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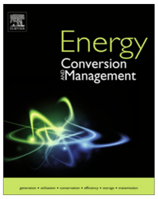

Experimental study on hydrogen production by lignite gasification in supercritical water fluidized bed reactor using external recycle of liquid residual

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ABSTRACT

The technology of supercritical water gasification provides a novel way to convert high-moisture lignite to hydrogen-rich products directly. According to the energy analysis of the whole system for supercritical water gasification, the energy recovery of liquid residual played a key role in the energy efficiency improvement. Moreover, previous research findings showed that some chemical compounds such as phenols and formic acid contained in liquid residual can be recycled to increase the yield of hydrogen. Therefore, an external recycle of liquid residual was used in the supercritical water fluidized bed system to recover not only the heat energy but also the chemical energy by re-gasification of the liquid residual. Besides, the separation of gaseous products from the system enhanced the gasification process. Hydrogen production experiments were operated in this system and the influence of operating temperature 470–550 °C, pressure 23–27 MPa, concentration 3–35 wt% and cycling flow rate 0–70 g/min were studied. The experimental results showed that hydrogen yield and carbon gasification efficiency reached 32 mol/kg and 82%, respectively, at 530 °C.

1. Introduction

Supercritical water (SCW) is water above the critical point (374 °C, 22.1 MPa) and has unique chemical/physical properties compared with that at ambient conditions. Under the supercritical condition, water becomes a nonpolar solvent because of the decreased hydrogen bond and the low dielectric constant, which improves the solubility of organic compounds and gases [1]. The high diffusivity and low viscosity [2] make it easy to diffuse in SCW for solute molecules. The high reactivity of SCW leads to the fast decomposition of polymeric structure and a high hydrogen yield in the gasification process [3].

SCW is used as an excellent medium for lignite gasification for the following reasons. (1) SCW can gasify lignite at relatively low temperature [4]. (2) The gaseous products are clean without the emission of gas containing N or S [5]. (3) The energy-consuming drying process can be avoided and supercritical water gasification (SCWG) is therefore considered an efficient way for the utilization of high-moisture lignite [6]. (4) CO_2 can be easily separated using a high-pressure separator and captured for the utilization of downstream [5]. (5) The properties of water such as ion product and dissociation constant can be adjust in wide range especially, so the free radical reaction or ionic reaction preferred reaction pathways can be adjusted [7].

The technology of SCWG has developed for more than thirty years since Modell [8] firstly proposed it and many attempts have been made to further enhance the gasification efficiency. Deshpande et al. [9] designed a high-pressure reactor for lignite and bituminous coal gasification in SCW, and coal was injected into an autoclave containing preheated supercritical water. Boukis et al. [10] established an experimental device called "VERENA", in which the feedstock was heated moderately to critical temperature in the heat exchanger to avoid the precipitation of inorganic salts, and brines and solids can be separated through a third output from the lowest part of the reactor to reduce fouling of the heat exchanger. D'Jesús et al. [11] established a down-flow reactor to not only improve the gasification efficiency but also eliminate the plugging problems. Ge et al. [12] conducted experiments to investigate the gasification characteristics using a quartz tube reactor, where the catalytic effect caused by reactor inner wall can be eliminated, and the complete gasification of lignite was obtained at 950 °C. Besides, supercritical water fluidized bed reactor was established and solved the blocking problems in traditional pipe flow continuous system to ensure continuous and stable

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gasification, in which Hongliulin coal was completely gasified with the H_2 yield of 77.5 mol/kg [13].

In the existing supercritical water gasification reactors, the high-efficiency conversion of coal has been achieved, but one of the main reasons for incomplete gasification is the production of phenolic compounds [14]. DiLeo et al. [15] at the University of Michigan studied the SCWG of phenol, where phenol was essentially completely converted to gaseous products mainly including H_2 and CO_2 at 600 °C when using three Ni wires as the catalyst. No char was formed and the yields of liquid-phase products were low. In SCWG process, macromolecular structures are produced by the cross-linking reactions of hydrolysis products [16], and residues or solid particles are formed during the repolymerization process. In the environment of water-phenol mixture, however, solid particles formed are almost completely diffused. So it benefits the gasification with phenol in liquid residual re-injected into the reactor. Okuda et al. [17] carried out lignin conversion experiments in SCW-phenol mixture at 400 °C, and the rapid depolymerization of lignin was achieved with no char formed, where the average molecular weights before and after the reaction were 2100 and 660, respectively, with the residence time of 1 h. Saisu et al. [18] conducted experiments to study the conversion of lignin in SCW-phenol mixture at 400 °C with an autoclave. The experimental results indicated that the yield of tetrahydrofuran-insoluble products as well as the molecular weight of tetrahydrofuran-soluble products decreased compared with those without phenol. In another word, phenol prevented heavier compounds formation and promoted reaction toward the lower molecules. In SCW, phenol might react with reactive sites of the large fragments, which suppressed the cross-linking reactions among reactive sites and greatly enhanced the decomposition of lignin to substances with lower molecular weights. Aida et al. [19] studied coal conversion in phenol-SCW mixture at 400 °C with Taiheiyo coal as the material, and the synergistic effect between SCW and phenol was found. The extraction rate with SCW-phenol was as high as 70% at the water/phenol rate of 4.5:0.5, while that with pure SCW was less than 60%. It was found that phenol seemed to act as a capping agent for reactive hydrolysis products to suppress the cross-linking reactions that might form macromolecules.

In addition, studies on the gasification of coal in SCW-HCOOH mixture have also been reported. Adschiri et al. [20] conducted experiments to study the conversion of Taiheiyo coal in supercritical toluene, SCW and SCW-HCOOH mixture, respectively, in a semi-batch reactor. It was declared that the coal conversion efficiency in SCW-HCOOH mixture was the highest which reached 80% at the condition of 380 °C, 35 MPa, because HCOOH played a role of hydrogenation, which greatly promoted the conversion of coal. Sato et al. [21] examined the upgrading of bitumen in HCOOH-SCW and the decomposition of bitumen in HCOOH-SCW provided higher asphaltene conversion efficiency and lower coke yield than that in pure SCW. HCOOH in SCW can enhance the bitumen conversion toward compounds with lower molecular weight probably due to its active species production in SCW.

According to the energy analysis of the reaction system for coal gasification, the recovery of the heat energy in liquid residual is believed to be effective in the energy efficiency improvement [22]. Besides, phenols and HCOOH are often found in the liquid residual for supercritical water gasification. Thus, based on the idea of chemical energy and heat energy recovery, a supercritical water fluidized bed system using external recycle of liquid residual was developed in this paper. This work is innovative because phenols and HCOOH in liquid residual were recovered and further converted to hydrogen-rich gas with the residual heat effectively recovered at the same time. Hydrogen production experiments by lignite gasification were conducted under different conditions in the system to obtain the optimized operating condition.

2. Experimental section

In this section, firstly, materials used in the experiments are given. Secondly, the experimental apparatus and its use are discussed. Thirdly, analysis methods for gaseous products and the feedstock are introduced. Finally, related characterization parameters for the evaluation of gasification characteristics are defined.

2.1. Material

Yimin lignite from China was selected as the feedstock and its elemental and proximate analyses were listed in Table 1. Sodium carboxymethyl cellulose (1.5 wt%) was added to ensure the stability and uniformity of the coal slurry. K_2CO_3 (1 wt%) was added as the catalyst [23] to promote the steam reforming and water gas shift reaction [24].

2.2. Apparatus and experimental procedures

SCW fluidized bed system using external recycle of liquid residual is shown in Fig. 1. The system is primarily composed of feeding, reaction and liquid residual recovery these three subsystems. The reactor is made from AISI316 with diameter and length of 30 mm and 915 mm, respectively, and the designed maximum temperature and pressure are respectively 650 °C and 30 MPa. Quartz sand is used as heat transfer medium and to avoid particle agglomeration or coalesce during fluidization. In the experimental process, the average temperature of five thermocouples fixed on the centerline of the reactor is selected as the reaction temperature and the pressure is measured using a pressure transducer (PA23/8465, Keller). The detailed basic operation descriptions of the system can be found in previous Ref. [25].

The recycle loop of thermal energy and chemical energy using the external recycle of liquid residual is seen as red color in Fig. 1. It can be seen that the recycle loop is composed of high-pressure separator, filter, high-pressure circulating pump, flow meter, preheater, reactor and heat regenerator. At the bottom of the high-pressure separator, part of the high-temperature fluid is extracted using the high-pressure circulation pump, mixed with fresh water, and then flows into the preheater. The preheated fluid enters the reactor for gasification, and the liquid residual after reaction finally flows through the heat regenerator and to the high-pressure separator. In the conventional systems, the energy of the large flow of high-temperature residue liquid cannot be recovered efficiently in the heat regenerator, so a cooler is needed to cool the high-temperature fluid to protect downstream process equipment, resulting in the low energy efficiency. In the improved system, however, the residue liquid is injected back into the fluidized bed reactor, which both reduces the energy demand of the preheater and saves fresh preheated water, and finally improves the energy efficiency of the whole system. Besides, the mixed fluid entering the reactor contains some amount of phenols and HCOOH, which effectively promotes the gasification reaction as mentioned above. Furthermore, because the solubility of CO_2 is greater than that of H_2, more H_2 is extracted in the high-pressure separator as product, causing the gasification reaction to proceed in the direction of H_2 production.

2.3. Analysis methods

The analysis of gaseous products was conducted on a gas chromatography (Agilent 7890A) with thermal conductivity detectors (TCD), and high-purity Ar was used as carrier gas. A carbon-2000 capillary column purchased from LanZhou Institute of Chemical Physics in China was used, operating at 60 °C for 1.5 min, followed