Upgrading of Bio-oils from the Fast Pyrolysis of Longan Wood over the Low Cost Catalysts in a Fluidized Bed Reactor

Chaturong Paenpong*, Weerapun Chunluang and Niwat Pratoomchai

Mechanical engineering department, Rajamangala University of Technology Lanna Tak

* Corresponding author. E-mail address: jaturong_p@yahoo.com

Abstract

The objective of this work was to upgrade the properties of bio-oil from fast pyrolysis of longan wood by using a low cost catalyst bed material in the fluidized bed reactor. The experiments in this work were performed in two sets. This first one was studied the effects of pyrolysis temperature on the product yield and properties of bio-oil in a fluidized bed reactor to determine the optimal conditions for liquid yield. The experiment were carried out at the pyrolysis temperatures of 450, 500 and 550 °C and sand was used as bed material. The second part was studied the effects of low cost catalyst bed material on the product yields and properties of bio-oil. The experiments were performed at the optimized pyrolysis temperature from the first set of experiments and sand, iron powder and natural zeolite were used as bed materials. The experimental results showed that increasing pyrolysis temperature from 450 - 550 $^{\circ}$ C reduced bio-oil yield while increasing the gas yields. The optimum pyrolysis temperature for obtaining highest bio-oil yield for longan wood was 450 °C which gave maximum bio-oil yield of 36.09 wt%. However, when considering the effect of a catalyst bed material which pyrolysis was performed at optimum temperature of 450°C. It was found that the natural zeolite bed gave the highest bio-oil yield of 36.09 wt%. When considering the effect of the catalyst bed materials on bio-oil properties, the sand bed gave the highest pH value (less acidic) and the lowest flash point in comparison with the iron powder and natural zeolite bed. While the bio-oil obtained from natural zeolite bed had the highest higher heating value (HHV) when compared with the sand bed and iron powder bed which the higher heating value of natural zeolite bed is about 2 time of typical bio-oil. Therefore, the term upgrading of bio-oils refers to increasing of heating value and reducing acidic when comparison typical bio-oil.

Keywords: Pyrolysis temperature, Fast pyrolysis, Bed materials, Longan wood pruning, fluidized-bed Reactor

Introduction

Currently, the global warming is a major problem in Thailand and the world. Thailand carbon dioxide emissions was approximate 0.8% of the world, which has a lower per capita emission rate than the world's carbon dioxide emissions average. The growth rate of Thailand's total carbon dioxide emissions has twice between 1991 and 2002 and the Thailand government recognized its contribution to global warming (Kisner, 2008).

The effects of climate change, including higher surface temperatures of the earth caused by greenhouse gases, floods, droughts, severe storms and sea level rise. The damage to agriculture, coastal tourism, and the capital city as consequences of climate change will have enormous economic, cultural and environmental impacts. The gradual increase of the temperature of the earth's surface caused by greenhouse gases which include water vapor, methane, nitrous oxide, and carbon dioxide. Hence, when the heat of sun energy touches them, they absorbed some of the heat which is basically trapped into our atmosphere.

Biomass is a type of renewable energy derived from plant and animals which include sawdust, wood, cardboard, and animal manure. The energy stored in a biomass is a renewable energy that can be converted



into liquid fuels. In comparison to petroleum resources, the liquid fuels from biomass is a carbon dioxide neutral process considering the global carbon balance (Zhang et al., 2009).

Thailand is an agricultural country, after harvesting there will be a large amount of agricultural residues which could be used as biomass energy. Biomass is the production of industrial-agricultural waste such as rice, sugarcane, corn, soybean, cassava/tapioca, cotton and various ground nuts. Addition, there are several other agricultural residues that can also be used for energy. Longan wood pruning was agricultural residue which could be used as alternative energy. In 2017, longan harvested area in Thailand has been at about 1,097,188 rai (Office of agricultural economics, 2018). Sasujit, Homduang, and Dussadee (2014) found that longan wood pruning obtained from longan harvested area has been an average yield of 459 kg / rai or about 123,708.3 ktoe/year (kilotonne of oil equivalent /year).

Agricultural residues could be used in a variety of ways to provide energy by direct combustion, gasification and fast pyrolysis. The advantage of fast pyrolysis is that it can directly produce a liquid fuel which can be readily stored and transported. (Bridgwater, Meier, & Radlein, 1999). Fast pyrolysis is a thermochemical process that is the rapidly heating of biomass occurring in the absence of oxygen from room temperature to moderate temperature (400-600 °C), short vapor residence time (1-2 s) and quenching of the vapor at the end of the process. The product of fast pyrolysis process are liquids fuel, gases and char. The liquid fuel form fast pyrolysis process is called bio-oil or bio-crude. Bio-oils are dark brown and fluid, be similar to a medium fuel oil in viscosity which is also sensitive to elevated temperatures when it undergoes oil properties change so it must to storage at low temperature. They have a higher heating value of about 16-19 MJ/kg compared with 42-44 MJ/kg for petroleum liquid fuels (Bridgwater & Peacocke, 2000).

The methods to improve the yield of high quality bio-oil can largely be categorized into two routes: the physical upgrading and the catalytic upgrading (Park et al., 2011). The physical upgrading were hot gas filtration (Paenpong, Inthidech, & Pattiya, 2013, Paenpong & Pattiya, 2016) emulsification (Chiaramonti et al., 2003a,b) and solvent addition (Oasmaa, Kuoppala, Selin, Gust, & Solantausta, 2004). Besides, the catalytic upgrading were hydrotreating (French et al., 2015, French, Stunkel, & Baldwin, 2011) and catalytic vapor cracking (Al-Sabawi, Chen, & Ng, 2012, Lorenzetti Conti, Fabbri, & Yanik, 2016, Mante, Agblevor, & McClung, 2013). One simple solution in pyrolysis is the introduction of catalysts to removing oxygen and increasing the heating value (Meesuk, Cao, Sato, Ogawa, & Takarada, 2011, Veses et al., 2014). In the technology of catalytic cracking, the vapors of bio-oils are upgraded at atmospheric pressure with catalysis. Oxygen is removed as H_2O , CO_2 and CO. route to Catalytic cracking technology presents a cheaper method convert oxygenated components from bio-oil into hydrocarbon. But catalytic cracking reactions lead to decrease of bio-oil yield (Zhang et al., 2009).

The commonly used bed materials for fast pyrolysis include silica sand, dolomite or catalysts. The bed material not only serves as the heat transfer medium, but it can act as the catalyst for the purpose of upgrading bio-oils (Basu, 2010). The bed material was in-bed operate which can provide better than ex-bed operate (Pütün, Uzun, & Pütün, 2006). According to Aho et al. (2008), the acidic zeolite catalysts were used as bed material in a fluidized bed reactor at pyrolysis temperature of 450 $^{\circ}$ C. The acidic zeolite catalysts bed gave the highest bio-oil yield which was 20.1 wt%, whereas the sand bed was 27.3 %. Pütün et al. (2006) studied to effect of pyrolysis temperature, natural zeolite content and sweeping gas flow rate in a fixed-bed reactor. From experimental, the bio-oil yield was 24.01 wt% at a pyrolysis temperature of 400 $^{\circ}$ C. While the

maximum bio-oil yield was 26.34 wt% at the temperature of 550 $^{\circ}$ C. When considering the high heating value of the bio-oil, the use of a natural zeolite as bed material increases high heating value of bio-oil. Li Briens, and Berruti (2015) elucidated the influence of silica sand, lignin char, activated lignin char, birch bark char, and foamed glass beads on yield and quality of bio-oil was investigated for a pyrolysis temperature of 550 $^{\circ}$ C. They found that the activated lignin char bed was the highest bio-oil yield of 43 wt%, less pyrolytic water and lower average molecular weight. Moreover, the use of a fluid catalytic cracking (FCC) catalysts as bed material on the fast pyrolysis of corncob in a fluidized bed reactor for a pyrolysis temperature of 550 $^{\circ}$ C (Zhang et al., 2009).They tests with and without catalyst percentages of 5, 10, 20 and 30 % in bed materials. It can be seen that the bio-oil yields decreased from 53 % to 47 % and 45% when increasing the catalyst percentages in bed materials from 5 % to 20 % and 30 %, respectively. But the higher heating value increased with the increase of the catalyst percentages.

According to the above-mentioned research studies, there were several advantages of the catalysts bed materials such as less pyrolytic water, lower average molecular weight, and increase higher heating value. In this research, a low cost catalyst such as sand, iron powder and natural zeolite were used as bed materials. In addition, no published research study has been carried out on the longan wood. Therefore, the objective of this work was upgrading of the bio-oil from fast pyrolysis of longan wood by using a low cost catalyst bed material. A low cost catalyst bed material was to upgrade the properties of bio-oil such as heating value and acidity. In this work, the experiments were performed in two sets. In the first set of experiments, the effects of pyrolysis temperature was investigated in a fluidized bed reactor to determine the optimal conditions for liquid yield. In addition, the effect of pyrolysis temperature on the properties of fast pyrolysis product were studies in this set. An initial set of experiments were carried out at temperatures of 450, 500 and 550 °C for optimizing the pyrolysis temperature for getting the maximum liquid product by using sand as bed materials. In the second set of experiments, the effect of catalyst bed material on the product yields and properties of fast pyrolysis temperature for getting the determine were performed at the optimized pyrolysis temperature from the first set of experiments and using sand, iron powder and natural zeolite as bed materials to investigate the effect of the catalyst bed material on yield and properties of fast pyrolysis product.

Methods and Materials

Feedstock analysis

The biomass in this work was longan wood pruning obtained from an orchard longan in the northern of Thailand. The longan wood pruning was ground and sieved to prepare a size fraction of 0.450-0.600 mm. Thereafter, it dried in an oven at 105 °C for 24 h reaching the moisture content of approximately 9 %, which to reduce the moisture content to below 10 wt% (Bridgwater et al., 1999). This is because the moisture in the longan wood pruning after pyrolysis processing would end up in the bio-oil which increasing the water content of bio-oil. The characteristics of the longan wood pruning was given in table 1. In this work, three bed material were the sand, iron powder and natural zeolite. The bed material were dried in a furnace at 550 °C and sieved to a particle size of 0.250-0.425 mm.



| Characteristics | Values | | | | |
|----------------------------------------------|--------------------------------------|--|--|--|--|
| Proximate analysis (wt %, dry basis) | | | | | |
| Ash | 2.6 | | | | |
| Volatile matter | 82.2 | | | | |
| Fixed carbon | 14.6 | | | | |
| Ultimate analysis (wt%, dry, ash-free basis) | | | | | |
| Carbon | 45.32 | | | | |
| Hydrogen | 7.22 | | | | |
| Nitrogen | 0.06 | | | | |
| Sulphur | 0.38 | | | | |
| Oxygen* | 47.02 | | | | |
| H/C molar ratio | 1.91 | | | | |
| O/C molar ratio | 0.78 | | | | |
| Molecular formula | CH _{1.91} O _{0.78} | | | | |
| High heating value (HHV)** (MJ/kg) | 12.55 | | | | |
| | | | | | |

* Calculated by difference ** Bomb calorimeter

Experimental apparatus

The experimental were carried out in a fluidized-bed reactor as shown in Figure 1. The biomass feeding rate of the fast pyrolysis unit was 100 g/h. The apparatus was mainly consisted of biomass feeding unit, pyrolysis reactor, char separator and liquid collection.

The biomass feeding unit consisted of DC electric motor and a biomass hopper. The electric motor was 12 VDC and 120 watt. It was connected with a PWM motor speed controller. The biomass hopper was made from acrylic tube with a diameter of 19 cm and a height of 40 cm. The inside of biomass hopper was a stainless steel (AISI 304) stirrer designed for sustain the feeding of the biomass into the reactor. The biomass feed rate was controlled by adjusting the 12 VDC motor speed and the nitrogen flow rates at the top of hopper (3.5 lpm) and at the feeding tube (4 lpm).

The pyrolysis reactor was made of stainless steel (AISI 304) pipe with an inner diameter of 5 cm and a height of 70 cm. Nitrogen gas flow rate of 9 lpm was used as fluidizing gas in the pyrolysis reactor. The reactor was installed in a maffle furnace. The electric heaters (6500 watt) were installed onto a maffle furnace to supply heat to the reactor. The pyrolysis temperature was controlled by PID at 450, 500 and 550 °C. A Type K thermocouple was located in the reactor to measure the pyrolysis temperature. The beds or fluidized medium $(300-425 \ \mu\text{m})$ in the fluidized bed were the sand, iron powder and natural zeolite. The char separator unit comprised two cyclone and a fixed bed hot filter which the temperature maintained at 380 – 420 °C. In this work, a cyclone was made of stainless steel (AISI 304) pipe with an inner diameter of 3.10 and 2.6 cm. The fixed bed hot filter with a diameter of 5 cm was made from stainless steel pipe (AISI 304). The inside of hot filter was filled with the cotton wool.



Figure 1 The fast pyrolysis unit schematic

The liquid collection was consists of a water condenser, an electrostatic precipitator and a cotton wool filter. The water condenser was stainless steel (AISI 304) pipe which cooled by water at the temperature was at 27-33 °C. The electrostatic precipitator was supplied by 25,000 VDC. The bio-oil collected by a water condenser and an electrostatic precipitator was contained in the oil pot. While a cotton wool filter was to capture some non-condensable gas that may exit the electrostatic precipitator.

Prior to the experiments it was necessary to prepare the setup. The first step was to weight and place the biomass hopper and langan wood, fluidized bed reactor, cyclone, hot filter, water condenser, oil pot, electrostatic precipitator and cotton wool filter. When all the pieces were in place, a leakage nitrogen gas test were performed by observing the pressure levels on the nitrogen gas tank by supplying nitrogen gas. The next step in the setup preparation were switched on furnace and electrostatic precipitator. After about 2 hr the fluidized bed reactor and furnace temperatures reached the desired values. The longan wood feeding started by AC. Electric motor was switched on and the nitrogen gas was to flow in the fast pyrolysis unit about 16.5 lpm. This process was allowed to proceed for about 1 hr. The reason to keep the experimental run time for 1 hr is that to produce enough bio-oil for the subsequent analyses. Next, the furnace, electrostatic precipitator and fluidized bed reactor were shut down and the reactor, cyclone and hot gas filter allowed to cool down. After about 2 hr, the biomass hopper was removed from the place and the remaining langan wood was weighed. It is possible to calculation the langan wood consumed during the experiment. Furthermore, fluidized bed reactor, cyclone, hot filter, water condenser, oil pot, electrostatic precipitator and cotton wool filter were removed and weighed separately. They were also weight before the experiment, thus it is possible to know the amount of bio-oil and char produced during the pyrolysis process. The total time for each experimental was about 5-6 hr. Given the number of experiments carried out in this work, the repetition of each experiment would have been impossible due to time constraint. The very accurate monitoring of the temperature was such that irregularity in the experiment caused by experimental errors or equipment malfunctions could be easily detected. Nevertheless, in order to ensure that the results were reproducible and significant for the purpose of this work. Reproducibility promoted in this work. The reproducibility in this work was verified by carrying out in three replicates and under a pyrolysis temperature of 500 °C and the biomass feed rate of 100 g/h. The



results of the product yields and statistical analysis were summarized in Table 2. Yildiz et al. (2013) was carried out the continuous catalytic fast pyrolysis of pine wood in the auger reactor. They found that relative spread are less than 10%, showing that the reproducibility of the experiments is good. From Table 2, this means that the reproducibility of the product yields obtained from fast pyrolysis of longan wood in the fluidized bed reactor is acceptable and considered sufficiently close to allow trend detection on basis of single experiments per set of conditions.

Table 2 Reproducibility

| Product | Average yield, Y (wt%) | Std dev, σ_{γ} (wt%) | Relative spread, $\sigma_{_Y}/Y 	imes 100\%$ (wt%) |
|---------|------------------------|----------------------------------|----------------------------------------------------|
| Bio-oil | 25.7 | 2.2 | 8.56 |
| Char | 15.20 | 1.5 | 9.87 |
| Gas | 59.10 | 5.8 | 9.81 |

Bio-oil analysis

1. The density of bio-oil was measured by allowing the bio-oil into a beaker of a known volume which was measured at room temperature (about 30 $^{\circ}$ C). The weight of bio-oil divided by the volume of bio-oil was calculated as the bulk density (kg/m³).

2. The pH value of bio-oil was measured by a PH-009 I Pometer pH meter. Prior to the analysis the pH meter with phosphate buffers solution of pH meter 4, 7 and 10.

3. The higher heating value (HHV) of bio-oil was measured with a 1341 Parr Bomb Calorimeter following ASTM D240-02 which was standardization test by benzoic acid.

4. The flash point of bio-oil were determined using an AIM 508 Aimil, Pensky-Martens Closed Cup flash point tester according to ASTM D 93-02. Natural gas flame and hot wire electric igniters have been found acceptable for use as the ignition source. The bio-oil volume of 75 ml were filled in a test cup which heated by the electric heaters in a rate of 5-6 °C/min. Natural gas flame was applied to the bio-oil vapor in the test cup at intervals of 1 °C starting from 60 °C. The temperature of bio-oil at atmospheric pressure of 101.3 kPa to just form a flammable were the flash point.

Fast pyrolysis products yields

The bio-oil and char yields were calculated by measuring their weights at begin and end of each experiment whereas the gas yield was determined from the difference. The fast pyrolysis product yields were calculated using the formulae below.

The bio-oil yield on a wet basis is given as a mass percentage of the wet longan wood mass which is given by

$$(bio-oil)_{yield} = \frac{mass_{bio-oil}}{mass_{longan \ wood}} \times 100 \tag{1}$$

Where $mass_{bio-oil}$ is the bio-oil mass in the oil pot and cotton wool filter, $mass_{longan_wood}$ is the longan wood mass which to feed into the fluidized bed reactor. In this work, the longan wood mass is about 100 g.

The char yield is calculated as the percentage of the wet longan wood mass which is given by



$$(char)_{yield} = \frac{mass_{char}}{mass_{longan \ wood}} \times 100$$
⁽²⁾

Where $mass_{char}$ is the char mass in the fluidized bed reactor, char pot and hot gas filter. The gases yield is calculated from the mass balance which if given by

$$(gases)_{yield} = 100 - (bio - oil)_{yield} - (char)_{yield}$$
(3)

Results and Discussion

The experiments in this work were performed in two sets. This first one was studied the effects of pyrolysis temperature on the yield and properties of fast pyrolysis product in a fluidized bed reactor to determine the optimal conditions for liquid yield. The second part was studied the effects of low cost catalyst bed material on the product yields and properties of bio-oil. The experiments were performed at the optimized pyrolysis temperature from the first set of experiments and sand, iron powder and natural zeolite were used as bed materials.

Effect of pyrolysis temperature on products yields

The effects of the pyrolysis temperature in the range from 450 to 550 °C on products yields are shown in Figure 2. The bed material was sand. As observed from the figure, conversion of longan wood pruning decreased with increase in pyrolysis temperature. It can be seen that the bio-oil yields decreased from 32.78 % to 26.81 % and 21.9% when increasing the pyrolysis temperature from 450 °C to 500 °C and 550 °C, respectively. Therefore, the maximum yield of bio-oil (32.78%) was obtained at a pyrolysis temperature of 450 °C. For char yield, when the pyrolysis temperature increased from 450 to 500 and 550 °C, the char yield decreased from 17.13 % to 15.46% and 13.41 %, but the gas yield continued to increase. The bio-oil and char yield decreased, while the gas yield continued to increase due to the increase of pyrolysis temperature may be because of the enhanced decomposition of the primary pyrolysis product such as bio-oil (pyrolysis vapor), char and gas, especially bio-oil and char could thermal or secondary cracking in the reactor leading to the increased proportion of the gas yield (Bridgwater et al., 1999, Paenpong et al., 2016). Therefore, the excess supply of heat by increasing the pyrolysis temperature, the longan wood could easily be converted form condensable gas.



Figure 2 Effect of pyrolysis temperature on the main product yields

Effect of the bed material type on products yields

The effect of the bed material type on products yields are shown in Figure 3. The optimum pyrolysis temperature from first part experiment was 450 °C, which it was used to optimizing this experiment. The experimental were conducted at the bed material type of either sand, iron powder or natural zeolite and pyrolysis temperature of 450 $^{\circ}$ C. The results found that the bed material type had significant effect on the yield of bio-oil. As shown in Figure 3, it seemed that the maximum bio-oil yield was obtained by using natural zeolite bed material, which was 36.09 % by weight. The bio-oil yields decreased from 36.09 % to 32.78 % and 23.25% by weight when usage sand and iron powder were bed material. Similarity, the maximum char yield was obtained by using natural zeolite bed material of 20.48 % by weight. Whereas the minimum char yield of the fast pyrolysis of longan wood pruning was 17.13 % by weight which occurred when applying sand bed material. This means the reduction of 2.18 %, when compared to utilization of the iron powder bed material. While looking at the gaseous product yield, which the minimum yield was 43.43 % by weight for natural zeolite bed material, reached the maximum value of 57.44 % by using the iron powder bed material. When considering the product yields of fast pyrolysis. It found that the iron powder bed material led to a diminution of the bio-oil yield and an increase of the gas yield, indicating significant thermal cracking of the pyrolysis vapor. According to the results reported by Williams et al. (1995), they found that the stainless steel ball-bearings bed material produced an increase in gas yield. Which both the iron powder and the stainless steel ball-bearings is the steel and had in the Fe compound were similar. Therefore, the thermal cracking may be occur due to usage iron powder bed material. The thermal cracking arise from the primary pyrolysis product (pyrolysis condensate gas) were transformed into secondary product (pyrolysis noncondensate gas) by the pyrolysis vapor produced create short-chained compounds by inducing cracking reaction on the high temperature iron powder surface. Moreover, the presence of Fe compound in the iron powder bed material produced an increase in gas yield may be due to an enhancement of the dehydrogenation reactions (Antonakou, Lappas, Nilsen, Bouzga, & Stöcker, 2006, Nilsen et al., 2007).



Figure 3 Effect of bed material type on the fast pyrolysis product yields at pyrolysis temperature of 450 °C

Effect of pyrolysis temperature and bed materials type on bio-oil properties

The properties of bio-oils obtained at different pyrolysis temperature and bed materials type are determined in comparison with ASTM burner fuel standard D7544-12 for fast pyrolysis bio-oil requirement data. The results are summarized in Table 3. The pH value gives the acidity level of the fast pyrolysis bio-oils which were corrosive to common construction materials such as carbon steel and aluminum. The effect of the pyrolysis temperature on the pH values can also be observed from the Run No. 1, 2 and 3. The pH values of bio-oil were in the range 4.2-5.1. The data in Table 3 show that the pH values decreased from 5.1 to 5.0 and 4.2 when increasing the pyrolysis temperature from 450 °C to 500 °C and 550 °C, respectively. The increase of pyrolysis temperature lead to increase acidic of bio-oil. The acidity of bio-oil is the sum of the acidity of the chemical compounds in the bio-oil such as formic acid, acetic acid, propionic acid and crotonic acid (Diebold, 2000). According to the results reported by Thangalazhy-Gopakumar et al. (2010) found that the increase of the pyrolysis temperature lead to the increase concentration of propionic and crotonic acid. Considering the effect of the bed materials type on the pH values is shown from the Run No. 1, 4 and 5. It was found that the sand bed (5.1) gave higher pH value than the iron powder (4.7) and natural zeolite bed (4.3). The pH value of the bio-oil produced in this work were obvious higher than the typical bio-oil (pH 2.0-3.8) reported by Garci a-Pèrez, Chaala, and Roy (2002).

| Table 3 Characteristics of bio-oils with different pyrolysis temperature and bed materials | type |
|--------------------------------------------------------------------------------------------|------|
|--------------------------------------------------------------------------------------------|------|

| Properties | Experimental condition | | | Bio-oil ASTM D7544-12** | | | |
|-------------------------------|------------------------|-------|-------|-------------------------|---------|-------------|-------------|
| | Run 1 | Run 2 | Run 3 | Run 4 | Run 5 | Grade G | Grade D |
| Pyrolysis temperature (°C) | 450 | 500 | 550 | 450 | 450 | _ | - |
| Bed materials type | Sand | Sand | Sand | Iron | Natural | - | - |
| | | | | powder | zeolite | | |
| pH | 5.1 | 5 | 4.2 | 4.7 | 4.3 | _ | _ |
| Density (kg/m ³) | 1200 | 1100 | 1100 | 1300 | 1300 | 1,100-1,300 | 1,100-1,300 |
| Flash point ([°] C) | 75 | 80 | 96 | 81 | 97 | 45 | 45 |
| High Heating Value(MJ/kg) | 28.3 | 31.3 | 32.7 | 27.9 | 29.0 | 15 | 15 |

**(Oasmaa, van de Beld, Saari, Elliott, & Solantausta, 2015)



The data in Table 3 show that the density of bio-oils produced from longan wood were in the range of $1,100-1,300 \text{ kg/m}^3$, which were similar to the ASTM D7544-12 requirement, whereas that had obvious higher than the diesel fuel (840 kg/m³). From data in Table 3 also shows that the influence of pyrolysis temperature and bed materials type on the density of bio-oil were negligible. The density of the typical bio-oil was in the range of $1,100-1,300 \text{ kg/m}^3$ (Oasmaa et al., 2015).

The flash point is the lowest temperature at which the test flame ignites the vapor above the fuel. The data in Table show that all of the bio-oils produced in this work had obvious higher flash point than the ASTM D7544-12 requirement. Considering the influence of pyrolysis temperature, increasing the pyrolysis temperature from 450 °C to 500 °C and 550 °C increased the flash point from 75 to 80 and 96 °C, respectively. The effect of bed materials type on the flash point of bio-oil is shown from the Run 1, 4 and 5 when the pyrolysis temperature was kept constant at 450 °C. It was found that the lowest flash point of biooil (75 °C) was obtained by using the sand bed. The flash of the typical bio-oil was in the range from 40 °C to 110 °C (Oasmaa et al., 2012).

From data in Table 3, when considering the heating values of bio-oil produced from the longan wood pruning. In this work, the high heating values were in the range of 28.3-32.7 MJ/kg. The effect of the pyrolysis temperature on the heating values can be observed from the Run No. 1, 2 and 3. It is obvious from Table 3 that the high heating values increased from 28.3 to 31.3 and 32.7 when increasing the pyrolysis temperature from $450 \,^{\circ}C$ to $500 \,^{\circ}C$ and $550 \,^{\circ}C$, respectively. Because, the increase in pyrolysis temperature actually leads to an increase in the content of carbon in the bio-oil and decrease in the content of oxygen in the bio-oil. Which this monotonous increase suggests the intensification of the deoxygenation process with increasing temperature (Garcia-Perez et al., 2008). When considering the effect of the bed materials type on the higher heating values, it found that the higher heating values from the sand, iron powder and natural zeolite bed were not different. The higher heating value of the typical bio-oil was in the range from 14 MJ/kg to 19 MJ/kg (Oasmaa et al., 2015).

Conclusion and Suggestion

In this study, longan wood pruning fast pyrolysis was carried out in a fluidized bed reactor using a low cost catalyst bed material. It was that increasing pyrolysis temperature from 450 - 550 °C reduced bio-oil yield while increasing the gas yields. The optimum pyrolysis temperature for obtaining highest bio-oil yield for longan wood was 450 °C which gave maximum bio-oil yield of 36.09 wt%. Moreover, the increase in pyrolysis temperature could lead to the increase of flash point and heating values while the pH value decrease. When considering the effect of a catalyst bed material which pyrolysis was performed at optimum temperature of 450 °C. It was found that the natural zeolite bed gave the highest bio-oil yield of 36.09 wt%. When considering the effect of the catalyst bed materials on bio-oil properties, the sand bed gave the highest pH value (less acidic) and the lowest flash point in comparison with the iron powder and natural zeolite bed. However, a low cost catalyst bed material also resulted in a significant decrease of the acidic of bio-oil (4.3-5.1) compared to the typical bio-oil (2-3). But the bio-oil obtained from natural zeolite bed had the highest higher heating value (HHV) when compared with the sand and iron powder bed, which the highest higher



heating value of natural zeolite bed is about 2 time higher than of typical bio-oil. In the case of the iron powder bed, it was found that the pH value, flash point and higher heating value were between that of the natural zeolite and sand bed. The results indicate that the natural zeolite bed is more effective for increase the bio-oil yield and the improvement of the higher heating value.

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