Investigation of Chemical-looping Gasification Characteristics of Chinese Western Coals with Hematite-CuO Oxygen Carrier

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Abstract. In order to realize highly efficient conversion of Chinese western bituminous coals into syngas, a series of chemical-looping gasification experiments was conducted with hematite-CuO oxygen carrier in a laboratory-scale fluidized-bed reactor. The results indicated that the gasification rate of Chinese western bituminous increased by 2-3 times after addition of a hematite-CuO oxygen carrier. Meanwhile, the syngas yields of Chinese western bituminous ranged from 1.84–2.04 m^3/kg, three times higher than that of lignite. This shows that the combination of chemical-looping technology and gasification of coal can achieve efficient conversion of Chinese/western bituminous coals. The temperature and the supply oxygen coefficient (O/C) all demonstrated a clear effect on the gasification rates and the gas yields. 10 cycles of redox experiments indicated that the hematite-CuO oxygen carriers have good recycled reaction characteristics. Those results provide theoretical guidance for the efficient conversion of Chinese western bituminous coals into syngas via chemical-looping gasification.

1.INTRODUCTION

Chemical-looping gasification is a new technology that converts solid fuel into syngas.[1] Choosing the right oxygen carrier and better operating conditions are some of the key issues in the chemical-looping gasification process.[2-6] Guo et al. suggested that multifunctional oxygen carrier compounds, such as Ca-based oxygen carriers with K or Na pendant groups, coupled with catalytic gasification, could effectively accelerate coal gasification, but the systems suffered alkali metal loss during the recycling process.[7, 8] Moreover, Cu-based oxygen carriers usually exhibit greater oxygen donating capacity and much higher reactivity, which can effectively accelerate char gasification.[9] Sintering of the oxygen carrier occurs and the syngas produced is consumed, which leads to degradation in the quality of the product gas.[10] The use of copper-iron oxygen carriers is expected to solve the above problems. However, the copper-iron oxygen carrier is mainly used in chemical-looping combustion.[11-13] Chemical-looping combustion and chemical-looping gasification serve different purposes and involve different processes. Chemical-looping combustion involves complete combustion to produce heat, while chemical-looping gasification results in the syngas.[14] Therefore, it is necessary to study the effect of the copper-iron oxygen carrier on the gasification rate of coals during chemical-looping gasification.

This paper investigated the effect of temperature and the supply oxygen coefficient (O/C) on the gasification rates and the syngas yields in laboratory-scale experiments utilizing a fluidized bed reactor. In addition, X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and N2 adsorption isotherm (BET) were carried out to verify the gasification characteristics of these coals.

2.EXPERIMENTAL

2.1.Materials

2.1.1.Coal

Coal samples include NX, SX, NM, XJ and YN sourced from coalfields in western China. Detailed and ultimate analyse results of the coal are shown in Table 1.

Table 1. Proximate and ultimate analyses of coal

S.	Proximate analysis w_t/%				Ultimate analysis w_t/%					LHV MJ/kg
	M	A	V	F_C	C	H	N	S	O	
NX	5.18	4.56	26.95	63.31	77.60	5.16	1.46	0.40	10.77	24.71
SX	7.10	5.88	29.71	57.31	69.08	7.17	0.76	0.30	14.03	25.23
XJ	9.06	3.55	28.07	59.32	76.06	3.50	0.29	0.44	15.83	23.34

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NM	11.52	5.07	27.26	56.15	74.08	4.91	0.70	0.02	14.29	26.58
YN	22.38	23.5	30.98	23.14	45.86	2.85	1.20	1.15	18.67	12.61

2.1.2.Oxygen carrier

A hematite-CuO oxygen carrier was prepared by mechanical mixing of 50 mol% Fe_2O_3 (in hematite) and 50 mol% CuO. The preparation method is as follows: Hematite (China, particle size< 0.075 mm), CuO (China , particle size < 0.075 mm) and deionized water were added to a colloid mill with a rotor speed set at ~6000 rpm and mixed for 4 min to reach homogeneity. The resultant slurry was dried at 120°C for 12 h in a ventilating dry box, followed by calcination at 950°C for 6h. The samples were sieved; and particles between 0.10 – 0.15 um were collected. The phases, morphological and pore structure of $CuFe_2O_4$ OCs were evaluated by the X-ray Diffraction (XRD), Scanning Electron Microscope (SEM) andN_2 adsorption analysis (BET), respectively.

2.2. Experimental Setup and Procedure

The reactions between coal and the hematite-CuO oxygen carrier were evaluated with a laboratory-scale fluidized bed reactor (310 stainless steel, with an inner diameter of 65mm and a height of 2900mm). The schematic diagram of the reactor system is as shown in Fig1. All the experiments were conducted in a laboratory-scale fluidized bed reactor with a constant gas flow of 2 L/min of steam, and N2 was applied during reduction. The superficial velocity in the reactor (U0) was ~3.8 times the minimum fluidizing velocity (Umf = 0.8 m/s) of the oxygen carrier particles. In each test, the mass of coal was kept at 3g and if the mass of the oxygen carrier was insufficient to balance the total sample weight at 60 g, silica sand with the same particle size served as the inert bed material.

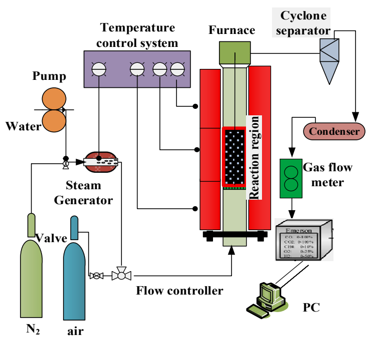

Fig.1 The schematic diagram of laboratory setup

In order to evaluate the four Chinese western bituminous coals, the gasification temperature was set to 900℃, O/C was 0.4 and the steam flow rate was fixed at the fluidization agent was 50 vol.% H2O. In order to determine the effects of temperature on the performance of chemical-looping gasification, the temperature increased from 800 to 950℃ at an interval of 50, O/C were set at 0.2,0.4,0.8,1.0 and the steam flow rate was fixed at the fluidization agent was 50 vol.% H2O. In order to examine the stability of the oxygen carrier, we conducted 10 cyclic redox tests with NX, the reaction temperature was kept at 900℃, the fluidization agent was 50 vol.% H2O and the O/C was 0.4. The oxidation and reduction stages were alternated with a 10 min N2 purge.

2.3.Data processing

O/C is calculated with the following formula:

$$\frac{O}{C}=\frac{R_{OC}\cdot m_{OC}}{\Phi_{coal}\cdot m_{coal}} \tag{1}$$

Where:

m_{OC} and m_{coal} denote the masses of the oxygen carrier and coal (kg), respectively; R_{OC} represents the theoretical oxygen transport capacity; Φ_{coal} is the oxygen needed for complete combustion per unit mass of coal.

The gas content (Y_i, m^3/kg) and syngas yield (G_{syn}, m^3/kg) are calculated as follows:

$$Y_i=\frac{\int_0^t F_{out}\cdot x_i\cdot dt}{\sum\int_0^t F_{out}\cdot x_i\cdot dt} \tag{2}$$

$$G_{syn}=\frac{\int_0^t F_{out}\cdot x_{CO}\cdot dt+\int_0^t F_{out}\cdot x_{H_2}\cdot dt+\int_0^t F_{out}\cdot x_{CH_4}\cdot dt}{m_{coal}} \tag{3}$$

where Fout denotes The volume flow rate of the outlet gas L/min; xi (i = CO2, CO, CH4 and H2) denotes the instantaneous volume fractions of gas in the outlet gas flow on a dry basis, vol %.

The gasification rate(r(t), %/min) is calculated as follows:

$$r(t)=\frac{dX_C}{dt} \tag{4}$$

The carbon conversion (XC, %) is calculated as follows:

$$X_C=\frac{\int_0^t F_{out}(x_{CO}+x_{CO_2}+x_{CH_4})dt}{n_C\cdot 22.4}\times 100\% \tag{5}$$

where nC is the total number of moles of coal containing carbon.

The reactivity index of gasification (R,min-1) is calculated as follows:

$$R=\frac{0.5}{\tau_{0.5}} \tag{6}$$

Where τ0.5 is defined as the time (min) when the gasification rate reaches 50% during gasification.

3.RESULTS AND DISCUSSION

3.1.Comparison of gasification and chemical-looping gasification in Chinese western coal

Fig.2 shows the gasification rate as a function of carbon conversion of Chinese western coals in gasification and chemical-looping gasification. According to Fig.2, the maximum gasification rates of coal gasification for NX, XJ, NM and SX coals are 0.029 %/min, 0.043 %/min, 0.034 %/min and 0.046 %/min, respectively, which are much lower than those with lignite. This can be ascribed to the differing reaction properties of different types of coal. This also shows that compared with lignite,

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Chinese western bituminous coal has a lower gasification rate and improvement is needed. In chemical-looping gasification with a hematite-CuO oxygen carrier, the maximum gasification rates of coal gasification for NX, XJ, NM and SX are 0.092 %/min, 0.092 %/min, 0.083 %/min, 0.083 %/min, distinctly higher than those in traditional coal gasification. This shows that the hematite-CuO oxygen carrier raises the gasification rates for NX, XJ, NM and SX coals. These increased gasification rates are primarily because that the hematite-CuO oxygen carrier reacted with char[15, 16].

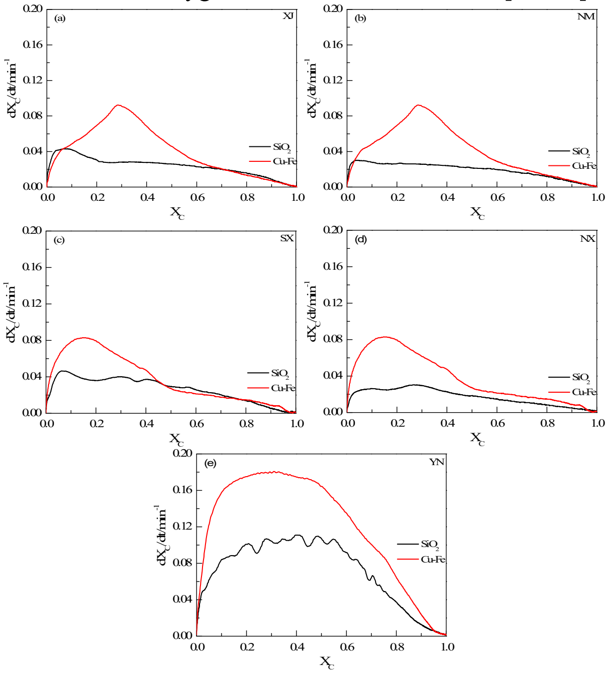

Fig.2 The gasification rate as a function of carbon conversion of Chinese western coals in gasification and chemical-looping *gasification; (a) XJ, (b) NM, (c) SX, (d) NX, (e) YN.*

Table 2 shows the gas content and syngas yields of traditional coal gasification and chemical-looping gasification for Chinese western coals. According to data in table 3, the syngas yields of NX, XJ, NM and SX with a hematite-CuO oxygen carrier are lower than those in traditional coal gasification. This is because the hematite-CuO oxygen carrier consumes some of the coal gasification products during gasification.[17] Moreover, the syngas yields of all four bituminous coals were approximately 3 times higher than those with YN lignite. This is because the YN coal contains a higher amount of moisture and a lower amount of carbon than the high rank bituminous coal.[18, 19]

Table 2. The gas content and syngas yields of coal gasification and chemical-looping gasification for Chinese western coals

Sample	Y_i (%)				G_{syn}(m^3/kg)
	CO_2	CO	H_2	CH_4	
NX /SiO_2	23.92	13.15	61.33	1.60	2.19
XJ /SiO_2	22.74	13.15	62.27	1.84	2.38
NM /SiO_2	21.11	15.73	61.01	2.15	2.22
SX /SiO_2	23.71	13.79	60.50	2.00	2.06
YN /SiO_2	33.47	10.06	53.58	2.89	1.05
NX /hematite-CuO	35.48	11.09	51.06	0.40	2.04
XJ /hematite-CuO	36.02	12.12	53.07	0.66	1.93
NM /hematite-CuO	34.57	10.68	54.08	1.50	1.94
SX /hematite-CuO	36.18	11.68	58.37	1.00	1.84
YN /hematite-CuO	43.62	8.82	45.66	1.80	0.74

In conclusion, despite a low gasification rate, Chinese western bituminous coal has a significant advantage in coal gasification technology thanks to its high syngas yield. And the gasification rate of the Chinese western bituminous coal increases by 2-3 times upon addition of a hematite-CuO oxygen carrier. This shows that the combination of chemical-looping technology and gasification of coal can achieve efficient conversion of Chinese western bituminous coal.

3.2.Effect of temperature on chemical-looping gasification

The reaction temperature is an important factor to the gasification rate and syngas yield in the chemical-looping gasification process.[17] Fig. 3 shows the effect of temperature on the reaction index and snygas yields of Chinese western bituminous coals with a hematite-CuO oxygen carrier. The coal gasification reaction indices of NX, XJ, NM and SX all increase as the temperature increases, mostly because of the endothermic nature of coal gasification and the fact that endothermic processes are fueled by temperature increases.[20] When the temperature increased from 800 °C to 950 °C for NX, NM, SX and XJ coals, syngas yields increased by 0.8-1 m3/kg, which suggested that temperature had a great effect on the gasification rate of Chinese western bituminous coals. For NX, NM, SX and XJ, an increased temperature increased the reaction index and syngas yield.

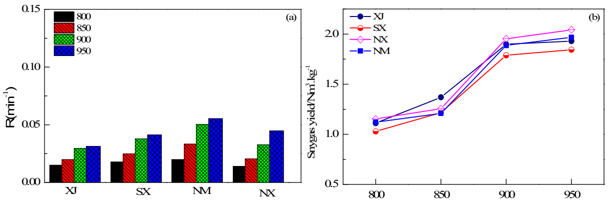

Fig. 3. Effect of temperature on reaction index (a) and snygas yield (b) of Chinese western bituminous with a hematite-CuO oxygen carrier

3.3.Effect of O/C on chemical-looping gasification

The oxygen carrier acts as an oxygen source and a heat carrier for coal gasification; thus the oxygen carrier in the reactor is absolutely vital for the performance of chemical-looping gasification. Fig. 4 shows the effect of O/C on the reaction index and syngas yield of four Chinese western bituminous coals with the hematite-CuO oxygen carrier. As shown in Fig. 4, as the O/C increased, the coal gasification reaction indices of NX, XJ, NM and SX also increased. This is because an increase in O/C generated more lattice oxygen, which resulted in greater syngas consumption.[7] The reduction in syngas fueled coal gasification. In addition, increasing the O/C facilitated the conversion of C, CO and CH4 into CO2, which served as a gasification agent that promoted coal gasification. However, as the O/C increased, the syngas yield decreased. Increasing O/C could efficiently improve the gasification rate of Chinese western bituminous coals, but the primary goal of chemical-looping gasification was to get a high syngas yield. Consequently, an appropriate O/C was a key factor to the efficient conversion of Chinese western bituminous coals into syngas via chemical-looping gasification. In addition, as we note here, for chemical looping gasification, O/C is the main factor to maintaining a heat balance between the two reactors to achieve a spontaneous process. But experiments in the current study were conducted in a batch fluidized bed reactor with an external electric furnace for heating. Therefore, it is necessary to further investigate the effect of O/C on the efficient conversion of Chinese western bituminous coals into syngas in the chemical-looping gasification interconnected fluidized bed.

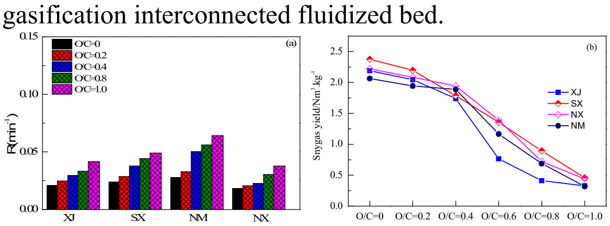

Fig. 4. Effect of O/C on the reaction index (a) and syngas yield (b) of four Chinese western bituminous with hematite-CuO oxygen carrier

3.4.Gasification variation during multiple redox cycles

Fig. 5 shows the syngas yields for NX over 10 cycles. There was little fluctuation in syngas yields over the 10 cycles. This indicated the stability of the hematite-CuO oxygen carrier used in chemical-looping gasification of Chinese western bituminous coals.

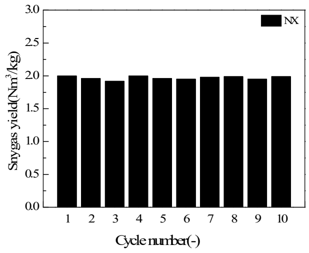

Fig. 5 Syngas variations of yield during 10 cycle tests of NX coals with a hematite-CuO oxygen carrier

3.5.Oxygen carrier characterization

Fig. 6 have shown the crystalline phase compositions of fresh and used oxygen carrier. A fresh hematite-CuO sample contained CuFe2O4 and SiO2. The formation of CuFe2O4 spinel was the reason for the synergistic reactivity of the oxygen carrier. For the hematite-CuO oxygen carrier in the initial reduction state cycle, Cu2+ was reduced to Cu0, while Fe3+ was reduced to Fe+8/3. This is consistent with results reported in literature.[20] After 10 redox cycles with NX in a fluidized bed reactor, the microscopic morphologies of hematite-CuO remained unchanged. And the stabilization morphologies of the hematite-CuO oxygen carrier during the redox cycle were clearly visible.

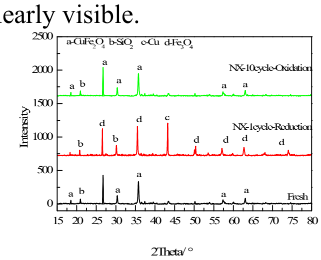

Fig. 6. XRD results of the fresh, cycle-1 reduction and after 10 oxidation cycles of NX with a hematite-CuO oxygen carrier

Typical SEM images of the fresh and 10-cycle hematite-CuO with NX are shown in Fig. 7. With respect to the particle surface morphology, the fresh oxygen carrier sample had a uniform morphology and smooth surface. After 10 cycles, the oxygen carrier surface was rather loose and featured a porous structure. This was due to the repeated reduction and oxidation processes of the gas-solid reaction which resulted in the formation of channels by the gaseous reactants and products.

Table 3 further illustrates that after 10 cycles, the specific surface area of the hematite-CuO oxygen carrier increased by 1 m2/g compared with that of fresh oxygen carrier. In addition, SEM-mapping analysis reveals that Cu and Fe were evenly distributed on the hematite-CuO surface for fresh and 10 cycles in chemical-looping gasification. CuFe2O4 created during the reaction between CuO and hematite is consistent with the characteristic peak of CuFe2O4 in the XRD patterns of the hematite-CuO oxygen carrier. Therefore, the hematite-CuO oxygen carrier showed good cyclic reaction characteristics during 10 cyclic regeneration experiments.

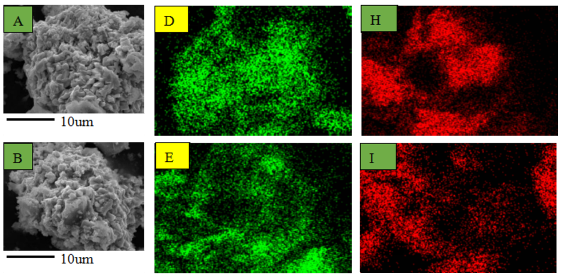

Fig. 7. SEM images of fresh samples (A) and after 10 cycles samples of NX (B) with a hematite-CuO oxygen carrier;Mapping-Fe: (D), (E); Mapping-Cu: (H), (I)

Table 3. The BET of Fresh and 10 Cycle hematite-CuO oxygen carrier

Sample	S_{BET}/(m^2/g)
Fresh	0.759
NX-10 Cycle	1.729

4.CONCLUSION

In this paper, we achieved highly efficient conversion of Chinese western bituminous coals based on the hematite-CuO oxygen carrier using a batch fluidized bed and drew the following conclusion:

(1) The gasification rates and syngas yields were used to compare five coals; Chinese western bituminous coals showed a higher syngas yield but a lower gasification rate than those in lignite, while the gasification rate of Chinese western bituminous coals increased by 2-3 times upon addition of a hematite-CuO oxygen carrier.

(2) The temperature and O/C all showed clear effects on the gasification rates and the syngas yields. An increased temperature could efficiently improve the gasification rates and syngas yield of Chinese western bituminous coals. Increasing O/C could also efficiently improve the gasification rates of Chinese western bituminous coals, while decreasing the syngas yield. An appropriate O/C was a key factor to the efficient conversion of Chinese western bituminous coals into syngas via chemical-looping gasification.

(3) 10 redox cycles were conducted for the verification of the gasification characteristics of Chinese western bituminous coals based on hematite-CuO oxygen carrier. The results showed the hematite-CuO oxygen carrier had good cyclic reaction characteristics.

Acknowledgments

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