Kinetic study of thermal decomposition of Shivee-Ovoo and Tavantolgoi coals

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ABSTRACT
The present research work deals with the behavior of the thermal decomposition of the coals from Shivee-Ovoo and Tavantolgoi deposits and the determination of the kinetic parameters of their thermal decomposition. Thermal decomposition experiments were performed at five different heating temperature rates (10, 20, 30, 40, 50°C/min) for two typical rank coal such as bituminite and lignite samples in an argon atmosphere temperature range from 25°C to 1000°C. The experimental results of thermogravimetric analysis of both Shivee-Ovoo and Tavantolgoi coal samples show that the heating rate increases weight loss was decreased as well as the maximum decomposition rate was slightly increased. First-time kinetic parameters such as activation energy and pre-exponential factor were calculated using model-free methods like Kissinger, Friedman and KAS for the Shivee-Ovoo and Tavantolgoi coal samples. The arithmetic average of activation energies calculated by the Kissenger, Friedman and KAS methods were 157.9, 188.6, and 203.6 kJ/mol for Shivee-Ovoo and 227.05, 129.2, and 131.1 kJ/mol for Tavantolgoi coal, respectively.

Keywords: *Coal, coal pyrolysis, kinetic, thermal, decomposition.*

1. INTRODUCTION

Mongolia is rich in coal, 9.8 billion tons of proven reserved resources and 162.3 billion tons of estimated resources including lignite, brown coal, and anthracite [1]. Baganuur, Aduunchuluun, Ovdugkhudag, Khoot, Tevshiin govi, Khoot, Shivee-Ovoo, and Tsaidam nuur deposits are counted as a brown coal basin that is centered in Mongolia's central economic region. Among them Baganuur and Shivee-Ovoo brown deposits are the largest in Mongolia [2]. In Mongolia, coal is now the main energy carrier for local thermal power plants and boilers, and there is almost no other form of large scale coal industry [3].
Last year's Mongolia exports about 15 million tons of raw coal by truck from Southern Gobi to China [2]. The biggest coal deposits are Tavantolgoi and Nariinsukhait located in the Southern Gobi near to the border with China [4]. Coal from the Tavantolgoi deposit has been assessed as bitumen, therefore it sufficient for beneficiation [5] and coke production [6]. Meanwhile, coal from Baganuur, Bayanteeg and Shivee-Ovoo deposits have been assessed as raw product for pyrolysis [7], hydrogenation [8] and gasification [9, 10].
Thermal characters of Mongolian coals have been widely studied in recent years to investigate the behavior of the thermal decomposition of brown coal, bituminous, and oil shale. Analysis of thermal properties of coal is crucial for the use of coal in industry. Most widely used methods such as differential thermal analysis and thermogravimetric analysis are to investigate the thermal characteristics of coal. These analyses have been extensively used to determine the characteristics of thermal decomposition and kinetic parameters [11].
The present work is focused on the investigation of kinetics of Shivee-Ovoo lignite coal and Tavantolgoi bitumen coal pyrolysis using a TGA apparatus under nonisothermal conditions. The obtained data were analyzed to determine the kinetic parameters for nonisothermal condition using three models: KAS, Kissenger and Friedman.

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2. MATERIALS AND METHODS

The Shivee-Ovoo coal deposit locates in the ''Dorno govi'' province while the Tavan tolgoi coal deposit is in the '' Umno govi '' province of Mongolia.
The analytical samples of coals of Shivee-ovoo and Tavan tolgoi deposits were prepared according to Mongolian National Standards (MNS) and main technical specifications including moisture (MNS 656-79), ash (MNS 652-79), volatile matter (MNS 654-79), caloric value (MNS 669-87) sulfur content (895-79) have been determined.

2.1. Materials

This investigation used lignite and bituminous as raw materials, indicated as Shivee-Ovoo (ShO) and Tavantolgoi (TT), respectively, to show the differences in pyrolysis behavior for coals with different structures. In order to be utilized, the coal samples were ground, pulverized, and sieved to a particle size of less than 74 µm.

2.2. Experimentals

Pyrolysis of the coals was carried out with thermogravimetry instrument (TG/DTA 7300, Hitachi, Japan). In each run, approximately 10 mg of coal was used in experiments. The sample was heated in argon (200 ml/min) from 25°C to 1000°C to record the weight loss. Heating rate were conducted at 10°C/min, 20°C/min, 30°C/min, 40°C/min, 50°C/min to obtain kinetic parameters and validate the models.

2.2.1. Kinetic analysis

In this section, the activation energy of coal pyrolysis was calculated by using iso conversional methods. Three model free methods including Kissenger (1), Friedman (2) and KAS (Kissinger Akahira Sunose) (3) were adopted to calculate activation energies [12].

$$\ln\left(\frac{B}{T^2 m}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RTm} \quad (1)$$

$$\ln\left(\frac{dx}{dt}\right) = \ln[Af(x)] - \frac{E_a}{RT} \quad (2)$$

$$\ln\left(\frac{B}{T^2}\right) = \ln\left(\frac{AR}{E_a g(x)}\right) - \frac{E_a}{RT} \quad (3)$$

Here, E_a:activation energy, A:pre-exponential factor

3. RESULTS

The results of technical as well as elemental analyses of Shivee – Ovoo and Tavantolgoi coals are shown in Table 1.

Table 1. The technical and elemental analyses data

Coals	*Elemental analysis, ^{daf} %*					
	C^{daf}	H^{daf}	S_t	N^{daf}	O^{*daf}	H/C
ShO	71.35	4.97	1.03	0.9	21.74	0.84
TT	84.0	5.0	0.98	0.3	9.72	0.7
Technical analysis						
Coals	W^a, %	A^d,%	V^{daf},%	Q^{daf}, kcal/kg		
ShO	13.41	21.17	42.57	6501		
TT	0.82	14.80	29.90	7524		

The Tavantolgoi calorific value and carbon content are higher and volatile matter and oxygen contents as well as the H/C ratio are lower than the Shivee-Ovoo coal. This clearly shows the higher degree of coalification of Tavantolgoi coal and indicates that more compact aromatic components predominates in its organic matrix. Both Shivee-Ovoo and Tavantolgoi coals have relatively low sulfur content ranging between 0.9–1.1%. The results from the FTIR spectrometric analysis are shown in Fig. 1.

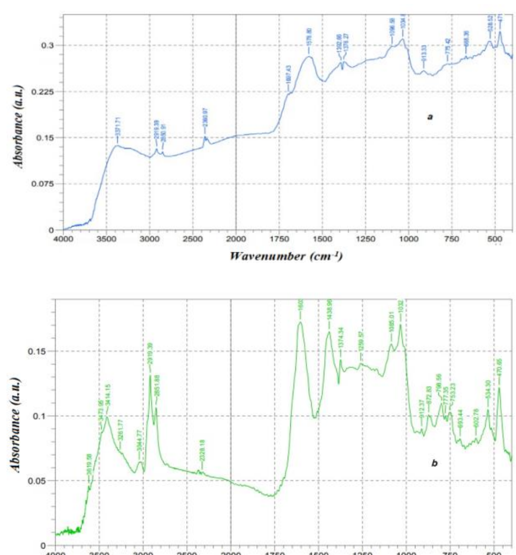


Figure 1. The results FTIR spectrometry analysis of Shivee-Ovoo (a) and Tavantolgoi coals (b)

It is seen that for raw Shivee-Ovoo coal, noticeable peaks found in the wavelengths of 3371 cm^{-1}, 2919 cm^{-1} and 2852 cm^{-1} which indicate the presence of hydroxyl and amines groups, as well as CH_2, CH_3 aliphatic groups. In the spectrum region of 1578 cm^{-1} aromatic compounds with C=C and C=O bond have been found. Also in the regions of 1261 cm^{-1}, 1097 cm^{-1} as well as 1033 cm^{-1}, simple ethers with C–O bond, at round 933–705 cm^{-1} polyaromatic and aromatic as well as aromatic hydrocarbon compounds have been found.

The FTIR spectrometry analysis shows that for Tavantolgoi raw coal, long-chain polymerized molecules are dominant, which are seen from branched weak spectrum. The Tavantolgoi coal is high-quality dense coal and there are no peaks of carboxyl and carbonyl groups at wavelength of 1680-1700 cm^{-1}, which means very weak oxidation degree. Adsorption of aromatic groups at around 700-900 cm^{-1} relatively weak indicating very small or absence of aromatic species in the coal macromolecule structure. At 1438 and 700-900 cm^{-1} region the adsorption of –CH by aromatics is weak. For the 1603 cm^{-1} region, the adsorption of -C=O bond attached to aromatic rings has been detected. CH_3, CH_2, CH groups attached to aliphatic and aromatic components have also been observed at round 2800-2900 cm^{-1}.

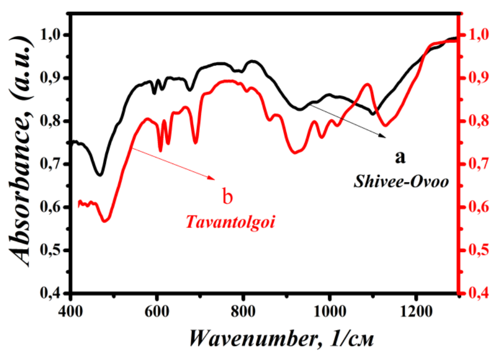


Figure 2. The results IR spectrometry analysis of mineral components of the Shivee-Ovoo coal (a) and Tavantolgoi coal (b)

The results of the FTIR spectrometry of the Shivee-Ovoo and Tavantolgoi coal ash are shown in Fig. 2. The adsorption of Si and Al oxides observed at 659-682 cm^{-1}. At the 1084-1105 cm^{-1}, the intensive adsorption of sulfate group S-O-, silica Si-O-, and certain adsorption of Ca, Mg attached to the carbonyl as well as carboxyl groups. For the region 1150 cm^{-1}, the Ca-O-, Si-O- bonds of the CaO and SiO_2- groups have been detected.
For Tavantolgoi coal ash, main adsorption peaks have been observed at the wavelengths of 400-1500 cm^{-1}, 412, 464, 528, 692, 779, 800, 1093, 1165, 1406 cm^{-1} and the adsorption shape, intensity and extensions are quite similar. Together with Si-O the Al-O bonds were detected at 412, 464, 528 cm^{-1}. However, at around 1093 cm^{-1} O-Si-O and O-Al-O bonds, at 779 cm^{-1} intensive quartz adsorption have been observed.
The chemical composition of the Shivee-Ovoo and Tavantolgoi coals ash were analyzed using the X-ray fluorescence analysis and the results are illustrated in Table 2. The IR spectrometry and X-ray fluorescence analyses show that Tavantolgoi coal ash contains high amount of SiO_2 and Al_2O_3. However, CaO, Fe_2O_3 and SiO_2 are predominant mineral components in the Shivee-Ovoo coal ash. The Shivee-Ovoo ash contains alkaline metals and their oxides, but the Tavantolgoi ash does not.

Table 2. The chemical composition of Shivee-Ovoo and Tavantolgoi coal ashes, %

Coals	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO
ShO	0.26	4.30	7.20	27.70	1.10	28.9
TT	-	-	15.75	77.61	0.52	1.89
Coals	TiO_2	Mn_2O_3	Fe_2O_3	SrO	P_2O_5	SO_3
ShO	1.20	1.60	8.40	0.18	-	19
TT	0.92	-	0.72	0.03	0.58	1.93

The ratio of (Fe_2O_3 + CaO + MgO + Na_2O + K_2O) / (SiO_2 + Al_2O_3 + TiO_2) for Shivee-Ovoo coal equals 1.2, which means ash is basic type (Class F). However, for Tavantolgoi coal this parameter is 0.033, which indicates acidic type of ash. Due to high SiO_2 content, the ash melting point of the Tavantolgoi coal ash would be high.
TGA studies of Shivee-Ovoo, Tavantolgoi coals have been performed with the purpose to find out their thermal decomposition behavior and to obtain kinetic parameters. The samples with selected size (<74μm) have been subjected to TGA experiment with five different heating rates ranging between 10-50 °C/min. The results are illustrated in Fig. 3-6.

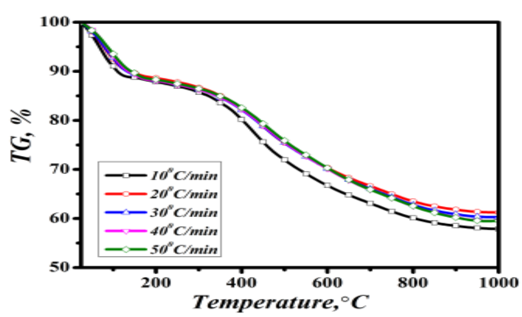


Figure 3. The TG curves vs the heating rates, (Shivee -Ovoo)

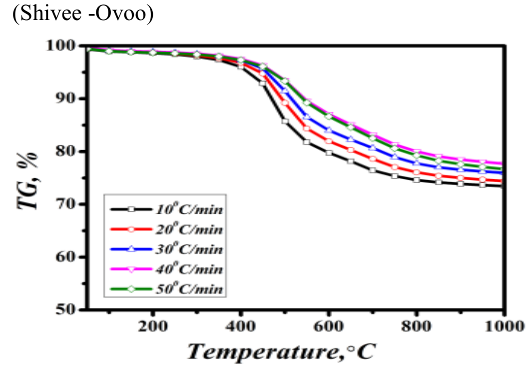


Figure 4. The TG curves vs the heating rates, (Tavantolgoi)

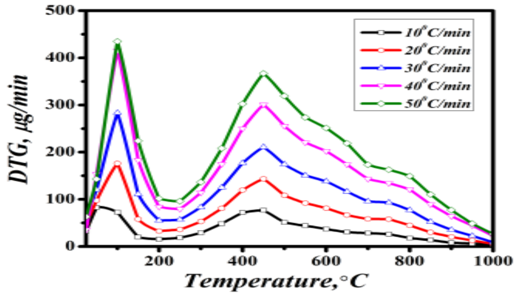


Figure 5. The DTG curves vs the heating rates, (Shivee -Ovoo)

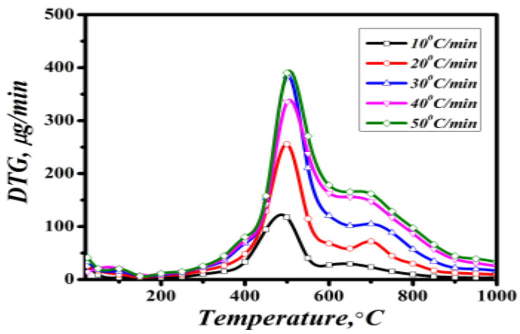


Figure 6. The DTG curves vs the heating rates (Tavantolgoi)

Although increasing the heating rate in the range of 10 – 50˚C/min for final temperature 1000˚C did not affect the asymptotic yield the total weight loss decreases with increasing heating rate. With increasing heating rate from 10˚C/min up to 50˚C/min, the corresponding weigth loss for Tavantolgoi and Shivee-Ovoo coals are 26.5 – 23.3% and 42.1 – 40.7%, respectively.

It is observed that with increasing heating rate, the rate of weight loss enhances (Fig. 5-6). For Shivee-Ovoo coal, the initial peak in the weight loss was observed in the temperature range of 50-100°C and the second peak caused by the rapid decomposition of organic mass happened at around 450°C. The rate of thermal decomposition is strongly dependent upon heating rate. Within the heating rate range employed the decomposition rate rises from 76.2 – 366.1 μr/min with increasing heating rate. For Tavantolgoi coal, the decomposition process initiates at around 100ºC and peaks at temperature of approxiamtely 500°C. At this point the rate of thermal decomposition of organic mass corresponds to 117.3 – 390.0 μr/min depending on the heating rate.When using the TGA analyzer, it is able to view the heat effect caused by the physical as well as chemical processes during the thermal decomposition. The results of DTA analyses of the Shivee-Ovoo and Tavantolgoi coals are plotted in Fig. 7- 8, respectively.

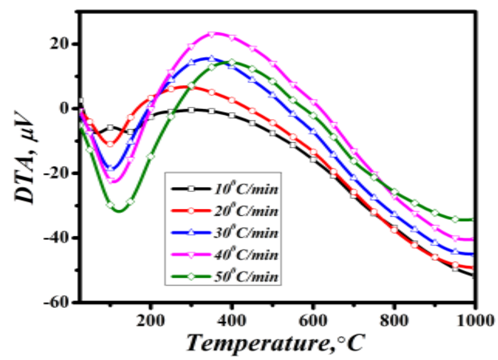


Figure 7. The DTA curves vs heating rates, (Shivee-Ovoo)

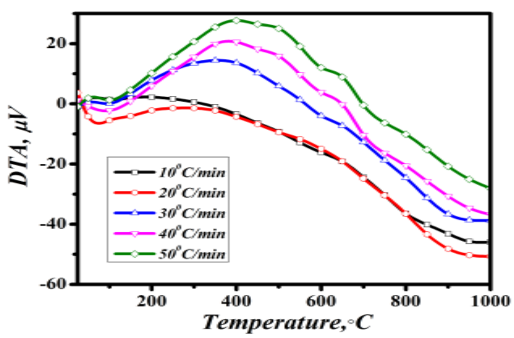
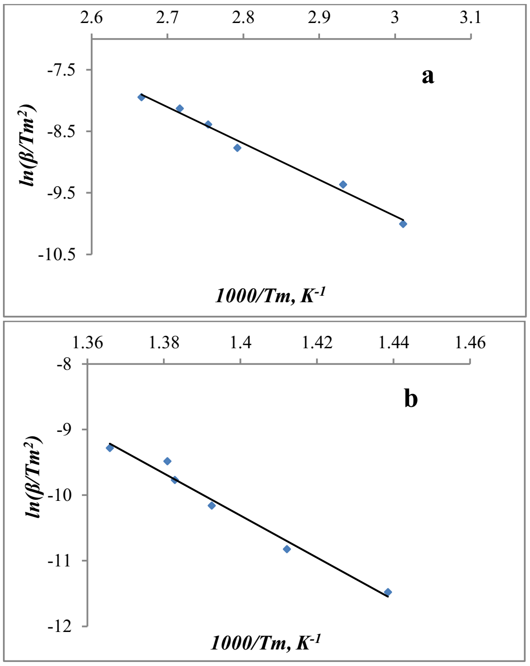


Figure 8. The DTA curves vs the heating rates, (Tavantolgoi)

The minimum point in the DTA curve was observed at temperature of approximately 100°C, which means water content in the coal vaporized and released from the organic mass indicating endothermic process. When conversion increases further curves climb up indicating exothermic process and it peaks at around 400 – 500°C. As the conversion progresses the curves move down clearly showing exothermic process is slowing.

In order to calculate the kinetic parameters for the thermal decomposition of Shivee-Ovoo and Tavantolgoi coals the parameters from the TG curves. As known we have performed non-isothermal TGA experiments with varying heating rates of 10°C/min, 20°C/min, 30 °C/min, 40°C/min, 50°C/min. The obtained results were analyzed and simulated employing model-free method such as Kissinger and isoconversion methods like Friedman and KAS and compared in order to analyze non-isothermal kinetic data and investigate thermal behavior of Mongolian coals. The basic equation employed for the determination of activation energy and pre-exponential is Arrhenius equation. According to Kissinger, the maximum reaction rate occurs with an increase in the reaction temperature. The degree of conversion at the peak temperature of the DTG curve is a constant at different heating rates. For Shivee-Ovoo coal, the conversion peaks correspond to the temperature regions of 25 – 300°C and 300 – 700°C. The Kissinger plots at different heating rates for Shivee-Ovoo coal are shown in Fig. 9.



a. 25-300°C, b. 300-700°C

Figure 9. Kissinger plot of Shivee-Ovoo pyrolysis at different heating rates

The kinetic parameters using Kissinger method were found by linear regression line which is shown in Fig. 9. In the case of Shivee-Ovoo coal, the activation energy and pre-exponential factor extracted from the slope and intercept are 49.1 kJ/mol, 2000 min^{-1} for the first peak and 266.73 kJ/mol, $1 \cdot 10^{15}$ min^{-1} for the second peak region, respectively.

The activation energy corresponding to the first peak is lower than that of the second peak could be attributed to the decomposition of higher molecular organic components for the second peak temperature region.

The activation energy and pre-exponential factor were calculated as a function of conversion by using isoconversional methods of KAS and Friedman. The isoconversional plots of these methods are shown in Fig. 10. Different ranges of conversion from 0.1 to 0.9 is considered for calculating the kinetic parameters based on isoconversional method.

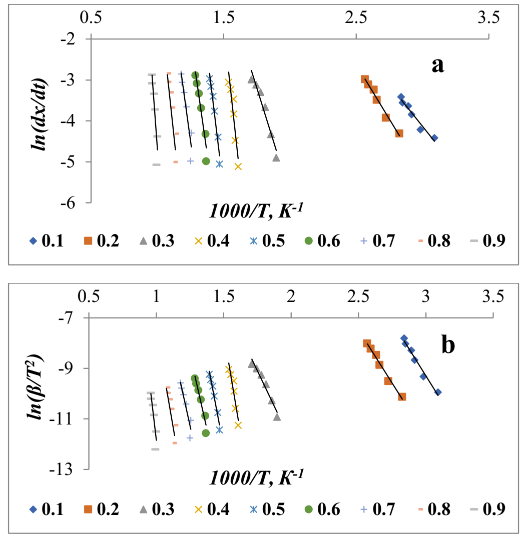


Figure 10. Friedman and KAS plots of Shivee-Ovoo coal pyrolysis at different values of conversion: a. Friedman, b. KAS

The arithmetic means of the activation energy calculated by Friedman and KAS methods were 188.6 and 203.6 kJ/mol respectively, which are different but close to average activation energy obtained from the Kissinger method (266.7 kJ/mol). The kinetic data obtained for pyrolysis of coal are found to agree closely with some of the literature data. However, the differences observed in the literature data can be attributed to the fact that the pyrolysis characteristics of coal highly depend on the properties of the coal which in turn differs based on origin of the coal.

The initial activation energy value was low due to cleavage of some weak bonds and elimination of volatile components from the coal matrix because at the beginning of the process all the strong bonds are not cleaved. Therefore, more activation energy is required to decompose these stable molecules

As a result of this process gaseous products such as H_2, CH_4, NH_3, CO are released forming high-molecular solid, coke. During the thermal decomposition of brown coals the aliphatic methyl or methylene groups bonded with ring-compounds are destructed at low temperatures, while oxygenated functional groups are decomposed at higher temperatures. Thermal cracking as well as the condensation of aromatic ring components require high activation energy.

The Kissinger plot of Tavantolgoi coal pyrolysis is shown in Fig. 11. The Friedman and KAS plots of Tavantolgoi coal pyrolysis are illustrated in Fig. 12.

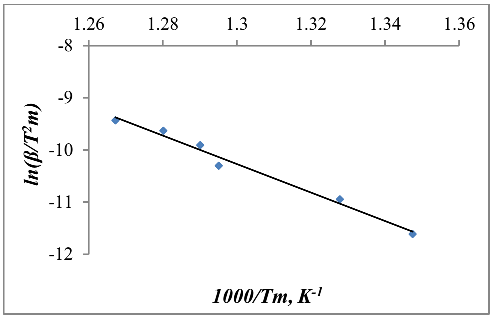


Figure 11. The Kissinger plot of the Tavantolgoi coal pyrolysis at different heating rates

From Fig. 11-12 plots have been calculated the kinetic parameters. In the Kissinger method the degree of conversion at the peak temperature (T_m) is a constant under different heating rates. The kinetic parameters using Kissinger method were found by linear regression line which is shown in Fig. 8. The activation energy and pre-exponential factor extracted from the slope and intercept are 227.05 kJ/mol and $9 \cdot 10^{17}$ min^{-1} respectively. The activation energy and pre-exponential factor were calculated as a function of conversion by using iso conversional methods of KAS and Friedman methods. The isoconversional plots of these methods are shown in Fig. 12. It is seen that the activation energy varies with conversion and the average value of activation energy calculated by the Friedman method is 129.2 kJ/mol. This value of this coal calculated by the KAS method is 131.1 kJ/mol.

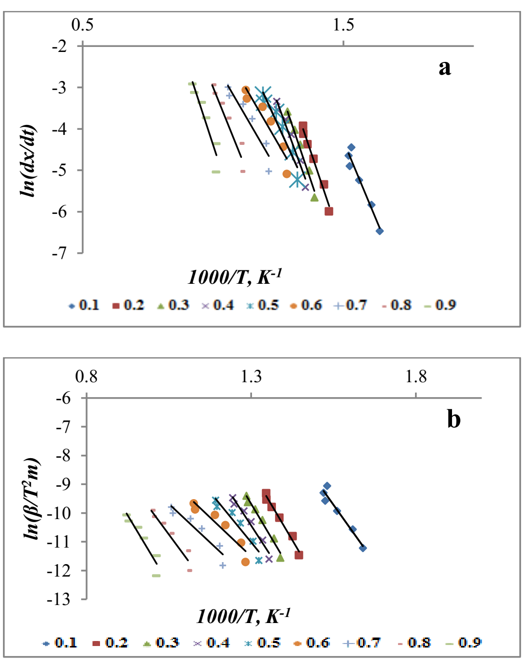


Figure 12. The Friedman and KAS plots of Tavantolgoi coal pyrolysis at different values of conversion:a. Friedman, b. KAS

These values were close to the activation energies obtained using Friedman abd KAS methods.

4. CONCLUSIONS

The Shivee-Ovoo and Tavantolgoi coal were studied using TGA analysis and the kinetic parameters were calculated. The conclusions are:

- When coal samples were pyrolyzed in the TGA with heating rate from 10ºC/min up to 50ºC/min the weight loss varied 40.7-42.1% for Shivee-Ovoo coal and 23.3-26.5% for Tavantolgoi coal. Depending on the heating rate the decomposition rate for the Shivee-Ovoo coal were 76.2-366.1 mg/min, those for Tavantolgoi coal were 117.3-390.0 mg/min respectively. With increasing heating rate the temperature at which maximum decomposition occurs enhanced.
- The arithmetic average of activation energies calculated by the Kissinger, Friedmann, KAS methods were 157.9, 188.6 and 203.6 kJ/mol for Shivee-Ovoo coal and 227.05, 129.2 and 131.1 kJ/mol for Tavantolgoi coal respectively.

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