The effect of various heating rate and final temperature towards heating value and activation energy on rice husk pyrolysis

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Abstract. Rice husk was residual waste which had content such other biomass, however it was still classified low in utilizing, thus it was needed efforts to improve the using values from the rice, the one of those was pyrolysis process. The determination of kinetic parameter was also studied to get the proper conditions where the pyrolysis became easier to occur. The heating rate variations of pyrolysis were 10°C/min, 30°C/min and 60°C/min while the final temperatures were 350°C, 450°C, 500°C and 600°C. The highest heating value of the char product was obtained with 3348.78 cal/g at the final temperature of 550°C and heating rate of 30°C/minute. The highest activation energy was shown at the final temperature of 550°C and heating rate of 60°C/minute. However, as heating value of char product was still under National Indonesian Standard minimal 5000.00 cal/g, thus char was not suitable to be used as an alternative fuel. Conversely, the tar produced has the highest heating value obtained which reached 7340.53 cal/g therefore tar of rice husk was more suitable to be utilized as bio oil.

Keywords: rice husk, pyrolysis, activation energy, global kinetics, heating value, char, tar.

1. Background
Indonesian’s Population is increasing every year causing increasing energy need which creates energy availability problem. For this reason, alternative energy is needed which can be used as reserve energy from untouched, one of which is in agriculture sector. Indonesia is an agricultural country with a rapidly growing agriculture sector because of its sufficient natural condition was sufficient. The one of abundant products was rice, according to the data of Indonesian Central Bureau of Statistics data in 2017 Indonesia produced more than 81 million tons of rice. To be cooked rice, the rice must be processed first, where in the process, there is a part of hard sheets, such scaly dry thing which is called rice husk. Husk is useful as grain protector from fungal attack and moisture reaction [1].

In the process of milling rice, it produced about 20% rice husk from the total of unpeeled rice weight [2], however utilizing rice husk was still relatively low because the content of high ashes, low nutrition and its characteristic was rough [3], its utilization was still limited in making bricks, roof tiles and agriculture. Due to abundant husk quantity and it was regarded as waste, thus it was needed utilization the waste of rice husk as alternative energy and it increased useful values from rice husk.

Rice husk had the content such as other biomass that if it was used as gasification starter, husk had low water content and the same size. Biomass utilization had to use the right technique, the one of effective techniques was pyrolysis. Pyrolysis was thermal degradation process of biomass at oxygen
environment which was limited [4], main products of pyrolysis were char, tar, and gas, where the comparison of the three products results depended on some conditions such as final temperature and holding time [5]. Advantages of pyrolysis were high conversion ratio from the product and it could be used as basis material of utilizing others [6], besides due to burning system without involving oxygen from atmosphere thus it was produced a little bit of CO₂.

Activation energy was minimal energy which was needed in order to happen burning reaction, activation energy was usually measured using thermogravimetry method [7]. Activation energy was denoted with a symbol of (Ea) in kilojoules per mol (kJ/mol) or kilocalorie per mol (kcal/mol). In exothermic and endothermic reaction needed energy from outside [8].

Decomposition reaction in pyrolysis process would be easier in reacting if it had lower activation energy. According to Chen et al. [9] if it was done various heating rate with constant temperature, thus activation energy would improve along with increasing heating rate. Material requirements which could be used as alternative energy had to have heating value above the standard. heating value was energy quantity which was released by the number of mass unit in the burning process. Biomass standard which was fixed by Badan Standar Nasional Indonesia [10] was minimally 5000.00 cal/g. Therefore, it was needed the treatment of rice husk for increasing heating value. This research was done a study about the impact of various final temperature and heating rate towards heating value and activation energy of product which was produced and the product was appropriate to be utilized.

2. Research Method

2.1. Method of Retrieving Data

Materials which were used in this research were rice husk that was easy to be sought and regarded as waste. Rice husk was often found in Klaten, Central Java, Indonesia.

2.2. Research Materials

The first step was preparation, including collecting, drying, crushing and sieving materials. Materials which were rice husk was crushing using crusher machine and sieved until those was passed in the size of 20 mesh. The second step was equipment and software installation, then it was done pyrolysis process of rice husk as 20 grams with heating reactor until the temperature which was desired. Various heating rate was 10°C/minute, 30°C/minute and 60°C/minute with final temperature of 550°C, and for the various final temperature was 350°C, 450°C, 500°C, and 600°C with heating rate of 30°C/minute. To remove oxygen in the reactor, it streamed nitrogen in the amount of one litre/minute, then it was done the testing of heating value based on ASTM (American Society for Testing and Materials) D2015 in PSPG laboratory (Pusat Studi Pangan dan Gizi) Gadjah Mada University, Yogyakarta for pyrolysis process of product and raw materials. Analysis which was done was the determination of activation energy using Arrhenius equation of the first order of kinetics reaction. Schematic of pyrolysis equipment which was used in this research was presented in Fig. 1.

![Experimental apparatus schematic](image_url)

**Figure 1.** Experimental apparatus schematic
2.3. Activation energy determination

Activation energy of pyrolysis process can be calculated by Arrhenius equation using first order reaction as the following equation:

\[
\frac{dx}{dt} = Ae^{\frac{E}{RT}}(1-x)
\]  

(1)

Where \(A\) is pre-exponential factor, \(E\) is activation energy, \(T\) is temperature, \(t\) is time, and \(x\) is pyrolysis conversion which can be calculated with this following equation:

\[
x = \frac{w_0 - w}{w_0 - w_f}
\]  

(2)

Where \(w_0\) is initial mass of the sample, \(w\) mass of the sample at the current temperature, and \(w_f\) is final mass of the char.

If \(\beta\) is heating rate constant, so:

\[
\beta = \frac{dT}{dt}
\]  

(3)

By rearranging equation (1) gives:

\[
\frac{dx}{dT} = \frac{A}{\beta} e^{\frac{E}{RT}}dT
\]  

(4)

\[
\frac{dx}{(1-x)} = \frac{A}{\beta} e^{\frac{E}{RT}}dT
\]  

(5)

By integrating equation (5) gives:

\[
-\ln(1-x) = \frac{A}{\beta} \int e^{\frac{E}{RT}}dT
\]  

(6)

Since \(\int e^{\frac{E}{RT}}dT\) has no exact integral, \(\int e^{\frac{E}{RT}}dT\) can be expressed as an asymptotic series and integrated, with the higher order terms ignored, and equation (6) becomes:

\[
-\ln(1-x) = \frac{ART^2}{\beta E} \left[ 1 - \frac{2RT}{E} \right] e^{\frac{E}{RT}}
\]  

(7)

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

(8)

Expressing equation (8) into logarithmic form gives:

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

(9)

If \(\frac{2RT}{E} \ll 1\) is assumed, so:
\[
\ln \left[ \frac{\ln (1-x)}{T^2} \right] = \ln \left( \frac{AR}{\beta E} \right) - \frac{E}{RT}
\]  \tag{10}

\( w \) and \( T \) for each minute can be used to determine \( x \) and by make a plot the relation between \( \ln \left[ \frac{\ln (1-x)}{T^2} \right] \) and \( 1/T \), gives a straight line with \( -E/R \) slope thus the activation energy can be defined.

3. Results and Discussions

Activation energy was determined using Arrhenius equation with the first order of kinetics reaction which was often called global kinetics, without looking at elementary reaction which was happened [7], it was used by global kinetics because in the biomass which had the content of lignin, cellulose and hemicellulose, that happened the reaction and composition of content were not surely known yet because the impact of other mineral content and interaction inter components [11]. The result of activation energy with various heating rate was presented in table 1 as follows:

| Heating rate (°C) | Activation Energy (kJ/mol) |
|-------------------|-----------------------------|
| 10                | 16.385                      |
| 30                | 27.215                      |
| 60                | 28.679                      |

Table 1 showed that heating rate got higher thus activation energy got more increasingly, due to the higher of heating rate would be more much formed free radicals which were caused the termination of covalent bond, the free radicals as a result that energy which was needed for bond termination that got higher [12], besides in pyrolysis process of the rising of heating rate would accelerate high temperature achievement as a result that decomposition process would also need high energy. This statement were appropriate with the statement of Singh [13] that the impact got bigger heating rate which caused getting higher from activation energy, the relation of activation energy and the various final temperature was presented in table 2 as follows:

| Final temperature (°C) | Activation Energy (kJ/mol) |
|------------------------|-----------------------------|
| 350                    | 20.27                       |
| 450                    | 20.80                       |
| 550                    | 27.21                       |
| 600                    | 21.34                       |

Table 2 showed that the final temperature got higher thus activation energy value also got bigger, activation energy was improved from the final temperature of 350°C to 550°C and it decreased drastically at the final temperature of 600°C which was specifically 27.21 kJ/mol becoming 8.74 kJ/mol, the measurement of activation energy could be difficult to be done due to the effect of char morphology and ash layer thickness at husk surface which would inhibited the process of oxygen diffusion and the in and out of gas at the sample [14]. The result of measurement which was showed table 1 and table 2 was not differently fallen with the measurement which was done by Mansaray and Ghaly [14] that
activation energy of rice straw was 30 kJ/mol and Suyitno [15] stated that activation energy of rice husk was 41.24 kJ/mol.

The test of heating value was done to know husk properness as fuel, where heating value got higher therefore it got better to be used as fuel, the test result of char heating value with the various final temperature was presented in table 3 as follows:

| Final temperature (°C) | Heating value (cal/g) |
|------------------------|-----------------------|
| 350                    | 2569.24               |
| 450                    | 2972.01               |
| 550                    | 3348.78               |
| 600                    | 2916.47               |

Table 3 showed that the final temperature got higher thus the heating value got bigger, because the increase of temperature caused the termination of lignocellulose bond which got much more so that pure carbon atom that was obtained got bigger [16] with the amount of carbon atom which was much therefore the heating value got higher. The highest heating value that had obtained was 3348.78 cal/g at final temperature 550°C and it decreased at the final temperature 600°C becoming 2916.47 cal/g, this could be caused many things.

Firstly, due to silica content which was high it could affect heating value that was produced, silica content got higher, ash content got higher thus the heating value got lower [17], secondly the above temperature of 500°C could happen continuous process which was biomass decomposition becoming ashes [18]. Besides at the final temperature of 600°C, there was allegedly burned char because the too high temperature so that it decreased heating value from its char [19]. The results of char heating value with the various heating rate were presented in table 4 as follows:

| Heating rate (°C) | Heating value (cal/g) |
|-------------------|-----------------------|
| 10                | 1496.83               |
| 30                | 3348.78               |
| 60                | 2938.94               |

Almost the same with the various final temperature of table 4 showed happening the increase of heating value and achieved the highest value at the heating rate of 30°C which was 3348.78 cal/g and happened the decrease at the rate of 60°C becoming 2938.94 cal/g this was expected because at the heating rate of 60°C/minute that there was burned char due to the highest heating so that it would decrease heating value [19], besides the phenomenon of secondary cracking could be happened the above temperature of 500°C, the secondary cracking which was happened at partical pores of material caused tar and gas which was produced transforming into char thus it affected char content [5].

Besides, char was also obtained tar, the test analysis of heating value from tar was presented in table 5 and table 6 as follows:
Table 5. The test of heating value from tar with final temperature various.

| Final temperature (°C) | Heating value (cal/g) |
|------------------------|-----------------------|
| 350                    | -                     |
| 450                    | 5399.33               |
| 550                    | 2252.15               |
| 600                    | 7340.53               |

Table 6. the test of heating value from tar with heating rate various.

| Heating rate (°C/minute) | Heating value (cal/g) |
|--------------------------|-----------------------|
| 10                       | -                     |
| 30                       | 2252.15               |
| 60                       | 4751.58               |

The heating at the low temperature of 350°C and the low heating rate of 10°C/minute did not produce tar or bio oil because at the low temperature it tended the formation of charcoal instead of bio oil and the process of decomposition slowly happened due to energy which was given on low besides it happened the formation of anhydro cellulose which also caused the formation bio oil becoming low [20]. The final temperature of pyrolysis got higher than the amount of bio oil which was produced it would be much more, as well as heating value, the heating value of bio oil pyrolysis would increase along with the increase of the final temperature [21]. The highest heating value of tar which was obtained was at the final temperature of 600°C as big as 7340.53 cal/g and the heating rate of 60°C/minute as big as 4751.58 cal/g.

The result of heating value from raw rice husk was 3347.22 cal/g, the data which was obtained at char in table 3 and 4 could be stated on low because it had the highest heating value of char which was almost the same with the heating value of raw husk and its heating value was under standard for biomass that was fixed by Badan Standar Nasional 01-6325-2000 [10] minimally 5000.00 cal/g, therefore rice husk charcoal with pyrolysis process was less appropriate to be utilized because it could not increase the heating value of rice husk, different with the heating value of tar which was obtained high until it reached 7340.53 cal/g, although not each of test result produces tar due to kinds of optimal condition, so that the pyrolysis process of rice husk tar was more appropriate for to be utilized because it was proven to be able to increase its heating value.

4. Conclusions
The result of research showed that the final temperature pyrolysis of 550°C and the heating rate of 30°C/minute produced the highest heating value for the product of char as big as 3348.78 cal/g, and for the highest activation energy at the final temperature of 550°C and the heating rate of 60°C/minute. However due to its value was almost the same with the value of raw husk then the product of char was less appropriate to be utilized because it could not increase its heating value, another side the highest heating value of tar which was obtained reached 7340.53 cal/g for the final temperature of 600°C and 4751.58 cal/g for the heating rate of 60°C/minute. Due to the highest heating value then tar was more appropriate to be utilized as bio oil.

References
[1] Chandra A, Miryanti Y, Widjaja L B and Pramudita A 2012 Isolasi dan karakterisasi silika dari sekam padi Research Report - Engineering Science 2 1-41
[2] Somaatmadja D 1980 *Sekam Gabah Sebagai Bahan Industri*: Badan Penelitian dan Pengembangan Industri

[3] Houston D 1972 *Rice Chemistry and Technology* (Minnesota: American Association of Cereal Chemist)

[4] Di Blasi C 2008 Modeling chemical and physical processes of wood and biomass pyrolysis *Prog. Energy Combust. Sci.* 34 1 47-90

[5] Himawanto D A 2012 Optimasi kondisi pirolisis sampah bambu guna mendapatkan energi terbesar *Buana sains* 12 2 35-8

[6] Kalita P, Mohan G, Pradeep Kumar G and Mahanta P 2009 Determination and comparison of kinetic parameters of low density biomass fuels *J. Renew. Sust. Energ.* 1 2 023109

[7] Himawanto D A 2013 Penentuan Energi Aktivasi Pembakaran Briket Char Sampah Kota Dengan Menggunakan Metoda Thermogravimetry Dan Isothermal Furnace *Rotasi* 15 3 35-42

[8] Atkins P 1999 *Kimia Fisika* Jilid 2 Jakarta: Erlangga

[9] Chen T, Zhang Y, Wang H, Lu W, Zhou Z, Zhang Y and Ren L 2014 Influence of pyrolysis temperature on characteristics and heavy metal adsorptive performance of biochar derived from municipal sewage sludge *Bioresour. Technol.* 164 47-54

[10] Nasional B S 2000 *Briket Arang Kayu SNI 01-6235-2000* Badan Standardisasi Nasional Jakarta

[11] Anca-Couce A 2016 Reaction mechanisms and multi-scale modelling of lignocellulosic biomass pyrolysis *Prog. Energy Combust. Sci.* 53 41-79

[12] Hao J, Zhang J, Qiao Y and Tian Y 2017 Effect of heating rate on thermal cracking characteristics and kinetics of Xinjiang oil sand bitumen by TG–FTIR *AIP Conf. Proc.* 1864 1 020002

[13] Singh R, Biswal B and Kumar S 2013 Determination of activation energy from pyrolysis of paper cup waste using thermogravimetric analysis *Research Journal ofRecent Sciences* 2 177-82

[14] Mansaray K and Ghaly A 1998 Thermal degradation of rice husks in nitrogen atmosphere *Bioresour. Technol.* 65 1-2 13-20

[15] Suyitno 2011 Perumusan Laju Reaksi dan Sifat-Sifat Pirolisis Lambat Sekam Padi Menggunakan Metode Analisis Termogravimetri *Jurnal Teknik Mesin UNS* 11 1 12-8

[16] Majedi F, Wijayanti W and Hamidi N 2016 Perubahan Massa dan Nilai Kalor Char dengan Variasi heating Rate dan Suhu pada Pirolisis Serbuk Kayu Mahoni (Swietenia Macrophylla) *Rotor* 9 2 59-64

[17] Ronsse F, Van Hecke S, Dickinson D and Prins W 2013 Production and characterization of slow pyrolysis biochar: influence of feedstock type and pyrolysis conditions *Geb Bioenergy* 5 2 104-15

[18] Iskandar T 2013 Identifikasi Nilai Kalor Biochar Dari Tongkol Jagung Dan Sekam Padi Pada Proses Pirolisis *Teknik Kimia* 7 1

[19] Mujiarto S and Suprianto T 2012 Pengaruh Variasi Heating Rate Proses Pirolisis Terhadap Karakteristik Pembakaran Briket Char Bambu *Jurnal Poros Teknik* 4 2 77-80

[20] Yan Q, Toghiani H, Yu F, Cai Z and Zhang J 2011 Effects of pyrolysis conditions on yield of bio-chars from pine chips *For. Prod. J.* 61 5 367-71

[21] Wijayanti W, Sasongko M N and Purnami 2016 The Calorific Value of Solid and liquid Yields Qonsequenced by Temperatures of Mahagony Pyrolysis *ARPN J. Eng. Appl. Sci.* 11 2 917-21