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Biochar potential evaluation of palm oil wastes through slow pyrolysis: Thermochemical characterization and pyrolytic kinetic studies

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HIGHLIGHTS

- PKS-char and EFB-char have high carbon contents of 59.92 and 53.78 wt%.
- HHV of PKS-char (27.50 MJ kg^{-1}) and EFB-char (26.18 MJ kg^{-1}) comparable with coal.
- High yields of PKS-char (37.07 wt%) and EFB-char (35.14 wt%) achieved by pyrolysis.
- Multi-step pyrolysis kinetics demonstrated by isoconversional KAS and FWO methods.

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ABSTRACT

This research investigated the potential of palm kernel shell (PKS), empty fruit bunch (EFB) and palm oil sludge (POS), abundantly available agricultural wastes, as feedstock for biochar production by slow pyrolysis (50 mL min^{-1} N_2 at 500 °C). Various characterization tests were performed to establish the thermochemical properties of the feedstocks and obtained biochars. PKS and EFB had higher lignin, volatiles, carbon and HHV, and lower ash than POS. The thermochemical conversion had enhanced the biofuel quality of PKS-char and EFB-char exhibiting increased HHV (26.18–27.50 MJ kg^{-1}) and fixed carbon (53.78–59.92%), and decreased moisture (1.03–2.26%). The kinetics of pyrolysis were evaluated by thermogravimetry at different heating rates (10–40 °C). The activation energies determined by Kissinger-Akahira-Sunose and Flynn-Wall-Ozawa models were similar, and comparable with literature data. The findings implied that PKS and EFB are very promising sources for biochars synthesis, and the obtained chars possessed significant biofuel potential.

1. Introduction

The increase in fossil fuel usage due to rapid industrialisation and population growth has resulted in detrimental impacts on the environment such as air pollution, global warming and climate change. This, in addition to diminishing fossil fuel reserves, poses a serious concern worldwide for governments and researchers alike. In response to this concern, many researchers have focussed on developing alternative routes for sustainable and clean energy production, especially biofuel from lignocellulosic wastes (Jeguirim et al., 2014a).

Biofuel from lignocellulosic materials is considered renewable, abundant and low cost since the feedstock is readily available worldwide in the forms of agricultural waste, forestry refuse, industrial biomass by-products, municipal sewage sludge, aquatic algae and plants (Chen et al., 2015; Jeguirim et al., 2014b; Liang et al., 2008). These solid wastes can be transformed into various biofuels such as syngas, bio-oil and biochar through gasification and pyrolysis (Jeguirim et al., 2014b). Comparing with standard fossil fuels, lignocellulosic wastes have lower nitrogen and sulphur composition hence harvesting biofuel from them would generate lesser toxic gases including nitrogen oxides and sulphur dioxide. Furthermore, production of biofuel would lead to comparatively lower carbon footprint since lignocellulosic wastes are part of nature's carbon cycle. Thus, the production of bioenergy from lignocellulosic wastes is more environmentally friendly (Lee et al., 2013).

Oil palm (*Elaeis guineensis*) is grown extensively in Malaysia with a total planted area of 5.74 million hectares in 2016. The production of edible oil from the palm fruits has reached 17.32 million tonnes per year (MPOB, 2016a). Apart from palm oil production, the industry also generates considerable amount of agricultural wastes such as palm kernel shell (PKS), empty fruit bunch (EFB)

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and palm oil sludge (POS). PKS and EFB are solid residues from fresh fruit bunch (FFB) after oil extraction, accounting for 4.5 and 22 wt% per tonne of FFB, respectively (Garcia-Nunez et al., 2016). Based on the FFB yield of 15.91 tonnes per hectare in 2016, the quantities of PKS and EFB generated were significant (MPOB, 2016a). Palm oil sludge (POS) is the semi-solid residue resulting from the treatment of palm oil mill effluent (POME) by acidification, anaerobic and aerobic methods. POS is generated in significant quantity in mills located throughout Malaysia due to the large amount of POME (800 dm^3 POME per tonne of FFB) resulting from high consumption of water in oil extraction and cleaning processes (Garcia-Nunez et al., 2016). The disposal of untreated POS, PKS and EFB could lead to adverse consequences on the environment. It is thus necessary to control the wastes discharge from palm oil industry.

This research involved re-utilizing the three major palm oil mill residues as feedstock for biochar thereby providing an attractive option for managing the wastes and imparting economic value. Biochar is a carbon rich and porous solid, often produced by slow pyrolysis of waste biomass without or with partial presence of oxygen (Creamer et al., 2014; Islam et al., 2016). The pyrolytic reaction releases moisture and volatiles in the biomass, leaving behind a porous structure whilst retaining the aromatic compounds and chemical functional groups (Tan et al., 2017). These desirable attributes enable biochar to be used in various applications such as soil amendment, energy production and pollution control. Biochar when added to soil can improve its fertility by enhancing nutrients and water retention (Beesley et al., 2011; Wang et al., 2014; Zhang et al., 2013). It has also been utilized as an effective pollutant adsorbent in environmental remediation (Creamer et al., 2014; Hodgson et al., 2016). A number of agricultural wastes such as pelletized grape vine and sunflower husks (Colantoni et al., 2016), paper mill sludge (Devi and Saroha, 2015), olive solid waste, date palm trunks, pine sawdust, *Posidonia oceanica* balls (Jeguirim et al., 2014b), rice husk and elm sawdust (Wang et al., 2014) have been pyrolyzed to biochars indicating the process versatility with regard to feedstock type.

The objectives of this research were to investigate the potential of PKS, EFB and POS as the precursor for biochar, and to evaluate the biofuel potential of the obtained chars. To date, a number of investigations have been reported on pyrolysis of palm oil residues by thermogravimetric (TG) analysis whereby the obtained data were analyzed using different kinetic models and/or model-free isoconversional approaches. For instance, Jeguirim et al. (2014a) examined the thermochemical conversion of PKS and palm mesocarp fibre (PMF) under nitrogen (N_2) atmosphere. PMF was determined to be the most suitable feedstock exhibiting the highest heating values. The pyrolysis kinetic was represented by devolatilization followed by char formation. Nyakuma et al. (2015) who assessed the potential of palm EFB as the pyrolysis feedstock reported that the pyrolytic kinetics were well represented by a model-free isoconversional method. Luangkiattikhun et al. (2008) studied the non-isothermal decomposition of palm shell, fibre and kernel, and determined that the experimental data were best fitted with the two step-parallel reactions model. Other similar works on palm oil residues reported in the literature include that by Yang et al. (2004) and Ma et al. (2015).

This research aims to compare the pyrolytic behaviour of PKS, EFB and POS sourced from the same palm oil mill. There are 453 FFB mills spread across Malaysia, and each mill operates with different parameters to process FFB from various plantations hence generating by-products of varying properties (MPOB, 2016b). In this work, the rationale behind the approach of using agricultural residues acquired from the same mill is to eliminate the possible influence of variation in milling and plantation conditions on the research findings (Luangkiattikhun et al., 2008; Ma et al., 2015; Yang et al., 2004). The physicochemical properties of the three biomasses and derived biochars were determined by Fourier transform infrared spectroscopy, bomb calorimetry, scanning electron microscopy, energy dispersive X-ray and proximate analysis. The pyrolysis kinetics were evaluated by TG analyzer, and the data obtained were correlated with the Kissinger-Akahira-Sunose and Flynn-Wall-Ozawa models.

2. Materials and methods

2.1. Preparation of biochars

PKS, EFB and POS were collected from Seri Ulu Langat Palm Oil Mill Sdn. Bhd., Dengkil, Selangor, Malaysia. The waste materials were washed repeatedly with distilled water to remove impurities and surface oil, and dried in an oven (Memmert, Germany) at 80 °C, for 72 h. The dried biomass were pulverized in a miller (Retsch SM 100, Germany) and then sieved to 0.5–2 mm particles using a vibratory sieve shaker (Retsch AS 200, Germany). The biomass particles was then pyrolyzed in a stainless steel bed reactor with internal diameter 0.04 m and length 1.22 m, placed in a horizontal tubular furnace (Carbolite CTF12, UK). The sample was heated to 500 °C at 10 °C min^{-1} under a N_2 flow of 50 mL min^{-1}. It was held up at this temperature for 1 h until complete degradation of hemicellulose and cellulose was achieved (Lee et al., 2013). The pyrolyzed products were referred to as PKS-char, EFB-char and POS-char. The char yield was determined based on the sample weight difference before and after pyrolysis.

2.2. Scanning electron microscopy

The morphological and elemental characteristics of PKS, EFB, POS and their corresponding biochars were examined by scanning electron microscope (SEM, Quanta 400F, USA) equipped with an energy dispersive X-ray (EDX) spectrometer and X-max detector (Oxford-Instruments INCA 400, UK). The sample was mounted on the SEM stub using double-side carbon tape and inserted into the chamber operated at approximately 1.4×10^{-3} Pa, between 10–20 kV accelerating voltages and 2500–10,000 times magnification.

2.3. Lignocellulose content determination

The extractives, hemicellulose, cellulose and lignin contents of the raw biomass were evaluated based on procedures described by Ayeni et al. (2013) and Tan et al. (2011). The extractives content was evaluated using a Soxhlet extractor in which 1 g of biomass was refluxed with 60 mL acetone at 60 °C for 6 h. The sample was then dried in the oven at 110 °C until a constant weight was achieved. The difference in the initial sample weight and final dried sample weight represented the extractives weight.

The hemicellulose content was determined by sodium hydroxide (NaOH) treatment. Approximately 1 g of extractive-free biomass was poured into an Erlenmeyer flask containing 150 mL NaOH of concentration 0.5 mol L^{-1}. The mixture was agitated in a waterbath shaker (Protech, Malaysia) at 150 rev min^{-1} and 80 °C for 3.5 h. The contents were filtered through a filter paper (Sartorius, Grade 293) and rinsed with excess distilled water until the pH of rinsing approached 7. The residue was then dried at 110 °C until its weight was constant. The sample weight difference before and after this treatment was taken as the hemicellulose weight.

The lignin content of biomass was determined by a two-step acid hydrolysis process. Approximately 300 mg of extractive-free biomass was treated with 3 mL sulphuric acid of concentration 14 mol L^{-1}. The mixture was agitated in the waterbath shaker at 150 rev min^{-1} and 30 °C for 2 h. Thereafter, 84 mL of distilled