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Emulsification of Bio-Oil and Diesel

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With a rich biomass resource from palm oil industry, Malaysia has high potential in developing the biofuel industry. Fast pyrolysis of biomass provides bio-oil, which has a wide range of projected applications that are comparable to that of the crude oil. Storage and processing of lignocellulosic bio-oil are not economically successful yet. Bio-oil has to undergo further downstream processing to attain right specifications for final applications. Emulsification of bio-oil with conventional fuel such as diesel is one of the direct applications projected for bio-oil. Since bio-oil is a complex mixture of polar and non-polar compounds, blending of bio-oil and diesel is a challenge. Fast pyrolysis of palm kernel shells (PKS) at 550 °C in a fixed bed reactor yielded 39.2 ± 5.0 wt% of bio-oil. The bio-oil was investigated for its properties and taken for emulsification studies. The impact of emulsification parameters on the combustion properties of bio-oil diesel emulsified mixture was performed by varying bio-oil, diesel, and surfactant ratios. With the aid of an optimisation tool, the emulsion samples achieved an optimised pH of 3.29, heating value of 42.19 MJ/kg and density of 0.86 g/cm^3.

1. Introduction

Among renewable energy sources, biomass shows the most potential in terms of its abundance. As the quantity of sulphur and nitrogen content is negligible, emissions from biomass conversion for energy generation does not pollute the environment. The use of lignocellulosic biomass as an energy source is attractive based on the fact that biomass materials are diverse in nature, exhibiting different behaviours in thermal processes (Braz and Crnkovic, 2014).

Malaysia is known as the largest exporter of palm oil, and currently accounts for 39 % of world palm oil production and 44 % of the world's total palm oil supply (MPOC, 2016). The large amount of waste produced simultaneously such as empty fruit brunches (EFB), fibre, PKS, and palm oil mill effluent (POME) are promising supplies of renewable energy.

The conversion of biomass to energy can be processed via pyrolysis, a thermo-chemical process. Pyrolysis converts biomass into liquid (bio-oil), gaseous fractions and solids (mainly bio-char) by adding heat to the biomass in the absence of oxygen at approximately 500 °C. Fast pyrolysis is designed to maximise liquid product according to the heating rate employed. However, there are many constraints for bio-oil to be applied as an energy candidate/source. The high water content in bio-oil affects the heating value, flame temperature, viscosity and atomisation, whereas high acidity causes the bio-oil to be very corrosive and unstable. The high oxygen content leads to lower energy density and immiscibility with hydrocarbons. Depending on the biomass feedstock and pyrolytic process conditions, viscosities of bio-oils vary greatly, which may negatively affect the atomisation of liquid during the combustion process in the engines. Due to the high water content, high acidity, high oxygen content, and high viscosity, and low heating value, bio-oil is unable to substitute diesel in the market currently (Xu et al., 2011). The upgrading of bio-oils is required to fine-tune the properties of bio-oil.

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One of the suitable methods for upgrading bio-oil is catalytic cracking of the pyrolysis product (Baniasadi et al., 2016).

Emulsification is one of the most convenient physical upgrading techniques for bio-oil, where immiscible bio-oil and diesel are blended into a homogenous stable system, with or without surfactants. The presence of polar compounds in bio-oil may cause undesirable stratification of bio-oil and diesel emulsion. Surfactants and agitation techniques have to be used (Majhi et al., 2012). Stability of the emulsion depends greatly on the surfactant chosen and the amount of surfactant added. Since the bio-oil is acidic in nature, only non-ionic surfactants can be used and there would be changes in the combustion properties of the mixture from that of diesel. Studies on the properties are required for further development of emulsified mixture for combustion applications. In this research, bio-oil was produced from PKS using fixed bed reactor. Upon analysing the properties of bio-oil, emulsification of bio-oil and diesel was carried out in the presence of surfactants at varying ratios and different bio-oil concentrations. The properties of each combination were analysed and compared.

2. Methodology

2.1 Biomass Collection and Analysis

PKS were collected from Seri Ulu Langat Palm Oil Mill Sdn. Bhd, Dengkil, Selangor, Malaysia. Diesel was obtained from a Shell petrol station in Semenyih, Selangor, Malaysia. PKS was dried in an oven at 75 ^{0}C for 16 h, and then ground to less than 5 mm. The remaining moisture content of the dried biomass was analysed from the weight difference of dried biomass before and after placement in the oven at 103 ˚C for 16 h according to ASTM E 871 standard. The heating value of the biomass was measured using Parr 6100 bomb calorimeter, whereas the ash content of biomass was measured using ASTM E 1755 standard. Ultimate analysis for the biomass was carried out using Perkin Elmer 2400 Elemental Analyser. The thermo-gravimetric analysis (TGA) of the biomass was done with Perkin Elmer TGA/DSC. Approximately 10 mg of biomass was heated from room temperature to 900 ˚C with a heating rate 20 ˚C /min in a nitrogen flow of 20 mL/min. All analyses were duplicated for consistency.

2.2 Fast Pyrolysis

Fast pyrolysis experiments were carried out in a stainless steel fixed bed reactor to obtain bio-oil from PKS. The furnace was pre-heated to 200 °C and held at that temperature for approximately 30 min. The reactor was filled with 120 g of biomass, and placed into the preheated furnace that was to be heated to 550 °C under nitrogen atmosphere. Then, the reactor was maintained at 550 °C for 15 min to ensure complete pyrolysis of biomass. As soon as fume in condenser was observed, nitrogen flow rate was lowered. Pyrolysis vapour was condensed the soonest possible by passing through a copper coil that was covered with ice, and collected in a condenser kept in ice-bath. The non-condensable gases were passed through a gas scrubber and released to the atmosphere. The bio-oil collected was refrigerated. Bio-char was collected at the end of the experiment after cooling the reactor to room temperature.

2.3 Product Analysis

The density of bio-oil was measured using Anton Parr DMA4500M density meter. The pH of bio-oil was measured using Eutech pH700 pH meter. 1 g of bio-oil was dissolved in ethanol, stirred, and filtered. The weight difference between the initial and dried filter paper was taken as the amount of solid content in the bio-oil. A Brookfield DV-E viscometer was used to measure the viscosity of the bio-oil. FT-IR Spectroscopy was done using Brunker IFS66v. The methods for analysing moisture content, heating value, and ash content, and ultimate analysis for bio-char were similar to that for biomass analysis as Section 2.1.

2.4 Emulsification

The emulsification of bio-oil and diesel with surfactants was carried out in a bottle with the lid closed. Two types of surfactants (Brij58 and Tween80) were used for emulsification. Emulsion behaviour of bio-oil and diesel reported by Ikura (2003) showed that fuel emulsion had a good stability of about 120 h when the bio-oil content was 10 - 20 % and the surfactant was 4 - 6 %. The bio-oil to diesel ratios ranged from 10 : 90 to 30:70, whereas the surfactant wt% ranged from 0 to 10 (based on the bio-oil amount) were used in this study. A 45 mm magnetic stirrer was used and the bottle was placed on a hot plate agitator. The temperature and the stirring speed were set to 25 °C and 350 rpm, for 30 min for all emulsion samples. The bottle was then removed from the agitator and the emulsion was analysed for its properties. Emulsification of bio-oil in diesel in the presence of both surfactants were conducted according to design of experiments (DOE) developed by Design-Expert software Version 6.0.0, Stat-Ease, Inc., and Minneapolis, MN, USA. Central composite design (CCD) was applied as it required lesser number of runs and yet provided a good accuracy as a full factorial model. In this study, a total of 26 runs were conducted with 1 centre point and an alpha value of 1.414. The constructed response surface methodology was used to model fit the parameters and the responses for density, pH, viscosity and higher heating value (HHV) were measured for each emulsion.

3. Results and Discussion

3.1 Physicochemical Characteristics of Palm Kernel Shell Biomass (PKS)

The production yield and the characteristics of bio-oil depend mainly on the physicochemical properties of feedstock. Moisture content of the biomass is of importance in producing bio-oil as it affects the heating value of bio-oil, where higher moisture content in biomass will result in higher moisture content in bio-oil. The PKS biomass was dried to a moisture content of 4.5 ± 1.0 wt%. The calorific value of PKS biomass indicated its potential to be used as a feedstock for energy generation and it was 16.9 ± 0.3 MJ/kg. The ash content of biomass was 1.9 ± 1.3 wt %. Ultimate analysis reveals that PKS contains 45.04 wt%, 5.91 wt%, 0.53 wt%, 1.21 wt%, and 45.41 wt% of carbon (C), hydrogen (H), sulphur (S), nitrogen (N), and oxygen (O).

TGA studies the change in the weight of the sample as a function of temperature and was used to analyse the pyrolysis behaviour of different samples. Both thermo-gravimetric (TG, wt%) and differential thermogravimetric (DTG, wt%/°C) of PKS biomass are shown in Figure 1.

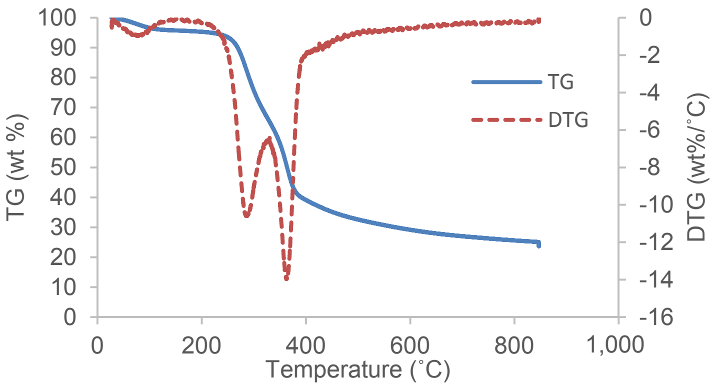

Figure 1: TG and DTG curves of biomass at heating rate of 20 °C /min

As observed from TGA curve, the weight loss began at a temperature of 100 °C, indicating the loss of unbound and bound moisture. As for the maximum weight loss that occurs at temperature range 280 - 400 ˚C, the volatile matters are from cellulose and hemicellulose, which can be confirmed from the analysis of DTG curve. The first peak at the DTG curve between 250 - 300 °C showed the decomposition of hemicellulose, while the second peak between 300 - 400 °C was contributed by the decomposition of cellulose. Lignin decomposed the slowest and the main decomposition happened slowly under the whole temperature range up to 900 °C (Yang et al., 2007). The results obtained were comparable to those reported by Asadullah et al. (2013), which showed that the thermal decomposition of PKS started at 210 °C. As discussed in the study, PKS contains a high fraction of lignin (44 %), creating difficulties for PKS to be pyrolysed for bio-oil production. Since lignin gives mechanical strength to holocellulose, the devolatilisation rate for cellulose and hemicellulose was slow.

3.2 Bio-oil Yield and Properties

Fast pyrolysis was carried out in a fixed bed reactor to produce bio-oil. It was observed that some vapour escaped from the condenser and was entrained with non-condensable gases due to insufficient residence time of vapours in condenser. This could be avoided by having two condensers installed in series (Asadullah et al., 2013). The yield of bio-oil achieved was about 39.2 ± 5.0 wt% on PKS weight basis. The gas and char yields were about 37.8 ± 1.9 wt% and 23.0 ± 5.1 wt%. This result defers from that obtained by Asadullah et al. (2013) who had successfully produced 44 – 56 % of bio-oil. The lower yield of the current study as compared with literature data was due to the difference in experimental conditions and set up. From analysis, the C, H, S, N, and O weight percentages of bio-oil are 23.41 wt%, 10.13 wt%, 0.04 wt%, 0.20 wt%, and 65.90 wt%; the C, H, N, S, and O content of bio-char as 64.83 wt%, 2.98 wt%, 0.49 wt%, 0.43 wt%, and 27.45 wt%.

The properties of bio-oil obtained from PKS biomass are listed in Table 1 and are compared to ASTM D7544 standard. The high density of bio-oil reflects the high molecular weight compounds. The viscosity of bio-oil was well within the values stated in the ASTM standard, which could be caused by the higher solid content in bio-oil. The bio-oil was produced without any filtration process and thus, might be a contributor to the high solid content in the bio-oil. As the PKS bio-oil produced did not meet the ASTM D7544 standards, further studies on improving the properties of bio-oil have to be conducted.

Table 1: Comparison between experimental properties of bio-oil and ASTM D7544

Property	Result	ASTM D7544
Density (kg/ m^3)	1,068 ± 0.97	1,100 - 1,300
pH	2.50	Report*
Viscosity (Cp)	5.7 ± 1.30	125 max
Heating value (MJ/kg)	13.8 ± 2.20	15 min
Solid content (%)	3.90 ± 0.70	2.5 max
Ash content (%)	0.26 ± 0.06	0.25 max

* Detailed information is required in reporting the results of the standard

Bio-oil usually contains some organic acids such as formic and acetic acids, which lower its pH to below 5. The bio-oil at lower pH can cause severe corrosion in the combustion and firing equipment. Chemical treatment for bio-oil is required to lower the acidity. The calorific value of PKS bio-oil was found to be 13.8 ± 2.2 MJ/kg, which was relatively low as compared to the calorific value for bio-oil produced from palm kernel cake (18.67 MJ/kg) published by Razuan et al. (2010). Low heating value of bio-oil indicated that the pyrolysis of lignin was ineffective and major components were derived from holocellulose. An improvement of pyrolysis conditions is required for the decomposition of lignin compounds, such as increasing pyrolysis temperature or increasing vapour residence time.

Figure 2 compares the TGA of both PKS bio-oil and diesel.

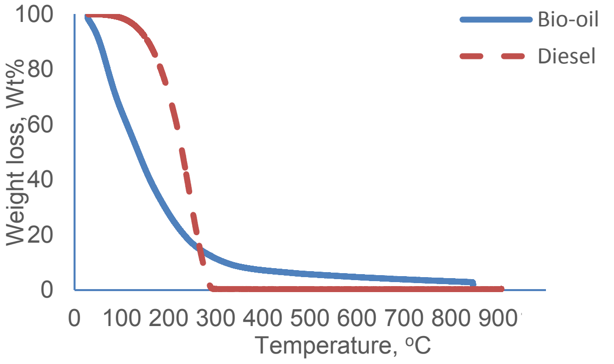

Figure 2: TGA comparison between PKS Bio-oil and Diesel

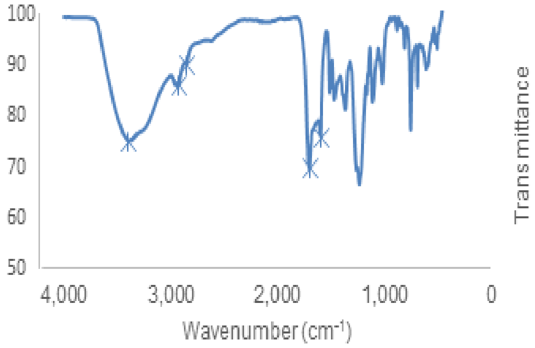

Figure 3: FTIR spectra of bio-oil

The thermogram in figure 2 shows that bio-oil degradation started at 30 °C whereas diesel was steady at around 75 °C, which confirmed the instable nature of bio-oil. The pyrolysis reaction of bio-oil varied from 30 – 350 °C, and even after, degradation proceeded in a slow rate. In the case of diesel, the pyrolysis reaction was limited to 75 – 280 °C. The thermogravimetric profile of bio-oil confirmed the presence of numerous compounds with different volatility. The diesel sample experienced a steep reduction in mass to 0 wt%, indicating that the diesel had been completely volatised. In contrast, even though bio-oil starts to lose volatile matters at a lower temperature, the process was gradual. Even at higher temperatures, the wt% of bio-oil was higher than that of diesel, revealing the higher solid content in bio-oil.

Figure 3 presents the FT-IR spectra of bio-oil and bio-char.

The results of bio-oil are similar to those reported by Nanda et al (2014). The presence of the broad band between 3, 000 cm^{-1} and 3, 700 cm^{-1} indicates O-H stretching vibration, attributed to the presence of phenol and alcohol in bio-oil. The peaks at 2, 852 cm^{-1} and 2, 934 cm^{-1} are both assigned to C-H stretching vibration. Peaks between 1,680 cm^{-1} and 1, 780 cm^{-1} confirms the presence of stretching vibrations of C-O from ketones and aldehydes. The peak at 1, 708 cm^{-1} can be assigned to C=O stretching due to the presence of ketones, quinones, and aldehyde groups. The presence of aromatics was supported by the peaks between 1, 580 cm^{-1} and 1, 650 cm^{-1}. The various peaks between 950 cm^{-1} and 1, 300 cm^{-1} are contributed by other functional groups such as different alcohol, phenols, ethers, and esters. Lignin peak at 1, 424 cm^{-1} aromatic ring modes (the peaks between 1, 513 cm^{-1} and 1, 597 cm^{-1}) were noticed in FTIR spectra of bio-char (not shown here).

3.3 Emulsification

The bio-oil contained significant amount of oxygen and water as compared to diesel. Therefore, bio-oil was immiscible with diesel. Hence, energy is needed to disperse this immiscible water phase into the diesel phase in the form of fine droplets. The current experiments showed that the energy supplied by mechanical agitation was not able to provide a stable emulsion. Therefore, results suggested to use ultrasound, which can produce smaller sized droplets to improve the stability of the emulsion. The effects of emulsification parameters on combustion properties are given in Figure 4.

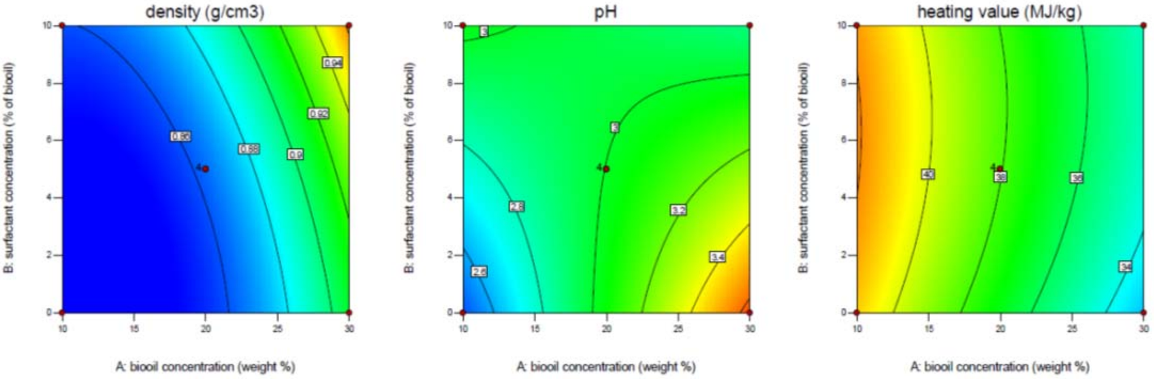

Figure 4: Contour graph on the effect of bio-oil concentration and surfactant concentration on combustion properties of bio-oil – diesel blend; (a) density, (b) pH, (c) heating value

As seen in Figure 4(a), the density of the emulsions changed significantly with the varying of bio-oil and surfactant concentrations, but not with the type of surfactant. As both of the bio-oil and surfactant concentrations increased, the density of the emulsion increased, showing that there was less likely to have chemical interaction between bio-oil and diesel but only physical interaction. The pH of the emulsions experienced a change with respect to the bio-oil and surfactant concentrations, and the type of surfactant used. As observed from Figure 4(b), pH of the emulsion increased with both bio-oil and surfactant concentrations. This observation was unexpected but favourable. The heating value of the emulsion was inversely proportional to bio-oil concentration but was not significantly affected by surfactant concentration, which is shown in Figure 4(c). The change in viscosity of the emulsions was insignificant at these limited ranges. A study by Ikura et al. (2003) concluded that as the bio-oil concentration increased, the viscosity of the bio-oil and diesel emulsion increased, which was in-contrast to current study. However, our results for HHV and density were as similar to those reported by Ikura et al. (2003). One of the future works that can be done is altering the agitation technique and speed. The reduction of the solid content of the bio-oil by using glass wool in the fixed bed reactor may be further studied as well. According to Martin et al. (2014), the key to producing an emulsion of two immiscible items is the surfactant chemical. Since the bio-oil produced is acidic in nature, only non-ionic surfactants can be used. When non-ionic surfactants are used, hydrophilic lipophilic balance (HLB) is important to choose the ideal surfactant mixture. Thus, a detailed study on the effects of surfactants on PKS derived bio-oil – diesel mixture have to be further studied.

The optimisation was based on the highest heating value, highest pH and the lowest density values possible. The results obtained from the emulsification experiments were evaluated by DOE software. DOE has selected the mixture ratio of 10 % bio-oil: 90 % diesel and 10 % surfactant as most significant sample for optimisation. Based on DOE prediction, four experiments were conducted using Brij and Tween surfactants. The experimental data were compared well to the data predicted by the DOE. The experimental data and DOE prediction of the four optimised samples are presented in Table 2.

Table 2: Comparison between experimental data and DOE prediction properties

Ratio (%)		Surfactant (wt%)	Heating Value (MJ/kg)	Viscosity (cP)	Density (g/cm^3)	pH
Diesel	Bio-oil					
			DOE Prediction			
90	10	10	42.19	5.67	0.86	3.29
			Experimental Data			
90	10	Tween, 10	41.38	5.96	0.86	4.10
90	10	Brij, 10	41.18	5.26	0.85	3.70

4. Conclusions

Bio-oil was produced from pyrolysis of palm kernel shell in a fixed bed reactor at a temperature of 550 °C. The bio-oil production yield was 39.2 ± 5.0 wt%. The density and viscosity were comparable with the ASTM D7544 specification. However, some of other properties of bio-oil did not meet ASTM standards. Emulsification of bio-oil in diesel was conducted by varying diesel:bio-oil ratio and surfactant concentrations. The optimum ratio was found to be 90 : 10 (diesel:bio-oil) and 10 wt% surfactant for maximum heating value and pH, and minimum density. The optimised emulsion samples had a predicted pH of 3.29, heating value of 42.19 MJ/kg and density of 0.86 g/cm^3. Experimental data were in good agreement with the predicted data. In order to enhance the accuracy of the results and to obtain a better insight on the emulsification of bio-oil and diesel, further studies will have to be carried out as proposed.

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