

OXYGEN-ENRICHED COMBUSTION OF LIGNITE

by

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The study is concerned on the oxygen-enriched combustion kinetics of lignite. Thermogravimetric experiments were carried out in a thermogravimetric analyzer under O₂/N₂ conditions, and operated at different heating rates ranging from 5 °C per minute to 25 °C per minute. Flynn-Wall-Ozawa method was used to calculate the kinetic parameter. The value of activation energy increased when the oxygen concentration varied from 21% to 70%.

Key words: activation energy, thermogravimetric analyzer, oxygen-enriched, lignite

Introduction

The lignite regions of Inner Mongolia account for 75% of the total quantity of lignite in China [1]. However, its low heating value limits its wide utilization in combustion. Most researchers have concluded that the coal combustion process is affected by the O₂ concentration [2].

Iso-conversional methods enable determination of kinetic parameters without knowledge of reaction mechanism, and Flynn- Ozawa-Wall (FOW) model allow the calculation of the activation energy of the process, which using dynamic integral and differential thermogravimetric (TG) curves obtained with several heating rates.

The main purpose of this work was to study the kinetics of lignite in oxygen-enriched atmosphere. The TG data were carried out by the application of FOW model. The effect of different oxygen concentration on the lignite combustion process was studied.

Solid state kinetics of the decomposition reaction can be described in eq. (1),

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

where α is the conversion extent, $\alpha = (W_0 - W_t)/(W_0 - W_\infty)$, W_0 and W_∞ are sample masses at the beginning, and the end of mass loss reaction, respectively, W_t is the sample mass at time t /temperature, $f(\alpha)$ – the reaction model, T – the temperature, $k(T)$ – the reaction rate constant which is described by Arrhenius equation, $k(T) = A \exp(-E/RT)$, where A is the pre-exponential factor, E – the apparent activation energy, and R – the gas constant [$= 8.314 \text{ J}(\text{mol}^{-1}\text{K}^{-1})$] [3]. Equation (1) can be converted into eq. (2) expressed as:

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$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta} \right) \exp \left(- \frac{E}{RT} \right) f(\alpha) \quad (2)$$

where β is the linear heating rate, $\beta = dT/dt$, and it is a constant.

Iso-conversional methods are originated from the integration of the kinetic equation.

Integration of eq. (2) gives rise to:

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp \left(- \frac{E}{RT} \right) dT \quad (3)$$

If E/RT is replaced by x , eq. (3) can be written as:

$$G(\alpha) = \frac{AE}{\beta R} \int_x^\infty \frac{\exp(-x)}{x^2} dx = \frac{AE}{\beta R} p(x) \quad (4)$$

The term $p(x)$ is the temperature integral and has no analytical form, but has many simplified approximations. The FOW uses a correlation of the heating rate of the samples, the activation energy and the inverse temperature. The derivation of this correlation is based on Doyle's approximation which is $\log[p(x)] \approx -2.315 + 0.457x$ [4].

It is evident that a linear plot of $\log\beta$ vs. the inverse temperature is sufficient enough in order to obtain the activation energy corresponding to each conversion step.

Experimental

A typical indigenous lignite was obtained from the Yuanbaoshan underground coal mine (YBS), in Inner Mongolia in China. The coal sample was sieved to less than 80 μm .

Table 1. Proximate and ultimate analysis of YBS lignite sample

Proximate [%]				Ultimate [%]					$Q_{\text{net,ar}}$ [MJkg ⁻¹]
M_{ad}	VM_d	FC_d	A_d	C_d	H_d	O_d	N_d	S_d	
11.42	30.56	39.49	29.92	59.58	3.39	5.45	1.35	0.28	17.468

ad – air dry basis, d – dry basis, M – moisture, VM – volatile matter, FC – fixed carbon, A – ash, and $Q_{\text{net,ar}}$ – net calorific value

Proximate analyses data, ultimate analyses data and calorific value are briefly summarized in tab. 1.

In this paper, thermal analysis of lignite combustion was performed on NETZCH –STA 409PC instruments. Approximately 10 mg of a coal sample

was heated from room temperature to 1000 °C, with the heating rate of 5, 10, and 25 °C per minute. Combustion tests were conducted in an O₂/N₂ atmosphere at the O₂ concentration of 21, 40, and 70 vol.%, respectively. The total gas flow was set to 80 ml per minute.

Combustion characteristic parameters of ignite temperature (T_{ig}), peak temperature (T_{max}), and burnout temperature (T_b) was determined by TG/DTG curves. [5].

Results and discussion

The TG curves of lignite samples are presented in fig. 1. It is evident from fig. 1(a) that the effect of oxygen concentration is almost negligible before 260 °C. When the oxygen concentration increased, The stage from 260 °C to 425-450 °C was characterized by a major weight loss, corresponded to the main release volatile and carbon combustion.

In figs. 1(b)-(c), TG curves present the same laws with fig. 1(a), while the major weight loss stage temperature presented from 270 °C to 435-480 °C in fig. 1(b), and from

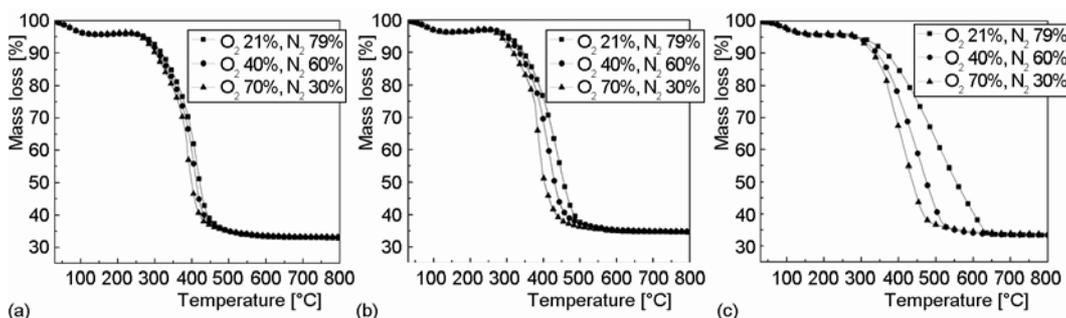


Figure 1. The TG profiles in different O₂ volume fraction with the heating rate of (a) 5 °C per min., (b) 10 °C per min., and (c) 25 °C per min.

290 °C to 470-615 °C in fig. 1(c). An increase of the heating rate tended to delay thermal reaction processes towards higher temperature, most probably due to increased thermal lag as at a given temperature.

The characteristic temperatures in different oxygen concentration and heating rate are shown in tab. 2. The kinetic parameters of activation energies were determined by iso-conversional FOW model. A plot of $\log\beta$ against $1/T$ is a straight line. From the slope of the line, activation energy (E) of the lignite in different oxygen concentration can be estimated at various conversions α .

Table 2. Characteristic temperatures in different oxygen concentration and heating rate

O ₂ :N ₂	Heating rate [°C per min.]	T _{ig} [°C]	T _{max} [°C]	T _b [°C]	O ₂ :N ₂	Heating rate [°C per min.]	T _{ig} [°C]	T _{max} [°C]	T _b [°C]
21:79	5	290.02	417.19	459.15	40:60	5	282.22	407.71	448.37
	10	314.93	439.73	497.33		10	296.09	410.71	467.21
	25	317.00	499.47	633.86		25	317.29	457.33	524.86
70:30	5	288.50	390.88	428.85					
	10	282.40	385.87	447.73					
	25	299.47	424.27	480.27					

Conversion varying from 0.2 to 0.8 were employed at different heating rates of 5 °C, 10 °C, and 25 °C per minute in fig. 2.

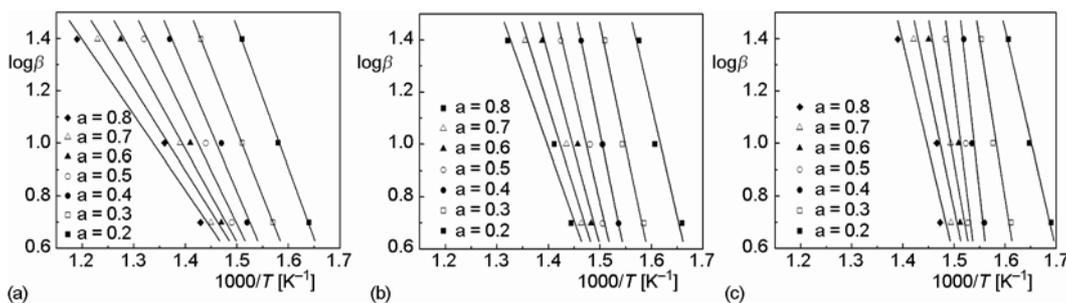


Figure 2. Iso-conversional determination of the kinetic parameters for lignite in the O₂ volume fraction of (a) 21%, (b) 40%, and (c) 70% (FWO method)

The active energies in $0.2 \leq \alpha \leq 0.8$ calculated by FWO method was listed in tab. 3. the average activation energy increased with the increase of oxygen concentration. The values of active energy decreased with the conversion extent increased in 21 vol.% O₂ concentration.

Table 3. The activation energies obtained by FWO method

α	O ₂ :N ₂ = 21:79		O ₂ :N ₂ = 40:60		O ₂ :N ₂ = 70:30	
	E [kJ mol ⁻¹]	R	E [kJ mol ⁻¹]	R	E [kJ mol ⁻¹]	R
0.2	97.96	-0.9994	146.43	-0.9734	151.97	-0.9961
0.3	90.81	-1.0000	166.85	-0.9908	214.37	-0.9827
0.4	83.00	-0.9939	175.42	-1.0000	310.06	-0.9801
0.5	72.14	-0.9882	150.85	-0.9902	251.54	-0.9342
0.6	63.25	-0.9904	128.04	-0.9844	169.93	-0.9200
0.7	55.21	-0.9844	111.05	-0.9831	143.33	-0.9231
0.8	51.05	-0.9878	98.46	-0.9834	128.83	-0.9306
Average	73.34		139.59		195.72	

The results can be explained that the high concentration of fixed carbon present in the lignite at the beginning of the combustion. Activation energy values decreased possibly due to the intense combustion of carbon, finally with the decrease in carbon content and increase in ash content.

Activation values increased first and then

decreased in the higher oxygen concentration (40 vol.% and 70 vol.%). At the beginning process the lower activation energy values was due to the volatile matter presents in the lignite, then the increase values before conversion 0.4 was attribute to the decrease of volatile matter and high concentration of fixed carbon. Activation energy values decreased after conversion 0.4 was due to the decrease in carbon content and increase in ash content.

Conclusions

It was obvious that the activation energy was increased with the increase of oxygen concentration. The values of active energy decreased with the conversion extent increased in 21 vol.% O₂ concentration. Activation values increased at the conversion of 0.2-0.4, then decreased when the conversion higher than 0.4 in 40 vol.% and 70 vol.% oxygen concentration.

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