Kinetics and thermodynamics study of organic waste combustion using thermogravimetric analysis

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Abstract. Urban waste in Malang becomes a significant problem due to its increasing volume and negative impact on the environment. An incineration process offers a solution to reduce waste. The thermochemical method is one of the routes to reduce waste volume effectively. This paper discussed the combustion of organic waste with thermogravimetric analysis in a non-isothermal mode in which temperature escalated from 25 to 1000°C by a heating ramp of 20°C/min. The process of burning organic waste is divided into three steps of decomposition, namely the step of moisture loss, decomposition and combustion of volatile matter and fixed carbon, and the final step of ash decomposition from the residual matters. The kinetic parameters calculated using the Coats-Redfern method at the main combustion step, resulting in activation energy of 99.37 kJ/mol and a pre-exponential factor of 6.01E+08/s.

1. Introduction
The increasing population and living standard impact household needs and consumption, which increases the municipal waste production rate [1–5]. It influences the environment since municipal solid waste not only holds in storage and landfill areas but also produces disturbing odors and gas emissions. Continuous stockpiling impacts the contamination of water sources in the ground [5,6]. With a population of around 894,653, Malang can generate significant amounts of waste, roughly 660 tons daily, consisting of household and industrial waste [7]. Municipal waste includes organic and synthetic waste, where synthetic waste is difficult to degrade by the environment [8]. The proper incineration process can prevent the accumulation of environmental waste by converting municipal waste into energy through thermochemical processes [9–11]. Reducing waste mass and volume by 70-90% can be reached by means of incineration [2]. Therefore, converting waste into valuable energy through the combustion process is a great challenge that must be in-depth studied with a deliberate effort to generate significant energy and decrease the environmental issue.

Combustion technology can be well perceived by identifying the kinetics parameters. A popular technique for studying combustion kinetics is thermogravimetric analysis (TGA) [8]. Azam et al. [12] examined the kinetic combustion of solid waste by applying four isoconversional methods (Friedman, Kissinger-Akahira-Sunose (KAS), Vyazovkin, and Flynn-Wall-Ozawa (FWO)), and the results were compared with low-rank coals. They showed that for solid wastes, altogether, isoconversional methods have almost the same trends of activation energy in the selected conversion zones (0.1-0.6 and 0.7-0.9). As for coal, the Friedman model showed a lower and inconsistent activation energy value compared to
the other selected isoconversional methods. Phasee & Areeprasert [13] have used hydrothermal treatment (HTT) to produce solid fuel from municipal solid waste (MSW), then it was analyzed by thermogravimetric technique. It was reported that the mass loss of raw-MSW by 56% occurred at the combustion temperature of 200-380°C, which was associated with organic and paper waste. In addition, the kinetic parameter analysis reported that HTT in the municipal waste combustion (MSW) process could increase the value of activation energy. The findings of this study can open a perspective of converting waste into environmentally friendly energy and provide an alternative option for waste management policies.

This research intended to determine the decomposition of organic waste combustion with thermogravimetric analysis, evaluate its combustion kinetics using the Coats-Redfern method as recommended by [14] and analyze the thermodynamic parameters.

2. Materials and method

2.1. Material preparation
Organic waste was accumulated collectively from five landfill sites in the city of Malang, including Brantas, Comboran, Merjosari, Tanjung, and Tidar. Ten types of organic waste included coconut shells, beans, dry leaves, straw, corn husks, peanut shells, banana peels, wood husks, coconut fibers, and corn cobs. They were sun-dried for two weeks and were cut into small particles by scissors and mashed. In order to equalize the size, the samples were filtered with a mesh size of 40. Then, the waste was mixed with a mass ratio of 1. The organic waste sample was stored later in a desiccator.

2.2. Thermogravimetric analysis
The characteristics of organic waste combustion were studied with a thermogravimetric analyzer (TG/DSC1 of Mettler Toledo Instrument). For each test, 10 mg of organic waste sample was poured into the Al2O3 crucible and then put into the TG furnace. In this combustion experiment, the atmospheric air was used with a flow rate of 100 ml/min. The heating escalation in the furnace was set at a rate of 20°C/min, and it was initiated from room temperature (25°C) and was completed at 1000°C. A thermogravimetric (TG) and derivative thermogravimetric (DTG) graphs were achieved during the testing process. Any mass losses were recorded based on time and temperature.

2.3. Kinetics method
The material experienced thermal degradation during the combustion process, and its degraded fraction presented as conversion (α), is defined as:

\[
\alpha = \frac{m_0 - m_t}{m_0 - m_f}
\]

where \(m_0\) is the initial mass of material; \(m_t\) is the mass at a time (t) and \(m_f\) is the final mass of the material. The rate of conversion denoted as \(\frac{da}{dt}\), expressed as:

\[
\frac{da}{dt} = kf(\alpha) = A e^{-\frac{E}{RT}} f(\alpha)
\]

where \(k\) is a temperature-dependent rate constant, and \(f(\alpha)\) is the temperature-independent reaction model. In the non-isothermal studies with heating rate \(\beta = \frac{dT}{dt}\), Equation (2) becomes:

\[
\frac{da}{dT} = \frac{A}{\beta} e^{-\frac{E}{RT}} f(\alpha)
\]

where \(E\) is the activation energy, \(A\) is the pre-exponential factor, \(R\) is the ideal gas constant, and \(T\) is the absolute temperature. By considering the \(n\)-order reaction, \(f(\alpha) = (1 - \alpha)^n\), thus Equation (3) converted to be:

\[
\frac{da}{(1-\alpha)^n} = \frac{A}{\beta} e^{-\frac{E}{R}} dT
\]
Equation (4) is the primary reference in calculating the kinetic parameters based on thermogravimetric (TG) graph data.

2.4. Thermodynamic parameters

The thermodynamic parameters could be determined based on the kinetic parameters obtained. The respective change in Gibbs free energy (ΔG), the change in entropy (ΔS), and the change in enthalpy (ΔH) were calculated based on the following equation:

$$\Delta G = E + R.Tm.\ln\left(\frac{k_B.Tm}{h.A}\right)$$  \hspace{1cm} (5)

$$\Delta H = E\alpha - R.T$$  \hspace{1cm} (6)

$$\Delta S = \frac{\Delta H - \Delta G}{Tm}$$  \hspace{1cm} (7)

where $k_B$ is the Boltzmann constant ($1.381 \times 10^{-23}$ J/K), $h$ is the Plank constant ($6,626 \times 10^{-34}$ J/s), and $Tm$ is the peak temperature on the DTG graph.

3. Results and discussion

3.1. Thermal characteristics

The thermal characteristics of organic waste combustion with a constant heating rate at 20°C/min in atmospheric air were depicted in the form of TG and DTG graphs, as shown in Figure 1. The graph of mass loss rate versus time (DTG) clearly showed three steps of decomposition in organic waste combustion. In step I, which occurred in the temperature range of 25-139°C, indicated the initial step of the combustion process was associated with moisture loss. Step II (139-601°C) was the main step of the decomposition and combustion of volatile matter and fixed carbon from organic waste, characterized by a fast mass degradation rate [14], with a significant mass loss of 63%. Step II was then divided into two zones. Zone I was the decomposition of organic waste characterized by a peak of DTG at a temperature of 294°C [13]. Zone II was the decomposition of coconut shell waste components characterized by the highest peak of DTG at a temperature of 339°C [15]. Step III (601-998°C) was the final step in the decomposition process of ash during the combustion process, accompanied by the oxidizing of the small amount of the remaining char from the previous step. Thus, it reduced the weight of biomass.

![Figure 1. TG and DTG combustions of organic waste](image-url)
3.2. Evaluation of kinetic parameters

Table 1 showed the temperature characteristics of organic waste combustion. In the step of main decomposition (Step II), the kinetic parameters were evaluated through the Coats-Redfern fitting model recommended by Acikallin [16].

Based on the integral of Equation (4), and in order to find an exact analytical solution, the equation is made simpler by bearing in mind that $2RT/E \ll 1$ so that it becomes Equation (8):

$$\ln g(\alpha) = -\frac{E}{RT} + \ln \left(\frac{AR}{\beta E}\right)$$

where, if value;

$n = 1$, then $g(\alpha) = -(\ln (1 - \alpha)/T^2)$,

$n \neq 1$, then $g(\alpha) = \{1 - ((1 - \alpha)(1 - n))/((1 - n)T^2)\}$.

| Step | Characteristics of temperature |
|------|-------------------------------|
|      | $T_i$ (°C) | $T_{max}$ (°C) | $T_f$ (°C) | $M_{max}$ (%/s) | Mass loss (%) |
| I    | 25 | 66.392 | 139.432 | -0.059322 | -10.39 |
| II   | 139.432 | 339.31 | 601.674 | -0.170196 | -73.29 |
| III  | 601.674 | 672.745 | 998.341 | -0.010625 | -86.84 |

Figure 2. $R^2$-n combustion of organic waste in step II with the Coats-Redfern method

Figure 2 showed the $R^2$-n plot in finding the highest correlation coefficient ($R^2$) that is correlated with the most proper $n$ value. The highest $R^2$ value of 0.989 was found at the selected $n$ value of 3.23. This $n$ value was then used to obtain the plot of $\ln g(\alpha)$ vs. $(1/T)$ to obtain the slope (-$E/R$) and intercept [$\ln ((AR)/(\beta E))$] as shown by Figure 3, in the conversion range of alpha $\alpha$ values which were calculated between 0.05-0.95.
As presented in Table 3, the average activation energy value of organic waste combustion at a heating rate of 20°C/min, which was analyzed with the Coats-Redfern method in the main decomposition step, was 99.37 kJ/mol. The associated pre-exponential factor value was 6.01E+08/s. The results indicated that the activation energy of organic waste was greater than a mixture of synthetic waste and microalgae *Spirulina platensis* by 57.77 kJ/mol [17] and coal by 34 kJ/mol [18]; however, this value was smaller than corn silk biomass by 207.37 kJ/mol [19]. Sukarni et al. [20] stated that the smaller the value of activation energy is, the less energy needed by a particle to start reacting will be. Thus, this results in the activation energy of organic waste becoming the essential data for proper designing the power generation system.

### Table 2. The kinetic parameters according to the Coats-Redfern method

| Step | Trendline equation | $R^2$ | Kinetic parameters |
|------|--------------------|-------|--------------------|
|      | $y = -11952x + 7.8297$ | 0.989 | $E_a$ (kJ/mol) | $A$ (1/s) | $n$ |
| II   |                    |       | 99.37            | 6.01E+08  | 3.23 |

#### 3.3. Thermodynamic parameters

Table 3 showed the thermodynamic parameters of organic waste combustion in the main decomposition step at the heating rate of 20°C/min. The values of $\Delta H$, $\Delta G$, $\Delta S$ were 96.85; 150.10 and -0.087 kJ/mol, respectively. The $\Delta G$ showed the magnitude of energy change in the system. Besides, $\Delta S$ showed the change in the degree of irregularity in the system, and $\Delta H$ represented the difference in the energy of the reagent and the activated complex for the dissociation of chemical bonds in the reagent.

### Table 3. Thermodynamic parameters

| Step | $E_a$ (kJ/mol) | Log $A$ (1/min) | $\Delta H$ (kJ/mol) | $\Delta G$ (kJ/mol) | $\Delta S$ (kJ/mol) |
|------|----------------|-----------------|---------------------|---------------------|---------------------|
| II   | 99.37          | 8.778           | 96.58               | 150.10              | -0.087              |
4. Conclusion
The characteristics of organic waste combustion have been analyzed to find the kinetics and thermodynamic parameters. Thermal decomposition of organic waste combustion is divided into three steps: the step of moisture loss, followed by decomposition of volatile matter and fixed carbon. The final step of combustion indicates the ash decomposition during the combustion. The organic waste combustion at the heating rate of 20°C/min showed the activation energy value at the main step of decomposition (in the range of 139-601°C) by 99.37 kJ/mol. Overall, the organic waste in Malang has the potential to be converted into valuable energy by combustion processes.

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