Co-Gasification of Cow Manure and Bituminous Coal: A Study on Reactivity, Synergistic Effect, and Char Structure Evolution

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ABSTRACT: As special waste biomass, cow manure (CM) is also the main pollutant in agricultural production. The combination of cow manure and coal is conducive to the sustainable development of energy and the solution to pollution problems. This work aims to investigate the co-gasification reactivity and synergy of cow manure and Meihuajing (MHJ) bituminous coal blends at 800–1100 °C using a thermogravimetric analyzer, and the correlation between char gasification reactivity and its structural characteristics is performed. The results indicate that the sensitivity of gasification reactivity to temperature is gradually weakened with the proportion of CM increasing. The synergistic effect on reactivity was observed in the co-gasification process of CM/MHJ. The addition of CM promoted the synergistic effect obviously at the low carbon conversion level, and the inhibitory effect with the CM addition on the order degree of char carbon structure was enhanced during the co-gasification process according to Raman spectroscopy analysis. The addition of CM promoted the porous structure evolutions, which make the pore size distribution and the specific surface developed remarkable. The changes in carbon and pore structures can be well related to the gasification reactivity. The findings in this study would be helpful in the understanding of the co-gasification synergy mechanism of cow manure and coal blends.

1. INTRODUCTION

As special waste biomass, cow manure (CM) is also the main pollutant in agricultural production. With economic growth and improvement of the quality of life, the development of livestock husbandry in China has steadily increased because of the demand for a large number of high-quality proteins, resulting in the production of large amounts of livestock manure and becoming a long-standing pollution source. Because of the serious waste of resources caused by the shortage of treatment technology, it is urgent to seek advanced technologies for the efficient and rational conversion of cow manure waste. Biomass gasification is one of the most promising routes to solve these environmental problems by converting manure into clean syngas for downstream synthesis and killing pathogenic bacteria at high temperatures.

Moreover, China is the main producer of coal resources, and coal accounts for more than 50% of the primary energy consumption structure in China. The status and role of the main energy are difficult to change, but it is facing long-term contradictions between reserve depletion and market demand growth. Co-gasification of cow manure and coal is expected to improve the utilization efficiency of these two kinds of feedstock, and it not only reduces coal consumption and treats livestock manure effectively but also reduces industrial catalyst cost and improves gasification reactivity since active alkali and alkaline earth metals (AAEMs) contained in waste biomass are natural catalysts. As special biomass, cow manure shows a higher energy yield and a higher comprehensive combustibility index than other manures. Therefore, research on co-gasification of manure and coal is rather important.

On the one hand, the changes in structural characteristics play a critical role during the char gasification process. On the other hand, the biochar gasification reactivity is directly governed by its structural properties. The pore structure of coal is very complex, and it contains a large number of visible cracks and nanoscale pores. Pores and fractures form a complex networked structure, which provides channels and places for gas flow and storage, respectively. These pore distributions determined the contact of the gasification agent with the carbon matrix during the gasification process and affected the gasification reactivity. So, our research mainly focused on the co-gasification reactivity and synergy of cow manure and bituminous coal blends and discussed the contributions of structural evolution on the reactivity improvement.

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reported that the carbon structure evolution in co-pyrolysis inhibits co-gasification of rice straw and bituminous coal in a CO\(_2\) atmosphere. Kerkkaiwan et al.\(^{24}\) found that the co-pyrolysis char of rice straw and sub-bituminous gave a higher gasification reactivity due to an increased surface area. Most studies have focused on co-pyrolysis and co-gasification of traditional crops and coal. Issac et al.\(^{25}\) studied the co-gasification of tyre char and lignite; in their work, the role of tyre char ash was studied specifically by mixing it with lignite char. The tyre char ash effect was also found to vary significantly with temperature by checking the gasification residue. As to the co-gasification of livestock manure and coal mixtures, nearly no work is reported.

Hence, the objective of this work is to explore the co-gasification reactivity and synergy of cow manure (CM) and Meihuajing (MHJ) bituminous coal blends using a thermogravimetric analyzer (TGA). The relationship between gasification reactivity and structural characteristics can be correlated using a laser Raman spectrometer and a physical adsorption analyzer. The findings from this work are essential for the application of co-gasification of cow manure and coal and provide guidance for the thermal conversion of cow manure as gasifier feedstock.

### 2. MATERIALS AND METHODS

#### 2.1. Raw Material Preparation

A special biomass cow manure (CM) from the local farms and a kind of bituminous coal, which is a typical gasification coal from Meihuajing (MHJ) mine in Ningdong energy and chemical industrial base in China, was used in this study. The properties of CM and MHJ are listed in Tables 1 and 2. Table 1 shows the proximate composition analysis of CM and MHJ.

#### 2.2. Char Preparation

A tubular furnace reactor was adopted to prepare the pyrolysis char sample. The schematic diagram of the tube furnace experiment system is shown in Figure 1. The pyrolysis procedures were as follows: about ~3 g of blended samples was put into the quartz tube with an alumina ceramic crucible (Al\(_2\)O\(_3\)) for heating in a tubular furnace. The reactor was heated to final pyrolysis temperatures (800, 900, 1000, 1100 °C) by a temperature-programmed device under 150 mL/min N\(_2\) atmosphere. The samples were held for 30 min at target temperatures to remove most of the volatile matter. Afterward, the samples were cooled to room temperature, and then the pyrolysis char at four different temperatures were obtained, respectively. The blending mass ratio of CM and MHJ was 1:3, 1:1, 3:1, respectively, and the corresponding char samples were marked as CMP, 1C3M, 1C1M, 3C1M, and MHJP.

#### 2.3. Isothermal Gasification Reactivity Analysis

The gasification experiments were carried out using a thermogravimetric analyzer (NETZSCH STA449-F3). About 10 mg of char sample was placed in an Al\(_2\)O\(_3\) crucible and heated from room temperature to target gasification temperatures (800, 900, 1000, 1100 °C) with a heating rate of 10 °C/min. High-purity Ar (99.999%) with a flow rate of 50 mL/min was used as the carrier gas. The atmosphere in the reactor then changed to CO\(_2\) with a flow rate of 120 mL/min, and isothermal gasification reactivity started. The weight-loss data can be obtained from TGA when weight-loss curves tended to be unchanged.

The carbon conversion \(X\) of char gasification can be calculated by eq 1\(^{26}\)

\[
X(t) = \frac{w_0 - w_t}{w_0 - w_\infty}
\]  

where \(w_0, w_\infty, w_t\) refer to initial, final, and instantaneous weights during the reaction, respectively.

The reactivity of the gasification reaction is quantitatively expressed by the gasification reaction index \(R_{0.9}\)\(^{27}\) which was defined as follows

\[
R_{0.9} = \frac{0.9}{t_{X=0.9}}
\]

where \(t_{X=0.9}\) represents gasification time when carbon conversion reaches 90%.

### 2.4. Chemical Structure Analysis

The carbon structure parameters of char samples were measured by a laser Raman
spectrometer (Thermo Fisher DXR). It is suitable for the analysis of carbon crystal using an argon-ion laser as the excitation light source, and the laser wavelength is 532 nm. The first level region was selected and the wavelength range of 800−2000 cm$^{-1}$ was measured. Several particles from each sample were randomly selected for multiarea test and the average values were used as the final result to ensure the accuracy of the data.

2.5. Physical Structure Characterization. The pore structure parameters of the char were measured by a physical adsorption analyzer (JW-BK 100C-01) with the nitrogen adsorption method. Prior to the gas adsorption measurements, the fresh chars were degassed in the adsorption system at 250 °C for at least 10 h. Nitrogen adsorption experiments were carried out at a temperature of 77 K and a relative pressure of 0.01−0.99. The specific surface area was calculated by the Brunauer−Emmett−Teller (BET) model, and the pore size distribution was obtained by the Barrett−Joyner−Halenda (BJH) method.

2.6. Scanning Electron Microscopy Coupled with Energy-Dispersive Spectroscopy (SEM−EDS) Analysis. The microstructure and element composition of the sample surface were analyzed by scanning electron microscopy coupled with energy-dispersive spectroscopy (SEM−EDS). The instrument system has a resolution of 3 nm, the effective detection area is 10 mm$^2$, the element detection range is Be
(beryllium)—Pu (plutonium), and the magnification range is 5–1,000,000 times and it can be adjusted continuously.

3. RESULTS AND DISCUSSION

3.1. Isothermal \( \text{CO}_2 \)-Gasification Reactivity of Samples

Gasification reactivity curves of CM, MHJ, and their blended samples at different temperatures are illustrated in Figure 2. As seen, the gasification time required to reach the same conversion level was obviously decreased with the increase of temperature from 800 to 1100 °C. As an illustration, it took about 3 h for CM to be gasified completely at 800 °C but 5 min at 1100 °C. At the same temperature, the gasification reactivity of CM is always better than that of MHJ. \( R_{0.9} \) was used as a quantitative index to evaluate the overall gasification reactivity of samples. The greater \( R_{0.9} \) means the higher gasification reactivity of the whole gasification reaction. \( R_{0.9} \) of samples at different temperatures is listed in Table 3. It can be seen that \( R_{0.9} \) increases with the increase of the reaction temperature and the proportion of CM. CM possesses much higher reactivity than MHJ, and mixing CM and MHJ was helpful for the enhancement of the whole gasification reactivity compared with single coal gasification.

To intuitively express the effect of temperature and mixing ratio on the reactivity of gasification reaction, the specific reactivity index was introduced, as shown in the following:

\[
\text{specific } R_{0.9} = \frac{R_{0.9,T}}{R_{0.9,800}}
\]

(4)

\[
\text{specific } R_{0.9}^{\prime} = \frac{R_{0.9,B}}{R_{0.9,MHJ}}
\]

(5)

where \( R_{0.9,T} \) represents the \( R_{0.9} \) of the sample at temperature \( T \); \( R_{0.9,800} \) represents the \( R_{0.9} \) at 800 °C; and \( R_{0.9,B} \) and \( R_{0.9,MHJ} \) represent the \( R_{0.9} \) of the blended samples and MHJ at different temperatures, respectively. Equations 4 and eq 1 can characterize the effects of temperature and mixing ratio on the reaction reactivity, respectively.

The higher the specific \( R_{0.9} \) value, the more obvious the positive effect of gasification temperature and CM mixing ratio on MHJ gasification reactivity. The specific \( R_{0.9} \) is illustrated in Figure 3. Figure 3a shows the effect of temperature on gasification reactivity; it can be seen that with the proportion of CM increasing, the sensitivity of gasification reactivity to temperature is gradually weakened. As an illustration of CM, the specific \( R_{0.9} \) is 15.0 and 15.3 at 1000 and 1100 °C, respectively. Figure 3b shows the effect of CM mixing ratio on gasification reactivity. The specific \( R_{0.9} \) value of MHJ was lower than that of CM at the same gasification temperature, indicating that the addition of CM can promote the coal gasification reaction. In addition, it is also found in Figure 3b that the promoting effect of CM on MHJ gasification reactivity is more significant at low temperatures, and with the increase of gasification temperature, the sensitivity of gasification reactivity to CM mixing ratio decreased gradually.

3.2. Synergy Behavior toward Co-Gasification Reactivity of Blended Samples

Figure 4 shows the calculated carbon conversion variations of CM/MHJ blends versus gasification temperature. By comparing the experimental reactivity curves with the calculated reactivity curves, the synergy behavior of CM and MHJ during co-gasification process could be determined. A higher experimental reactivity curve means that there was a synergistic effect during co-gasification, whereas a higher calculated reactivity curve means an inhibitory effect.\(^{16}\) As seen from Figure 4, the experimental reactivity curves of blended samples were always higher than the corresponding calculated reactivity curves during co-gasification process, demonstrating that the synergistic effect existed in the entire co-gasification process of CM/MHJ blended chars. By comparing the synergistic effect at different temperatures, it can be found that the overall synergistic effect at 1000 and 1100 °C was weakened. This could be explained as the high temperature greatly shortened the gasification time and was favorable for the gasification reaction. The increases of temperature were beneficial to increase the energy of the carbon atoms in coal char so that the carbon bonds in the aromatic ring of the coal could be easily broken and generated more active carbon molecules. The effective collision times between activated carbon molecules and gasification agent...
were increased, hence the gasification reaction rate was accelerated.29

To quantitatively investigate the cooperative behavior evolution in co-gasification process, the synergy factor $A_{X,T}$ was proposed as eq 6.30 When $A > 1$, it indicates that a synergistic effect existed in co-gasification process otherwise an inhibition effect existed. The larger $A$ value implied more obvious synergistic effect on the co-gasification reactivity

$$A_{X,T} = \frac{t_{X,T,\text{cal}}}{t_{X,T,\text{exp}}}$$

where $t_{X,T,\text{cal}}$ and $t_{X,T,\text{exp}}$ represent the calculated and experimental gasification time required for carbon conversion of $X$ when char samples are gasified at a temperature of $T$, respectively.

Blended samples gasified at 900 °C were taken as examples. The blending mass ratios of CM and MHJ were 1:3, 1:1, and 3:1, respectively, and the corresponding samples are labeled as $1C3M$-900, $1C1M$-900, and $3C1M$-900. Synergy factor variations with carbon conversion during blended char co-gasification at 900 °C are shown in Figure 5. As seen, synergy factors increased with increasing CM proportion. At the same carbon conversion rate, the order of the synergy factor $A_{X,T}$ value is $3C1M$-900 > $1C1M$-900 > $1C3M$-900. For $3C1M$-900, with the increase of conversions, $A_{X,T}$ showed a low decrease trend and then increased when the conversion level reached 0.5. The phenomenon was different from synergy behavior variations on co-gasification reactivity of $1C3M$-900. Synergy behavior on co-gasification reactivity of $1C3M$-900 was presented as a decreasing inhibition effect first and turned into an enhanced synergistic effect with further reaction.

$A_{0.9,900}$ could be used to evaluate the overall synergy behavior toward co-gasification reactivity.31 When the carbon conversion is 0.9, the synergy factor $A_{0.9,900}$ values of $3C1M$-900, $1C1M$-900, and $1C3M$-900 were 2.61, 2.01, and 1.14, respectively. At the low conversion level, taking the carbon conversion 0.9 as an example.
conversion of 0.2 as an example, the synergy factor values of 3C1M-900, 1C1M-900, and 1C3M-900 were 2.64, 1.15, and 0.82, respectively. The interaction behavior toward co-gasification reactivity of samples was transformed from an inhibition effect to a synergistic effect with the addition of CM. The results mean that the addition of CM promoted the synergistic effect on the whole gasification process, especially at the low conversion level.

3.3. Structural Characteristics Analysis. 3.3.1. Carbon Structure Change of Char. Char was produced by pyrolysis at a high temperature, and the carbon microcrystal structure composed of the carbon skeleton was left. The structural evolution of char has been studied by Raman spectroscopy, which was suitable for analyzing the structural characteristics of biochars. The structural features of chars can be evaluated by analyzing the intensities of the major Raman bands. WIRE 3.4 software was used to separate and fit the original Raman spectra, and different carbon structure parameters were obtained. Referring to the methods of Sheng33 and Wu et al., the original Raman spectrum was resolved into four Lorentzian bands (D1, D2, D4, G) and one Gaussian band (D3). The D1 band appearing at the wavelength of 1350 cm⁻¹ represented a defect structure and heteroatoms in the graphite lattice, and the G band appearing at the wavelength of 1580 cm⁻¹ represented an ideal vibration mode of graphite lattice. The area ratio between D1 band and G band (D1/I_G) reflects the crystalline or graphite-like carbon structures, and the I_D1/I_all band area ratio can evaluate the content of the large aromatic ring and the order of carbon. Thus, the D1/I_G and I_D1/I_all values were used as quantitative parameters to evaluate the order degree of the carbon structure of the measured samples. The typical Raman spectrum of the resulting char and band distributions is shown in Figure 6.

![Typical Raman spectra of MHJP.](image)

The decrease of I_D1/I_G values and the increase of I_D1/I_all values indicate that the order degree of char structure increases. The Raman band area ratios I_D1/I_G and I_D1/I_all of different blended chars are listed in Table 4. As seen, the I_D1/I_G values of different char samples decrease with increasing pyrolysis temperature, indicating that the order degree of carbon microcrystalline structure of the char sample increases. This is because the organic matter in the relatively loose structures such as oxygen-containing functional groups, aliphatic side chains and bridge bonds, and small aromatic clusters gradually falls off with the pyrolysis temperature increasing. Then, dehydrocondensation of the remaining aromatic ring structure (mainly three or more rings) occurs, and the size of the aromatic carbon skeleton gradually increases until it is close to the graphite structure. According to some studies, this is mainly because AAEMs can promote the decomposition of the large aromatic rings and induce the increase of the small aromatic ring systems. During the co-pyrolysis process, the decrease in concentrations of small aromatic rings of CMP and the increase in amorphous carbon of MHJP imply that AAEMs migrate from CMP to MHJP.

Also, the addition of CM has a significant effect on the I_D1/I_G of gasification char. Under the same gasification temperature, the order of I_D1/I_G values of different char samples is as follows: MHJP < 1C3M < 1C1M < 3C1M < CMP, indicating that the CM additive was beneficial to slow down the graphitization process of carbon microcrystallite structure in char samples during gasification. The inhibitory effect of graphitization was more obvious at a low temperature. Also, the Raman band ratio of char samples with and without CM additive was quite different. At high temperatures, the difference of I_D1/I_G and I_D1/I_all values decreases for CM blends; this indicates that the inhibitory effect of CM on the graphitization process for coal char carbon structure and the promotion effect of CM on the increase of amorphous carbon structure during char gasification were weakened at high temperatures.

3.3.2. Pore Structure Evolution of Chars. Table 5 shows the BET specific surface area and the BJH average pore width of different blending samples measured by N₂ adsorption experiments. The results show that the A_BET of CMP is

| Table 4. Raman Spectroscopic Band Area Ratio of Different Blended Chars |
|-----------------------------|-----------------------------|-----------------------------|
| temperature (°C) | CMP | 3C1M | 1C1M | 1C3M | MHJP |
| 800 | 16.332 (0.049) | 14.883 (0.055) | 13.612 (0.059) | 13.505 (0.093) | 6.089 (0.114) |
| 900 | 14.221 (0.058) | 10.501 (0.056) | 13.135 (0.061) | 12.714 (0.090) | 5.793 (0.118) |
| 1000 | 12.912 (0.062) | 11.978 (0.066) | 11.062 (0.073) | 13.336 (0.088) | 5.586 (0.124) |
| 1100 | 11.112 (0.074) | 10.935 (0.078) | 10.202 (0.080) | 14.347 (0.084) | 5.523 (0.130) |

| Table 5. Pore Structure Parameters of Char Samples from Pyrolysis at 1100 °C |
|-----------------------------|-----------------------------|
| samples | A_BET (m²/g) | pore volume (cm³/g) |
| CMP | 170 | 0.17 |
| 3C1M | 137 | 0.13 |
| 1C1M | 69 | 0.07 |
| 1C3M | 15 | 0.03 |
| MHJP | 4 | 0.01 |
40.19 times greater than that of MHJP, indicating that the pore structure of CMP developed more and the mass-transfer resistance of CMP was less. The surface characteristic of char samples is shown in Figure 7. It can be seen that the CMP possessed more crack structures than MHJP. The red circular region represented the ash supported by the char surface, and the darker region is the carbon crystal structure of the char samples. Compared with CMP, the surface structure of MHJP was more compact, and fewer pore structures and higher fixed carbon content were observed. From Figure 7b, it can be seen that a lot of minerals attached to the surface of CMP. Manures typically contain high organic content and cellulosic composition owing to the bacterial and chemical reactivity along animals’ digestive track, therefore the CM contains cellulose, lignin, hemicelluloses, and other plant characteristics; the pore size was obviously larger than that of MHJP, which was beneficial to the entry of the gasification agent, thus promoting the gasification reaction rate. The distribution of MHJP and CMP particles at the blending ratio of 1:1 is uniform, as seen in Figure 7c. The close contact between MHJP and CMP was beneficial to the increasing of the residence time of the gasification agent during the co-gasification process and was also beneficial to the catalysis of active alkali and alkaline earth metals (AAEMs) in CMP.

Table 6 gives the element composition of the particle surface of different samples, and a higher content of AAEMs existed in the blending samples compared with MHJP. Hence, CMP with higher reactivity would improve the whole gasification reactivity of char samples by mixing with MHJP.

Figure 8 shows the pore size distribution of different char samples from pyrolysis at 1100 °C. The results show that with the addition of CM, the range of pore size changes is mainly between 2 and 10 nm. This indicates that the addition of CM promotes the development of mixed char samples to a smaller pore size structure. It can be seen that with the increase of the CM content in blended char, the proportion of pore size below 2–10 nm increases, while the proportion of pore size distribution more than 50 nm decreases relatively. The
contribution of the smaller pore to the surface area is larger, which makes the gasified char of CMP have a larger $A_{BET}$.

3.4. Relationship between Char Gasification Reactivity and Structural Characteristics. The gasification reactivity of chars is closely related to its physicochemical structure. The order degree of carbon structure, the specific surface area, and pore volume will affect the degree of difficulty of gasification agent diffuse into the structure of the carbon layer during gasification process, which determines the gasification reactivity of char.

As known from the above analysis, the inhibitory effect with the CM addition on the order degree of char carbon structure was enhanced during co-gasification. Figure 9 shows the relationship between carbon structure $I_{D1}/I_G$ and gasification reactivity $R_{0.9}$. The relationship between $R_{0.9}$ and $I_{D1}/I_G$ of MHJP at different gasification temperatures is shown in Figure 9a, and Figure 9b shows the relationship between $R_{0.9}$ and $I_{D1}/I_G$ of char samples at different mixing ratios. The $I_{D1}/I_G$ value of gasification char was consistent with the changing trend of gasification reactivity of char samples; it was concluded that the order degree of carbon microcrystal structure was also an important structural parameter to characterize the reactivity of char on co-gasification. This result was expected because the char sample with highly active AAEM concentration and low degree of graphitization was believed to be more reactive.38,39

Based on both the SEM–EDS and $A_{BET}$ results, the gasification reactivity of MHJ was relatively low. From Table 6, it can be seen that MHJP has a higher fixed carbon content and CMP is rich in AAEMs. The content of AAEMs in co-pyrolysis char was higher than that in MHJP. It can be explained that the co-pyrolysis process of MHJP and CMP will load a certain amount of CM ash on the surface of MHJP particles. Besides, the CMP in mixtures would react first during co-gasification process owing to its high reactivity. With the consumption of CMP, the AAEM-rich ash of CMP was gradually released and transferred to MHJP, resulting in the enhancement of gasification reactivity. Moreover, the close contact between MHJP and CMP was beneficial to the co-gasification reaction between them. The residence time of the gasification agent on the co-gasification process was increased. It was also beneficial to the catalysis of AAEMs in CM char for co-gasification. As seen in Figure 8, at the same temperature, a larger specific surface area and pore volume are helpful for higher gasification reactivity. Compared with other char samples, the proportion of pore distribution at 2–10 nm in CMP was the largest, which also corresponded to the highest gasification reactivity for CM.

4. CONCLUSIONS

Co-gasification reactivity and synergy of cow manure and bituminous coal blends were investigated. The synergistic effect existed in the co-gasification process of CM/MHJ blended samples. The promoting effect of CM on MHJ gasification reactivity is more significant at low temperatures. With the proportion of CM increasing, the sensitivity of gasification reactivity to temperature is gradually weakened. The pore size distribution developed to a smaller range at a higher CMP proportion, and a larger specific surface area was obtained.

Additionally, the changes in carbon structure and pore structure can be well related to the gasification reactivity. During the co-gasification process, the inhibitory effect on the order degree of char carbon structure was enhanced with increasing CM, resulting in the continuous enhancement of gasification reactivity. The addition of CM promotes the porous structure evolution, which made the pore size distribution and the specific surface area developed remarkable. Correspondingly, the gasification reactivity was improved.

Figure 8. Pore size distribution of different blended char samples.

Figure 9. Effects of (a) gasification temperature and (b) blending ratios on carbon structure $I_{D1}/I_G$ and gasification reactivity $R_{0.9}$. 16786 http://dx.doi.org/10.1021/acsomega.0c01785 ACS Omega 2020, 5, 16779–16788
Moreover, the evolutions of the pore structure had an impact on the gasification characteristics at higher temperatures. The carbon structure changes of CMP during co-pyrolysis contributed more to the co-gasification reactivity at the early stage.

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**Notes**

The authors declare no competing financial interest.

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