Hydrogen production by non-catalytic partial oxidation of coal in supercritical water: The study on reaction kinetics

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ABSTRACT

Supercritical water gasification (SCWG) has attracted great attention for efficient and clean coal conversion recently. A novel kinetic model of non-catalytic partial oxidation of coal in supercritical water (SCW) that describes formation and consumption of gas products (H_2, CO, CH_4 and CO_2) is reported in this paper. The model comprises 7 reactions, and the reaction rate constants are obtained by fitting the experimental data. Activation energy analysis indicates that steam reforming of fixed carbon (FC) is the rate-determining step for the complete gasification of coal. Once CH_4 is produced by pyrolysis of coal, steam reforming of CH_4 will be the rate-determining step for directional hydrogen production.

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Introduction

Coal is both an energy resource and organic chemical feedstock [1]. China is the largest user and producer of coal [2], and coal will continue to be the most important component of energy production in China [3]. However, the adverse effect of coal utilization on environment limits the growth in coal consumption [4–7], which stimulates new research for efficient and clean way of coal utilization.

SCW attracts great attention as a medium for organic chemistry because of its environmentally benign chemical processes [8], and it has special physical and chemical properties. The dielectric constant is very lower, and the persistence and number of hydrogen bonds are both diminished. As a result, SCW has complete miscibility with many organic compounds and gases. Therefore, chemical reaction could proceed in a single fluid phase, which reduces the mass transfer limitation of reaction [8]. SCWG of coal is a recently developed technology for effective and clean coal conversion [9–11]. The formation of SO_x and NO_x, could be hindered at the relatively low reaction temperature, and emissions of fine ashes could be excluded because of closeness of system [4,7]. In addition, a high-pressure separator could be used to separate CO_2 from the reaction system easily without employing specialized and expensive equipment [9].

Considerable research has been focused on SCWG of coal. SCWG of coal was firstly conducted by Modell in MIT in 1978, and only 8% of bituminous coal was converted to gas due to the temperature limitation [12]. Cheng et al. [13] studied

pyrolysis of Xiaolongtan lignite in SCW with an autoclave, and found that about 68% of carbon that was not gasified centralized as residual char at 550 °C. General Atomics supported by DOE conducted supercritical water partial oxidation of 40 wt% high-sulfur coal to generate H_2 in a small vessel at 620 °C, and obtained poor gasification of coal because of insufficient temperature and solids residence time [14—16]. Yamaguchi et al. [17] studied the non-catalytic SCWG of Victorian brown coal in quartz tubes. Coal was not completely gasified due to the residue char in each reactor after the SCWG reaction. Su et al. [18] investigated SCWG of Zhundong coal in quartz reactors, and found that coal was almost completely gasified at 850 °C after 15 min. In my previous study [19], non-catalytic SCWG of coal in quartz reactors was conducted. Lignite and bituminous coal were completely gasified at 950 °C and 980 °C separately as ER (Equivalent Ratio of oxidant. There is no oxidant added as ER equals 0; Coal is completely oxidized as ER equals 1) equaled 0.1 and 0.2 respectively. Wang et al. [20] conducted catalytic gasification of low rank coals in SCW in an autoclave at 690 °C and 30 MPa, and found that $Ca(OH)_2$ had a strong effect on the decomposition of coal and catalyzed the gasification of char, resulting in the increasing H_2 yield. Lin et al. [21] realized more than 90% of carbon conversion in an autoclave at 973 K by using 0.1 g of coal, 0.05 g of NaOH and 0.6 g of $Ca(OH)_2$ within 30 min. In my previous study on catalytic SCWG of coal with alkaline catalysts in a micro bath reactor [22], coal was completely gasified with the weight ratio of K_2CO_3 to coal equaling to 1 at 700 °C and 25 MPa. Zhang et al. [23] found that both KOH and CaO catalyzed gasification of coal, and the use of partial oxidation could rapidly heat the gasification medium in a flow-type reaction system, resulting in less char formation and more H_2 yield. Li et al. [24] realized the continuous and stable gasification of 16 wt% of coal in a continuous flow system, and found that K_2CO_3 had better catalytic effect that Raney-Ni. Jin et al. [25] conducted SCWG of Zhundong coal in a fluidized bed reactor, and found that 40 wt% of coal was almost gasified completely at the reaction temperature range of 620—660 °C.

The research above mainly shows the influences of main operating parameters on the gasification characteristics, and then the development of kinetic study is asked for understanding the reaction mechanism and searching for the reaction rate-determining step. Vostrikov et al. [5] investigated the kinetics of coal particle pack conversion in SCW at 500—750 °C, 30 MPa and 60—720 s. Dependences of conversion rate on temperature, reaction time and degree of coal conversion were investigated with an assumption of the Arrhenius dependence and the first-order reaction, and activation energy of conversion is 103 kJ/mol. Wang et al. [26] investigated coal oxidation kinetics in SCW with a bench-scale semicontinuous installation, and found that coal oxidation in SCW was a pseudo-first-order process and the activation energy is 154.65 kJ/mol. Su et al. [18] investigated SCWG kinetics of Zhundong coal with quartz reactors. A kinetic model of CE (carbon gasification efficiency = amount of carbon in gas products/amount of carbon in coal × 100%) was established by considering the effects of both temperature and coal concentration, and it could be used to predict the gasification of Zhundong coal in SCW. Jin et al. [27] investigated the kinetic

model of char gasification in SCW by using homogeneous, non-reacted core and random pore models, and found that random pore model was fittest and the activation energy is 125.43 kJ/mol.

The kinetics study above was concentrated on total conversion of coal, and did not analyze the production and consumption paths of gases. In fact, the gas products especially H_2 are of the most concern for SCWG of coal, and the reaction routes are little known recently. Resende et al. [28] reported the first quantitative kinetic model for SCWG of lignin and cellulose that describes the formation and consumption of gaseous species. The model used a lumping form to handle numerous intermediate compounds. Other researchers also studied the kinetic model of xylose [29], algal phospholipid [30], algal [31], lignin [32], glycerol [33], formaldehyde [34] and so on by using the similar method. However, the models above are not suitable for SCWG of coal since the different structure and composition of coal leading to different reaction pathway. Jin et al. [35] established a SCWG kinetic model of coal mainly focusing on the gaseous products (H_2, CO, CH_4 and CO_2), and seven reactions were the main reaction pathways, which showed that steam reforming reaction produced the most H_2. The refractory liquid products was thought to be difficult to be gasified once formed, and gasification of them was the rate-determining step for complete gasification, However, in previous literature [13,17,19], residual char is consistently thought to be the main factor that impedes complete gasification of coal according experimental results.

In this paper, the kinetics study that describes the formation and consumption of gas products is carried out to understand the mechanism of non-catalytic partial oxidation of coal in SCW. Residual char is thought to be the refractory product. The reaction rate constants are obtained by fitting the experimental data by using the least squares method. The formation and consumption pathway and rate of gaseous species are also analyzed.

Kinetic model

A simplified reaction pathway is shown in Fig. 1 (ash is not taken into consideration because it doesn't refer to the gasification reaction we care about). The model is based on reaction routes in the previous literature on SCWG [13,17—19,22,24,25,35,36]. It concentrates on the reactions involving gaseous species (H_2, CO, CH_4 and CO_2). When coal are added into SCW, volatiles (CH_4, CO_2 et al.) and liquid intermediates are produced as the pyrolysis, hydrolysis, liquefaction and extraction reaction of coal proceeds, leaving fixed carbon. In previous literature [13], the amount of liquid intermediates decreases with the increasing temperature, and is less than 10% of solid residue at 550 °C. Herein, the liquid intermediates will be much less when oxidant is added at a higher temperature range of 600—800 °C. Therefore, the liquid intermediates and their liquid reactions are negligible in order to simplify the reaction model. The steam reforming reaction and oxidation of fixed carbon would produce H_2, CO, CH_4 and H_2O, leaving char. The homogeneous reaction model is assumed for the solid reaction. The model assumes that the