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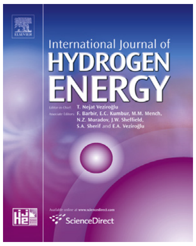

Hydrogen production by non-catalytic partial oxidation of coal in supercritical water: Explore the way to complete gasification of lignite and bituminous coal

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ABSTRACT

Supercritical water gasification (SCWG) of coal is a promising technology for clean coal utilization. In this paper, hydrogen production by non-catalytic partial oxidation of coal was systematically investigated in supercritical water (SCW) with quartz batch reactors for the first time. The influences of the main operating parameters including residence time, temperature, oxidant equivalent ratio (ER) and feed concentration on the gasification characteristics of coal were investigated. The experimental results showed that H_2 yield and carbon gasification efficiency (CE) increased with increasing temperature and decreasing feed concentration. CE increased with increasing ER, and H_2 yield peaked when ER equaled 0.1. CE increased quickly within 1 min and then tended to be stable between 2 and 3 min. In particular, complete gasification of lignite was obtained at 950 °C when ER equaled 0.1, as for bituminous coal, at a higher temperature of 980 °C when ER equaled 0.2.

1. Introduction

Coal is important as an energy resource and organic chemical feedstock in the 21st century [1]. China is the world's largest producer and user of coal, and coal supplies 75% of energy demand and 95% of thermal electric power generation in China [2]. However, the negative effect of coal utilization on environment and related expense for maintaining environmental safety restrain the growth in coal consumption [3–6], and this stimulates the research for clean and efficient methods of coal conversion.

SCW ($T > 374$ °C and $P > 22.1$ MPa) is attracting increasing attention as a medium for organic chemistry for its more "green" or environmentally benign chemical processes. The properties of SCW are quite different from those of ambient liquid water. The dielectric constant is much lower, and the number and persistence of hydrogen bonds are both diminished. As a result, SCW behaves like organic solvents so that many organic compounds and gases have complete miscibility with SCW. Therefore, SCW provides a single fluid phase for chemical reaction, which reduces the mass transfer limitation of reaction [7]. The solvent power and diffusivity of SCW can be also easily controlled by operation conditions, so it is easy to separate gases from SCW by simply reducing the reaction temperature and pressure [8].

Gasification or oxidation of coal in SCW is a newly developed technology for clean and effective conversion of coal. It is reported that energy efficiency of power generation from

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oxidation of coal in SCW is higher than those of conventional coal power plants at the same steam conditions [9]. Moreover, the relatively low temperature of SCWG of coal impedes formation of NO_x and SO_x, and closeness of the system excludes emissions of fine ashes [3,6]. Cheng et al. [8] studied conversion of Xiaolongtan lignite in sub- and supercritical water with an autoclave in the temperature range of 350–550 °C, and found that the key factor affecting the product distribution was reaction temperature, and about 68% of carbon in the form of residue char was not gasified under 550 °C. Li et al. [10] conducted SCWG of coal with a continuous flow system. The incomplete gasification was obtained and the increase of coal concentration led to a decrease in CE and H_2 yield, and the similar case was also found by Jin et al. [11] and Zhang et al. [12]. Yamaguchi et al. [13] investigated the non-catalytic gasification characteristics of Victorian brown coal in SCW by using a novel immersion technique with quartz reactors, and found that the SCWG of coal was not complete due to the residual coal char observed in all the reactors after the SCWG reactions. Incomplete gasification of coal hinders the commercial development of SCWG, so an important job is to explore the way to complete gasification of coal at present.

Coal char contains plenty of phenolic structures, which are difficult to be gasified and are regarded as the ‘last hurdle’ to get over for complete gasification [10,12,14]. Therefore, once the feedstock is partially converted into char, it is hardly gasified, resulting in low product gas yield and gasification efficiency [13]. To decompose the aromatic compounds and realize the complete gasification, radical reaction led by radical derivatives such as hydrogen peroxide will help [15]. In addition, oxidant provides an in situ heat resource to heat the gasification medium rapidly through the sensitive temperature range, resulting in less tar and char formation [16,17], because tar-forming and condensation reactions are known to be favored by long residence time at lower temperature [18]. Some researches on partial oxidation in SCW for various biomass and model compounds were carried out [19–23], and it was reported that oxidant could improve the gasification efficiency and decrease the production of char.

A novel high-throughput screening technique proposed by Potic et al. [24] was used to conduct SCWG reaction with the quartz reactors. Unlike the autoclave method, the technique enables rapid heating and cooling. Furthermore, the method allows SCWG reactions to be conducted in an environment free of catalytic surfaces. Hence, it is possible to precisely characterize the SCWG reaction. In this work, to realize the complete gasification of coal, non-catalytic partial oxidation of coal in SCW with quartz reactors was conducted for the first time. The effects of various operating parameters on gasification characteristics of coal were investigated, and the related reaction mechanism was also clarified.

Table 2 – Predicted inner pressures at each temperature according to thermodynamic property of pure water.

Temperature (°C)	600	700	800	900	950	980
Pressure (MPa)	20.5	23.6	26.7	29.7	31.2	32.0

2. Experimental method

2.1. Materials

Yimin lignite and Shenmu bituminous coal (air-dried basis) were used as feedstock, and the elemental and proximate analysis is listed in Table 1. Particle sizes of coal were in the range of 100–150 μm. Hydrogen peroxide solution (30 wt%), in which the molecule of H_2O_2 was used as oxidant, was purchased from the Tianjin Chemistry Factory.

2.2. Experimental apparatus and procedure

200 mm length of quartz capillaries with inner and outer diameters of 1.5 and 3 mm respectively were employed for the experiment. One end of the quartz capillary was sealed, and the other open.

A certain amount of coal, according to its concentration, was measured by using a precision electronic balance and loaded into a quartz capillary. Then the 30 wt% hydrogen peroxide solution was diluted to the desired concentration according to required ER assuming that a molecule of H_2O_2 provided half a molecule of O_2 [25], and 20 mg of the solution was injected into the quartz capillary by using a 50 μL micro syringe (If ER equaled 0, only ultrapure water was added into the quartz capillary). The reaction pressure could be calculated according to thermodynamic property of pure water. The predicted inner pressures at each temperature are listed in Table 2. After that, the air inside the capillary was replaced by argon in a chamber coupled with a vacuum pump. At last, the open end of quartz capillary was flame-sealed by oxyhydrogen flame.

The sealed quartz reactor was heated by using an electric furnace. The temperature of furnace was measured by a K

Table 1 – Elemental and proximate analysis of the Yimin lignite and Shenmu bituminous coal.

Coal	Elemental analysis[a] (wt%)					Proximate analysis[b] (wt%)			
	C	H	N	S	O[c]	Moisture	Ash	Volatiles	Fixed carbon
Lignite	61.42	4.93	0.86	0.29	32.50	18.42	15.64	32.21	33.73
Bituminous coal	82.33	4.76	1.14	0.74	11.02	10.97	2.48	31.38	55.17

a Dry and ash-free basis (daf).
b Air-dried basis (ad).
c By difference.