



Utilization of palm oil sludge through pyrolysis for bio-oil and bio-char production



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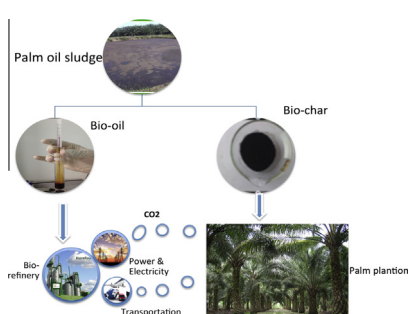
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HIGHLIGHTS

- Palm oil sludge was pyrolyzed to get value added materials: bio-oil and bio-char.
- Listed properties of bio-oil met the ASTM specifications as a fuel.
- Adsorption efficiency of bio-char was comparable to that of activated carbon.
- Pyrolysis can be effectively used for the safe disposal of palm oil sludge.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, pyrolysis technique was utilized for converting palm oil sludge to value added materials: bio-oil (liquid fuel) and bio-char (soil amendment). The bio-oil yield obtained was 27.4 ± 1.7 wt.% having a heating value of 22.2 ± 3.7 MJ/kg and a negligible ash content of 0.23 ± 0.01 wt.%. The pH of bio-oil was in alkaline region. The bio-char yielded 49.9 ± 0.3 wt.%, which was further investigated for sorption efficiency by adsorbing metal (Cd^{2+} ions) from water. The removal efficiency of Cd^{2+} was $89.4 \pm 2\%$, which was almost similar to the removal efficiency of a commercial activated carbon. The adsorption isotherm was well described by Langmuir model. Therefore, pyrolysis is proved as an efficient tool for palm oil sludge management, where the waste was converted into valuable products.

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1. Introduction

Malaysia plays a major role in palm oil industry as the second largest producer and world's largest exporter of palm oil. Palm oil industries produce a substantial amount of agricultural wastes, which present a great opportunity for harnessing biomass energy

in an eco-friendly and commercially viable manner (Ng et al., 2012). Empty fruit bunch, mesocarp fiber, fronds, trunk and shell are the major biomass available from oil palm tree. In addition to these biomass feedstocks, palm oil mill produces great amount of palm oil mill effluent (POME), which is considered as a major source of renewable energy. One of the major wastes produced during POME treatment is waste sludge and the growing amount of this waste needs serious attention. Compared to other wastes from palm oil mill, sludge cannot be used as a feedstock for most

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of the renewable energy processes. Another application of sludge is as an adsorbent by carbonization (Gobi and Vadivelu, 2013). Palm oil sludge is normally disposed in palm oil plantations, which can bring hygienic issues in addition to environmental pollution.

At present, fast pyrolysis of biomass is a well-known technology for liquid fuel production because of high oil yield and high energy density compared to virgin biomass. In pyrolysis, the organic part of biomass is converted into carbon rich solid (char) and volatile matters (liquid and gases). Pyrolysis can handle different types of feedstocks ranging from lignocellulosic biomass to sewage sludge (Kim and Parker, 2008; Thangalazhy-Gopakumar, 2010). It is easy to construct and operate a pyrolysis plant nearby the source of feedstock and the products can be easily transported to existing refineries for further processing.

The solid product (bio-char) can be used as an adsorbent for wastewater treatment and as a soil amendment to enhance the fertility. As a soil amendment, bio-char fertilize the soil without environmental and hygienic issues. Bio-char in the soil act as a sink for atmosphere carbon dioxide, helps to retain nitrogen, sulfur, phosphorous, calcium and organic matter in the soil and thus prevent soil leakage (Lehmann, 2007). As an adsorbent, bio-char remove metal dyes and other pollutants from surface or wastewater.

Current project utilize the palm oil sludge (after aerobic and anaerobic treatment) from wastewater treatment plant of palm oil mill, which is normally disposed as soil amendment for palm oil plantations. Direct disposal of sludge in plantation will bring serious hygienic issues to public. To the author's knowledge, any other work was done with this sludge other than direct disposal. The utilization of sludge through pyrolysis would be a new tool for solid waste treatment effectively. Normal carbonization of sludge provides only char where pyrolysis would provide both liquid and char products. Moreover, this was waste to energy production. In this project, bio-oil was produced from palm oil sludge and the physical properties were analyzed and compared with ASTM standards. Current project would also assess the bio-char application as adsorbent for metal (cadmium) removal from water. Herein, the sludge converted as char, simultaneously producing a value added product (liquid fuel), which can bring money for palm oil mills.

2. Methods

2.1. Sludge preparation and characterization

Palm oil sludge used in this study was obtained from Seri Ulu Langat Palm Oil Mill Sdn Bhd, Dengkil, Selangor, Malaysia. The sludge was already treated for complete oil recovery and passed through acidification, anaerobic and aerobic ponds in effluent treatment section. The sludge collected was dried in an oven at 65 °C for 72 h. The dried sludge was ground using a granulator and sieved. The sample fraction 2.00–3.35 mm was used for pyrolysis. The moisture content of the sludge (wet basis) was determined by calculating the weight loss of a sample by heating it in an oven at 103 °C for 16 h. Ash content in the sludge was measured using ASTM E 1755 standard. Higher heating value (HHV) of the sludge was measured using an oxygen bomb calorimeter (IKA, model C2000). Thermo-gravimetric behavior of sludge biomass was analyzed in a thermo gravimetric analyzer (TA Instruments, TGA Q500) under nitrogen environment. In TGA analysis, a known amount (approximately 5 mg) of sludge was taken and heated from ambient temperature to 800 °C at different heating rates of 10, 20, 30, and 40 °C/min and hold at final temperature for 10 min. A nitrogen flow rate of 100 mL/min was maintained during the analysis. All experiments were run in duplicates to confirm reproducibility.

2.2. Pyrolysis

Pyrolysis was done in a fixed bed quartz reactor (75 mm OD and 700 mm length), which was heated using a single-zone tube furnace (Carbolite, Model CTF 12/75/700). 200 g of sludge was filled inside the reactor and the reactor was placed in the furnace. Initially the reactor was purged with nitrogen flow of 0.6 L/min and a little flow was maintained during the pyrolysis for inert atmosphere. The furnace was heated with a heating rate of 100 °C/min, however, the actual heating rate of the sample was not measured. Once the furnace temperature reached at 550 °C, the temperature was maintained until the white fumes finished. Two glass condensers were used in series to condense the vapors. The condensers were placed in ice bath where the temperature was around 2–4 °C. The non-condensed gas was vented out. Weight of bio-oil and bio-char was measured and calculated as the weight percentage of biomass. The experiment was run in triplicates to confirm reproducibility.

2.3. Bio-oil analysis

Physical and chemical analyses of bio-oil including pH, ash content, solid content, and heating value were determined. The pH measurement was performed with a digital pH meter (Eutech Instrument, pH 510). The solid content in the bio-oil was measured as ethanol insoluble portion. Briefly, one gram of bio-oil was added into a beaker containing 100 mL ethanol and mixed well. The solution was then filtered through a dried and pre-weighed filter paper (1 µm pore size) followed by drying in an oven at 105 °C for 30 min. The insoluble portion remained on the dried filter paper was weighed. HHV and ash content were also determined as discussed in Section 2.1. Each measurement was repeated thrice and the average values were reported in the paper.

Bio-oil compounds were identified by injecting a dilute sample (300 mg bio-oil in 20 mL methanol) to an Agilent 7890 GC/5975MS using a HP-5MS column (30 m; 0.25 mm i.d.; 0.25 mm film thickness). Oven temperature program was as follows: 40 °C for 2 min, subsequently increased to 250 °C at 10 °C/min, and the final temperature was held for 3 min. Helium (99.99% purity) was flowed as carrier gas at 1.25 mL/min. The injector and the GC/MS interface were kept at constant temperatures of 280 and 100 °C, respectively. Compounds were analyzed over a mass per change (m/z) range of 50–550 and identified by comparing the mass spectra with the NIST (National Institute of Standards and Technology) mass spectral library.

2.4. Bio-char activation

The collected bio-char was ground and sieved to obtain similar particle sizes of 600 microns to 1.18 mm as that of activated carbon. Before adsorption studies, the bio-char was activated by 1.0 M KOH solution. Initially, bio-char was mixed with the KOH solution at a 1:1 mass ratio, and then placed on a hot plate for 4 h at a temperature of 60 °C to evaporate all the water. After evaporation, the mixture was dried in an oven for 24 h at 100 °C. The dried bio-char was washed with distilled water, filtered using a vacuum filtration unit, and dried again to make ready for adsorption.

2.5. Adsorption studies

Activated bio-char and activated carbon (R&M Chemicals, Malaysia) of similar particle sizes were used to investigate the removal of cadmium from water. The initial concentration of Cd²⁺ 1 mg/L was taken for batch studies. The agitation speed, adsorbent dosage, and the contact time were kept at 125 rpm,

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