A Novel Approach for Analyzing Thermal Properties of Sewage Sludge

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Abstract

A comparative analysis between combustion and pyrolysis of sewage sludge was studied using TG analysis. Non-isothermal kinetic analysis was used to evaluate the Arrhenius activation energy and the pre-exponential factor. The kinetic parameters were calculated using three isoconversional methods: a Friedman, a Kissinger-Akahira-Sunose, and a Flynn-Wall-Ozawa. The average values of activation energy for sewage sludge combustion are E_a = 151.01, 163.37 and 161.47 kJ/mol calculated by Friedman, FWO and KAS methods, respectively. Our comprehensive experimental approach rendered new information concerning the sludge's behavior during combustion and pyrolysis and determined the activation energy using three isoconversional methods for the studied samples.

Introduction

The sewage sludge production and disposal is increasing rapidly in Poland. The disposal is limited because of EU Directive 86/278/EC which prohibits the use of untreated sludge on agricultural land, unless it is injected or incorporated into the soil. The main problems are the high percentage of stored sewage sludge and a lack of installations for its thermal utilization. Thermal processes can be used for the conversion of large quantities of sewage sludge into useful energy. Processes of thermal utilization of sludge can be developed at existing installations (heating plants, power plants, or cement plants) or in newly built facilities. Thermal methods of sewage-sludge utilization should be preceded by dehydration and drying of sludge. A significant reduction in sludge quantity is achieved through digestion. Thermal processes allow for a significant reduction in the weight and volume of transformed sewage sludge [1]. There are several thermal technologies for utilizing municipal sewage sludge to obtain useful forms of energy, such as combustion, pyrolysis, gasification, and co-combustion processes [2-7]. Wether and Ogada have presented comprehensive review of sewage sludge combustion mechanism [2]. The knowledge of the combustion mechanisms of sludge is important; because the heterogeneous reactions of sewage sludge combustion process is more complex than the coal combustion. The combustion of solid residue occurs in the partial processes of drying, pyrolysis, ignition, combustion of volatile matter and residual char. Pyrolysis is one of the methods for the treatment of sewage sludge [5,6,8]. Pyrolysis process is the process through which organic substances are thermally decomposed in an oxygen-free atmosphere. Generally, pyrolysis demands the heating of the sludge in the absence of oxygen, which leads to production of carbon, tar and gases [5].

The elementary composition of sewage sludge and the contents of trace elements and inorganic compounds are very important factors that should be investigated in energy and environmental aspects. The municipal sewage sludge from waste water treatment plant contains a lot of organic matter and some heavy metals and pathogenic organisms. Chemistry of sewage sludge has a high diversity and variability caused by biochemical changes in time. The main combustible component in sewage sludge is carbon (c.a. 30 % C). Sewage sludge has a significantly high content of the volatiles, and also the trace metals, which are harmful substances because of gaseous emission and deposition in ashes. The content of trace elements in sewage sludge is the most important factor in deposit and thermal treatment. The concentration and composition of trace elements in sewage sludge depend on municipal activities. The heavy metals exist in the form of hydroxides, carbonates, phosphates, silicates, and sulphates.

Knowledge of the thermal behaviour (combustion and pyrolysis) and chemical composition of sewage sludge is necessary for design of energy units as well as the effective use as an alternative fuel. In this paper, studies of combustion and pyrolysis processes of sewage sludge have been performed. Thermal techniques, in particular thermogravimetric analysis (TG, DTG, DTA) allow to get information about thermal behaviour, the reactivity of sewage sludge in a simple and straightforward way [9-12] and to study kinetics [13-15]. The advantages of thermogravimetric analysis are its rapid assessment of the fuel value, the temperatures at which combustion starts and ends, and other characteristics like maximum reactivity temperature, ash amount and total combustion time. Thermal Analysis (TA) determines a set of methods for study of the selected physical properties of the substance under the temperature influence. Sometimes, simultaneously, the environment (pressure, atmosphere, chemical composition) can be changed. Thermogravimetry (TG) is a technique which monitors the sample mass as a function of temperature or time when the sample is subjected to a controlled temperature program. Differential thermogravimetry (DTG) is based on the rate of weight loss. DTG profiles make it possible to know, for example, the weight loss which is taking place at a temperature during the combustion process. Differential thermal analysis (DTA) enables measuring the thermal effects during the studied process. The obtained peaks correspond to

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exothermal or endothermal effects which allow to explain the thermal behaviour of fuel.

The most important applications of thermal analysis is kinetics calculations. The kinetic parameters such as activation energy and pre-exponential factor could be obtained by methods for analysing non-isothermal solid-state kinetic. Solid state kinetic data are the major interest in combustion processes. The kinetic studies of coal, oil and biomass (wood biomass, sewage sludge etc.) combustion has been studied by many research group [16-25]. In non-isothermal kinetics, the Friedman (F), Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) methods are the most often used isoconversional methods [16-18, 25].

Generally, the kinetic of reactions in solid-state are described by equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where α is conversion defined as follows:

$$\alpha = \frac{m_{i0}-m_a}{m_{i0}-m_f} \tag{2}$$

where: m_{i0} – the initial mass of the sample, m_a – the actual mass, m_f – mass after combustion.

The rate constant k is determined by the temperature and is given by the Arrhenius equation:

$$k(T) = A\,e^{-\frac{E_a}{RT}} \tag{3}$$

where R is gas constant (8.314 kJ/mol), T is the temperature in Kelvin and A (1/min) – pre-exponential factor, E_a – activation energy (kJ/mol) are constants which describe the properties of the material. The combination of these two equations (1) and (3) gives the fundamental expression (4) of analytical methods to calculate kinetic parameters, on the basis of the TG results:

$$\frac{d\alpha}{dt} = A\cdot f(\alpha)\cdot e^{-\frac{E_a}{RT}} \tag{4}$$

The expression of the function $f(\alpha)= (1-\alpha)$ and its derivative $g(\alpha) = -ln(1-\alpha)$ are used to describe solid-state first order reaction. The equation including reaction order n takes the form:

$$\frac{d\alpha}{dt} = A\cdot(1-\alpha)^n\cdot e^{-\frac{E_a}{RT}} \tag{5}$$

For non-isothermal TG experiments in which a sample is heated at a constant rate ($\beta = \frac{dT}{dt}$ – heating rate) the equation (5) is given by:

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\cdot f(\alpha)\cdot e^{-\frac{E_a}{RT}} \tag{6a}$$

The equation (6a) express the fraction of materials conversion during temperature change.

Integration of equation (6a) yields:

$$g(\alpha) = \frac{A}{\beta}\int_0^T e^{-\frac{E_a}{RT}}\,dT \tag{6b}$$

If x is given by E_a/RT and integration limits transformed equation (6b) becomes:

$$g(\alpha) = \frac{AE_a}{\beta R}\int_0^\infty \frac{e^{-x}}{x^2}dx = \frac{AE_a}{\beta R}p(x) \tag{7}$$

Friedman method is one of the isoconversion method. The method allows to obtain the temperature dependence of the rate constant. Applying logarithm of both sides of equation (6a):

$$\beta\frac{d\alpha}{dT} = A\cdot e^{\frac{-E_a}{RT}}f(\alpha) \tag{8}$$

gives:

$$\ln\left[\beta\frac{d\alpha}{dT}\right] = \ln[A_\alpha f(\alpha)] - \frac{E_{a,\alpha}}{RT_\alpha} \tag{9}$$

Hence, a plot of $ln(\beta d\alpha/dT)$ versus $1/T$ at each α gives E_a from the slope of the plot.

The Kissinger-Akahira-Sunose method is based on the equation:

$$\ln\left(\frac{\beta}{T_\alpha^2}\right) = \ln\left(\frac{A_\alpha R}{E_{a\alpha}g(\alpha)}\right) - \frac{E_{a\alpha}}{RT_\alpha} \tag{10}$$

The apparent activation energy can be obtained from a plot of $ln(\beta/T_a^2)$ versus $1/T$ for a given value of conversion α, where the slope is equal to $-E_\alpha/R$.

Flynn-Wall-Ozawa method is based on the following equation:

$$\ln\beta = \ln\left[\frac{0.0048E_a}{Rg(\alpha)}\right] - 1.0516\frac{E_a}{RT} \tag{11}$$

The activation energy can be determined by measuring the temperatures corresponding to fixed values of α from experiments at different heating rates.

The main aims of this study were estimating the behaviour of the three types of sewage sludge during combustion and pyrolysis processes using thermogravimetric analysis and the activation energy (Ea) according to conversion degree (α) using the Friedman, KAS and FWO isoconversional methods under non-isothermal conditions. The paper presents the experimental results which are important and novel with respect to other papers because it analyses combustion and pyrolysis and determines the activation energy using three isoconversional methods for each one of the three studied samples of sludge.

Experimental

In this experimental study, sewage sludge were used as renewable energy sources. The sewage sludge samples (SS1, SS2, and SS3) were obtained from Polish wastewater treatment plants. Sludge stabilisation treatment was done by anaerobic digestion, dehydration and thermal drying.

The elemental analysis and the calorific values of the studied samples are presented in Table 1. The properties, including volatile matter, ash, moisture content, heating value, and chemical composition, were determined according to the European standards. The Elemental Analyser Truespec CHN Leco was used to determine the carbon, hydrogen and nitrogen content. The LECO CHN628 is a combustion elemental C, H, and N instrument that utilizes only pure oxygen in furnace, ensuring complete combustion and superior recovery of the elements of interest. The sulphur content was analysed using an ICP-OES Vista Varian apparatus. The thermogravimetric analyses were conducted using a Mettler Toledo TGA/SDTA 851 apparatus. The TGA instrument was calibrated using indium, zinc and aluminium. Its accuracy was equal to 10^{-6} g. For the thermal analyses (TG/DTG), the samples were placed in alumina crucibles. Approximately 15 mg of sample were heated from ambient temperature to 800 °C at a constant rates: 5, 10, 20 and 40 °C/min in a 40 ml/min flow of air and 5, 10 and 20 °C/min of argon. The argon flow rate ensures an inert atmosphere on the sample

during studied pyrolysis process. Each sample had to be measured under exactly the same conditions, including temperature range, atmosphere, and heating rate. The TG curves for each of the samples were obtained as the outputs for combustion and pyrolysis processes. The TG curves presented the weight loss via temperature. The DTG curves (weight loss rate) was calculated ($dm/dt =$ $f(t)$, where m – mass sample, t - time).

Results and Discussion

The chemical composition (CHN), moisture and ash content as well as calorific value of sewage sludge samples are shown in Table 1. The sewage sludge samples have variable characteristics depending on the type of process used at the wastewater treatment plant. Typical raw sewage sludge has a moisture content of approximately 95 %, but these samples were analysed after thermal drying process. The dry sludge, on average, consists of 65 % organic and combustible components and 35 % ash. As can be observed, the chemical composition of studied sludge is typical. The sewage sludge samples have not very low carbon content ($28.9 \div 33.1$ %) and a high oxygen content comparing to other kind of renewable fuels. The hydrogen content is high in comparison with coal, however the sulphur content is lower, for studied samples in the range from 0.57 % to 1.1 %. Thus, SS3 sludge has the highest sulphur content (1.1 wt.%), while the SS1 sludge has the highest contents of hydrogen and nitrogen. Sludge can provide all nitrogen (N) and/or phosphorus (P) for plant growth. On the other side, high content of nitrogen in sewage sludge could be drawback during their combustion, on account of high NO_x emission. The sewage sludge is characterized by a much lower HHV than coal, because of the former's higher inorganic content. The calorific value of sewage sludge is determined by its moisture and ash contents. The drying process of sewage sludge and the depth of the waste treatment configuration have direct impact on calorific value. SS1 sample has the highest value (13.12 MJ/kg) of HHV for 32 % ash content.

Table 1
Ultimate and proximate analysis of sewage sludge samples (SS1, SS2, SS3), (M - moisture, A – ash, [a] calculated by difference, [b] high heat value) [26].

	% C	% H	% N	% S	% O
SS1	32.3	4.9	5.3	0.57	24.9
SS2	33.1	4.8	4.8	0.64	20.4
SS3	28.9	4.4	4.1	1.1	20.2
	% M	% A	HHV[b] MJ/kg		
SS1	19.1	32.0	13.12		
SS2	4.2	36.2	12.79		
SS3	5.3	36.0	12.24		

Figures 1 – 3 show differential thermogravimetric curves (DTG) obtained from combustion processes of studied sewage sludge samples by different heating rate

(5, 10, 20 and 40 °C/min). With the increasing heating rate the DTG curves have similar shape but with the different maximum. The most evident influence of heating rate is observed for SS1 and SS2 sludge samples. The percentage of weight loss is about 78 % at heating rate 10 °C/min, while at 5, 20 and 40 °C/min is 70 % for sewage sludge SS1 combustion. In the case SS2 sludge at 5 °C/min the lowest mass loss is observed (55 %), the effect of residue yield is not observed for other heating rate. DTG curves for sludge SS3 present typical heating rate influence (Fig. 3).
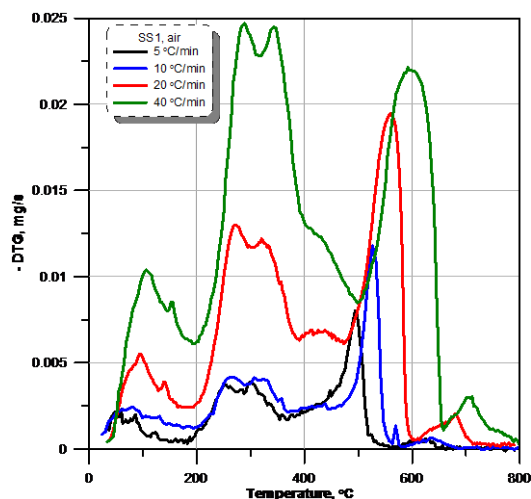

Fig. 1. DTG curves for sewage sludge SS1 at 5, 10, 20 and 40 °C/min in air atmosphere.
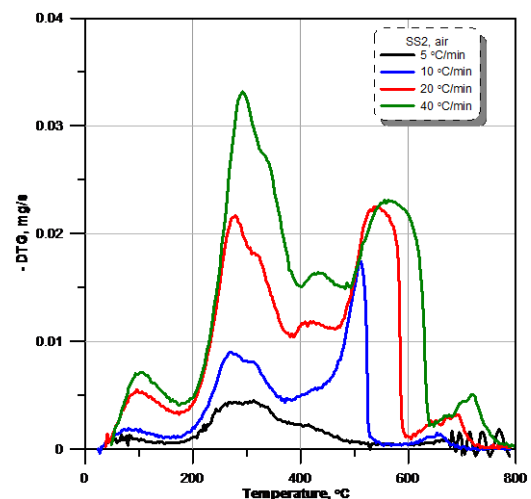

Fig. 2. DTG curves for sewage sludge SS2 at 5, 10, 20 and 40 °C/min in air atmosphere.

With the increasing of heating rate the studied processes end in higher temperatures. The influence of heating rate is evidently observed on DTG curves, peaks are wider and the rates of the decomposition are higher. From the obtained results we can conclude that sewage sludge combustion processes present can be divided into three stages for all sewage sludge samples: beginning of the decomposition, main decomposition and final stage.

The first stage, corresponding to the dehydration and drying process, takes place up to c.a. 200 °C. The first weight loss rate peaks result from vaporization of moisture.
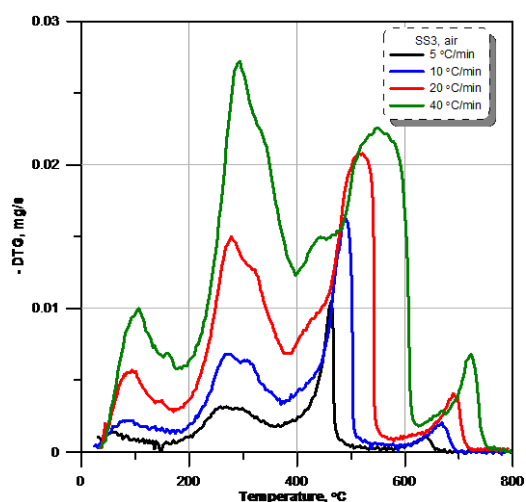

Fig. 3. DTG curves for sewage sludge SS3 at 5, 10, 20 and 40 °C/min in air atmosphere.

The non-isothermal kinetic study of sewage sludge's weight loss during the combustion and pyrolysis was performed. Differential and integral isoconversional methods, namely Friedman, KAS and FWO, were used to determine activation energies E_a at several conversion degrees (α) assuming one-step kinetics. Two sets of heating rates (β = 5, 10, 20, 40 K/min and β = 5, 10, 20 K/min) were used to examine kinetics of combustion and pyrolysis respectively.

Table 2
Values of activation energy Ea (average) obtained by Friedman, FWO, KAS methods for combustion and pyrolysis processes of studied sludge samples.

	Model		
	Friedman	FWO	KAS
	E_a, kJ/mol		
SS1			
Combustion	146.72	151.87	148.88
Pyrolysis	199.47	189.90	189.79
SS2			
Combustion	168.33	165.70	163.84
Pyrolysis	178.34	176.04	175.24
SS3			
Combustion	151.01	163.37	161.47
Pyrolysis	219.79	196.92	195.98

Methods used in analysis of measured data can be applied only within certain ranges of E_a/RT as dictated by Doyle's approximation of exponential integral i.e. following inequalities must hold: $20 \leq E_a/RT \leq 60$ for FWO method, $20 \leq E_a/RT \leq 50$ for KAS method, only those E_a's are considered in final calculations. Figures

10 - 13 present plots of $\ln(\beta d\alpha/dT)$, $\ln(\beta/T^2)$ vs. 1/T for different conversion degrees (α = 0.1 - 0.9) and correspond to the data from combustion and pyrolysis of the sewage sludge SS1. The activation energy is obtained from the slope of the line of appropriate conversion degree α. Mean values for E_a are summarized in Table 2. All methods used gave very close mean values for particular sample and considered process (see Table 2 and Figs 4 - 8 for SS1 sample). The activation energies of combustion are between 140 kJ/mol and 168 kJ/mol, whereas the pyrolysis activation energies are higher and include between 175 kJ/mol and 220 kJ/mol. This is consistent with the fact that we need more external energy for decomposition by pyrolysis, while we do not need this extra energy during combustion, because of energy released from exothermic reactions and overall weight loss by gasification and combustion. Evaluation of activation energies using KAS and FWO methods must be performed keeping in mind that approximations of temperature integrals hold only for reduced activation energy (E_a /RT) from finite interval ([20,50] for KAS and [20,60] for FWO). Data sets used for mean E_a computation were selected in order to fulfill mentioned restrictions. Conversion degrees used for computation of E_a mean value in case of Friedman method were the same as implied by the restrictions for KAS and FWO.
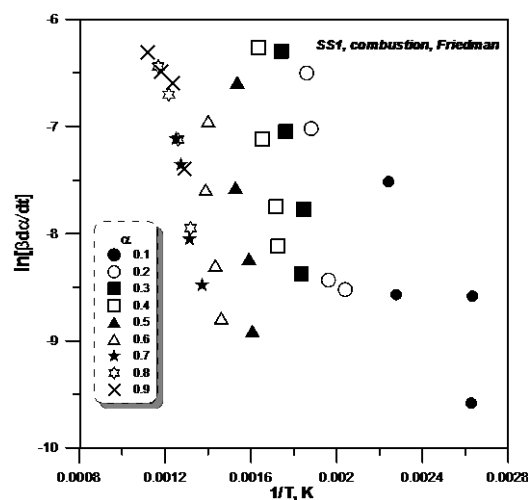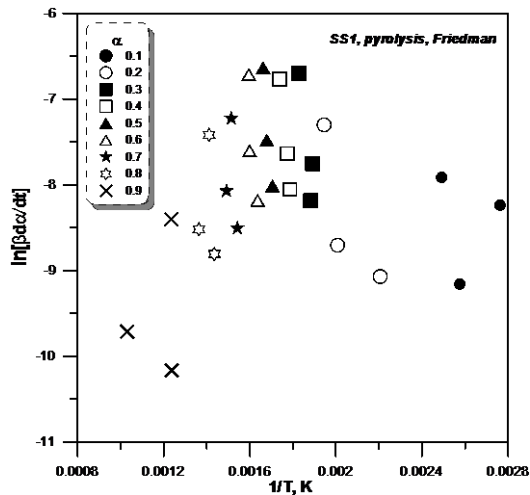

Fig. 4. Plots of fitting to kinetic model proposed by Friedman under non-isothermal conditions for various conversion corresponding to the combustion of sewage sludge SS1.

Conclusions

The thermal behavior and kinetic characteristic of three sewage sludge samples were studied of different heating rates (5, 10, 20 and 40 °C/min) under air and argon atmosphere. The effect of heating rate affected the TG/DTG curve profiles for each studied sludge samples. The maximum weight loss rate of samples obviously increase with the increase of heating rate. Some differences were found between combustion and pyrolysis process profiles of sewage sludge samples

which resulted from the chemical composition. The obtained data defined the temperature range of sewage sludge combustion and pyrolysis processes. The experimental data allowed to determine kinetic parameters to better understanding the thermal processes. The novelty of this study was applied the three non-isothermal isoconversional methods: Friedman, KAS and FWO to obtain activation energy values for combustion and pyrolysis of sewage sludge. E_a values obtained for combustion were lower than corresponding with pyrolysis. The obtained mean energy values are comparable with literature data.

Fig. 5. Plots of fitting to kinetic model proposed by Friedman under non-isothermal conditions for various conversion corresponding to the pyrolysis of sewage sludge SS1.
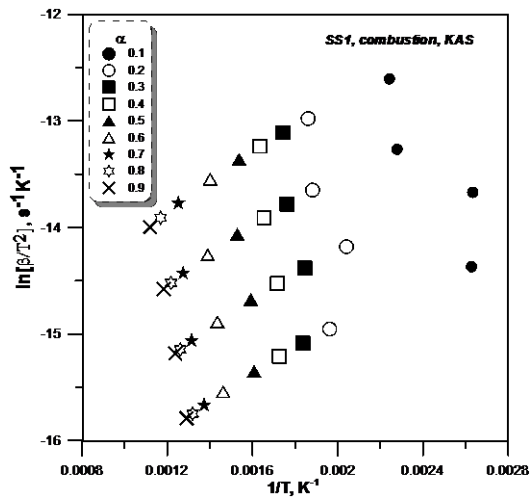

Fig. 6. Plots of fitting to kinetic model proposed by Kissinger-Akahira-Sunose under non-isothermal conditions for various conversion corresponding to the combustion of sewage sludge SS1.
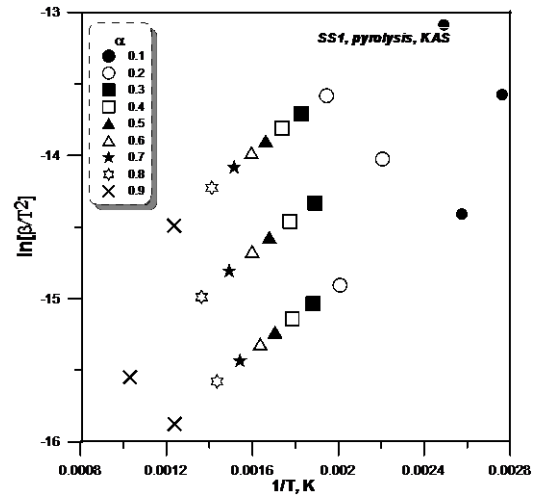

Fig. 7. Plots of fitting to kinetic model proposed by Kissinger-Akahira-Sunose under non-isothermal conditions for various conversion corresponding to the pyrolysis of sewage sludge SS1.
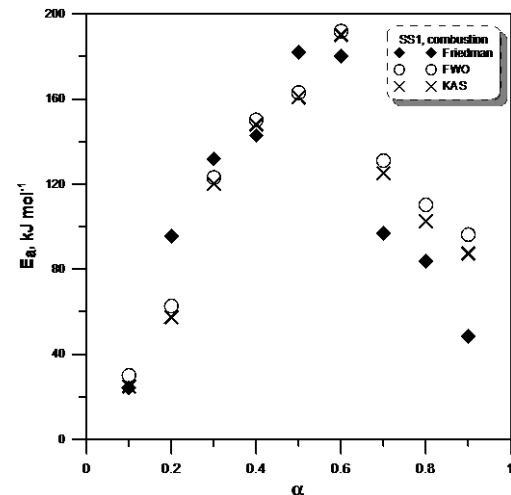

Fig. 8. Curves of the activation energy (E_a) via the degree of conversion (α) resulted using Friedman, FWO and KAS methods for the combustion of sewage sludge SS1.

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