International Conference on Applied Energy 2019
Aug 12-15, 2019, Västerås, Sweden
Paper ID: 567

THERMAL EFFECT AND KINETIC ANALYSIS ON CO-PYROLYSIS OF LOW-RANK COAL WITH CELLULOSE FROM BIOMASS

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ABSTRACT

The prospect of using biomass alone is broad, but there are a number of problems that make it difficult to achieve real profitability. In this paper, the thermal effects and reaction kinetics of cellulose and low-rank coal mixing at different mixing rates (25 wt%, 50 wt.% and 75 wt.%) and different heating rates (10 ^{o}C·min^{-1}, 20 ^{o}C·min^{-1}, 40 ^{o}C·min^{-1}) were studied via thermogravimetric analyzer(TGA). The addition of low-rank coal can promote the formation of volatile substances in the co-pyrolysis process, and the degree of synergy is closely related to the heating rate and blending ratio. The kinetic results show that the average activation is 244.44 kJ·mol^{-1} and 164.41 kJ·mol^{-1} when the low-rank coal blending ratio is 25% and 50%.

Keywords: low-rank coal, cellulose, co-pyrolysis, thermal effect, kinetic analysis

1. INTRODUCTION

Although the utilization of biomass alone is promising, it is difficult to achieve real profitability due to high storage and storage costs of raw materials and low energy density. Coal and biomass are similar and complementary. Many scholars have used them together. It is believed that co-pyrolysis can improve the economic performance of biomass. The pyrolysis mechanism is crucial for product selection[1-4]. Similarly, for thermochemical conversion processes such as combustion or gasification, how to clarify the reaction mechanism and kinetics of the initial pyrolysis process is extremely necessary[5].

For the co-pyrolysis reaction of biomass and coal, the mutual coordination between the two products during the pyrolysis reaction will affect the final yield and quality of the product. Chen et al [6]used coal and corn stover as raw materials to study the effect of heating rate and straw ratio on coal and co-pyrolysis via TGA. It was found that corn straw hindered the release of volatiles from the blend. Zhang et al [7] studied the distribution of co-pyrolysis products of pine chips and sub-bituminous coal in free-fall reactors, and found that the mixing of sub-bituminous coal can increase the yield of tar and reduce the yield of small-molecule hydrocarbons. In addition, the synergy between the two can reduce asphaltenes in the tar and improve its quality. Most of the previous studies have focused on the actual agroforestry waste and coal co-pyrolysis. The pyrolysis product distribution and related characteristic parameters are obtained by changing the pyrolysis conditions and mixing ratio. Most of the previous researches focused on the actual agroforestry waste and coal co-pyrolysis, and obtained the distribution of co-pyrolysis products and related characteristic parameters by changing the pyrolysis conditions and mixing ratio. However, due to the wide variety and diversity of biomass sources, many scholars have different conclusions on the co-pyrolysis characteristics, the co-pyrolysis product distribution and the co-pyrolysis kinetics. Some scholars believe that the structural similarity between biomass and low-rank coal is higher than between biomass and high-rank coal, and the interaction between biomass and low-grade coal is more obvious than between biomass and high-grade coal [8, 9].

Therefore, this paper aims to study the kinetics and product distribution of cellulose (CE) and low-rank coal(LC) in co-pyrolysis from the important organic composition of biomass and the low-rank coal of Shenfu. The synergistic mechanism and product distribution, heat coupling and kinetic characteristics of the two under slow pyrolysis conditions were studied, which

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Selection and peer-review under responsibility of the scientific committee of the 11th Int. Conf. on Applied Energy (ICAE2019).

provided a theoretical basis for efficient conversion and utilization of biomass and coal.

Table 1. Proximate and ultimate analyses of CE and LC.

	LC	CE
Proximate analysis (wt. %, ad)		
Moisture, M	4.18	4.67
Ash, A	15.38	0.07
Volatile, V	30.56	93.37
Fixed carbon, FC	49.88	1.89
Ultimate analysis (wt. %, daf)		
Carbon, C	79.31	51.47
Hydrogen, H	4.72	2.87
Nitrogen, N	1.03	1.69
Sulfur, S^t	1.3	0.03
Oxygen, O^c	13.38	43.98
ad: Air-dried; daf: Dry ash-free; t: Total content; c: Calculated by difference.		

Table 2. Thermal behavior of pyrolysis parameters from co-pyrolysis of CE and LC under 20 $^{o}C\cdot min^{-1}$

Parameters		CE	LC
T_{in}(°C)	Initial devolatilization temperature	317	108
$R_{\max}$(%·min^{-1})	Maximum decomposition rate	-48.83	-2.68
$T_{\max}$(°C)	Temperature of maximum decomposition rate	352	464
$\Delta T_{1/2}$(°C)	Temperature interval when $R_{\mathrm{d}}/R_{\max}$=1/2	29.3	101.2
D_{i}(10^{-8}%·min^{-1}·$^{o}C^{-3}$)	Devolatilization index of the sample	1493.42	52.86
Solid yield(%)	Initial devolatilization temperature	10.51	68.21
W_{Exp} (%)	Experimental weight lose	89.49	31.79
W_{Cal}(%)	Calculated weight lose	-	-

2. MATERIALS AND METHODS

2.1 Materials

The powdered cellulose used in the experiment was purchased from Sigma–Aldrich Co., Ltd., and the coal sample was collected from Shenfu, northern Shaanxi. The coal sample is first ground by a sample pulverizer 5E-PC1-100, and then sampled and sieved through a standard sieve machine 5E-SS200 to sample 200 mesh, and dried for use. Industrial analysis and elemental analysis of the samples are shown in Table 1. The coal was mixed with cellulose according to the mass fraction of 25%, 50% and 75%, stirred by a shaker and placed in a dry container for use. The samples were named CE-LC-3-1, CE-LC-1-1. , CE-LC-1-3.

2.2 Experimental method

The experiment used the HCT-3 differential thermal analyzer of Beijing Henven Instrument to test the slow pyrolysis behavior of the mixture of cellulose and coal. A 10 mg sample was taken for each experiment, and first purged with high-purity argon at a volume flow rate of 60 mL·min-1 for 1 hour to purge the air in the gas path. Then, it was raised from 25 °C to 850 °C at three different heating rates of 10 $^{o}C\cdot min^{-1}$, 20 $^{o}C\cdot min^{-1}$ and 40 $^{o}C\cdot min^{-1}$. The gas phase products generated during the reaction were monitored in real time by an on-line mass spectrometer, and each experiment was repeated three times to ensure reproducibility of the experiment. Detailed information on data processing and analysis methods can be found in previous studies [10-13].

3. RESULTS AND DISCUSSION

3.1 Pyrolysis characteristics

The results of the relevant pyrolysis characteristic parameters calculated from the TG and DTG data are listed in Table 2, and it can be found that the initial pyrolysis temperature of the mixture is reduced due to the addition of low-rank coal. Cellulose and low-rank coals have different maximum decomposition rates and their relative temperatures due to their structural differences[14]. The maximum decomposition rate decreases with the increase of low rank coal. The maximum weight loss rate is lower than that of the single material. Especially under the mixing of 25% low rank coal, there may be some synergistic effect, which makes the mixed pyrolysis. The reaction can be carried out at a lower temperature. Calculating the weight loss according to the respective coke yields, comparing the experimental values with the theoretical values, it can be found that the total weight loss of the co-pyrolysis of each mixed sample is higher than the calculated value, especially 6.25% when the 25% low-rank coal is blended. It is suggested that there may be a positive synergistic effect between the cellulose and the low rank coal on the formation of volatile products (Shui et al., 2017) [15].

3.2 Synergistic effect

Figure 1 shows the TG and DTG curves for slow pyrolysis of cellulose and low-rank coal at different mixing ratios. From the TG curve, the experimental values before 300 °C are not much different from the theoretical values. The experimental curves and theoretical curves are different in the main pyrolysis range of 322 °C ~376 °C, and the experimental values of weight loss rate are lower than the theoretical values. At 390 °C this difference reached a maximum and remained until the end of the reaction, indicating a certain synergy.

Comparing the theoretical and experimental DTG curves in Figure 1 (b), the peak experiment between 322 °C and 376 °C is significantly different from the expected one. It can be seen that the experimental value of the maximum weight loss rate in this temperature range is compared with the theoretical value. The value is high, which may be caused by the temperature hysteresis effect of the addition of low-rank coal for cellulose. The addition of low-rank coal accelerates the rate of thermal decomposition of cellulose, which may be one of the direct causes of the synergistic effect of weight loss. The synergistic effect of each mixed sample

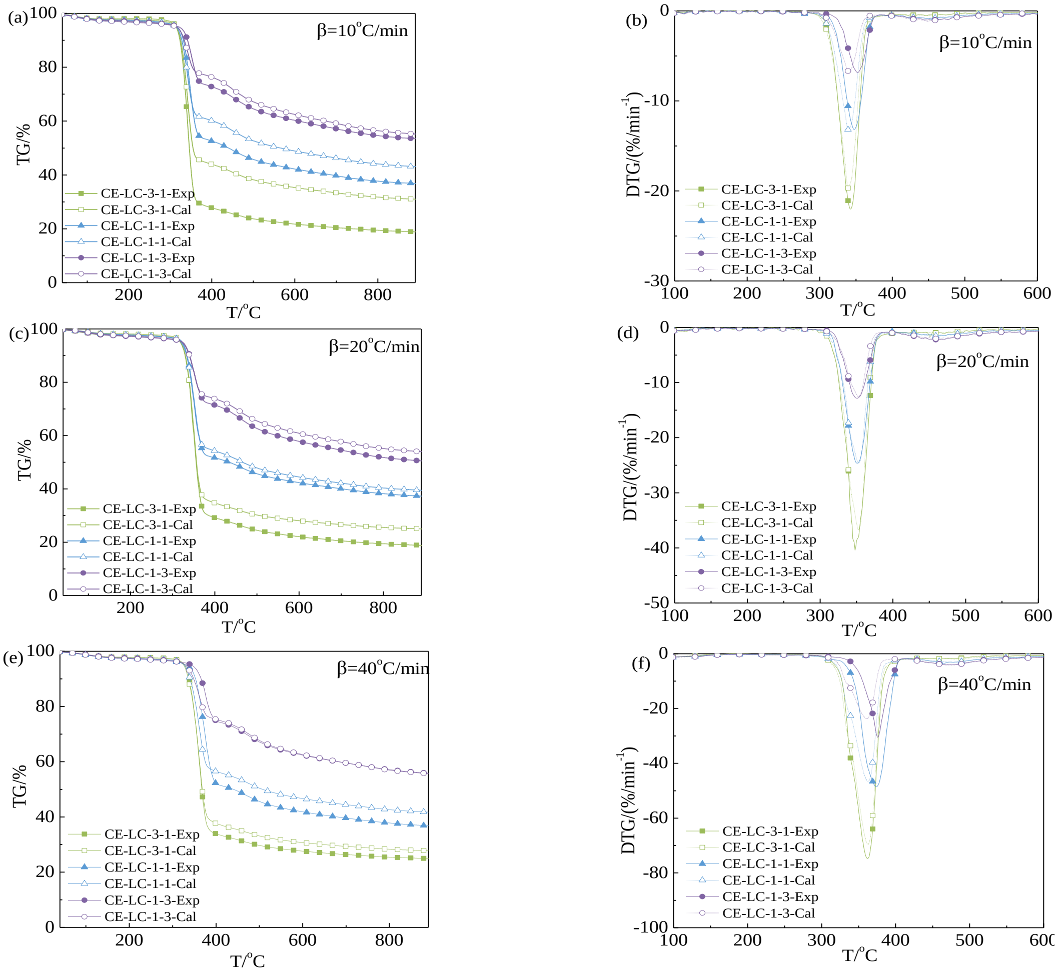

Fig 1. Comparison of experimental and theoretical values of TG and DTG for different mixed samples at different heating rates.

also has a certain relationship with the heating rate. The lower heating rate may be beneficial to the synergy of the two. When the heating rate is low, the response time of cellulose and low-rank coal particles reaching the same temperature is prolonged, which is beneficial to the sufficient contact reaction between the two reactants; on the other hand, the temperature difference between the surface and the interior of the cellulose and low-rank coal particles can be reduced, which in turn affects the pyrolysis process inside the two particles.

4. CONCLUSIONS

In this work, the thermal effects and kinetics analysis of cellulose and low-rank coal at different ratios were studied at different heating rates. The addition of low-rank coal can promote the formation of volatile substances in the process of co-pyrolysis, and the low-rank coal in the middle and low content is more likely to produce synergy than the low-rank coal in the high content. The kinetic results show that the average activation energy is the lowest when the low-rank coal blending ratio is 25% and 50%, which are 244.44 kJ·mol^{-1} and 164.41 kJ·mol^{-1}, respectively.

ACKNOWLEDGEMENT

This work was supported by the National Natural Science Foundation of China (Grant No: 51606149), the China Postdoctoral Science Foundation (Grant No: 2019M653626), the Fundamental Research Funds for the Central Universities (xjj2017021), the Promotion Plan forYoung People of Shaanxi Association for Science and Technology (20180402), the Natural Science Basic Research Plan in ShaanxiProvince of China (Program No. 2018JQ2008), and the Technology Foundation for Selected Overseas Chinese Scholar in Shaanxi Province (Grant No: 2018015).

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