Synergistic Analysis of Co-combustion of Sunflower Straw and Coal Gangue

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Coal gangue and sunflower straw biomass from Xilingguole, Inner Mongolia, China and Ulanqab Tsining District, Inner Mongolia, China, respectively, were burned separately and mixed in different proportions. The synergistic effect was analyzed by comparing the actual mixed combustion curve with the theoretical mixed combustion curve. The bar chart and TR (the mean of the difference between the experimental and calculated was divided by the mean of the calculated values) value curve were used to show the synergistic effect. The results showed that the synergistic effect of coal gangue and sunflower straw was optimal when the ratio (sunflower straw:coal gangue) was 2:8.

Keywords: Biomass; Coal gangue; Synergy

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INTRODUCTION

Energy greatly influences a country's development and progress. Global primary energy consumption grew by an average of 2.2% in 2017, and China's energy consumption rose by 3.1% (NBS 2018a). For the 17th year in a row, China was the world's largest energy producer (NBS 2018a). Every year, China consumes more resources than it produces. As economic development and scientific and technological progress accelerate the pace of life, the disparity between resource consumption and production continues to grow. For China and the rest of the world, a solution to this disparity is urgently needed (NBS 2018b).

Sung *et al.* (2016) found that the co-combustion of biomass and bituminous coal has a synergistic effect. The thermochemical properties of coal gangue, soybean straw, sawdust, and mixtures prepared with different proportions were determined by thermogravimetric analysis. Zhou *et al.* (2017) found that the ignition performance and thermal reactivity of coal gangue could be improved by adding biomass. The co-pyrolysis of corncob and coal gangue in a fiber tube resistance furnace was carried out by Liu (2017). The ratios of coal gangue to corncob were 20% and 40%, the temperature was over 200 °C, and the co-pyrolysis of corncob and coal gangue had a certain synergistic effect. There is yet to be sufficient research on the synergistic effect of biomass and coal gangue in different proportions was studied. The coal gangue from Xilinguole, Inner Mongolia, China and sunflower straw in Jining, Inner Mongolia, China were studied.

Although the mixing of biomass and coal gangue is a physical mixing process, the mixed combustion characteristics of biomass and coal gangue are not a simple superposition of the two combustion characteristics. Due to the different compositions

and properties of biomass and coal gangue, there can be mutual promotion or inhibition in the process of co-firing. Therefore, to provide a strong theoretical basis for practical application in the future, it is necessary to study the interaction between biomass and coal gangue. Synergetics is the brainchild of German physicist Hermann Haken (Haken 1989). He proposed it in the 1970s as a discipline to study the laws of coordination between subsystems within a system. The theory can be summarized in three aspects (Wang *et al.* 2017; Pan 2018; Zhao 2018), which include synergy, the principle of servo, and the selforganization principle.

EXPERIMENTAL

Preparation and Basic Characteristics of Experimental Samples

The coal gangue came from Xilingol coal field, Inner Mongolia, China and the sunflower straw came from Ulanqab Tsining District farmland, Inner Mongolia, China. After the preliminary post-drying (First, it was put into the room for natural drying for 24 h, and then it was put into a drying oven at 80 °C for 2 h. The dried samples were taken out and put into a grinding mill for grinding. Finally, the test samples were taken out by method of coning and quartering.) and grinding treatment of the above experimental materials, in accordance with ASTM D197-87 (2012), post-drying at 120 °C for 12 h, the size of sieving particles was 120 mesh.

The sunflower straw was added to lignite at weight ratio of 20%, 30%, 40%, 50%, 60%, 70%, and 80%. The blends were mixed a total amount of 10 g in all proportions to ensure the uniformity. The proximate analysis, *i.e.* moisture (Mad), ash (Aad), volatile matter (Vad), and fixed carbon (FCad), and the elemental analysis of materials was used to calculate the calorific value (Qb.ad) and combustion products of materials. Generally, the five elements C, H, O, N, and S are mainly analyzed in this type of assay. The proximate analysis and elemental analysis of the materials are shown in Table 1.

Proximate Analysis					Element Analysis					
Sample Description	<i>M</i> ad (%)	A _{ad} (%)	V _{ad} (%)	FC _{ad} (%)	Q _{b.ad} (kJ • kg ⁻¹)	C _{ad} (%)	H _{ad} (%)	O _{ad} (%)	N _{ad} (%)	S _{ad} (%)
Coal gangue	1.5 6	69.04	17.07	12.33	8986	24.84	1.37	1.69	0.41	1.09
Sunflower straw	1.9 3	8.54	71.69	17.84	15757	44.23	5.64	38.30	1.17	0.19

Table 1. Proximate Analysis Value and Element Analysis Values of TestSamples (Mass Fraction)

Experimental Setup and Method

The combustion experiment was carried out via a Setaram Setsys Evo thermal analyzer (France Setaram Instrument Company, Caluire-et-Cuire, France). At the beginning of the test, the thermal analyzer was preheated for 20 min. At the same time, Ar was used as the protecting gas and N₂ was used as carrier gas (O₂ was injected during combustion). The gas flow rate was 30 mL/min. The samples, which weighed about 10 mg, were put it into Al₂O₃ crucibles, and the furnace was heated from 40 °C to 1000 °C at a heating rate of 30 °C/min, and the cooling water was opened to start the test. All the tests were carried out at least twice to ensure the repeatability.

SYNERGY ANALYSIS

According to the synergy method, three methods were used to compare and analyze the combustion synergy:

(1) The theoretical values were compared with the experimental values to study the synergistic effect. TG/DTG analysis provides precise real-time information of mass variation versus time or temperature from a view of macroscopic scale, which is a common method for investigations on thermal behaviors and properties. If the theoretical calculation curves did not coincide with the experimental curves completely, then it would indicate a synergistic effect. The algorithm was as follows, Eq. 1,

 $TG_{The} = x_b \xi \overline{\omega}_b + x_g \xi \overline{\omega}_g$ (1) where TG_{The} are the calculated data according to the "rule of mixtures" calculation, $\overline{\omega}_b$ is a separate biomass combustion of weight loss rate value, $\overline{\omega}_g$ is the experimental value of

weight loss rate of coal gangue burning alone,
$$x_b$$
 is the proportion of biomass in mixed samples, and x_g is the proportion of coal gangue in mixed solid samples,

$$DTG_{The} = x_b \xi_b + x_g \xi_g \tag{2}$$

where DTG_{The} are the calculated data according to the "rule of mixtures" calculation, ξ_b is the experimental value of weight loss rate of biomass burning alone, ξ_g is the experimental value of weight loss rate of coal gangue burning alone x_b is the proportion of biomass in mixed samples, and x_g is the proportion of coal gangue in mixed solid samples.

(2) The following formula (Eq. 3) was used to process the data and draw a histogram to compare and analyze the effect of synergy. Equation 3 is as follows:

$$\left|\frac{TG_{\rm Ex} - TG_{\rm The}}{TG_{\rm The}}\right| \times 100\% \tag{3}$$

(3) An impact index, TR, was introduced to describe the degree of interaction between each stage. The mean of the difference between the experimental and calculated values was divided by the mean of the calculated values (recorded as TR) to analyze the effects of the combustion process. The formula for TR was as follows (Eq. 4) (Liang 2017),

$$TR = \left[\sum_{i=1}^{n} \left(\xi_{exp}^{i} - \xi_{cal}^{i}\right)\right] / n\xi_{cal}^{mean}$$

$$\tag{4}$$

where ξ_{exp}^{i} is the experimental value of point I, ξ_{cal}^{i} is the calculated value of point I, and ξ_{cal}^{mean} is the average of calculated values. When TR > 0, the reaction is benefited. When Tr < 0, the reaction is inhibited.

Synergistic Analysis Results

As displayed in Table 1, the carbon content of sunflower straw was higher than that of coal gangue, which meant that it needed more time to complete the pyrolysis process. The H/C atomic ratio of sunflower straw was 2.31 times that of coal gangue. It is known that high H content can produce more H free radicals during pyrolysis process, which helps to improve the quality of liquid and gaseous fuels (Li *et al.* 2015). Therefore, more H free radicals could be expected to be generated when blending sunflower straw in coal gangue, leading a promoting synergistic effect. Moreover, the sunflower straw had high volatile matter content (71.7%), which suggests high reactivity and volatility. This favored an increase in oil yield (Grioui *et al.* 2019). Therefore, the co-combustion process makes fuller use of the advantages of each fuel and to make up for their shortcomings.

The experimental curves and theoretical curves (the curves calculated according to the "rule of mixtures") of the TG and DTG of sunflower straw and coal gangue mixed combustion in different proportions are shown in Fig. 1. The experimental and theoretical curves did not completely coincide, and most of the theoretical curves were above the actual curves. The results showed that sunflower straw had a synergistic effect when it was mixed with coal gangue in different proportions.

Comparison of the TG experimental curve with the theoretical curve found that the weight loss rate in the actual mixed combustion process was greater than that in the theoretical mixed combustion. Comparison of the DTG experimental curve with the theoretical curve showed that the actual weight loss of the DTG curve was lower than the theoretical weight loss in the devolatilization and combustion stages of fixed carbon. This was because the synergy between the two phases was not shown in the magnitude of the weight loss, but in whether the combustion reaction was more complete.







Fig. 1. The TG and DTG curves of the theoretical and experimental values of sunflower straw and coal gangue mixed combustion in different ratios: (a) 2:8; (b) 3:7; (c) 4:6; (d) 5:5; (e) 6:4; (f) 7:3; (g) 8:2

The theoretical and experimental values of the mixed combustion of sunflower straw and coal gangue were calculated to obtain the data shown in Table 2 and the column graph shown in Fig. 2. The results showed that sunflower straw and coal gangue ratios of 2:8 and 8:2 were more suitable than the other ratios.

The TR value curve of the mixed combustion of sunflower straw and coal gangue is shown in Fig. 3. Figure 3 shows that the TR value of the mixed combustion of sunflower straw and coal gangue was mostly greater than 0, which indicated that the whole process benefited combustion. The TR value curve of sunflower straw and coal gangue at a ratio of 2:8 was better than other ratios. In other words, there was a maximum in synergy when the ratio of sunflower straw to coal gangue ratio was 2:8. The reason for this phenomenon was that pyrolysis of sunflower straw's cellulose produces a large number of hydrogen radical fragments, which promoted the cracking of coal gangue (Wu *et al.* 2018; 2019a,b,c).

The TR value of the mixed combustion of two kinds of biomass and coal gangue was less than zero at the initial stage of combustion, which was unfavorable for the reaction. Because the initial combustion is mainly water evaporation, as a part of the mixed sample, biomass is weaker than coal gangue in water evaporation capacity because the water content of both biomass is larger than that of coal gangue. Meng *et al.* (2016) reported that synergetic effect from co-combustion could be attributed to the formation of OH and H radicals from the combustion process of biomass. Thus, the radicals transferred from biomass to the coal gangue structure, leading to the improvement in the decomposition of coal gangue.

In general, the synergistic effects of coal gangue and sunflower straw is mainly derived from three aspects: (1) the effects of different components, including volatile matter, fixed carbon and ash composition; (2) secondary reaction between pyrolysis products, including free radical reaction and gasification reaction (Li et al, 2015); and (3) the different thermal conductivity between fuels (Li *et al.* 2015).

Ratio of Sunflower Straw:Coal Gangue	$\left \frac{TG_{\text{Test}} - TG_{\text{Theoretical}}}{TG_{\text{Theoretical}}}\right \times 100\%$
2:8	12.8%
3:7	4.6%
4:6	3.3%
5:5	6.7%
6:4	8.3%
7:3	5.0%
8:2	12.5%

Table 2. Data Processing Table



Fig. 2. Collaborative column analysis diagram



Fig. 3. The TR value curve

CONCLUSIONS

- 1. The theoretical TG curve of mixed combustion, based on a linear rule of mixtures calculation, did not completely coincide with the actual TG curve of the same mixing ratio, and the theoretical DTG curve of mixed combustion did not completely coincide with the actual DTG curve of the same mixing ratio. These findings showed that there was a synergistic effect between biomass and coal gangue beyond the simple superimposition of biomass and coal gangue combustion alone.
- 2. Comparison of the column charts revealed that the biomass and coal gangue ratios of 2:8 and 8:2 were better than the other ratios. In addition, the synergistic effect of mixed combustion of sunflower straw and coal gangue was better than that of corn straw and coal gangue.
- 3. The TR curve showed that the best synergistic effect was obtained when the ratio of biomass to coal gangue was 2:8 in the mixed combustion test.

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