

# Thermogravimetric analysis of combustion characteristics and kinetic parameters of pulverized coals in oxy-fuel atmosphere

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**Abstract** Temperature programmed combustions (TPC) of Yang-Quan anthracite, Liao-Cheng lean coal and Li-Yan bituminous coal in oxy-fuel atmosphere were conducted in a thermogravimetric analyzer and characteristic parameters were deduced from the TG-DTG curves. The results showed that combustion got harder to progress as the coalification degree increasing. Within range of 40%, effect of heightening O<sub>2</sub> concentration favored the combustion process, but beyond this zone, the effect leveled off. The model-fitting mathematical approach was used to evaluate the kinetic triplet ( $f(\alpha)$ ,  $E$ ,  $A$ ) through Coats–Redfern method. The calculation showed that  $D_3$ -Jander was the proper reaction model and the evaluations of  $E$  and  $A$  validated the experimental results.

**Keywords** Thermogravimetric analysis · Oxy-fuel combustion · Characteristic parameters · Model-fitting approach · Kinetic triplet

## Introduction

The greenhouse effect generated by carbon dioxide has gained considerable attentions recently, and as a major source of CO<sub>2</sub>, coal-fired power plants should take measures to abate CO<sub>2</sub> emission compulsorily. Normally, the CO<sub>2</sub> concentration in conventional coal–air combustion flue gas is just 14–16% and the direct sequestration is not

feasible economically for this low value concentration. Aimed at this intractable matter, the oxy-fuel combustion technology [1–3] was developed for the capture of CO<sub>2</sub> expelled from power plants. This technology is also called O<sub>2</sub>/CO<sub>2</sub> combustion technology with coal combustion proceeding in mixture of oxygen and recycled flue gases (RFG) to tackle CO<sub>2</sub> emission. During the process, as the oxidant required for combustion, O<sub>2</sub> is separated from air and then mixed with RFG. Subsequently, a highly concentrated CO<sub>2</sub>, achieving 95%, flue gas is produced, which is economically used for deep sea CO<sub>2</sub> storage and enhanced oil recovery toward the low carbon economy. Also, this technology possesses advantages of suppressing thermal NO<sub>x</sub> formation for its reduction or completely elimination nitrogen from air for pure O<sub>2</sub>. At the same time, net combustion gas volume falls down at higher O<sub>2</sub> feed concentration contributing to a higher boiler thermal efficiency with lower sensible heat loss in flue gas and a lower oxy-fuel plant investment by reducing the corresponding flue gas cleaning equipment.

It is expected that coal combustion proceeding in O<sub>2</sub>/CO<sub>2</sub> mixtures is different from the one in conventional air and investigations were conducted on coal ignition, mass loss rate, flame stability and heat transfer behavior [4–7]. Liu [4] found that, for a larger specific heat of CO<sub>2</sub>, an initial O<sub>2</sub> concentration of 30% or higher in oxy-fuel combustion was required to produce the same temperature profiles as those in air combustion. Tan et al. [5] found that the O<sub>2</sub>/RFG flames were much less brighter and more compact than conventional flames which was not even possible to maintain stable flames and in their investigations, the O<sub>2</sub> concentration was valued as 35% in the combustion feed gas for the same heat flux and temperature profiles as the air atmosphere. Kiqa et al. [6] investigated the flame propagation speed of pulverized-coal cloud in a

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microgravity combustion chamber and the results showed that the flame propagation speed in O<sub>2</sub>/CO<sub>2</sub> atmosphere was markedly lower compared with that in O<sub>2</sub>/N<sub>2</sub> and O<sub>2</sub>/Ar and it could be improved by increasing the O<sub>2</sub> concentration. Borrego [7] conducted the drop tube experiments and revealed that a higher amount of O<sub>2</sub> in CO<sub>2</sub> than in N<sub>2</sub> was needed to achieve similar burnout levels but char reactivity and micropore surface area were analogical in air and O<sub>2</sub>/RFG atmospheres. Previous studies [4–7], as mentioned above, were mainly focused on the O<sub>2</sub>/RFG coal combustion rules of mass loss rate, flame stability and furnace temperature profile, and they validated the feasibility of this technology to some extent. But investigation of the reaction mechanism and kinetic parameters during coal combustion in oxy-fuel atmosphere were not substantive referred which was an important aspect for a profound understanding of the O<sub>2</sub>/RFG combustion technology.

Thermogravimetric (TG) was traditionally performed by measuring a change in the extensive property, mass, through analysis method. This method has been widely used for the assessment of the combustion behavior of fossil fuel and sewage sludge [8–15]. Some studies were conducted in isothermal settings, but this method required some time to reach the experimental temperature. It would be inconvenient if a solid-state process reached its maximum reaction rate at the beginning of the transformation. So, more accurate researches should be done in non-isothermal settings to determine the kinetic parameters of coal combustion during which sample was heated at a constant rate [9]. Characteristic parameters during combustion like ignition temperature, peak of mass loss rate and its temperature, burn out efficiency and its temperature, could be achieved from TG-DTG curves. Further, the kinetic parameters, namely, the reaction model,  $f(\alpha)$ , the pre-exponential factor,  $A$ , and the activation energy,  $E$  (the so-called kinetic triplet) could be deduced.

Among the mathematical approaches performed for the kinetics parameters in TPC, two kind methods could be taken into consideration: modeling-fitting and isoconversional (free model) [12]. The anterior one was conducted under only one heating rate and the latter one was performed under at least three different heating rates. This study was to investigate coal combustion characteristic with different O<sub>2</sub> concentrations in oxy-fuel TPC and the change of reaction atmosphere was the principal part. So, the modeling-fitting approach with single heating rate was applied to analysis the kinetics parameters. Traditionally, two defections existed in the modeling-fitting approach. The first was that the reaction model  $f(\alpha)$  was pre-assumed and the  $k(T)$  and  $f(\alpha)$  were evaluated together. Thus, the data derived from this approach varied much with different  $f(\alpha)$  chosen but could be fit the corresponding  $f(\alpha)$  well

under the “kinetic compensation effect” [12]. The second problem was that the pre-assumed  $f(\alpha)$  made the solid-state reaction one-step process which factually was consisted of series of parallel and sequential reactions. For the accurate evaluation of the kinetic triplet in different oxy-fuel atmospheres under only one heating rate, some remediation was taken in this study. One was that relationship between  $A$  and  $E$  was established based on the Arrhenius equation for compensating the error of the pre-assumed reaction model departing from the right but unknown kinetic model. The other was taking the different reaction models into consideration for the model-fitting approach and the one whose correlative coefficient the most equaling to 1 would be the proper model. The detailed description would be mentioned in the kinetic parameters evaluation section.

The objective of this study was to investigate the combustion proceedings of three kinds of coals in O<sub>2</sub>/CO<sub>2</sub> mixtures and gain the corresponding characteristic parameters from the TG-DTG curves. Further, kinetic triplet ( $f(\alpha)$ ,  $E$ ,  $A$ ) were deduced from thermogravimetric analysis through Coats–Redfern method to validate the experimental results. Also, the relationship between the evaluated values of  $A$  and  $E$  were established through linearity regression.

## Experimental

### Materials used

Three kinds of representative coal abundant in China were emphasized in this study and denominated according to their locations: YQ (Yang-Quan anthracite), LC (Liao-Cheng lean coal) and LY (Li-Yan bituminous coal). Proximate and ultimate analysis of these tested coals was conducted in accordance with GB/T212-2001 and GB/T476-2001 (National Standard of China) and the data were listed in Table 1. After crushed and sieved to  $74 \times 10^{-6}$  m size, the coal samples were pretreated in the oven for 12 h under 378 K to eliminate the outer water. Then coal samples were then stored in sealed desiccator at room temperature for use.

**Table 1** Proximate and elementary analysis of tested coal samples

Coal types	Proximate analysis/%				Elementary analysis/%				
	$M_{ad}$	$A_{ad}$	$V_{ad}$	$FC_{ad}$	$C_{ad}$	$H_{ad}$	$O_{ad}$	$N_{ad}$	$S_{ad}$
YQ	1.92	28.93	8.94	63.21	61.56	2.38	2.61	0.76	3.76
LC	1.59	31.65	14.06	52.40	61.30	2.81	3.21	1.20	0.83
LY	2.50	16.36	31.69	49.45	70.31	4.32	5.84	1.17	2.00

*ad* air-dried basis

## Temperature programmed combustion

The experiments were performed in a TGA/SDTA851e thermogravimetric analyzer with the sample mass loss percentage (TG signal) and mass loss rate (DTG signal) as functions of time or temperature recorded continuously under the temperature programmed combustion (TPC). During the experiments, the temperature increased from 298 to 1273 K at a linear heating rate of 0.33 K/s. Reaction atmosphere required in chamber was fulfilled by mixing O<sub>2</sub> (99.97% purity) with CO<sub>2</sub> (99.90% purity) and the gas flux was kept  $1.67 \times 10^{-6} \text{ m}^3/\text{s}$  at the gauge pressure of 1 atm (101 kPa) constantly to suppress the mass-transfer effect at a minimum. The O<sub>2</sub> concentration in mixtures was valued 10–60% through adjusting the valve to supply the required oxygen atmosphere for coal combustion. At the same time, the chamber blowing gas, N<sub>2</sub> (99.99% purity), was fixed at a flux of  $5 \times 10^{-7} \text{ m}^3/\text{s}$ . Sample was quantified as  $(10 \pm 0.02) \times 10^{-6} \text{ kg}$  in a crucible at the beginning of every experiment. When data derived from TG-DTG curves were analyzed, they would be dealt with taking the original sample mass into consideration to eliminate the effect of mass different on the process. To ascertain the stability of the experimental system, some measurements were brought up twice at the beginning period of the whole experimental process, which were under conditions of 20% O<sub>2</sub> concentration for the three tested samples. The detailed TG-DTG curves and educed data are shown in corresponding section which validates the stability of the experimental system.

## Results and discussion

### Characteristic of coal combustion proceeding

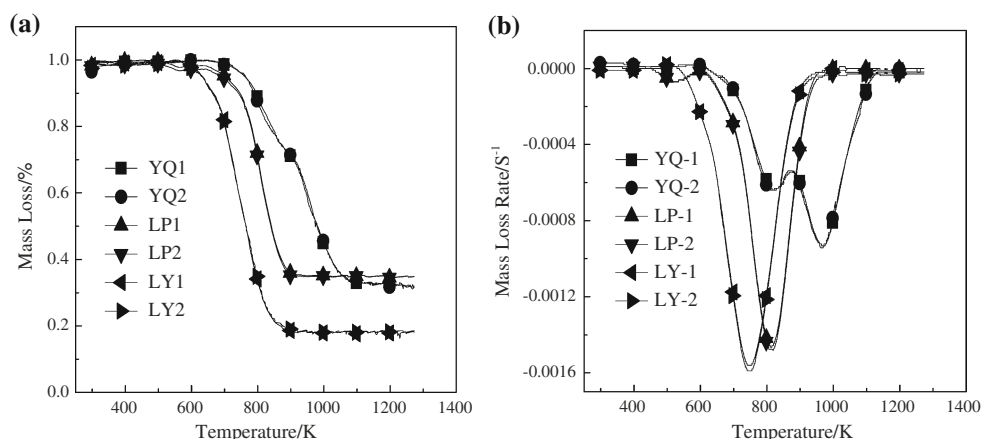
The TG and DTG curves for YQ, LC and LY in repeated TPC were shown in Fig. 1a and b, respectively. From these figures, some characteristic parameters [10, 11] were

obtained in order to evaluate the combustibility of the tested coal samples.  $T_v$ , the volatile matter initiation temperature where the rate of mass loss reached  $5 \times 10^{-5}$  after the loss of moisture and oxygen chemisorption.  $T_b$ , the burnout temperature where the mass loss rate achieved  $5 \times 10^{-5}$  after peak of the mass loss rate.  $\eta$ , the burnout efficiency corresponding to the  $T_b$ .  $DTG_{\max}$ , the maximum of mass loss rate (referred to the bigger one if multiple peaks appeared) and the corresponding temperature  $T_{\max}$ .  $\Delta T_{1/2}$ , the half peak width which is the temperature difference between two temperatures at the mass loss rate value equaling 0.5 times of  $DTG_{\max}$ . Integration combustion parameter [16],  $H_F = T_{\max} \times \ln[\Delta T_{1/2}/DTG_{\max}] \times 10^{-3}$ , described the whole process of coal combustion and it represented the rate and intensity of this proceeding. Also, this parameter reflected the flame stability after ignition. With  $H_F$  decreasing, the combustion characteristic got better.

Coals were highly heterogeneous in their chemical composition and physical properties and their combustion proceedings consisted of complex reaction occurring parallel and sequential, basically including, evolution the outer and inner water, release primary volatile and oxidation of residual volatile and the principal carbon [17]. Before the onset of combustion, all three coals were observed a net weight gain in TG-DTG curves due to the physisorption and chemisorption [18]. In following stages, different coals presented distinct laws depending on their coalification degree.

The deeper coalification coal, YQ, containing high fixed-carbon and low volatile owned the tight particle surface and long loops in molecular structure [19] which made the DTG curves show two peaks. In low temperature, releasing and combusting of the volatile shaped the first mass loss peak at 822 K (YQ-1). But intensity of combustion at this temperature was not enough to ignite the residual volatile and carbon and reaction trailed off temporarily. As temperature increasing, the residual volatile

**Fig. 1** a TG and b DTG curves for YQ, LC and LY (oxy-fuel atmosphere, 20% O<sub>2</sub> concentration) (Note: YQ-1 and YQ-2 were the twice experimental results under the same condition and LC and LY were the same as YQ)



and the principal carbon were ignited intensely under the heat transfer effect to form the second mass loss peak at 968 K. This peak was dominant compared with the anterior one and most of combustible constituent was accomplished during this stage. As for the lower coalification coals, LC and LY, they presented similar combustion laws in TPC which could be seen in Fig. 1b. Both of them shaped only one prominent peak in DTG curves and there was no obvious boundary for the combustion of volatile and carbon. Also, it was deduced that the lower coalification degree, the bigger peak value of the mass loss rate and the lower temperature it achieving the peak. The peak temperature for LY-1 was 748 K and the corresponding value for LC-1 was shifted toward higher temperature by 65 K. It was noticeable that there was a fluctuation with a very narrow shoulder in LC-1 DTG curve at low temperature range 499–550 K which accompanied a feeble mass loss of 1.88% for the combustible constituent, but the factuality needed further investigation.

The characteristic parameters deduced from TG-DTG curves were shown in Table 2 which represented the combustion laws for YQ, LC and LY directly in the view of statistical consideration. It was seen that, as the coalification degree increasing, the  $H_F$  value got increment accordingly. Namely, the combustion characteristic was not good for the deeper coalification coals compared with the lower ones. And the burnout efficiency for LY-1 was 3.22% higher than the one for YQ-1. Also the current for the parameters of  $T_v$ ,  $T_b$ ,  $T_{max}$  and  $DTG_{max}$  validated the above description. An exception was the  $\Delta T_{1/2}$  for LC-1 and LY-1, but this difference was small compared with effect of  $T_{max}$  and  $DTG_{max}$  which did not impact the orderliness of  $H_F$ . In conclusion, as the integration combustion parameter,  $H_F$  presented the combustion law more exactly.

At the same time, it was seen from Fig. 1 that the TG-DTG curves of the repeated experiments overlapped each other mainly. Also, the corresponding values of characteristic parameters, shown in Table 2, for the repeated experiments varied little. All of these validated the stability of the experimental system and the experiments with different  $O_2$  concentrations in oxy-fuel atmosphere would be conducted based on these in the next section.

## Coal combustion in oxy-fuel atmosphere with different $O_2$ concentrations

Figure 2 showed the DTG curves for LC in TPC with different  $O_2$  concentrations and the corresponding characteristic parameters were listed in Table 3. It was seen that LC in TPC presented similar law with different  $O_2$  concentrations but the values of parameters varied (It was in expectation that YQ and LY gained the similar currents, but were not exhibited here). Obviously, 10%  $O_2$  concentration was inadequate for LC combustion progress grew to the maximum rate and made the combustion occur in a longer zone, labeling a bigger value of half peak width, 195 K. It was also deduced that the peak of mass loss rate was much smaller than the ones derived from thicker  $O_2$  concentrations and the corresponding temperature was shifted to a higher value. It maybe resulted from the insufficient  $O_2$  supplement in high temperature zone where oxidation reaction was very intensive and the course was in a oxygen diffusion controlling stage [20]. As  $O_2$  concentration increasing,  $H_F$  values decreased and combustion characteristic got better gradually, for the volatile initiation temperature, burnout temperature and the mass loss peak temperature moved toward low temperature zone as a whole. Also, the half peak width got narrower and maximum mass loss rate become intensive. All of these proved that  $O_2$  strengthened the combustion course in a certain

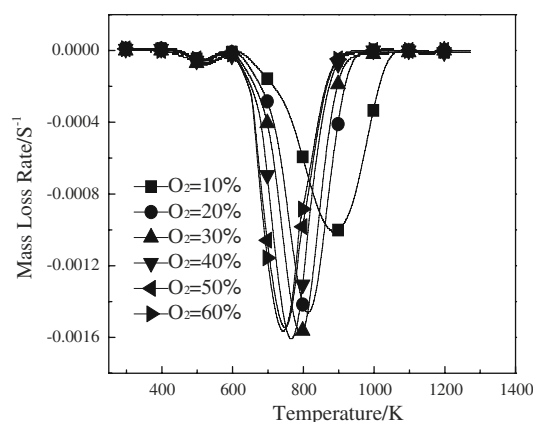


Fig. 2 DTG curves for LC with different  $O_2$  concentrations

**Table 2** Characteristic parameters of YQ, LC and LY in TPC with 20%  $O_2$  concentration

Coal types	$T_v$ /K	$T_b$ /K	$\eta$ /%	$T_{max}$ /K	$DTG_{max} \times 10^4/S^{-1}$	$\Delta T_{1/2}$ /K	$H_F \times 10^{-3}$
YQ-1	661	1116	95.35	968	9.32	267	12.163
YQ-2	670	1112	94.92	965	9.42	270	12.132
LC-1	633	942	95.56	813	14.66	130	9.262
LC-2	629	953	96.09	818	14.82	132	9.325
LY-1	557	921	98.57	748	15.6	162	8.639
LY-2	552	932	98.08	743	15.9	160	8.564

**Table 3** Characteristic parameters of LC in TPC with different O<sub>2</sub> concentrations

O <sub>2</sub> concentration (%)	T <sub>v</sub> /K	T <sub>b</sub> /K	η/%	T <sub>max</sub> /K	DTG <sub>max</sub> × 10 <sup>4</sup> /S <sup>-1</sup>	ΔT <sub>1/2</sub> /K	H <sub>F</sub> × 10 <sup>-3</sup>
10	650	1041	95.48	886	10.11	195	10.782
20	633	942	95.56	813	14.66	130	9.262
30	619	928	95.68	792	15.70	124	8.931
40	612	902	95.99	766	16.06	120	8.596
50	611	898	96.51	748	15.45	134	8.505
60	611	896	96.17	743	15.65	129	8.411

degree. In high O<sub>2</sub> concentration situations, abundant of O<sub>2</sub> penetrating to the particle surface made the combustion a dynamic controlling stage. So, when O<sub>2</sub> concentration got beyond 40%, its effect would become feeble. Either the DTG curves or the deduced parameters leveled off for O<sub>2</sub> concentration in range 40–60%. In another aspect, excessive oxygen in mixtures of O<sub>2</sub>/CO<sub>2</sub> depressed the RFG ratio and made the oxy-fuel technology meaningless. Taking the burnout efficiency into consideration which varied less in rang 10-60% of O<sub>2</sub> concentration shown in Table 3, it was concluded that O<sub>2</sub> concentration in oxy-fuel combustion atmosphere should not exceed 40% and this answered the results of previous studies [1–5].

Kinetics parameters in oxy-fuel TPC

The kinetic equation of heterogeneous solid-state thermal transformation in TPC could be generally described as [8, 9, 12]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \rightarrow \beta \frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right)f(\alpha) \quad (1)$$

where α is the degree of reaction, α = (M<sub>0</sub> - M<sub>t</sub>)/(M<sub>0</sub> - M<sub>f</sub>) (M<sub>t</sub> is the mass of the sample at time t/temperature T, M<sub>0</sub> and M<sub>f</sub> are the mass of the sample at the beginning and at the end of the mass loss reaction, respectively), t is the time, k (T) is the rate constant described by the Arrhenius equation, namely, k(T) = A · exp(-E/RT) (A is the pre-exponential Arrhenius factor, E is the activation energy and R is the gas constant), f(α) is the reaction model, T is the temperature and β is the heating rate (β = dT/dt = constant).

The starting temperature can be set as T = 0 K for the reaction rate at the starting temperature is negligible. The variables can then be separated and Eq. 1 can be integrated as:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = G(\alpha) = \frac{A}{\beta} \cdot \int_0^T \exp\left(-\frac{E}{RT}\right) dT. \quad (2)$$

Among the model-fitting methods considering single thermoanalytical curve for evaluating kinetic triplet (f(α), A, E), the Coats–Redfern [21] method was the most

employed one in previous studies. Therefore, the Eq. 2 was transformed into:

$$\ln \frac{G(\alpha)}{T^2} = \ln \left[ \frac{AR}{\beta E} \left( 1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT}. \quad (3)$$

For the normal reaction temperature zone and most E values evaluated previously, especially the coal combustion process, the RT/E << 1 in Eq. 3 and then the (1 - 2RT/E) ≈ 1 with an approximative hypothesis. Subsequently, the integrated kinetic equation was finally presented as:

$$\ln \frac{G(\alpha)}{T^2} = \ln \left( \frac{AR}{\beta E} \right) - \frac{E}{RT}. \quad (4)$$

At certain temperatures, the plot ln[G(α)/T<sup>2</sup>] vs. 1/T obtained from a series of experiments should be a straight line, and thus the activation energy is obtained with slope -E/R. Subsequently, the pre-exponential factor is obtained from the intercept. In this analysis, the kinetic parameters were evaluated with the corresponding DTG curve divided into low temperature section and high temperature section by the peak of the mass loss rate. In each section, four α values were selected, either heightened by 0.1 toward high temperature or reduced by 0.1 toward low temperature. Thus, the activation energy and pre-exponential factor were average ones in an appointed temperature section.

The normal heterogeneous solid-state reaction models [22], mainly including A<sub>1</sub>, A<sub>1</sub>, R<sub>1</sub>, R<sub>2</sub>, D<sub>1</sub>, D<sub>2</sub>, D<sub>3</sub>, D<sub>4</sub>, were mentioned in this study for the proper model-fitting method. Compared with each other, the D<sub>3</sub>-Jander model equation, which was expressed as f(α) = 3(1 - α)<sup>2/3</sup> (2(1 - (1 - α)<sup>1/3</sup>)) with G(α) = (1 - (1 - α)<sup>1/3</sup>)<sup>2</sup>, was the better one considering the deduced -R (shown in Figs. 3a and b, LC combustion with different O<sub>2</sub> concentrations in oxy-fuel atmosphere) in this study. It was seen that, in high temperature zone, the evaluated values of ln[G(α)/T<sup>2</sup>] and 1/T presented better correlative characteristic, but in low temperature zone, especially for O<sub>2</sub> concentrations of 50 and 60% this characteristic got worse. Maybe, some distinct reaction mechanism dominated in this high O<sub>2</sub> concentration section and hoped to get answer in further investigation.

It was seen in Table 4 that, the values of A for YQ were much smaller than LC and LY, but with a similar E values

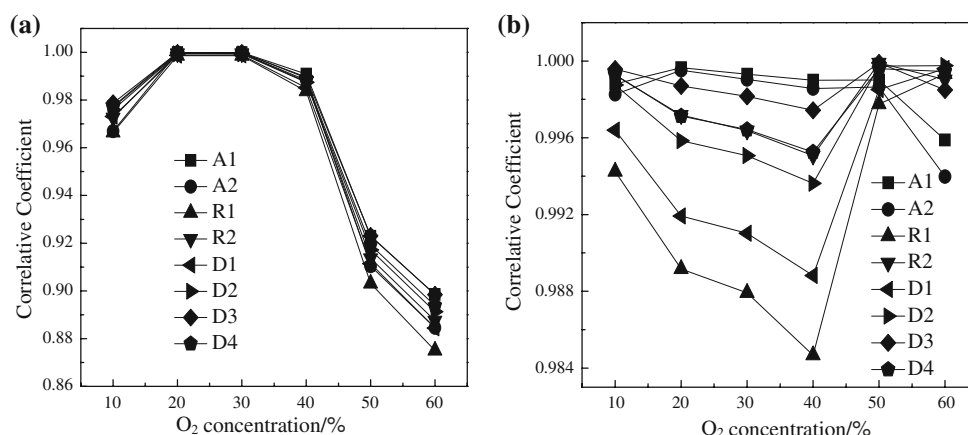


for the three coals. Although the  $E$  value for LC in low temperature was some bigger, its corresponding  $A$  was markedly increased in magnitude. At the same time, the corresponding low and high temperature zones for the principle mass loss of YQ were also shifted to higher temperature sections compared with LC and LY. The change current of  $A$  and  $E$  in Table 4 matched the data presented in Fig. 1 and Table 2 validating the forepart analysis.

Also, the calculated values of kinetic parameters for repeated experiments were shown in Table 4. It was concluded that values of activation energy deduced from the twice experiments changed little for a certain kind coal sample in either low or high temperature, though the referred temperature zone was not overlapped absolutely. And the corresponding values of standard deviations were small as a result. For YQ, LC and LY, the standard deviations were 4.242, 8.556, 3.394  $\text{kJ mol}^{-1}$  in low temperature zone and 3.748, 8.272, 6.435  $\text{kJ mol}^{-1}$  in high temperature zone, respectively.

The kinetic parameters of LC in oxy-fuel combustion with different  $\text{O}_2$  concentrations were listed in Table 5. Based on the curves in Fig. 2 and data in Table 3, it was seen that the combustion in 10%  $\text{O}_2$  concentration was hard to progress for the pre-exponential factor was evidently less compared with other  $\text{O}_2$  concentrations. Another aspect for 10%  $\text{O}_2$  concentration was that the reaction zone was broadened and shifted toward high temperature zone. Increasing the  $\text{O}_2$  concentration, the  $A$  values got increment, accordingly, and also the increased  $E$  values. But on the whole, the increment of  $A$  values dominated and the combustion characteristic improved with the reaction zone moving toward low temperature. As for 40–60% concentration, the effects of heightening  $\text{O}_2$  concentration further become invalid. So,  $\text{O}_2$  concentration in oxy-fuel combustion should vary between 20–40%, for combustion process got hard in low  $\text{O}_2$  concentration and the effect of heightening  $\text{O}_2$  concentration was not obvious if concentration exceeding 40%.

**Fig. 3** The correlative coefficients of different reaction models. **a** Low temperature zone and **b** high temperature zone



**Table 4** Kinetic parameters of YQ, LC and LY in TPC with 20%  $\text{O}_2$  concentration

Coal types	Temperature/K	$E/\text{kJ mol}^{-1}$	$A/\text{S}^{-1}$	$-R$
YQ-1	884–968	110.7	$6.00\text{E} + 02$	0.97381
	968–1074	114.0	$6.17\text{E} + 02$	0.99679
YQ-2	883–965	116.7	$6.38\text{E} + 02$	0.98096
	965–1074	108.7	$2.16\text{E} + 02$	0.99782
LC-1	775–813	248.2	$4.82\text{E} + 12$	0.99978
	813–855	177.3	$1.56\text{E} + 08$	0.99870
LC-2	782–818	236.1	$1.69\text{E} + 12$	0.99958
	818–865	161	$1.92\text{E} + 07$	0.99915
LY-1	699–748	171.2	$4.11\text{E} + 08$	0.99472
	748–799	125.1	$2.74\text{E} + 05$	0.99917
LY-2	693–743	176.0	$1.15\text{E} + 09$	0.99887
	743–796	116.0	$3.43\text{E} + 04$	0.99977

At the same time, the changes of  $A$  and  $E$  values with different  $\text{O}_2$  concentrations were not out-of-order for the determination of Arrhenius law,  $k = A \cdot \exp(-E/RT)$ . In other words, changes obeyed certain rule, and basically they were in the same current which could be explained by the “kinetic compensation effect” [12]. The linearity regression was made for the evaluated kinetic parameters of  $A$  and  $E$  in the model-fitting method (shown in Table 5) and expressed as:

$$\ln A = 0.1919E - 16.733 \quad (\text{low temperature zone})$$

$$\ln A = 0.1465E - 6.957 \quad (\text{high temperature zone}).$$

It is seen from Table 6 that, different values of activation energy were achieved from previous studies of other workers. Mainly, two aspects induced this result. One was that the experiments were not conducted under identical conditions and this included the different tested objects, heating rates, reaction atmospheres, etc. The other was the way in which the experimental data were dealt with. All of these factors resulted in the different values of activation energy.

**Table 5** Kinetic parameters of LC in TPC with different O<sub>2</sub> concentrations

O <sub>2</sub> concentration (%)	Temperature/K	<i>E</i> /kJ mol <sup>-1</sup>	<i>A</i> /S <sup>-1</sup>	- <i>R</i>
10	822–887	161.7	2.61E + 06	0.97868
	887–951	136.5	4.04E + 04	0.99958
20	775–813	248.2	4.82E + 12	0.99978
	813–855	177.3	1.56E + 08	0.99870
30	756–792	249.2	3.58E + 13	0.99979
	792–834	167.7	5.44E + 07	0.99816
40	739–766	312.2	2.68E + 18	0.98972
	766–809	154.4	1.84E + 07	0.99743
50	720–748	290.3	3.38E + 17	0.92307
	748–797	127.5	2.79E + 05	0.99990
60	719–743	316.5	2.01E + 19	0.89841
	743–797	115.1	3.41E + 04	0.99849

**Table 6** Comparison of activation energy values in this study with results of other workers

Reference	<i>E</i> /kJ mol <sup>-1</sup>	Reference	<i>E</i> /kJ mol <sup>-1</sup>
Present study	110.7–316.5	[12]	132–150
[8]	222.9–254.2	[14]	27.4–46.7
[9]	50–130	[23]	80–120

## Conclusions

This paper studied the combustion characteristics and kinetic parameters of pulverized coals in oxy-fuel atmosphere by using the thermogravimetric analysis and the following conclusions were obtained:

1. In oxy-fuel atmosphere, the deeper coalification sample got harder combustion progress compared with lower degree ones.
2. To get a better combustion process, sufficient oxygen must be provided and 10% O<sub>2</sub> concentration was inadequate for a favorable process. But, once the concentration exceeded 40%, O<sub>2</sub> prompted effect become feeble. So, O<sub>2</sub> concentration should vary in range of 40% for flexibility of the oxy-fuel combustion.
3. The model-fitting mathematical approach was well fitted for the evaluation of kinetic parameters and the Coats–Redfern method was applied in this study. The calculation showed that the *D*<sub>3</sub>-Jander was the proper equation for the reaction model. The change current of *A* and *E* with different O<sub>2</sub> concentrations could be presented as the “kinetic compensation effect” which could made linearity regression inherent in the Arrhenius law.

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