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Release of Ca during coal pyrolysis and char gasification in H_2O, CO_2 and their mixtures

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ABSTRACT

The release characteristics of Ca during a Chinese bituminous coal pyrolysis and char gasification in different gasifying agents was studied. Residual chars with different carbon conversion levels were obtained by gasifying in a quartz fixed-bed reactor under H_2O, CO_2, and H_2O/CO_2 atmospheres at 800–1000 °C. Sequential chemical extraction and microwave digestion were used to determine the modes of occurrence of Ca in chars. X-ray diffraction and scanning electron microscopy were used to analyze the ash composition and the morphology of minerals. The contents of Ca in chars were measured by atomic absorption spectroscopy. The results indicate that water-soluble form and HCl-soluble form Ca transforms mainly into gas phase during pyrolysis. The release ratio of Ca at 800 °C under different atmospheres is $H_2O/CO_2 > H_2O > CO_2$. The main reason is that minerals are more prone to sintering in CO_2 atmosphere. The interaction of H_2O and CO_2 can expand pores, which precipitate the minerals to the char surface and release into the gas phase. Increasing temperature induces the collapse of the pore structure which changed the release rule of Ca. The composition of the ash obtained from gasification at 1000 °C in CO_2, H_2O and H_2O/CO_2 are nearly same.

1. Introduction

Coal gasification is one of the effective ways to achieve clean and efficient utilization of coal [1,2]. H_2O is usually used as a gasifying agent in the actual industry, but char-H_2O and char-CO_2 reactions are occurring simultaneously in gasifier. The issue of coal gasification with H_2O and CO_2 has attracted wide attention, and so many studies have been focused on these [3–5]. Our previous work also done some research about coal gasification with H_2O and CO_2, and found that the reactivity of coal char gasification with H_2O/CO_2 mixtures was better than that with pure H_2O or CO_2 in specific conditions, due to the synergistic effect between H_2O and CO_2 [6], which Ca played a main catalytic role. The synergistic effect is obvious at low temperature, and disappears as the temperature increase.

Previous studies shown that Ca has catalytic effect on coal gasification [7,8], its concentration and dispersion are the factors affect the gasification rate [9]. But Ca also has certain disadvantages: slagging, corrosion and clogging of gasifier [10,11]. Many researchers have studied the release behavior of Ca during coal pyrolysis and char gasification. Quyn et al. [12] investigatived the release behavior of Ca during pyrolysis and gasification of Victoria brown coal, and they found that the release of Ca in the coal was mainly in the form of carboxylates, and Na was easier to release than Ca and Mg. Matsuoka et al. [13] investigatived the transformation of Ca in low rank coals during gasification, they found that most of Ca and Mg remain in the coal char and react to form a low melting point of ash, while Na and K were easily release during the gasification and its reaction with the minerals in the coal does not affect the characteristic of the coal char. There are also some studies on release behavior of alkali and alkaline earth metallic species (AAEMs) during coal pyrolysis and char gasification. Kosminski et al. [14] investigatived the release of Na in low-rank coal during gasification, found that Na retained in the coal produce Na_2CO_3 in both CO_2 and H_2O atmospheres at 850 °C, and the loss of Na was combine with chloride ions, the release of sodium and chloride from coal containing sodium chloride was disproportionate. Ma et al. [15] investigatived the transformation of AAEMs during the gasification at high temperature and found AAEMs generally converted to aluminosilicate at high temperature. The existing form of Ca in coal and char is different, in order to distinguish the different existing forms of AAEMs, Benson et al. [16] divided AAEMs into four forms: water-soluble form, ion-exchangeable form, HCl-soluble form, and stable form with the sequential chemical extraction method. Wei et al. [17] extracted alkali metal in Inner Mongolia lignite coal char from pyrolysis and gasification with this method, found that stable form of Na in coal char were

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Table. 1
Proximate and ultimate analyses of the coal sample.

Proximate analysis (wt%)			Ultimate analysis (wt%), daf				
M_{ad}	A_{ad}	V_{daf}	C	H	O*	N	S
12.8	3.1	29.0	79.2	3.9	16.0	0.6	0.3

[ad] air-dried basis, [daf] dry and ash free basis, *by difference

Table. 2
Chemical compositions of the coal ash.

Ash chemical composition(wt%)									
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	SO_3	K_2O	Na_2O	Others
34.7	4.7	5.7	29.2	11.5	0.2	11.0	0.2	2.1	0.8

mostly formed during pyrolysis, which were mainly in the form of aluminosilicate. K was mainly stable in coal, and HCl-soluble form of K increased during gasification process. Moreover, there were some researchers [18–21] studied release of AAEMs during the biomass gasification or coal and biomass co-gasification, also reached similar conclusions.

The investigation about release of Ca in pyrolysis and gasification has made some progress. However, there is less research on the release of Ca during gasification under CO_2, H_2O and H_2O/CO_2 atmospheres according to the author's best knowledge. Therefore, the aim of this work is to investigate the occurrence and release of Ca under different gasification agents, to better explain the catalytic effect of Ca on coal gasification and the mechanism of synergistic effect, and to prevent damage to gasifier equipments.

2. Experimental

2.1. Coal sample

A low rank bituminous coal, rich in Ca, from Yining County in Xinjiang, China was used in this study (abbreviated as YN). The proximate and ultimate analyses of YN were shown in Table 1. And the ash analyses of the coal were shown in Table 2.

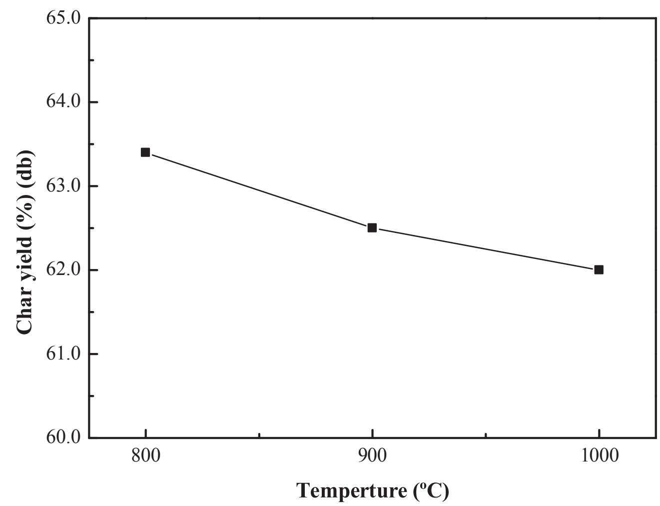

Fig. 2. Char yield of YN coal as a function of temperature.

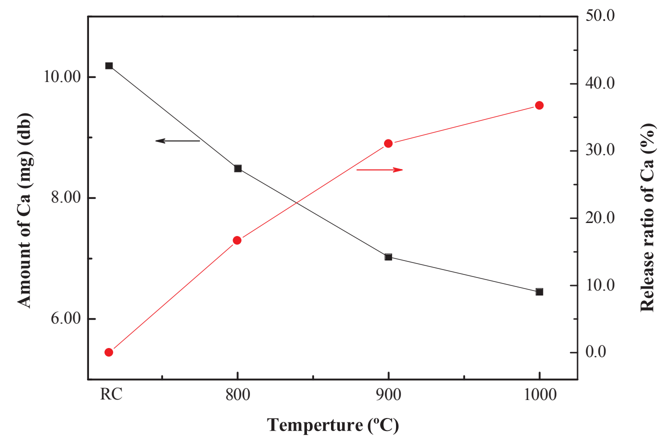

Fig. 3. Amount of Ca in per gram of raw coal and release ratio of Ca during pyrolysis process.

2.2. Char preparation

The coal was pulverized and sieved to obtain a particle size between 1.0–1.4 mm. Pyrolysis and gasification experiments were conducted in a designed quartz fixed-bed reactor which was shown in Fig. 1. The

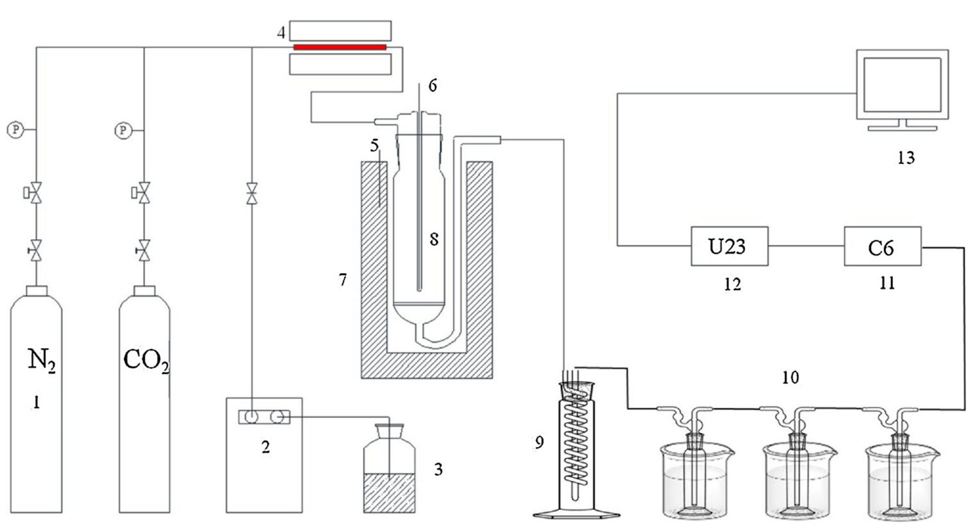

Fig. 1. Schematic diagram of the quartz fixed-bed reactor. (1 Cylinders; 2 Pump; 3 Deionized water; 4 Preheater; 5 Controller thermocouple; 6 Sample thermocouple; 7 Furnace; 8 Quartz tube reactor; 9 Graham condenser; 10 Gas-washing bottle; 11 Online gas analyzer; 12 Online gas analyzer; 13 Computer).