



BIOREFINERY CONCEPT ON JACKFRUIT PEEL WASTE: BIO-OIL UPGRADING

Cynthia Widjaja, Yovita Djojarahardjo, Alfin Kurniawan, Wenny Irawaty and Felycia Edi Soetaredjo

Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan, Surabaya, Indonesia

E-Mail: felyciae@yahoo.com

ABSTRACT

Jackfruit peel waste is utilized to produce bio-oil using a slow pyrolysis process. However, the high water content of bio-oil gives detrimental impacts such as less lubrication action and low calorific value during the combustion process. Therefore, upgrading process of bio-oil is necessary before its application to substitute fuel for the commercial or industrial burner. Various technologies have been developed for bio-oil upgrading: sub/supercritical fluids, solvent addition, and steam reforming. These methods possess some disadvantages: energy-intensive, low efficiency, high cost, and reduce yield also valuable organic compounds in bio-oil. The removal of water in bio-oil by adsorption technique using low-cost adsorbents (silica gel and natural zeolite) was studied in this work. The adsorption-based purification method can be a new viable alternative to conventional methods, owing to its advantages: simple, high selectivity, low cost, and wide adaptability from laboratory- to industrial-scale operation. Purification of bio-oil using silica gel and zeolite could decrease water content reduced from 40.09% to 27.6% and 25.06%. Zeolite has higher maximum adsorption capacity (q_m) and Equilibrium constant of adsorption process (K_L) than Silica gel. Zeolite is the best material to obtain the greatest water reduction during bio-oil purification.

Keywords: biorefinery, bio-oil upgrading, adsorption, jackfruit peel.

1. INTRODUCTION

Increasing energy needs and the depletion of fossil fuel reserves of non-renewable pose a considerable challenge to find alternative energy sources like lignocelluloses biomass as feedstock alternatives to fossil fuels. Advantages in the utilization of biomass include: biomass is a natural resource that can be renewed and abundant availability in the world; contents in the biomass free of sulfur and other harmful elements; biomass is carbon neutral so as not to cause pollution to the environment (Xu *et al.*, 2012).

Biorefinery concept has been developed to replace the use of fossil fuels with biomass. This concept provides maximum benefit and minimum waste in the use of natural raw materials. One of the renewable fuels and environmentally friendly by the idea of the biorefinery is bio-oil obtained by pyrolysis process. In pyrolysis, decomposition or chemical breakdown of biomass occurs at high temperatures in inert conditions. Biomass converted directly into solids (bio-char), liquid products (bio-oil), and biogas. With further processing, bio-oil can be converted into a more pure fuel. Biochar can be used as an adsorbent or solid fuel. Non-condensable gases containing CO, CO₂, H₂ and N₂ will be reused as fuel for the pyrolysis reactor.

Thermochemical conversion of biomass includes some processes such as hydrothermal liquefaction, gasification, and pyrolysis (Park *et al.*, 2012). Hydrothermal liquefaction process requires high temperatures and pressures to maintain the water is still in the liquid phase, and supercritical conditions are thereby increasing the cost of the process (Xiu and Shahbazi, 2012). In the gasification process, the main products produced in the form of gases such as H₂, CO, and CH₄ by partial oxidation of biomass (Park *et al.*, 2012). Pyrolysis is a process to decompose biomass into gas, bio-oil (liquid),

and char (solid) without the presence of oxygen. Taking into account the cost of the process and the desired main product, pyrolysis is the best solution to obtain an optimal bio-oil.

Indonesia is a country that known as jackfruit producing areas where is quite large. Jackfruit can grow not based on the season so it can be harvested throughout the year. Utilization of jackfruit impact on increasing the volume of jackfruit peels wastes significantly. The impact of organic waste jackfruit peels includes proliferation of pathogenic bacteria in the jackfruit peel waste accumulate if not taken seriously. The use of jackfruit peel waste as raw material for the manufacture of bio-oil can increase the economic value of jackfruit peel waste and reduce the amount of waste that can have an adverse impact on the environment.

However, bio-oil cannot use directly because limited by the problems of high viscosity, ash content, low heating value, instability, high corrosiveness, and also high water (Xiu and Shahbazi, 2012). Therefore, the purification process of bio-oil before bio-oil be used was applied. Bio-oil refining process has been widely studied. The process of purification is conducted by removing the oxygen content (Adjaye and Bakhshi, 1995), the acidic nature (Zhang *et al.*, 2006), and water content. In this study, the purification process is more emphasis on the removal of moisture content. To remove water in the bio-oil can be done by several methods such adsorption, and distillation. In the distillation process, the organic compounds in bio-oil that can be dissolved in water will come separated from bio-oil that would reduce the organic compound in bio-oil. Therefore, this study used zeolite and silica gel for a study about adsorption method on the crude bio-oil. This adsorbent serves to separate the water contained in the bio-oil without changing the organic compound inside the bio-oil.



2. MATERIALS AND METHODS

2.1 Materials

Jackfruit peel waste was collected from fruit market in Surabaya, East Java, Indonesia. Zeolite was purchased from Sigma Aldrich and silica gel 60M was purchased from Macherey-Nagel.

2.2 Raw material preparation

Jackfruit peels were cleaned and dried in an oven for 3 days at 105 °C (ASTM E1756-08). The dried jackfruit peel was then grounded using a grinder to form a powder and keep in a desiccator.

2.3 Characterization of raw material

The proximate analysis of the jackfruit peel is carried out based on the ASTM standards. The moisture content was analyzed by moisture balance at 110°C (ASTM D4442-07), the volatile matter was analyzed by tube furnace for 7 minutes at 700 °C (ASTM D-3175-11), and the ash was analyzed by muffle furnace for 3h at 600 °C (ASTM E1755-01). The fixed carbon was determined by subtraction of the biomass weight by total weight of moisture, volatile matter and ash. The ultimate analysis determines the content of carbon (C), nitrogen (N), hydrogen (H), oxygen (O), and sulfur (S). The ultimate analysis was determined by an elemental analyzer. Thermogravimetric analysis (TGA) determines the level of thermal stability. The thermal stability of jackfruit peel was studied using a Diamond TG/DTA (Perkin, Elmer, Japan). The temperature was varied from 40 °C to 900 °C. Following the method of before (Yuliana *et al.*, 2004) a sample (5.4 mg) was placed in a platinum pan and heated at 10 °C/min. Nitrogen (3.7 bar) was allowed to pass through the system at 20 mL/min during the process.

2.4 Pyrolysis process

Fifty grams of jackfruit peel powder was put in a tank biomass, and nitrogen will be introduced into the system at a rate 4 Liter/minute to maintain inert conditions. Furthermore, the reactor was heated to the desired temperature (400-650 °C) for 2 hours. Gases and vapors produced were then passed through a two multilevel condenser which the condensed vapor (bio-oil) was collected in a container. After the pyrolysis process was completed, the system will be cooled to room temperature. Biochar and bio-oil were weighted to obtain the yield of biochar and bio-oil. The yield of gas was calculated with 100% to reduce the yield of bio-oil and biochar. The best yield of bio-oil was continuously processed to obtain bio-oil which is used in the purification process.

2.5 Bio-oil upgrading process

Adsorbent material (silica gel and zeolite) were dried in an oven at 110 °C for 3 h before used for upgrading process. 1 mL of bio-oil was mixed with 0.6 gram adsorbent materials (silica gel or zeolite) for a certain time (2; 4; 8; 12; 16; 20; and 24 hours) for kinetic analysis. On the other hand, 1 mL of bio-oil was mixed

with different mass of adsorbent materials (0.1; 0.2; 0.3; 0.4; 0.5; and 0, 6 gram) for 24 hours. After purification process, the refining materials were filtered from bio-oil. The water content of bio-oil before and after purification was determined using Karl Fischer (ASTM E203).

2.6 Characterization of bio-oil

The calorific value of bio-oil was determined by bomb calorimeter (ASTM D240). Other physicochemical properties were analyzed as follow: pH using pH meter (ASTM E70), viscosity using viscosimeter Brookfield (ASTM D445), density using pycnometer (ASTM D4052), ash content (ASTM D482) and flash point (ASTM D93). Also, use GC/MS that completed with DB-5 MS column (30-meter x 0.25 mm x 0.25 µm) on static condition for chemical compound identification inside bio-oil (before and after purification) by comparing with National Taiwan University (NTU) database of the sample.

3. RESULTS AND DISCUSSIONS

3.1 Characterization of raw material

From the proximate result, jackfruit peel, as a raw material in this study, has a high amount of volatile compound (70%) that can be converted to bio-oil during the pyrolysis process. Because of drying before pyrolysis process, jackfruit peel has low water content (3.9%). The lower moisture content in raw material, the more viscous of bio-oil that be produced. Beside of that, low ash content (1.7%) made the quality of biochar higher.

From the elemental result, jackfruit peel had high carbon (46.64%) related to hydrocarbon as the organic compound in the pyrolysis product. High oxygen content (42.85%) result means a high possibility of the organic compound which contains oxygen, such as alcohol, ether, aldehyde, ketone, carboxylic acid, ester, and others in the raw material. Low nitrogen (0.6%) and sulfur content (1.51%) showed that jackfruit peel as raw material produced an environmental friendly bio-oil with low emission of NO_x and SO_x.

Thermogravimetric analysis (TGA) used to figure out the level of jackfruit peel thermal stability in specific temperature that shown in Figure-1. Reduction weight of the raw material is caused by loss of volatile matter as temperature function. Below 200 °C, weight loss is relevant to evaporation of water and short chain carbon in jackfruit peel. Decomposition of hemicelluloses and cellulose is the major stage in biomass pyrolysis with significant weight loss that initiated at 200 °C and ended at 400 °C. Further decomposition at 400 °C until 600 °C is attributed to lignin degradation. However, decomposition of lignin occurs gradually at a very low rate during the whole temperature range (Haykiri *et al.*, 2010). This phenomenon is closely related to the lignin's complex structure (Yang *et al.*, 2007).

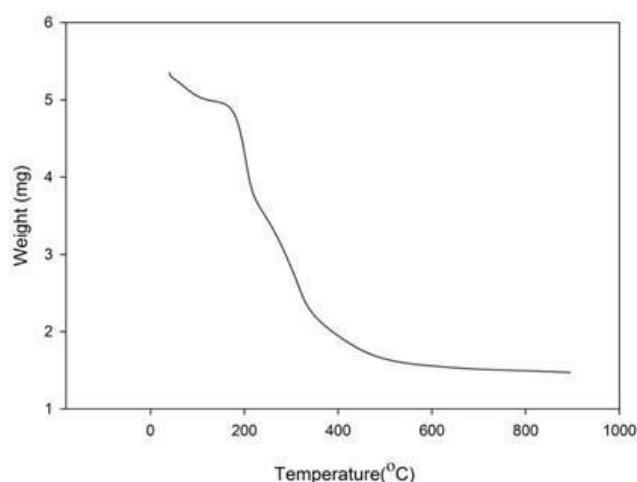


Figure-1. Thermal stability of Jackfruit peel.

3.2 Pyrolysis process

In pyrolysis process, biomass was heating in inert condition and caused the increase of organic vapor. Organic vapor was then condensed into a liquid that is known as bio-oil. The solid remaining after pyrolysis process called bio-char. So, the products of pyrolysis process are bio-oil, biochar, and vapor that cannot be condensed (gas).

To study the effect of temperature to the distribution of pyrolysis product, jackfruit peel as a raw material was put in the pyrolysis reactor with desired temperature (400 °C until 650 °C) and nitrogen flow rate was 4 L/min for 2 hours. From Figure-2, the yield of bio-oil increased gradually with increase of temperature. Optimal temperature of pyrolysis to obtain a maximal yield of bio-oil (51.9%) is 600 °C. At 600 °C, the yield of biochar and gas obtained were 28.6% and 19.5%, respectively. As the temperature increased, the yield of solid (bio-char) decreased while the yield of gases increased. The reduction of the char yield was the effect increasing of temperature due to the primary cracking of jackfruit peel increased on a higher temperature. At a temperature above 600 °C, a combination of secondary thermal decomposition of liquid and solid product enhances the yield of gas. At 650 °C, the yield of bio-oil

and biochar decreased to 46.8% and 23.5%, which was related to significant increase of gas produced (increased 10.2%).

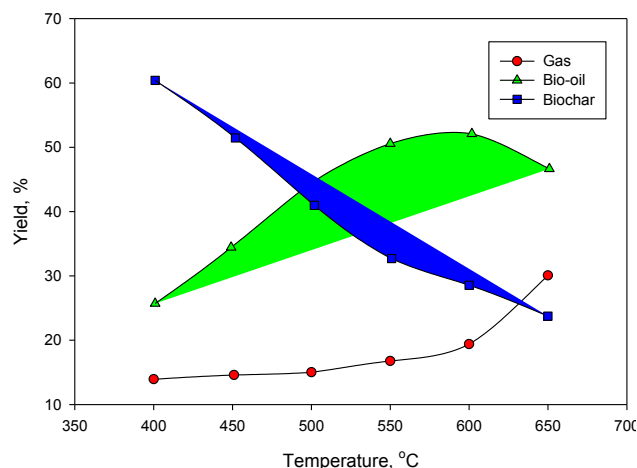


Figure-2. Temperature effect to Pyrolysis product from Jackfruit peel.

3.3 Bio-oil upgrading

Bio-oil was obtained using optimal temperature of pyrolysis process (600 °C) as fixed variable for upgrading process. Bio-oil from pyrolysis process has high water content that also causes low calorific value. Upgrading using adsorbent to reduce moisture content in bio-oil were needed for increasing heating value and viscosity. The effect of time and mass of adsorbent was studied to optimize the reduction of water in bio-oil.

3.3.1 Characterization of adsorbents

In this study, the adsorbents that have been used zeolite and silica gel. The analysis for adsorbent by using Scanning Electron Microscope (SEM). From figure 3, the topography of zeolite and silica gel are diverse. The zeolite has tetrahedron shape that improves the surface area and also the adsorption of the bio-oil. Beside of that, the silica gel has bigger size than zeolite. However, the surface of zeolite is smoother than silica gel.

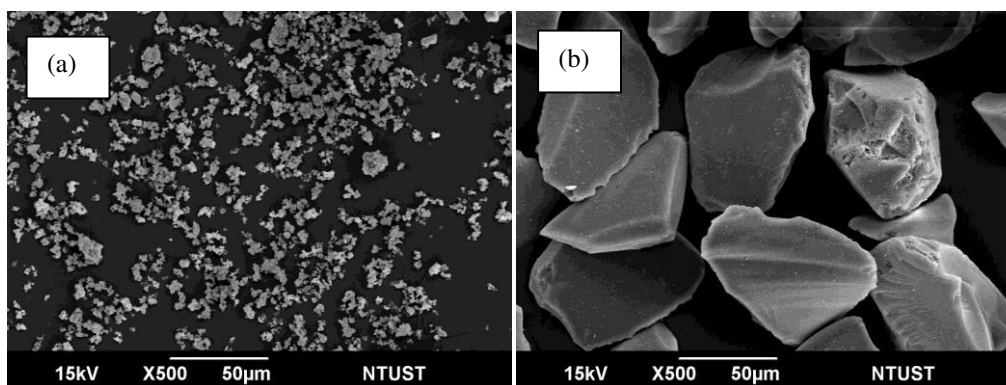


Figure-3. SEM images of (a) zeolite, and (b) silica gel.



3.3.2 Kinetic analysis

A series of batch experiments were conducted to assess the optimum time necessary to obtain a maximum adsorption of water onto silica gel and zeolite. Adsorption of water in bio-oil for upgrading process by using 0.6 grams adsorbent (zeolite or silica gel) at a certain time (from 2 to 24 h) was studied to get equilibrium time with maximum adsorption that can be seen in Figure-4. The water content of bio-oil before and after purification was

determined using Karl Fischer (ASTM E203). q_t (mmol water adsorbed/gram adsorbent) was calculated from the difference of water concentration before and after upgrading process per mass of adsorbent. Water adsorbed increased by the function of time. The maximum adsorption achieved on retention time 24h. After 24 h process of adsorption, the concentration of water in bio-oil reduced from 40.9% to 25.02% or 27.60% using zeolite or silica gel as an adsorbent.

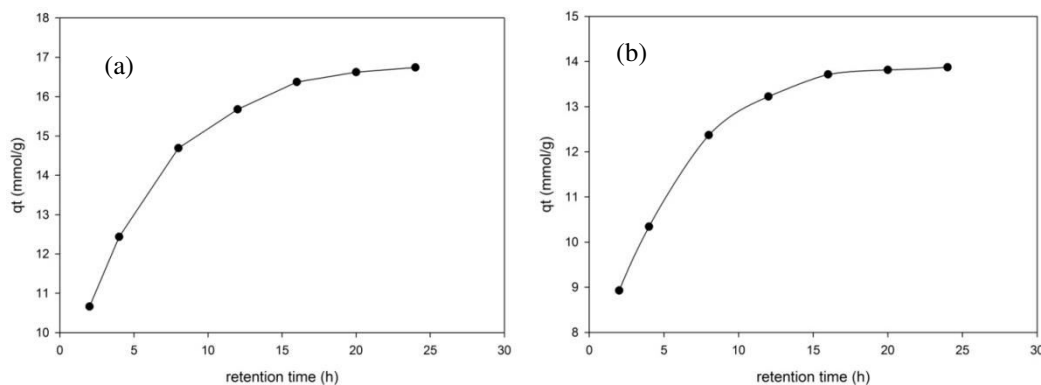


Figure-4. Kinetic of water adsorption onto (a) zeolite, and (b) silica gel.

3.3.3 Isotherm analysis

To describe the adsorption isotherms, experimental values were obtained for adsorption of water in bio-oil using a variation of mass adsorbent (zeolite and silica gel) from 0.1 until 0.6 grams using equilibrium time (24 h). The water content of bio-oil before and after upgrading process was determined using Karl Fischer (ASTM E203). q_e (mmol water adsorbed/gram adsorbent) calculated from the difference of water concentration before and after upgrading process per mass of adsorbent. Figure-5 shows the experimental data mmol water adsorbed per gram adsorbent in equilibrium time (q_e) versus concentration of water in solution at equilibrium conditions (C_e) that fitted by Langmuir models. The experimental data are represented by symbols and the Langmuir model as solid lines.

The adsorption equilibrium data of water on adsorbent was calculated by using Langmuir model. The Langmuir model was originally developed to represent

chemisorption on a set of well-defined localized adsorption sites having same adsorption energy, independent of the surface coverage and with no interaction between adsorbed molecules. Maximum adsorption is noticed when the surface of adsorbent is covered with a monolayer of adsorbate (Langmuir *et al.*, 1918). The Langmuir adsorption isotherm is given by:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

where q_e represent the amount of water adsorbed per unit weight of adsorbent (mmol/g), q_m the amount of water adsorbed (mmol) per gram of adsorbent required for monolayer coverage of the surface (monolayer capacity), C_e the concentration of water in bio-oil at equilibrium condition (mmol/L) and K_L is the constant of Langmuir related to the equilibrium constant of adsorption process.

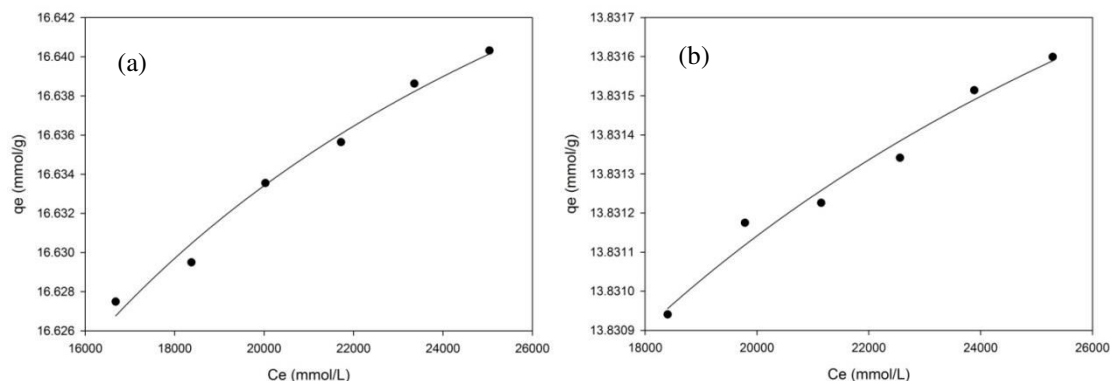


Figure-5. Isotherm adsorption of water onto (a) zeolite, and (b) silica gel.



Figure-5 clearly shows that the Langmuir equation can describe the experimental data fairly well. The equation parameters were calculated using nonlinear regression fitting using Sigmaplot software. Adsorption of water from bio-oil by using zeolite and silica gel fitted with Langmuir equation with regression coefficient 0.99 and 0.98. Zeolite (16.67 mmol/g) has higher maximum adsorption capacity (q_m) than silica gel (13.83 mmol/g). The equilibrium constant of adsorption process (K_L) using zeolite (0.02 L/mmol) as adsorbent was higher than silica gel (0.32 L/mmol), that showed zeolite has a higher affinity for water to the active surface. This phenomenon also shows zeolite has higher surface adsorption efficiency than silica gel.

3.4 Characterization of bio-oil

The characterisation of bio-oil before and after purification process using 0.6 grams adsorbent for 24 hours. After adsorption process using silica gel and zeolite, the water content in bio-oil reduced from 40.09% to 27.60% and 25.06%. Therefore, quality of bio-oil was increased as shown the increasing of gross calorific value from 14.85 MJ/kg to 42.1 MJ/kg and 44.3 MJ/kg. After upgrading process, kinematic viscosity at 40 °C also increased from 29.2 cSt to 32.9 cSt and 34.5 cSt that give more machine lubrication effect. Low ash content of bio-oil represents that bio-oil is environmental friendly fuel. Physicochemical properties of bio-oil after upgrading process fulfilled ASTM 7544-12 requirements as a substitute fuel for the commercial or industrial burner as indicated in Table-1.

Table-1. The physicochemical properties of bio-oil.

Properties	CrudeBio-oil	Bio-oil upgrading using Silica gel	Bio-oil upgrading using Zeolite	ASTM 7544-12
Gross calorific value (MJ/kg)	14.85	42.1	44.3	>15
Water content (%wt)	40.09	27.60	25.02	<30
Kinematic viscosity (cSt) at 40°C	29.2	32.9	34.5	<125
Density (kg/dm ³)	1.1	1.2	1.2	1.1 – 1.3
Ash content (%wt)	0.1	0.1	0.1	<0.15
pH	4.27	4.30	4.33	-
Flash point (°C)	79	72	70	>45

The chemical composition of bio-oil was characterized using GC/MS. Since the pyrolysis process involved into very complex reactions, there is no specific trend of the organic composition of bio-oil. Bio-oil is very complex mixtures that consist of different chemical species derived from depolymerization and fragmentation of main biomass components, covering a wide range of

molecular weights (Bertero *et al.*, 2012). As indicated in Table-2, the organic fraction of bio-oil contains acids, esters, ethers, aldehydes, ketones, phenols, alcohols, hydrocarbons, and other organic compounds and some unidentified organic compounds. There was no significant difference for the organic compound in bio-oil after and before upgrading process.

**Table-2.** Chemical composition of bio-oil.

Compounds (wt%, dry basis)	Crude bio-oil	Bio-oil after upgrading using silica gel	Bio-oil after upgrading using zeolite
Acids	23.84	20.49	19.82
Alcohols	4.03	3.94	3.74
Aldehydes and ketons	12.39	13.08	12.09
Esters	13.72	14.82	15.95
Ethers	8.17	9.37	8.62
Phenols	10.32	11.84	12.48
Furans	5.18	4.02	5.91
Hydrocarbons and its derivative	3.41	4.1	3.84
Nitrogen compounds	0.95	0.57	0.69
Oxygenated cyclic compounds	3.14	2.88	2.97
Unknowns	14.85	14.89	13.89

4. CONCLUSIONS

The yield of bio-oil increased gradually with the increase in temperature. Optimal temperature of pyrolysis to obtain a maximal yield of bio-oil (51.9%) is 600 °C. At a temperature above 600 °C, secondary thermal decomposition of liquid product decrease the yield of bio-oil. Upgrading process of bio-oil using 0.6grams adsorbent for 24 h resulted in highest water reduction in bio-oil. After adsorption process using silica gel and zeolite, moisture content in bio-oil reduced from 40.09% to 27.6% and 25.06%. Zeolite has higher maximum adsorption capacity (q_m) and Equilibrium constant of adsorption process (K_L) than Silica gel. Zeolite is the best material to obtain the greatest water reduction during bio-oil purification. After upgrading process, moisture content in bio-oil reduced and increased the quality of bio-oil as shown the increased of gross calorific value and kinematic viscosity. Physicochemical properties of bio-oil after upgrading process were fulfilled ASTM 7544-12 as a substitute fuel for the commercial or industrial burner. There was no significant difference for the organic compound in bio-oil after and before upgrading process.

REFERENCES

- Adjaye J.D. and N.N. Bakhshi. 1995. Catalytic conversion of a biomass-derived oil to fuels and chemicals I: Model compound studies and reaction pathways. *Biomass & bioenergy*. 8(3): 131-149.
- Bertero M., de la Puente G. and Sedran U. 2012. Fuels from bio-oils: Bio-oil production from different residual sources, characterization and thermal conditioning. *Fuel*. 95(0): 263-271.
- Haykiri-Acma H., Yaman S. and Kucukbayrak S. 2010. Comparison of the thermal reactivities of isolated lignin and holocellulose during pyrolysis. *Fuel Processing Technology*. 9 (7): 759-764.
- Langmuir I. 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society*. 40(9): 1361-1403.
- Park Y.K., *et al.* 2012. Wild reed of Suncheon Bay: Potential bio-energy source. *Renewable Energy*. 42: 168-172.
- Xiu S. and A. Shahbazi. 2012. Bio-oil production and upgrading research: A review. *Renewable and Sustainable Energy Reviews*. 16(7): 4406-4414.
- Xu J., *et al.* 2012. Liquefaction of sawdust in hot compressed ethanol for the production of bio-oils. *Process Safety and Environmental Protection*. 90(4): 333-338.
- Yang H., Yan R., Chen H., Lee D. H. and Zheng C. 2007. Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel*. 86(12-13): 1781-1788.
- Yuliana M., Huynh L.-H., Ho Q.-P., Truong C.-T. and Ju Y.-H. 2012. Defatted cashew nut shell starch as renewable polymeric material: Isolation and characterization. *Carbohydrate Polymers*. 87(4): 2576-2581.
- Zhang Q., *et al.* 2006. Upgrading bio-oil over different solid catalysts. *Energy and Fuels*. 20(6): 2717-2720.