A Non-isothermal Thermogravimetric Kinetic Analysis of Malaysian Sewage Sludge

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Abstract. Dewatered sewage sludge is one of the largest contributors of waste material in Malaysia and it indirectly elevates local environmental problems. Previous studies have indicated sewage sludge as a potential alternative fuel based on its higher heating values. To explore sewage sludge as an alternative solid fuel will not only address energy demand issues, it will also mitigate long term disposal problems related with the waste material. Further information on combustion characteristics of this material is required before any links to power generation applications can be established. In this work the combustion characteristics of Malaysian sewage sludge was studied by means of thermogravimetric analysis (TGA) under different heating rates (10, 20 30 and 40 K/min). Non-isothermal thermogravimetric data were used to assess the kinetics of the combustion of sewage sludge by the application of Ozawa–Flynn– Wall and Vyazovkin kinetic models. The average activation energies were found to be 82 and 79 kJ/ mol respectively. The average reaction order corresponding to sewage sludge combustion was 0.11.

1 Introduction

The treatment and disposal of domestic dewatered sewage sludge is slowly increasing the operation cost of waste water treatment companies due to increasing in population and this is especially critical in urban areas of Malaysia. There are numerous environmental and health risk issues associated with the current disposal route of treated domestic sewage sludge, in which if not mitigated will cause serious problems to the country. In 2007, the yearly feed-rate of domestic wastewater entering waste water treatment plants throughout the country was estimated at 4.9 million cubic meters results in an annual disposal cost of US$ 0.3 billion [1], [2]. Special consideration has to be given to the handling of DWS as it is laden with harmful pathogens that threaten the health of human beings [3]. Globally there are various options of managing DWS ranging from its disposal into landfills to various post processing techniques such as incineration, thermal treatment and direct use as fertilizers. To the authors' knowledge, there has been minimal effort in exploring the energy recovery options of the treated DWS produced at local treatment plants. Before embarking on the energy recovery option, it is important to gauge the suitability of DWS as fuel or energy source. Thermogravimetric analysis (TGA) is able to provide a rapid assessment of the fuel value and to determine at which temperatures the reaction starts and ends and can be used to measure the maximum reactivity temperature or total

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combustion time [4]. TGA can also be used to determine thermal degradation characteristics and kinetic parameters to provide general information on overall reaction kinetics [5].

In the available literature, analytical measurements using the TGA have been largely used to characterize the thermal decomposition of solid fuels such as coal [6] and different types of biomass. Shenet et al [7] investigated the combustion kinetics of four different wood based solid fuels under an oxidative atmosphere with TGA and found the respective mass loss and ignition characteristics. The thermal decompositions of palm kernel shell (PKS) and palm oil fronds (POF) using TGA under non-isothermal conditions have been widely studied and reported in numerous publications. Khan et al. [8] reported the activation energy, pre-exponential factor and order of reaction for a temperature range between 50 and 900°C using a heating rate of 20 °C/min. Other related studies investigated the co – combustion of sewage sludge with coal using TGA [3], [4], [6], [9]–[11]. In these studies, a wide range of variation in the values of the kinetic parameters and the TGA DTG characteristics were observed for sewage sludge. The large uncertainties in the results made it difficult to predict the kinetic parameters of sewage sludge from a variety of locations and thus suggested that further tests would be required to determine the kinetics parameters of samples which are dependent on process and environmental conditions. It is also found that, very few published research is available on the use of the iso-conversional (i.e., model-free) method to calculate the kinetic parameters of sewage sludge, which is recommended for obtaining reliable and consistent kinetic information [12]. Published research work on the characteristics and kinetic parameters of Malaysian sewage sludge through the use of TGA is also unavailable.

The objective of this paper is to fill in the research gap in characterization studies of sewage sludge using non-isothermal thermogravimetric kinetic analysis by applying the Ozawa–Flynn– Wall (Ozawa, 1965; Flynn and Wall, 1966) and the Vyazovkin (Vyazovkin, 1997) kinetic models, which, will allow the calculation of the activation energy and reaction order of sewage sludge combustion.

2 Experimental

The sewage sludge samples used in this study were collected from a mechanical waste water treatment plant in the city of Kuala Lumpur. The samples were first dried in an oven at 105°C to record the moisture content. Experimental procedures were carried out to measure the heating values and chemical compositions. The average values of the measured chemical and physical properties of the sludge samples are summarized in Table 1.

TABLE I.   PROPERTIES OF SLUDGE SAMPLES

Property	Proximate analysis (wt %)				Ultimate analysis (wt %)					Heating value (MJ/Kg)
	Moisture content	Volatile matter	Fixed carbon	Ash	Carbon	Hydrogen	Nitrogen	Sulfure	Oxygen	
Average	10	40	18	32	33	5	6	1.2	54.8	15.7

Samples of 10 mg each were analyzed in the TGA starting from room temperature to 850°C under an air flow. Four different heating rates, β, of 10 $Kmin^{-1}$, 20 $Kmin^{-1}$, 30 $Kmin^{-1}$, and 40 $Kmin^{-1}$ were chosen based on their suitability in homogeneous ignition and to minimize heat mass transfer effects as suggested by Sanchez et al [9]. One key feature of the TGA is its ability to determine the solid state reactions in a combustion process for which the mathematical descriptions are commonly defined in terms of their kinetic parameters, activation energy, E, and the Arrhenius parameter, A. An algebraic expression of the kinetic model for the solid state reactions related to the experimental data were previously proposed by many resources [3], [4], [9], [10], [13], as a function of the fractional conversion α, whereby $f(\alpha)$ can be written as:

$$\frac{d\alpha}{dt} = Ae^{-E/RT} f(\alpha)$$

(1)

The two common techniques used to find the kinetic parameters are Model Fitting for the identification of kinetic reaction models and Iso-Conversional i.e. model-free for which the rate of decomposition must follow Eq.(1) [9], [10] .The iso-conversional method is more widely used compared to the fitting models as it provides the ability to compute kinetic parameters without prefixing the reaction order [4], [10], [14].. In contrast, the model-fitting kinetic method generally involves the use of a single heating rate, which will result in a variation of activation energy values due to mass and heat transfer effects [9] . In the model free method the rate of heterogeneous solid-state reactions described in Eq. (1), as suggested by [4], [9]–[11], [14], can be transformed into a non-isothermal rate expression, as a function of temperature at constant heating rate β,

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = g(\alpha) = \frac{A}{\beta} \int_{T_o}^T e^{-E/RT} dT$$

(2)

The model free method requires input from a series of TG experiments which are carried out at different heating rates for at least three different β values as suggested by [3], [9], [10]. Based on Eq. (2), a considerable number of approaches to derive kinetic parameters have been developed. One approach suggested in[9]–[11] is to obtain the activation energy from dynamic data known as the Flynn, Wall and Ozawa approach which involves measuring the temperatures corresponding to fixed values of α from experiments at different heating rates. This is one of the integral approaches used to calculate the activation energy without prefixing the reaction order as gives by:

$$\ln(\beta) = \ln\left[\frac{AE}{Rg(\alpha)}\right] - 5.331 - 1.052\frac{E}{RT}$$

(3)

From Eq. (3), the activation energy, E can be estimated by plotting ln (β) vs. 1/T at different conversion values (α). Another method to calculate the activation energy was developed by Vyazovkin and Lesnikovick [4], [10], [11].

$$\ln\frac{\beta}{T^2} = \ln\left[\frac{RA}{Eg(\alpha)}\right] - \frac{E}{R}\frac{1}{T}$$

(4)

For each conversion value (α), the ln (β/T_2) vs. 1/T plot will give a straight line with an –E/R slope from which E is obtained as a function of the conversion. In order to determine the reaction order, Avrami's theory is used to describe the variation of the degree of conversion with temperature and heating rate, and results in the following equation[9] :

$$\ln\left[-\ln(1-\alpha(T)\right] = \ln A - \frac{E}{RT} - n\ln\beta$$

(5)

A plot of ln [-ln (1 – α (T))] vs. ln β, obtained at the same temperature from a number of isotherms taken at different heating rates, would yield straight lines whose slope will have the value of the reaction order or the Flynn–Wall–Ozawa exponent, n [9].

3 Results and discussion.

The TG curves obtained for the sewage sludge samples in this work at heating rates (β) of 10 K/ min, 20 K/min, 30 K/ min and 40 K/ min are shown in Fig. 1. The five different conversion percentages (α) (20, 30, 40, 50 and 60%) are also indicated in the figure. The heating rate (temperature scan rate) tended to slightly increase the start and end temperatures of each stage.The plots of log β vs. 1/T corresponding to the several conversion degrees are shown in Fig. 2. The trends in the plots allowed for the ctivation energy E to be calculated.
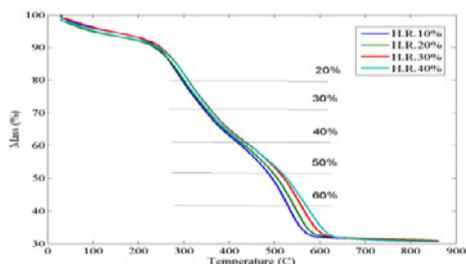
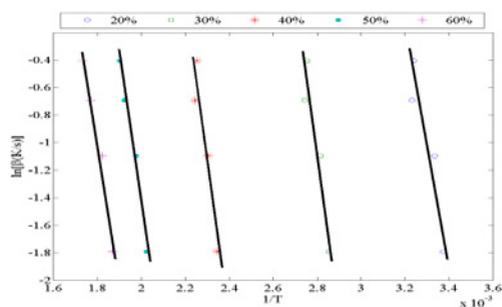Fig.1. TG curves corresponding to the combustion of sewage sludge at different heating rate

Fig.2. Curves of fitting to kinetic model proposed by Ozawa–Flynn–Wall

Fig. 3 shows the plot of ln ($\beta/T2$) vs. $1/T$ corresponding to the several conversion degrees (α). The slopes corresponding to linear fittings together with the corresponding correlation coefficients (R^2) and calculated activation energy using the Ozawa–Flynn–Wall and the Vyazovkin and Lesnikovick approaches are listed in Table 2. As it is listed in Table 2 the correlation coefficients obtained by the Vyazovkin and Lesnikovick is lower than the values obtained by the Ozawa–Flynn–Wall approach in all cases. The Ozawa–Flynn–Wall approach was also found to result in higher activation energy values compared to the Vyazovkin and Lesnikovick approach and this finding is consistent with earlier work by [4], [10]. The activation energies for both these approaches were estimated at 82 and 79 kJ/ mol, respectively. Otero et al [4], [10] calculated the activation energy for the combustion of two types of sewage sludge in Spain using the above mentioned approaches and found the values to be 138.1, 126.2 and 99.3 85.7 kJ/mol respectively. Separetely, M.E. Sanchez et al. reported the activation energy of sewage sludge, also in Spain, using the Ozawa–Flynn–Wall approach to be 143 kJ/mol [9]. Comparing previous work to the results presented in this paper, the activation energies of sewage sludge appear to vary significantly. This observation is believed to be related to the content and also to the structure of the samples which is a direct result of the process used in the sewage treatment plants [3] . Comparing coal which is a common power plant solid fuel with the sewage sludge used here, the activation energy of sewage sludge is noticeable higher than coal [4], [10], [14] and lower than animal manure (AM) and the organic fraction of municipal solid waste (OFMSW) [9]. To calculate the reaction order of the sewage sludge, the ln [-ln (1 –α (T))] vs. ln β relationship was plotted as shown in Fig. 4. The reaction order varied from 0.05 almost zero (zero reaction order) to 0.2, Sanchez et al. mentioned the reaction order is not constant throughout the reaction which is evidence of the multiple step process, according to their finding the reaction order of sewage sludge vary from 0.08 to around 0.23 with an average value of 0.14. This is higher than the reaction order carried out in this study 0.11 [9].

TABLE II.   SLOPES, CORRELATION COEFFICIENTS AND ACTIVATION ENERGIES OF SEWAGE SLUDGE

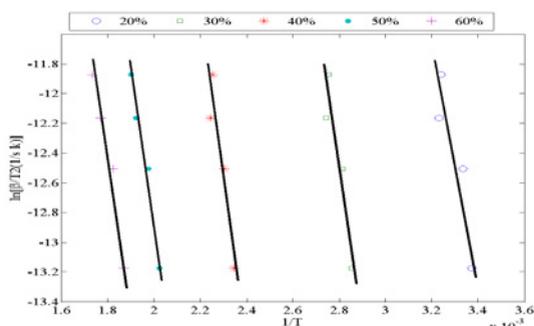| Conversion %	Vyazovkin and Lesnikovick model			Ozawa–Flynn–Wall model		
	Slope	R2	Activation energy (KJ/mol)	Slope	R2	Activation energy (KJ/mol)
20	7.4043	0.85	61.56305	8.01	0.87	63.30717
30	10.164	0.88	84.50858	10.879	0.89	85.98236
40	11.318	0.90	94.10351	12.253	0.91	96.8418
50	9.792	0.97	81.41558	10.812	0.98	85.45283
60	8.82	0.96	73.33389	9.931	0.97	78.48983

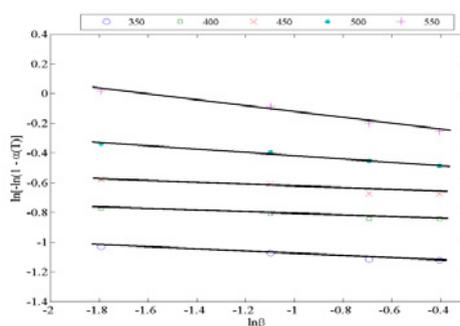Fig.3. Curves of fitting to kinetic model proposed by Vyazovkinand Lesnikovick

Fig.4. Curves of fitting corresponding to the reaction order n for different temperatures

4 Conclusions

The combustion of Malaysian sewage sludge was analyzed by the model-free method under non-isothermal condition. The activation energies obtained by the Ozawa–Flynn– Wall approach was relatively higher than the Vyazovkin approach. -The respective values are slightly lower than those reported in the literature for other locations but higher than coal. The reaction order was found to vary along the reaction pathway. The average reaction order corresponding to combustion of sewage sludge was 0.11. TG and DTG curves showed that sewage sludge exhibit three distinct reaction zones during the combustion corresponding to moisture content released and volatile matter and fixed carbon combustion.

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