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The Combustion Behavior and Kinetics of Dost (Oltu) Coal

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ABSTRACT

TGA/DTA analysis was used to have the knowledge on the combustion behavior and kinetics of Dost coal. The thermal analysis data were obtained at different heating rates (1, 2.5, 5, and 10 $Kmin^{-1}$) in air atmosphere from 298 to 1273 K. It is seen that when the heating rates increase, the ignition temperature and the burn out temperature increase. It is also determined the kinetic parameters by using two model-free methods, i.e. Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO). The activation energies (E_a) calculated by KAS and FWO methods were 81.38 and 87.82 kJ mol^{-1}.

Keywords: Coal, Combustion, Thermal Analysis, KAS-FWO

Dost (Oltu) Kömürünün Yanma Davranışı ve Kinetiği

ÖZ

Dost kömürünün yanma davranışı ve kinetiği hakkında bilgi elde etmek için TG/DTA analizi yapılmıştır. Termal analiz verileri hava atmosferinde 298 K'den 1273 K'e kadar farklı ısıtma hızlarında (1, 2.5, 5 ve 10 K dak^{-1}) elde edilmiştir. Isıtma hızı arttıkça tutuşma sıcaklığı ve sönme sıcaklıklarının da arttığı görülmektedir. Ayrıca serbest-model olan Kissinger-Akahira-Sunose (KAS) ve Flynn-Wall-Ozawa (FWO) metotlarını kullanarak kinetik parametreler tanımlanmaktadır. KAS ve FWO metotlarıyla hesaplanan aktivasyon enerjileri (Ea) sırasıyla 81.38 ve 87.82 kJ mol^{-1}'dir.

Anahtar kelimeler: Kömür, Yanma, Termal Analiz, KAS-FWO

1. Introduction

Coal is a complex combination of organic and inorganic matter. Coal is an important resource for providing around 22% of world energy supply. In our country, the main sources used for electricity production are natural gas, coal and renewable energy. 25 % of this production is obtained from coal (41% from natural gas, 33% from renewable energy) (Tahmasabi et al., 2013; Kök, 2007). According to the carbon and energy content, coals can be classified as peat, lignite, sub-bituminous, bituminous and anthracite. The composition and structure (the chemical and physical properties) of coal for oxidation process have an important role. Two coals having the same rank (carbon content) may exhibit significant differences in ways they undergo the oxidation process. The oxygen absorption of coal depends on coal rank and declines with a rising of this value (Wang et al., 2003).

Low-rank coal can be mixed with high-rank coal in order to provide the fuel needs of power plants and to prevent the disruption at the thermal performance (Pipatmanomai et

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al., 2009; Luxsanayotin et al., 2010). The combustion characteristics of a fuel before it is used in energy production must be determined. It plays an important role for safe and efficient operation at the power plants. There are different methods for the definition of the activity or combustion behavior of solid fuels, such as lignite, bituminous coals and petroleum coke. Especially, thermoanalytical tools such as differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and differential thermal analysis (DTA) play an important role among these methods (Kök, 2007; Jayaraman et al., 2013).

TGA is very useful in making effective predictions on the chemical and physical properties of coal. One person can easily analyze a large scale combustion system in TGA, it would demand a larger labor and much more money in other systems. It is advantageous in terms of precision and speed. TGA is an instrumental analysis that can be used to distinguish the burning profiles of different coals (Li, 2005).

Thermal analysis technique can also be used to determine and to compare the kinetic factors of solid-state decomposition reactions (especially, the combustion and the pyrolysis process of coal and woods) (Elbeyli et al., 2006; Sis 2009; Varol et al., 2010; Gil et al., 2010). There are many models to find kinetic parameters and to investigate the mechanisms of solid-state decomposition reactions thanks to the TG/DTG.

The Model-Free Kinetics method (i.e. KAS, FWO) applies an iso-conversional technique to calculate the effective activation energy as a function of the conversion extent of a chemical reaction.

1.1. KAS method

The method [Kissinger 1956; Akahira and Sunose 1971] consists of the terms as follows:

$$\ln\frac{\beta}{T^2} = \ln\left[\frac{AR}{E}\right] - \frac{E}{RT} + ln\frac{df(\alpha)}{d\alpha} \quad (1)$$

The activation energy, E, is calculated from the slope of the plot of $\ln\beta/T^2$ versus 1/T, at the given α, in constant heating rate conditions.

1.2. FWO method

The linear equation of the method [Flynn and Wall 1966; Ozawa 1965] is written as follows:

$$\log(\beta) = \log\left(\frac{AE}{g(\alpha)R}\right) - 2.315 - 0.457\left(\frac{E}{RT}\right) \quad (2)$$

This equation can be rearranged as Eq. 2:

$$\ln(\beta) = \ln\left(\frac{AE}{g(\alpha)R}\right) - 5.331 - 1.052\left(\frac{E}{RT}\right) \quad (3)$$

The activation energy, E, is calculated from the slope of lnβ versus 1/T plot.

The aim of this work is to determine the non-isothermal kinetic data and the combustion profile of Dost coal through thermal apparatus. The kinetics of thermal combustion of coal was obtained by applying separately both KAS and FWO methods to thermogravimetric data. The activation energy was calculated for combustion process.

2. Materials and Methods

2.1. Sample preparation

Coal used in this study was provided from Erzurum, Oltu. The samples were crushed and ground. A particle size of between 74-125 μm was used in experiments. The samples were stored in a vacuum dessicator to avoid from the oxygen and humidity of air. The elemental and chemical analyses of the samples were carried out and given in Table 1.

Table 1. The elemental and chemical analyses of the samples (on air dry basis)

Dost	C	H	N	S	Ash	Vol. mat	Fixed Carbon
%	28.17	2,92	1.27	2.20	49.57	42.23	8.20

2.2. Thermal analysis

Thermogravimetric analysis of the coal samples was performed on an NETZSCH STA 409 PC Luxx. The calcined α-Al_2O_3 powder as the standard reference was used. The samples (~20 mg, particle size) were put into a platinum crucible, and heated from 298 K to 1273 K at 1, 2.5, 5, 10 $Kmin^{-1}$ heating rates in air atmosphere. The data were used to determine the combustion kinetics.

3. Result and Discussion

It is seen that the coal has low fixed carbon and high ash at Table 1. The structure of the coal is not support the clean combustion conditions because of sulfur, nitrogen and ash content; the emissions of nitrogen oxides from this coal will not probably be minimal.

3.1. TG-DTG analysis

Figure 1, and 2 show the TG and DTG profiles of coal at heating rates of 1, 2.5, 5, and 10 K min^{-1} under air atmosphere from 298 to 1273 K. A higher heating rate has a short reaction time, and the temperature needed for the combustion of sample will be also higher. Thus, the combustion process shifts to right. High heating rates will reason simultaneous evolution and ignition of volatiles, but devolatilization will occur prior to ignition and combustion at lower heating rates. As a result, the ignition temperature and the burn-out temperature rise (Li, 2005).

As can be seen from Table 2, it can be obtained from DTG curves the important features as the ignition, peak-max, and the burn-out temperature. The ignition temperature indicates that the fixed carbon of coal starts to burn. The max-peak temperature (maximum weight loss rate) is the most important feature at the DTG profiles. The order of reactivity of coal is assessed primarily depending on the peak temperature. The coals with lower peak temperature can be easily ignited and burned (Marinova et al., 2009). When this temperature is higher, the coal is less reactive. It is seen that the max-peak and the burn out temperatures are affected by the changing of

the heating rate. The higher value of the burn out temperature depends on the higher heating rate. The high burn-out temperature has the meaning that the coal burns efficiently.

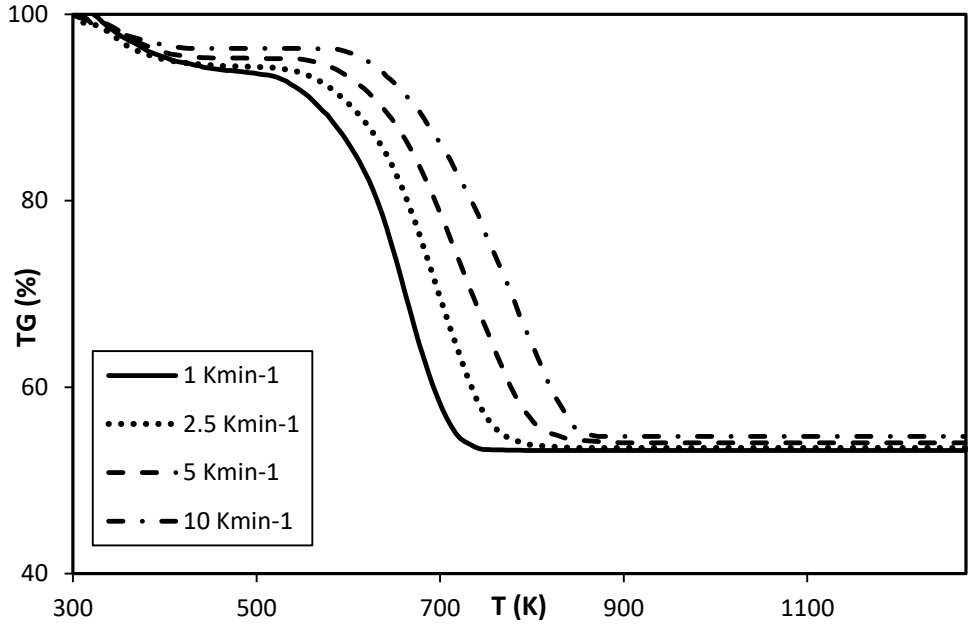

Figure. 1. TG curves of Dost coal at difference heating rates

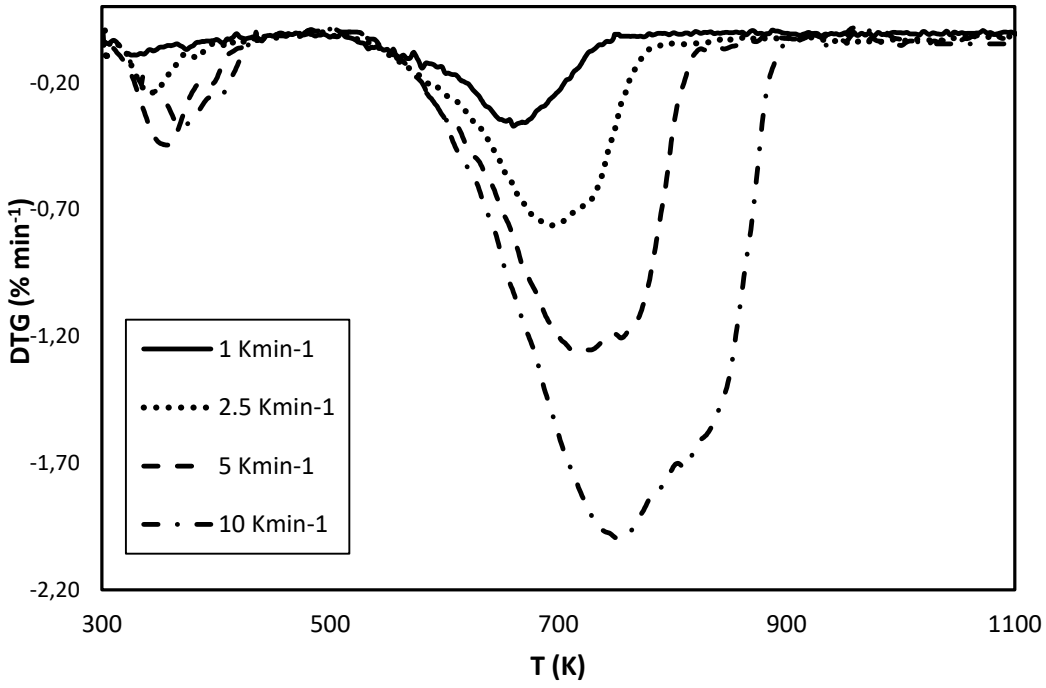

Figure 2. DTG curves of Dost coal

Table 2. Tsh, Tig, Tpeak-max, and Tb-out temperatures from DTG profile

Heating rate (K min-1)	Tig	Tpeak-max	Tb-out
10	239	480	630
5	258	456	600
2.5	293	424	527
1	308	389	480

The combustion characteristic of Dost coal consists of two step degradation at Figure 1. At first step, the release of moisture and light volatile compounds up to 512 K for 1 Kmin^{-1} occurs. The second step is the main combustion region in the range of approximately from 512 K to 1073 K for low heating rate (1 Kmin^{-1}). The fixed carbon burns in this state. Namely, the char is oxidized after volatiles are removed from coal.

2.3. Kinetic analysis

The combustion reaction is very complex. Since the coal consists from numerous components, it takes place the parallel, consecutive, and reversible reactions at the combustion process. The kinetic parameters on conversion can be obtained from TG-DTG data which includes mass loss curves obtained at different heating rates. As can be seen at Figure 3, the conversion value (α) at each temperature was obtained from the TG data.

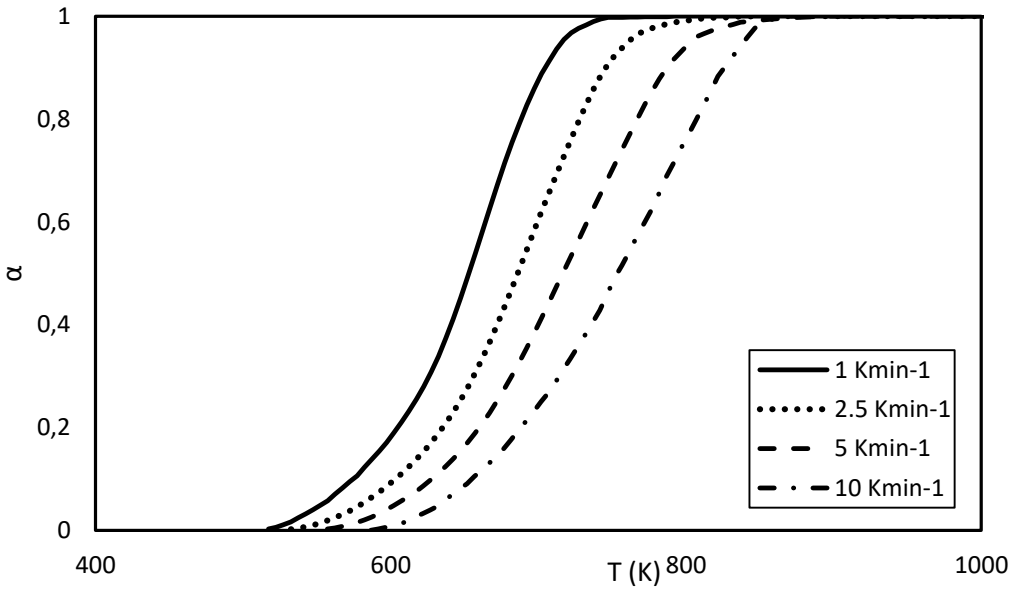

Figure 3. The conversion values versus temperatures

According to KAS method, the activation energies ($-E_a/R$) were obtained from the slope of the plot of ln (β/T^2) versus 1/T (Figure 4a) in between 0.1-0.9 values of α by using Eq.1. E_a and correlation coefficients (r^2) are tabulated in Table 3. Ea values were calculated by FWO method, too. The curves fit were graphed for ln β versus 1/T (Figure 4b). All activation energies have high correlation coefficient (r^2). It is mentioned above that TG plots have two step degradations. But, we selected only the main combustion region (second step degradation). It removes the moisture and light volatiles up to 512 K at first step. Due to the fact that we focus on the main combustion process, the kinetic parameters are not calculated for the first step as in the literature (Yorulmaz, 2009). This approach was applied for each heating rates.

There are the linear curves being rather parallel and having same slopes in Figure 4 (a, b), so the Ea values in all the range are close to each other. The average activation energy for the combustion process was calculated as 81.38 kJ mol^{-1} with the KAS method, and 87.82 kJ mol^{-1} with the FWO method in Table 3. Ea values obtained from these methods are very close to each other. The Ea versus conversion (α) was plotted in Figure 5.

It is seen that the activation energy has nearly a constant value; it changes within the narrow band, about 79±12 kJ mol^{-1}. In the literature, it is point out that the activation energy values for the combustion reactions of the different rank coals range between 54 and 92 kJ mol^{-1} (Kök, 2005). The activation energy calculated for combustion process of Dost coal having high ash and low rank is in this range.

3. Conclusion

In this study, the combustion behavior and kinetics of Dost (Oltu) coal having low fixed carbon and high ash were investigated. The simultaneous thermal analysis (TG-DTG) methods were used to determine the burning profile of coal at the four different heating rates from 298 to 1273 K. While at the same time and in the same temperature region a higher heating rate has a short reaction time and therefore the temperature needed for the sample to decompose is also higher. This causes the maximum rate curve to shift to the right.

TG and DTG measurements indicated that thermal behavior of coal has two-stage degradation. At the first stage, it was occurred due to the mass loss of moisture and of light volatile compounds at up to 512 K. The second stage proceeds from 512 K to the final temperature in which the main decomposition process takes places. It is seen that the ignition, the max-peak and the burn out temperatures are affected by the changing of the heating rate. The kinetic parameters under non-isothermal conditions based on the FWO and KAS methods were calculated. It is observed that the activation energy of the combustion process is almost constant with the conversion value.

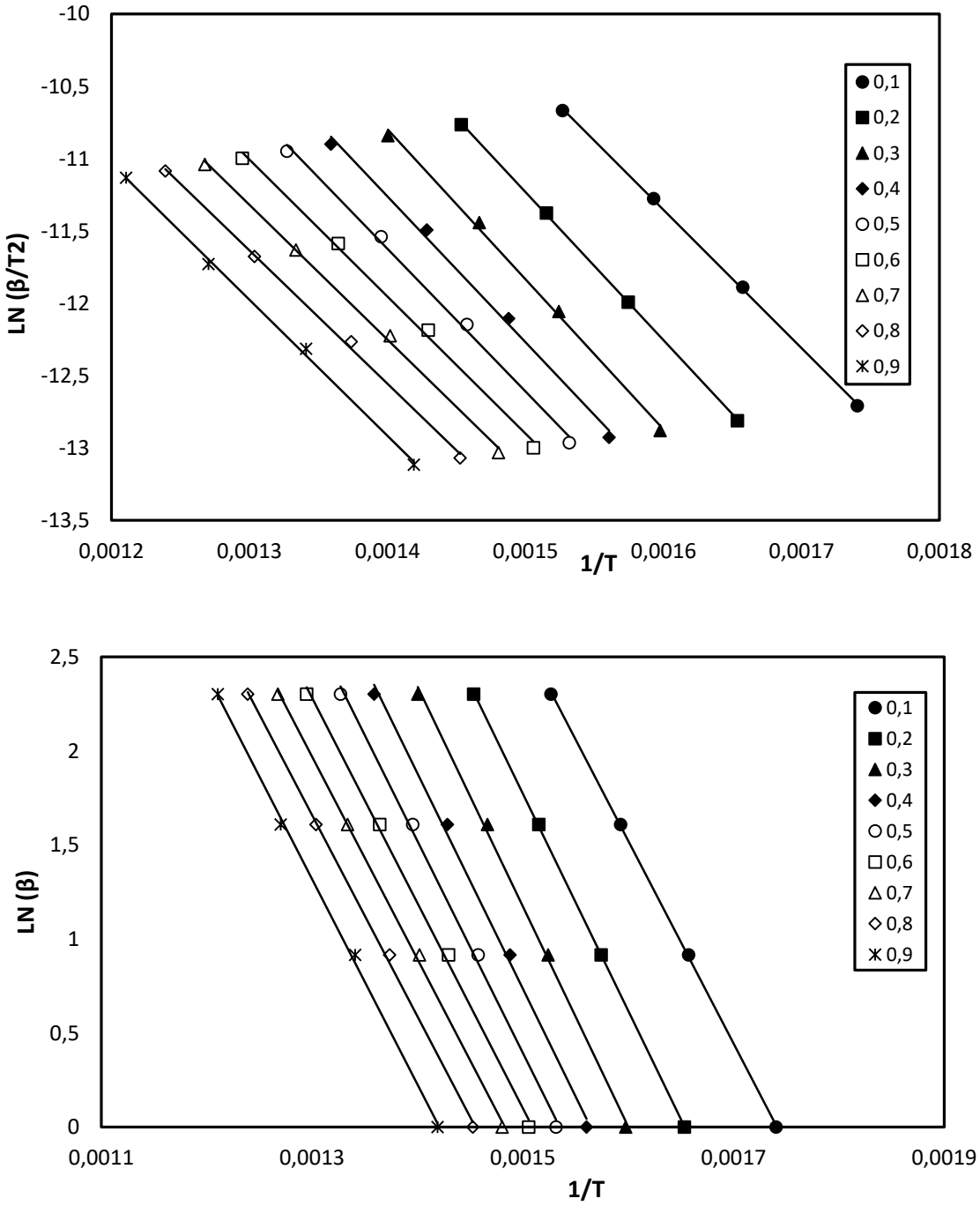

Figure 4. Isoconversional and non-isothermal determination of the kinetic parameters obtained

(a) KAS method (b) the FWO method

Table 3. Activation Energies (E_a) and correlation coefficients (r^2) calculated by KAS and FWO methods for the combustion of Dost-coal

α	**KAS method**		**FWO method**	
	E_a/kJ mol^{-1}	r^2	E_a/kJ mol^{-1}	r^2
0.1	79.42±1.38	0.9998	85.19±0.09	0.9999
0.2	85.13±0.08	0.9999	91.09±0.06	0.9999
0.3	86.22±1.36	0.9976	92.51±1.23	0.9983
0.4	83.78±2.40	0.9957	90.48±2.19	0.9970
0.5	81.91±1.78	0.9968	88.93±1.59	0.9978
0.6	78.77±1.66	0.9970	86.18±1.46	0.9980
0.7	77.45±0.87	0.9984	85.14±0.07	0.9990
0.8	76.62±0.86	0.9984	84.59±0.07	0.9990
0.9	83.09±0.95	0.9982	86.28±0.09	0.9988
Av	81.38±1.26	**0.9979**	87.82±0.76	**0.9986**

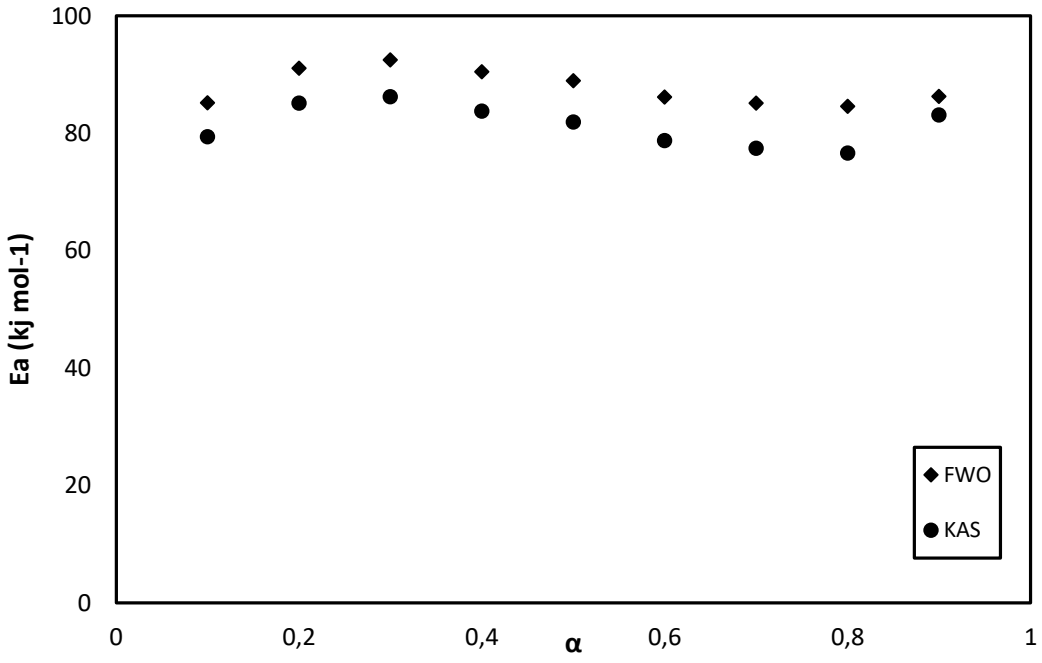

Figure 5. The activation energy as a function of conversion

4. Acknowledgement

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