

KINETIC ANALYSIS OF CO-COMBUSTION OF OIL SHALE SEMI-COKE WITH BITUMINOUS COAL

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Utilization of the semi-coke collected from oil shale retorts is very important and advantageous. Due to the inflammable property, co-combustion of semi-coke with other good quality solid fuels could be effectual. In this research, a kinetic study of the combustion of oil shale semi-coke (SC) mixed with bituminous coal (C) was carried out by thermogravimetric analysis at different heating rates. Popescu's method was applied to analyze the kinetic mechanisms of combustion of oil shale semi-coke, bituminous coal and their blends; Flynn-Wall-Ozawa method was employed to determine the activation energies of those combustion reactions. Based on the obtained results, it was concluded that three-dimensional diffusion model could be implemented either for the combustion process of oil shale semi-coke or for bituminous coal while for their blends the model of random nucleation and growth could be applied. The activation energies of oil shale semi-coke and the blends of semi-coke and bituminous coal decreased in the beginning, and then increased during the combustion process. Activation energies of the blends decreased with increasing amount of bituminous coal.

Introduction

Oil shale is a solid-state organic-rich sedimentary rock and combustible material with high ash content. According to its released heat, the total reserve of oil shale ranks second after coal. Oil shale can be burnt in boilers, and also can be retorted to produce shale oil. Retorts for processing oil shale have been built in Estonia, Brazil, Australia, China, etc. Oil shale is regarded as a supplemental energy source having economic and social benefits [1, 2]. Semi-coke is the solid residue left after oil shale retorting, containing phenols, polycyclic aromatic hydrocarbons (PAHs) and oil products that are potential pollutants to the environment [3]. Thus, it is very important to deal

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with deposits of semi-coke. Although the property of the oil shale semi-coke depends on the conditions of retorting process and varies greatly, semi-coke has always been considered as a potential fuel. Considering that oil shale semi-coke has usually high ash content, low volatile matter content, low calorific value, and is difficult to burn [4, 5], it will be the best way to burn semi-coke with other solid fuels, such as coal, biomass, oil shale, sewage sludge and their blends [6–10].

According to the results of the research, this paper proposes a method for processing semi-coke by mixing it with bituminous coal in circulating fluidized bed boiler. The ash left over from the burning process could be utilized as the building material if its carbon content is less than 2%. Based on this idea, thermogravimetric analysis was applied to investigate the process of co-combustion of semi-coke and bituminous coal.

Thermogravimetric analysis (TGA) of oil shale samples has been extensively used for determining combustion characteristics. TGA may be carried out in isothermal or non-isothermal conditions, the latter is being used more and more as it has several advantages over the isothermal method. First, experimental time is shorter. Second, the errors due to the thermal induction period are eliminated. Third, it simulates better the conditions expected at large-scale oil-shale retorting processes. So, many researchers have applied non-isothermal TGA to investigate the decomposition process and decomposition kinetics of oil shale. The present investigation is an experimental study on the samples of oil shale semi-coke, bituminous coal and their blends on TGA apparatus under non-isothermal conditions. The experimental data were analyzed to determine kinetic parameters – activation energy and the functions of kinetic mechanism.

Experimental

Materials

Oil shale semi-coke (SC) used in this work was collected from Huadian oil shale retort factory in Jilin Province, China. Bituminous coal (C) used in this research was gathered from Jixi deposit, located in Heilongjiang Province, China. Chemical analyses of two samples are presented in Table 1. Bituminous coal was mixed with oil shale semi-coke in three different mass percentages in the blend (10, 20 and 30 %) and marked as M1, M2, M3, respectively. Particle size of the blends was less than 200 μm .

Table 1. Proximate and ultimate analysis of the samples

Sample	Proximate analysis, wt%				$Q_{\text{ad.net}}$, J/g	Ultimate analysis, wt%				
	M_{ad}	V_{ad}	A_{ad}	FC_{ad}		C_{ad}	H_{ad}	O_{ad}	N_{ad}	S_{ad}
SC	0.89	10.44	82.62	6.09	3868.29	11.29	0.35	4.21	0.11	0.53
C	4.51	28.63	34.93	31.92	18343.15	44.13	4.01	11.38	0.53	0.50

Apparatus and experimental procedures

Thermogravimetric tests were performed using a PerkinElmer thermogravimetric analyzer Pyris1 TGA. The weight loss and weight loss rate were continuously recorded under dynamic conditions as a function of time or temperature, in the temperature range of 0–1000 °C. The sensitivity of the weight precision of this instrument is 0.1 µg. To eliminate the effects of heat and mass-transfer limitations, and ensure both – the reproducibility of TG experiments and accuracy of kinetic analysis, several pre-screening TG experiments were conducted. TGA were carried out using 6–8 mg samples. The constant air flow rate was 100 mL/min. The temperature of the TGA was linearly increased with the heating rate of 10, 20, 40 °C/min from ambient temperature up to 850 °C. The same experiment was repeated at least twice to ensure the repeatability and the accuracy of the test data.

Results and discussion

Combustion of samples

Conversion degree α is defined by the following equation:

$$\alpha = \frac{W_t - W_0}{W_f - W_0}, \quad (1)$$

where

W_t – the weight of the sample at a given time t ;
 W_0, W_f – the weight at the beginning and at the end of the TG reaction being analysed.

Using equation (1), according to the results of related TG experiments, the relation of conversion degree vs. temperature at different heating rates could be calculated and shown in Fig. 1.

Based on the related TG experiments, DTG curves could be calculated as shown in Fig. 2. It was found that combustion of semi-coke includes three temperature ranges: ambient temperature –130 °C, 450–650 °C and 650–850 °C, respectively. The first stage is the moisture loss; in the second stage the combustion of volatile matter and fixed carbon takes place and the final is mineral matter decomposition stage. But coal combustion is different from that of semi-coke. In case of coal there are only two reaction regions: the moisture loss and combustion of combustible matter. The combustion of mixture of semi-coke and coal was more similar to the combustion of semi-coke.

In Table 2 four combustion characteristics calculated for given heating rates can be seen, including the ignition temperatures (T_i), maximum combustion rate (DTG_{max}), the temperature corresponding to the maximum combustion rate (T_{max}) and burn-out temperature (T_h). It was found that due to the thermal lag, increase in the heating rate also increases the values of T_i ,

T_{max} and T_h . The DTG_{max} value increases with an increase in the heating rates for all samples.

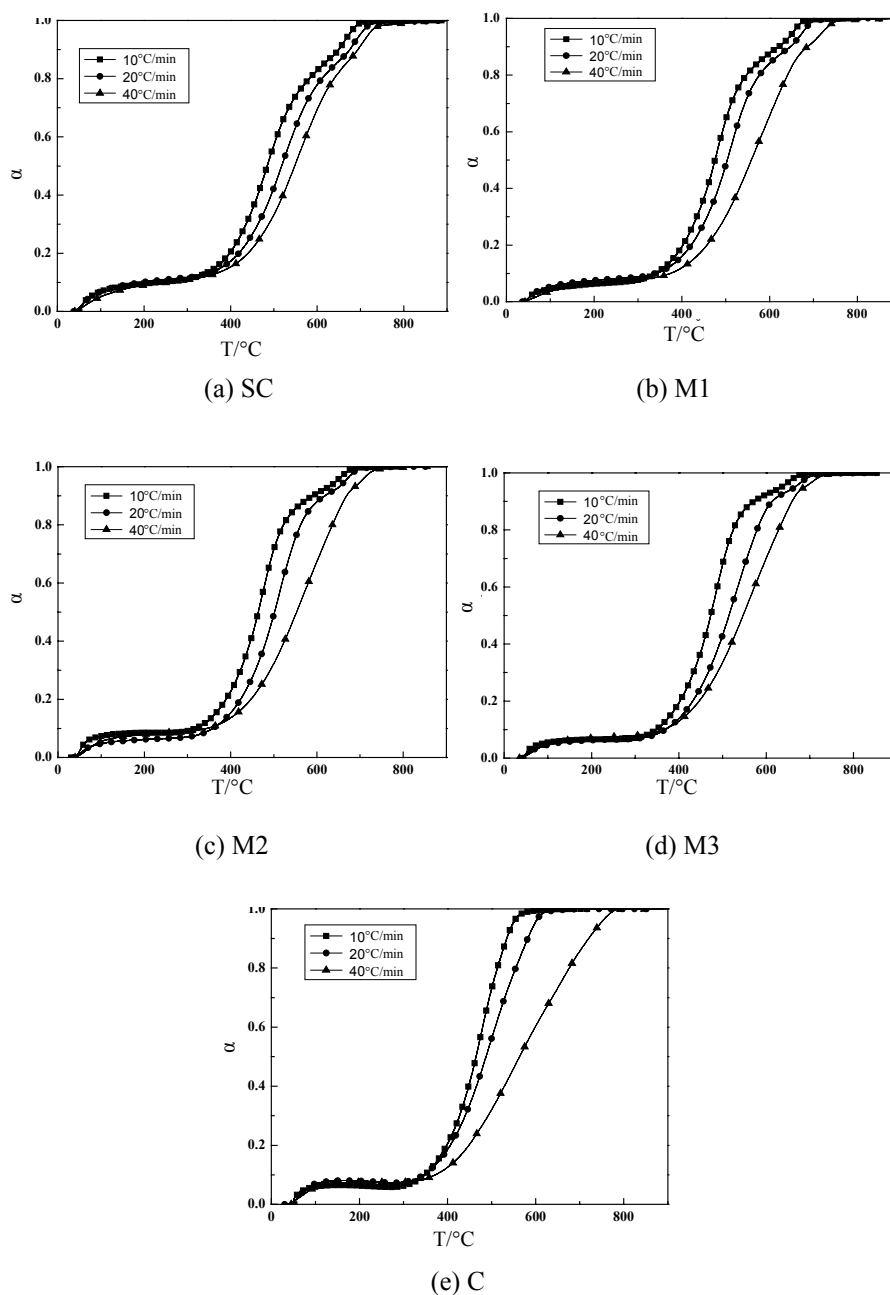


Fig. 1. Experimental (α, T) curves at different heating rates: (a) semi-coke; (b), (c) and (d) mixture of semi-coke and bituminous coal; (e) bituminous coal.

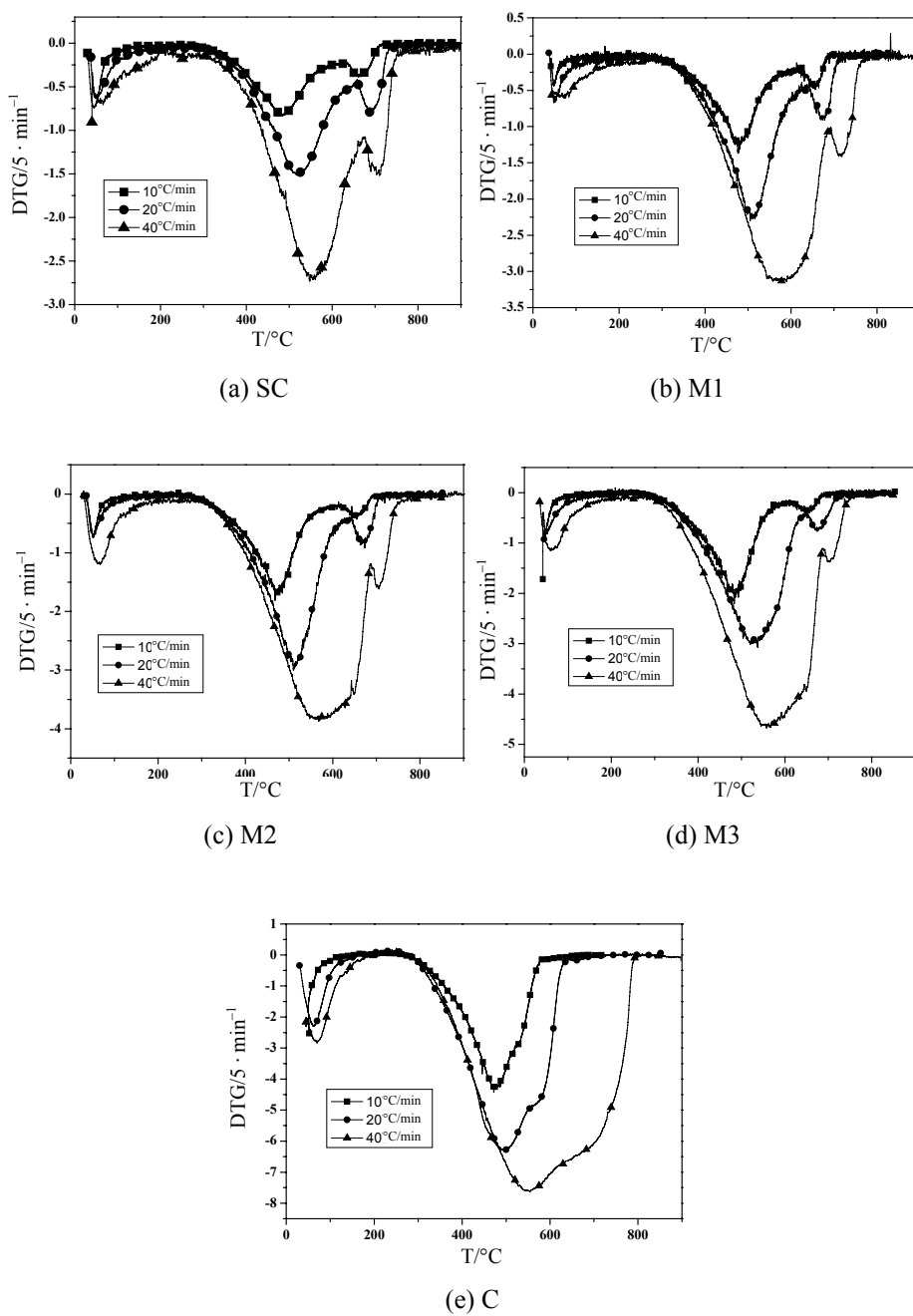


Fig. 2. DTG curves of the samples at different heating rates.

Table 2. Combustion characteristics of the samples

Sample	β , °Cmin ⁻¹	T_{is} , °C	DTG _{max} , %min ⁻¹	T_{max} , °C	T_h , °C
SC	10	397.2	0.80	484.8	690.5
	20	431.5	1.50	516.4	716.1
	40	442.5	2.71	557.8	739.9
M1	10	406.3	1.29	477.3	671.2
	20	428.3	2.30	511.7	690.8
	40	443.3	3.14	579.9	737.6
M2	10	399.1	1.70	474.6	671.2
	20	427.3	2.91	514.2	684.3
	40	434.5	3.85	576.4	729.2
M3	10	415.0	2.01	484.2	661.5
	20	424.5	3.48	513.5	680.1
	40	436.7	4.63	561.0	715.9
C	10	395.9	4.28	475.9	561.7
	20	398.3	6.27	497.3	611.6
	40	413.0	7.62	555.2	767.7

Determination of the kinetic mechanism

The reaction for the heterogeneous processes of the semi-coke blends with air under non-isothermal conditions in TGA depends only on the conversion degree α and temperature T , as expressed below by the following equation:

$$\frac{d\alpha}{dt} = f(\alpha)k(T), \quad (2)$$

where t is time.

By the usual change of the variable time into temperature, equation (2) could be changed into equation (3):

$$\frac{d\alpha}{dT} = \frac{1}{\beta} f(\alpha)k(T), \quad (3)$$

where $\beta = dT/dt$ is the heating rate.

In the related experiments the heating rate is being kept constant. Therefore, equation (3) could be integrated as below:

$$\int_{\alpha_m}^{\alpha_n} \frac{dx}{f(x)} = \frac{1}{\beta} \int_{T_m}^{T_n} k(y)dy, \quad (4)$$

where

α_m, α_n – two different degrees of conversion;
 T_m, T_n – temperatures of corresponding α_m, α_n studied in this research.

If the left side and the right side of the equation (4) are defined as equation (5) and equation (6):

$$F(\alpha)_{mn} = \int_{\alpha_m}^{\alpha_n} \frac{dx}{f(x)} \quad (5)$$

and

$$I(T)_{mn} = \int_{T_m}^{T_n} k(y)dy, \quad (6)$$

then equation (4) could be simplified and shown in equation (7) as follows:

$$F_{mn} = \frac{1}{\beta} I_{mn}. \quad (7)$$

With the help of the various conversion functions, given in Table 4, the values of F_{mn1} , F_{mn2} , ..., can be calculated according to the equation (5), and for each conversion function $f(\alpha)$, three values are obtained. As the temperatures T_m and T_n are the same for all experiments, according to the equation (6), it could be inferred that I_{mn} is constant and, from equation (7), F_{mn} was adopted as the variable at the y-axis and $1/\beta$ at the x-axis, a straight line could be formed between F_{mn} and $1/\beta$ with the intercept as zero if the proper analytical form of $f(\alpha)$ is chosen. In practice, the best correlation coefficient (R) can be used to choose the proper kinetic function. This method is based on several curves proposed by Popescu in 1996 [11]. Many authors disagree with the methods based on deriving kinetic parameters from TG/DTG curves, because incoherent results could be gained but Olivella and Heras confirm that Popescu's method is the most accurate method for deriving kinetic parameters from TG curves of oil shale and coal pyrolysis. [12].

The combustion reaction occurs mainly in the stage where combustion of volatile matter and fixed carbon takes place (450–650 °C), so T_m is considered to be 450 °C, T_n is 650 °C, and the corresponding conversion degrees for each combustion stage are given in Table 3. In addition the samples of semi-coke and bituminous coal were provided as references.

Table 3. Conversion degrees corresponding to the temperatures of the samples

β_i , °C/min	SC		M1		M2		M3		C	
	α_m	α_n	α_m	α_n	α_m	α_n	α_m	α_n	α_m	α_n
10	0.35	0.90	0.36	0.96	0.42	0.96	0.37	0.97	0.41	1.00
20	0.26	0.86	0.28	0.90	0.28	0.93	0.25	0.94	0.34	0.99
40	0.22	0.82	0.19	0.83	0.21	0.85	0.21	0.87	0.20	0.73

According to [13], applying data from Table 3 to the equation (7), a plot of F_{mn} vs. $1/\beta$ for all samples is obtained. There are nine reaction models available [14], to provide better linear relationship. The nine models, the correlation coefficients (R) and standard deviation (SD) for each plot of

samples are given in Table 4 and Table 5. It can be seen from Table 5 that the best correlation coefficient appeared when the three dimensional diffusion reaction mechanisms (Function B) applied during combustion of oil shale semi-coke or bituminous coal. Similar results are also obtained by Zhang [15]. Function G is the best for the blends of oil shale semi-coke and bituminous coal.

Table 4. Nine typical models for kinetic reaction [14]

No.	Reaction model	Reaction mechanism	Integral form $F(\alpha)$	Differential form $f(\alpha)$
A	Jander's equation	Spherical symmetry three dimensional diffusion	$[1-(1-\alpha)^{\frac{1}{3}}]^2$	$\frac{3}{2}(1-\alpha)^{\frac{2}{3}}[1-(1-\alpha)^{\frac{1}{3}}]^{-1}$
B	Zhuravlev-Lesokhin-Tempelmann (ZLT) equation	Three dimensional diffusion	$[(1-\alpha)^{\frac{1}{3}}-1]^2$	$\frac{3}{2}(1-\alpha)^{\frac{4}{3}}[(1-\alpha)^{\frac{1}{3}}-1]^{-1}$
C	Maple's equation (first-order)	One step random nucleation and growth	$-\ln(1-\alpha)$	$1-\alpha$
D	Avrami-Erofeev equation	Random nucleation and growth $n = 3/2$	$[-\ln(1-\alpha)]^{\frac{3}{2}}$	$\frac{2}{3}(1-\alpha)[- \ln(1-\alpha)]^{-\frac{1}{2}}$
E	Avrami-Erofeev equation	Random nucleation and growth $n = 2$	$[-\ln(1-\alpha)]^2$	$\frac{1}{2}(1-\alpha)[- \ln(1-\alpha)]^{-1}$
F	Avrami-Erofeev equation	Random nucleation and growth $n = 3$	$[-\ln(1-\alpha)]^3$	$\frac{1}{3}(1-\alpha)[- \ln(1-\alpha)]^{-2}$
G	Avrami-Erofeev equation	Random nucleation and growth $n=4$	$[-\ln(1-\alpha)]^4$	$\frac{1}{4}(1-\alpha)[- \ln(1-\alpha)]^{-3}$
H	Reaction order	Chemical reaction $n = 1$	$(1-\alpha)^{-1} - 1$	$(1-\alpha)^2$
I	Reaction order	Chemical reaction $n = 3/2$	$(1-\alpha)^{-\frac{1}{2}}$	$2(1-\alpha)^{\frac{3}{2}}$

Table 5. Linear fitting results of the kinetic mechanism functions

No.	SC		M1		M2		M3		C	
	R	SD	R	SD	R	SD	R	SD	R	SD
A	0.99437	0.0049	0.92113	0.0610	0.89013	0.0800	0.91677	0.0808	0.86485	0.2127
B	0.99984	0.0070	0.99493	0.1313	0.98827	0.2711	0.99865	0.1329	0.99491	4.5966
C	0.99190	0.0273	0.90032	0.3891	0.86600	0.5270	0.90969	0.4936	0.90856	1.3520
D	0.99642	0.0494	0.94480	0.6528	0.92216	0.9333	0.95103	0.8733	0.93428	3.4879
E	0.99831	0.0703	0.97011	0.9323	0.95406	1.4350	0.97490	1.3137	0.95532	7.9410
F	0.99983	0.0713	0.99451	1.2877	0.98573	2.7634	0.99645	1.9061	0.98280	8.6293
G	0.99983	0.1983	0.99994	0.4005	0.99657	4.4080	0.99944	2.7559	0.99368	2.7722
H	0.99981	0.0445	0.99422	0.8511	0.98895	1.6200	0.99944	0.5462	0.98952	6.4396
I	0.99814	0.0229	0.96682	0.3322	0.95256	0.4991	0.97889	0.4283	0.98820	2.5704

Determination of the activation energy

The activation energy is determined by Flynn-Wall-Ozawa (FWO) method. The following equation has been used to obtain the activation energy, which can be calculated from the plot of $\ln \beta$ versus $1/T$ by fitting to a straight line [14, 16].

$$\ln \beta = \ln \frac{AE}{F(\alpha)R} - 5.3305 - 1.052 \frac{E}{RT} \quad (8)$$

Applying equation (8) on the data from Fig. 1 a plot of $\ln \beta$ vs. $1/T$ for all samples was obtained. The results are shown in Fig. 3. The activation energies

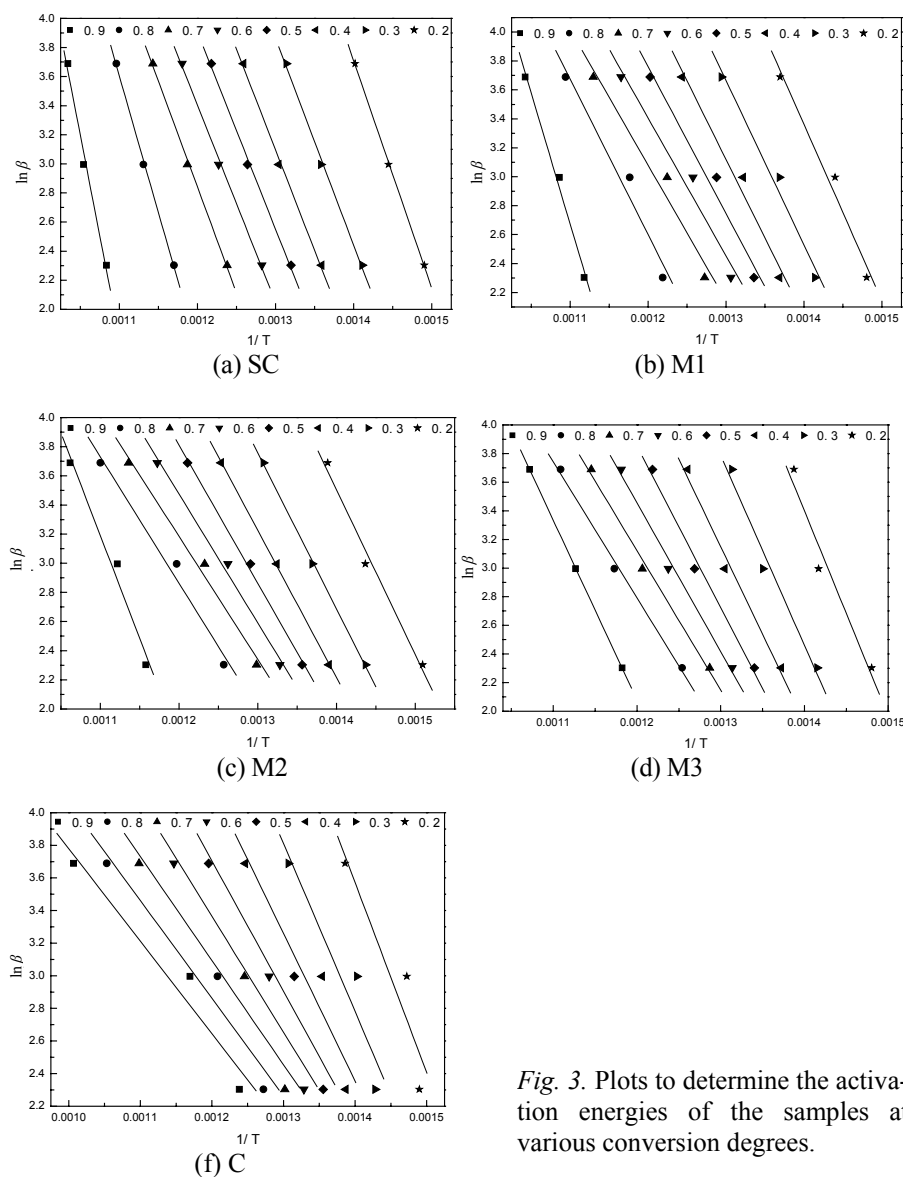


Fig. 3. Plots to determine the activation energies of the samples at various conversion degrees.

(E_{exp}) determined from the slope of $\ln \beta$ versus $1/T$ plots from $\alpha = 0.2$ to 0.9 , represent the main combustion region. The results are shown in Table 6.

Table 6. Activation energies by FWO method, kJ/mol

α	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
SC	124	112	109	107	107	115	148	220
M1	96	90	86	80	75	74	85	143
M2	89	85	80	75	70	67	69	112
M3	94	82	73	66	59	55	54	60
C	92	81	71	63	56	50	47	44

According to Table 6, it could be found that activation energies of oil shale semi-coke are the highest and activation energies of bituminous coal are the lowest at the same degree of conversion. The E_{exp} values of the blends are between those of bituminous coal and semi-coke. For oil shale semi-coke, bituminous coal, and their mixtures, high activation energy means that the reaction requires more energy from the surroundings. The change of activation energy shows that different blending ratios of oil shale semi-coke and bituminous coal present different reactivity at different conversion degrees. As inferred from Table 6, the higher is the proportion of bituminous coal in the blend, the closer is the value of activation energy E of the mixture to that of coal. For oil shale semi-coke and all the blends, the obtained activation energies decreased at the early stages, and then increased in at the later stage. When $\alpha = 0.2$, the values of E_{exp} of M1, M2, M3 were all smaller than their values of E_{cac} . It means that the ignition characteristics of the blends were improved compared to the oil shale semi-coke when less coal was added into the mix. The stage after $\alpha=0.8$, which is considered as the decomposition of carbonate minerals of oil shale semi-coke, the E of oil shale semi-coke and the blends increase dramatically, and the activation energy values are quite similar to the limestone decomposition (182.56 kJ/mol) [17]. In all, combustion reactions of oil shale semi-coke, bituminous coal and their blends are very complex multistep reactions and further research should be performed in the future.

According to Table 7, the activation energy value obtained in this study was smaller compared with those from the literature [10, 12] and it was found that those activation energies were different, although the same kinetic method was used. The great disparity may have risen from the differences in such experimental factors as different sample, heating rate, flow rate, etc. [18].

Table 7. Comparison of values of the activation energy (E) with those reported in the literature

Reference	Sample	E_{mean}^* (E)/ kJmol ⁻¹
present study	SC	117
	M1	84
	M2	76
	M3	69
	C	63.39
[10]	semianthracite	67.3
[12]	Mequinenza coal	138
	Canizara coal	108
	Rib-3 oil shale	248
	Rib-7 oil shale	384

Note: *The activation energy E_{mean} was calculated as arithmetic average of several E values obtained for the different conversion degrees ($\alpha \leq 0.8$, except for Sample C) shown in Table 6.

Conclusion

Co-combustion of semi-coke from oil shale retorts with bituminous coal at different mass ratios was investigated in this research by means of TGA. The reaction mechanisms involved were explored by the method put forward by Popescu, and the activation energy was further calculated by FWO method. The conclusions made after the study are the following:

- (1) Regarding the combustion process, there are three stages for the blends and semi-coke: moisture loss, combustion of volatile matter and fixed carbon, and decomposition of mineral matter. Regarding the combustion of coal, there are only two reaction regions: moisture loss stage and combustion of volatile matter and fixed carbon.
- (2) Reaction mechanism involving the combustion of semi-coke or bituminous coal alone was described by the three dimensional diffusion model (B). For their blends random nucleation and growth (G) reaction mechanism was implemented.
- (3) In the same conversion degree, the activation energies decrease with increasing of the ratio of bituminous coal in the blend. Furthermore, they are lower than those calculated as the algebraic sums of those from each separate component. Reactivity of bituminous coal is better than that of oil shale semi-coke, and it is improved for the blends with increasing of the ratio of bituminous coal.

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