Study of kinetic and thermal decomposition from municipal solid waste pellets using model-fitting methods

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Abstract. Reaction rate model could be determined from kinetic characteristics. Kinetic and thermal decomposition of municipal solid waste (MSW) pellets, consist of organic material, plastic, paper and leaves, with tapioca flour as binder (0%, 3%, and 6%) were studied in thermogravimetric analyzer from temperature 50 °C to 800 °C at heating rate 10 °C/min in N₂ atmospheres. The kinetic parameter were determined by Model Fitting or Coats Redfern Methods with different kinetic reaction model. Results of this study have shown that MSW pellets in various binder has activation energy values 64.64 kJ/mol and 22.06 kJ/mol for 0%, 68.83 kJ/mol and 21.99 kJ/mol for 3%, and 69.29 kJ/mol and 22.62 kJ/mol for 6% at temperature ranges between 200 °C – 400 °C and 400 °C – 500 °C respectively in typical three dimensional diffusion (D3) mechanism kinetic reaction model.

Keywords: kinetic study, Model-Fitting methods, municipal solid waste, pellet, thermal decomposition

1. Introduction

Population growth and lifestyle changes are inseparable parts of life in the world. However, these developments often have a negative impact on the surrounding environment, one of which is the presence of large amounts of municipal solid waste (MSW) [1–3]. On average, organic waste (food scraps and garden waste) is the largest part of the world's MSW, followed by paper and cardboard, plastics, glass, metal, wood, rubber and leather, and other waste [4]. The composition of MSW depends on each country's current level of development; More developed the country often the lower amount of organic waste [5]. In Indonesia, the average waste generation reaches 0.24 - 0.33 kg / capita / day with a composition that is dominated by organic waste [6–8].

There are many technologies for treating municipal solid waste, such as landfill, recycling, biological treatment, and thermal treatment. The cost of biological treatments is cheaper than the latter, but it is difficult to control bacterial growth and it takes a long time to reduce MSW [5]. That is why thermal treatment is more commonly chosen as a treatment for MSW in developed country. MSW is a very variable and heterogeneous multi-component material [9], so its calorific values are inconsistent. The use of MSW as fuels in thermal treatment especially gasification process results the low energy efficiency, so that to increase the efficiency, uniformity and compaction is required. Therefore, MSW is pelletized to reach uniformity.
Kinetic and thermal decomposition of pelletized MSW are needed for modelling reactors, like gasification and incineration reactors. Reaction rate of pelletized MSW can determine on how devolatization begins and how much contents of devolatization process products are. Currently, MSW can be approached as lignocellulose fuel since organic waste is the highest share of MSW. Usually, researchers use Di Blasi’s reaction rates to model a pyrolysis process of lignocellulose fuel [10]. However, the simulation results might be unreliable due to heterogeneity of MSW. That is why this research would find the kinetic of pelletized MSW.

This research would analyze kinetic characterization of pelletized MSW using thermogravimetric analysis (TGA). TGA is a powerful deformation tool commonly used in materials analysis [11]. There are researches that used TGA to determine thermal decomposition mechanism of organic wastes and MSW [12–16]. To perform kinetics analysis, there are many methods that can be used, but the method most often used is the Coats-Redfern method or call model fitting method. This method use an appropriate model of the integral function from various reaction mechanism [17,18]. Although many researches related to the kinetic characteristics of MSW have been conducted, the composition of MSW has unique variations in each region. In this study, which continues previous research [19], we examined the kinetics and thermal decomposition of MSW pellets using the composition of the waste entering the Bantargebang landfill from DKI Jakarta, Indonesia.

2. Material and methods

2.1. Material

The materials used are pellet from municipal solid waste with tapioca as binder. Composition of municipal solid waste simulated the composition of waste generation in Jakarta, which consist of 70% organic waste, 12% plastic, 10% paper and 8% leaves. Tapioca which one of favorite binder for mass production added 0%, 3%, and 12% in pellet production. Before used, tapioca flour diluted with water in a ratio of 1:4 and cooked.

2.2. Characterization of pellets

This study is a continuation of the previous paper[19]. In the previous paper, the physical characteristics of the MSW pellets have been described. Pellets have a diameter range of 7.8–8.2 mm with a length of 23.6–24.0 mm and a weight of 1.16–1.36 grams per unit of pellet. Other characteristics can be seen in Table 1.

| Binder Adding | Density (kg/m³) | Durability (%) | Moisture Content (%) | Hardness (kgF) | Caloric Value (kCal/kg) |
|---------------|----------------|----------------|----------------------|----------------|------------------------|
| 0%            | 490.9          | 0.704          | 5.19                 | 12.1           | 4360.84                |
| 3%            | 435.1          | 0.532          | 8.09                 | 10.4           | 3783.02                |
| 6%            | 383.9          | 0.686          | 13.21                | 10.0           | 3290.71                |

2.3. Thermogravimetric Analyzer (TGA).

Pellets are tested in Center for Materials Processing and Failure Analysis (CMPFA) University of Indonesia using Simultaneous Thermal Analyzer (STA) 6000 - Perkin Elmer. Approximately 10-15 mg of sample was put into TGA (STA 6000) and heated from temperatures 50 °C to 800 °C at heating rate 10 °C/min in N₂ atmospheres.

2.4. Coats redfern methods

Kinetics is the study of the dependence of chemical reactions on time and temperature. Material kinetics can be studied by measuring the properties of a material when heated (non-isothermal) or under
isothermal conditions [20]. In this process, there is a change in the sample weight which can be written by weight loss rate equation (1).

\[ \alpha = \frac{W_0 - W_t}{W_0 - W_f} \]  

(1)

Where \( \alpha \) is the conversion or weight loss rate, \( W_0 \) is the initial weight of the sample (mg), \( W_t \) is the weight of the sample at a given time (mg) and \( W_f \) is the final mass of the sample (mg). In isothermal conditions, the solid fuel decomposition rate is a linear function of the reaction rate constant (k) with the conversion function \( f(\alpha) \) as expressed in Eq. (2). However, in non-isothermal conditions, the solid fuel decomposition rate will be affected by the heating rate \( \frac{dT}{dt} \) or \( \beta \), so the equation may be define as in Eq (3).

\[ \frac{d\alpha}{dt} = kf(\alpha) \]  

(2)

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

(3)

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

(3)

The reaction rate constant is described in the Arrhenius equation as follows on Eq (4)

\[ k = Ae^{\left(\frac{E}{RT}\right)} \]  

(4)

Where \( A \) is the pre-exponential factor (min\(^{-1}\)), \( E \) is the activation energy (kJ/mol), \( R \) is the universal gas constant (8.314 Jmol\(^{-1}\)K\(^{-1}\)) and \( T \) is the absolute temperature (K). By substitution Arrhenius equation to solid fuel decomposition rate equation under non-isothermal conditions, gives on Eq (5).

\[ \frac{d\alpha}{dT} = \frac{A}{R} e^{\left(\frac{-E}{RT}\right)} f(\alpha) \]  

(5)

Equation (5) is known as the general equation of TGA curve [20]. Integration this equation, gives on Eq (6), where \( g(\alpha) \) is the integrated reaction model and this is dependent on the reaction mechanism followed by the solid fuel.

\[ g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T e^{\left(\frac{-E}{RT}\right)} dT \]  

(6)

Various reaction mechanism of \( g(\alpha) \) are listed in Table 2. Coats-Redfern Methods uses asymptotic series for the resolution of Eq (6), gives Eq (7).

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

(7)

Since asymptotic approximation used to solve integral equations, the number of \( \frac{2RT}{k} \ll 1 \), so this number is neglected [16,18] and gives the final equation for this method, shown in Eq (8).
\[ \ln \left( \frac{g(\alpha)}{T^2} \right) = \ln \left( \frac{AR}{\beta E} \right) - \frac{E}{R T} \] (8)

By linear fitting of \( \ln \left( \frac{g(\alpha)}{T^2} \right) \) versus \( \frac{1}{T} \) for each reaction mechanism, the reaction order can be achieved. Energy activation (E) determined from the slope and pre-exponential factor (A) determined from the intercept of linear fitting equation. The highest coefficient of determination \( (R^2) \) among linear fittings represent a possible model of the reaction mechanism that occurs.

**Table 2.** Expressions of \( g(\alpha) \) based on various reaction mechanisms [18,21]

| Reaction Mechanism                        | Symbol | \( g(\alpha) \)                        |
|-------------------------------------------|--------|----------------------------------------|
| Nucleation reaction models                |        |                                        |
| Avrami-Erofè (n=2)                        | A2     | \([-ln(1 - \alpha)]^{1/2}\)            |
| Avrami-Erofè (n=3)                        | A3     | \([-ln(1 - \alpha)]^{1/3}\)            |
| Avrami-Erofè (n=4)                        | A4     | \([-ln(1 - \alpha)]^{1/4}\)            |
| Power law                                 | P2     | \( \alpha^{1/2} \)                     |
| Power law                                 | P3     | \( \alpha^{1/3} \)                     |
| Power law                                 | P4     | \( \alpha^{1/4} \)                     |
| Phase boundary reaction models            |        |                                        |
| 2D, shrinking cylinder                    | R2     | \( 1 - (1 - \alpha)^{1/2} \)           |
| 3D, contraction of sphere                 | R3     | \( 1 - (1 - \alpha)^{1/3} \)           |
| Diffusion controlled models               |        |                                        |
| One-dimensional diffusion                 | D1     | \( \alpha^2 \)                         |
| Two-dimensional diffusion, cylindrical symmetry | D2     | \( \alpha + [(1 - \alpha) \times \ln(1 - \alpha)] \) |
| Three-dimensional diffusion, spherical symmetry (Jander) | D3     | \( 1 - (1 - \alpha)^{1/3} \) \] ^2 |
| Three-dimensional diffusion, cylindrical symmetry | D4     | \( 1 - \frac{2\alpha}{3} - (1 - \alpha)^{2/3} \) |
| Chemical reaction models                  |        |                                        |
| First order                               | F1     | \( -ln(1 - \alpha) \)                  |
| Second order                              | F2     | \( [(1 - \alpha)^{-1} - 1] \)           |
| Third order                               | F3     | \( [(1 - \alpha)^{-2} - 1] /2 \)        |

### 3. Results and Discussion

#### 3.1. Thermal decomposition

**Figure 1** shows the results of thermo gravimetric (TG) analysis and derivative of thermo gravimetric (DTG) analysis for pellet of municipal solid waste in various binder composition. Based on **Figure 1**, the thermal behaviour between various binders composition have a same trends and range of peak temperature [16].

The TG curve shows three main stage of degradation. First stage in temperature less than 200 °C is evaporation of moisture content and highly volatile materials by 4% - 7%. The second stage in temperature ranges 200 °C - 400 °C is degradation of lignocellulose biomass by 33% - 46%. The third stage in temperature 400 °C - 500 °C is plastic degradation and hemicellulose degradation by 8% - 11%. The residue after 800 °C is ranging from 28% - 50%. The activation energy (E) is presented on Table 3.
Figure 1. TG and DTG curves of various pellets sample.

Table 3. Calculation of activation energy (E) and pre-exponential factor (A).

|      | 0% | 3% | 6% |
|------|----|----|----|
| R²   |    |    |    |
| E    |    |    |    |
| A    |    |    |    |

Peak 1 (Temperature 200 °C – 400 °C)

|      | R² | E   | A   |
|------|----|-----|-----|
| A2   |    | 0.9343 | 10.67 | 7.26E-03 | 0.9516 | 11.71 | 9.57E-03 | 0.9549 | 11.86 | 1.01E-02 |
| A3   |    | 0.8152 | 4.03  | 7.64E-04 | 0.8765 | 4.73  | 1.01E-03 | 0.8860 | 4.83  | 1.06E-03 |
| A4   |    | 0.1893 | 0.71  | 7.12E-05 | 0.4563 | 1.24  | 1.36E-04 | 0.4974 | 1.31  | 1.47E-04 |
| P2   |    | 0.8561 | 6.65  | 1.67E-03 | 0.9039 | 7.72  | 2.36E-03 | 0.9098 | 7.77  | 2.40E-03 |
| P3   |    | 0.3351 | 1.35  | 1.32E-04 | 0.5807 | 2.07  | 2.30E-04 | 0.5995 | 2.10  | 2.35E-04 |
| R2   |    | 0.9610 | 26.33 | 1.44E-01 | 0.9712 | 28.45 | 2.28E-01 | 0.9734 | 28.63 | 2.41E-01 |
| R3   |    | 0.9637 | 27.70 | 1.42E-01 | 0.9728 | 29.80 | 2.22E-01 | 0.9748 | 30.02 | 2.37E-01 |
| D1   |    | 0.9658 | 54.33 | 6.69E+01 | 0.9747 | 58.60 | 1.57E+02 | 0.9765 | 58.78 | 1.66E+02 |
| D2   |    | 0.9701 | 59.11 | 1.20E+02 | 0.9777 | 63.35 | 2.76E+02 | 0.9793 | 63.65 | 3.02E+02 |
| D3   |    | 0.9736 | 64.64 | 1.15E+02 | 0.9797 | 68.83 | 2.58E+02 | 0.9812 | 69.29 | 2.93E+02 |
| D4   |    | 0.9715 | 60.94 | 4.34E+01 | 0.9785 | 65.17 | 9.90E+01 | 0.9802 | 65.52 | 1.09E+02 |
| F1   |    | 0.9676 | 30.58 | 9.61E-01 | 0.9746 | 32.66 | 1.48E+00 | 0.9761 | 32.97 | 1.61E+00 |
| F2   |    | 0.9696 | 40.47 | 1.46E+01 | 0.9715 | 42.41 | 2.11E+01 | 0.9714 | 43.05 | 2.49E+01 |
| F3   |    | 0.9632 | 52.11 | 3.27E+02 | 0.9611 | 53.85 | 4.38E+02 | 0.9595 | 54.90 | 5.74E+02 |

Peak 2 (Temperature 400 °C – 500 °C)

|      | R² | E   | A   |
|------|----|-----|-----|
| R2   |    | 0.7772 | 2.68  | 1.54E-04 | 0.5245 | 2.69  | 1.52E-04 | 0.4305 | 2.90  | 1.72E-04 |
| R3   |    | 0.8959 | 5.07  | 3.28E-04 | 0.7184 | 5.04  | 3.18E-04 | 0.6312 | 5.36  | 3.61E-04 |
| D1   |    | 0.9260 | 6.00  | 6.94E-04 | 0.8399 | 6.14  | 7.12E-04 | 0.7545 | 6.15  | 7.23E-04 |
| D2   |    | 0.9650 | 12.28 | 3.06E-03 | 0.9020 | 12.37 | 3.03E-03 | 0.8496 | 12.56 | 3.24E-03 |
| D3   |    | 0.9749 | 22.06 | 1.03E-02 | 0.9193 | 21.99 | 9.73E-03 | 0.8789 | 22.62 | 1.14E-02 |
| D4   |    | 0.9703 | 15.44 | 1.71E-03 | 0.9105 | 15.48 | 1.66E-03 | 0.8639 | 15.81 | 1.83E-03 |
| F1   |    | 0.9484 | 10.69 | 6.92E-03 | 0.8394 | 10.57 | 6.51E-03 | 0.7778 | 11.16 | 7.73E-03 |
| F2   |    | 0.9684 | 34.18 | 2.90E+00 | 0.9008 | 33.57 | 2.44E+00 | 0.8608 | 35.51 | 3.70E+00 |
| F3   |    | 0.9709 | 65.34 | 3.22E+03 | 0.9117 | 64.07 | 2.32E+03 | 0.8763 | 67.85 | 4.93E+03 |
3.2. Activation Energy
Activation energy is minimum amount of energy that is required to activate atoms or molecules to a condition in which they can undergo chemical transformation or physical transport. Table 3 shows the calculation of activation energy in various reaction mechanism for peak 1 or temperature range 200 °C - 400 °C and for peak 2 or temperature range 400 °C - 500 °C.

Based on Table 3, variations of binder composition do not affect the value of the activation energy. The activation energy value of pellets is in the range 64.64 kJ/mol - 69.29 kJ/mol for peak 1 and the range 21.99 kJ/mol - 22.62 kJ/mol for peak 2. Pre-exponential factor has a value of 1.15x10^2 min^(-1) - 2.92x10^2 min^(-1) and 9.73x10^3 min^(-1) - 1.03x10^3 min^(-1), respectively.

3.3. Kinetic reaction model.
There are four major groups of reaction mechanisms calculated in this study, namely nucleation reaction models (A2, A3, A4, P2, P3, and P4), phase boundary reaction models (R2 and R3), diffusion controlled models (D1, D2, D3, and D4) and chemical reaction models (F1, F2, and F3). In this calculation the reaction mechanism which gives a negative activation energy value will be ignored [22]. The results show that the reaction mechanism that comes closest to the process that occurs is the Three-dimensional diffusion, spherical symmetry (Jander) mechanism (D3).

4. Conclusion
In this study, kinetics and thermal decomposition of municipal solid waste pellet were investigated using thermogravimetric analyzer. The results shown that thermal decomposition were divided in three stage, such as evaporation of moisture content, degradation of lignocellulose, and plastic degradation and hemicellulose degradation. There is no significant different due to addition of binder in thermal decomposition. In parallel results the activation energy values in various binder has 64.63 kJ/mol and 22.05 kJ/mol for 0 %, 68.83 kJ/mol and 21.99 kJ/mol for 3 %, and 69.29 kJ/mol and 22.62 kJ/mol for 6 % at temperature ranges between 200 °C – 400 °C and 400 °C – 500 °C respectively in typical three dimensional diffusion (D3) mechanism kinetic reaction model.

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