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Metal oxide-catalyzed hydrothermal liquefaction of Malaysian oil palm biomass to bio-oil under supercritical condition

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ABSTRACT

Effect of metal oxide catalysts such as CaO, MgO, MnO, ZnO, NiO, SnO, CeO_2, Al_2O_3 and La_2O_3 on supercritical hydrothermal liquefaction of empty fruit bunch (EFB) derived from oil palm residues to bio-oil were studied in terms of product yields and characteristics. EFB, water and 1.0 wt% metal oxide were loaded into an Inconel batch reactor, heated to 390 °C to reach 25 MPa at reaction time of 1 h. Among the tested catalysts, four most active metal oxides with lower electronegativity such as CaO, MnO, La_2O_3 and CeO_2 were selected, and gave maximum relative yield of bio-oil at about 1.40 times that without catalyst. Based on GC–MS and FT-IR analyses, the presence of phenol and its derivatives, ketone, other aromatic compounds and carboxylic acid in bio-oils obtained were confirmed. Thermogravimetric (TG) analysis of obtained bio-oils showed three stages of thermal degradation behaviour. Modified Reverchon-Sesti Osseo model provides good fit for the experimental yield of bio-oil formed with the four most active metal oxide catalysts.

1. Introduction

The tropical climate of Malaysia makes it a suitable place for cultivating oil palm. With numerous large plantations, the industry has become significant to Malaysia's economic development in its capacity as the main global producer and exporter of palm oil [1]. In year 2011, oil palm plantation reached 4.98 million hectares and the export revenue of its oil had reached RM60 billions in year 2010 [2,3]. The massive cultivation of oil palm has been generating a considerable amount of biomass every year. The total amount of dry oil palm biomass production including empty fruit bunch (EFB), palm mesocarp fibres (PMF) and palm kernel shell (PKS) has reached 34.4 million tonnes in year 2010 [3]. EFB is classified as the main by-products, as it constitutes approximately 56% of total dry oil palm biomass produced in year 2010. EFB is a lignocellulosic biomass consisting of hemicelluloses (26.9%), cellulose (26.6%), lignin (18.6%) as well as extractives and ash (27.9%) [4,5].

In recent years, the oil palm biomass has been considered as a potential source for renewable energy and value-added natural products. Its utilization can mitigate environmental impact of its disposal, which can also reduce global over-dependency on non-renewable energy such as crude oil, natural gas and coal. One of many approaches for its utilization is the use of thermochemical method, which is a promising route to convert oil palm biomass into liquid products generally referred to as bio-oil. This bio-oil, also known as bio-crude, consists of a mixture of oxygenated compounds such as alcohols, carboxylic acid, aldehydes, ketones, ether, esters, phenols and other aromatic compounds. Its composition indicates that this can be used as renewable energy source, and can also be upgraded to other useful products such as resin, fertilizers, food flavourings and other fine organic chemicals. It is normally dark-brown in colour, with slightly viscous properties and has pungent odour similar to gasoline and diesel.

Thermochemical methods for bio-oil production include liquefaction using solvents (e.g. water or organic liquids), pyrolysis and gasification process. Thermochemical liquefaction, the method that utilizes any liquid solvent, gains attention in this study as its advantages outweigh pyrolysis. Pyrolysis is the process where thermal

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decomposition and degradation of organic substances, such as lignocellulosic biomass, to generate a mixture of condensable vapour, gas and char in the absence of oxygen at near atmospheric condition. The mixture of condensable vapour produced can be quenched and condensed to form bio-oil. Thermochemical liquefaction produces liquid products by decomposing the complex structure of biomass with hot and pressurized solvent such as water, methanol, ethanol and acetone by hydrolysis, and then further extracted with a solvent to obtain the bio-oil [6]. The generation of bio-oil based on mechanisms such as biomass depolymerisation, cleavage of C—C bond in biomass structure, dehydration, decarboxylation, deamination and finally the recombination of reactive fragments [7]. Liquefaction requires lower operating temperature (approximately 250–400 °C) and higher pressure (5–20 MPa) compared to pyrolysis (temperature at 500–800 °C) [6]. Therefore, it is expected that the energy consumption of liquefaction should be lower compared to pyrolysis. The use of solvent in liquefaction dilutes the concentration of products, thus capable of preventing cross-linking and recombination reactions from occurring [8]. Liquefaction method is able to convert wet biomass without the need of drying compared to pyrolysis [4]. Also, the bio-oil produced from liquefaction has lower oxygen, water and sulphur content, thus better quality of bio-oil compared to that obtained by pyrolysis. On the other hand, liquefaction method outweighs pyrolysis by producing lower amount of gas and char products while maintaining higher bio-oil yield [6].

Supercritical hydrothermal liquefaction was applied in this work due to its attractive characteristics compared to pyrolysis process. Water is used as solvent in this study because it is "green", cheap, abundant, non-poisonous and non-flammable compared to other organic solvent. Above the critical point (critical temperature of 374 °C and critical pressure of 22.1 MPa), the obtained supercritical water has liquid-like, gaseous-like and low dielectric constant properties that promote high compressibility and diffusivity that enhance separation, extraction and solubility of organic compounds [6]. In addition, water also acts as a natural catalyst. Supercritical water is able to enhance the self-dissociation of H_2O to H^+ and OH^- for hydrolysis and decomposition of biomass [9]. Chan et al. was able to obtain a maximum bio-oil yield of 38.5 wt% by performing subcritical and supercritical hydrothermal liquefaction of EFB, PMF and PKS under the optimum condition of 390 °C and 25 MPa (supercritical water) [6]. Thus, it has proven the feasibility of biomass liquefaction under supercritical water conditions obtaining relatively high bio-oil yield.

Apart from that, catalytic hydrothermal liquefaction is widely investigated by researchers to increase bio-oil yield and strengthen its characteristics especially by using alkali catalyst which has generated promising results. Sun et al. carried out direct liquefaction of paulownias in hot compressed water by using iron (Fe) and Na_2CO_3 catalyst [10], obtaining maximum bio-crude with 36.34 wt% yield at 300 °C and 10 min of reaction time, with minimum amount of solid residue. Nevertheless, only a few studies have been carried out on supercritical hydrothermal liquefaction of EFB to bio-oil by using metal oxide as catalyst. Metal oxide consists of positive metal ions (cations), having Lewis acid sites that act as electron acceptor and negative oxygen ions (anions), which are proton acceptors or Bronsted bases [11]. Base strength and basic site concentration of metal oxide affect its catalytic activity. Therefore, metal oxide properties can also be further related with pH value and electronegativity. Metal oxide has been applied widely for biodiesel synthesis, reduction, oxidation and hydrolysis reaction. Metal oxide with stronger basicity promotes higher catalytic activity. Shi et al. obtained high bio-crude yield of 32.5 wt% by using lanthanum oxide (La_2O_3) as catalyst in hydrothermal liquefaction of rice husk at 300 °C, 10 min reaction time and 5 of water/rice husk ratio [12]. Nickel (II) Oxide (NiO) is not effective in increasing bio-oil yield for the liquefaction of microalga, *Sprulina platensis*, instead it favours gas formation [13].

Table 1
Amount of EFB and distilled water required for hydrothermal liquefaction.

Temperature (°C)	Pressure (MPa)	Amount of EFB required (g)	Amount of distilled water required (g)
360	25	0.5182	5.1823
390	25	0.1909	1.9092
450	25	0.0961	0.9607

The objective of this work was to study the effects of various metal oxides in catalysing hydrothermal liquefaction of oil palm biomass to bio-oil under supercritical condition. The bio-oil produced using the four most active metal oxide catalysts were analyzed for their chemical composition and thermal degradation behaviour. The kinetic of formation was also fitted to the modified Reverchon-Sesti Osseo model.

2. Experimental

2.1. Materials

Empty fruit bunch (EFB) was supplied by a local Malaysian palm oil industry, and was obtained from Biomass Processing Laboratory, Center of Biofuel and Biochemical Research, Mission Oriented Research (Green Technology), Chemical Engineering Department of Universiti Teknologi PETRONAS (UTP). This was processed to particle sizes of less than 710 μm and was utilized as feedstock. The preparation and characterization of EFB regarding its structural and elemental composition as well as high heating values (HHV) were reported in the literature by Chan et al. [6]. The metal oxide used were zinc oxide (ZnO), aluminium oxide (Al_2O_3), calcium oxide (CaO), nickel (II) oxide (NiO), magnesium oxide (MgO), manganese (II) oxide (MnO), cerium (IV) oxide (CeO_2), tin (II) oxide (SnO) and lanthanum oxide (La_2O_3) with surface area in the range of 7–10 m^2/g as provided by the chemical suppliers.

2.2. Supercritical hydrothermal liquefaction method

The main starting materials used in this study were empty fruit bunch (EFB), distilled water and metal oxide, which serves as catalyst. Preliminary runs were conducted at 390 °C (above the critical temperature of water), 25 MPa and reaction time of 1 h, the optimum condition for the hydrothermal liquefaction as reported by Chan et al. [6].

To investigate the effect of temperatures, experiments at 360 °C and 450 °C were also conducted. Furthermore, reaction time was varied from 15–960 min in order to investigate their effects on the yield of bio-oil. The amount of EFB and distilled water used was at a ratio of 1:10. The amount of EFB and distilled water required at respective temperature and pressure was calculated using Water V3.3 software developed by Summit Research Corporation (Santa Fe, USA) as also reported by Chan et al. [6]. The amount of EFB and water required were reported in Table 1.

The amount of metal oxide, calculated using Eq. (1), was fixed at 1.0 wt% all throughout the study, unless otherwise specified.

$$\%wt\,metal\,oxide = \frac{weight\ of\ metal\ oxide}{weight\ of\ solution} \times 100 \quad (1)$$

The experiment was started by loading EFB, distilled water and metal oxide catalyst into an 8.8 ml Inconel batch reactor, then the mixture was mildly stirred. The batch reactor was closed, then inserted into the furnace and heated from atmospheric condition up to the desired conditions (*i. e.* T = 390 °C, P = 25 MPa, t = 1 h). After the reaction time has elapsed, the reactor was removed from the

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