Tar Kinetic Parameters of Pyrolysis Processes of Brem, Plastic, and Durian Skin Waste with Temperature Variations on A Rotary Kiln

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Abstract. Pyrolysis is a decomposition process chemical ingredient by adding the heating process without oxygen, where is the raw material/biomass will experience the breakdown of chemical structures to the gas phase. It produced char, tar, and gas. This research uses a rotary kiln system, in which the pyrolysis tube is rotated at low speed. Biomass in a rotating pyrolysis tube has an even heat. The pyrolysis temperature used in this research is 523K, 573K, 623K, 673K, The heat in the pyrolysis tube comes from heating the LPG stove. The heating is adjusted in such a way that the heat can be reached at the desired temperature. The tar formed in the pyrolysis process is calculated its kinetic rate value. The biomass used in this study is a waste of brem, plastic, and durian skin. The results showed that with increasing temperature, the tar volume would increase. The value of the kinetic rate is strongly influenced by variations in pyrolysis temperature. The pyrolysis temperature is large, so the kinetic rate is also large. The best kinetic rate at a temperature of 673 K in all biomass. The type of biomass can affect the kinetic rate. Plastic waste biomass has the smallest kinetic rate value compared to other biomass. The density of bio-oil will decrease with increasing pyrolysis temperature.

1. Introduction

In 2112 is the limit of coal availability. By 2042, fossil fuels from petroleum will run out. So that only coal is available as a fossil fuel [1]. One of the processes to obtain new and renewable fuels is pyrolysis. This process produces alternative fuels, namely Char (charcoal), tar (bio-oil), and gas. Tar (bio-oil) can be processed into biodiesel [2]. Pyrolysis is the process of breaking (decomposing) biomass through a heating process with little or no oxygen. Biomass in the pyrolysis process will undergo a breakdown of the chemical structure into a gas phase. The temperature of the pyrolysis process is between 500 - 800°C. The relative amount of pyrolysis main products (Char, Tar, and Gas) depends on operating parameters, biomass properties, and pyrolysis process system [3]. At a temperature of 400 - 550°C, the atomic bond breaking process occurs in biomass which produces bio-oil in a short time. The higher the temperature, the more likely the product gas is. While Char is produced at low temperatures [4]. Tar can be produced from the pyrolysis process and can be formed in 3 time zones, namely (i) (≥500°C) (ii) low heating rate, and (iii) (≤ 400°C) [5]. Biomass can come from an industrial, plantation, livestock waste, biomass contains hydrocarbon compounds so that it can be made as fuel and power plants ([6]. Pyrolysis research can be done with fixed tube or rotary kiln pyrolysis. Fixed tube pyrolysis research uses organic and non-organic materials: mahogany[7], plastic waste[8], brem waste [2].
bagasse[9], durian skin [10], [11]. The pyrolysis rotary kiln research uses organic and non-organic materials, such as durian skin[12], mahogany[6], tire waste [13], solid waste [14].

In this pyrolysis research using waste biomass brem, plastic, and durian skin. Brem is one of the typical snacks of the city of Madiun, East Java, Indonesia. Brem is produced from the fermentation process of glutinous rice which is extracted from the starch. The waste that has been taken from the brem production in the factory is 1.5-3 tons per month, so it is very potential as biomass in the pyrolysis process[15]. One of the waste products that are difficult to decompose is plastic waste. Indonesia is a very large contributor to plastic waste, namely 1.29 million metric tons [16]. Durian is one of the unique fruits of Asia and Indonesia. A material can be called biomass if it contains lignocellulosic elements, durian skin meets these requirements [17].

An important factor in overcoming the energy crisis is finding and making renewable fuels that can be used as a substitute for fossil energy. Based on the description that has been stated, the researcher is interested in the tar kinetic parameters of pyrolysis processes of brem, plastic, and durian skin waste with temperature variations on rotary kiln. This research was conducted by conducting direct testing of the rotary kiln pyrolysis system with waste biomass of brem, plastic, and durian skin. The test for each biomass is carried out separately, not mixed. The research objective was to determine the tar characteristics of each biomass including volume, kinetic rate, and density. The expected results in this research are that new fuels consisting of tar (bio-oil) as a substitute for crude oil. The equation to find out the value of the kinetic rate tar is the equation of change in volume per unit of time [18]:

\[ \frac{dV}{dt} = k \cdot f \left[ \frac{V - V_\infty}{V_0 - V_\infty} \right] \]  \hspace{1cm} (1)

where is the fraction of change in volume per unit time (gr/minute), k is the constant rate of addition of tar volume, V is the volume of tar at any time, V_0 is tar volume at the start of time and V_\infty is the final tar volume of the process. The equations of k[19]:

\[ k = A \cdot e^{-\frac{E_a}{RT}} \]  \hspace{1cm} (2)

here k is the rate constant (minute-1), E_a is the activation energy (kJ/mol), R is The absolut temperature (K), A is the pre-exponential factor (minute-1). Equation 2 can be formed into equation 3.

\[ k = A \cdot e^{-\frac{a}{T}} \]  \hspace{1cm} (3)

Where a is the slope = E_a/R [7]. The logarithmic form of equation 2 becomes to be a straight line equation to get the value of activation energy and pre-exponential factor.

\[ \ln k = \frac{-E_a}{R} \frac{1}{T} + \ln A \]

\[ y = a \cdot x + c \]  \hspace{1cm} (4)

2. Research Method

This research is an experimental study consisting of independent variables (variations in pyrolysis temperature) and dependent variables (tar volume, density, and heating value) in the experimental group. In tar formation, the kinetic rate of tar testing and calculation can be found. The pyrolysis system used is a rotary kiln system. The pyrolysis process uses temperature variations of 523K, 573K, 623K, and 673K, pyrolysis time of 180 minutes, and a nitrogen rate of 3 L/minute. The biomass used is a waste of brem, plastic, and durian skin.
The biomass samples were dried to a moisture content <4%. The sample size is uniform with a size of 0.7 mm. 500 g of biomass sample was inserted into the pyrolysis tube and closed. \( \text{N}_2 \) gas with a flow rate of 3 L/minute has flowed into the pyrolysis heating room until the \( \text{O}_2 \) level is <2% of the volume of the heating chamber and opens the exhaust valve on the pyrolysis tube so that \( \text{O}_2 \) gas comes out. After that, the rotary kiln tube was heated with temperature variations of 523K, 573K, 623K, and 673K. This test is carried out on Brem waste, Plastic, and trowel durian separately.

3. Result and Analysis

Figure (2), to calculate the constant rate of formation of char/rate constant (k) with a final temperature of 523 K at 33 minutes (equation 1)

\[
\frac{dy}{dt} = k \cdot f \left[ \frac{V - V_0}{V_0 - V_c} \right] 
\]

\[
\frac{159 - 156}{3} = k \left[ \frac{159 - 161}{0 - 161} \right] 
\]

\[
k = 0.001965 \text{ minute}^{-1}
\]
Fig. 2. Graph of tar addition and temperature increase at the final temperature of 523 K with brem waste biomass

From the k value, the ln k is calculated which will later be linked to the 1/T value to find a linear equation that can be used to find the exponential equation of k for the final temperature of 523K. Using the graph below, where the graph is obtained by finding ln k and 1/T is in the form of Kelvin (figure 3). This calculation is carried out for all biomass waste of brem, plastic, and durian skin at temperatures of 523K, 573K, 623K, and 673K.

Fig. 3. The kinetic rate of brem waste tar formation at the final temperature is 523K

From figure 3, we get a straight line equation: \( y = -2806.5x + 9.3126 \). With equation 4 can the value of \( k \) be \( k = 11076.71 . e^{-2806.5/T} \). In the same way, the k exponential equation will be obtained for each temperature and biomass of brem waste, plastic waste, and durian skin waste.

**Table 1.** Equation k for temperature 523K, 573K, 623K, 673K with brem waste biomass

| Temperature (K) | k (minute^{-1}) |
|-----------------|------------------|
| 523             | \( k = 11076.71 . e^{-2806.5/T} \) |
| 573             | \( k = 81.06084 . e^{-993.38/T} \) |
| 623             | \( k = 17452614 . e^{-736.7/T} \) |
| 673             | \( k = 1037.843 . e^{-203.5/T} \) |

**Table 2.** Equation k for temperatures 523K, 573K, 623K, 673K with plastic waste biomass

| Temperature (K) | k (minute^{-1}) |
|-----------------|------------------|
| 523             | \( k = 12.99546 . e^{-1329.9/T} \) |
| 573             | \( k = 29.72832 . e^{-1706/T} \) |
Table 3. Equation for temperature 523K, 573K, 623K, 673K with durian skin waste biomass

| Temperatur (K) | k (minute$^{-1}$) |
|---------------|------------------|
| 523           | $k = 9,48489 \cdot e^{-579,61/T}$ |
| 573           | $k = 147,4958 \cdot e^{-1647,7/T}$ |
| 623           | $k = 149,3511 \cdot e^{-1999,9/T}$ |
| 673           | $k = 96,27416 \cdot e^{-1178,4/T}$ |

Fig. 4. Plot of the constant/kinetic rate (k) formation of the brem waste tar

Fig. 5. Plot of the constant/kinetic rate (k) formation of plastic waste tar
From the exponential equation for each temperature and biomass (tables 1, 2, and 3), the exponential equation \( k \) for each biomass can be calculated, by entering the temperature value in equation \( k \), then making it the \( \ln k \) value and the temperature value is made \( 1/T \) (figures 4, 5, and 6).

From figures 4, 5, and 6, a linear equation is obtained for:
- **Brem waste**
  \[ y = -1420.5x + 6246 \]
- **Plastic waste**
  \[ y = -5556.3x + 10312 \]
- **Skin durian waste**
  \[ y = -3298.9x + 75336 \]

In the same way as equation 4, the exponential equation \( k \) for each biomass is obtained:
- **Brem waste**
  \[ k = 514.1937 \cdot e^{-1420.5/T} \]
- **Plastic waste**
  \[ k = 30091.56 \cdot e^{-5556.35/T} \]
- **Skin durian waste**
  \[ k = 1869.825 \cdot e^{-3298.9/T} \]

In the form of the equation table \( k \) (Tables 4, 5, 6) the values of \( E_a \) and \( A \) (equation 2) with biomass waste brem, plastic waste, and durian skin waste. Suppose the value of \( T \) is entered equal to 523 K to calculate the value of \( k \).

**Table 7.** Exponential equation \( k \), \( E_a \) and \( A \) with biomass waste brem, plastic and durian skin waste

| Biomassa           | Exponential equation          | \( E_a \) (kJ. mol\(^{-1}\)) | \( A \) (minute\(^{-1}\)) |
|--------------------|-------------------------------|-------------------------------|---------------------------|
| brem waste         | \( k = 514.1937 \cdot e^{-1420.5/T} \) | 11810                         | 514,1937                  |
| plastic waste      | \( k = 30091.56 \cdot e^{-5556.35/T} \) | 46195.1                       | 30091.56                  |
| skin durian waste  | \( k = 1869.825 \cdot e^{-3298.9/T} \) | 27427.0546                    | 1869.825                  |

From the \( k \) exponential equation in table 7, the \( k \) values are obtained at each temperature and biomass (table 8).

**Table 8.** Value of \( k \) at each temperature and biomass

| Temperatur (K) | Brem Waste | Plastic Waste | Skin Durian Waste |
|---------------|------------|---------------|-------------------|
|               | Value \( k \) (menit\(^{-1}\)) | Value \( k \) (menit\(^{-1}\)) | Value \( k \) (menit\(^{-1}\)) |
| 523           | 34.00605802 | 0.732053829   | 3.407406828       |
| 573           | 43.10083173 | 1.849916979   | 5.908294295       |
| 623           | 52.688882216| 4.028442671   | 9.378456505       |
| 673           | 62.9626948  | 7.814505305   | 13.89899802       |
From table 8, the k value of plastic biomass has the smallest value compared to other biomass. The k value in plastic biomass is small because it has a small moisture content so it is easy to form a small volume of tar to validate additions tar volume with the equation the value of k which is obtained by increasing the tar volume testing, then we put it again into The initial calculation, from 3 to 180 minutes with 3 minute intervals in equation 1.

\[
\frac{V_3-V_0}{3} = k \left[ \frac{V_3-V_0}{V_0-V_0} \right]
\]

\[
\frac{V_3-0}{3} = k = 514,1937 \cdot e^{-1.420.5/T} \left[ \frac{V_3-161}{V_0-161} \right]
\]  \hspace{1cm} (7)

With the calculation of equation 5 get the tar volume change value with the calculation method, which if depicted on the graph can be seen at Figures 7, 8, and 9.

Fig. 7. The graph of the addition of test tar volume with the addition of tar volume calculated by the kinetic equation with brem waste biomass

Caption:
a. The blue graph line indicates an increase in test tar volume
b. The red graph line indicates the increase in tar volume calculated
Fig. 8 The graph of the addition of test tar volume with the addition of tar volume calculated by the kinetic equation with plastic waste biomass

Caption:
a. The blue graph line indicates an increase in test tar volume
b. The red graph line indicates the increase in tar volume calculated
Fig. 9. The graph of the addition of test tar volume with the addition of tar volume calculated by the kinetic equation with Durian skin waste biomass

Caption:

a. The blue graph line indicates an increase in test tar volume
b. The red graph line indicates the increase in tar volume calculated

c. Temperatures of 623K
d. Temperatures of 673K

For Figures 7, 8, and 9 graphs of the actual addition of tar volume with the addition of tar volume calculated by the kinetic equation at temperatures of 523, 573, 623, and 673 K with biomass waste brem, plastic, and durian skin. Where the graph of the addition of the actual tar volume with the addition of the tar volume calculated from the kinetic equation for each biomass can be seen that the value of the addition of the tar volume calculated is close to the value of the addition of the actual tar volume so that the kinetic equation of each biomass (see tables 7 and 8) is close to accuracy. There are several points that the test volume is heavier than the calculated volume, this happens because at certain temperatures the biomass is easier to break down its atomic bonds so that the gas becomes more abundant and the tar volume automatically increases.
In Figure 10, the tar density is also affected by temperature variations in the pyrolysis process of brem waste, plastic, and durian skin. The content or composition of hydrocarbons in the tar will affect the value of the tar density, where the more hydrocarbons contained in the tar, the more stretched the molecular density and the lower the tar density value.

4. Conclusion

The tar kinetic parameters of pyrolysis processes of brem, plastic, and durian skin waste with temperature variations on a rotary kiln, with the following conclusions:

a. The results showed that with increasing temperature, the tar volume would increase. The value of the kinetic rate is strongly influenced by variations in pyrolysis temperature. The pyrolysis temperature is large, so the kinetic rate is also large. The best kinetic rate at a temperature of 673 K in all biomass. The type of biomass can affect the kinetic rate. Plastic waste biomass has the smallest kinetic rate value compared to other biomass.

b. The tar density is also affected by temperature variations in the pyrolysis process of brem waste, plastic, and durian skin.

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