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Kinetics study for sodium transformation in supercritical water gasification of Zhundong coal

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ABSTRACT

Zhundong coal (ZDC) has attracted much attention due to its high alkali metal content which can lead to a series of problems such as furnace slagging and ash fouling. Supercritical water gasification (SCWG) become a better choice for ZDC coal utilization because of its unique chemical and physical properties. The transformation mechanism of alkali metals during SCWG process was different from conventional ways of coal utilization. Systematic research about it could hardly be found. In this study, ZDC was used to explore sodium transformation mechanism and kinetics during supercritical water gasification under typical conditions. We got four kinds of sodium including the water-soluble fraction (L1), the carboxylic matrix-associated fraction (L2), the macromolecular organic group-associated fraction (L3), and the inorganic silicate mineral fraction (L4) through sequential extraction method after SCWG. A reaction pathway of sodium transformation in supercritical water gasification was proposed. A quantitative kinetic model for describing sodium transformation mechanism was developed. Finally, it was found that, L1 played an important role in catalytic process and mineral in coal weaken the catalytic process by combining with L1. L2 and L3 served as the two important intermediate products in the coal gasification, which explained the catalytic mechanism of sodium. L3 showed better reactivity. Sodium finally tended to deposit in the form of $NaSiAlO_4$ (L4) which was stable and environmentally friendly. All of these could provide basis for high-efficiency utilization of ZDC and the design of a reactor.

Introduction

A coalfield with a predicted reserve of more than 390 billion tons of high-quality coal was found in Xinjiang Uygur Autonomous Region of China [1–4]. Due to the unique coal-forming environment and geological features, coal explored from that coalfield is characterized by its low rank, inflammability, ease of burnout, medium/high water content, low ash content, high volatile content, moderate heat value, high alkali-metal content. All these characteristics result in problems of fouling, slagging and corrosion of the heat exchange surface and boiler wall during its direct combustion in boilers in power plants [5–8]. These problems not only reduce the heat transfer efficiency of the heat

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exchange surface but also affect the operational safety and life of boilers [9].

The effect of alkali metal on the conventional utilization of ZDC had been investigated by many researchers. Most of them paid attention to the effect of alkali metals on the solid production. Lin [10] investigated the initial deposition feature during high-temperature pressurized pyrolysis of a typical ZDC. The transformation of potassium, sodium, calcium and magnesium with the increasing of pressure and temperature was obtained, and the compounds of the outlet were analyzed. Zhang [11–13] investigated sodium transformation of ZDC, and found that the coal ash was located in a high melting temperature zone, which would help to avoid agglomeration and defluidization phenomena. Song [5] investigated the influence of alkali and alkaline earth metal on slagging and fouling of Zhundong coal at different air equivalence ratios in circulating fluidized bed. All of these research were conducted in either the oxidizing atmosphere or high temperature reach up to 1000 °C due to the low reactivity of reaction media, which would easily lead to the volatilization of alkali metal and arise slagging of flue. So new technologies should be developed for a clean and efficient utilization method of ZDC.

SCWG has become one of the most potential ways to make use of many different feedstock [14,15], especially for dealing with coal of a special type such as high-sulphur coal, high-ash coal, high-alkali metal coal. Because of the unique chemical and physical properties of supercritical water [16,17], coal can be gasified into hydrogen-rich mixed gas with high efficiency at an experiment temperature lower than 750°C [18–20], which contributed to the immobilization of alkali metal into solid residue at the bottom of reactor and avoid influencing the downstream process. Meanwhile, alkali metal showed good catalytic effect in many gasification processes [21]. Alkali metal compounds were chosen as the catalysts in most SCWG process, even in the investigation of the supercritical water gasification mechanism of some intermediate products [22–24]. As a result, SCWG of ZDC could not only prevent the slagging problem, but also make use of the catalytic effect of alkali metal.

Lots of research had been done on alkali metal catalytic gasification in supercritical water. Ge [25] explored complete gasification of coal in supercritical water with alkaline catalysts such as NaOH, Na_2CO_3, KOH, K_2CO_3 and $Ca(OH)_2$, and found that alkaline catalysts influence the surface of the char. Cao [26,27] conducted SCWG of wheat straw black liquor in a batch reactor, and tried to recycle the alkali metal by the way of regulating the fluid temperature. Chen [28] investigated the transformation of potassium and sodium in supercritical water oxidation gasification. Hydrogen peroxide was used as oxidizing agent. However, most research just paid attention to the catalytic effect of different alkali metal compounds, and the additional content of them was almost empirical value. Little research had been conducted to systematically introduce the transformation mechanism, kinetic process and catalytic mechanism of alkali metal in supercritical water. So it is necessary to conduct an investigation to reveal these problems, which will help to instruct the design of a reactor for clean and efficient utilization of ZDC.

The present study was focused on the transformation characteristics of sodium in ZDC. Chemical sequential extraction method [29] was used to separate sodium in different occurrences, and their contents were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES). We examined the effect of temperature and residence time on gasification efficiency and sodium distribution, then a reaction pathway of sodium transformation in supercritical water gasification of ZDC was proposed accordingly and a quantitative kinetics model to describe sodium transformation mechanism was also developed. By calculating and analyzing the kinetic parameters, we found out the dominant reactions in the process influenced the transformation of sodium mostly and the catalytic mechanism of sodium. The role of four kinds of sodium played in the gasification process was also presented. In terms of the conclusions we obtained, some instructions were given to optimize the use of alkali metal catalyst and improve the design of the reactor.

Experiment section

Coal sample

The coal employed in this investigation was obtained from Wucaiwan, Xinjiang Uygur Autonomous Region of China. The coal was broken and ground to obtain particles smaller than 0.2 mm. The elemental analysis and industrial analysis of lignite were shown in Table 1. Both of them were air dried basis.

Apparatus and experimental procedures

Supercritical water gasification of ZDC was conducted in an autoclave which was manufactured with Inconel 625, and the design limitation of the autoclave is 750°C and 35 MPa with chamber volume of 567 ml. The schematic diagram of the experimental system was illustrated in Fig. 1. The system mainly consisted of an argon bottle, an autoclave, an electric furnace, a temperature controller, data acquisition, a gas flowmeter and some needle valves. Meanwhile, heat preservation cotton was also used in the top of the autoclave to make temperature increasing at a high rate.

Coal (0.6122 g), deionized water (30 g) and potassium carbonate (0.0306 g) were put in the bottom of the autoclave. After packaging the autoclave, high-purity argon was used twice to make sure that air in the autoclave was completely purged. The autoclave was then heated to the operation condition (650°C–750°C,25 MPa), and kept from 1 min to 30 min. After every single experiment, the autoclave was cooled down to

Table 1 – Elemental and industrial analysis data of ZDC.

Ultimate analysis (wt%)				Industrial analysis (wt%)				HHV (MJ/kg)
C	H	N	S	M_{ad}	A_{ad}	V_{ad}	FC_{ad}	
68.45	4.68	0.93	1.05	6.63	10.58	24.42	58.37	21.56

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