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Effects of Blast Furnace Slag with Iron Ore Containing Rare Earth Elements on Combustion Characteristics of Pulverized Coal

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Abstract: The combustion characteristics of pulverized coal when using blast furnace slag charged with iron ore containing rare earth elements as a composite catalyst were investigated by thermo gravimetric analysis. The results show that the combustion char acteristics of pulverized coal loaded with 21.3% by weight of blast furnace slag containing 15% rare earth ore are better than those of others. It is also indicated that the composite catalyst promotes combustion of volatiles and also performs well for carbon residue. The mechanism of promotion by the composite catalyst was explored. The kinetic parameters calculated by the Coats-Redfern model show that the activation energy(E) was reduced by10 kJ/mol, the time of combustion was shortened by 3min, pre-exponential factor(A) reached 2.7×10^4/min and general combustion characteristic index (S)was 1.09.

Keywords: Pulverized coal (PC), catalyst, thermo gravimetric analysis, rare earth ore, blast furnace slag, kinetic model.

1. INTRODUCTION

Studies have been conducted to improve the characteristics of pulverized coal (PC) to shorten combustion time during its passage through the raceway, increase coke ration, and reduce costs. Previous reports show that adding a catalyst provides an efficient mechanism for combustion [1]. Alkali, alkaline-earth metal, transition metal, and rare-earth compounds have been widely used as catalysts [2-5]. Alkali compounds are hazardous, while transition metal compounds exhibit beneficial effects [6]. Shen and co-workers [7] found that oxygen decomposition of MnO_2 accelerates burning speeds in Northeastern University. ZHANG and co-workers [8] found that CeO_2 improves the combustion of carbon in University of Science &Technology Beijing.

The combustion of PC can be divided into three stages displaying different mechanisms. Many disadvantages for single catalysts have been discovered. Herein, the combustion characteristics of PC and parameters such as the activation energy and pre-exponential factor at different catalyst loading are discussed. The mechanism has also been tentatively explored.

2. MATERIAL AND METHODS

2.1. Experimental Materials

The results of ultimate and proximate analysis of PC are shown in Table **1**.

Table 1. Ultimate, proximate analysis and calorific value of coal sample.

Grade	Percentage								Constant Volume Heating Value (J/g)
	FC_{ad}	A_{ad}	V_{ad}	C_{ad}	H_{ad}	O_{ad}	N_{ad}	S_{ad}	
PC	68.76	8.07	23.38	75.66	3.91	10.64	0.75	0.27	28667.72

Note: FCad, Vad, and Aad were based on air-dried samples.

The composition of blast furnace (BF) slag is shown in Table **2**.

Table 2. Composition of BF slag.

Percentage				
CaO	MgO	SiO_2	Al_2O_3	Remain
41.66	15.3	28.18	11.54	3.32

Note: FCad, Vad, and Aad were based on air-dried samples.

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The percentage of elements of iron ore containing rear earth elements is shown in Table **3**.

Table 3. Percentage of elements in ore.

Percentage					
Fe	**Ca**	**F**	**La**	**Y**	**Remain**
32.03	14.21	12.08	1.34	0.03	40.31

The slag is taken from Baogang group which locates in Inner Mongolia Autonomous Region.

2.2. Experimental Design

An HCT-3 differential thermo analysis apparatus was manufactured by Beijing Hengjiu. The system includes a balance, a control system for temperature and atmosphere, and a computer.

The PC was dried at 105°C for 2h. The ration BF slag to iron ore containing rare-earth elements was kept constant at 17:3. The weight of coal was 14.5±0.1mg, and the volume of the Al2O3crucible was 0.06ml. Air was flowed at100 ml/min, and the temperature increased at the rate of 10°C /min from room temperature. The thermo gravimetric (TG) and differential thermo gravimetric (DTG) curves were recorded automatically by using the attached computer. The variations in experiments are shown in Table **4**.

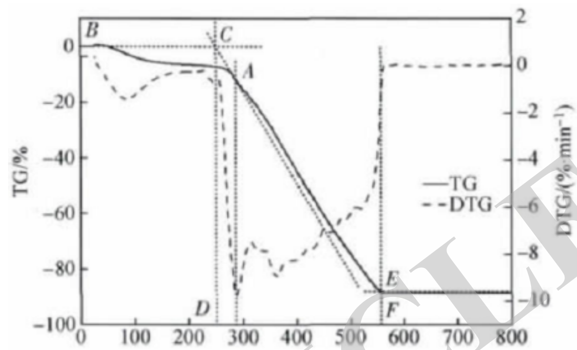

Fig. (1). Determination of ignition temperature.

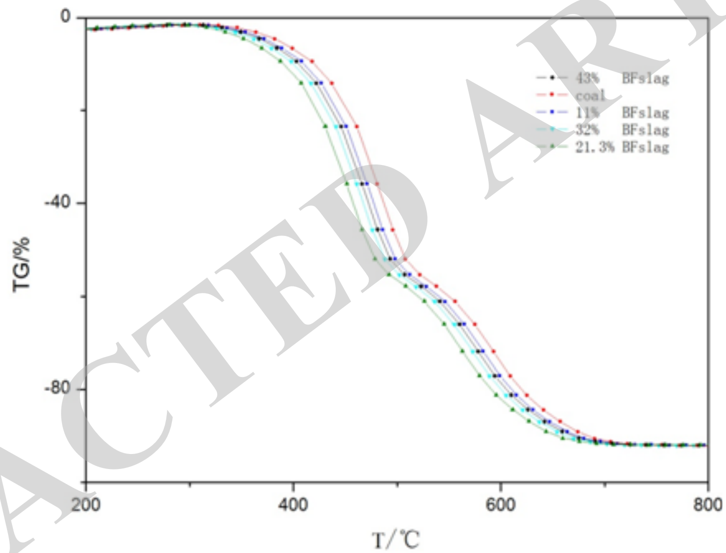

Fig. (2). TG curves of samples.

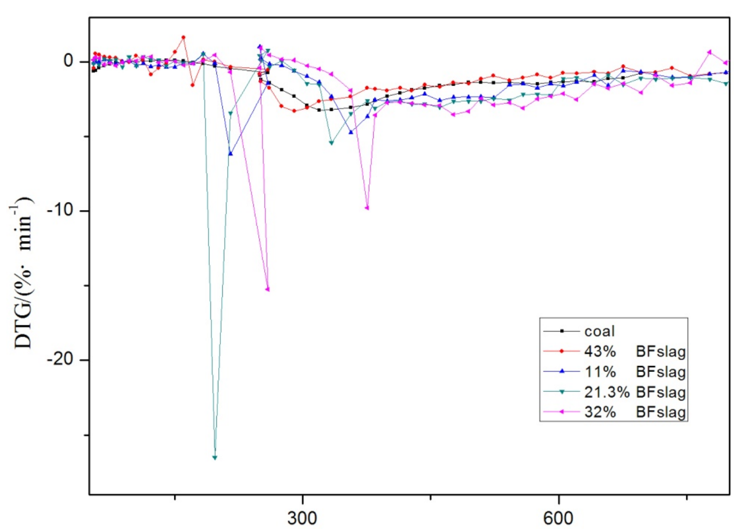

Fig. (3). DTG curves of samples.

Table 4. Experimental variations.

NO.	Catalyst	Percentage
1	0	0
2	BF slag	11
3		21.3
4		32
5		43

2.3. Evaluating the Indicator of Combustion

The general combustion characteristic index S [9] was used as an indicator of combustion, where a larger value indicates better combustion. S can be expressed by the following equation (1):

$$S = \frac{\left(\frac{dw}{dt}\right)_{\max}\left(\frac{dw}{dt}\right)_{mean}}{T_I^2 T_F} \quad (1)$$

where, $(dw/dt)_{max}$ is the maximum combustion rate,(%/min); $(dw/dt)_{mean}$ is the average combustion rate, (%/min); T_I is the ignition temperature, K, and T_F is the burn-off temperature, K.

The method [4] used for determining the ignition temperature is shown in Fig. (**1**).

A perpendicular line drawn from the peak of the DTG curve intersects the TG curve at point A. The tangent line from point A intersects horizontally at point C. The temperature at point C was taken as the ignition temperature. The temperature at which the sample lost 98% of the total weight was taken as the burn-off temperature (E). The time was also determined.

3. RESULTS AND ANALYSIS

3.1. TG and DTG

The effects of the catalyst on the combustion characteristics at different content ratios are shown in Figs. (**2**, **3**).

The TG curve shows that an increase in catalyst content improves the combustion characteristics of PC. The ignition temperature decreases and the rate of combustion increases. The most effective combustion was achieved when the content of the catalyst was 21.3wt%.

The momentary weight loss rate is shown by the DTG curve. The shape of the curve gets sharper and reaches a peak at a content of 21.3wt%. The position of the peak shifts in relation to the type and content of catalyst.

3.2. Effects of Catalyst on Combustion Parameters

The combustion parameters of PC are shown in Table **5**.

T_I, ignition temperature, K;T_1, peak temperature, K;T_F, burn-off temperature, K.

PC combustion becomes more efficient with the inclusion of a catalyst, with the most effective being the third group shown in Table **5**. T_I decreases to 699.5 K, T_1 decreases to723.3K, and T_F decreases to 880.5 K. The maximum and average weight losses are 8.39%/min and 5.61%/min, respectively. The process time was shortened by 3min and the value of S was 1.09.

A lower ignition temperature means the catalyst can cause the lixiviation of volatiles at an earlier stage. The

Table 5. Combustion parameters of PC with catalyst.

Percentage	T_I/K	T_1/K	(dw/dt)max/(%·min^{-1})	(dw/dt)mean/(%·min^{-1})	T_F/K	t/min	S×10^7/((%·min^{-1})^2·K^{-3})
0	723.3	739.1	6.89	5.07	915.3	19.7	0.730
11	709.6	737.2	6.99	5.41	890.6	18.1	0.843
21.3	699.5	723.3	8.39	5.61	880.5	16.8	1.09
32	707.8	741.5	7.59	5.52	895.3	17.8	0.934
43	705.4	745.4	7.39	5.35	890.8	18.5	0.892

Table 6. Parameters of combustion.

Percentage	Temperature Range (K)	Activation Energy (kJ/mol)	pre-Exponential Factor (min^{-1})	R^2	K α	
					713 K	823 K
0	703-900	97.58	1.9×10^4	0.9971	0.0412	0.425
11	709-890	91.14	2.4×10^4	0.9851	0.0533	0.575
21.3	699-880	82.03	2.7×10^4	0.9942	0.0621	0.753
32	707-895	86.21	2.1×10^4	0.9911	0.0596	0.588
43	705-890	90.55	1.5×10^4	0.9766	0.0588	0.573

combustion of volatiles accelerates the process and increases the speed of the reaction.

The best combustion efficiency at 21.3% catalyst content indicates that only a small amount of the catalyst is required, beyond which the catalyst coats the PC particles and blocks the pathway of oxygen, which further reduces diffusion and limits the efficiency.

3.3. Kinetic Analysis

During the non-isothermal and heterogeneous process [10-11], the linear equation of $\mathrm{d}\alpha/\mathrm{dt}$, reaction rate constant k, and combustion function f(α) can be expressed in the following way:

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

where, α is the rate of conversion, A is the pre-exponential factor, and E is the activation energy.

f(α) is expressed in the following way:

$$f(\alpha) = (1-\alpha)^n \quad (3)$$

where, n is the order of reaction.

α is expressed in the following way:

$$\alpha = \frac{m_i - m_t}{m_i - m_\infty} \quad (4)$$

where, m_i is the initial mass, m_t: is the mass at time t, and m_∞ is the final mass.

The heating rate (β) is expressed in the following way:

$$\beta = \frac{dT}{dt} \quad (5)$$

Introducing equations (3) and (5) in (2) gives

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)dT \quad (6)$$

The order of PC combustion is 1. Taking the integral of (6)gives,

$$\ln\left(-\frac{\ln(1-\alpha)}{T^2}\right) = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad (7)$$

When $\frac{E}{RT} \geq 1$ and $\left(1-\frac{2RT}{E}\right) \approx 1$ cause, $\ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right]$ as is constant at normal temperature. The linear equation y=kx+b can be achieved through line-fitting. The activation energy(E)and pre-exponential factor (A)were calculated by using the slope coefficient $k=-\frac{E}{R}$ and intercept $b=\ln\frac{AR}{\beta E}$.

The fitting results in the different content of catalyst are shown in Figs. (**3-8**).

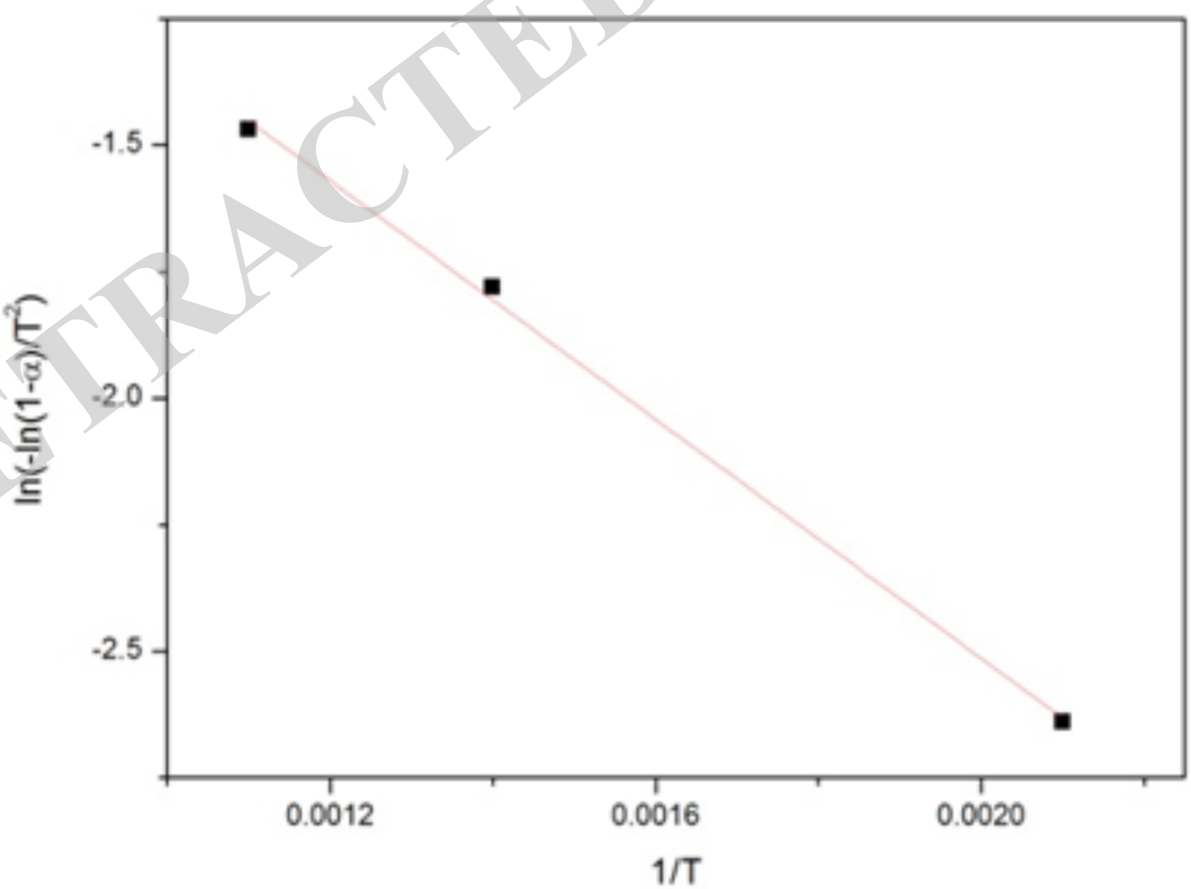

Fig. (4). The content of catalyst is 0.

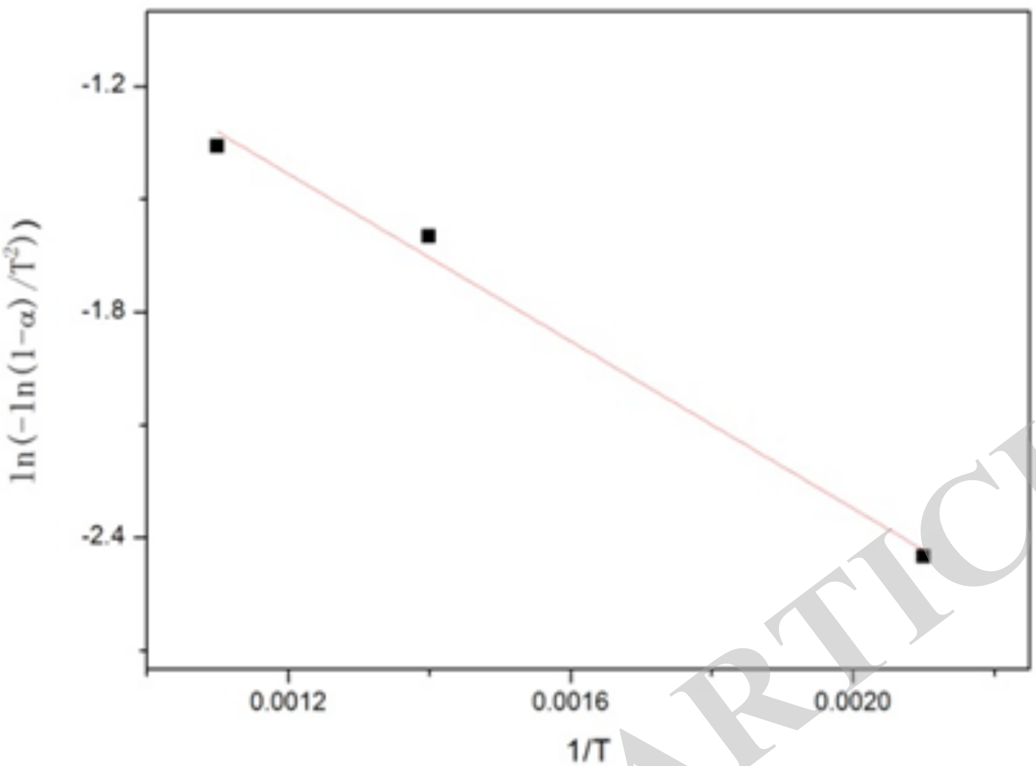

Fig. (5). The content of catalyst is 11%.

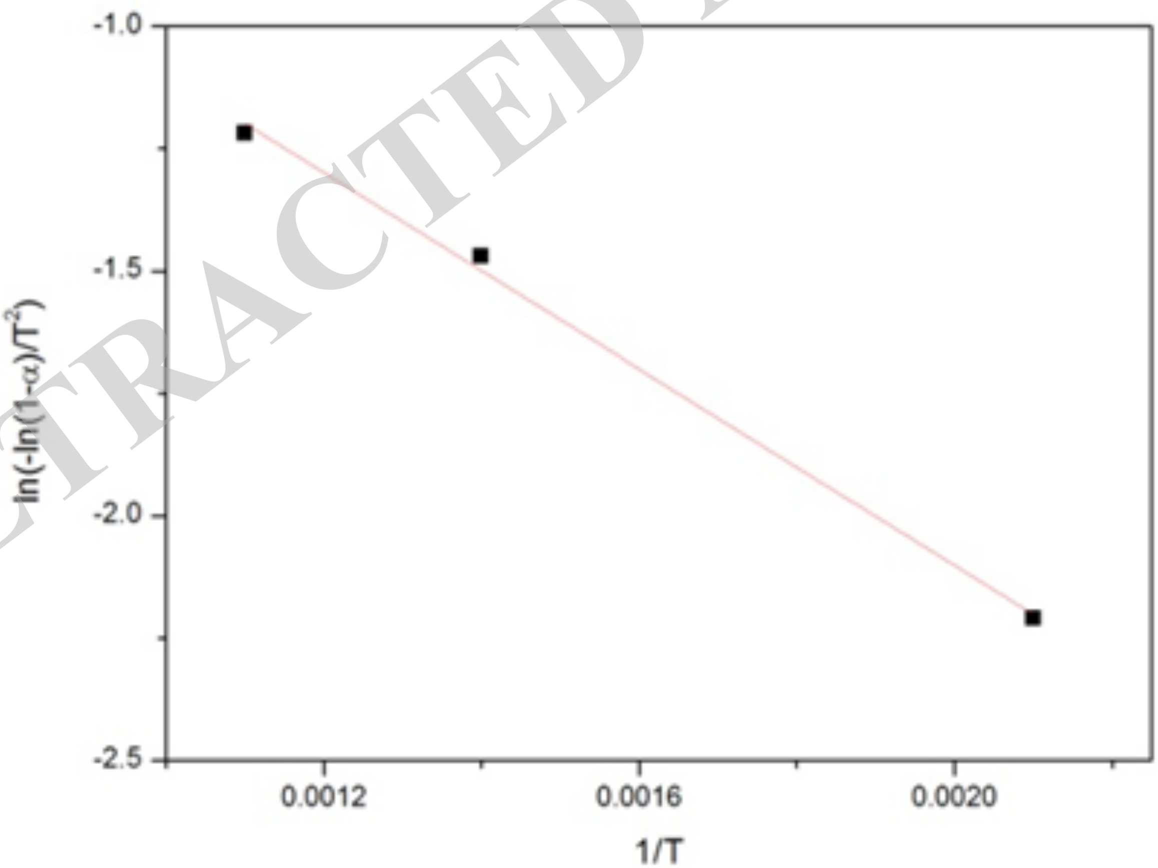

Fig. (6). The content of catalyst is 21.3%.

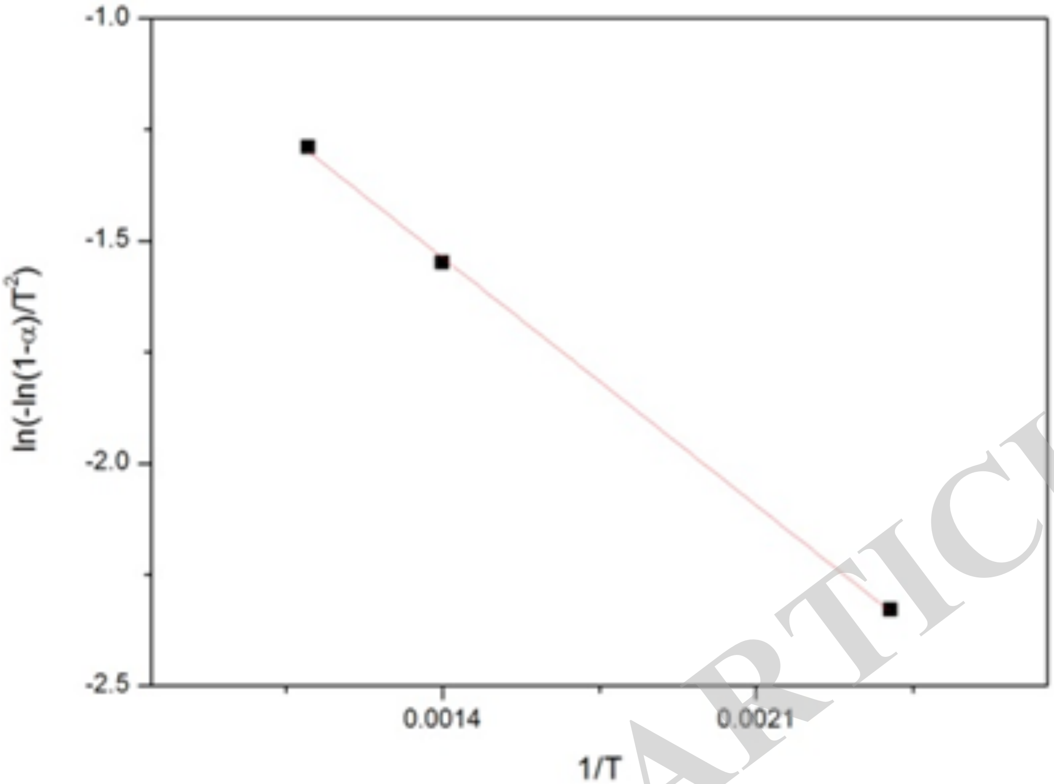

Fig. (7). The content of catalyst is 32%.

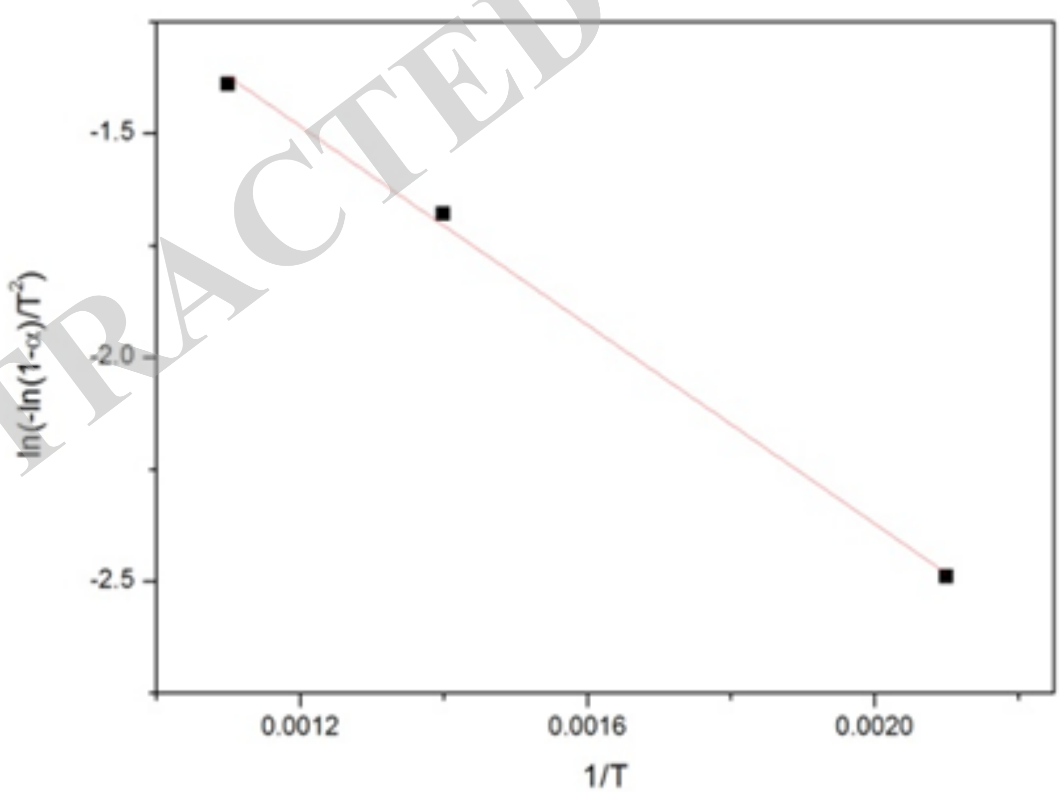

Fig. (8). The content of catalyst is 43%.

The kinetics parameters achieved by the method above are shown in Table **6**.

The range of coefficients is 0.9766-0.9971.What the range of coefficients shows a good correlation to the function.

When the ignition temperature decreases, the activation energy is reduced by10kJ/mol and the time of combustion shortens by around 3min. The value of the pre-exponential factor ranged from 1.9×10^4-2.7×10^4/min. To check the effect of the catalyst under different temperatures, Kα was also calculated and the results are shown in Table **6**.

K_α can be defined as the following way,

K_α=(-E/RT).Where, R, gas constant, 8.314J/(mol·K), other parameters as mentioned above.

The process of thermolytic dissociation can be divided into two parts dehydrogenation condensation and decarburization cracking.

Dehydrogenation condensation occurs when the hydrogen bond is broken so that the aromatic products such as benzene, ortho-xylene and paraffin can be condensed to form coke. Decarburization occurs when the covalent carbon bond is broken, and then the formation of active free radicals continues to split the coal into smaller gaseous molecules. Combustion occurs after contact with oxygen.

It is well known that compound catalysts provide better effects than single catalysts. BF slag with iron ore containing rare-earth elements can improve the combustion characteristics of PC.

Undersaturation improves the combustion properties by increasing the combustion rate in the presence of rare earth elements. The electronic shell structure produces the characters of a metastable state; vacancies and ions format the current rate, which can absorb O_2, O^{2-}, and O^- to accelerate the process of combustion.

At the initial stage of combustion, the reduction environment reduces Fe_2O_3 to FeO. The reverse reaction happens in the absence of the environment. With the help of Fe^{2+} and Fe^{3+}, oxygen is transported through a series of reactions as follows.

$$C+O\rightleftarrows C[O] \rightleftarrows C_XO_Y;C_XO_Y\rightleftarrows CO+CO_2;\ CO_2\rightleftarrows CO) \quad (8)$$

The results accelerate the process of combustion.

Another reason for improved combustion was attributed to lattice defects and vacancies in compounds which favor the inclusion of oxygen. Further studies need to be conducted to gain a deeper understanding.

CONCLUSION

1) According to the results of thermo gravimetric analysis, BF slag with iron ore containing rare earth elements as a composite catalyst improved combustion characteristics of PC, with the most efficient catalyst content being 21.3wt%.
2) The catalysts can improve the combustion of volatiles and carbon residue; however, the improvement was more prominent for the latter.
3) The regulation of combustion characteristics of PC with different contents was explored. Results of the kinetic analysis show that the best case was determined to have an activation energy and a pre-exponential factor of 82.03 kJ/mol and2.7×10^4 min^{-1}, respectively.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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