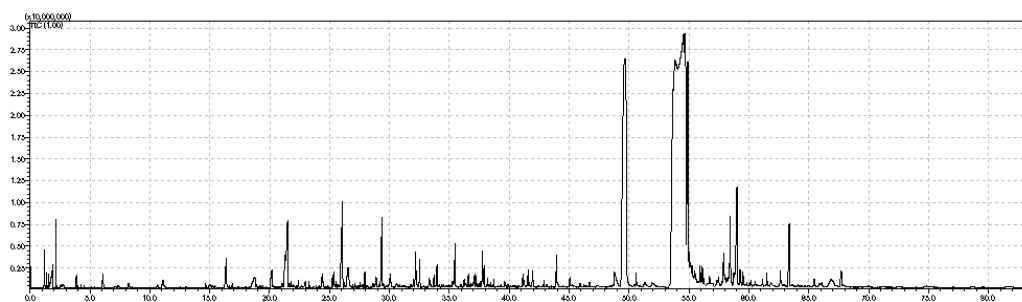
Retention time (min)	Area (%)	Name
54.6	29.87	9-Octadecenoic acid, methyl ester, (E)-
53.9	18.70	9,12-Octadecadienoic acid (Z,Z)-, methyl ester
49.6	15.25	Hexadecanoic acid, methyl ester
55.0	8.76	Methyl stearate
59.0	1.87	Methyl 18-methylnonadecanoate
58.5	1.71	cis-11-Eicosenoic acid, methyl ester
63.4	1.18	Docosanoic acid, methyl ester
26.0	1.00	Creosol
21.4	0.84	Phenol, 2-methoxy-
66.9	0.76	9-Octadecenoic acid, 1,2,3-propanetriyl ester, (E,E,E)-

**Table 7. Main components in the blend oil with 5:5 (bio-oil/biodiesel) mixing ratio.**

Retention time (min)	Area (%)	Name
54.7	29.26	9-Octadecenoic acid, methyl ester, (E)-
53.9	17.94	9,12-Octadecadienoic acid (Z,Z)-, methyl ester
49.7	12.9	Hexadecanoic acid, methyl ester
54.9	8.04	Methyl stearate
59.0	2.42	Methyl 18-methylnonadecanoate
21.5	2.28	Phenol, 2-methoxy-
26.1	1.95	Creosol
58.5	1.33	cis-11-Eicosenoic acid, methyl ester
29.4	1.14	Phenol, 4-ethyl-2-methoxy-
63.4	0.92	Docosanoic acid, methyl ester

As shown in Figures 6, 7 and 8, with the increase of the ratio of bio-oil, the components of the bio-oil (retention time before 45 minutes) was increasing. The most obvious ones are 2-methoxy-Phenol (retention time = 21.4 minutes), Creosol (retention time = 26.0 minutes), 4-ethyl-2-methoxy-Phenol (retention time = 29.3 minutes), 2-methoxy-4-(1-propenyl)-(Z)-Phenol (Retention Time = 33.9 minutes), 1-(4-hydroxy-3-methoxyphenyl)-2-Propanone (Retention Time = 39.4 minutes), and Methyl tetradecanoate (Retention Time = 44.0 minutes). Phenol, ketone, ester with simple structures and a lot of short carbon chain acid, alcohol and ester, such as formic acid, acetic acid, acetone, methanol, and so on, were also easier to be mixed into the upper layer.

**Figure 6. Ion current of the blend oil with 1:9 (bio-oil/biodiesel) mixing ratio.****Figure 7. Ion current of the blend oil with 3:7 (bio-oil/biodiesel) mixing ratio.**



**Figure 8. Ion current of the blend oil with 5:5 (bio-oil/biodiesel) mixing ratio.**

The composition of lower layer of the mixtures was also detected. Table 8 shows the result from 5:5 (bio-oil/biodiesel) mixing ratio mixtures. Some substances abundant in raw bio-oil were not detected in the upper layer mixed liquid. The retention time of these substances were between 20 minutes to 40 minutes. These substances are mainly long chain organics with carbon ring and should be the main components which absolutely cannot be mixed into the upper layer mixtures.

**Table 8. Main components in the lower layer from 5:5 (bio-oil/biodiesel) mixing ratio mixtures.**

Retention time (min)	Area (%)	Name
53.6	9.72	9,12-Octadecadienoic acid (Z,Z)-, methyl ester
40.3	6.57	.beta.-D-Glucopyranose, 1,6-anhydro-
39.4	4.97	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-
21.4	3.14	Phenol, 2-methoxy-
26.0	2.53	Creosol
22.4	2.39	Cyclopropyl carbinol
26.9	2.30	Catechol
22.1	2.27	Pentanoic acid, 4-oxo-
27.1	2.14	2H-Pyran, tetrahydro-2-[(tetrahydro-2-furyl)methoxy]-
18.9	1.99	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-
2.0	1.89	Acetic acid
2.2	1.83	2-Propanone, 1-hydroxy-
49.2	1.72	1-Heptanol, 2,4-dimethyl-, (R,R)-(+)-
41.7	1.65	Homovanillic acid
11.3	1.51	2(5H)-Furanone
30.3	1.51	1,2-Benzenediol, 3-methyl-
37.1	1.27	.alpha.-D-Glucopyranose, 4-O-.beta.-D-galactopyranosyl-
39.7	1.24	4-Ethoxy-3-anisaldehyde
1.6	1.16	Acetaldehyde, hydroxy-
32.0	1.12	Phenol, 2,6-dimethoxy-
23.1	1.11	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-
27.8	1.00	2-Deoxy-D-galactose

### 3.7. Analysis of Stability

The stability was examined after 3 months. By visual inspection, no phase separation occurred in the upper layer. Table 9 shows the chemical compositions detected by GC-MS after 3 months were a little changed. The slight percentage change in detected area of ion current was not significant in the trend, and more likely to come from inaccuracy of the apparatus.

**Table 9. Main components of upper layer mixtures after 3 months.**

Name	Area (%)		
	bio-oil/biodiesel=1:9	bio-oil/biodiesel=3:7	bio-oil/biodiesel=5:5
9-Octadecenoic acid, methyl ester, (E)-	31.77	30.64	31.61
9,12-Octadecadienoic acid (Z,Z)-, methyl ester	18.28	18.71	18.05
Hexadecanoic acid, methyl ester	14.71	14.32	12.96
Methyl stearate	8.09	8.86	8.87
Methyl 18-methylnonadecanoate	1.32	2.02	2.45
Phenol, 2-methoxy-	0.12	0.81	2.01
Creosol	0.14	0.97	1.72
cis-11-Eicosenoic acid, methyl ester	2.22	1.86	1.17
Phenol, 4-ethyl-2-methoxy-	0.05	0.39	0.92
Docosanoic acid, methyl ester	1.29	1.02	0.80

The main characteristics of three types of upper layer mixtures after 3 months were listed in Table 10. It can be seen that the upper layer solution was still stable after 3 months because almost no change in element content and physical properties.

**Table 10. Main characteristics of the upper layer mixtures after 3 months.**

Bio-oil:Biodiesel	5:5	3:7	1:9
C (%)	74.1	74.7	76.1
H (%)	11.1	11.4	12.4
N (%)	0.0	0.0	0.0
O (%)	15.80	15.30	14.68
Ash (%)	0.1	0.1	0.0
Density (g/cm <sup>3</sup> )	0.95	0.91	0.88
Kinetic viscosity (mm <sup>2</sup> /s @ 40 °C)	4.85	4.61	3.98

### 3.8. Explanation of the blending result

It can be considered that both the solution and the emulsification occurred in the mixing process. The complexity of the blending reaction is that the bio-oil itself is an emulsified liquid. Hundreds of

compounds in bio-oil are of different properties. There are both high polar components (water, acids and alcohols) and low polar components (esters, ethers and phenolics) in it. These components are not completely mutual soluble. If water will be added, the precipitation happens immediately. It proves that water insoluble molecules form the continuous phase of the emulsified liquid. Water and water soluble materials are dispersed as micelles in bio-oil. Some multipolar compounds act as emulsifiers to stabilize the structures.

After mixed with biodiesel, the main structures of bio-oil changed into a biodiesel-based structure since the main components in the upper mixture were coming from biodiesel. Material which was dissolved in biodiesel or could react with biodiesel formed a new continuous phase in which very little moisture was contained. With the increase of the ratio of the bio-oil, the components in the bio-oil emulsified or dissolved was increasing. The most obvious examples are 2-methoxy-Phenol, Creosol, 4-ethyl-2-methoxy-Phenol, 2-methoxy-4-(1-propenyl)-(Z)-Phenol, 1-(4-hydroxy-3-methoxyphenyl)-2-Propanone and Methyl tetradecanoate. Phenol, ketone and ester with simple structures are also easy to be emulsified in the mixtures, such as formic acid, acetic acid, acetone, methanol, and so on. Plenty of long chain organics which contain carbon ring was not soluble in the fatty acid. A portion of the biodiesel was also detected in the lower layer. It means that the two phases are partially miscible emulsion. That is why the stratification started when the stirring was stopped.

The mixed proportion from bio-oil into the upper layer increased as the initial bio-oil mixing ratio decreased and the limit was 25%. Water and other substances of high polarity mainly remained in the lower layer. These high polarity substances were much easier to resolve into high polarity liquid, bio-oil, than resolved or emulsified into the upper layer, which was mainly low polarity substances, biodiesel.

#### 4. Conclusion

The stable and high quality blend oils were able to be produced by mixing bio-oil and biodiesel without any additives as an upper layer of the stratified mixture. The mixing process needed a long time exceeding 10 hours for each mixture to achieve the maximum CP (changed proportion of bio-oil) value while 95% of the maximum CP value could be achieved in the first hour of mixing. Heating contributed to accelerate the mixing process but did not affect the maximum CP value. By reducing the initial bio-oil mixing ratio, the maximum CP value of 25% by weight of the bio-oil was achieved.

The upper layer mixture showed desirable properties in regards to the viscosity, the water content and the oxygen content compared to the raw bio-oil. The analysis of the upper layer mixtures (blend oils) discovered no components accounting for the vast majority in bio-oil. Most of the components in bio-oil contained oxygen element. Long carbon chain fatty acid esters dominated the main properties of biodiesel. Phenol, ketone, ester with simple structures are easier to be emulsified or resolved in the upper layer mixture. methyl octadecene and methyl hexadecanoate dominate the main properties of the upper layer mixed fuels. The main ingredients of the blend oils were nearly the same as biodiesel, regardless of the mixing ratios. Compared with biodiesel which can be used in internal combustion engines, the blend oils showed similar characteristics on centane index, HHV and viscosity. The application of these blend oils in and internal combustion engine should be tested in the next step.

## Conflict of interest

All authors declare no conflicts of interest in this paper.

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