Catalytic Upgrading of Bio-oil Produced from Pyrolysis of Rice Husk

Asriadi Sakka* and Kunio Yoshikawa

Department of Transdisciplinary Science and Engineering, Suzukakedai Campus, Tokyo Institute of Technology, Kanagawa prefecture 226-8503, Japan

* corresponding author: asdyasriadi@gmail.com

Abstract. Rice husk is one of the most widely available agriculture residues. It was a promising eco-friendly alternative source of renewable energy in the context of current energy scenarios. Fast pyrolysis technologies can transform rice husk into bio-oil considering its physical and chemical properties. Catalytic pyrolysis experiments have been carried out on Japanese rice husk to obtain bio-oil using a fixed-bed pyrolysis reactor with the use of the catalyst and comparison was done to analyze the changes in the bio-oil properties and yield. The fast pyrolysis of rice husk has been performed in the temperature range of 400-600 °C using the experimental pyrolysis reactor. The objective of this research is to explore the possibility to upgrade bio-oil produced from rice husk. The catalytic cracking is the most promising bio-oil upgrading processes, and it can remove oxygenated compounds from bio-oil via H₂O, CO and CO₂. The result showed that by using two heating units, even without catalyst, the upgrading was achieved well. In this research, two heating units were employed so that the raw bio-oil will separate in the first heating unit and the cracking in the second heating unit. The raw rice husk bio-oil produced and the upgraded bio-oil were characterized by measuring their element content, water content and the chemical composition of its organic fraction. The catalysts used were HZSM-5 zeolite and other non-commercial catalyst like rice husk ash which were appropriately effective in the bio-oil crack upgrading to reduce cost.

1. Introduction
Biomass energy is one of the most widely explored research fields in energy and environmental science. The bio-oil can be produced from renewable biomass feedstock such as wood, grass, rice husk and any agricultural waste. Rice husk is a by product from rice mills and it is considered as main food in many countries like China, Japan, Indonesia, Pakistan, Bangladesh, Malaysia etc. because of food habit of the population and weather condition. Along with the rice production, a large amount of rice husks are produced into untreated waste or burned waste that generate air pollution. One of the ways to convert the solid rice husk such as fast pyrolysis oil produced.

The fast pyrolysis of rice husk is a thermochemical process in which rice husk is heated in the temperature range of 400 – 600 °C in absence of air decomposing the rice husk into three products; bio-char, bio-oil and pyrolysis gas. Generally, the raw bio-oil has to be upgraded because of its high viscosity. There various bio-oil upgrading processes, but catalytic cracking method shows better potential. Thermal instability and corrosiveness present many obstacles to the substitution of fossil derived fuels by bio-oils. So, an upgrading process by reducing the oxygen content is required before
its application [3]. The catalytic cracking method is mainly in the medium temperature and the atmospheric pressure by adding catalysts for bio-oil upgrade. The macromolecules contained in the bio-oil crack into small molecules, the oxygen element is removed in the form of CO$_2$, CO and H$_2$O. However, CO$_2$ is a more ideal form of deoxydation, because it removes more oxygen than CO and easier to separate from the liquid than H$_2$O.

The catalyst used were HZSM-5 zeolite and rice husk ash (RHA). The HZSM-5 zeolite is commonly used in bio-oil upgrading by the cracking and the new one of non-commercial catalyst like RHA which were appropriately effective in the bio-oil crack upgrading to reduce cost. The result showed that by using two heating units, even without catalyst that the upgrading was achieved well. The cataclytic cracking promoted the deoxygenation rate and further improved the quality of the upgraded oil compared with non-catalytic cracking case. The biggest problem of the catalytic cracking process is in the activation of the catalyst caused by coking problems. The catalyst deactivation occurred from the inside to outside. In order to maintain the activity of the catalyst, Guo et al. [4] used tetralin as a solvent that tetralin is produced by the catalytic hydrogenation of naphthalene, mixed with bio-oil at a ratio 1 : 1 to lower the viscosity of the bio-oil and improve the stability and maintain the life of the catalyst. It is reported that the inactivation can be avoided with this additive. However, in this research, no additive was used for the purpose to realize the cracking with the lowest cost. The fixed bed cracking is chosen in this experiment for its simple equipment requirements.

The goal of this study was to obtain the quality of bio-oil after upgraded better than raw rice husk bio-oil produced. The effects of HZSM-5 zeolite catalyst and RHA catalyst on products yields and quality were examined to verify its acticity and selectivity not only to obtain the quality but also to reduce the cost.

2. Material and Methods

2.1. Feedstock preparation and characterizations
Raw rice husk was collected from Japanese local paddy mill that shows in figure 1. Before being used, rice husk sample was first screened to remove coarse contaminants, and then dried. Rice husks are processed into heavy liquid bio-oil through fast pyrolysis reactor. The rice husk bio-oil produced was upgraded using catalytic cracking method. The elemental analysis and properties of the raw rice husk are listed in Table 1.

![Figure 1. Rice husk as raw feedstock.](image-url)
Table 1. The elemental analysis and properties of the raw rice husk.

| Ultimate Analysis    | (wt.%) |
|----------------------|--------|
| Carbon               | 39.78  |
| Hydrogen             | 5.69   |
| Nitrogen             | 0.71   |
| Sulphur              | 0.1    |
| Oxygen               | 53.72  |

| Proximate Analysis   | (wt.%) |
|----------------------|--------|
| Moisture             | 14.45  |
| Volatiles            | 65.76  |
| Ash                  | 13.27  |
| Fixed Carbon         | 15.52  |

| Heating Values       | (MJ/kg) |
|----------------------|---------|
| HHV                  | 17.32   |
| LHV                  | 15.91   |

2.2. Catalysts preparation and characterizations

The HZSM-5 (SiO₂/Al₂O₃ molar ratio = 22.3) was purchased from Zeolite Company in Tokyo, Japan. The HZSM-5 catalysts were dried at 100 °C for 2 h and the mixture was calcined at 550 °C for 4 h under the air atmosphere.

Rice husk ash (RHA) was produced by raw rice husk. It was burnt using an electric furnace available at the Tokyo Institute of Technology, Japan. The incineration process of rice husk was performed in accordance with the process described by Zein et al. [5]. It is expected that more than 90% amorphous silica can be produced by this process. After proper the incineration, the produced RHA was received. Its properties of comparison between commercial catalyst and non-commercial catalyst are listed in table 2.

Table 2. Properties of the catalysts.

| Materials                  | RHA | HZSM-5 |
|----------------------------|-----|--------|
| SiO₂/Al₂O₃ (mol/mol)        | 87.91| 40     |
| Spesific surface area (m²/g)| 320.4| 330    |
| Pore size (nm)              | 11.2 | 5.8    |
| Average Particle size (µm)  | 7.59 | 10     |
| Acid Density (mmol/g)       | 2.21 | 1.3    |

2.3. Experimental design and procedure

The schematic diagram of the experimental set-up is shown in figure 2. The raw bio-oil was firstly introduced into the first heating unit and then introduced into the second heating unit with or without packing of the catalyst. As a carrier gas, N₂ gas was fed at the flow rate of 10mL/min from the top of the first heating unit for the continuous withdrawal of the products and the maintenance of the inert atmosphere during the cracking. The product flowing out from the bottom of the second heating unit was in gaseous form, and was condensed in a glass receiver submerged in an ice-water bath. Non-condensable gases were collected in a gas bag. A filter was placed between the ice-water bath receiver and the gas bag for recovering condensable vapor which might leak from the condenser.
The second heating unit was filled with 15 g catalyst (the catalytic cracking) while the first heating unit was filled with 30 g of the raw bio-oil. The first heating unit was heated to a specified temperature after the second heating unit was heated to 500 °C for 60 minutes.

The liquid products were collected and quantitatively measured in the pre-weighted glass receiver. The non-condensable gas products were collected and measured by the water displacement method. The amount of the solid residue left in the first heating unit was measured by weighing the first heating unit before and after the experiment. The solid products consisted of the coke left in the first heating unit and the coke on the catalyst weighed by the difference. The amount of condensable vapors recovered in the filter was also weighed by the difference and the weight was added to the liquid products yield.

The following characteristics were determined: the elemental analysis of C, H, O, the moisture content, the ash content, the density, the high heating value (HHV), the cetane index, the kinetic viscosity and the chemical composition. The ash content and the elemental analysis of C, H were determined by JM10 at 950 °C. The elemental analysis of O was determined by Vario micro cube at 1150 °C. The moisture content was measured using the Karl Fischer method in accordance with the standards JIS K 2275. HHV was determined in accordance with the standards JIS K 2279. The kinetic viscosity was measured by the ostwald viscometer at 40 °C. The cetane index was calculated in accordance with the standards JIS K 2280-5.

GC-MS is the technique used in the analyses of the product oil composition. A Rxi®-5Sil MS Column was used in the GC and helium was selected as the carrier gas. The oven heating profile was set at an increase of 5 °C /min from 30 to 280 °C.

3. Results and discussion

3.1. Bio-oil production from rice husk

Bio-oil production from rice husk is a dark brown, it is flowing liquid with a distinctive smell that a heavy crude oil pyrolysis has produced. Bio-oil is a complex mixture, which consists of several hundreds of organic compounds, mainly including alcohols, acids, aldehydes, esters, ketones, phenols as well as lignin-derived oligomers [6] that can be upgraded the quality as well as depend on each properties of bio-oil production from biomass.

Table 3 shows the comparison of selected properties between rice husk bio-oil produced and bio-oil upgraded using two different catalysts. The properties of the rice husk bio-oil produced that have the water content of bio-oil derived from pyrolysis of rice husk is 27.14 wt.%, the oxygen contents in bio-oil derived from pyrolysis of rice husk is 54.23 wt.% and the acid value is 87.56 mg KOH/g. So, a conclusion can be drawn that the rice husk bio-oils have much high properties before upgrading.
Bio-oil upgraded with RHA catalyst and HZSM-5 catalyst that a significant decrease, the values of water content are 19.6 wt.% and 15.4 wt.%, the oxygen contents are 42.2 wt.% and 37.23 wt.%, and the acid values are 67.4 wt.% and 54.8 wt.%, respectively. In the other elemental analysis has been increased about the elemental analysis value especially in carbon and HHV. The carbon content of RH bio-oil produced was 38.76 wt.% and increased to 45.61 wt.% and 65.10 wt.%, the HHV content are 16 wt.% and increased to 26.5 wt.% and 29.77 wt.% with bio-oil upgraded using RHA catalyst and HZSM-5 catalyst respectively. Even as hydrogen levels are increased but the hydrogen was not totally changed.

Table 3. Comparison of selected properties of the rice husk bio-oil produced and bio-oil upgraded

| Ultimate analysis (wt.%) | RH bio-oil produced | Bio-oil upgraded (RHA catalyst) | Bio-oil upgraded (HZSM-5 catalyst) |
|-------------------------|---------------------|---------------------------------|-----------------------------------|
| C                       | 38.76               | 45.61                           | 65.10                             |
| H                       | 7.31                | 7.51                            | 7.58                              |
| N                       | 0.17                | 0.12                            | 0.11                              |
| S                       | 0.0                 | 0.0                             | 0.0                               |
| O                       | 54.23               | 42.2                            | 37.23                             |

Elemental analysis

| HHV (MJ/Kg)   | 16          | 26.5                    | 29.77                    |
|---------------|-------------|-------------------------|--------------------------|
| Acid Value (mg KOH/g) | 87.56      | 67.4                    | 54.8                     |
| Water content (wt.%) | 27.14      | 19.6                    | 15.4                     |
| Density (g/ml) | 1.27        | 1.29                    | 1.32                     |
| Kinematic viscosity (m²/s@45°C) | 12 | 4.87               | 4.35                     |
| pH            | 2.4         | 2.3                     | 2.1                      |
| Ash           | -           | -                       | -                        |

3.2. Cracking Upgrading of Bio-oil

Figure 3 shows the comparison of bio-oil upgraded using HZSM-5 and RHA catalyst. These are the different colour between bio-oil produced by RHA catalyst in the left vial and bio-oil produced by HZSM-5 catalyst in the right vial.

![Figure 3. Bio-oil upgraded using RHA dan HZSM-5 catalyst.](image)

The experiments were repeated two times with changing the catalyst in the second heating unit and replacing the residue in the first unit with new bio-oil. Figure 4 and figure 5 shows the GCMS analysis results that a few different of two analyses although the graphs seems mostly similar because it comes from the same feedstock but different catalysts.
Figures 4 and 5 shows the analysis results of two runs at 260 °C. It was clear that the first peak happened after 10 min because at that time is starting time in MS methods which referred to small molecule, the target product. The comparison of analysis between bio-oil using RHA catalyst and HZSM-5 catalyst seems different about the number of peaks and end running time. End running time of analysis using HZSM-5 is increased especially in 90 min to 99 min.

Though hundreds of organics were detected, if picking out the highest 20 peaks in Figure 4, and the highest 29 peaks in Figure 5. The area of these peaks have the similarity more than 90 %. In order to see the change clearly, the main components of the liquid product especially in both of cracking at the temperature 260 °C, the organics are listed in table 4 and 5.

Table 4. Main components of the liquid product in the first cracking run at 260 °C.

| Peak | Ret. Time | Area % | Name                                   |
|------|-----------|--------|----------------------------------------|
| 1    | 8.313     | 0.43   | 3-Penten-2-one                         |
| 2    | 11.195    | 1.14   | Cyclohexanone                           |
| 3    | 15.235    | 3.76   | Benzene                                |
| 4    | 21.048    | 3.55   | 2-Propanone, 1-hydroxy-                |
| 5    | 25.759    | 3.44   | 2-Cyclopenten-1-one                    |
| 6    | 26.993    | 1.17   | 2-Cyclopenten-1-one, 2-methyl-         |
The main components could be divided into 4 classes. The first one is oxygen-containing small molecules with the retention time from 7 to 10 min, the main components of which are kinds of butanenitrile, furan and imidazole. The second class is cyclopentanone with the retention time of 10 to 28 min. The third class with the retention time from 28 to 75 min are phenols. The fourth one was the materials whose retention time were later than 75 min, mainly containing fatty acid macromolecular structural substances. The area proportions of these four classes are listed in Table 6.
Table 6. Component classification of the bio-oil

|                  | Small molecule | Cyclopentanone | Phenols  | Macromolecule |
|------------------|----------------|----------------|----------|---------------|
| Retention time (min) | < 10          | 10 ~ 28        | 28 ~ 75  | > 75          |
| Area (%)         | 5.20%         | 11.70%         | 69.35%   | 13.75%        |

Bio-oil has high acidity and high content of organic acids, of which acetic acid content should be detected in the product, but actually not. The deoxygenation pathway of acid is the decarboxylation and the dehydration. It can be presumed that acetic acid firstly removes H₂O and CO₂ to generate acetone, then the acetone is decarboxylated to ethylene, and then aromatization of ethylene resulted in aromatic compounds. In addition, according to the carbenium reaction mechanism, the HZSM-5 catalyst provides proton conjugation with oxygen in the acetic acid to form alkenes and carbocations and removed H₂O.

4. Conclusion
The bio-oil can be upgraded in a process with two heating unit with the zeolite catalyst. The main reaction of the cracking is the deoxygenation of phenols. The zeolite catalyst contributes to promote the deoxygenation rate. However, utilization of zeolite catalyst results in a decrease of the liquid product yield. As a liquid fuel, the properties of the catalytic cracked oil using HZSM-5 catalyst better than RHA catalyst. The hundreds of components in the raw bio-oil can be divided into 4 classes: small molecules, cyclopentanone, phenols and macromolecules. Small molecules are not the main cause of the catalyst deactivation. Phenols slightly deactivate the catalyst. The contact of macromolecules with zeolite is a big problem causing the deactivation. A lower separation temperature in the first heating unit helps to alleviate the inactivation reaction.

Acknowledgements
Author would like to thank for Yoshikawa Laboratory, Tokyo Institute of Technology who support anything of this research and The Indonesia Endowment Fund for Education (LPDP), Ministry of Finance of Republic Indonesia who support my scholarship

References
[1] Shouyun C, Lin W, Xianhui Z, Yinbin H, Douglas R, Changling Q, John K and Yong Y 2015 AIMS Energy 2 pp 227-240
[2] Jamil M, Khan M, Karim M, Kaish A and Zain M 2016 Construction and Building Materials 128 pp 185-198
[3] Zhang Q, Chang J, Wang T and Xu Y 2007 Energy Conversion and Management 48 pp 87-92
[4] Guo X, Zheng Y, Zhang B and Chen J 2009 Biomass and Bioenergy 33 pp 1469-1473
[5] Zain M, Islam M, Mahmud F and Jamil M 2011 Construction and Building Materials 25 pp 798 – 805
[6] Shuangning X and Abolghasem S 2012 Renewable and Sustainable Energy Reviews 16 pp 4406 – 4414