Kinetic and Synergetic Effect Analysis of the Co-Combustion of Coal Blended with Polyurethane Materials

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1. INTRODUCTION

Polyurethane has good mechanical and sealing properties. Polyurethane is light, with high expansion multiples, low production cost, and convenient to use. Therefore, polyurethane is widely applied in coal mines to reinforce broken layers, to fill caving areas in gob, to construct gob sealing walls, and to seal air and water leakage channels. In coal mines, polyurethane material is used by injecting an isocyanate and polyester polyol slurry into the cracks of broken layers. The mixture combines with the broken coal and rock and forms a strengthened gelatinous solid. During the injection of the mixture slurry, isocyanate and polyester polyol react violently and release a large amount of heat. In recent years, some fire accidents, which were caused using polyurethane material to reinforce broken layers, have occurred in coal mines. Therefore, research on the combustion of polyurethane and coal blends has become a new topic.

Polyurethane is a kind of porous material. The oxygen index of polyurethane without flame retardant treatment is lower than 18. It is easy to ignite and its burning speed is very high. It releases a lot of heat and toxic gases when polyurethane is burning. Therefore, its combustion performance limits the application of polyurethane material. Jiang used semiconversional methods to calculate the pyrolysis kinetic parameters of rigid polyurethane and identified the volatile product by Py-MC/Ms. Font investigated the pyrolysis kinetic parameters and gas release laws of polyurethane in an inert gas atmosphere. Jomaa found that the pyrolysis process of polyurethane consisted of several independent pyrolysis reactions. Jiao divided the polyurethane combustion process in an air atmosphere into three main stages and divided the polyurethane pyrolysis process in a nitrogen atmosphere into two stages. The urethane bonds in polyurethane were decomposed into isocyanate above 200 °C, and aliphatic and alcohol volatiles were then produced during polyurethane pyrolysis when the temperature increased. In the temperature range of 300–500 °C, the dominant volatile products are primary amines, secondary amines, vinyl ethers, and CO2. Many scholars have studied the flame retardant treatment of polyurethane. Flame retardant additives will change the combustion performance and gas release laws of polyurethane. Singh provided a detailed summary of the ignition, combustion, toxicity, and fire retardancy properties of polyurethane and pointed out that the addition of flame retardant additives would inevitably affect the physical and mechanical properties of polyurethane. Wu, Hu, and Liu improved the flame resistance and mechanical properties of polyurethane.
through the addition of flame retardant additives and inorganic materials to the polyurethane used in coal mines and applied it in practice.\textsuperscript{3,13,14}

Coal is another main reactant of the spontaneous combustion, which occurred in broken layers strengthened by polyurethane. Coal spontaneous combustion is a major cause of mine fires, which leads to health hazards, casualties, safety accidents, and environmental pollution.\textsuperscript{15,16} Experimental studies have shown that the processes of coal spontaneous combustion are very complicated, and there are many factors that impact it, such as the coalification degree, particle size, moisture content, and ventilation conditions.\textsuperscript{17,18} Deng and Zhang researched the spontaneous combustion and gas release laws of samples from different coal seams by temperature programming experiments. With the coalification degree increasing, the exothermic rate in the early stage of spontaneous combustion decreased, the oxygen consumption rate decreased, and the tendency of spontaneous combustion weakened.\textsuperscript{19,20} Researchers have applied thermogravimetric analysis (TGA) to investigate the weight loss processes, characteristic temperatures, dynamic parameters, pyrolysis products, and gas release laws of different coals.\textsuperscript{21–23}

Studies have shown that the kinetics will substantially change during co-combustion processes, and synergetic effects occur between different materials.\textsuperscript{24–27} Many scholars have researched the synergetic effects during the co-combustion of different materials. Sun calculated the co-combustion kinetic parameters of oil shale and semicoke by the distributed apparent activation energy model (DAEM) and divided the TG curve of combustion into different stages with the logistic function.\textsuperscript{28} Liu divided the combustion processes of oil shale blended with biomass into different stages and calculated their kinetic parameters. He found that the mixing ratio and the heating rate were the main factors influencing the synergetic effects during co-combustion processes.\textsuperscript{29} Qin, Wang, and Liu researched the synergetic effects during co-combustion of different proportions of semicoke or oil shale blended with biomass by comparing the root-mean-square (RMS) error and mean error (MR) of the corresponding theoretical and experimental TG curves.\textsuperscript{25,30,31} Qu adopted a synergistic parameter synergetic index (SI) based on the contrast between theoretical and experimental TG and DTA curves to analyze synergetic effects and then analyzed the synergetic effects during the co-combustion of coal blended with biomass from the catalytic and noncatalytic effects.\textsuperscript{32}

With the increasing application of polyurethane materials in coal mines, more and more spontaneous combustion accidents occurred in goafs containing polyurethane. At present, the research on the mechanism and synergetic effects of the polyurethane and coal co-combustion processes is insufficient. In this paper, we researched their dynamic laws by TGA experiments. We also analyze the synergetic laws of different mixing ratio samples during their co-combustion. The results will provide a further explanation of the spontaneous combustion that occurred in goafs containing polyurethane. It will provide a theoretical basis for the prevention and treatment of spontaneous coal combustion accidents.

2. EXPERIMENTAL SECTION

2.1. Materials. The experimental coal samples were anthracite samples collected from the working face of the Gaobo coal mine in the city of Changzhi, Shanxi Province, China. The samples of polyurethane were also the reinforcing materials used in this coal mine. This polyurethane consisted of two components: black and white materials. The main component of the black material was polyisocyanate (PAPI), which was of industrial grade and produced by BASE SE, Germany. The main component of the white materials was polyether polyol N-4110, which was of industrial grade and produced by the Jiangsu Zhongshan Company. A small amount of auxiliary ingredients, such as a catalyst, a chain extender, a flame retardant, and a foam stabilizer, were also included in the white materials. According to the actual construction requirements of the coal mine, the samples used in this research were rigid polyurethane foams prepared with a 1:1 volume ratio of black and white materials. The experimental testing results showed that the reaction initiation time of this kind of polyurethane was 1 min 10 ± 5 s, the expansion time was 3 min 10 s ± 3 s, and the reaction completion time was 5 min 15 ± 5 s. The coal and polyurethane samples were pulverized before the experiments and dried at 80 °C for 24 h in a nitrogen atmosphere. The proximate and elemental analysis results of the samples are summarized in Table 1.

2.2. Experiment. The calorific values of the coal, polyurethane, and blended samples were tested with the ZDHW-6B miniature automatic calorimeter manufactured in China according to the ASTM standard method,\textsuperscript{28} and three repeated experiments were performed on each sample.

The thermogravimetric experiments were conducted with a NETZSCH STA-449-F3 thermal synthesis analyzer. In the experiments, there were seven different proportions of coal blended with polyurethane among the samples that were smaller than 200 mesh. The samples weighing approximately 10 mg were heated from 30 to 800 °C at a heating rate of 2 °C/min in a synthetic air atmosphere (80% N₂ and 20% O₂) to simulate the spontaneous combustion process, and three repeated experiments were performed for each sample. The sample and experimental parameters are listed in Table 2.

2.3. Combustion Characteristic Parameters. In this paper, \( T_b, T_i, DTG_{\text{max}} \), and \( T_{\text{max}} \) are four characteristic parameters of the combustion process, were investigated. \( T_i \) is the ignition temperature, which characterizes the difficulty of ignition of the samples. \( T_b \) is the burning out temperature, and the lower \( T_b \) is, the easier it is for the samples to burn out. \( DTG_{\text{max}} \) is the maximum mass loss rate and its corresponding temperature is \( T_{\text{max}} \). When \( DTG_{\text{max}} \) is high and \( T_{\text{max}} \) is low, the combustion speed and stability are high. There were two other combustion indexes to characterize the combustion properties of the samples. One index was the comprehensive combustion index \( S \), which characterizes the combustion properties of the

| sample            | proximate analysis | elemental analysis |
|-------------------|--------------------|--------------------|
|                   | Mad (%) | Vad (%) | Aad (%) | FCad (%) | N (%) | C (%) | H (%) | S (%) | O (%) |
| coal              | 0.69    | 15.53   | 7.93    | 75.86    | 1.51  | 83.00 | 2.75  | 2.77  | 9.97  |
| polyurethane      | 3.66    | 88.72   | 1.33    | 6.29     | 6.32  | 60.50 | 6.03  | 0.00  | 27.15 |

Table 1. Proximate Analysis and Elemental Analysis Results of the Coal and Polyurethane samples
samples. The better are the combustion properties, the higher is S. The calculation equation of S is expressed as eq 1.33

\[ S = \frac{\text{DTG}_{\text{max}} \times \text{DTG}_{\text{mean}}}{T^2_b \times T_b}, \]  

where \( \text{DTG}_{\text{mean}} \) is the average mass loss rate.

The other combustion stability index was \( R_w \), which characterizes the combustion stability of the samples. When the combustion stability increases, \( R_w \) increases. The calculation equation of \( R_w \) is shown below (eq 2).34

\[ R_w = - \frac{\text{DTG}_{\text{max}}}{T_b} \]  

2.4. Synergistic Effect Analysis Theory. During the co-combustion process, reactant interactions cause changes in the combustion mechanism. Co-combustion processes are not simply the result of the superposition of separate combustion products and exotherms, but there is mutual promotion or inhibition. This mutual promotion or inhibition is called the synergistic effect. There are large differences between the combustion processes of coal and polyurethane. There will be even larger differences between their co-combustion processes. The synergistic effects will change their dynamic mechanism. In this paper, the synergistic effects of the co-combustion processes are investigated by analyzing the theoretical and experimental calorific values and TG-DTG theoretical and experimental curves of the samples of coal blended with polyurethane at different ratios. The calculation method of the theoretical curves of the co-combustion process is shown in eqs 3, 4, and 5.31,32,35,36

\[ \frac{dW}{dt}_{\text{cal}} = \alpha_{\text{coal}} \times \left( \frac{dW}{dt} \right)_C + \omega_{\text{PU}} \times \left( \frac{dW}{dt} \right)_{\text{PU}}, \]  

\[ Q_{\text{cal}} = \alpha_{\text{coal}} \times Q_C + \omega_{\text{PU}} \times Q_{\text{PU}}, \]  

\[ E_{\text{cal}} = \alpha_{\text{coal}} \times E_C + \omega_{\text{PU}} \times E_{\text{PU}}, \]

where \( \left( \frac{dW}{dt} \right)_{\text{cal}} \) is the calculated mass loss rate of the blended sample (%/min), \( \left( \frac{dW}{dt} \right)_C \) and \( \left( \frac{dW}{dt} \right)_{\text{PU}} \) are the experimental mass loss rates of coal and polyurethane, respectively (%/min), \( \alpha_{\text{coal}} \) and \( \omega_{\text{ PU}} \) are the proportions of coal and polyurethane, respectively (%), \( Q_{\text{cal}} \) is the calculated calorific value of the blended sample (kJ/kg), \( Q_C \) and \( Q_{\text{PU}} \) are the experimental calorific values of coal and polyurethane, respectively (kJ/kg), \( E_{\text{cal}} \) is the calculated activation energy of the blended sample (kJ/mol), and \( E_C \) and \( E_{\text{PU}} \) are the experimental activation energies of coal and polyurethane, respectively (kJ/mol).

If there were no synergistic effects during the co-combustion processes of coal blended with polyurethane, the difference between the theoretical and experimental curves at corresponding points would be almost 0. If the experimental curves are below the theoretical curves, this suggests that the actual burning speed is higher than the theoretical burning speed. As a result, coal and polyurethane promote each other during the co-combustion process. In contrast, if the experimental curves are above the theoretical curves, this suggests that the actual burning speed is lower than the theoretical burning speed. Coal and polyurethane inhibit each other during the co-combustion process.37-39 In this paper, the relative root-mean-square error (RMS) was adopted to describe the synergistic effects during co-combustion. The calculation of the RMS index is shown in eq 6.35,36

\[ \text{RMS} = \frac{1}{n} \times \sum_{i=1}^{n} \left( \frac{x_{\text{exp}} - x_{\text{cal}}}{x_{\text{exp}}} \right)^2 \]  

where \( x_{\text{exp}} \) and \( x_{\text{cal}} \) are the experimental and theoretical values, respectively.

In this synergistic effect analysis, the higher is the RMS index, the larger is the deviation between the theoretical and experimental curves and the stronger are the synergistic effects.

2.5. Kinetic Analysis Theory. According to the first-order Arhenius law, the kinetics of the pyrolysis and combustion of coal and polyurethane follow the following equations21,22

\[ \frac{d\alpha}{dt} = k \times f(\alpha) \]  

\[ G(\alpha) = kt \]  

\[ \alpha = \frac{W_0 - W_i}{W_0 - W_\infty} \]  

\[ k = A \times \exp \left( \frac{-E}{RT} \right) \]  

\[ T = T_0 + \beta \]  

where \( \alpha \) is the loss fraction, %; \( t \) is the time, s; \( k \) is a temperature-dependent constant; \( f(\alpha) \) is the mechanism function; \( W_0, W_i, \) and \( W_\infty \) are the initial weight, the weight at time \( t \), and the weight at the end of combustion, respectively; \( A, E, T, \) and \( R \) are the pre-exponential factor, the apparent activation energy, the temperature, and the universal gas constant, respectively; \( T \) and \( T_0 \) are the temperature at time \( t \) and the initial temperature, respectively; \( K_i \) and \( \beta \) is the heating rate, K/min.

Combining eqs 7, 10, and 11 yields the Ozawa equation

\[ \lg \beta = \lg \left( \frac{AE}{RG(\alpha)} \right) - 2.315 - 0.4567 \times \frac{E}{RT} \]  

The Flynn–Wall–Ozawa (FWO) method is used to calculate the activation energy during the combustion process.40

According to the above equation, for \( Y_i = \lg \beta \), and \( X_i = 1/T \), \( Y_i \) varies linearly with \( X_i \) and the slope and the intercept of the curve are \( a = -0.4567 \times E/R \) and \( b = \beta \). Where, \( AE, \beta, \) and \( E/RT \) are the activation energy, reaction rate, and slope of the Ozawa equation, respectively. At \( \beta \) values of 2, 5, and 10 K/min, we can obtain the activation energy at corresponding \( \alpha \) values.
3. RESULTS AND DISCUSSION

3.1. Calorific Value of the Blended Samples. Figure 1 shows the calorific values of the coal, polyurethane, and blended samples. The calorific value of coal is 35534 kJ/kg, and the calorific value of polyurethane is 26642 kJ/kg. Sample PU-C-4 attains the highest calorific value at 35927 kJ/kg. Sample PU-C-1 attains the lowest calorific value at 34270 kJ/kg. The theoretically calculated calorific value of the blended samples can be obtained with eq 4. The theoretical calorific values of the blended samples decrease with increasing mixing ratio. When the mixing ratio is lower than 1:15, the experimental calorific values of the blended samples are lower than the theoretically calculated calorific values. Sample PU-C-1 (with a mixing ratio of 1:25) exhibits the maximum negative difference, and its experimental calorific value is 2.62% lower than its theoretical calorific value. When the mixing ratio is higher than 1:15, the experimental calorific values of the blended samples are higher than the theoretically calculated calorific values. Sample PU-C-5 (with a mixing ratio of 1:5) attains the largest positive difference between the experimental and theoretical calorific values of 4.54%.

Therefore, synergetic effects occur during the co-combustion process of coal blended with polyurethane. When the mixing ratio of the blended samples is lower than 1:15, the heat release of co-combustion decreases and the synergetic effects are inhibited. When the mixing ratio of the blended samples is higher than 1:15, the heat release of co-combustion increases and the synergetic effects are promoted.

The combustion process of coal is complicated. It mainly consists of three processes: coal oxidation, coal pyrolysis, and coal combustion. These three processes overlap each other. First, coal comes into contact with oxygen. When the temperature increases, the active functional groups of coal combine with oxygen and then form peroxides and free radicals and release heat. The heat release leads to an increase in the temperature and the oxygen-containing functional groups and large molecular branches in coal pyrolyze to generate combustible volatiles, tar and fixed carbon. Coal continues to pyrolyze and releases heat. When the temperature reaches the ignition point of coal, the combustible volatiles are ignited, which release more heat and gases. Then, the reaction speed and temperature increase, and the residual fixed carbon formed during pyrolysis begins to burn.49

The ignition temperature of polyurethane is much lower than that of coal, and its burning speed is higher than that of coal. The combustion process of polyurethane mainly consists of depolymerization, branch breaking, secondary polymer pyrolysis, and fixed-carbon burning. Polyurethane has a high hydrogen content and low carbon content. It contains many hydroxyl and active groups.8,40 During the co-combustion of coal blended with polyurethane, from 200 to 300 °C, polyurethane starts pyrolyzing first and releases heat and free radicals, while coal absorbs oxygen. From 350 to 550 °C, coal begins to pyrolyze and burn, while the pyrolysis of polyurethane is finished, and the fixed carbon begins to burn. The mixing ratio imposes a major influence on the co-combustion process. When the mixing ratio is lower than 1:15, polyurethane suppresses combustion, and when the mixing ratio is higher than 1:15, polyurethane promotes combustion.

3.2. Combustion Characteristics of the Blended Samples. Figure 2 shows the thermogravimetric curves of the coal, polyurethane, and mixed samples at heating rates of 2, 5, and 10 K/min.

For coal (sample C), its DTG curve exhibits a weight gain peak and a weight loss peak. The weight gain peak is caused by the weight increase due to oxygen absorption by coal. Alkyl branches, oxygen-containing functional groups, and small molecular groups break from the main structure of coal and form free radical groups that then combine with oxygen.41,42 When the temperature increases, the cyclic macromolecular structures of coal begin to break and produce more free radical groups. Thereafter, more oxygen is absorbed, and the mass growth rate increases. Chemical oxygen absorption is enhanced. During this process, the weight gain due to oxygen absorption exceeds the weight loss due to pyrolysis. The DTG curve of coal reflects weight gain. The weight loss peak is caused by coal pyrolysis and burning. As the temperature increases, coal continues to pyrolyze and releases heat and many combustible volatiles. When the temperature reaches the ignition point of coal, the aromatic ring structure in coal begins to pyrolyze, and the volatiles and fixed carbon begin to burn. Tars are generated, and a large amount of CO and CO₂ is...
produced. Finally, the weight loss rate and the heat release rate reach their peak values.

The weight gain due to oxygen absorption decreases with increasing heating rate. The reaction rate of oxygen absorption is limited. The higher is the heating rate, the shorter is the contact time between coal and oxygen and the lower is the weight gain due to oxygen absorption. The weight loss peaks move to higher temperatures and increase with increasing heating rate. Because the pyrolysis rate of coal is low, product escape requires a certain time. With increasing heating rate, products are not released quickly enough, and the temperature difference between the particles of the samples increases.

Figure 2. TG and DTG curves of the blended samples.
The characteristic temperature of the blended samples is listed in Table 3. The characteristic temperature of the same sample increases with increasing heating rate. The heating rate increase leads to the enhancement of the temperature gradient of the inner and outer surfaces of the samples. Then, the sample heat transfer efficiency decreases and the characteristic temperature of the samples increases. The ignition temperature $T_i$ of the blended samples decreases with increasing mixing ratio. When the mixing ratio is lower than 1:15, the ignition temperature of the blended samples is higher than that of the coal sample, and the synergetic effects are expressed as inhibitory effects. When the mixing ratio is higher than 1:15, the ignition temperature of the blended samples is lower than that of the coal sample, and the synergetic effects are manifested as promoting effects.

For the different blended samples, the temperature $T_{\text{max}}$ at which the maximum weight loss rate occurs and the temperature $T_b$ at which combustion ends are almost equal. The combustion process of the polyurethane, coal, and blended samples is almost the same at high temperatures. During the combustion process, the main reaction is fixed-carbon combustion. As a result, the mixing ratio has little influence on the high-temperature combustion stage of the blended samples.

The results of the comprehensive combustion index $S$ and combustion stability index $R_w$ of the mixed samples of polyurethane and coal are summarized in Table 4. The $S$ and $R_w$ values of polyurethane are higher than those of coal. When the mixing ratio is higher than 1:15, the comprehensive combustion index of the blended samples is higher than that of the coal sample. The higher is the mixing ratio, the better is the combustion performance. The combustion stability indexes of the blended samples are lower than those of the polyurethane and coal samples. From 200 to 400 °C, polyurethane loses the most weight due to pyrolysis and burning, while from 400 to 600 °C, coal loses the most weight. The stability of the blended samples decreases.
In the coal, which compete with coal oxygen absorption and promote Polyurethane pyrolysis provides heat and free radicals to the are Polyurethane pyrolysis and coal oxygen absorption.

than those in the other stages. In this stage, the main reactions from 30 to 350 °C, while at a heating rate of 10 K/min, the second stage is from 500 to 600 °C. The volatile content of polyurethane is higher than 80%. There are many hydroxyl groups, carbonyl groups, and other unstable polymers in polyurethane. During the co-combustion process of the blended samples, more free radicals are produced than during the combustion process of coal, which accelerates combustion.\textsuperscript{48} The other reason is that the synergetic effects are related to the energy supply during the combustion process. When the mixing ratio of the blended samples is low, the heat release during the co-combustion process is low. There is an insufficient energy supply during the co-combustion process, and as a result, the reactions slow down. When the mixing ratio of the blended samples is high, more heat is released during the co-combustion process, and the reactions are accelerated.

The RMS values of the blended samples at the different heating rates exhibit the strongest synergetic effects. Sample PU-C-1 (with a mixing ratio of 1:25) achieves the smallest RMS value, and its synergetic effects are the weakest. The synergetic effects in the first stage during the co-combustion process of the blended samples are the most significant. There are two reasons for the occurrence of the synergetic effects. One reason is that polyurethane changes the volatile types and content of the blended samples. The hydrogen-to-carbon molar ratio of polyurethane is much higher than that of coal \((\text{H/C})_{\text{PU}} = 1.2\) vs \((\text{H/C})_{\text{C}} = 0.4\). The volatile content of polyurethane is higher than 80%. There are many hydroxyl groups, carbonyl groups, and other unstable polymers in polyurethane. During the co-combustion process of the blended samples, more free radicals are produced than during the combustion process of coal, which accelerates combustion.\textsuperscript{48} The other reason is that the synergetic effects are related to the energy supply during the combustion process. When the mixing ratio of the blended samples is low, the heat release during the co-combustion process is low. There is an insufficient energy supply during the co-combustion process, and as a result, the reactions slow down. When the mixing ratio of the blended samples is high, more heat is released during the co-combustion process, and the reactions are accelerated.

The RMS values of the blended samples at the different heating rates exhibit the same trend with the temperature. When the heating rate increases, the RMS values of the same samples at the same temperature increase, and the synergetic effects become stronger. Because the acceleration of the heating rate leads to an increased reaction rate, the synergetic effects become more significant. At a heating rate of 5 K/min, the second stage is from 450 to 550 °C, while at a heating rate of 10 K/min, the second stage is from 500 to 600 °C. Heating rate acceleration leads to a lag in the thermal weight loss.

3.3. Synergetic Effect Analysis of the Blended Samples. The RMS values of the different blended-sample DTG curves at the three heating rates can be calculated with eq 5. The results are shown in Figure 4.

According to the RMS values of the different samples, the co-combustion process of the blended samples can be divided into three stages. At a heating rate of 2 K/min, the first stage is from 30 to 350 °C, and the RMS values in this stage are higher than those in the other stages. In this stage, the main reactions are polyurethane pyrolysis and coal oxygen absorption. Polyurethane pyrolysis provides heat and free radicals to the coal, which compete with coal oxygen absorption and promote coal pyrolysis.\textsuperscript{8,31,46} In the first stage, the synergetic effects are distinct. The second stage is from 400 to 500 °C, and the RMS values in this stage are nearly 0. In this stage, the main reaction is the combustion of fixed carbon, and there is nearly no difference in fixed-carbon combustion between coal and polyurethane. There are almost no synergetic effects in this stage. The third stage is from 550 to 800 °C, and the RMS values in this stage are larger than 0. In this stage, the combustion residues of polyurethane and coal agglomerate. There are certain synergetic effects in this stage.

The DTG RMS values of the different blended samples at the same temperature increase with increasing mixing ratio. Sample PU-C-5 (with a mixing ratio of 1:5) attains the largest RMS value, and its combustion process exhibits the strongest synergetic effects. Sample PU-C-1 (with a mixing ratio of 1:25) achieves the smallest RMS value, and its synergetic effects are the weakest. The synergetic effects in the first stage during the co-combustion process of the blended samples are the most significant. There are two reasons for the occurrence of the synergetic effects. One reason is that polyurethane changes the volatile types and content of the blended samples. The hydrogen-to-carbon molar ratio of polyurethane is much higher than that of coal \((\text{H/C})_{\text{PU}} = 1.2\) vs \((\text{H/C})_{\text{C}} = 0.4\). The volatile content of polyurethane is higher than 80%. There are many hydroxyl groups, carbonyl groups, and other unstable polymers in polyurethane. During the co-combustion process of the blended samples, more free radicals are produced than during the combustion process of coal, which accelerates combustion.\textsuperscript{48} The other reason is that the synergetic effects are related to the energy supply during the combustion process. When the mixing ratio of the blended samples is low, the heat release during the co-combustion process is low. There is an insufficient energy supply during the co-combustion process, and as a result, the reactions slow down. When the mixing ratio of the blended samples is high, more heat is released during the co-combustion process, and the reactions are accelerated.

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3.4. Kinetic Analysis of Co-Combustion. In this paper, the FWO method is used to calculate the apparent activation
energy of the coal, polyurethane, and blended samples during the co-combustion process. The results are shown in Figure 5a.

According to eq 5, the theoretically calculated apparent activation energy of the blended samples can be obtained. The difference between the experimental and theoretical activation energies is shown in Figure 5b.

During the combustion process of coal, when $5\% < \alpha < 50\%$, the activation energy ranges from 125.0 to 135.0 kJ/mol. At $\alpha = 20\%$, the activation energy reaches a maximum of 132.68 kJ/mol. When $50\% < \alpha < 95\%$, the activation energy decreases. At $\alpha = 95\%$, the activation energy reaches a minimum of 103.15 kJ/mol.

During the combustion process of polyurethane, when $5\% < \alpha < 40\%$, the activation energy gradually increases. At $\alpha = 10\%$, the activation energy reaches a minimum of 96.14 kJ/mol. At $\alpha = 40\%$, the activation energy reaches a maximum of 200.89 kJ/mol. When $40\% < \alpha < 55\%$, the activation energy decreases. At $\alpha = 55\%$, the activation energy is 112.47 kJ/mol. When $55\% < \alpha < 75\%$, the activation energy increases. At $\alpha = 80\%$, the activation energy is 161.55 kJ/mol. When $75\% < \alpha < 95\%$, the activation energy increases. At $\alpha = 95\%$, the activation energy is 134.28 kJ/mol.

During the co-combustion process of the blended samples, when $5\% < \alpha < 50\%$, the activation energy at the same temperature decreases as the mixing ratio increases. Sample PU-C-5 (with a mixing ratio of 1:5) achieves the lowest activation energy. When $50\% < \alpha < 95\%$, the activation energy of the blended and coal samples is nearly equal. The mixing ratio has a major influence on the early stage of co-combustion. However, there is no notable influence on the late stage of co-combustion. Polyurethane has a higher volatile content than coal. The pyrolysis and burning processes of polyurethane mainly occur in the temperature range from 150 to 350 °C. Therefore, the synergetic effects of the early stage of co-combustion increase with increasing mixing ratio.

When the mixing ratio is lower than 1:15, for $5\% < \alpha < 50\%$, the activation energy of the blended samples is higher than that of the coal sample. When the mixing ratio is higher than 1:15, for $5\% < \alpha < 50\%$, the activation energy of the blended samples is lower than that of the coal sample. According to Figure 4b, there is a large difference between the experimental and theoretically calculated activation energies of the blended samples, and the synergetic effects are notable. When the mixing ratios are 1:25 and 1:20, the experimental activation energy is higher than the theoretical activation energy, and the synergetic effects are expressed as inhibitory effects. When the mixing ratios are 1:15, 1:10, and 1:5, the experimental activation energy is lower than the theoretical activation energy, and the synergetic effects are manifested as promoting effects.

Energy and free radicals are the main two factors in the co-combustion process of the blended samples. The pyrolysis and combustion of polyurethane consume a large amount of oxygen, and its heat release is lower than that of coal. Polyurethane is easier to pyrolyze and oxidize than coal. When the mixing ratio is low, the temperature in the early stage of co-combustion is low. It produces a small amount of energy and free radicals by the pyrolysis and oxidation of polyurethane. During this process, the oxygen absorption of coal competes with the pyrolysis of polyurethane. The activation energy increases and the synergetic effects are expressed as inhibitory effects. As the temperature rises, the main reactions of co-combustion are the pyrolysis of coal and the combustion of fixed carbon. There are almost no synergetic effects in this stage. When the mixing ratio is high, the pyrolysis and the combustion rates of polyurethane in the early stage increase. There is more energy and additional free radicals are released, which promotes the pyrolysis of coal. The activation energy in this stage decreases and the synergetic effects are manifested as promoting effects.

4. CONCLUSIONS

(1) There are synergetic effects during the co-combustion process of coal blended with polyurethane. When the mixing ratio is lower than 1:15, the ignition temperatures of the blended samples are higher, the calorific values are lower than that of the coal sample. The activation energy in the early stage of co-combustion increases and the synergetic effects are expressed as inhibitory effects. When the mixing ratio is higher than 1:15, the ignition temperatures of the blended samples are lower, and the calorific values are higher than that of the coal sample. The activation energy in the early stage of co-combustion decreases and the synergetic effects are
manifested as promoting effects. The synergetic effects become more significant with increasing heating rate.

(2) According to the magnitude of the synergetic effects, the co-combustion of coal blended with polyurethane can be divided into three stages. In the first stage, the main reactions are the pyrolysis of polyurethane and the oxygen absorption of coal. The synergetic effects are the most significant. In the second stage, the main reaction is the combustion of fixed carbon, and the synergetic effects are nearly zero. In the third stage, there are some synergetic effects because the combustion residues agglomerate.

(3) The co-combustion process is mainly influenced by two factors, energy and free radicals. During co-combustion, polyurethane influences the pyrolysis and oxygen absorption of the blended samples before the temperature reaches the ignition temperature. When the mixing ratio is low, polyurethane pyrolysisis competes with coal oxygen absorption, the activation energy increases and the synergetic effects are expressed as inhibitory effects. When the mixing ratio is high, polyurethane pyrolysis provides heat and free radicals, which accelerate the pyrolysis process of coal, and the activation energy decreases.

[800x800]

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Notes

The authors declare no competing financial interest.

Acknowledgments

The authors gratefully acknowledge the support of the National Nature Science Foundation of China (51874313) and the National Key Research and Development Program of China (2018YFC0808101).

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