Kinetics of Co-Gasification of Low-Quality Lean Coal and Biomass

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The co-gasification behaviors of composite samples of biomass and lean coal were investigated under a CO_2 atmosphere. The composite behaviors were determined based on thermogravimetric analysis and the Coats-Redfern method. These methods were used to analyze the kinetics of the processes. The results showed that the temperature ranges of the lean coal, biomasses, and the gasification ability of each biomass were different, and the coordination effects of each biomass varied. The addition of alkali metals had little influence on the pyrolysis efficiency and the peak temperature of composite samples of soybean stalk and lean coal, but it did promote gasification. In the processes of pyrolysis and gasification, composite samples of soybean stalk and lean coal exhibited lower activation energies than unmixed samples, but there was no significant enhancement with the extra alkali metal.

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INTRODUCTION

Because of the overuse of fossil fuels, the world's energy and environmental problems have become increasingly prominent. Thus, making rational use of fossil fuels and seeking new sources of energy are important. Biomass energy is widespread in nature; it has a high volatiles component, low ash content, high carbon activity, and low nitrogen and sulfur contents. All of these are advantages of biomass energy (Pu *et al*. 2006). Biomass gasification technology is one of the major biomass energy conversion technologies (Porbatzki *et al*. 2011). It has broad application prospects because of its high conversion efficiency, simple usage, inexpensiveness, and the fact that it is free from the restrictions of fuel regionalism (Xu *et al*. 2014). Co-gasification of biomass and coal can be regarded as a bridge to the use of both fossil and renewable fuels; the synergistic effect makes the oil tar burn completely, which reduces pollution (Brown and Liu 2000).

Many related studies have reported co-gasification of coal and biomass. McLendon *et al*. (2004), Kajitani *et al*. (2010), and Aigner *et al*. (2011) found that the co-gasification process has no obvious synergistic effect, while other studies (Sjöström *et al*. 1999; Li *et al*. 2008; Howaniec *et al*. 2011) found that there is one. Pan *et al*. (2000) studied a small continuous fluidized bed and found that a suitable mixing ratio can increase the co-gasification process of low-grade coal and biomass; Collot *et al.* (1999) studied a static bed and a fluidized bed with respect to co-pyrolysis and co-gasification, respectively, and found a synergistic effect in the former but not in the latter.

Gasification in a CO_2 atmosphere not only can use carbon dioxide, but it also can reduce the consumption of solid carbon, so it is an energy-saving alternative. In this work,

a thermal gravimetric analysis method was applied to study the gasification reaction of a mixture of different biomasses and coal under a CO_2 atmosphere, considering various characteristics of coal and biomass as well as various catalyst effects. Additionally, a dynamic analysis of the gasification reaction was performed.

EXPERIMENTAL

Test Samples and Test Methods

The primary purpose of this experiment was to study the gasification characteristics of different mixtures of coal and biomass in a carbon dioxide atmosphere. By mixing up coal and biomass uniformly at different proportions, and with the thermo-gravimetric analysis from samples with different ratios, the weight change of various samples, with and without catalysis, can be determined.

Materials

Corn stalks, bean stalks, peanut shells, and lean coal were purchased in Chongqing. These materials were dried, ground, and sieved to a certain degree of fineness. The sample particle sizes ranged from 7.5 μm to 10.6 μm. Proximate analysis of the samples is shown in Table 1, and ash composition analysis of lean coal is shown in Table 2.

Table 1. Proximate Analysis of Biomass and Lean Coal (wt %, ad)

Samples	Ash $_{ad}$	Moisture $_{ad}$	Volatile $_{ad}$	Fixed carbon $_{ad}$
Cornstalk	8.45	6.60	71.06	13.89
Peanut shells	4.99	7.08	72.94	14.99
Soybean stalk	5.67	7.48	71.40	15.45
Lean coal	33.47	1.47	15.62	49.43

Ad: as determined basis

Table 2. Ash Composition Analysis of Lean Coal (wt %)

SiO_2	Al_2O_3	Fe_2O_3	CaO	TiO_2	MgO	K_2O	Na_2O	SO_3	P_2O_5
49.99	22.12	11.07	5.88	2.77	1.04	0.86	0.34	5.24	0.69

Test Instruments and Procedures

The experiment was conducted in a STA409P (Netzsch, Germany) comprehensive thermal analyzer. Approximately 15 mg of char sample was placed in an Al_2O_3 crucible. High-purity CO_2 was chosen as a carrier gas, and the gas flow was set to 50 mL/min. Throughout the experiment the sample was kept in the middle of the reactor with a heating rate of 25 °C/min up to a final temperature of 1400 °C. An analysis of changes in the various samples was carried out using the thermal analyzer. After the experiment, the apparatus was cooled to room temperature and samples were taken out of the crucible. The results were then analyzed to obtain the gasification characteristics.

Table 3. List of Samples

| Number	Sample	Number	Sample
1	Cornstalk	11	Peanut shells:coal=1:1
2	Cornstalk:coal=2:1	12	Peanut shells:coal=1:2
3	Cornstalk:coal=1:1	13	Coal
4	Cornstalk:coal=1:2	14	Sample 8:NaCl=9:1
5	Soybean stalk	15	Sample 8:MgCl$_2$=9:1
6	Soybean stalk:coal=2:1	16	Sample 8:KCl=9:1
7	Soybean stalk:coal=1:1	17	Sample 8:K$_2$CO$_3$=9:1
8	Soybean stalk:coal=1:2	18	Sample 8:CaCO$_3$=19:1
9	Peanut shells	19	Sample 8:CaCO$_3$=9:1
10	Peanut shells:coal=2:1		

RESULTS AND DISCUSSION

Analysis of Gasification Process of Coal, Biomass, and Their Mixture

Figure 1 shows DG and DTG curves from three different gasification reactions of biomass and coal. The biomass gasification process can be divided into three stages: the heating dehydration stage, volatile gas precipitation (pyrolysis) stage, and coke reaction stage. The coal gasification process is compartmentalized in two stages: the dehydration stage of devolatilization (pyrolysis) and coke gasification stage.

The gasification stages of different samples occurred at different temperatures. For example, the lean coal pyrolysis temperature was higher (393 to 749 °C) compared to that of the biomass, the rate peak of mass loss was less steep, and the pyrolysis process was slower. Coal started the depolymerization reaction and decomposition between 300 and 600 °C and started to precipitate the tar and volatiles to generate char. Above 600 °C, the char started the polycondensation reaction and generated coke. When the temperature exceeded 850 °C, the reaction $CO_2 + C \rightarrow 2CO$ became faster, which accelerated the weight loss of coal.

The pyrolysis temperatures for the three biomasses were low (major temperature ranges: 157 to 635 °C), and the pyrolysis process was fast. TG curves of the biomass gasification process were composed of two large shoulder peaks and a tailing peak. The two shoulder peaks represent the pyrolysis stage and coke gasification stage, respectively. The internal ether bonds (R-O-R) of straw biomass are relatively weak. The pyrolysis range of hemicellulose is 200 to 315 °C, the pyrolysis range of cellulose is 315 to 400 °C, and the lignin range is from 160 to 900 °C (Zhang *et al.* 2011). In the process of biomass pyrolysis, the first shoulder peak is primarily the hemicellulose and cellulose pyrolysis overlap, and the second shoulder peak is mostly the overlapping peaks from lignin pyrolysis and gasification of coke.

Figure 1 (TG) shows that within the experimental temperature range, the samples exhibited different weight loss rates at the end of the reaction: corn stalk > peanut shells > soybean straw > coal. In Fig. 1 (DTG), the maximum pyrolysis loss rate of different biomasses varied: corn stalk (25.040%/min) > peanut shell (19.326%/min) > bean stalk (18.233%/min).
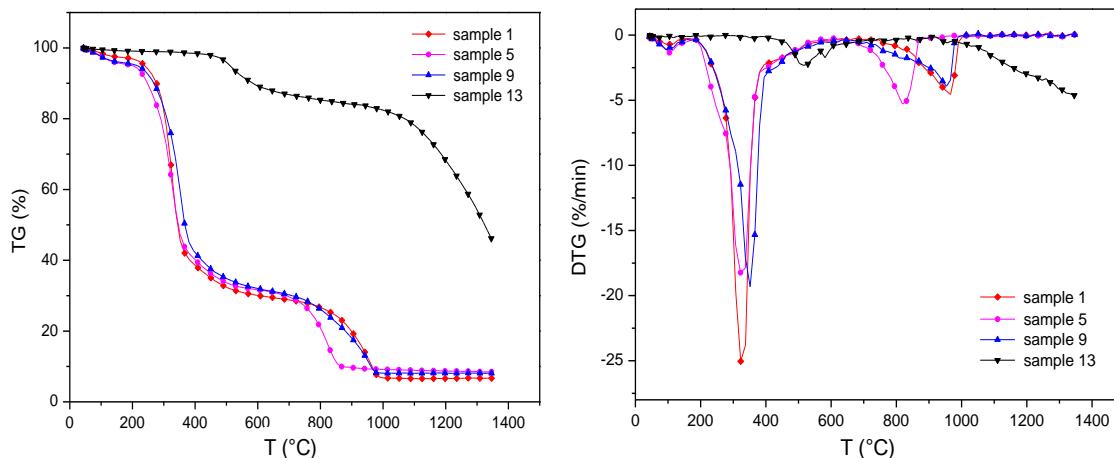
Fig. 1. TG and DTG curves of three kinds of biomass and coal

The coal and biomass were mixed in various proportions. Gasification was carried out in an atmosphere of CO_2, and the corresponding TG curves and DTG curves are shown in Figs. 2 through 4. The TG curves demonstrate that an increase in the quality loss rate of the mixed samples resulted with increasing biomass proportions. Two reasons explained below are the probable causes of this trend. First, biomass has a higher volatile matter content than coal. Second, as the biomass mixing proportion is increased, the mineral content is increased, making the catalytic effect more obvious. It can be seen from the DTG curves that an increase in biomass proportion made the gasification peak (maximum weight loss rate) increase and lowered the time to reach the peak. When reaching the end temperature, the weight loss of coal, tar, and biomass were greater in comparison to each of them separately. This shows that in the process of gasification, a synergistic effect was produced. Also, different biomasses have different gasification efficiency: bean stalk < peanut shells < corn stalk. The final mixing of the sample after weight loss show: bean stalk mixture > corn stalk mixture > peanut shell mixture. This suggests that the bean stalk had the strongest synergistic effect with coal, followed by peanut shells, and corn stalk had the weakest. The main reason for the synergy is that the alkali metal elements (K, Na, Ca) in the biomass promote the carbon gasification reaction as catalyst, and the carbon conversion rate increases significantly.
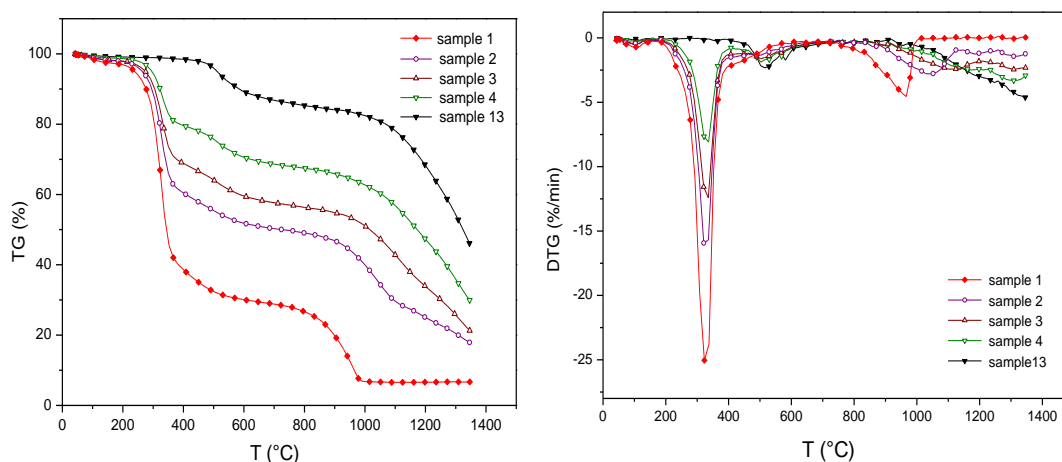
Fig. 2. TG and DTG curves of cornstalk and coal mixtures of different proportions
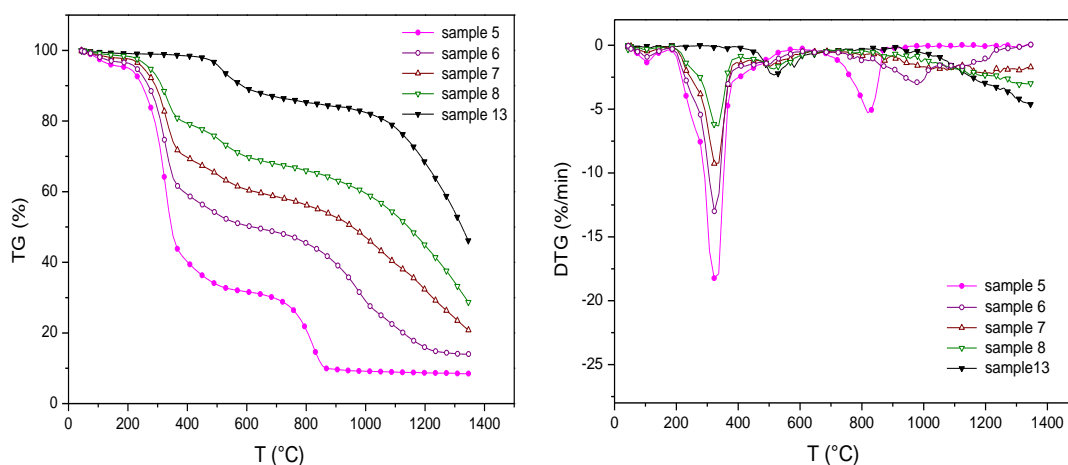
Fig. 3. TG and DTG curves of soybean stalk and coal mixtures of different proportions
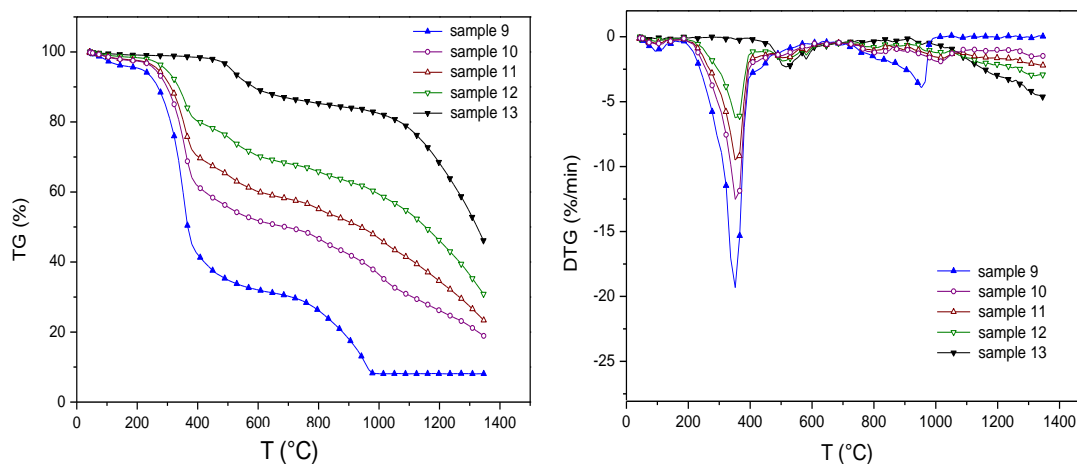

Fig. 4. TG and DTG curves of peanut shells and coal mixtures of different proportions

Effect of Adding an Alkali Metal Mixture

Various amounts of alkali metals were added to sample 8 (soybean straw:coal = 1:2) to obtain six kinds of samples (Samples 14 to 19). These samples were gasified under the same reaction conditions. Figure 5 displays DG and DTG curves, respectively, of the samples with various proportions of alkali metal. It can be seen from TG curve that the starting point of pyrolysis was the same, while the peak value was different. The maximum pyrolysis temperature of sample 15 was the lowest, and the minimum pyrolysis temperature of sample 16 was the highest, while the sample 8 pyrolyzed corresponding to the peak mass loss rate was maximum. This shows that adding an alkali catalyst does not affect the pyrolysis rate and peak temperature. In the gasification region, the samples with alkali metal added produced an extra peak at temperatures ranging from 900 to 1000 °C, which is seen as a pyrolysis peak just next to the gasification peak (Zhang *et al*. 2009). Under the same conditions, Sample 8 had no such gasification peak. This suggests that the alkali metal plays a catalytic role in the gasification reaction of the mixture, and the catalysis ability is as follows: $K_2CO_3 > NaCl > KCl > MgCl_2$.

Additionally, when reaching the melting point, the alkali metal will absorb heat, resulting in a decrease in the mass loss rate in a short period of time. When the alkali metal proportion was low, this part of the energy loss (the alkali metal absorb heat while melt) was not obvious.
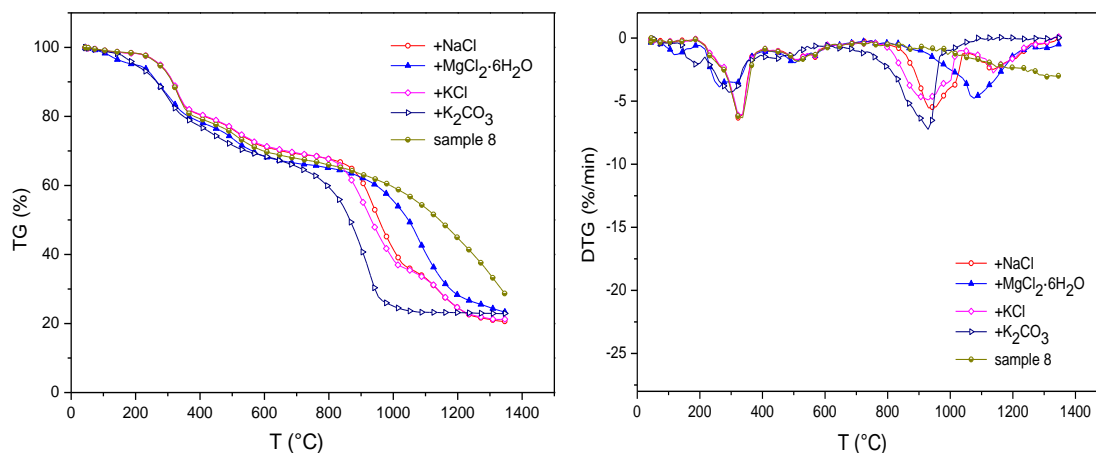
Fig. 5. TG and DTG curves of samples with different alkali metals

The TG and DTG curves shown in Fig. 6, respectively, were produced from Sample 8 with various proportions of $CaCO_3$ under the original gasification conditions. The TG curves show that the final mass loss rate of a sample with added $CaCO_3$ was also lower than the samples with no catalysts added. As can be seen from Fig. 6 (DTG), the pyrolysis processes of samples with added $CaCO_3$ (Samples 18 and 19) and Sample 8 with no alkali metal were essentially the same. This is because the thermal decomposition temperature of $CaCO_3$ was 825 °C; when the temperature is higher than this, the decomposed product from $CaCO_3 \rightarrow CaO$ is an obvious catalyst for the gasification of the biomass and coal mixture (Perander *et al.* 2015).

When the temperature was around 905 °C, there was one more gasification peak in the curve than can be seen from Sample 8, and the gasification peak of the sample with 10% $CaCO_3$ (Sample 19) was significantly higher than that from the 5% $CaCO_3$ sample (Sample 18), which suggests that catalyst effects became more obvious with increasing volume of Ca.
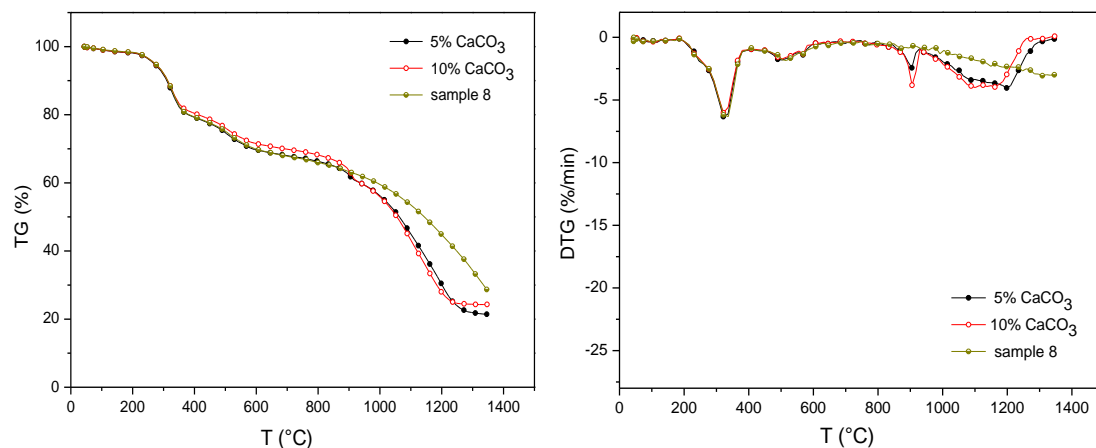
Fig. 6. TG and DTG curves of sample 8 with $CaCO_3$ of different proportions

Kinetic Analysis

Kinetic analysis was used to analyze the pyrolysis of coal and biomass using the Coats-Redfern method. The pyrolysis kinetic equation of coal and biomass is described as follows,

$$\alpha' = kf(\alpha) = k(1-\alpha)^n \tag{1}$$

where α is the conversion of the combustible material, $\alpha = \dfrac{m_o - m_i}{m_0 - m_\infty}$, α' is the derivative of α, and k is the rate constant based on the reaction temperature, T,

$$\frac{d\alpha}{dT} = \frac{A}{\varphi}\exp\left[-\frac{E}{RT}\right](1-\alpha)^n \tag{2}$$

where φ is the constant rate of temperature rise, A is the pre-exponential factor, and E is the activation energy. Equation 2 was integrated with the Coats-Redfern method. When n = 1, Eq. 2 can be written as Eq. 3:

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\varphi E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \tag{3}$$

When n $\neq$ 1, Eq. 2 can be written as Eq. 4:

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln\left[\frac{AR}{\varphi E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \tag{4}$$

As $\dfrac{2E}{RT} \gg 1$, $(1-\dfrac{2RT}{E}) \approx 1$, the first formula at the right end of Eq. (3) and Eq. (4) is approximately equal to $\ln(\dfrac{AR}{\varphi E})$.

When n = 1, a line with the slope $-\dfrac{E}{R}$ is obtained in the plot of $\ln[\dfrac{-\ln(1-\alpha)}{T^2}]$ *versus* $\dfrac{1}{T}$. By analyzing the line, one can obtain the activation energy (*E*) and pre-exponential factor (*A*).

The kinetic model can describe the pyrolysis and gasification process during the co-gasification of biomass and coal. The results of a dynamic analysis of the pyrolysis process of 19 samples using the Coats-Redfern method are shown in Table 4.

As can be seen from the curves, the activation energy of the lean coal in the pyrolysis stage was 67.68 kJ/mol, which is slightly lower than that of corn stalks but higher than that of soybean stalk and peanut shells. The activation energy of the mixed sample with corn stalks does not appear to have great volatility compared with lean coal, while the activation energies of the mixed samples with soybean stalks and peanut shells were decreased compared with that of lean coal.

Among all samples with added alkali metal, sample with K_2CO_3 and $MgCl_2 \cdot 6H_2O$ had obviously lower activation energies.

Table 4. Pyrolysis Kinetic Parameters in Gasification Process

Sample	Temperature ranges (°C)	E (kJ.mol^{-1})	A (min^{-1})	Correlation Coefficient
Sample 1	278～352	71.928	5.185E+5	0.99681
Sample 2	276～351	66.221	1.002E+5	0.99729
Sample 3	275～365	57.289	1.078E+4	0.99235
Sample 4	261～351	57.411	7.914E+3	0.99474
Sample 5	216～380	38.621	3.786E+2	0.99362
Sample 6	217～381	35.089	1.129E+2	0.99287
Sample 7	217～381	36.179	1.053E+2	0.99479
Sample 8	216～351	35.655	71.018	0.99624
Sample 9	232～395	40.292	3.903E+2	0.99185
Sample 10	262～409	41.061	2.913E+2	0.99196
Sample 11	276～380	42.370	3.307E+2	0.99825
Sample 12	247～394	37.360	74.865	0.99591
Sample 13	476～555	67.682	9.929E+2	0.99379
Sample 14	232～352	37.136	86.894	0.99704
Sample 15	262～337	16.371	0.917	0.99468
Sample 16	277～366	37.481	90.733	0.99112
Sample 17	262～337	18.596	1.729	0.99489
Sample 18	291～351	40.322	1.957E+2	0.99739
Sample 19	276～351	39.191	1.493E+2	0.99793

Table 5. Gasification Kinetic Parameters in Gasification Process

Sample	Temperature ranges (°C)	E (kJ.mol^{-1})	A (min^{-1})	Correlation Coefficient
Sample 1	918~954	77.863	9.086E+2	0.99007
Sample 2	1173~1284	30.271	1.215	0.99105
Sample 3	1027~1284	35.132	1.599	0.99123
Sample 4	1088~1223	40.837	2.212	0.99503
Sample 5	807~856	103.501	5.553E+4	0.99451
Sample 6	1076~1186	45.253	9.182	0.99135
Sample 7	1004~1137	16.840	0.168	0.99908
Sample 8	1137~1247	45.975	4.088	0.99530
Sample 9	821~869	11.630	0.179	0.99138
Sample 10	1065~1149	7.735	0.047	0.99396
Sample 11	1113~1223	25.057	0.518	0.99235
Sample 12	1125~1235	39.075	2.003	0.99540
Sample 13	1271~1321	193.450	1.209E+6	0.99238
Sample 14	919~967	75.011	2.290E+2	0.99994
Sample 15	1051~1125	82.622	2.746E+2	0.99938
Sample 16	870~978	58.318	41.043	0.99952
Sample 17	893~941	120.001	8.049E+4	0.99305
Sample 18	1137~1210	94.351	6.356E+2	0.99248
Sample 19	1064~1174	83.166	2.715E+2	0.99369

The results of a dynamic analysis of the gasification process of 19 samples using the Coats-Redfern method are shown in Table 5.

The activation energy of sample 13 was significantly higher than that of other samples such as the Peanut shells (sample 9) at this stage of gasification. The activation energy of the biomass mixed with cornstalk was less than that of coal. So was cornstalk, and the activation energy decreased with increasing cornstalk ratio. The activation energy of the biomass mixed with soybean stalk was obviously less than that of coal and soybean stalk, but the effect of the stalk ratio on the activation energy was not apparent. The activation energy of the sample added the high proportion of peanut shell was obviously decreased, while it was much higher than the sample added the low proportion of peanut shells.

The activation energy of Sample 8 mixed with alkali metal was greater than the original sample; thus, the sample with alkali metal required more energy to initiate the reaction.

CONCLUSIONS

1. The weight loss during the co-gasification of lean coal and biomass is greater than that of individual components above 1000 °C, which indicates that a synergistic effect takes place in co-gasification.

2. The synergistic effect between soybean stalk and coal is strongest, followed by peanut shell, and the synergistic effect of cornstalk is the weakest.

3. A variety of alkali metals (soil) have a catalytic role on the gasification reaction between biomass and lean coal, and the catalysis ability is as follows: $K_2CO_3 > NaCl > KCl > MgCl_2$.

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