Activation energy of domestic wastewater sludge in combustion process by using thermogravimetric analysis

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Abstract. The increasing demand of energy and environmental problem due to the consumption of fossil fuel has led the exploration of biomass fuel as an alternative energy. One of the potential biomass feedstocks that is available in Malaysia is Domestic Wastewater Sludge (DWS). In this study, DWS fuel characterization and the effect of experimental condition such as gaseous atmosphere, heating rate and particle size to the thermal behaviour of DWS has been carried out. In addition, kinetic parameter such as activation energy was determined by using the isoconversional model free kinetic method, Flynn Wall Ozawa (FWO) model. Furthermore, lower heating rate and smaller particle size of DWS produced more volatile gas (84.51%), resulted to low ignition temperature (209°C) and low burnout temperature (515°C). Higher volatile indicates that it can accelerate the ignition process. In addition, low ignition temperature and low burnout temperature reveal that DWS can be ignited easily and shorten the time for combustion process. Based on the finding, the average activation energy for combustion of DWS which is about 143.86 kJ/mol.

1. Introduction
Emissions of greenhouse gases from fossil fuels and an ever-growing demand for energy source and with a limited supply of fossil fuels are the current pressing global problems which need a sustainable solution. Biomass is one of the available sources of renewable energy that has become a great interest at the national and global level. Historically, biomass has been utilized by mankind since centuries ago when burned woods were used to cook and warm the environment [1]. The fossil fuel has become the world’s main energy source for the past few decades [2-4]. This is due to the high demands from industrialization and population growth are the factors that increase the consumption of fossil fuel. Nonetheless, biomass is still believed to be a viable option to reduce the dependency on the fossil fuel. It is found that the biomass energy is a sustainable, abundant and environmentally friendly energy source that available to explore [5]. At present, biomass-based energy is used in developing countries for direct consumption such as cooking, and in industrialized countries for conversion into secondary energy such as heat and biofuel [6-8]. Among all the biomass available in Malaysia, the waste derived from wastewater treatment plant namely Domestic Wastewater Sludge (DWS) is one of the less explored biomass energy sources as it has a huge potential as solid fuel for energy recovery. This potential biomass source is classified in the industry waste group and require high operational cost to dispose. Currently, the main disposal method for DWS that has been practice in Malaysia is by landfilling. However, most of the landfill have reach its capacity whereas the volume of DWS keeps increasing.
annually [6]. Therefore, converting this waste to biofuel by Thermochemical Conversion (TCC) process will reduce the disposal problem as well as contribution to a new source of energy.

However, the details study on the combustion characteristics and kinetics study are very important. Through this study, it can provide a useful information and important data about the characteristic of the biomass as its degradation during the TCC process. This can be achieved using Thermogravimetric Analysis (TGA), which is the most popular technique in thermal analysis studies [9-11]. TGA can be applied to study the thermal degradation of biomass as well as the reaction kinetic determination. However, the mechanism occurred during the analysis relies on the controlled variable and experimental condition. For example, the heating rate, physical properties of material and the ambient gaseous in which the reaction takes place, always have significant effect to the degradation process [12-19]. Therefore, it is important to study the factors affecting thermal behaviour of DWS. In this study, TGA was carried out in oxygen and nitrogen atmosphere to study the behaviour of DWS combustion.

2. Methodology

In this study, the sample of DWS was collected at the Universiti Teknologi Petronas (UTP) wastewater treatment plant. The sample of DWS was fully dried in an oven at temperature of 105 ºC for 24 hours. The dried sample was then crushed and sieved using to form a regular shape. The TGA analysis was performed by using Thermogravimetric Analyser (TGA) LABSYS Evo Setaram. In this research, non-isothermal experiment was practiced as the temperature in the TGA was increased from 30 ºC to 800 ºC. After 800 ºC, there is no significant effect on the thermal degrading has been observed which determine the temperature limit on this experiment. There are four different heating rates were observed in this study which are 5, 10, 15 and 20 K/min. This type of heating rate may reduce the mass transfer and temperature gradient effect [15]. In addition, the particle size of DWS was fixed at 0.425 mm.

Based on the previous researcher, Flynn-Wall-Ozawa (FWO) iso-conversional model free kinetic method normally used to calculate the activation energy as contribute to reliable and accurate result [15]. FWO model is implemented by using several experiment conditions of non-isothermal experiments at varies of heating rate as stated in equation (1) [9,15,16]:

\[
\ln(\beta) = \ln \left[ \frac{AE_a}{Rg(\alpha)} \right] - 5.33 - 1.052 \frac{E_a}{RT}
\]

Hence, a graph of \( \ln(\beta) \) vs \( 1/T \) is plotted and the determination of the activation energy can be calculated from the slope of the straight line produced in the plotted graph.

3. Results and discussion

The evaluation of activation energy of DWS combustion and pyrolysis were performed by kinetic analysis. This was done by using the FWO iso-conversional model free kinetic method. Based on this method, there are four different heating rates were studied. TG and DTG curves of DWS at four different heating rates in combustion process. Then, the temperature corresponding to conversion degrees at each heating rate, \( \beta \) was chosen. Subsequently, the curves of \( \ln(\beta) \) versus \( 1/T \) were plotted. Figure 1 show the linear fitting for TGA combustion. Based on the curves, it can be seen that the nine straight lines are produced denote nine conversion degree, \( \alpha \) was selected ranged from 0.1 until 0.9. In addition, the value of \( 1/T \) decreases with the increases the value of \( \alpha \) as the value of temperature directly proportional to the value of \( \alpha \). The four dots at each line represent four different heating rate which are 5, 10, 15 and 20 K/min. Based on the graph, the value of \( \ln(\beta) \) increase directly proportional to the value of the heating rates. However, there is different in gradient value for each \( \alpha \) which can be explain in details in figure 2.
Table 1 shows the gradient of FWO linear fitting, $m$, correlation coefficient, $R^2$ and the value of activation energy, $E_a$, under oxidative atmosphere. It can be observed that the smooth linearity of data can be proved by the straight line which is achieves $R^2$ above 0.9 for combustion which is gives an accurate value for activation energy, $E_a$. Lastly, the activation energy is calculated by using the FWO aforementioned equation.

**Table 1.** Slope of FWO linear fitting, correlation coefficient, $R^2$ and calculated activation energy, $E_a$.

| Combustion | Slope, $m$ | $R^2$ | $E_a$ [kJ/mol] |
|------------|------------|-------|-----------------|
| 0.1        | -16.92     | 0.9461| 133.77          |
| 0.2        | -16.04     | 0.9245| 126.92          |
| 0.3        | -17.52     | 0.9431| 138.35          |
| 0.4        | -20.07     | 0.9728| 158.62          |
| 0.5        | -26.42     | 0.9604| 208.71          |
| 0.6        | -31.05     | 0.9031| 245.42          |
| 0.7        | -20.04     | 0.9983| 158.67          |
| 0.8        | -21.21     | 0.9976| 167.74          |
| 0.9        | -27.12     | 0.9965| 214.43          |

Figure 2 displays the $E_a$ obtained for every conversion. In general, the activation energy $E_a$ obtained is different at each conversion. Therefore, a unique reaction mechanism at every degradation stage can be assumed. In addition, $E_a$ value and conversion are correlated and dependent upon each other due to a complex multistep mechanism that occurred in a solid state [1]. Similarly, Cheng et al. [2] stated that distribution value of $E_a$ is plausible during the whole decomposition process because thermal
decomposition is a sequence reaction that occurred simultaneous and continuously. This resulted to an individual value of $E_a$.

![Comparison of $E_a$ at each conversion for DWS TGA under $O_2$.](image)

**Figure 2.** Comparison of $E_a$ at each conversion for DWS TGA under $O_2$.

Activation energy value is slightly increase when the conversion increase for TGA pyrolysis. However, a slight drop of $E_a$ at conversion of 0.2 can be seen before a sudden rise took place at conversion around 0.5 and 0.6. The activation energy, $E_a$, reached its maximum value at conversion 0.6 reveal that high activation energy is required for devolatilization stage which occurred at around $T = 300 \, ^\circ C$ in TGA combustion. After a while, $E_a$ drop drastically at conversion 0.7 due to the completion of devolatilization process at 400 °C. The $E_a$ of DWS combustion slightly increased again because more energy is needed for char oxidation process. The average activation energy for combustion obtained in this study was 172.5 kJ/mol respectively.

4. Conclusion

Based on finding of this study, the average activation energy of DWS is low which is about 172.5 kJ/mol for combustion. Lower activation energy reveals that it has high reactivity and minimum energy required for the decomposition process is low.

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