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Liquefaction of palm kernel shell in sub- and supercritical water for bio-oil production

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ABSTRACT

The heavy palm oil industry in Malaysia has generated various oil palm biomass residues. These residues can be converted into liquids (bio-oil) for replacing fossil-based fuels and chemicals. Studies on the conversion of these residues to bio-oil via pyrolysis technology are widely available in the literature. However, thermochemical liquefaction of oil palm biomass for bio-oil production is rarely studied and reported. In this study, palm kernel shell (PKS) was hydrothermally liquefied under subcritical and supercritical conditions to produce bio-oil. Effects of reaction temperature, pressure and biomass-to-water ratio on the characteristics of bio-oil were investigated. The bio-oils were analyzed for their chemical compositions (by GC–MS and FT-IR) and higher heating values (HHV). It was found that phenolic compounds were the main constituents of bio-oils derived from PKS for all reaction conditions investigated. Based on the chemical composition of the bio-oil, a general reaction pathway of hydrothermal liquefaction of PKS was postulated. The HHV of the bio-oils ranged from 10.5 to 16.1 MJ/kg, which were comparable to the findings reported in the literature.

1. Introduction

In view of current critical issues such as the escalating global energy demands and the environmental deterioration due to extensive use of fossil fuels, the need to shift our dependence to renewable and sustainable energy alternatives is vital [1]. In this context, utilization of biomass has proved to be a feasible solution as it is the main source of carbon, which can be converted to biofuels and biochemicals [2]. Besides, biomass is considered to be one of the potential alternatives due to its abundance, carbon neutrality and renewability [3].

Pyrolysis and liquefaction are the major thermochemical treatments employed to convert biomass to liquid products such as bio-oil [4]. In liquefaction process, solvent at elevated temperature and pressure serves as a good medium and reactant to depolymerise the complex macromolecular structure of biomass, generating liquid products (bio-oil) [5]. Compared to pyrolysis, liquefaction process is a promising conversion technology in terms of energy requirement, operating cost and process viability [6]. Liquefaction process usually operates at lower temperatures (<400 °C) and relatively higher pressure of 5–30 MPa [7]. In addition, liquefaction is also suitable to convert high-moisture-containing biomass, and often results in bio-oil with superior quality compared to pyrolysis process [8]. The presence of solvent lowers the process temperature and concentration of products, hence inhibits the formation of tar and char [9,10].

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The operating parameters of liquefaction process play significant roles in determining the yield and quality of bio-oil products. Dimitriadis and Bezergianni (2017) and Huang and Yuan (2015) comprehensively reviewed on the liquefaction technology in converting various types of biomass feedstocks to bio-oil, summarizing state-of-the-art knowledge of this technology to date [11,12]. Jena et al. (2011) investigated the effect of liquefaction temperature, reaction time and solid concentration on the yield and properties of bio-oils produced from *Spirulina platensis* [13]. Sun et al. (2011) reported the FT-IR analysis of bio-oils produced from paulownia at different liquefaction temperatures [14]. The physical property and chemical composition of bio-oils produced from hydrothermal liquefaction of wheat straw were investigated by Patil et al. (2014) [15]. Zhu et al. (2015) found out that better quality of bio-oil (higher HHV and lower oxygen content) was obtained for liquefaction at higher temperature, while the relative contents of phenolics and carboxylic acids in the bio-oils decreased with increasing temperature [16]. Durak and Aysu (2016) liquefied *Datura stramonium* L. plant stems at various temperatures with (colemanite and borax) and without catalysts and reported that the chemical compounds in bio-oil produced were similar [17]. Malins studied the effect of temperature, pressure, reaction time, catalyst loading and biomass-to-water ratio in hydrothermal liquefaction of birch sawdust and reported that the bio-oil produced constituted suitable chemical compounds for conversion to bio-based hydrocarbons [18].

As one of the top producers of palm oil in the world, Malaysia has generated a substantial amount of oil palm (*Elaeis guianensis*) wastes, creating problems such as disposal difficulties and increased operating cost of oil palm mills [19]. These wastes were utilized as feedstocks in various liquefaction studies for the conversion to bio-oil. Previously, the effects of solvent and catalyst on the quality of bio-oils produced from liquefaction of oil palm fruit press fiber were reported [20,21]. Akhtar et al. (2010) reported the effect of alkalis on the chemical composition of bio-oils derived from empty fruit bunch (EFB) via liquefaction by hot compressed water [22]. Yim et al. (2017) studied the effect of metal-oxide catalysts on the yield and quality, as well as the thermal degradation behaviour of the bio-oils derived from EFB via supercritical hydrothermal liquefaction [23].

To the best of our knowledge, the study on effects of operating parameters of hydrothermal liquefaction on the yield and quality of bio-oil derived from palm kernel shell (PKS) is limited and has not been widely reported so far. Among various types of oil palm biomass wastes, PKS has the highest higher heating value (HHV) of ~18.46–20.09 MJ/kg [24,25] and lignin content of ~44.0–50.7% [19,26], which is a prospective feedstock to be converted and upgraded into biofuel and bio-oil rich in phenolic and aromatic compounds. HHV is a common parameter considered in the context of biofuel production (for heat and power generation) whereas the chemical content of feedstock is influential in determining the major chemical compounds in bio-oil, which is an important aspect in bio-oil upgrading process into biochemicals. As such, in this study, the effects of reaction temperature, pressure and biomass-to-water ratio on the yield and properties of bio-oils produced from PKS were investigated and reported. The bio-oils were characterized by their chemical compositions and HHVs. Based on the chemical compounds detected in the bio-oils, a simplified reaction pathway for the liquefaction of PKS under sub- and supercritical hydrothermal conditions was postulated.

2. Materials and methods

2.1. Feedstock preparation

The supply of raw PKS and the pretreatment process were reported in our previous works [27,28]. Structural analysis of PKS was performed by Forest Research Institute Malaysia (FRIM) while ultimate analysis was performed using a LECO CHNS Analyzer. Proximate analysis was performed using thermogravimetric analyzer (TGA) following the procedures and method reported in the literature [29]. HHV was estimated based on the result of proximate analysis and correlation reported in the literature [29]. The characteristics of PKS are shown in Table 1. All measurements and analyses were performed twice to ensure the repeatability of the results.

2.2. Hydrothermal liquefaction of PKS

PKS was liquefied at various conditions to produce bio-oil. PKS and distilled water were loaded into the reactor according to the specified biomass-to-water ratio for reaction time of 1 h. Liquefaction of PKS was performed using an 8.8 ml Inconel batch reactor placed in a reactor furnace with mechanical stirring with a cyclic horizontal swing span of 2 cm at a frequency of 60 cycles/min. The densities of water at various reaction conditions were determined using Water V3.3 software developed by Summit Research Corporation (Santa Fe, USA) prior to the experiments. Based on the density, suitable amount of distilled water was loaded into the reactor such that it would produce the desired

Table 1
Characteristics of PKS.

Structural content	
Hemicellulose (%)	24.1
Cellulose (%)	24.6
Lignin (%)	45.4
Ultimate analysis (dry basis)	
C (%)	50.31
H (%)	6.05
N (%)	0.46
S (%)	0.00
O[a] (%)	43.18
Proximate analysis (dry basis)	
Volatile matter (%)	80.71
Fixed carbon (%)	14.68
Ash content[a] (%)	4.61
Higher heating value (MJ/kg)	18.5

[a] Calculated by difference.

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