Upgrading of bio-oil from the pyrolysis of biomass over the rice husk ash catalysts

B Sutrisno and A Hidayat
Chemical Engineering Department, University of Islam Indonesia
Jalan Kaliurang km 14.5 Yogyakarta 55584, Indonesia

E-mail : arif.hidayat@uii.ac.id

Abstract. The pyrolysis oils are complex mixtures of organic compounds that exhibit a wide spectrum of chemical functionality, and generally contain some water. Their direct use as fuels may present some difficulties due to their high viscosity, poor heating value, corrosiveness and instability. For possible future use as replacements for hydrocarbon chemical feedstocks and fuels, the liquids will require considerable upgrading to improve its characteristics. By esterification of the bio oil as the upgrading method, the properties of the bio-oil could be improved. In the paper, the upgrading of a bio-oil obtained by pyrolysis was studied over rice husk ash catalysts. The raw bio-oil was produced by pyrolysis of rice husk. From the experiment results, it can be concluded that the densities of upgraded bio-oil were reduced from 1.24 to 0.95 g.cm⁻³, and the higher heating value increased from 16.0 to 27.2 MJ/kg and the acidity of upgraded bio-oil was also alleviated from 2.3 to 4.4. The results of gas chromatography-mass spectrometry (GC–MS) and FT-IR analysis showed that the ester compounds in the upgraded bio-oil increased. It is possible to improve the properties of bio-oil by esterifying the raw bio-oil.

1. Introduction
The global energy crisis and environmental concerns have boosted research initiatives on alternatives for fossil energy and has encouraged the exploration of renewable resources such as biomass for increased energy generation [1]. Thermochemical techniques for bio-oil production including fast pyrolysis liquefaction and byproduct oil collection from slow pyrolysis are gradually being developed and recommended. Fast pyrolysis has been developed considerably as a front technology for efficient conversion of biomass into a liquid product known as bio-oil, which can be used as a potential substitute for fossil fuels. This technology is industrially feasible and has advantage in terms of reduced cost[1–3]. Great progress in fast pyrolysis of biomass has been achieved, and liquid product yield is more than 70% on dry feed [4, 5]. However, bio-oil is not as good as fossil fuels and the drawbacks including high acidity, low heating value, high corrosiveness, high viscosity and poor stability limit its usage as high grade/transportation fuel. Consequently, upgrading of bio-oil before utilization is desirable to obtain a liquid product that can be used in a wider variety of applications. The current upgrading methods include catalytic hydrogenation, catalytic cracking and catalytic esterification [6–8]. The presence of a large amount of organic acids (formic acid, acetic acid and propionic acid) is the main reason for the strong acidity, high corrosiveness and poor stability of bio-oil [9–11].

Esterification reaction is an upgrading method that can convert carboxylic acids in bio-oil to esters. It is not only able to reduce corrosiveness of the bio-oil but can also prohibit some reactions catalyzed by these acids, for example, the reactions of oligomers or polymer formation (homopolymerization of aldehydes, phenol/aldehyde polymerizations, etc.) This treatment could be an attractive method for improving bio-oil properties due to its ease of operation, low investment cost and avoiding secondary reactions that may occur at high operating temperatures. Although limited studies on bio-oil upgrading by esterification reaction have been reported thus far, this upgrading technique is still the topic of recent interest. Doshi et al. (2005) upgraded the bio-oil derived from fast pyrolysis of sewage sludge.
via esterification using H$_2$SO$_4$ as a liquid acid catalyst. It was found that odor of the treated oil was improved from an extremely annoying level to a not annoying level (ASTM D1833-87) with about four times reduction in viscosity and up to 9% increasing in heating value. However, using solid catalyst in place of H$_2$SO$_4$ to reduce corrosion problem was also proposed. It is noted that increasing amount of alcohol for the esterification reaction can reduce heating value of the upgraded oil and therefore alcohol separation by fractional distillation would be needed in this process. Later, several researchers improved the process by using various types of solid acid catalyst and/or recovery of the alcohol by distillation [6-8]. Junming et al. (2008) reported that density and acidity were reduced (1.16 to about 0.93 g/cm$^3$ for density and pH from 2.82 to 6.21) and the gross calorific value increased from 14.3 to 23 MJ/kg using ethanol as a reactant and SO$_2^2$-ZrO$_2$ as a catalyst at the reaction temperature of 55-77 °C. Mahfud et al. (2007) treated the bio-oil with a higher boiling point alcohol of n-butanol in the presence of a solid acid catalyst of Nafion SAC13 at 50-80 °C under reduced pressure of less than 10 kPa. The results indicated that the upgraded oil properties were improved, particularly the heating value and viscosity but the acidity was still close to that of the raw bio-oil. In studying the effect of catalyst type, Zhang et al. (2006) used solid acid catalyst 40SiO$_2$/TiO$_2$-SO$_4^2$- and solid base catalyst 30K$_2$CO$_3$/Al$_2$O$_3$-NaOH to compare their effectiveness. It was found that acidity of the bio-oil was lowered by the use of both catalysts but the solid acid catalyst was capable of converting volatile and nonvolatile organic acids into more esters. However, the strong acidification of solid acid catalyst tended to intensify the acidity of bio-oil.

Rice (Oryza sativa L.) is a primary source of food for billions of people and it covers 1% of the earth's surface. Globally, approximately 600 million tons of rice is produced each year. For every 1000 kg of paddy milled, about 220 kg (22%) of husk is produced. Rice husk (RH) is therefore an agricultural residue abundantly available in rice producing countries. Much of the husk produced from the processing of rice is either burnt or dumped as waste. RH is composed of 20% ash, 38% cellulose, 22% lignin, 18% pentose and 2% other organic components. Silica can be pyrolyzed at elevated temperature to form rice husk ash (RHA). RHA as biomass has promising role with high silica content (87–99%) and available abundantly, being a low cost waste source as amorphous silica precursors. Each tons of rice produces 200 kg of rice husk, and with the complete combustion will be generated 40 kg of RHA. Recently, about 146 million tons of RHA was produced annually worldwide and efforts are being made to overcome this environmental issue by utilization this material as catalyst support. In this research, the upgrading bio-oil from pyrolysis of biomass on rice husk ash as catalysts was studied.

2. Experimental

2.1. Materials

Rice husk ash (RHA) was collected from rice mills in Bantul Province, D.I. Yogyakarta, Indonesia. Methanol (analytical grade, Merck) was used for esterification reaction. Sulfuric acid p.a. (98 wt.%) was supplied from Merck.

2.2. Catalyst Preparation

RHA was ground to powder (particle size ≤ 0.28 nm) and sieved with a 200 mesh sieve. Then, 10 g of powdered ash was washed with 60 mL of 0.1 mol L$^{-1}$HCl for 1 h, and neutralized with deionized water. The washing step is to remove the trace of minerals/metal (Al, Ca, K, Mg, Mn and Na) contained in RHA and organic compounds. Finally, the clean ash was dried in an oven at 105 °C for 2 h. The sulfonation of RHA was performed using the following procedure. RHA (5.0 grams) and a concentrated H$_2$SO$_4$ (98%) solution (100 mL) were placed into a 100 mL Teflon-tube autoclave. In this procedure, 5 grams of the RHA was immersed in 100 ml concentrated H$_2$SO$_4$ (98%) at 423 K for 12 hours. The product was then washed with hot distilled water until no sulphate ions were detected in the wash water and then dried.
2.3. Catalyst Characterization

The crystalline phase of the catalyst sample was confirmed using a powder X-ray diffractometer coupled with Cu Kα radiation. The surface areas (based on the BET equation), pore volumes and average pore diameter for the RHA and RHA catalyst were measured by N₂ adsorption–desorption isotherm apparatus. A FTIR spectrophotometer was used to characterize the chemical structure of alkali metal silicate at 400-4000 cm⁻¹ range. The acid density of the catalysts was estimated by a titration analysis.

2.4. Esterification Reaction

Bio-oil required for this research was produced from rice husk ash with a size of 1-3 mm and moisture content of 8-10% on dry-weight basis. Bio-oil was produced by the fast pyrolysis process performed at a temperature of 450 °C with nitrogen carrier gas. The batch esterification was performed at a laboratory scale. A hot plate with a magnetic stirrer was used for heating the mixture in a three-neck 250 mL round bottom-flask fitted with a water-cooled reflux condenser. The round bottom-flask was held in a water bath to maintain the temperature. The esterification was performed by addition of 20 wt.% of methanol in the presence of RHA catalyst (4 wt.% of raw bio-oil) at a temperature of 60°C for 90 min. As a control raw bio-oil was also esterified without application of pretreatment by following the same esterification procedure as described above. In each experiment, once the reaction was complete, the liquid products were cooled to room temperature. The mixture was collected in centrifuge test tubes and which were centrifuged to separate the resulting aqueous and organic phases; the time for centrifuging to separation ranged from 2 to 4 h. Both phases were separated and weighed for mass balance computation. The composition of raw bio-oil and upgraded bio-oil was determined using the GC-MS (Gas Chromatography Mass Spectroscopy) instrument. The acid values were analyzed by titration procedure for the evaluation of free residual acidity. The physical properties of bio-oil such as density, kinematic viscosity, pH, and water content were characterized by commonly standard methods. Meanwhile, higher heating values (HHVs) were determined by bomb calorimeter.

3. Results and Discussion

3.1. Textural characterization

The catalyst characteristics, including the BET surface area, the average pore size, and the total pore volume of the RHA and RHA catalyst are presented in Table 1. The RHA had low surface areas. The acid treatment by sulfonation improved the surface area characteristics by opening the pores of the material. The acid treatment of the partially carbonized material improved the surface area from 1.510 to 3.140 m²/g. Meanwhile, the average pore size diameter decrease from 139.767 to 66.3547 nm. The larger pore size diameter would make the reactant molecules easily to access to the internal catalyst. The total acid density of the carbon solid acid catalyst was measured using a back titration method. The SO₃H density of the catalyst was significantly increasing after sulfonation. The catalyst exhibits high catalytic acid density.

| Materials                  | RHA   | RHA/catalyst |
|----------------------------|-------|--------------|
| BET specific surface area  | 1.510 | 3.140        |
| Total pore volume (cm³/g)  | 0.1055| 0.1042       |
| Average pore diameter (nm) | 139.767| 66.3547    |
| Acid density (mmol/g)      | 0.05  | 2.24         |

The presence of amorphous silica in RHA and RHA catalyst were confirmed from the X-ray diffraction patterns shown in Figure 1. The RHA spectrum showed silica in the form of cristobalite (SiO₂ polymorph formed during RHA combustion process) and tridymite as the major crystalline phase. The SiO₂ (quartz) peaks could be observed for RHA catalysts.
In this study we have applied esterification to upgrade bio-oil from pyrolysis of biomass. Figure 2 compares acid values of raw bio-oil and the upgraded bio-oil. Figure 1 indicates that after pretreatment of raw bio-oil with esterification reaction the acid values decreased from 89.54 mg KOH/g to 56.82 mg KOH/g. The low acid values of the upgraded bio-oil indicated the conversion of carbonyl compounds (mainly aldehydes and ketones) and alcohols to carboxylic acids.

Table 2 shows a comparison of physical and chemical properties of raw bio-oil and upgraded bio-oil after esterification reaction. As shown in Table 1, after pretreatment the acid value of upgraded bio-oil decrease to 89.54 mg KOH/g from 56.82 mg KOH/g the value of raw bio-oil. The decreasing of acid value indicates the oxidation of aldehydes/ketones and alcohols to acids. The viscosity decreased from 12.0 to 9.2 cSt, water content decrease from 31.4 to 4.7%. The HHV of the oxidized product increased from 16.0 to 27.2 MJ/kg. Density decreased from 1.2 to 0.95 g/ml and pH was reduced to 2.3 from 4.1. Oxygen content increased somewhat from 53.9 to 55.3 wt.%. This oxygen content was resulted from both increased acid and water content.
Table 2. Comparison of physical and chemical properties of raw bio-oil and upgraded bio-oil

| Properties                              | Raw bio-oil | Upgraded bio-oil |
|-----------------------------------------|-------------|------------------|
| HHV (MJ/Kg)                             | 16          | 27.2             |
| Acid Value (mg KOH/g)                   | 89.54       | 56.82            |
| Water content (%)                       | 31.4        | 4.7              |
| Density (g/ml)                          | 1.24        | 0.95             |
| Kinematic viscosity, 40 °C (cSt)       | 12          | 9.2              |
| pH                                      | 2.3         | 4.4              |
| Elemental analysis (%)                  |             |                  |
| C                                       | 39.1        | 64.7             |
| H                                       | 7.7         | 9.8              |
| N                                       | 0.3         | 0.4              |
| O                                       | 52.8        | 25.1             |

Carbon content of upgraded bio-oil nearly doubled from 39.1 to 64.7 that of raw bio-oil. Hydrogen content was higher for upgraded bio-oil at 9.8% compared to the 7.7% of raw bio-oil. Nitrogen increased from 0.3% for raw bio-oil to 0.4% for upgraded bio-oil. Upgraded bio-oil oxygen content was reduced by the esterification of raw bio-oil with a decrease from 52.8 to 25.1%. Therefore, the esterification of raw bio-oil to produce upgraded bio-oil substantially increased the quality of its most important characteristics (HHV, acid value, water, hydrogen and oxygen content, and pH value); density and viscosity remain essentially the same. The only negative change was the small increase in nitrogen content.

Figure 3 compares the FTIR spectra of raw bio-oil and upgraded bio-oil. Characteristic vibrational modes are observed at 1650-1710 cm\(^{-1}\) (C=O stretching) and 3600-3000 cm\(^{-1}\) (-OH stretching). It was observed that C=O stretching was decreased and OH stretching was intensified, indicating that carbonyl compounds (mainly aldehydes and ketones) were converted to carboxylic acids. The bands at
1100-1300 cm⁻¹ was corresponding to C-O stretching. An adsorption peak at 1710 cm⁻¹ which attributed to C=O stretching. The band around 2850-2980 cm⁻¹ is due to aliphatic CH stretching. The bands at 3600-3000 cm⁻¹ can be assigned to the stretching vibration of OH stretching. From Figure 3, it was evident that after esterification reaction C=O stretching peak was decreased and OH stretching was intensified. The decreasing of C=O stretching peak and increasing of OH stretching indicate increase in carboxylic acids after esterification reaction. Furthermore, on esterification the intensity of CH stretching band dramatically increased and OH absorption band is significantly decreased due to conversion of carboxylic acids to esters and decrease in water content. As shown in Figure 2, it is clear that the decreasing of OH stretching peak of upgraded bio-oil is significantly higher than raw bio-oil; which implies that conversion of acids to esters and separation of water after esterification of upgraded bio-oil was improved compare to the esterification of raw bio-oil.

Table 3. Raw bio-oil and upgraded bio-oil chemical composition analysis by GC-MS with area percentages.

| Compound name | Area (%) | Compound name | Area (%) |
|---------------|----------|---------------|----------|
| Ethanone, 1-(4-hydroxy-3-methoxyphenol) | 19.55 | 1-Butanol | 34.12 |
| Phenol, 2-methoxy-4-methyl- | 10.81 | Acetic acid, butyl ester | 8.99 |
| Acetic acid | 5.1 | Propanoic acid, butyl ester | 3.04 |
| Phenol, 2-methoxy- | 4.15 | Butanoic acid, octyl ester | 2.69 |
| 2-Propanone, 1-hydroxy | 3.63 | Phenol, 4-methyl | 2.59 |
| Phenol, 2-methoxy-3-(2-propenyl)- | 3.28 | Cyclopentanone, 2-methyl | 2.51 |
| Phenol, 2-methoxy-4-propyl- | 3.16 | Phenol, 5-methoxy-2,3-dimethyl | 2.06 |
| Phenol, 4-ethyl-2-methoxy- | 2.61 | Benzaldehyde, 3,4-dihydroxy | 1.99 |
| 3,4-Anhydro-d-galactosan | 2.1 | Hexanoic acid, butyl ester | 1.96 |
| Benzenecetic acid, alpha-hydroxy- | 1.96 | Pentanoic acid, butyl ester | 1.82 |
| Furfural | 1.94 | 3-Undecene, 6-methyl- | 1.47 |
| Acetic acid, fluoro-ethyl ester | 1.93 | Oxalic acid, isobutylnonyl ester | 1.36 |
| Hexanoic acid, 1-methylhexyl ester | 1.85 | Cyclohexanone, 2-butyl | 1.08 |
| 2-Cyclopenten-1-one, 2-hydroxy-3-methyl | 1.84 | Ethanol, 2-(4-(1,1-dimethylpropyl)) | 1.07 |
| Acetic acid, 1-methylethyl ester | 1.82 | Phenol, 2-ethyl-6-methyl | 1.04 |
| 2-Furancarboxaldehyde, 5-methyl- | 1.78 | 3-Methyl cyclopentanone | 0.89 |
| Eugenol | 1.78 | 2-Heptanone | 0.88 |
| Phenol, 2-methoxy-4-(1-propenyl)- | 1.65 | Cyclohexanone, 3-dimethyl | 0.87 |
| Heptanoic acid | 1.42 | Cyclopropane, trimethyl methylene | 0.86 |
| 2-Cyclopenten-1-one, 2-hydroxy- | 1.42 | Cyclopentane, 1,2,3,3,5-pentamethyl | 0.86 |
| Vanillin | 1.39 | Phenol, 4-propyl | 0.84 |
| 1,2-Benzenediol, 4-methyl- | 1.31 | 4-(N-Dimethylamino)phenol, acetate | 0.83 |
| 4-Hydroxy-2-methylacetophenone | 1.27 | Cyclohexanone, 2,3-dimethyl | 0.83 |
| 3-Methoxy-4-methylaniline | 1.25 |
| Glutaraldehyde | 1.16 |
| Phenol, 2-methyl- | 1.14 |
Table 3 shows the chemical composition of raw bio-oil and upgraded bio-oil analyzed by GC-MS. Approximately 50 chemical compounds were identified by GC-MS in both samples. As shown in this section the major chemical compounds present in the upgraded bio-oil are esters, ethers, ketones, phenols and alcohols.

4. Conclusions
From the experiment results, it can be concluded that the densities of upgraded bio-oil were reduced from 1.24 to 0.95 and g cm$^{-3}$, and the higher heating value increased from 16.0 to 27.2 MJ/kg and the acidity of upgraded bio-oil was also alleviated from 2.3 to 4.4. The results of gas chromatography-mass spectrometry (GC–MS) and FT-IR analysis showed that the ester compounds in the upgraded bio-oil increased. It is possible to improve the properties of bio-oil by esterifying the raw bio-oil.

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References
[1] Bridgwater A V, Meier D, Radlein D 1999 Org. Geochem. 30(12) 1479–1493
[2] Fatimah I, Hidayat A, Setiawan K H 2010 Asian J. Chem. 22 (5) 3793
[3] Hidayat A, Rochmadi, Wijaya K, Nurdiawati A, Kurniawan W, Hinode H, Yoshikawa K and Budiman A 2015 Energy Procedia 75 969
[4] Hidayat A, Rochmadi, Wijaya K, Hinode H, Budiman A 2013 Asian J. Chem. 25 (3) 1569-1579
[5] Bridgwater A V, Peacocke G V C 2000 Sustainable Renewable Energy Rev 4 (1)1–73
[6] Qin T F 2006 Biomass Chemical Engineering 40(suppl) s78–s85
[7] Czernik S, Bridgwater A V 2004 Energy Fuels 18(2) 590–598
[8] Xu J M, Jiang J C, Lu Y J 2007 Modern Chemical Industry 27(7) 13–17
[9] Zhang Q, Chang J, Wang T J, Wu C Z, Xu Y, Zhu X F 2006 Journal of Fuel Chemistry and Technology 34(6) 680–683
[10] Branca C, Giudicianni P, Dibiasi C 2003 Ind. Eng. Chem. Res. 42(14) 3190–3202
[11] Mohan D, Pittman C U, Steele P H 2006 Energ. Fuels 20(3) 848–889
[12] Oasmaa A, Kuoppal A, Solantausta Y 2003 Energ.Fuels 17 (2) 433–443
[13] Doshi V A, Vuthaluru H B and Bastow T 2005 Fuel Process. Technol. 86(8) 885
[14] Junming X, Jianchun J, Yunjuan S, Yanju L 2008 Biomass Bioenerg. 32(11) 1056
[15] Mahfud F H, Melian-Cabrera I, Manurung R, Heeres H J 2007 Process Saf. Environ. Prot. 85(B5) 466
[16] ZhangQ., ChangJ, Wang Tand XuY(2006)Energ. Fuels20(6)2717.