Towards Commercialization of Alternative Biofuel: Improving the Stability of Pyrolysis Liquid by Physical Fractionation

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Abstract

Amidst climate change and global energy crises, the need for renewable and low-carbon fuels is increasingly dire. Many fuels derived from biological sources have emerged as promising contenders, due to their low-carbon life cycles, comparable performance to conventional fossil fuels, and prospects of being produced from domestic feedstock. Besides already commercialized biodiesel and bioethanol, alternatives such as pyrolysis liquids are also gaining momentum. Pyrolysis liquid, also known as bio-oil, is a dark brown, free-flowing organic liquid that is a product of fast pyrolysis, which is rapid heating of biomass in the absence of air. The use of bio-oil in boilers and engines has been shown in several studies, and it was estimated by the International Energy Agency to be the lowest-cost liquid biomass-based fuel. Nonetheless, before commercialization, certain aspects of bio-oil's quality, especially its storage stability, need to be improved. The inherently low stability of bio-oil is tied to its "aging" during the storage period when bio-oil experiences phase separation and increasing acidity and viscosity. Previous studies suggested that removing bio-oil's light compounds, which participate in aging reactions and could pose problems when used in engines, would improve the bio-oil's stability. The objective of this work is, thus, to improve the stability of bio-oil by physical separation and removal of the light-compound fraction. The work endeavored to maximize the yield of more stable bio-oil and removal of light compounds, while trying to minimize the amount of time, energy, and resources required. Combinations of different processes, such as liquid-liquid extraction and vacuum evaporation, were tested, and key conditions were varied and analyzed. The results showed that fractionation using water as an extracting liquid, which is a relatively cheap resource, at a water-bio-oil ratio of 5 vol% could effectively remove the light compounds from bio-oil and improve its qualities.

Keywords*:* bio-oil, pyrolysis fuel, stability improvement

1. Introduction

The demand for transportation fuels is increasing, yet the supply becomes increasingly limited. Consequently, renewable fuels from biological sources, such as bio-diesel, biogas, and bio-oil, are gaining more interest. Bio-oil is a product of pyrolysis, which is a thermal conversion of biomass under oxygen-free conditions [1-3]. It is also known pyrolysis oils, pyrolysis liquids, bio-crude oil, wood liquids, wood

oil, liquid smoke, wood distillates, pyroligneous acid, and liquid wood. It consists of oxygenated compounds such as water, acids, aldehydes, ketones, phenol, and other complex compounds derived from carbohydrates and lignin [4]. These oxygenated compounds are the cause of high acidity and viscosity, and relative low energy density (16-18 MJ/kg, which is about 40-45 wt% of hydrocarbon fuels [5]). Due to the high oxygen content, bio-oil is reactive and thermally unstable. Therefore, upgrading processes, such as chemical upgrading (including catalytic esterification, catalytic hydroprocessing, and catalytic cracking) and physical upgrading (including char removal, hot vapor filtration or distillation, liquid chromatography, centrifugation, liquid filtration, solvent addition, and extraction or fractionation of organic acids) are need [3, 6-8]. These process separate bio-oil into less complex compounds. The improved bio-oil can be a transportation fuel substitute or used in stationary power production. One of the commonly used upgrading methods is solvent-fractionation with toluene, methanol, diethyl ether, dichloromethane, n-hexane, or water, depending on the polarity and solubility [4-5]. Among these solvents, water is the most ubiquitous and in expensive.

This study, thus, focuses on using water fractionation as a method to improve bio-oil's properties. When fractionated by water, bio-oil is separated into two parts. The first part is the water-soluble fraction (WSF), which is composed of high-polarity compounds, such as formic acid, acetic acid, and ketones. The second part is the water-insoluble fraction (WIF), comprising low-polarity compounds, including phenolic compounds that originate from lignin called pyrolytic lignin [2, 6]. This study aims to improve the stability of bio-oil by physical separation and removal of the light fraction. While water fractionation is the focus, other processes, such as ethyl acetate extraction and vacuum evaporation, were also tested and analyzed.

2. Experimental

2.1 Materials

The bio-oil used in this study was obtained from a charcoal production, using various wood chips, in Japan. The properties of the starting bio-oil are listed in Table 1.

Table 1 Properties of the bio-oil

Property	Value
Density at 15 ^{o}C	1.1781 g/cm^{3}
Water content	4.3745 wt%
Acidity	81.38 mg KOH/g oil
pH	2.29
Viscosity at 40 ^{o}C	114.5 cP
Heating vale	25.80 MJ/kg
Particle size distribution (D_{50})	1.37 micron
Molecular weight distribution	665
Element analysis	
C	65.04 wt%
H	7.55 wt%
N	0.20 wt%
O	27.21 wt%

2.2 Method

The water fractionation of bio oil was achieved by slowly dropping bio-oil into ice-cooled distilled water, base on the work by B. Scholze and D. Meier [9]. In different experiments, the water-to-bio-oil ratio was varied between 5:1, 10:1, 15:1 and 20:1 by volume. After the

dropping, the mixture was stirring with a homogenizer at 6000 rpm for 2 hours. In this stirring process, the WIF separated from the WSF solution. Then, the WSF was filtered out, and the distilled water was added to the WIF, which was subsequently stirred for 4 hours. Finally, the WSF was removed by filter again. The remaining WIF, which appeared sticky, was dried in a vacuum oven at 30 °C, whereas the WSF was evaporated in rotary evaporator at 40 °C to remove moisture and calculate the yield. The flowchart of the process described above is shown in Fig. 1. In addition to this fractionation-with-water method, bio-oil fractionation with ethyl acetate and vacuum evaporation of bio-oil were also studied for comparison. In the case of fractionation with ethyl acetate (EA), the ethyl acetate soluble fraction (EASF) is the lignin-rich fraction, which is equivalent to the WIF in the fractionation-with-water method.

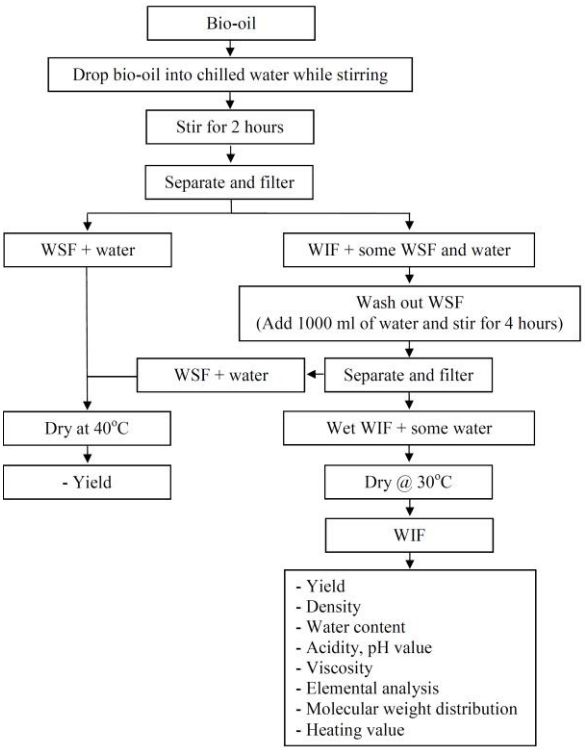

Fig. 1 Water fractionation process

2.3 Analysis

The density was determined at 15 °C by a density meter. The water content was measured by Karl Fischer titration method using 809 Titrando. The acidity was measured by titrating the sample with 0.0801 normal (N) of KOH using 809 Titrando, while the pH values were measured using 826 pH mobile. The viscosity was measured by using a viscosity meter at 40 °C. The heating values were measured with a bomb calorimeter. The molecular weight distribution of bio-oil was determined using gel permeation chromatography (GPC) technique. The elemental analysis was measured with a CHN analyzer to determine carbon, hydrogen, and nitrogen content, while the oxygen content was calculated.

3. Results and discussion

The water fractionation of bio-oil with various water-to-bio-oil ratios showed that the yields of lignin-rich WIF ranged from 31 to 24 wt% of whole bio-oil, as shown in Fig. 2, while the red-brown WSF increased with higher water-to-bio-oil ratios, from 40 to 50 wt%. The results indicated that high water-to-bio-oil ratios had higher ability to separate the WSF from the whole bio-oil. About 24-29 wt% was lost during fractionation process, mostly due to materials sticking to the equipment. The yields of WIF in this study were higher than the WIF in the work by Schvlze et al., which varied from 13.5 to 27.7%, based on water free oil [9], but were close to those obtained through water fractionation by Ba et al. [2]. In any case, the yield of WIF in bio-oil depends on characteristics of the feedstock, the pyrolysis conditions, and the solubility of bio-oil [2].

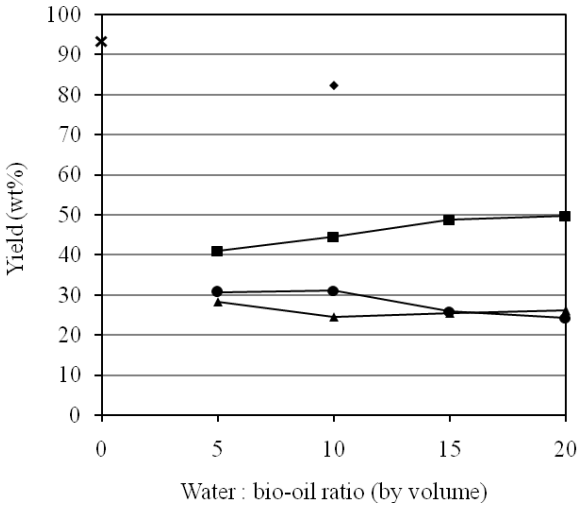

Fig. 2 Yield of WIF (●), WSF (■), loss from water fractionation (▲) with various water-to-bio-oil ratio; EA-extraction at 10:1 EA-to-bio-oil ratio (◆); and vacuum evaporation of whole bio-oil (✕)

For the ethyl acetate extraction and vacuum evaporation of bio-oil, the products' yields were very high, as shown in Fig. 2; however, the properties of the products were very similar to those of the starting bio-oil.

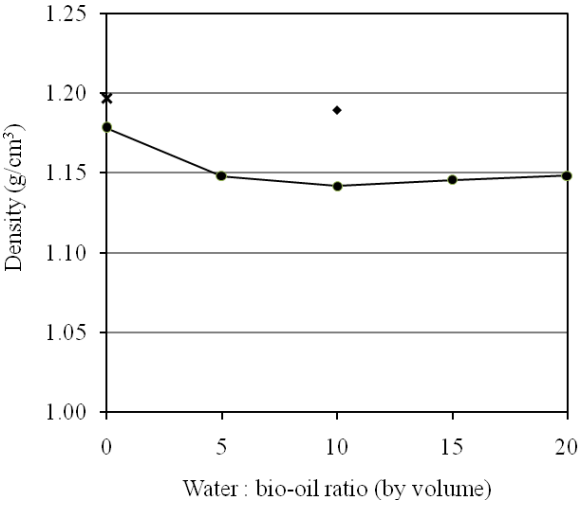

Fig. 3 Density of WIF from water fractionation (●), EA-extraction at 10:1 EA-to-bio-oil ratio (◆), and vacuum evaporation of whole bio-oil (✕)

The density of the WIF was lower than that of the whole bio-oil and did not vary across the water-to-bio-oil ratios, as shown in Fig. 3. This density drop was due to the fact that the WSF, which had higher density in the range of 1.23195-1.26621 g/cm^3, was removed. On the other hand, vacuum evaporation produced higher-density products, due to the water loss in the evaporation.

The water-content values of the products are presented in Fig. 4. It can be seen that the water content of all samples was lower than that of the whole bio-oil. This was because the water was evaporated in a vacuum oven at the end of the fractionation process. The water content decreased with rising water-to-bio-oil ratio, except for the 10:1 ratio, which appeared to be the lowest, showing that in general more of the WSF could be separated from the WIF at the high ratios. The ethyl acetate extraction and vacuum evaporation created products with lower water content, due to the use of a rotary evaporator instead of a vacuum oven, which had lower heat diffusion and evaporation rates.

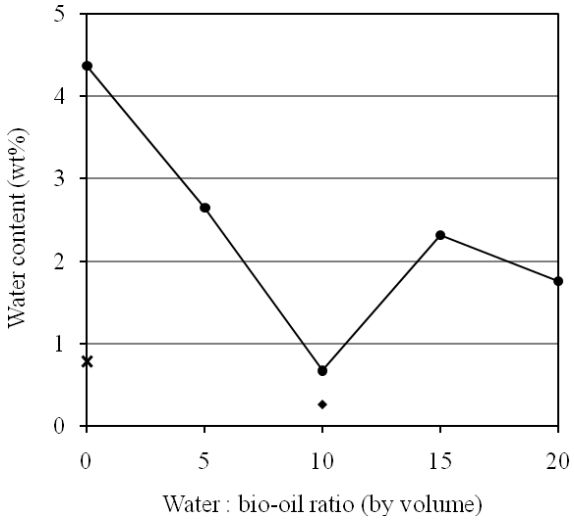

Fig. 4 Water content of WIF from water fractionation (●), EA-extraction at 10:1 EA-to-bio-oil ratio (◆), and vacuum evaporation of whole bio-oil (✕)

As show in Fig. 5, the vacuum evaporation and ethyl acetate extraction of bio-oil could only slightly reduce the acidity of bio-oil. The acidity reduction by the fractionation by water, on the other hand, was drastic. The water-to-bio-oil ratios of 5:1 and 10:1 were able to reduce the acidity more than the higher ratios. In the vacuum evaporation case, the still-high acidity of bio-oil may be due to the boiling point of acids, which are higher than that of water (e.g., at standard atmospheric pressure, the boiling points of acetic and formic acids are 118-119 °C and 100.7 °C, respectively [6], [10]). Thus, the vacuum evaporation could lower the water content of the bio-oil, but not its acidity.

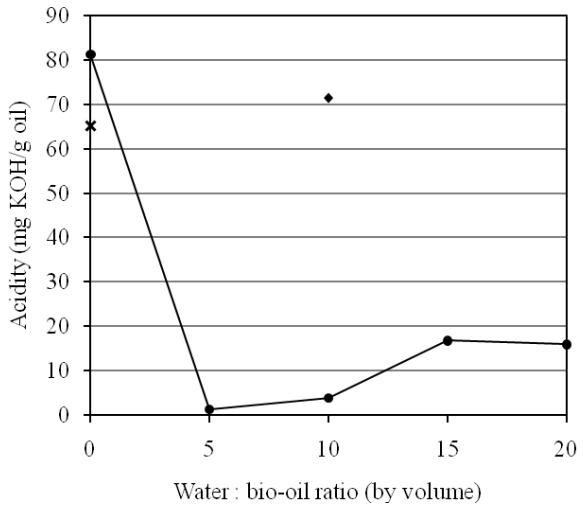

Fig. 5 Acidity of WIF from water fractionation (●), EA-extraction at 10:1 EA-to-bio-oil ratio (◆), and vacuum evaporation of whole bio-oil (×)

Fig. 6 showed that the pH of the WIF from water fractionation were generally higher than the starting bio-oil. In contrast, the pH of lignin from the vacuum evaporation and ethyl acetate extraction were lower than that of the whole bio-oil, which is consistent with the high acidity.

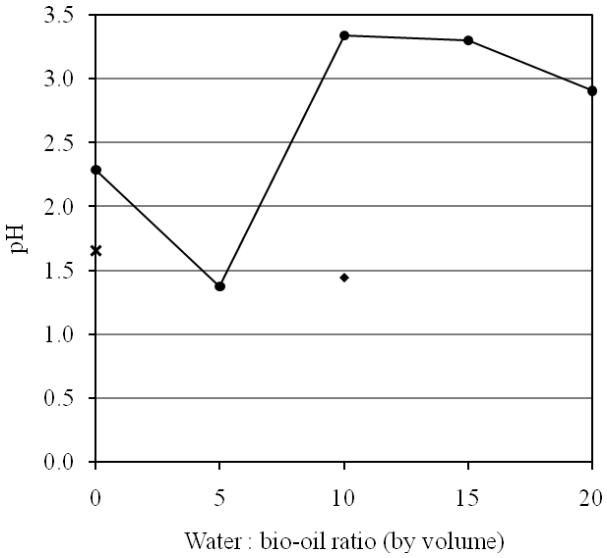

Fig. 6 pH of WIF from water fractionation (●), EA-extraction at 10:1 EA-to-bio-oil ratio (◆), and vacuum evaporation of whole bio-oil (×)

The viscosity of the WIF increased with the water-to-bio-oil ratio, as shown in Fig. 7, while the viscosity of the products from the vacuum evaporation and ethyl acetate extraction were slightly higher than that of the whole bio-oil. The rise in viscosity for higher water-to-bio-oil ratio could be due to the lower water content; however, that could not be the only factor as the water content of the WIF from the 15:1 and 20:1 ratios was not very low. Another explanation is that there were still some more WSF that had not been separated from the WIF in the low water-to-bio-oil ratio cases. Since the WSF had lower viscosity, it would have diluted the WIF, hence the lower viscosity in the low water-to-bio-oil ratio cases.

In Fig. 8, the heating values of the products from the vacuum evaporation and ethyl acetate extraction were 27.0 and 26.9 MJ/kg, respectively, which were similar to that of the whole bio-oil (25.8 MJ/kg). On the other hand, the WIF from the water fractionation had heating

values in the range from 25.8-31.0 MJ/kg. This was due to the increased carbon content and reduced oxygen content and water content, compared to the starting bio-oil (Table. 2). The different water-to-bio-oil ratios did not significantly affect the heating value.

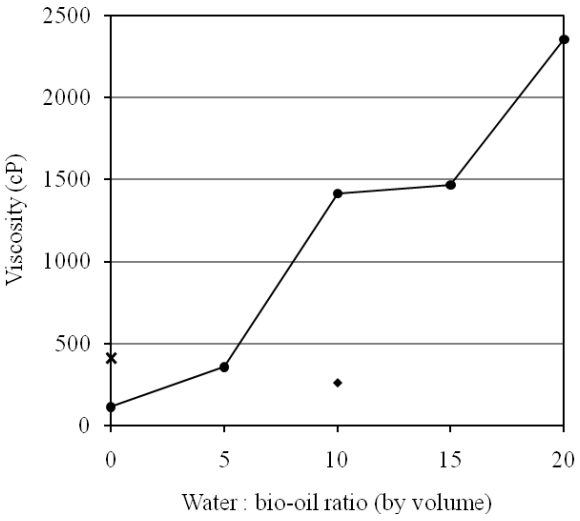

Fig. 7 Viscosity of WIF from water fractionation (●), EA-extraction at 10:1 EA-to-bio-oil ratio (◆), and vacuum evaporation of whole bio-oil (✕)

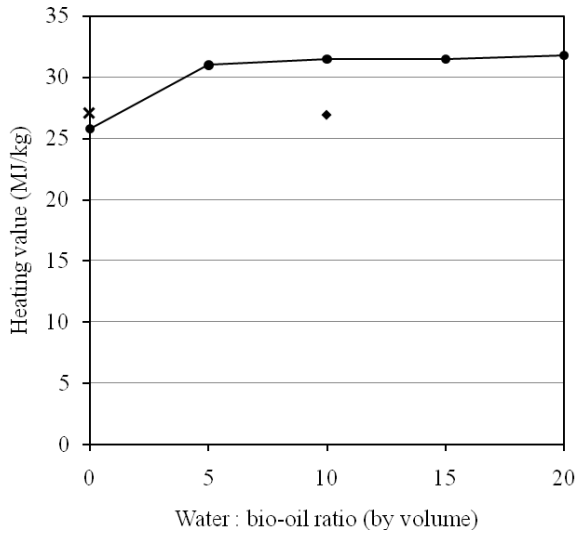

Fig. 8 Heating value of WIF from water fractionation (●), EA-extraction at 10:1 EA-to-bio-oil ratio (◆), and vacuum evaporation of whole bio-oil (✕)

The results from the elemental analysis are shown in Table 2. The WIF obtained from the different water-to-bio-oil ratios had nearly equal amount of carbon, hydrogen, nitrogen, and oxygen content. It is clear that water fractionation could produce WIF that had higher carbon content and lower oxygen content, compared to the starting, whole bio-oil. The higher carbon content explains the higher heating values of WIF obtained from water fractionation. High oxygen content is undesirable because it causes high reactively and low thermal stability in bio-oil [2]. Thus, by lowering the oxygen content, the water fractionation improved the bio-oil's stability. The products from ethyl acetate extraction and vacuum evaporation did not have higher carbon content or lower oxygen content than the starting bio-oil. This explains why the heating values of these products were close to that of the whole bio-oil. Meanwhile, the hydrogen and nitrogen content of all samples were similar.

The molecular weight distribution of all samples is showed in Table 3. It can be seen that the weight average, number average and polydispersity of WIF and EASF were reduced from those of the whole bio-oil. The weight averages of WIF and EASF were about half of that of the whole bio-oil, which indicated that water and ethyl acetate could crack the structure of bio-oil [2].

Table 2 Elemental analysis of whole bio-oil, water-insoluble fraction (WIF), ethyl acetate soluble fraction (EASF), and vacuum evaporation of whole bio oil

Sample	Element analysis (wt%)			
	C[a]	H[a]	N[a]	O[b]
Whole bio-oil	65.04	7.55	0.20	27.21
WIF (5:1 water-to-bio-oil ratio)	71.24	7.45	0.15	21.16
WIF (10:1 water-to-bio-oil ratio)	71.36	7.45	0.21	20.97
EASF[c]	62.58	7.16	0.17	30.09
Vacuum evaporation of whole bio oil	63.39	7.05	0.09	29.47

[a] The value from measurement.

[b] Calculated by difference.

[c] The waterless Ethyl acetate soluble fraction which is extract with ethyl extraction (1:1 wt%) for 10 minutes base on NREL bio-oil solvent method [1].

Table. 3 Molecular weight distribution of the water-insoluble fraction (WIF), ethyl acetate soluble fraction (EASF) and whole bio-oil

Sample	Molecular weight (g/mol)		
	Weight average, M_w	Number average, M_n	Polydispersity, M_w/M_n
Whole bio-oil	665	508	1.31
WIF[a]	317	254	1.24
EASF[b]	276	229	1.20

[a] Values from 10:1 water-to-bio-oil ratio.

[b] The waterless Ethyl acetate soluble fraction which is extract with ethyl extraction (1:1 wt%) for 10 minutes base on NREL bio-oil solvent method [1].

4. Conclusion

Bio-oil fractionation with water could improve the chemical and physical properties of bio-oil. Up to 30.69% yield of WIF, 2.6536 wt% water content, 1.29 mg KOH/g-oil acidity, and 31.00 MJ/kg heating value could be achieved at 5:1 water-to-bio-oil ratio, as a result from the increased carbon content and lowered oxygen content. The viscosity of 357.1 cP at 40 $^{\circ}$C was higher than that of the whole bio-oil but could be improved by other means.

5. Acknowledgements

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6. References

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