Rice Husk Fuel Pellet: Characterization on Physical and Thermogravimetric (TGA) Combustion Properties

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Abstract. Recently, the demand for biomass fuel pellet is increasing leading to the use of agricultural waste as the feedstock alternative to the wood pellet. In this study, the rice husk was developed into fuel pellet and characterized its physical and combustion properties. The pelleting used a flat-die roller type pelleting machine. The pre-treatments were reducing the size and mixing with a 4% gelatinized tapioca starch as the binder. The single pellet had an average diameter of 8 mm, length of 28.7 mm and weight of 1.8 g/pellet. The rice husk bulk density increased from 145 kg/m3 in raw form into 511 kg/m3 in pellet form. There were no significant different changes in pellet dimension after 14 days of pelleting. The combustion properties were analyzed using thermogravimetric analyses (TGA). The TGA analyses were conducted using oxygen at a flow rate of 50 ml/min; the heating rates were 10°/min, 20°/min and 30°/min heated up to 950°C. This study found that the ignition and the burnout temperatures were at about 276°C and 448°C, respectively. As to the non-woody characteristic of higher cellulose than woody biomass, the rice husk pellet had a higher conversion rate at lower temperatures than that of wood pellet.

1. Introduction
The use of agro-industrial waste as bioenergy resources may have some advantages both economic and environmental. As a waste, it is generally cheap and predictable based on the related production capacity of the plant. Environmentally, the re-use and re-cycle of the waste could significantly solve the problem of dumping or open burning. This type of organic waste may come from a wide range of agricultural processes, animal solid excretion and herbaceous plants. Straw, grasses, crop stubble and trash are typical non-woody biomass from agricultural field waste. On the other hand, rice husk, palm oil waste, cane bagasse and animal excreta is the non-woody biomass waste from agricultural processing plants. In Indonesia, rice husk is usually found in rice mills. Rice as a staple food has increased in production to fulfill the increased of consumption due to high population growth. The by-product of rice processing plants, in the form of rice husks and hulls, is also increased.

Some of the agro-industrial wastes particularly the non-woody type are not fully utilized yet as the biomass energy resource. The main problems are irregular size, low density, low calorific value and
high ash or tar contents. Rice husk contains approximately 40% cellulose, 30% lignin group, and 20% silica [1]. Rice husk, as highest cellulose can be categorized as non-woody and having low density, 83-125 kg/m³ [2]. In Indonesia, some of the rice husk, in a raw form, is recently utilized as fuel for drying grains or making bricks. Due to the low density, the transportation cost is relatively high; even the transportation cost is sometimes more expensive than the price of rice husk itself. Another technical problem related to the low density is unstable combustion causing the low combustion efficiency. An alternative to process the biomass fuel for having higher density is transforming it into briquette or pellets.

Biomass fuel pellet is a tradable commodity, popular in Europe, USA and East Asian countries. The production of wood pellet in the global market is increasing from 19 million tonnes in 2012 to 27 million tonnes in 2015 [3]. The main resource of fuel pellet at this moment is sawdust, however, some of the non-woody has become an alternative resource. The standard for non-woody pellets is stated in ISO 17225: 2014 part 6 [4]. At this time, the rice husk pellet has appeared in the markets. Indonesian Center for Agricultural Engineering Research and Development (ICAERD) studied the rice husk pellet production in 2018. This paper presents the process of production and investigation in the pellet’s physical properties and thermogravimetric (TGA) analyses in combustion.

2. Methods

2.1. Material and equipment
The rice husk pellets were produced from a line production of biomass pellet developed by ICAERD. The machinery consists of a disc mill for size reduction, mixer and a pellet mill (figure 1). The pellet mill is a rotating plate and static roller press type, a mill generally used for commercial pellet production.

![Figure 1. Rice husk pellet production](image)

The rice husk for pellet production was originating from rice mills nearby Desa Situgadung, Kabupaten Tangerang, Banten. The average density and moisture contents were 140 kg/m³ and 10% wb respectively. The pre-treatment in the production of pellets was size reduction and mixing with a binder of 4% blend of gelatinized tapioca. Water was also added during the process of pelleting. The moisture of feeding materials entering into the pellet mill was about 30%. The samples of rice husk pellets (Fig 2) were randomly taken from the production for physical and TGA Analyses.
2.2. Pellet dimension and relax density
Analysis of pellet dimensions was carried out by taking 50 pellet samples randomly. Each pellet is measured in length, diameter and weight, and bulk density. Considering it as a cylinder, a single pellet density can be calculated based on its own dimension. Measurement of pellet dimensions is done twice. First, one day after pellet production and second 14 days after storage, called relaxed density [5] Measurement of pellets after storage (14 days) was carried out to determine whether the changes in the relaxed density during the storage period after pellet production.

Statistical analysis using T-test paired was conducted to determine the significant change in relax density. Statistical analysis was performed with Microsoft Excel software.

2.3. Thermogravimetric analyses (TGA)
The thermogravimetric analyses were conducted in Pusat Laboratorium Terpadu, UIN Syarif Hidayatullah Jakarta. The thermo analyses were performed in TG Analyzer Q500 instrument. The samples were 30-50 mg per experiment. The oxygen at flow rate of 50 ml/min was used as the carrier gas. The samples were heated from the ambient temperature up to 950°C. The heating rates applied 10°C/min, 20°C/min and 30°C/min. The obtained results were in the form of the remaining masses or processed into the derivatives. To reduce the noise data, the moving average trend lines were used.

Ignition and burnout temperatures
Obtained from the TGA and DTG combustion curves, the ignition and the burnout temperatures for rice husk pellet can be defined. The ignition temperature is the minimum temperature at which fuel ignites spontaneously without any external source of ignition; while the burnout temperature indicates the maximum temperature of the fuel at which the sample is almost completely consumed during burning [6]. There are several methods of determining ignition and burnout temperatures of a fuel based on TGA and DTG curves. Those are intersection method, conversion method and deviation method. Further description of those methods has been reviewed by Lu and Chen [6]. In this study, the intersection method was applied.
Thermo-kinetic model analyses

The empirical kinetic behavior data of TGA is often presented as plot of the residual mass portion or mass conversion against a time or a temperature. The mass conversion, $\alpha$, at a time, $t$, or temperature, $T$, can be denoted as

$$\alpha = \frac{m_0 - m}{m_0 - m_e}$$

(1)

Where as $m_0$ is initial mass,

$m$ is the instantaneous mass

$m_e$ is the end mass

The data of function, $\alpha$, is then used to model the kinetic decomposition of that particular material. The kinetic rate of thermal decomposition can be expressed as a single step kinetic equation [7]:

$$\frac{d\alpha}{dt} = k(T) f(\alpha)$$

(2)

whereas $f(\alpha)$ is the conversion model of $\alpha$, the extent of conversion.

$k(T)$ is the reaction rate constant at temperature $T$.

This equation expresses the rate of mass conversion as a product of two function $f(\alpha)$ and $k(T)$ which depend on time and temperature. Those three variables are also known as the kinetic triplets. The reaction rate constant almost universally follows the Arrhenius equation [7]:

$$k(T) = A e^{-\frac{E}{RT}}$$

(3)

whereas $k$ is reaction rate constant $(s^{-1})$

$A$ is pre-exponential factor $(s^{-1})$

$E$ is activation of energy $(J.mol^{-1})$

$R$ is gas constant $(J.K^{-1} mol^{-1})$

$T$ is temperature $(K)$

In the empirical data analyses, the activation energy can be calculated from the temperature coefficient of the overall reaction rates, while the value of pre-exponential factor is a scaling factor of the overall reaction rates. The examination of experimental TGA analyses can be either from isothermal or non-isothermal condition. For both analyses, there exists two approaches to determine the model of reaction [7]. The first is by the forced fitting of the experimental data to the different reaction models and the second one is the free method. Free method approach utilizes data from the multiple constant heating rates figures.
or/and temperatures. Using the multiple data of TG/DTG curves, the kinetic triplets were approximated from the isothermal/iso-conversional condition. Models which follow this approach are: Flynn-Wall, Flynn-Wall-Ozawa (FWO), Kissinger, Kissinger-Akihara-Sunose (KAS) and Friedman methods [8].

In this study, the KAS model was adapted. This model takes an iso-conversion point of the DTG curves for calculation. In this study, the temperatures at α = 50% conversion were applied to the model. The reaction model is described as follow:

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

(4)

Whereas \( \beta \) constant heating rate
A is pre-exponential factor (s\(^{-1}\))
E is activation of energy (J.mol\(^{-1}\))
R is gas constant (J.K\(^{-1}\) mol\(^{-1}\))
T is temperature (K)
The \( \left( \frac{-E}{Rf(\alpha)} \right) \) value is the slope of \( \ln \left( \frac{\beta}{T^2} \right) \) to 1/T.

3. Results and Discussions

3.1. Rice husk pellet production

The process of producing rice husk pellets depends on various factors such as humidity, pressing equipment temperature, ambient temperature, type of biomass, particle size and material composition. The temperature increase inside the pressing chamber may be as a result of friction from the roller presses, rotating plate and the pressed material. The temperature on the pressing plate, in addition to roller pressure, is an important factor in getting good quality pellets. Low temperatures prevent the polymer softening process from the phase of glass transition into the phase plastic. On the other hand, high temperatures above 80°C would damage the polymer, so the material is too dry and even the plastic structure is not formed in the outside layer of the pellets. Rice husk itself contains a high amount of silica, about 12-18% [2]. The silica can also affect to high friction which could fasten the heating process in the pressing chamber. However, it could cause overheated, hence the pelleting was not successful. The water mists can be added to the chamber during the pressing for keeping the machine cool. Based on the experiences in this activity, the optimum temperature of the pressing chamber should be kept in the ranges of 60-80°C to form the good quality of rice husk pellets.

Table 1 presents the proximate and ultimate of the produced pellets. It can be seen that the water content of the pellet is approximately 7%, the volatile content is 68%, the ash content is 18%.

| Table 1. Proximate analyses of rice husk pellet |
|-----------------------------------------------|
| **Proximate** | %, as received |
| Moisture     | 7.42          |
| Volatiles    | 68.98         |
| Ash          | 18.07         |
| Fixed carbon | 12.95         |
| Heating value, HHV (MJ/kg)                     | 15.2          |

The proximate content of this rice husk pellet is similar to that of the rice husk in raw bulk form. It has been reported that, in bulk form, rice husk consists of 60–65% volatile matter, 10–15% fixed carbon, and 17–23% ash [2]. Thus it can be assumed that the addition of 4% tapioca adhesive might not significantly
change the proximate composition of the rice husk. The ash content of this husk pellet was still quite high, at 18%, similar to those in bulk form.

The problem of application biomass in raw form, particularly the low density type of biomass, was the high residual solid formation due to unstable combustion and low conversion efficiency. In contrast, the dense biomass in pellet form produced a less residual mass of combustion. The process of controlling the air to fuel ratio would be easier in a uniform size and feed rate of fuel; leading to higher combustion efficiency.

3.2. Rice husk pellets dimension

This process of pelleting could increase the rice husk density from 140 kg/m³ to 511 kg/m³ (table 2). The average dimension of the pellet after a day of production compared to that after 14 days of storage is presented as in table 2.

| Dimension of rice husk pellets | Initial | After 14 days storage |
|-------------------------------|---------|----------------------|
| Length, average               | 28.7 mm | 28.7 mm              |
| Diameter, average             | 8.1 mm  | 8.1 mm               |
| Weight, average               | 1.83 g/piece | 1.82 g/piece       |
| Density, average              |         |                      |
| Single pellet                 | 1.25 kg/m³ | 1.25 kg/m³         |
| Bulk                          | N/A     | 511 kg/m³            |

Relax density pellets are changes in single pellet density, calculated based on the average single pellet density at the start of production compared to after 14 days of storage [5]. If the change in pellet dimensions is significant, the pellet production process is technically unsuccessful. Table 2 shows a small change in weight after storage, however, the t-test paired data of pellet dimension before and after storage shows an insignificant change in dimension. It can be concluded that the form of pellet was not changed during storage.

ISO 17225-6 Graded non-woody pellet stated that the pellet dimension should be in the diameter between 6 to 25 mm, and the length is within 3.15-50 mm. The ash content should be not higher than 6% for A grade or not higher than 10% for B grade. The bulk density should also higher than 600 kg/m³. This rice husk pellet is farther than the grade both for ash content and bulk density. Moreover, high silica in the ash of rice husk would react to the iron material equipment forming iron-silicate. Then, this paper suggests reducing the ash as well as increase the bulk density of rice husk pellet by blending it with wood material in pellets. Blending should be done with the materials which can reduce the ash content as well as increase the pellet density. However, ISO 17225-6 is specific for fuel pellet standard applied for households and commercial uses, not for industrial use. The industry which applies less iron material equipment for its energy conversion may still utilize this pure rice husk pellet. The silica by-products would be then recycled to form other usable materials, such as the mix materials for making bricks, concrete, asphalt etc.

3.3. TGA analyses

In general, there are three phases in the thermal decomposition of biomass during combustion. The first is the release of water or drying stage. This occurs in the temperature up to 150°C. The second is the fastest release of the volatile content, namely oxidative pyrolysis, which can occur at a different temperature, specific for each material and its composition. Next stage is a slow volatile release counted with char heterogeneous reaction as indicated by the slow decomposition rate [9]. Figure 4 shows the mass decomposition (TG) of rice husk pellet at TGA analyses using oxygen as a gas carrier at heating constant 10 °C/min. The rate of mass reduction during heating (DTG) is also shown by the curve of derivative mass loss (DTG). Figure 4 shows the high mass loss occurred at a heating temperature between 250°C and 300°C, next the second high mass loss was at ~400-450°C. The high mass losses were shown by the peaks in the
DTG curve. It can be seen that the heating at 500°C forward would release only the residue of combustion, the ash. The ash residue was at about 20%.

Using analyses as in figure 3, the ignition point occurred at temperature 276°C. A fast oxidation pyrolysis occurred which was reducing the weight up to 69%. At first highest mass reduction, cellulose was degraded which mainly contained of condensable [10]. Another research also reported that for most natural fibers approximately 60% of the thermal decomposition occurred within a temperature range between 215 and 310 °C [11]. Next, a slow reduction, about 3.6% of masses, were deducted from the temperature of 300 °C up to 448°C. A gradual reduction was then seen between 300-600°C, indicating the slow phase of pyrolysis. The mass reduction in this zone had been detected as xylan and lignin [10]. Xylan is a group of hemicellulose found in plant cell walls. The zone of 600°C forward was mainly ash. The silica in rice husk is an amorphous form, so it is easy to be breakable during ash formation [2].

Effect of heating constant in the mass conversion can be seen in Figure 5. Slightly higher temperatures of ignition and burnout at the higher constant heating rate applied. This relation has been used to calculate the mathematic model of mass reduction in the thermo-kinetic behavior of fuel. This empirical data can be used widely in several applications, one of them is as a parameter design of a predictive fuel behavior applying in a combustor.
Figure 5. The available weight (TG Curve) during thermal combustion analyses at different heating rates

The Kissinger-Akihara-Sunose (KAS) model (equation 4) was applied to predict the kinetic model of mass degradation of the combustion reaction at TGA analyses. The empirical kinetic properties of this rice husk pellet resulted from the TGA Combustion analyses is summarized as in table 3.

Table 3. Thermal degradation in kinetic combustion of rice husk pellet

| Heating rate | Peak 1 | Peak 2 | Ignition and burnout |
|--------------|--------|--------|----------------------|
|              | $T_{\text{max}}$ | $r_{\text{max}}$ | $T_{\text{max}}$ | $r_{\text{max}}$ | $T_i$ | $T_b$ |
| 10 °C/min    | 271    | 2.4    | 415                  | 0.04              | 272.8 | 429.0 |
| 20 °C/min    | 274    | 2.2    | 439                  | 0.04              | 277.4 | 453.2 |
| 30 °C/min    | 283    | 2.0    | 469                  | 0.05              | 278.7 | 462.0 |
| **Average**  |        |        |                      |                   | 276.3 | 448.1 |

Activation energy (kJ. Mol$^{-1}$) 
$E = 188.9$

Pre-exponential factor ($s^{-1}$) 
$A = 3.62 \times 10^{13}$

The activation energy, according to Arrhenius theory, is a minimum amount of energy that must be first acquired by reactions to transform it into products. At an absolute temperature $T$, at fraction of molecules with their kinetic energy greater than activation energy can change into products of reactions. Arrhenius provided a physical justification and interpretation for the formula. Currently, it is often seen as an empirical relationship [7]. The collision theory states that in order to reactive, molecules must first collide. The reactant molecules must get closer than a certain distance. These molecular distances are, however, difficult to measure. In the Arrhenius theory, the pre-exponential factor, $A$, can be re-interpreted as the number of collisions per second occurring with the proper orientation to react. Then, it can also be
called a frequency factor. The pre-exponential factor, $A$, is a constant that can be derived experimentally or numerically from a regression data [7].

Figure 5 and table 3 show the highest peaks occurred at 271-283°C. At these points, high masses reduction drastically took place. The volatiles was mainly degraded, reacting homogeneously or heterogeneously. In this paper, the activation energy approached using the KAS method at $\alpha = 50\%$ conversion (equation 4) was approximately 188.9 kJ/mol. For comparison, a study has analyzed the thermal degradation of several varieties of rice husk, using the gas carrier oxygen [12]. Similar to our study, two distinct reaction zones were observed for all varieties of rice husk. The activation energies for the first zone were in the range of 142.7–188.5 k J mol$^{-1}$ [12].

4. Conclusions
Rice husk is a by-product of rice mill. In Indonesia, the rice husk is not fully utilized yet and often found dumped in the rice mill plants. The low density of rice husk often causes the high cost of transportation. The form of fuel pellet, the biomass fuel is denser and uniform. The dense and uniform biomass solid fuel can significantly improve the energy conversion efficiency and reduce the technical problems related to inconsistent of combustion or gasification of raw form biomass fuel. Wood pellet is a tradable commodity, well-applied in Europe and East Asian countries. A rice husk pellet has appeared in the global market. This study developed the rice husk pellet and analyzed the physical and the kinetic thermal degradation using oxygen as the gas carrier.

The rice husk was pelleted using a rotating plate and static roller press type pellet mill, the general type of mill used in biomass pellet production. The 4% weight of gelatinized starch was used as the binder. The densification increased the bulk density from 140 kg/m$^3$ to 511 kg/m$^3$. The optimum temperature of the pressing chamber should be kept in the ranges of 60-80°C to form the good quality of rice husk pellets. The proximate of this rice husk pellet is similar to that of the rice husk in raw bulk form. High ash at about 18% dry weight, which is mainly silica content, was detected from proximate analyses. The industry which applies less iron material equipment for its energy conversion can utilize this rice husk pellet. Furthermore, silica by-products can be then recycled to form other usable materials, such as the mix materials for making bricks, concrete, asphalt etc.

The results of TGA combustion analyses using oxygen as the gas carrier resulted in two distinct reaction zones of thermal degradation. The first zone occurred at range temperatures of 250-300°C and the second at 410-470°C. The ignition and burning out temperatures were at averagely 276°C and 448°C, respectively. The Kissinger-Akihara-Sunose (KAS) model approximated the activation energy of 188.9 kJ/mol for the first zone reaction of highest mass reduction.

5. References
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