



Bench scale catalytic fast pyrolysis of empty fruit bunches over low cost catalysts and HZSM-5 using a fixed bed reactor



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ABSTRACT

The performance of HZSM-5 and low cost catalysts, such as the spent fluid catalytic cracking (FCC) catalyst, bentonite, dolomite, and olivine, on the production of high-quality bio-oil during the catalytic pyrolysis of empty fruit bunches (EFBs) was compared in a bench scale fixed bed reactor. The spent FCC and HZSM-5 catalysts showed higher cracking performance than bentonite, dolomite, and olivine. The catalytic pyrolysis of EFB over the spent FCC catalyst showed higher selectivity to phenol (31.5%) and alkyl phenols (26.0%) due to the effective dealkylation of guaiacols and syringols, whereas HZSM-5 provided the higher selectivity to aromatic hydrocarbons (40.4%). The catalytic pyrolysis of EFB over the spent FCC catalyst and HZSM-5 produced bio-oil with a higher heating value (28.44–31.18 MJ/kg) than other bio-oils obtained over bentonite (27.89 MJ/kg) and olivine (16.83 MJ/kg). The bio-oils obtained from the catalytic pyrolysis of EFB over the spent FCC and HZSM-5 catalysts also had a lower viscosity (7.0–13.5 mm²/s) than those (13.8–22.1 mm²/s) over the other catalysts, even after accelerated aging at 80 °C for 1 day.

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1. Introduction

The increasing energy crisis, air contamination, and greenhouse gas emissions have become important worldwide issues due to the massive use and depletion of fossil fuels (Mitchell, 2003). In this situation, biomass is being considered as a solution to produce renewable energy and reduce the dependence on fossil fuels (Jernström et al., 2017). A range of thermal technologies, such as torrefaction (Iroba et al., 2017), pyrolysis (Kim et al., 2016a), and gasification (Wilk and Hofbauer, 2016), have been studied for the production of high quality fuels and chemicals from biomass. Among them, pyrolysis, which is the thermal decomposition of polymeric materials at intermediate temperatures between 400

and 600 °C under non-oxygen atmospheres, is considered one of the most suitable methods for producing high-yield and high-quality bio-oil from biomass (Tchapda and Pisupati, 2014). The bio-oil produced by pyrolysis has a huge potential to replace the petroleum-based chemical feedstock or fuels as a cleaner product that is sustainable due to the carbon (CO₂) neutrality of biomass. In this regard, pyrolysis studies of many types of biomass, such as wood (Mohan et al., 2006), fruit peel (Kim et al., 2015b), miscanthus (Heo et al., 2010), algae (Bae et al., 2011), and its main components, hemicellulose (Patwardhan et al., 2011), cellulose (Jiang et al., 2016), and lignin (Kim et al., 2016b), have been performed to evaluate the feasibility of these feedstocks for the production of bio-oil in recent decades. The amount and quality of bio-oil were influenced largely by the lignocellulosic composition and ash content of biomass (Yildiz et al., 2015). Although a large amount of bio-oil can be obtained from the pyrolysis of biomass, it is unsuitable for direct use as a fuel or chemical because of the low quality of biomass pyrolysis oil (Mamaeva et al., 2017) caused by the high

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water content, high oxygen content (Lee et al., 2017), and thermal instability (Lee et al., 2016).

Empty fruit bunches (EFBs) are abundant biomass species harvested mainly in the subtropics (Shinoj et al., 2011). The amount of waste EFB is increasing rapidly due to increasing cultivation of palm (Vijaya et al., 2008). Although waste EFB can be used to produce organic fertilizer or burnt to generate steam for the production of electricity (Palamae et al., 2014), most of the waste is dumped in landfill without proper treatment. This means that a large amount of EFB can be used as a feedstock for the production of bio-fuel and/or chemicals (Chang, 2014), and the pyrolysis of EFB can be a candidate method for producing large amounts of bio-oil from EFB. Sukiran et al. (2009) obtained 42.28% bio-oil from the pyrolysis of EFB at 500 °C using a fluidized bed reactor; the calorific value of the bio-oil produced ranged from 20 to 21 MJ/kg. Abdullah and Gerhauser (2008) improved the yield of bio-oil further using the ash-removed EFB by a washing pretreatment. Although large amounts of bio-oil can be produced by the pyrolysis of EFB, its direct use as a fuel or chemical is still difficult due to the low quality of bio-oil caused by the large quantities of unstable oxygen-containing compounds (Rodionova et al., 2017). The catalytic pyrolysis of EFB has been attempted as a means of overcoming the limitations to the use of EFB pyrolysis oil. Auta et al. (2014) used Ca(OH)₂ as a catalyst for the catalytic pyrolysis of EFB and reported an improved selectivity to phenolic compounds, that can be used as a valuable chemical feedstock.

Many types of catalysts, such as metal oxides (Yoshikawa et al., 2014), activated charcoal (Eibner et al., 2017), and microporous zeolites (Kim et al., 2015a) and mesoporous materials (Kim et al., 2017), have been tested for the catalytic pyrolysis of biomass. Of these, HZSM-5 has been identified as the most appropriate catalyst to produce high-quality bio-oil with a higher selectivity to aromatic hydrocarbons because of its high acidity and suitable pore size.

Veses et al. (2015) attempted the use of low cost materials, such as clay minerals for the catalytic pyrolysis of biomass. A spent fluid catalytic cracking (FCC) catalyst, a by-product obtained from an oil-cracking refinery plant, also has potential for the catalytic pyrolysis of polymeric materials because it still has high acidity that can promote the aromatization reactions of pyrolysis vapors. Barbarias et al. (2015) reported the catalytic effects of spent FCC catalyst on the catalytic cracking of plastic waste. They obtained high yields of gasoline (52 wt %) and light olefins (28 wt %) from the catalytic pyrolysis of high density polyethylene over the spent FCC catalyst, which indicates that the spent FCC catalyst can provide sufficient cracking efficiency for biomass pyrolysis. Zhang et al. (2013) also examined the effects of different catalysts on the production of aromatics and olefins via the catalytic pyrolysis of straw biomass and found that the spent FCC catalyst exhibited high selectivity to benzene and ethylene. The use of spent FCC catalyst for the catalytic pyrolysis of plastics or biomass is meaningful because it can be a possible way of recycling spent FCC catalysts (Ferella et al., 2016). Other catalysts, such as bentonite (Sulman et al., 2009), dolomite (Vassilatos et al., 1992), and olivine (Devi et al., 2005), have potential use in the production of high-quality bio-oil via the catalytic pyrolysis of biomass but their catalytic effects have not been studied systematically. The use of these catalysts might be a solution to produce value-added products not only from EFB, but also from other biomass. The economics of the catalytic pyrolysis process can be improved using highly active and inexpensive catalysts.

In this study, the performance of HZSM-5, spent FCC catalyst, other low cost catalysts, such as bentonite, dolomite, and olivine, on the catalytic pyrolysis of EFB were evaluated using a fixed bed reactor. The chemical composition of the products (gas and bio-oil) was analyzed by gas chromatography-mass spectrometry/flame ionization detector/thermal conductivity detector (GC-MS/FID/

TCD). The heating value and viscosity of the fresh and aged bio-oils obtained from the catalytic pyrolysis of EFB were also measured to evaluate the stability of the product bio-oil.

2. Experimental

2.1. Sample

EFB of oil palm harvested in Indonesia, *Elaeis guineensis*, was dried at 110 °C for 24 h, milled, and sieved to make a particle size between 400 and 600 μm. Table 1 lists the ultimate and proximate analysis results of EFB.

2.2. Catalysts

Dolomite, olivine, and spent FCC catalyst were obtained from local companies in Korea. Bentonite and silica sand were purchased from Sigma Aldrich. HZSM-5(30, SiO₂/Al₂O₃ = 30) was supplied by Zeolyst International. Before the catalytic pyrolysis experiments, dolomite was calcined at 800 °C for 2 h, and the other catalysts were calcined at 550 °C for 3 h and kept in a desiccator. BET analysis results showed that HZSM-5 has the highest surface area (405 m²/g), followed by spent FCC (171 m²/g), bentonite (19 m²/g), dolomite (9 m²/g), and olivine (2 m²/g). This indicates that HZSM-5 and spent FCC have a significantly larger surface area than the other catalysts, which can have a positive impact on their activity. Table S3 and Fig. S1 (Supplementary Information) present the analysis results of the pore size and acidity.

2.3. Catalytic pyrolysis and product analysis

Fig. 1 shows a schematic diagram of the fixed-bed reactor used in this study. The reactor consisted of a furnace, four cooling condensers using air or anti-freezing liquid cooling, and a gas sampling bag (20 L Tedlar). For the thermal and catalytic pyrolysis of EFB over each catalyst, a mixture of EFB (50 g) and catalyst (50 g) was loaded onto the sample position at ambient temperature and 500 mL/min of nitrogen gas was supplied to the system for 30 min before the reaction to purge the residual air inside the reactor. After nitrogen purging, the furnace was heated to the target temperature, 400, 500, or 600 °C. When the furnace temperature was stabilized, fast pyrolysis was initiated by sliding the furnace from the standby position to the reaction position. During reaction time (1 h), the pyrolysis vapor emitted from the furnace was condensed in four condensers and the emission gas emitted from the last condenser was collected in the gas sampling bag. After the experiments, the yields of solid residue and condensed bio-oil were obtained by checking their weights directly and the gas yield was calculated by subtracting the summed weights of the solid residue and liquid from that of the reactant. The chemical compositions of the bio-oil

Table 1
Proximate and ultimate analysis of EFB.

Sample		EFB
Proximate analysis ^a (wt. %)	Moisture	5.5
	Volatiles	78.8
	Fixed carbon	13.4
	Ash	2.3
Ultimate analysis ^a (wt. %)	C	42.6
	H	5.7
	O ^b	39.5
	N	1.7
	S	<0.3

^a Based on dried sample.

^b By difference.

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