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Hydrogen production by Zhundong coal gasification in supercritical water

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ABSTRACT

The high sodium content of Zhundong coal restricts its application in direct combustion and supercritical water gasification is a promising clean and efficient coal conversion technology. To obtain the gasification and sodium distribution characteristics of Zhundong coal in supercritical water, experimental investigations were conducted in autoclaves and supercritical water fluidized bed reactors. The experimental results showed that as the concentration of Zhundong coal slurry decreased or the residence time increased, more sodium was released from the solid phase in autoclaves. Carbon gasification efficiency of more than 95% was obtained with the coal slurry of 30 wt%~40 wt% in the fluidized bed reactor. Less than 0.07% sodium was released from the reactor, in other words, most of the sodium remaining could be collected and caused no pollution and fouling problems for downstream process. Supercritical water fluidized bed reactor appeared to be a promising reactor for supercritical water gasification of Zhundong coal.

Introduction

Coal accounts for the main part of energy resources in China and will play a dominant role in the next decades [1]. Direct combustion of coal in the gas phase has caused serious environmental pollution and safety problems. Zhundong coalfield has huge exploitable reserves of 164 Gt [2,3], however, direct combustion of Zhundong coal is restricted for its high alkali metal content. Because alkali metal lowers the ash fusion temperature and leads to serious fouling and slagging on the boiler water wall quickly [4–8].

Efficient and clean Zhundong coal utilization method is urgently needed and advanced coal conversion methods such as pyrolysis or gasification were investigated [9,10]. Much attention was paid to the effect of sodium upon the gasification results and solid foundation was built for the clean conversion of Zhundong coal [5,11–13]. However traditional gasification and pyrolysis were conducted in gas phase, and sodium containing fly ash may exist in the raw gas. Therefore, special fly ash separation device is necessary to prevent slagging problems. Supercritical water gasification technology attracts people's attention due to the unique chemical and physical properties of supercritical water [14–17]. Supercritical water provides a homogenous and rapid reacting medium for clean coal conversion [18–26]. The main conversion product is hydrogen, which is believed to be one of the most promising fuel in this century [27,28]. Moreover, the solubility of inorganic matter in supercritical water is quite limited, which makes the separation of unwanted inorganic slats

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easier [29–33]. MODAR SCWO [29] reactor used reverse-flow vessel to recover the slats with a small steam at the bottom of the reactor. Vogel [34] investigated the separation of inorganic salt in the process of biomass gasification to recover the salts as fertilizer and also avoid catalyst poisoning. Tester [35] discussed several commercial approaches that have been developed and/or used to control salt precipitation and solids buildup in SCWO systems. Cao [36,37] conducted supercritical water gasification of black liquid, and investigated the alkali recovery from supercritical water fluidized bed reactor. Therefore, supercritical water gasification might be a good choice for coal with high sodium content.

The element transformations were examined by researchers. For example, the transformations of Pb, Mn, Ni, Cu, Zn, Cd and Cr during the supercritical water treatment of used tires were studied by Chen [38]. Nitrogen [39–41] and sulfur [42–44] transformation characteristics were investigated in the supercritical water environment from the point of view of pollution reduction. Su [3] conducted the gasification of Zhundong coal in supercritical water with a quartz tube reactor to omit the unwanted catalytic effect of the reactor wall and obtained a kinetic model for Zhundong coal gasification. However, the distribution characteristics of sodium were beyond the discussion. This manuscript investigated Zhundong coal gasification in supercritical water with autoclaves and fluidized bed reactor, and attention was paid to the sodium transformation characteristics.

Materials and experimental method

Coal sample

Table 1 showed the elemental analysis and the proximate analysis of Zhundong coal. It can be observed that the moisture content is as high as 17.1%, which also restricts the widespread application of Zhundong coal [15,45,46]. The coal ash analysis is seen in Table 2 and it can be seen that the sodium content is 3.40 wt% and potassium content is 1.05 wt %. The coal particle size used in experiments was in the range of 75–150 μm.

Table 2 – Coal ash analysis of Zhundong coal.

Content	Fe_2O_3	Al_2O_3	CaO	MgO	TiO_2	SiO_2
Fraction (wt%)	8.96	11.80	17.69	1.80	0.64	42.20
Content	SO_3	K_2O	Na_2O	MnO_2	P_2O_5	
Fraction (wt%)	11.30	1.05	3.40	0.13	0.14	

Apparatus and experimental procedures

Supercritical water gasification reactions were conducted in high-through autoclaves for batch experiments and in fluidized bed reactor system for continuous experiments. The autoclave material is Hastelloy C276. The depth and the effective volume of the autoclave are 20 mm and 10 mL respectively. The designed temperature and pressure of are 750 °C and 30 MPa respectively. The average heating rate inside the reactor was about 70 °C/min. More details of the autoclave were noted in the reference [17].

The fluidized bed reactor has supercritical water as fluidizing agent. A distributor made of sintered metal with an average pore diameter of 50 μm is located in the bottom of the reactor. The sintered metal is provided by Northwest Institute for Nonferrous Metal Research. Water preheated to the desired temperature flows through the distributor to form a fluidization state [47,48]. Zhundong coal-water-slurry flows into the reactor above the distributor. The fluidized bed reactor is constructed of 316 stainless steel and the design temperature and pressure are 700 °C and 30 MPa respectively. The inner diameter of the reactor is 40 mm, and the height of the reactor is 1650 mm.

Analytical methods and data interpretation

The composition of the gaseous products was analyzed by gas chromatography (Agilent 7890A) with thermal conductivity detectors (TCDs) and high-purity argon was used as the carrier gas. The yield of gas was measured by wet gas flow meter. The determination of the sodium content in the aqueous or solid sample was conducted in inductively coupled plasma-atomic emission spectrometry (ICP-AES, IRIS Intrepid II, Thermo Scientific). Carbon gasification efficiency and hydrogen yield were selected to evaluate the gasification characteristics and defined as follows [17]:

CE (Carbon gasification Efficiency) = (total carbon in the gaseous products)/(total carbon in Zhundong coal) × 100(%)

Gas yield = (molar amount of a certain component of the gaseous products)/(mass of Zhundong coal) (mol/kg).

Results and discussion

Effect of concentration

High concentration means high handling capacity of Zhundong coal in reactors, however, high concentration of feedstock may be overloaded for a certain reactor. The effects of concentration upon Zhundong coal gasification results were investigated in autoclaves as seen in Fig. 1. When the concentration of Zhundong coal was 5 wt%, the main gas fraction

Table 1 – Element and proximate analysis of Zhundong coal.

Elemental analysis (wt %)					Proximate analysis (wt %)				Qb,ad (MJ/kg)
C	H	S	N	O[a]	M	A	V	FC	
56.99	2.4	0.47	0.46	12.62	17.1	9.96	23.91	49.03	20.46

[a] By difference.

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