Thermogravimetric investigation of *Reutealis Trisperma* (Blanco) airy shaw and iron sand as bed material at different heating rates pyrolysis

I M Rajendra[1,2], I N S Winaya[2], A Ghurri[2], I K G Wirawan[2]

[1] Department of Mechanical Engineering, Politeknik Negeri Bali, Kampus Bukit Jimbaran, Bali, Indonesia
[2] Study Program of Mechanical Engineering, Faculty of Engineering, University of Udayana, Bali, Indonesia

E-mail: maderajendra@pnb.ac.id

Abstract. This study observed the effect of bed material in the pyrolysis process. Also, other parameter such as the heating rate have been observed. The biomass studied is Sunan Candlenut cake. This biomass is a potential commodity as a producer of biodiesel. Through the method of mechanical press and esterification, it will leave waste in the form of a cake that still contains crude oil. Trapped oil can be converted into bio-oil through the pyrolysis technique. Parameters that affect the pyrolysis process include the addition of bed material and heating rate. Pyrolysis of this candlenut cake has been tested to determine the amount of activation energy. Heating rates are varied to 5, 10 and 20 K per minute and bed material used is iron sand. The testing instruments uses Thermogravimetric Analysis (TGA). The results show that the lowest activation energy of 15.497 [KJ/mol] is achieved when added iron sand at the heating rate of 10 K per minute.

1. Introduction

Nowadays, the issue of scarcity of fossil energy sources has become the world's attention. While in Indonesia, energy reserves from fossil are estimated to last only for the next 23 years [1]. To anticipate these conditions, the Indonesian government issued a policy that directs efforts to achieve national energy security by 2050. The aim of that policy is to support the development of Indonesia into a developed country. The efforts which are carried out include increasing the processing of coal, gas, geothermal energy, biofuels and new renewable energy. One of the potential energies is energy from biomass, because its availability is very abundant.

Most of biomass decomposition research aimed to obtain bio-oil as the main product which is then processed into biodiesel. Research on biodiesel that has been done so far includes processing of Jatropha Curcas, Nyamplung, Kepuh, Kesambi and Bintaro [2]. The research has not succeeded optimally. Therefore, research on the use of plant species whose seeds produce oil (bioenergy plants) as raw material for making biodiesel needs to be continually carried out and improved. One plant that is very potential as a producer of bioenergy is Sunan Candlenut (*Reutealis Trisperma* (Blanco) Airy Shaw). The advantages of this plant have been considered in the National Energy Policy (KEN) of Indonesia in

2014. In that policy, there is a direction that aims to develop research that ends in the production process of Sunan Candlenut commodities into bioenergy [3].

Sunan Candlenut is different from the type of candlenut vegetable which is commonly used as a spice ingredient. The content of fatty acids in Sunan Candlenut oil consists of stearic acid, oleic, linoleic, and α -eleostearic. This oil contains poison, therefore it cannot be consumed. Sunan Candlenut consists of fruit peel (62-68%), shell (11-16%) and kernel (16-27%). This kernel contains crude oil which is quite high above 50% which approaches solar [4].

Processing Sunan Candlenut into crude oil which is a biodiesel feedstock requires several stages of the process. Starting from collecting crops, stripping, drying, extracting oil and refining oil, then processing it into biodiesel through an esterification process. At the stage of extracting seeds into crude oil is done by pressing. This stage will leave waste in the form of a cake or pulp. At present, the waste is only processed into briquettes and activated charcoal. This cake still contains around 12.9% crude oil but it is difficult to remove by pressing [2]. One technique that can be applied to convert biomass into an energy source is through a thermochemical conversion process, such as pyrolysis, gasification and combustion [5].

Pyrolysis is the decomposition of thermochemical biomass into several useful products that take place without the presence of oxygen. During pyrolysis, large and complex bonds of hydrocarbon molecules will break down into smaller molecules in the form of gas, liquid, and charcoal. Pyrolysis is usually carried out in the temperature range 300 to 650°C [6]. The pyrolysis process aims to accelerate the decomposition reaction and shorten the long hydrocarbon chain so that it is easy to condense into bio-oil. The reaction can be accelerated by increasing the heating rate and adding bed material. Some studies concluded that most of the bed materials used were able to increase the amount of bio-oil [7]. The material that has the potential as a bed material is iron sand which is widely spread in the territory of Indonesia. The use of iron sand is currently not optimal even though iron oxide (Fe3O4) contained in iron sand is actually very potential to be processed into various high value industrial products, among these are steel, colouring, ink, magnetic recording media, ferrite magnets and bed material [8].

The addition of bed material aims to reduce energy requirements during the process. The amount of energy needed for decomposition is called activation energy, which is an estimate of the amount of heat (energy) needed in pyrolysis to convert biomass into bio-oil, biochar, and gas products. The knowledge about activation energy is very important for predicting suitable process behaviour and reactor design [9]. Activation energy can be determined through kinetic rate analysis which is the rate of energy change during the pyrolysis process. Changes due to decomposition can be determined based on biomass mass reduction or increase in volume of pyrolysis products. Kinetic rate testing can use a pyrolysis reactor or TGA (Thermogravimetric analysis) test equipment [10-13]. Kinetic rate analysis can be determined using formulas found in several methods [14,15].

This study observed the pyrolysis behaviour of Sunan Candlenut cake by adding iron sand as a bed material at different heating rates. The behaviour was studied based on the TGA test data which was analysed using the kinetic rate method to determine the amount of activation energy.

2. Materials and methods

2.1. Material

Sunan Candlenut seeds as the material in this research were obtained from plantations in Garut Regency, West Java Province. Candlenut seeds are peeled from the shell, then dried in the sun for 1 day, then pressed using a hydraulic press with compressive strength of 140.6 KN. Residual pulp is chopped to homogenize the size to an average of 1 mm, then dried in an electric oven at 110°C for 6 hours to reduce humidity.

The iron sands are taken from the slopes of Mount Batur, Kintamani Bangli, Bali. First, sand is sieved to get a size between mesh 30 and 40. The first washing used water and dried it in an electric oven at 110°C for 3 hours, then immersed in 2 mol NaOH, for 24 hours then rinsed with Aquades to the neutral pH. The next process is calcination to activate the granules by heating in the furnace at a temperature of 400ºC for 3 hours.

Proximate testing of Sunan Candlenut cake to know the contents of the moisture, volatiles, fixed carbon Ash using a TGA (Thermogravimetric Analysis) 701 (LECO) test, following the ASTM D7582 MVA BIOMASS standard.

2.2. Test method

Thermogravimetric data are based on the results of testing using a TGA-701 (LECO), under continuous nitrogen gas flow at 20 mL.min^{-1}. Non-Bed Material (NBM) testing was carried out on 1.2 g of Sunan Candlenut cake samples. While testing with the addition of bed material the composition of 1.0 g of Iron Sand is mixed evenly with 0.2 g of Sunan Candlenut cake. All samples were hydrolyzed at operating temperatures dynamically starting from room temperature to 1023 K at variations in Heating Rates (HR) 5, 10 and 20 K.min^{-1}. Mass data, time and temperature are recorded using TGA software. Sample preparation and TGA test equipment are shown in Figure 1.

Figure 1. Preparation of samples and TGA equipment.

2.3. Kinetic model

The kinetic rate model applied in the biomass pyrolysis process in this study is the One-Stage Global Single Reaction. Pyrolysis was modeled as a one-step reaction assuming biomass experienced overall decomposition into volatile and ash products. This analysis uses the rate of decrease in mass measured experimentally, where the rate of pyrolysis depends on the mass of the biomass that is not decomposed [6]. The kinetic model is calculated based on changes in biomass mass *(k)* formulated by the following equation:

$$k = \frac{m_o - m}{m_o - m_f} \quad (1)$$

Where m_o and m_f are respectively the values of the initial and final masses and m is the change in mass that occurs during measurement. Then, by substituting k which is similar to the Arrhenius equation [14] therefore, k can be formulated as Equation (2).

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (2)$$

Where k is the constant rate (s^{-1}), E_a is the activation energy (kJ.mol^{-1}), R is the gas constanta (8.314 J.K^{-1}mol^{-1}), T is the Temperature (K), A is the pre-exponential factor (minute^{-1}). Equation 2 is converted to logarithmic form into a straight-line equation to get the activation and pre-exponential factor values into Equation 3.

$$ln\, k = \frac{-E_a}{R}\frac{1}{T} + ln\, A \quad (3)$$

$$y = mx + c \tag{4}$$

The Equation 4 is a straight line equation from regression between *ln k* versus *1/T* in Equation 3. The activation energy can be calculated based on the gradient *(m)* of the equation.

3. Results and discussion

3.1. Proximate analysis of Sunan Candlenut cake

Sunan Candlenut cake has a high oil content. This property makes it potential as a raw material for biofuels. High oil content is indicated by high volatile values through proximate analysis test. The following results of the proximate analysis test are shown in Table 1.

Table 1. Proximate analysis Sunan Candlenut cake

Type of test	Result (%) *
Moisture	3.76
Volatile	90.26
Fixed Carbon	3.05
Ash	2.94

*dry basis

3.2. Thermogravimetric analysis

Thermal decomposition that occurs in the pyrolysis process causes changes in the form of the solid phase into a gas or vapor phase which is then cooled into a liquid product (bio-oil) and is a fuel called biofuel. These changes when viewed from the solid phase there will be a decrease in mass during the time of pyrolysis. The comparison of mass changes at any time to the initial mass is the basis for calculating kinetic rates. Thermal decomposition of biomass occurs through stages such as heating, Torre faction, pyrolysis, and gasification where the stages depend on the temperature of the process. To determine the temperature of pyrolysis that occurs it can be analysed based on the graph of the test results shown in Figure 2.

In Figure 2 (upper) it can be seen the difference in heating rate causes a different weight loss percentage. The mass change in the heating rate of $5 K.min^{-1}$ is slower than the heating rate of $10 K.min^{-1}$ and the fastest occurs at the heating rate of $20 K.min^{-1}$. However, in each group it was seen that the addition of bed material caused changes to be slightly faster than NBM. Pyrolysis which aims to produce bio-oil products occurs at the heating stage of volatile components. This component experiences a decomposition reaction in a fast time because of its easy to change by heat. Based on the proximate test results as shown in Table 1, Sunan Candlenut cake has a volatile content of 90.26%. in other words, Sunan Candlenut is volatile. In the pyrolysis process the changes in dominant mass occur at this stage. To determine the temperature range, the dominant change can be analysed based on the derivative change curve at the reaction temperature, as shown in Figure 2 (below). Of all the test samples it was seen that the volatile component pyrolysis temperature began at 383 K, indicated by increasing the derivative curve to the peak temperatures between 663 to 689 K and ending at 860 K. Therefore, the pyrolysis temperature range to be used in the subsequent kinetic rate analysis is 383 to 860 K. higher than that pyrolysis still occurs but the main product is charcoal or ash and fixed carbon. At the beginning, a lower temperature is a heating process that aims to reduce humidity. In the graph also shows that samples with different heating rates give different derivative values. The highest value occurs at a heating rate of $20 K.min^{-1}$ for samples with addition or non-bed material. The next smaller percentages are 10 and $5 K.min^{-1}$, respectively. This shows that the heating rate in the pyrolysis process causes different levels of mass degradation.

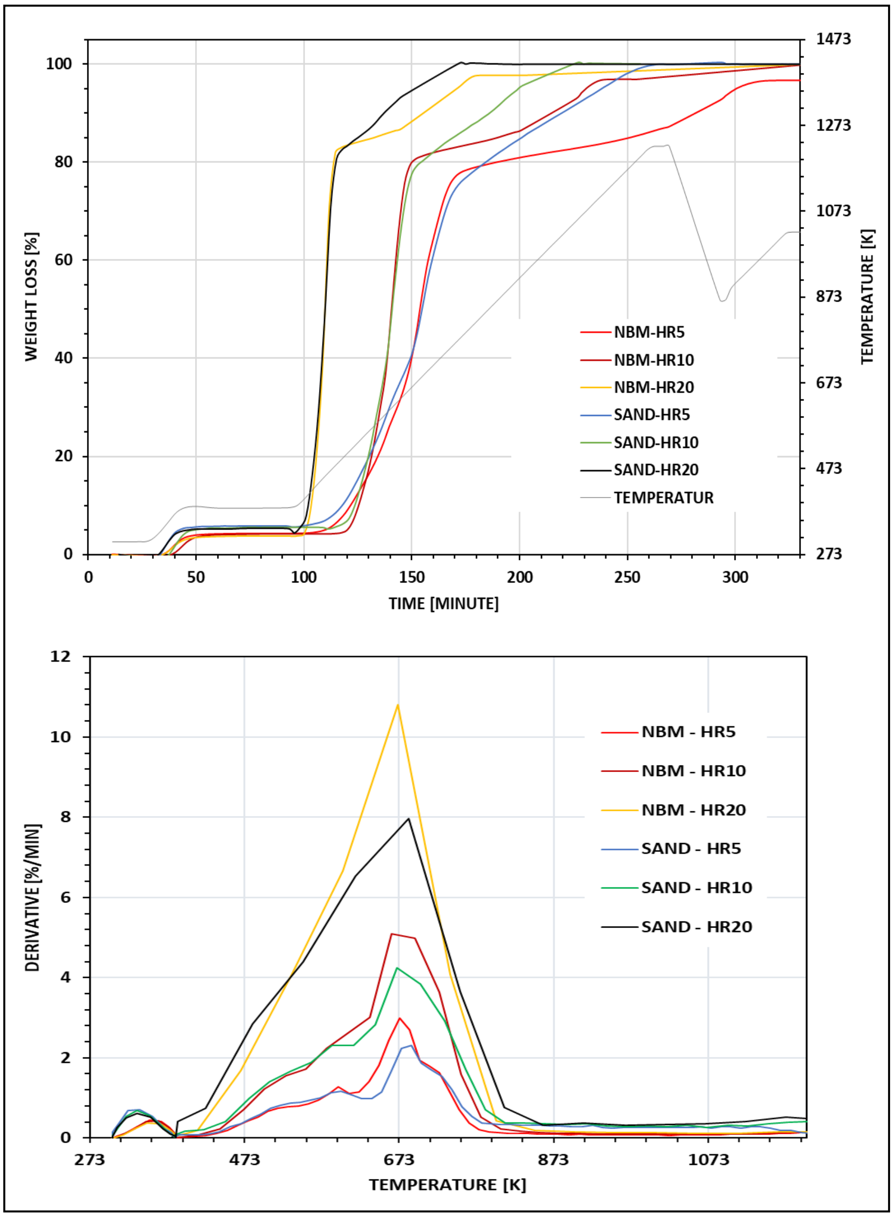

Figure 2. TG (upper) and DTG (below) curves for Sunan Candlenut NBM and with iron sand as bed material at different heating rates.

3.3. Rate constant

Based on the data weight of the TGA test results, then the kinetic rate analysis is determined by calculating the constant rate (k) in the pyrolysis temperature range above. The value of k is calculated using equation 1, based on data on mass changes to temperature during the pyrolysis process. The graph of the constant rate of pyrolysis temperature is shown in Figure 3.

The graph shows that the six curves have almost the same trends. If observed in more detail, there is a slight trend difference in these curves, where the NBM sample group shows a steeper curve than the sample using bed material. In the temperature range of 383 K to 663 K, the NBM sample group was lower than the sample added with iron sand. However, after that temperature, the trend is reversed, where the NBM group shows a higher rate constant. A temperature difference of about 25 degrees occurs between two sample groups to get the same rate constant. This confirms that the bed material functions as heat storage so that the conversion runs simultaneously and is more stable.

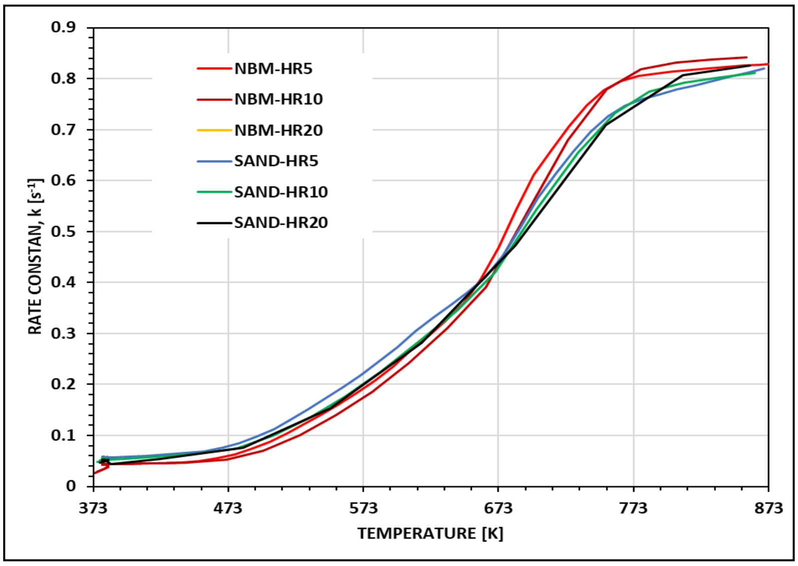

Figure 3. Rate constant *(k)* based on changes in mass to temperature during pyrolysis.

3.4. Activation energy (E_a)

To determine the amount of activation energy (E_a) can be calculated using Equation 4. The component *y* represents *ln k* while *x* represents $1/T$. Both of these values are obtained from the conversion of rate constant (k) and temperature (T). Then, plotting is done on the graph of the kinetic rate, where on the y axis there is *ln k* and the *x* axis is $1/T$. The relationship curve of the two components is presented by linear regression so that the straight line equation gradient is obtained where the value represents the formula $-E_a/R$. The graph of plotting data results is shown in Figure 4.

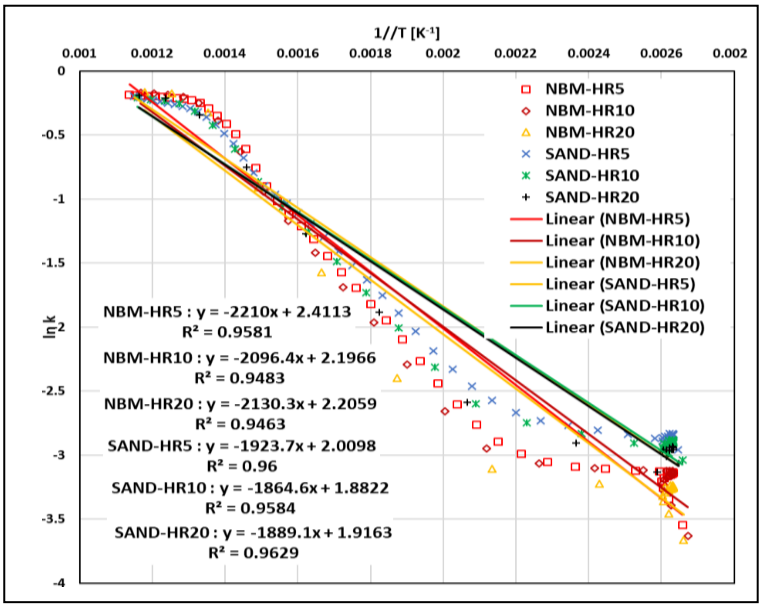

Figure 4. Kinetic rate by one-stage global single reactions method on pyrolysis of Sunan Candlenut.

Table 2. Results of activation energy calculation (E_a).

Sample	HR	Slope	R gas	$-E_a$	E_a (KJ/mol)	R^2
NBM	5	-2210	8.314	-18373.9	18.374	0.9581
NBM	10	-2096	8.314	-17426.1	17.426	0.9483
NBM	20	-2130	8.314	-17708.8	17.709	0.9463
				average	17.836	
Iron Sand	5	-1923	8.314	-15987.8	15.988	0.9600
Iron Sand	10	-1864	8.314	-15497.3	15.497	0.9584
Iron Sand	20	-1889	8.314	-15705.1	15.705	0.9629
				average	15.730	

Based on the average value of activation energy each sample group showed a significant difference in value. The addition of bed material in pyrolysis requires lower energy than without bed material (NBM). Based on the heating rate in each group showed that the activation energy at the heating rate of 5 K.min^{-1} then decreased at the heating rate of 10 K.min^{-1} and increased again at the heating rate of 20 K.min^{-1}. At the heating rate 5 K.min^{-1} the greatest activation energy, this is caused by decomposition reactions that occur more slowly so that the change in solid phase into gas takes longer so that the energy needed to start the reaction is also getting bigger. While the heating rate of 20 K.min^{-1} has a shorter reaction because the reaction temperature is faster but the energy needed to accelerate the reaction is also greater. Based on the amount of activation energy, the best pyrolysis process from sunan candlenut in this study was to use iron sand as bed material with a heating rate of 10 K.min^{-1}.

4. Conclusions
An investigation using TGA for Sunan Candlenut cake and iron sand as bed material at the pyrolysis heating rate of 5, 10 and 20 K.min^{-1} was carried out. Sunan candlenut cake has a high volatile content, almost 90.26%, which has the potential to be produced as bio-oil as an energy source in the future. The results showed that the lowest activation energy of 15.497 [KJ/mol] was achieved when added iron sand at the heating rate of 10 K.min^{-1}. The average activation energy without bed material (NBM) shows a value of 17,836 KJ/mol while using iron sand shows a value of 15,730 KJ/mol. This shows the use of iron sand as a bed material can reduce the energy needed.

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