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Experimental study on Zhundong coal gasification in supercritical water with a quartz reactor: Reaction kinetics and pathway

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ABSTRACT

China has fairly rich reserves of Zhundong coal but the utilization of it is limited due to the high alkali metal content which can cause great troubles in a traditional boiler. Supercritical water gasification is a novel thermochemical conversion technique to convert wet feedstock into hydrogen-rich gas product with near zero emission. Reaction kinetics of Zhundong coal gasification in supercritical water was investigated with a quartz reactor in this study. The effects of reaction temperature (650–850 °C) and coal concentration (5–15 wt%) on the gasification behavior were investigated in a wide range of residence time (0–30 min). Experimental results showed that the experimental method employed presents good performance in revealing the continuous change of gas formation with residence time. Carbon gasification efficiency can reach nearly 100% at 850 °C with the residence time of 15 min and the mole fraction of hydrogen was more than 50%. A simplified gasification reaction pathway was also claimed at the end. The results show a promising prospect of Zhundong coal conversion in supercritical water and provide some useful information for reaction kinetics model establishment of coal gasification in supercritical water.

Introduction

China's energy production and consumption will continue to be dominated by coal for a long time in the future. Zhundong coal explored in recent years in northwest China is a great energy resource, which has exploitable reserves of 164 Gt [1]. However, serious problems were encountered when it was burned in a traditional boiler because of its high moisture content and high alkali metal content [2]. In a conventional coal-fired boiler with Zhundong coal as fuel, fouling and slagging occur easily due to the high alkali metal (Na, K) content. The high alkali metal content lowers the ash fusion temperature, therefore ash melts easily in the burning of coal and slags again on the boiler water wall which quickly leads to serious fouling and slagging. This causes heat transfer deterioration of the boiler heating surface, which may lead to serious safety accident. In addition to that, sulfur and nitrogen

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oxides and carbon dioxide emitted during the coal combustion in a traditional boiler pollute the environment seriously [3]. Supercritical water gasification (SCWG) provides a promising way to convert biomass and coal into hydrogen-rich gas product with near zero emission. The wet feedstock with high moisture content (even more than 30 wt%) can be directly processed in supercritical water (SCW) without the energy-intensive drying step, which can save much energy [4]. The relatively low reaction temperature (below 850 °C) in SCW is typically below the ash fusion temperature hence ash after reaction will be easily discharged in the form of solid residue. The fouling and slagging problems can be avoided consequently. The unique properties of supercritical water, such as high diffusion rate, low viscosity and good miscibility with gases, hydrocarbons and aromatic compounds make it an excellent reaction media for the wet feedstock conversion [5,6].

Since Modell [7] firstly reported that solid or liquid organic material was gasified in SCW and high heating value gas was produced, more and more attention has been paid to SCWG in recent years for its high efficient and clean style. Deshpande et al. [8] early in 1984 developed an autoclave apparatus for the conversion of lignite and bituminous coal and found that large quantity of char was formed. Thereafter, Various coal, raw biomass or wastes were used as the materials for SCWG [9–13]. In general, the experimental devices employed above are batch-type and some specific gasification characteristics and results were obtained. Concerning about the drawbacks of batch-type reactor for industrialization application of this technology, continuous flow reactor for SCWG was developed by researchers around the world. Vostrikov et al. [14,15] studied conversion of single coal particle of diameter 1–5 mm in a supercritical H_2O/O_2 fluid with a semibatch reactor at a pressure of 30 MPa and a temperature of 673–1023 K. Department of Energy in the USA [16] also performed related research of coal conversion in supercritical water. In China, studies on coal gasification in SCW with continuous flow reactor were also reported [17–19]. Zhang et al. [18] from the Institute of Coal Chemistry in Shanxi established an experimental apparatus operating with continuous feeding of coal water slurry within the temperature 550–650 °C, and pressure 20–30 MPa and found that addition of H_2O_2 can improve the carbon gasification efficiency and hydrogen yield. Based on the conception of supercritical water fluidized bed reactor proposed by Matsumura and Minowa [20], a fluidized bed reactor was successfully developed by SKLMF in 2008 [21,22], which showed good performance in improving heat and mass transfer and high hydrogen output was obtained. Yamaguchi et al. [23] employed an immersion technique with a quartz reactor to study the effect of various operating parameters on Victorian brown coal gasification in supercritical water and found that coal was not converted completely and the reaction was far from equilibrium state.

The quartz reactor, proposed early by Potic et al. [24], provides a convenient and low-cost way to search an optimal operation condition and to investigate the gasification reaction kinetics in SCWG. On one hand, the experimental apparatus mentioned above are made of alloy material thus experiments parameter range are limited due to the extreme operating condition. However, the quartz reactor can withstand an operating condition with the pressure up to 45 MPa and the temperature up to 1000 °C according to our experimental test. Therefore the condition for complete gasification can be detected, which may be a good guide for us to improve the performance of existing reactor. On the other hand, as we know, chemical reaction kinetics involved in a specific chemical process is essential for the design of reactors. Therefore, more precise experimental data may contribute to studies on reaction kinetic model of coal gasification in SCW. However, for alloy material reactor, the heating rate is relatively slow and it has an obvious effect on the gasification efficiency and gas yield [25], thus the accurate kinetics data at a constant temperature are difficult to be obtained. For continuous flow or the fluidized reactor, the reaction temperature distribution are not uniform in the entire reactor, according to researches [19,21] thus it could not grasp the gasification characteristics at a specific constant reaction temperature. Unlike the autoclave reactor, quartz reactor ensures rapid heating and cooling and an environment free of catalytic wall [23]. Gasification in a quartz reactor can be thought to proceed with a constant temperature in the entire residence time, thus eliminating effects of the reactor wall and temperature rising process. Therefore it can be employed to characterize change trend of gas formation with residence time at a given temperature more precisely. The data obtained will be meaningful for chemical kinetics model establishment of SCWG, which can be very instructional for reactor design and optimization.

Coal gasification in SCW is a very complicated process with a large amount of physical and chemical phenomena involved. The exhaustive reaction pathway remains not very clear until now. The reaction kinetics study with a quartz reactor also helps a lot in accessing knowledge of coal gasification pathway in SCW. Therefore, the method utilizing quartz capillary as reactor was employed to investigate coal gasification in SCW in this study.

Materials and experimental method

Coal sample

The elemental and proximate analysis results of Zhundong coal are shown in Table 1. The coal particle size was in the range from 75 to 150 μm. Here, N and S are thought to deposit in the form of inorganic salts [26] and the effect of alkali

Table 1 – Elemental and proximate analysis of Zhundong coal (as received basis).

Elemental analysis (wt%)					Proximate analysis (wt%)			
C	H	N	S	O[a]	M	A	V	FC
56.99	2.40	0.47	0.46	12.62	17.1	9.96	23.91	49.03

[a] By difference.