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Bio-oil from Jackfruit Peel Waste

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Abstract

Fossil fuels such as petroleum, charcoal, and natural gas sources are the main energy sources at present, but considering their natural limitation in availability and the fact that they are not renewable, there exists a growing need of developing bio-fuel production. Biomass has received considerable attention as a sustainable feedstock that can replace diminishing fossil fuels for the production of energy, especially for the transportation sector. JackfruitwasteisabundantinIndonesiamake itpotentiallyas one of thegreenrefineryfeedstockforthe manufacture ofbio-fuel.As intermediate of bio-fuel,jackfruitpeelsisprocessed intobio-oil. Pyrolysis, a thermochemical conversion process under oxygen-absent condition is an attractive way to convert biomass into bio-oil.In this study, the pyrolysis experiments were carried out ina fixed-bedreactor at a range of temperature of400-600°C, heating rate range between 10-50°C/min, and a range of nitrogen flow between 2-4litre/min. The aims of this work were to explore the effects of pyrolysis conditions and to identify the optimum condition for obtaining the highest bio-oil yield.The effect of nitrogen flow rate and heating rate on the yield of bio-oil were insignificant. The most important parameter in the bio-oil production was the temperature of the pyrolysis process.The yield of bio-oil initially increased with temperature (up to 550°C) then further increase of temperature resulting in the decreased of bio-oil yield. Results showed that the highest bio-oil yield (52.6%)wasobtainedat 550°C with nitrogen flow rate of 4L/min and heating rate of 50°C/min. The thermal degradation of jackfruit peel was also studied using thermogravimetric analysis (TGA). Gas chromatography (GC-MS) was used to identify the organic fraction of bio-oil. The water content in the bio-oil product was determined by volumetric Karl-Fischer titration. The physicochemical properties of bio-oil produced from pyrolysis of jackfruit peels such as gross calorific value, pH, kinematic viscosity, density, sulfur content, ash content, pour point and flash point were determined and compared to ASTM standard of bio-oil (ASTM 7544).

Keyword: Pyrolysis; jackfruit peel, bio-oil

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1. Introduction

The increasing usage of fossil fuel in the world causes two major issues which are the depletion of nonrenewable resource and the increasing of glass house emission gas which effect to the world climate. Energy crisis is the main reason to explore different kinds of renewable alternative energies, one of which is bio-fuel. Bio-ethanol, bio-diesel, andbio-oil can be classified into bio-fuel. However, in the application, bio-ethanol and bio-diesel have some defects since bio-ethanol and bio-diesel use foodstuffas raw material. Vegetable oil was used to produce bio-diesel[1] and mono-sugars were used to produce bio-ethanol[2]. Moreover, bio-ethanol needs long fermentation process while bio-diesel also needs methanol in which can be acquired from methane gas which also nonrenewable source. The consideration of the weaknesses of bio-ethanol and bio-diesel makes bio-oil is an exactly great alternative.

Based on the methodology process, the technology to convert biomass to fuel can be classified into three categories; thermochemical, thermal, and biochemical conversion. Biomass thermochemical conversion includes a number of processes such as liquefaction, gasification, and pyrolysis[3]. Liquefaction process needs high temperature and pressure to keep the water stay on the liquid phase and supercritical condition[4]hence increase the production cost. The main product of gasification is gaseous product such as H_2, CO, and CH_4 through partial oxidation of biomass[4]. Pyrolysis is the process of chemical breakdown in biomass into gas, bio-oil (liquid), and char (solid) without the existence of oxygen. Considering the production cost and the desired main product, pyrolysis is the best solution to obtain bio-oil optimally.

Biomass is environmental friendly raw material which can be potentially used to produce bio-oil. In choosing biomass as the raw material, thorough consideration of the raw material characteristic is needed; the raw materials should possess high volatile matter content. The level of volatile matter shows the amount of organic compound which can evaporate into vapors during the pyrolysis process. The organic vapor, able to be condensed, is bio-oil. Jackfruitisabundantly availableinIndonesiamake its waste haspotentialapplication as one of thegreen refinery feedstockforthe manufacture ofbio-fuel;wherejackfruitpeelscan beprocessed intobio-oil.

Several studies on the utilization of the agricultural waste for bio-oil production are available in the literature[5-7]. In their studies, Pattiya and his co-workers using cassava rhizomes and stalk as the biomass material, and the reactors used in their studies were fluidised-bed reactor[5,7] and free-fall reactor[6]. In this study, jackfruit peel was employed as the rawmaterial for bio-oil production, and the pyrolysis process was carried out in a fixed-bed reactor.

1. Experimental section

2.1. Preparation and characterization of raw materials

Jackfruit peel was obtained from jackfruit chips factory in Sidoarjo, East Java, Indonesia. Prior to use, thejackfruit peel was washed several times with tab water to remove the dirt and other organic materials.Subsequently,clean jackfruit peel was dried in an oven at 100°C for 24 hours until itsmoisture content around5%. Dried Jackfruit peel was then pulverized until its particle size 80/100 mesh.Ultimate analysis of jackfruit peel was performedusing a Perkin-Elmer 2400 CHNS/O elemental analyser, while theproximate analysis was conducted using standard ASTM procedures as follow: ASTM D4442-07 procedure for water content, ASTM E1755-01 for ash content, and ASTM D-3175-11 for the content of volatile matter. The fixed carbon content was obtained from the subtraction of 100% with the percentage moisture content, ash content and volatile matter. Analysis of heating value was performed using ASTM procedure D5865-12 in an oxygen bomb calorimeter apparatus and the results obtained was 17.9 MJ/kg.

2.2. Thermogravimetric analysis (TGA)

Gravimetric analysis was conducted to measure the levels of thermal stability of the material.The testwas conducted in a TGA/DSC 1 STAR System (Mettler-Toledo) with a nitrogen flow of 70 mL/min and the rate of heating and cooling $10^{o}C/min$. The weight of sample used in this testwas 10 mg and maintained at a temperature of $700^{o}C$.

2.3. Fixed-bed pyrolysis process

The pyrolysis of jackfruit peel was carried out in a fixed-bed reactor.The experimental procedure is described as follows: 200 grams of jackfruit peelpowder was put into the reactor. Subsequently, nitrogen gas was flown into the system at a certain flow rate(2-4 L/min) to remove the airfrom the system in order to reach an inert atmosphere condition. The reactor was heated withcertain heating rate (10-50^{o}C/min)until the temperature reached the desired temperature(400-700°C) and maintained at constant conditions for 2 hours. During the pyrolysis process, the resulting gases and vapours products were flown into double stages condenser to condense the vapours into liquid product. The liquid products (called as bio-oil) were collected in a glass vessel. Cotton wool filters were attached at the end of the condenserto capture hydrocarbons which have low partial pressure. The un-condensable and carrier gases were passed into gas volume flow meter. After 2 hours, the reactor was cooled rapidly until it reaches room temperature to prevent any further reaction. The resulting solid product (char) and liquid product (bio-oil) wereweighted by analytical balance (Precisa 3000D).

2.4. Characterization of bio-oil

The chemical composition of bio-oil were analysedby GC/MS Shimadzu QP2010 equipped with DB-5 MS column (30m x 0.25mm x 0.25µm). Injector temperature was set at 250^{o}C and oven temperature was programmed at 60°C for 1 minute and then increased to 300^{o}C with a heating rate 10^{o}C/min and maintained for 20 minutes. Helium was used as the carrier gas at a flow rate of 1.5 mL/min.The detector temperature was set at 230^{o}C. Sample was injected into the column with a split ratio of 1:30. The identification of the chemical composition of bio-oil was conducted by comparing the sample chromatogram with the database in the GC/MS library and the data base of the National Institute of Standards and Technology (NIST). The calorific value of the bio-oil was measured using the oxygen bomb calorimeter based on ASTM D240. Physical and chemical properties of the bio-oil were analysed by ASTM standards as follow: density (ASTM 4052), pH (ASTM E70), kinematic viscosity (ASTM D445), pyrolysis solid content (ASTM D7579), moisture content (ASTM E203), sulfure content (ASTM D4294), ash content (ASTM D482), pour point (ASTM D97), and the flash point (ASTM D93).

3. Result and Discussion

3.1. Raw Material Characterization

3.1.1. Proximate and Ultimate Analysis

Proximate and ultimateanalyses of jackfruit peel are summarized in Table1.Based on the proximate analysis, it can be seen that the volatile matter content in the Jackfruit peel waste is quite high, an indication that this biomass was suitable precursor for bio-oil production. In the pyrolysis process, the volatile matterin the jackfruit peel was decomposedand evaporated into smaller carbon chain of organic compounds, some part of it were condensable (called as bio-oil) and un-condensable gases contains CO_2, CO, CH_4, etc.

Table 1.Characteristic of Jackfruit Peel

Analysis	% Weight	Analysis	% Weight
Proximate		Ultimate	
Water	4.8	Carbon	63.60
Ash	2	Hydrogen	7.84
Volatile matter	74	Oxygen	27.92
Fix carbon	19.2	Nitrogen	0.61
		Sulphur	0.03

From the ultimate analysis, highcarbon content (63.60%) indicates that organic compounds produced in the pyrolysisprocessgenerally form ofhydrocarbons. The presence ofoxygenwhichranks the second largest(27.92%) aftercarbonindicatesthe formation of oxygenated organic compounds such asalcohols, ethers, aldehydes, ketones, carboxylicacids, esters, andothers also occurred. The low sulphur(0.03%) andnitrogen(0.61%) content is strong indication that thebio-oil produced becomesan environmental friendlyfuel.

3.1.2. Thermogravimetric Analysis (TGA)

TGA is used to determine the thermal stability of jackfruitpeel during the heating process. Weight reduction caused by the release of volatile compounds was observed as a function of temperature. Figure 1 shows the TGA curve of jackfruit peel.

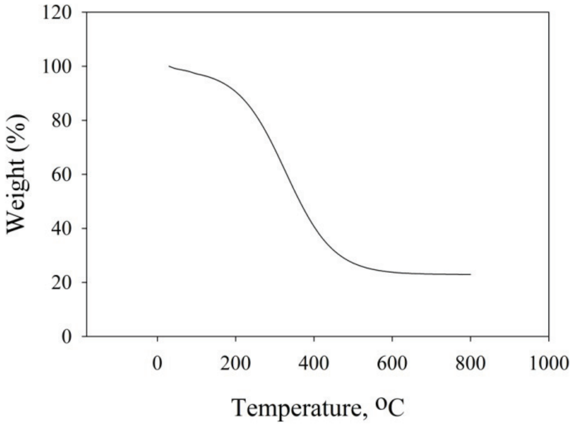
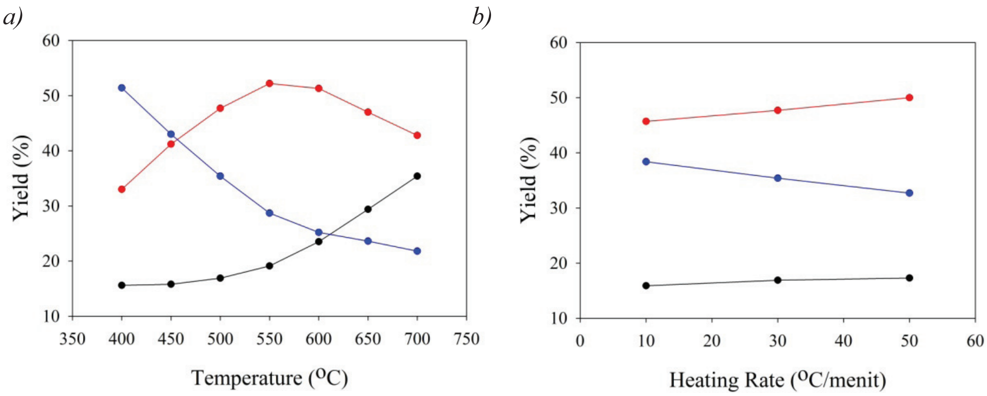


Fig1. TGA of Jackfruit Peel

At temperatures below 200°C, weight reduction of jackfruit peel is dominantly caused by the evaporation of the water of the solid structure. Jackfruit peel weight decreased significantly at temperatures 200-400°C. This is caused by the decomposition of cellulose and hemicellulose in jackfruit peel. At temperatures above 400°C, weight reduction of jackfruit peel is caused by the decomposition of lignin[7,8].

3.2. Effect ofoperating conditionsonthe yieldof bio-oil produced

The effect of operating conditions such as temperature, heating rate, and nitrogen gas flow rateon the yield of char, tar (bio-oil), and pyrolysis gases can be seen in Figure 2.



c)

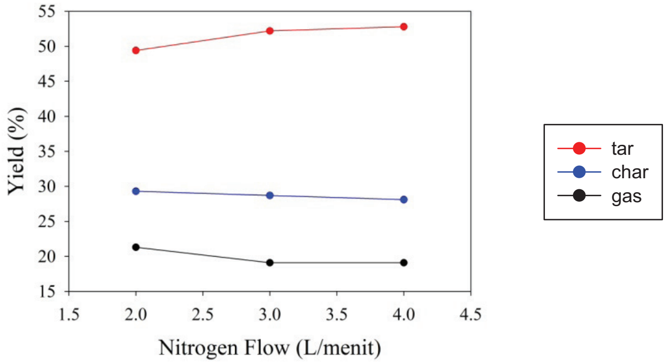


Fig2.Effect of a) temperature b) heatingrate c)nitrogen flow on the pyrolysis yield of jackfruit peel

3.2.1. Temperature

To determine the effect of temperature on the yield of pyrolysis products, the experiments were carried out at severaltemperatures(400, 450, 500, 550, 600, 650, and 700°C) with nitrogen flow and heating rate of 3L/minutes 30°C/minutes, respectively. Figure 2a clearly indicates that the yield of bio-oil (tar) increase with the increase of temperature. At temperatures 550°C, the maximum yield of bio-oil (51.8%) was obtained. However, with further increase of temperature, the decrease of the bio-oil yield is observed due to the secondary cracking. At temperature more than 550°C, some of the bio-oil decomposed into smaller compounds in the form of gases such as CO_2, CH_4, CO, and others. The decomposition of bio-oil into un-condensable gases become more and more with the increase of temperature (above 550°) leading to the increase of gas yield. A significant increase in gas yield during the secondary cracking is obvious as seen in Figure 2a.

3.2.2. Heating rate

Heating rate is the speed of heating the reactor to achieve the desired temperature. To study the influence of the heating rate, the pyrolysis process wasconductedat several different heating rates(10, 20, and 50°C/minute) at a temperature of 550°C and nitrogen flow of 3L/minute. The increase of the heating rate affects to the production of pyrolysis products in which increase the percentage yield of bio-oil and gas, whereas decrease in the char yield obtained as seen in Figure 2b. At low heating rate, the formation of char is more dominant than bio-oil and gases due to the slow release of the volatile compounds from the solid matrices, secondary cracking of trapped volatile matters occurred within the solid matrices, therefore it enhanced the formation of char. In contrast, at high heating rates, the release or evaporation of volatile matters occurred faster and most of the volatile compounds were converted into bio-oil and gas. At high heating rate, the occurrence of secondary cracking can be minimized.

3.2.3. Nitrogen flow

Nitrogen gas was used as the carrier gas and to maintain the system in inert condition. The effect of nitrogen flow rate on the yield of the pyrolysis products was studied at temperature of 550°C and heating rate of 50°C/min. The flow rates of nitrogen used in this study were 2, 3, and 4 L/min. The increases of nitrogen flow increase the result of bio-oil. The high flow of nitrogen encourages the release of organic vapours from the solid particle and exits the reactor faster therefore it minimizes the occurrence of secondary cracking. However, the effect of the nitrogen flow on the yield of bio-oil is not significant as indicated in Figure 2c.

3.3. Pyrolysis products characteristic

3.3.1. Bio-oil characteristic

3.3.1.1. Water and organic content of bio-oil

The organic and water content in the bio-oil obtained at pyrolysis of jackfruit peel at various temperatures and heating rate of 50°C and nitrogen flow of 4 L/min are summarized in Table 2.

Table 2.Water and organic contentinbio-oil of jackfruit peel

Temperature, °C	Water, %	Organic, %
400	23.6	76.4
450	21.5	78.5
500	18.2	81.8
550	14.8	85.2
600	17.0	83.0
650	19.1	80.9
700	20.3	79.7

Thewater contentinbio-oil samplesobtainedfromthisstudywasbetween14.8% -23.6%. The water contentinbio-oil dependsonseveral factors such asthe original water contentin theraw materials, the performance ofthe reactorpyrolysis, heating rateandpyrolysistemperature. The water contentinbio-oil has significant effect onfuel quality. The higher content ofwaterwillcause thebio-oil more difficult to be ignited and hasa low calorific value. At a temperature of550°C, the bio-oil produced has the best quality which isthe lowestwater content(14.8%) and the highest organic content(85.2%). The increase intemperature increasesthe organic contentin thebio-oil produced. At the temperature reaches more than 550°C, the organic content in bio-oil decreased due tosecondary cracking of organic compounds, some of the organic compounds were converted to gases and some to water.

3.3.1.2. Chemical composition of bio-oil

GC-MS was used to determine the chemical composition of the bio-oil obtained from the pyrolysis process at optimum condition (temperatureof 550°C at a heating rate50°C/ min and 4L/ min). The chemical composition of the bio-oil pyrolysis results are influenced by jackfruit peel (raw material) used and the condition of the pyrolysis process. In the ultimate analysis found that jackfruit peel had the highest levels of carbon and oxygen than the other elements that cause bio-oil product is composed of hydrocarbons containing oxygen such as carboxylic acids (22.38%), alcohols (4.14%), aldehydes and ketones (20.87%), esters (7.14%), ethers (4.25%), phenols (18.4%), furan (7.37%), hydrocarbon and derived (2.13%), nitrogen compound (1.64%)and oxygenated cyclic compounds (3.91%).

3.3.1.3. Bio-oilcharacteristic

Before the bio-oil is used as fuel, the characterization is needed to determine its quality. Characterization of bio-oil obtained from pyrolysis at optimum condition (temperature 550°C, 50°C/min heating rate and nitrogen flow 4L/min) can be seen in Table 3,in this table we also compared with the standard from ASTM 7544. The bio-oil obtained in this experiment has acidic valuedue to the acidic compounds such as formic acid, acetic acid, propionicacid, butanoic acid, and others. Solids content of pyrolysis is one property that is important in the application of bio-oil. Ideally, the smaller the solid content, the quality of bio-oil is better because high levels of solids that can cause blockage and erosion in the pipe or pump system. High levels of solids disrupt the stability of the viscosity of bio-oil after a certain period. Ash content in bio-oil pyrolysis associated with solid content as it contains ash solids pyrolysis. By eliminating solids in the bio-oil, the ash content of the bio-oil is also reduced[7]. High viscosity will cause poor atomization processes and incomplete combustion[9].

Table 3.The physicochemical properties of bio-oil (550ºC).

Properties	Bio-oil	ASTM 7544
Gross calorific value (Mj/kg)	29.3	min 15
pH	4.3	-
Kinematic Viscosity (cSt) at 40ºC	31.8	max 125
Density (kg/dm^3) at 20ºC	1.4	1.1-1.3
Pyrolysis solid content (wt %)	0.1	max 2.5
Water content (%wt.)	14.8	max 30
Sulfur content (%wt.)	0.01	max 0.05
Ash content (%wt.)	0.06	max 0.25
Flash Point (ºC)	84	min 45
Pour Point (ºC)	-10	max -9

4. CONCLUSION

Jackfruit peel was used as the raw material in pyrolysis to obtain bio-oil. The influences of nitrogen flow rate, heating rate, and the pyrolysis temperature were also examined to find the highest yield of bio-oil. The most important parameter was the pyrolysis temperature. GC-MS analysis showed that the bio-oil consist of acids, alcohols, sugars, aldehydes, ketones, esters, ethers, phenols, furans, hydrocarbons derived, nitrogen compounds, and oxygenated cyclic compounds. Thermogravimetric Analysis (TGA) was employed to determine thermal stability of jackfruit peel during thermal processing.

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