Kinetic studies and performance analysis of Indonesian rice husk pyrolysis

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Abstract. Rice husk is abundantly available biomass in Indonesia and it can be a potential source of high-value energy source. In the present work, pyrolysis of rice husk was subjected to various temperature and used as a method to produce bio-oil. The decomposition profile of rice was examined at different heating rates (10, 20, 30, and 40°C/min) using a thermogravimetric analysis (TGA) method. The pyrolysis kinetics were evaluated using three different kinetic models: Kissinger-Akahira-Sunose (KAS), Ozawa-Flynn-Wall (OFW), and Coats-Redfern (CR). The activation energy for KAS, OFW, and CR was centered at 251.62 kJ/mol, 253.32 kJ/mol, and 33.92 kJ/mol, respectively. Varying activation energy with conversion was observed, which reveals that the pyrolysis of rice husk processes through complex reaction. The production of bio-oil from rice husk using pyrolysis method was studied at different temperature conditions (300, 400, 500, 600°C). Results showed that bio-oil and gas products increase at higher temperature. The highest yield of bio-oil was produced at 600°C with 46.3 grams (37 wt%). The specific test showed that the density, viscosity, and acid value of bio-oil decreased at higher temperatures indicating that different pyrolysis conditions might lead to the different bio-oil quality.

1. Introduction
Petroleum-based products such as fuel and chemicals are slackening in energy supplied. Hence, alternative energy such as biomass is not only directed to alternative fuel sources but also more benignant fuels for industrial sectors. Biomass such as rice husk, corn cobs, and cotton stalks are potential for energy sources. Indonesia as an agricultural country has expanded rice production by around 59.2 million tonnes in 2018 [1]. Technologies for biomass utilization are not well-established in Indonesia. Rice husk yield was attained in 20% of rice production [2]. Recently, rice husk utilization is disposed of as agricultural waste, however, rice husk has the potential for producing electricity and can be used in the cement industry. Biomass waste such as rice husk could be converted into high-value energy since it has low nitrogen and sulfur content. Rice husk contains 34.4% cellulose that favorable for liquid fuel production [3].
Biomass can be converted to liquid, gases, or solid fuel products through various methods, which are combustion, gasification, and pyrolysis. Pyrolysis is a thermal degradation process that takes place in an inert atmosphere with the absence of oxygen. The range temperature of pyrolysis is 200-800°C. Large biopolymers (20,000-400,000 a.m.u) break into smaller molecules (less than 200 a.m.u) in pyrolysis process [4]. Biomass was used as feed in pyrolysis process to produce decomposed products including solid char, gas, and bio-oil or a liquid, with low viscosity that contains complex mixture such as aldehydes, ketones, and carboxylic acids. Pyrolysis also can produce advanced materials such as carbon materials including carbon nanotubes and graphene-like materials [5].

Kinetic studies of pyrolysis may help better understanding and planning of industrial process since kinetic modelling of chemical and physical can be beneficial for process design and optimization. Non-isothermal thermogravimetric analysis (TGA) is verified as a method for the understanding of kinetic pyrolysis. Saddawi et al. reported that TGA methods have been used in a wide temperature range and followed with various model fitting kinetics such as iso-conversional methods [6,7]. Iso-conversional methods can provide the estimation of the kinetic parameters with rather accurate results compared to the other methods since it is considered using a single-step process, with the presumption that activation energy as a function of the heating rate and temperature determined as the total reaction [8]. The activation energy, as kinetic parameters did not change during the conversion range in iso-conversional methods.

This work was designed to determine the rice husk pyrolysis kinetic parameters. The rice husk pyrolysis kinetics study is figured out in thermogravimetric analysis which is conducted with TGA-DSC 600, while main pyrolysis experiment as well as for pyrolysis product examination are held using a fixed bed reactor.

2. Methods

2.1. Materials and characterization
The rice husk was provided by the local rice milling industry in West Java, Indonesia. It was first dried at 105°C for 24 h. After grinding, the rice husk was sieved to obtain a uniform size particle, 10 mesh by cutting mill. The sample was characterized using elemental analysis, which was performed using NC Technology Organic Elemental Analyzer ECS8020. The moisture content was estimated gravimetrically before and after drying. Ultimate analysis dry ash free basis of rice husk is presented in Table 1.

| Element | Mass Composition (%) |
|---------|----------------------|
| C       | 32.29                |
| H       | 4.31                 |
| O       | 43.08                |
| N       | 0.28                 |

2.2. Thermogravimetric analysis
The instrument involved in thermogravimetric analysis (TGA) of rice husk was TGA-DSC 600. The TGA process was referred to ASTM-E43 operational standard. About 12-14 mg of rice husk sample was heated from room temperature to 600°C using various heating rate conditions (10, 20, 30, 40, and 50°C min⁻¹) with an inert atmosphere of N₂, as a purge gas, was injected into the system with a flowrate of 100 mL/min.

2.3. Pyrolysis process
The pyrolysis observed in this work was slow pyrolysis and was assisted with fixed bed reactor. Pyrolysis was held with 125 g of rice husk under various temperatures 300, 400, 500, and 600°C. The reactor temperature was held isothermally for 50 minutes when reached the end of pyrolysis temperature. The produced char and bio-oil was collected in the flask.
Physicochemical analysis for bio-oil encompassed density and viscosity were identified. Density measurement was performed with pycnometer. Bio-oil viscosity was explored through Ostwald Viscometer. The bio-oil functional group was then identified using Thermo-scientific Fourier Transform Infrared Spectroscopy.

Bio-oil acid value was identified under titrimetric analysis. It was solubilized in ethanol and then was dripped with phenolphthalein (PP) indicator. This solution was titrated with 0.1 mol/L potassium hydroxide (KOH). The indicator color change was carefully monitored and KOH amount for the indicator color change was recorded.

### 2.4. Pyrolysis kinetic parameters determination

Three different kinetic models were occupied in the present study, namely Kissinger-Akahira-Sunose (KAS), Ozawa-Flynn-Wall (OFW), and Coats-Redfern (CR) method [9]. KAS equation follows differential form as served below:

\[
\ln \left( \frac{\beta}{T^2} \right) = -\frac{E_a}{R} \left( \frac{1}{T} \right) - \ln \left[ \frac{A \cdot E_a}{R \cdot g(\alpha)} \right]
\]

where \( \beta \), Heating rate, °C/min; \( A \), Pre-exponential factor, s\(^{-1}\); \( E \), Activation energy, kJ/mol; \( R \), Gas constants, J/kg.K; \( \alpha \), Mass conversion; \( T \), Temperature, °C.

The linear plot of the curve \( \ln \left( \frac{\beta}{T^2} \right) \) versus the inverse temperature produces the activation energy value corresponding to each conversion step.

OFW method is another iso-conversional method which is also widely found in kinetic study. It is determined from global kinetic equation [8]. The formula for OFW method is based on the integral form of the kinetic curve from TG analysis and the correlation is based on Doyle’s approximation [10].

\[
\log \beta = \log \left( \frac{A \cdot E_a}{R \cdot g(\alpha)} \right) - 2.315 - 0.4567 \frac{E_a}{R} \left( \frac{1}{T} \right)
\]

where \( \beta \), Heating rate, °C/min; \( A \), Pre-exponential factor, s\(^{-1}\); \( E \), Activation energy, kJ/mol; \( R \), Gas constants, J/kg.K; \( \alpha \), Mass conversion; \( T \), Temperature, °C. The slope of the curve \( \log \beta \) vs \( \left( \frac{1}{T} \right) \) obtain the activation energy for the specified conversion.

Another method was developed by Coats-Redfern could predict the activation energy and pre-exponential factor from pyrolysis process [11]. This equation was given below:

\[
\ln \left[ \frac{g(\alpha)}{T^2} \right] = \ln \left[ \frac{AR}{\beta E} \left( 1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT}
\]

where \( \beta \), Heating rate, °C/min; \( A \), Pre-exponential factor, s\(^{-1}\); \( E \), Activation energy, kJ/mol; \( R \), Gas constants, J/kg.K; \( \alpha \), Mass conversion; \( T \), Temperature, °C; \( n \), the order reaction. The slope of the curve \( \left[ \frac{g(\alpha)}{T^2} \right] \) vs \( \left( \frac{1}{T} \right) \) to obtain the activation energy and pre-exponential factor.

### 3. Results and discussion

#### 3.1. Thermal decomposition characterization at different heating rate condition

Figure 1 shows the thermal decomposition curves of rice husk pyrolysis at various heating rate conditions (10, 20, 30, and 40°C). The thermal gravimetric curves of rice husk at different heating rates of pyrolysis have the same trend curves and typical appearance of lignocellulosic material decomposition. The peaks of biomass decomposition are detected in DTG curves. The biomass decomposition appeared below temperature 100°C or can clearly observe at first peak in Figure 1(b). It
indicated that water content starts to evaporate, followed by a large amount of weight loss in temperature range 200-450°C which can be seen at second or the highest peak in DTG curves. By comparing the DTG peaks at different heating rates, it can be observed that by increasing the heating rate, the DTG curve can be more cusptate and the fraction decomposed was higher.

Figure 1. Thermal gravimetric curves (a) and DTG curves (b) of rice husk pyrolysis at various heating rates.

According to TG-DTG curves, rice husk pyrolysis process is divided into several stages. Biomass was absorbing heat to decompose and break down the molecules. The first stage occurs before 100°C where the water content in biomass (about 4-7%) is evaporated. TG curves almost stagnant at second stage around 100-240°C when slow decomposing and polymerization to break down the larger molecules started. From temperature 240-450°C, large molecules of rice husk decomposed into small molecules which consist of gas and condensable volatile elements. The percent weight loss was about 50-65%. It is indicated that the main phase of the pyrolysis occurred. The last stage (char production) undergoes at temperature exceeding 450°C and is considered to be C-C and C-H bonds further cracking phase [12].

3.2. Kinetic parameters

Biomass pyrolysis follows a complicated process since biomass has various chemical compositions of components. In this study, the pyrolysis kinetic parameters were determined with three different kinetic methods, i.e. Kissinger-Akahira-Sunose (KAS) and Ozawa-Flynn-Wall (OFW) as iso-conversional methods [9] and Coats-Redfern (CR) model. KAS and OFW methods assume that the kinetics of the reactions does not depend on the heating rate and the reaction conversion of biomass into products as
one-step process. Iso-conversional method also has the advantages of avoiding a potential error in different assumptions of mechanism reaction function.

Figure 2(a) and (b) show the linear plot of the curve \( \ln \left( \frac{\beta}{T^2} \right) \) vs \( \frac{1}{T} \) and \( \log \beta \) vs \( \frac{1}{T} \) at different conversion to determine the kinetic parameters using KAS and OFW methods respectively. The calculated activation energies and correlation coefficient can be obtained through further calculation as listed in Table 2. Both methods have a high correlation coefficient. Each conversion for both methods has slightly different activation energies. The lowest values of activation energy for KAS and OFW about 211 kJ/mol and the highest value is 283.142 kJ/mol for KAS and 294.749 kJ/mol for OFW. It is evidenced that pyrolysis progresses through multi-step kinetics with various apparent activation energies [8,13].

**Figure 2.** Estimation of activation energy using (a) KAS method and (b) OFW method.

**Table 2.** Estimation of activation energies (\( E_a \)), Pre-exponential factor (\( A \)), and correlation coefficients for different conversion values using the KAS and OFW methods.
The CR plot is showed in Figure 3 and the results for activation energy and Arrhenius pre-exponential factor are summarized in Table 3 below. Coats-Redfern equation was simulated with mampel (first-order) reaction and geometrical contraction models at different heating rates.

![Figure 3. Estimation of activation energy using CR method.](image)

### Table 3. Estimation of activation energies (Ea), Pre-exponential factor (A), and correlation coefficients for different conversion values using CR method

| β   | Ea     | A       | Correlation coefficient |
|-----|--------|---------|------------------------|
| 10  | 34.298 | 11.30E+04 | 0.975                  |
| 20  | 32.711 | 13.99E+04 | 0.968                  |
| 30  | 31.928 | 16.48E+04 | 0.974                  |
| 40  | 31.329 | 18.19E+04 | 0.976                  |

3.3. Pyrolysis product
Figure 4 shows the liquid product or bio-oil increase at higher temperature, reaching 46.3 g (37\% wt) at 600°C. On the other hand, the solid product or charcoal has decreasing trend at higher temperature. The highest amount of charcoal obtained, 82.7 g (66\% wt), is subjected to a temperature of 300°C. The pyrolysis temperature condition will increase the breaking rate of volatile compounds in rice husk.

The pyrolysis process also produces gas products consist of H₂, CO, CO₂, CH₄, and a limited amount of hydrocarbon gas which cannot be condensed with a condenser and will exit into gas products [14]. Bio-oil obtained is the result of the condensation of gases formed during the pyrolysis process. According to Atadana et al, liquid product contains more complex compounds such as pyrone, catechol, syringol, guaiacol, water, vanillin, furan carboxaldehyde, isoeugenol, acetic acid, formic acid, and carboxylic acid [15].

From figure 5, bio-oil contain functional groups such as alcohol groups with O-H stretch vibration at wavenumber 3550-3200 cm⁻¹, C-H stretch vibrations at wavenumber 2990-2850 cm⁻¹ indicate the presence of alkane groups, C=O stretch vibrations at wavenumber 1715-1680 cm⁻¹ and 1700-1665 cm⁻¹ represent the aldehyde and ketone groups, then the vibration C=C stretch at wavenumber 1625-1440 cm⁻¹ and C-H bend at wavenumber 900-680 cm⁻¹ are attributed to the aromatic groups, C=C stretch vibration at wavenumber 1650-1600 cm⁻¹ is attributed to alkene groups, while C=O stretch vibrations at wavenumber 1320-1000 cm⁻¹ denote the presence of alcohol, carboxylic acids, esters, and ether. The solid product or charcoal is a component of the remaining biomass. The highest yield of char produces at low temperature or below 500°C.

Figure 6 shows the bio-oil characteristic analysis at different temperatures which includes density, viscosity, total acid number, and water content. The highest acid number at temperature 300°C with 78.4 mg KOH/g sample and the lowest acid number at temperature 600°C, with 58.24 mg KOH/g sample. Various research showed the same results that the acid number will decrease with the heating time and the reaction temperature, the lowest acid number indicates a reduction in the fatty acid content in bio-oil due to an increase in the temperature of the pyrolysis process [16,17].
Furthermore, density is a unit that represents the mass or weight of an object relative to the volume of the solution. Because it relates to the mass of an object, the main factor that affects or the weight of the molecules that make up the substance. The decreasing bio-oil density is found at higher temperature. Figure 6 shows the density of the bio-oil produced is closer to the density of water (1 g/mL) than to the density of biodiesel (0.867 g/mL) since the water content of bio-oil is above 90%-wt.
4. Conclusion
The present work revealed different approaches for kinetic study using iso-conversional methods including KAS and OFW model and CR method to estimate the kinetic parameters. The results of thermal decomposition of rice husk showed in the temperature range 100-650°C, followed by the stagnant curves that indicate no more decomposition process occurred above temperature 650°C for all different heating rate conditions. The bio-oil products from rice husk pyrolysis have potential as an alternative for fuel since it contains hydrocarbon functions with low sulphur content.

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