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CO-PYROLYSIS KINETICS ANALYSIS OF STONE COAL AND BIOMASS FOR VANADIUM EXTRACTION

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In this paper, co-pyrolysis of stone coal and biomass was performed. The activation energy of pyrolysis was analyzed, and the mechanism of biomass on the stone coal pyrolysis was discussed. The results show that biomass contributed to the pyrolysis of stone coal. The optimum pyrolysis heating rate of the biomass and stone coal was 25 °C/min and 20 °C/min respectively. The alkaline and alkaline earth metals derived from biomass pyrolysis improved thermal decompose of stone coal, yet stone coal inhibited biomass pyrolysis under co-pyrolysis conditions. The promotion of corn stalk on the stone coal pyrolysis was better than that of sawdust.

Key words: vanadium extraction, co-pyrolysis kinetics, stone coal, biomass, activation energy

INTRODUCTION

Vanadium can significantly improve the common welding performance of low carbon steel. Stone coal, containing massive vanadium resource, is the mainly source of Chinese vanadium products [1]. However, stone coal has a poor effect of vanadium extraction for its low calorific value. A certain proportion of the auxiliary fuel is added to improve this problem. Technology of mixing biomass and stone coal to extract vanadium is a new process with less pollution and better efficiency of vanadium extraction [2]. Therefore, further study of stone coal and biomass co-pyrolysis dynamics can reveal the co-pyrolysis characteristics and the pyrolysis mechanism of stone coal. Much research has been done on the co-pyrolysis of biomass and coal [3-4], and various kinetic models are formed, of which the Coats-Redfem integral method is the most extensive [5].

In this paper, the activation energy/ E was analyzed during the co-pyrolysis of biomass and stone coal, and the interaction in pyrolysis was discussed. Pyrolysis dynamics model and reaction order were determined. Activation energy/ E and pre-exponential factor/ A were calculated. This study provides a reference for the process of vanadium extraction from stone coal.

MATERIALS AND METHODS

The stone coal as raw materials was collected from Hubei province in China. The auxiliary fuel was corn stalk and sawdust from Liaoning province. The stone coal and the biomass were ground to a particle size of 0,15 mm or less. The two kinds of biomass were mixed respectively with stone coal in a certain proportion.

The experiment was carried out by The Setsys Evolution synchronous thermal analyzer manufactured by the French Seth Rahm Company. The carrier gas was high purity nitrogen and the flow rate was 40 ml/min. The thermal analyzer was first introduced 0,5 hours nitrogen before the experiment. Empty crucible was used as dynamic baseline calibration. The weight of each sample was 7 mg.

The analysis of the samples was shown in Table 1 and Table 2. The Coats-Redfem integration method was selected to process the solid thermal decomposition velocity equation.

Table 1 **Industrial analysis**

Samples	M_{ad} /%	A_{ad} /%	V_{ad} /%	FC_{ad}/%
Stone coal	0,53	63,72	6,21	29,54
Corn stalk	7,62	12,59	62,21	17,58
Sawdust	7,53	2,79	73,28	16,41

Where: M_{ad} - moisture; Aad - ash; V_{ad} - volatile; FC_{ad} - fixed carbon

Table 2 **Elementary analysis**

Samples	C_{ad}/%	H_{ad}/%	O_{ad}/%	N_{ad}/%	S_{ad}/%
Stone coal	29,20	0,38	3,13	0,01	2,83
Corn stalk	43,68	4,32	33,62	0,71	0,22
Sawdust	46,72	5,73	37,63	1,18	0

RESULTS AND DISCUSSION

The pyrolysis interval of each reaction stage was solved and the conversion rate of 0,1 – 0,9 in each interval were fitted on the basis of Thermal Gravity Analysis / Differential Thermal Gravity (TG / DTG) data. Assuming that the reaction series was 1, the linear correlation coefficient was found to be above - 0,995 by calculation.

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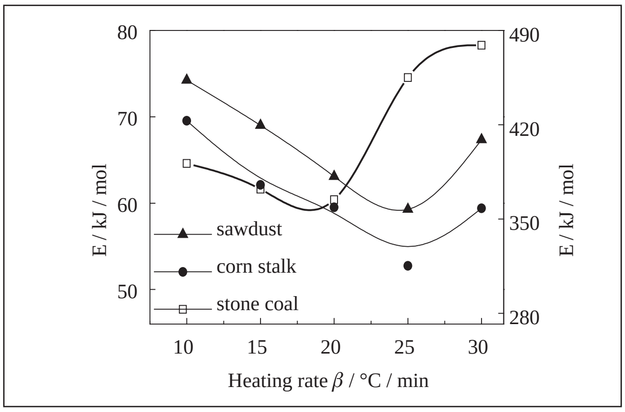

Figure 1 Pyrolysis activation energy of biomass and stone coal

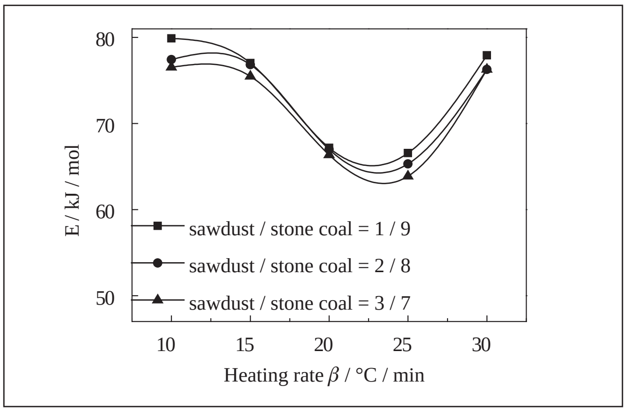

Figure 2 Co-pyrolysis activation energy of sawdust

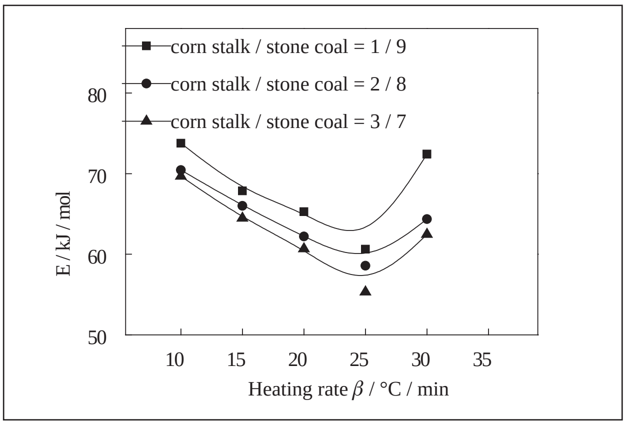

Figure 3 Co-pyrolysis activation energy of corn stalk

It illustrated that the fitted curve was consistent with the actual curve. The linear correlation coefficients of the fitting equation at different heating rate were between 0,97514 – 0,9999, indicating that the assuming reaction series was reasonable. Therefore, the kinetic studies in this paper were based on first-order reaction kinetics.

Pyrolysis kinetic analysis of individual samples

Figure 1 shows that the activation energy of the three samples decreased first and then increased under different heating rate, and the minimum activation energy of biomass and stone coal occurred at 25 °C / min and 20 °C / min respectively. The reason was that slower heating rate caused the sample energy to accumulate slowly, resulting in a slow reaction, thus requiring a higher activation energy. Faster heating rates lead to delayed heat transfer, which tends to result in higher activation energy for pyrolysis of the samples.

The activation energy required for biomass pyrolysis was lower than that of stone coal. The reason was a large number of high bond energy C = C bonds in stone coal. It was also found that the activation energy required for corn stalk pyrolysis was lower than that of sawdust. The reason was the high content of lignin in sawdust but the high content of cellulose and hemicelluloses in corn stalks. Therefore, the stronger molecular cross-linking effect of sawdust makes the activation energy required for pyrolysis higher than that required for corn stalks.

Kinetic analysis of the biomass in the co-pyrolysis

Kinetic calculations were performed for the co-pyrolysis of biomass and stone coal with different blending ratios at different heating rate (Figure 2, Figure 3). The results show that the required pyrolysis activation energy of the biomass decreased gradually with the increase of its mixing ratio, but more than that of the individual pyrolysis at the same heating rate. This phenomenon indicated that the stone coal suppressed the normal pyrolysis of biomass and the inhibition gradually diminished with the increase of biomass. Taking the heating rate of 25 °C / min as an example, the activation energy required for sawdust and corn stalk in the co-pyrolysis increased by approximately (5,2 – 7,5) kJ / mol and (2,5-8,6) respectively, comparing to single pyrolysis. The activation energy in the biomass pyrolysis decreased first and then increased with the accelerating of the heating rate. The activation energy required for biomass pyrolysis attained minimum when the heating rate was 25 °C / min.

Kinetic analysis of the stone coal in the co-pyrolysis

Figure 4 and Figure 5 indicate that the activation energy required for stone coal in the co-pyrolysis was less than in independent pyrolysis at different heating rate. Thus, the addition of biomass was more conducive to the stone coal pyrolysis. The effect of biomass on the pyrolysis of stone coal was strengthened gradually with the increase of the biomass in the mixture. The activation energy required for the stone coal pyrolysis was still decreasing and then increasing with the accelerating of the heating rate under the same mixture ratio.

Selectivity of stone coal to biomass

Figure 6 shows that the effect of corn stalk on the pyrolysis of stone coal was better than sawdust on stone coal, and the difference was more obvious with the increase of heating rate.

When the stone coal was mixed with 20 % biomass at the heating rate of 20 °C / min, activation energy of

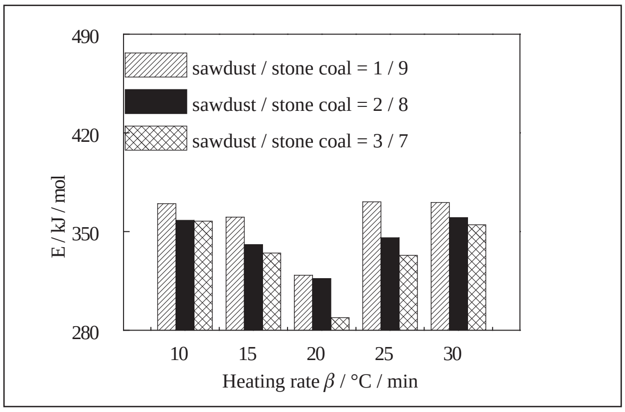

Figure 4 Pyrolysis activation energy of stone coal in the sawdust / stone coal mixture

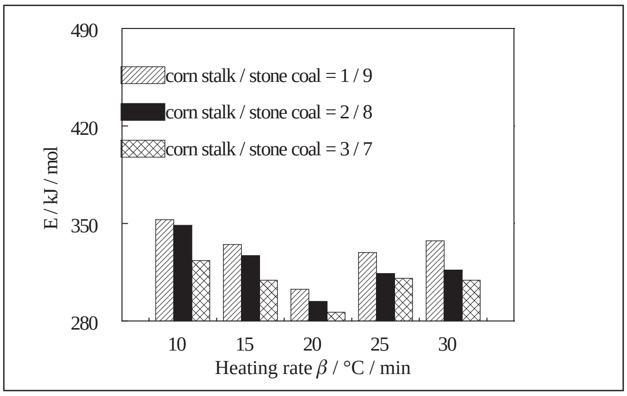

Figure 5 Pyrolysis activation energy of stone coal in the corn stalk / stone coal mixture

the stone coal in the co-pyrolysis of corn stalk / stone coal was reduced by about 22,5 kJ/mol comparing to that of stalk / stone coal mixture.

X-ray fluorescence(XRF)

Table 3 **XRF results of bomass ash / wt. %**

Biomass	K_2O	CaO	MgO	SiO_2
Sawdust	28,36	21,04	10,63	10,20
Corn stalk	0,52	14,01	18,11	39,96
Biomass	P_2O_5	Na_2O	Al_2O_3	Fe_2O_3
Sawdust	8,64	4,86	2,36	1,81
Corn stalk	—	20	6,02	1,42

Table 3 shows that the two biomass ash contains a large amount of alkaline earth metals such as CaO and MgO. The total content of sawdust is 31,67 % and the corn stalk is 32,12 %. A large number of alkaline earth metals reacted with harmful gases, such as H_2S and COS produced by the pyrolysis of stone coal. The formation of H_2O and CO_2 resulted in less sulfide produced from the stone coal pyrolysis, which promoted the further reaction.

The two kinds of biomass pyrolysis ash also contains substantial K_2O and Na_2O, which was 20,52 % in the corn stalk ash and 33,22 % in the sawdust ash. The literatures shows that alkali metals and their oxides had a significant catalytic effect on the pyrolysis of stone coal [6]. Therefore, the pyrolysis effect of corn stalk on stone coal was better than the sawdust on stone coal with the same addition ratio.

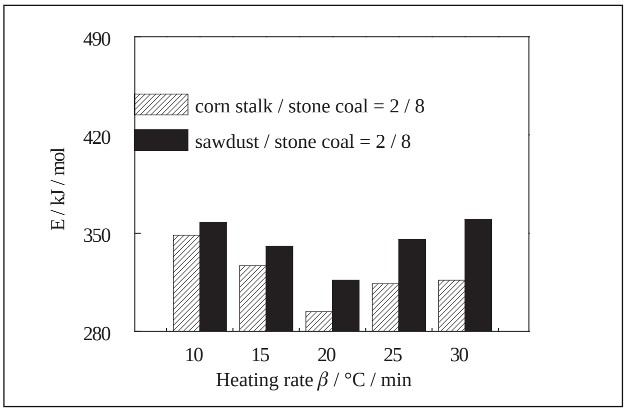

Figure 6 Effect of biomass type on activation energy of stone coal during co-pyrolysis

CONCLUSION

The pyrolysis activation energy of stone coal was much larger than that of biomass during the pyrolysis, and the pyrolysis activation energy of the corn stalk was less than the sawdust. The pyrolysis activation energy of the stone coal was first reduced and then increased with the acceleration of the heating rate. The optimum pyrolysis heating rate was 20 °C / min.

Stone coal inhibited the biomass pyrolysis but the biomass promoted the stone coal pyrolysis in the co-pyrolysis. The co-pyrolysis of cornstalk and stone coal was better than sawdust and stone coal. The main reason was that the content of alkali metal and alkaline earth metal in the ash of corn stalk was obviously higher than that of sawdust, which had a positive effect on the pyrolysis of stone coal.

Acknowledgments

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Note:Kun Liu is responsible for English language, China