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Use of palm oil decanter cake as a new substrate for the production of bio-oil by vacuum pyrolysis

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ABSTRACT

The present study was carried out to investigate the potential of palm oil decanter cake (PDC) for bio-oil production at various temperatures by vacuum pyrolysis. PDC was first dried in oven at 105 °C for 24 h to remove moisture and ground to particle size of 0.85–2 mm. Pyrolysis experiments were carried out at 400, 450, 500, 550 and 600 °C, with heating rate of 15 °C/min. The highest yield of bio-oil (22.12 wt%) was obtained at pyrolysis temperature of 500 °C. The chemical characterization of bio-oil was studied using ^{1}H NMR, FTIR, CHNS analyzer and GC–MS. The other properties like pH, calorific value and thermal volatilization were also determined. The pH value recorded to be 6.38, which is found to be higher as compared to other bio-oils. The calorific value of PDC bio-oil found to be 36.79 MJ/kg, which is slightly lower than that of conventional liquid fuel such as gasoline and diesel fuel. However, the bio-oil obtained from PDC has better fuel characteristics than that of bio-oil derived from palm kernel shell (PKS).

1. Introduction

World's energy consumption is increasing significantly in recent decade due to economic and population growth. International Energy Agency forecasts that global energy demand will increase by one third from 2007 to 2035. However, the share of fossil fuel in world's energy mix will decrease from 82% to 76% in 2035 while renewables share in primary energy use rises to 18% in 2035, from 13% in 2011 [1]. In addition, depletion of fossil fuel resources and uncertainty of oil price encourage the search for biomass based renewable energy sources due to their local availability, affordability and sustainability. Employing biomass as energy source is likely to be an attractive option for reducing greenhouse gas emission due to its ability to deliver a significant reduction in net carbon emission when compared with fossil fuels [2–4]. Combustion of biomass is considered to be CO_2 neutral as it can be captured from atmosphere by photosynthesis process [5,6].

Oil palm industries can be considered as potential resources for generation of renewable energy. From the processing of fresh fruit bunch (FFB), palm oil milling plant produces 23.5 wt% as crude palm oil (CPO), 5.2 wt% as crude palm kernel oil (CPKO) while the rest, 71.3 wt%, is released into the environment in the form of solid or aqueous phase [7]. Decanter cake (PDC) is generated by palm oil milling plant from three-phase CPO purification. The production rate of PDC is about 4–5 wt% of fresh fruit bunch processed. This is equivalent to around 3.6 million tonnes of PDC generated by Malaysian palm oil industries in 2012. At the oil palm mill site, the PDC generated take up a lot of space. Moreover when dried, the PDC become fire hazard and contribute toward increasing the amount of suspended particles in the vicinities of mills. Recently, PDC has been utilized as feedstock for the production of cellulose and polyose [8,9], bio-surfactant [10], bio-butanol [11], and bio-diesel [12]. So far, there is no report on thermal conversion of PDC into bio-oil through pyrolysis process.

Biomass is converted into energy sources through thermal, biological, mechanical or physical processes [13]. Biomass is heated in the absence of oxygen to 275–675 °C during thermal conversion via pyrolysis to produce portion of gas, liquid (condensable gases) and carbon rich solids [14]. The relative amount of each fraction depends on the initial feedstock type and mode of pyrolysis. Fast pyrolysis (residence time less than 2 s) at 400–600 °C produces up to 75% liquid fraction, while slow pyrolysis generates lesser liquid fraction and more solid fraction. A specific process, gasification, converts almost 90% of biomass into gas fraction [15]. Pyrolysis for liquids production is currently of particular interest as the liquid can be stored and transported, and used for chemicals synthesis or as an energy carrier [13].

Vacuum pyrolysis is usually conducted in slow or intermediate rate pyrolysis mode. Vacuum pump is employed to evacuate the air

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before heat treatment of biomass and withdraw the vapor during thermal decomposition of biomass. Typically, yield of liquids by vacuum pyrolysis is about 20–40 wt%, which is comparable with that of slow pyrolysis [16]. Simple reactor design and no requirement of inert gas made up the advantage of vacuum pyrolysis compared to fast pyrolysis mode. Liquid product of pyrolysis is usually divided into two phases: aqueous phase and non-aqueous phase. The aqueous phase pyrolysis liquid contains lower molecular weight oxygenated organic compound, while organic compounds particularly aromatics becomes main constituent of non-aqueous phase [17]. Bio-oil obtained by pyrolysis process typically contains 55–65 wt% C, 5–7 wt% H, 28–40 wt% O and small amount of N and S (less than 0.5 wt%) [18].

Generally, bio-oil compounds can be classified into acids, esters, linear aldehydes and ketones, cyclic ketones, furans, alcohols and sugars, ethers, phenols, phenolic ethers, oxygenated cyclic compounds, hydrocarbons and derivatives, and nitrogen compounds [19,20]. However, several factors e.g. feedstock type, pyrolysis condition, condensation procedures determines the chemical compositions of bio-oils [21]. High oxygen content of bio-oil is a major concern since it causes the instability of bio-oil, low calorific value and high acidity [22]. It can be resolved by upgrading through hydro-treatment process over heterogeneous catalysts [23,24].

Lignocellulosic biomass wastes are commonly used as substrate in bio-oil production via pyrolysis. In addition edible/non-edible oil cakes were also considered as potential raw materials for bio-oil production. The pyrolysis of soybean oil cake [25], rapeseed oil cake [26,27], sunflower [28], palm kernel cake [29,30], and sesame cake [31] has already been reported. The oil content of PDC was reported to be about 11.5 wt% [12]; therefore, it has the potential to be utilized as bio-oil substrate. A commercially viable process for converting PDC into bio-oil would facilitate removal of PDC, ensure formation of useful valuable by product and make the oil palm industry eco-friendly. Therefore, the present study was aimed to convert PDC into bio-oil through vacuum pyrolysis. The study also discusses the effect of pyrolysis condition on product distribution, and properties of PDC bio-oil in comparison with PKS bio-oil.

2. Materials and methods

2.1. Materials

PDC and PKS were collected from LKPP Sdn. Bhd. palm oil milling plant in Lepar Hilir, Kuantan, Pahang, Malaysia. The samples were dried in oven at 105 °C for 24 h to remove moisture. Dried decanter cake was then ground and sieved to obtain the particle size of 0.85–2 mm.

2.2. Vacuum pyrolysis

The pyrolysis of biomass was carried out in a cylindrical stainless steel reactor with inner diameter of 6.5 cm and height of 12 cm. The pyrolysis apparatus is illustrated in Fig. 1. About 300 g of biomass was loaded into the reactor that was then sealed and positioned into a muffle furnace. A vacuum pump was used to evacuate the air inside the reactor and kept the pressure below 30 kPa. The reactor was heated at 15 °C/min to the desired reaction temperature of 400, 450, 500, 550 and 600 °C. Vapor evacuated from the pyrolysis process was condensed using water condenser and water-ice condenser traps. Uncondensed gases were discharged into air properly. The pyrolysis processes was terminated after an hour at the final temperature or when liquid was not produced anymore. Liquid product separated into two phases: organic and aqueous phase. The organic phase obtained i.e. the bio-oil, is labelled as PDC-400, PDC-450, PDC-500, PDC-550, and PDC-600, with the pyrolysis temperature serving as part of the label. For comparison purposes, dried PKS was also pyrolyzed at 500 °C. The bio-oil produced was labelled as PKS-500. All of the bio-oil samples were analyzed to determine their properties and chemical compositions.

2.3. Characterization of bio-oil

2.3.1. Higher heating value

Calorific value of bio-oils was measured using IKA C-200 oxygen bomb calorimeter. Approximately 0.2 g of bio-oil was placed into a quartz crucible inside the combustion chamber. Pure oxygen gas was introduced into the chamber until 30 bar pressure was achieved. Two litres of tap water at temperature range of 20–23 °C was added inside the calorimeter surrounding the chamber. After five minutes of stirring, the water temperature became stable and the samples were ignited. The changes in water temperature were monitored until it remained constant. Differences of initial and final temperature were used to calculate the heating value of the samples. The calorimeter heat capacity was calibrated using benzoic acid as reference.

2.3.2. pH

Mettler Toledo SevenEasy pH meter was used to determine the pH of bio-oil. Each measurement was done in triplicate to give the average of the measurements.

2.3.3. Viscosity and density

Dynamic viscosity of bio-oils was determined by Brookfields DV-II+ viscometer equipped with Small Sample Adapter. Density of bio-oil was measured using KEM Densitometer. Viscosity and density of Automotive Diesel Oil (Caltex) were also measured for comparison purpose.

2.3.4. Elemental analysis

The composition of C, H, and N elements in bio-oil were determined by Elementar CHONS Analyzer. Oxygen content of bio-oil was calculated by differences.

2.3.5. Fourier transform infrared spectrometry

FTIR spectra of the bio-oils were obtained by Perkin Elmer Spectrometer. A thin film of bio-oil was placed between KBr plates and 100 scans of spectrum in 400–4000 cm^{-1} range were accumulated. A blank KBr plate was used as background of the measurement.

2.3.6. ^{1}H nuclear magnetic resonance

The nature of hydrogen in the bio-oil and the aliphatic, olefinic and aromatic components in bio oils were examined by Bruker NMR. Bio-oil sample was diluted into deuterated chloroform as solvent prior to analysis.

2.3.7. Gas chromatography–mass spectrometry

Analysis of bio-oil composition was performed on HP 6895 GC–MS equipped with Agilent 5973 mass selective detector. A HP DB-Wax capillary column (30 m × 0.25 mm × 0.25 μm) was employed to separate the constituents. Bio-oil was diluted in hexane then 1 μL sample was injected into column at 250 °C. Helium was used as carrier gas at flow rate of 1 mL/min. Oven temperature was programmed from 40 to 250 °C with heat ramp 8 °C/min, held at initial and final temperature for 10 min.

2.3.8. Thermogravimetry analysis

Thermal volatilization of bio-oil was evaluated by Mettler Toledo TGA/DSC unit. Experiments were performed involving 5 mg sample, 50 mL/min nitrogen flow with 10 °C/min heating