Catalytic fast pyrolysis of durian rind using silica-alumina catalyst: Effects of pyrolysis parameters

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ABSTRACT

Silica-alumina catalyst was prepared and used in the catalytic fast pyrolysis of durian rind in a drop-type two-stage reactor. The effects of catalytic temperature (400 °C–600 °C) and catalyst-to-durian rind ratio (1:30–3:30) were evaluated. Bio-oil yield was increased with increased catalytic temperature due to considerable dehydration process, but it was reduced with high catalyst loading due to the overcracking of organics into light gases. Silica-alumina catalyst possessed good selectivity and the products changed according to the temperature. The major components in bio-oil were hydrocarbons, furan derivatives, and aromatic compounds at 400 °C, 500 °C, and 600 °C, respectively. The hydrogen and carbon contents of bio-oil were reduced with high catalyst loading due to the overcracking of organics, and the deoxygenation process became unfavorable. The silica-alumina catalyst worked well in catalytic fast pyrolysis of durian rind, and the condition may be adjusted based on the desired products.

1. Introduction

Fast pyrolysis is a promising method to convert lignocellulosic biomass into useful energy forms (mainly bio-oil). Researchers investigated the products obtained by pyrolysis of different biomasses, such as citrus fruit peels (Kim et al., 2016), coconut shell waste (Ali et al., 2017), pine wood (Sun et al., 2017), and forestry waste (Hu et al., 2017). Bio-oil is a thick dark-brown liquid that may consist of more than 300 oxygenates. The advantages of converting lignocellulosic biomass into bio-oil are as follows: (1) bio-oil contains less impurities that are left in solid biochar, e.g., inorganic minerals, (2) easy transportation, (3) higher energy content than that of raw feedstocks, and (4) lower sulfur content than that of petroleum (Bulushev and Ross, 2011). However, crude bio-oil should be further improved due to its high O/C ratio. Bio-oil experiences drawbacks due to high oxygen level because it is chemically and thermally unstable; it is also corrosive due to the presence of organic acids. Although it is known as bio-oil, this energy form is immiscible with petrofuel because of its high polarity and hydrophilic properties (Mohan et al., 2006). Furthermore, bio-oil is highly viscous due to the presence of large molecules with long carbon chain length (approximately 100), which is considerably longer than those of gasoline (5–10 branched alkanes and aromatics) and diesel (12–20 linear alkanes). Thus, the major approaches for the improvement of bio-oil are deoxygenation and cracking.

The active oxygenates in bio-oil can be removed through different chemical routes, such as cracking, aromatization, aldol condensation, and hydrotreatment (Liu et al., 2014). These chemical routes present their own advantages and disadvantages. Catalytic cracking is one of the most widely applied methods because it can be performed under atmospheric pressure without hydrogen requirement. In catalytic cracking, oxygen can be removed in the form of H_2O, CO, and CO_2 through dehydration, decarbonylation, and decarboxylation, respectively. The removal of oxygen in CO_2 form is more preferred than those in H_2O and CO because it can minimize the need for external hydrogen supply (Christoforou et al., 2018). Catalysts are used to promote selectivity in oxygen removal; they can also help convert free radicals into stable components.

The application of different catalysts, such as metal oxides and solid acids, in catalytic bio-oil cracking has been widely studied. Solid acids are extensively used in catalytic cracking due to its acidic nature that can help promote the rupture of C−C and C−O bonds (Aho et al., 2013). Liu et al. (2014) reported that Al_2O_3 can promote the formation of aromatic compounds, such as polycyclic aromatic hydrocarbons. SiO_2 with low acidity can also help remove oxygenates and inhibit coke formation on the catalyst due to its medium porosity. Thus, alumino-silicates, such as ZSM-5 and HZSM-5, are widely used in catalytic pyrolysis. These materials display strong Brønsted acidity; thus, they are active in oxygenate cracking. Strong acidity will enhance the cracking activity and hydrogen transfer capability of the catalyst. Consequently, many aromatics and hydrocarbons are formed (Liu et al.,

2014). Adhikari et al. (2014) improved raw lignin by using zeolites with different SiO_2/Al_2O_3 ratios (SARs). They found that the catalyst can promote the conversion of guaiacols (methoxy phenols) into aromatic hydrocarbons by direct deoxygenation. Furthermore, the activity of high-acidity zeolites (low SAR) is higher than those of low-acidity zeolites; therefore, many aromatic products are produced. Engtrakul et al. (2016) found that the acidic site density of ZSM-5 affects the product yield distribution and selectivity of aromatic products. Moreover, the increased total number of acidic sites on the catalyst will reduce the selectivity toward substituted aromatics; by contrast, it will increase the selectivity of polycyclic aromatics.

Microporous structure limits the accessibility of large molecules to diffuse into the pores and provides high selectivity to produce aromatic compounds. Nevertheless, coke formation and catalyst deactivation are major problems that should be addressed. To overcome catalyst deactivation, formation of coke on the external surface of catalyst should be inhibited (Kabir and Hameed, 2017) and the surface area of catalyst should be increased to avoid the immediate deactivation of active acidic sites.

Malaysia is one of the largest producers of durian (*Durio zibethinus* L.), with an estimated annual production of more than 300,000 MT (Manshor et al., 2014). Durian rind accounts for 65%–70% of the whole fruit. This nonedible fruit shell and the seeds will be disposed as wastes. The improper disposal of durian waste, such as burning or disposal in an open space, will create environmental issues. Durian rind contains high amount of cellulosic materials that can be converted into value-added chemicals, such as phenolic compounds (Tan et al., 2017).

In the present work, a silica-alumina catalyst was used to improve the durian rind pyrolysis product yield and composition. This study also investigated the properties of silica-alumina catalyst and its effects on product yield and bio-oil chemical distribution. The effects of catalytic temperature (400 °C–600 °C) and catalyst-to-durian rind ratio (1:30–3:30) on product yield and chemical distribution were determined to understand the behavior of silica-alumina catalyst in the catalytic pyrolysis process.

2. Materials and methods

2.1. Materials

Durian rind was acquired from a local market in Nibong Tebal, Malaysia. It was washed, dried, ground, sieved to 1–2 mm, and kept in an air-tight container prior to usage. The proximate and ultimate analyses, lignocellulosic compositions, and heating values of durian rind were reported previously (Tan et al., 2017). Detailed characterization methods of durian rind can be found in the literature (Khanday et al., 2016).

Tetraethyl orthosilicate (TEOS, 98%), aluminum nitrate nonahydrate ($Al(NO_3)_3·9H_2O$, ≥ 98.5%), hexadecyltrimethylammonium bromide (CTAB, ≥ 97%), ammonia solution (NH_3, ≥ 25%), and toluene ($C_6H_5CH_3$, ≥ 99.5%) were purchased from Merck, Malaysia. Ethanol (EtOH, 95%) was acquired from R&M Chemical, Malaysia.

2.2. Silica-alumina catalyst synthesis

Silica-alumina catalyst was synthesized by modifying the preparation method described in literature (Sheng and Zeng, 2015). TEOS, Al(NO_3)$_3$·9H$_2$O, and CTAB were used as silica source, aluminum source, and structure-directing template, respectively. Organic phase was prepared by dissolving 1.5 g of CTAB and 1.8 mL of TEOS in a mixture of toluene (6 mL) and EtOH (240 mL). The solution was stirred until the template was completely dissolved. Approximately, 0.3 g of Al(NO_3)$_3$·9H$_2$O and 7.5 mL of NH$_3$ were added to 260 mL of deionized water under vigorous stirring. The aqueous solution was poured into the organic phase and aged for 4 h at room temperature. The precipitated white product was centrifuged, washed with ethanol, and

dried at 105 °C in the oven. The white solid was calcined at 600 °C in air atmosphere for 4 h.

2.3. Silica-alumina catalyst characterization

2.3.1. Surface area and porosity measurement

N_2 sorption isotherms were measured at −196 °C by using Autosorb I (Quantachrome Corporation, USA). The catalyst was degassed under vacuum condition at 350 °C for 4 h prior to the N_2 sorption measurement. The physical property of catalyst surface and pore size distribution were determined by Brumauer–Emmett–Teller and Barrett–Joyner–Halenda methods, respectively.

2.3.2. X-ray diffraction (XRD)

The structure, crystal phase, and crystallite size of silica-alumina catalyst were characterized by XRD using a SIEMENS XRD D5000 equipment. Copper Kα radiation at 30 mA/40 kV was used as the X-ray source. An alumina sample holder was used to pack the catalyst, and the sample was scanned in a step-scan mode over the angular 2θ range of 5°–70° with a scanning rate of 2°/min.

2.3.3. Scanning electron microscopy with energy dispersive X-ray spectrometry

FESEM (Zeiss SUPRA 35VP, Germany) was utilized to capture the image of surface morphology and the textural structure of the catalyst. Energy-dispersive spectroscopy (X-ray Microanalysis System Ametek EDAX-GENESIS 2000) was used for elemental analysis. The sample was sputtered with an ultrathin gold layer prior to analysis to prevent the charging of specimen.

2.3.4. Surface acidity measurement by titration method

The catalyst surface acidity, which can be determined by titration, is crucial in catalytic pyrolysis. Approximately 0.1 g of silica-alumina catalyst was shaken in 50 mL of NaOH (0.05 M) solution for 24 h. The solid was separated by centrifugation. One drop of phenolphthalein was added to 10 mL of the solution and titrated with HCl (0.05 M) solution until the solution became transparent. The experiment was repeated three times to obtain the average volume of acid solution used to neutralize the excess NaOH. The number of acidic sites was calculated on the basis of the assumption that the NaOH solution neutralized all the acidic groups.

2.4. Fast catalytic pyrolysis in a drop-type two-stage reactor

A downflow drop-type two-stage pyrolysis reactor was used to perform the fast catalytic pyrolysis study. The thermal decomposition of durian rind without catalyst was conducted in the first stage (pyrolysis bed), and the catalytic upgrading of pyrolysis product was operated in the second stage (catalyst bed). The detailed experimental procedures had been previously reported (Tan et al., 2017). In brief, 3 g of durian rind was volatilized in the first stage at 650 °C under nitrogen atmosphere (200 mL/min). Afterward, the pyrolysis vapor was passed through the catalytic bed (catalyst-to-durian rind ratio of 1:30, 2:30 or 3:30) at 400 °C, 500 °C, or 600 °C to investigate the catalyst performance at different catalytic temperatures. The condensable vapor was condensed in a cooling trap with circulating ethylene glycol solution at −4 °C. The gas product was collected in a gas bag and analyzed using GC-TCD (Agilent 7890A equipped with Carboxen-1010 PLOT Capillary GC Column) to determine the gas composition.

2.5. Bio-oil property determination

The chemical distributions of the liquid products were analyzed by using GC-MS analysis on Perkin Elmer Clarus 600/600 T. The column used for chromatographic separation was a fused silica capillary column HP–INNOWAX. The GC oven temperature was programmed to