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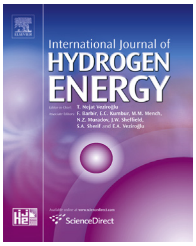

Hydrogen production by semicoke gasification with a supercritical water fluidized bed reactor

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ABSTRACT

Semicoke powders with particle size less than 6 mm are by-products during the pyrolysis of coal. Direct combustion of semicoke powders is difficult due to the low volatile content. Supercritical water gasification might provide an efficient conversion method for semicoke powders. In order to determine the optimum conditions of gasification of semicoke with the supercritical water fluidized bed reactor, the influences of the main operating parameters including temperature (540–660 °C), feedstock concentration (10–30 wt%), flow rate of preheated water (40–80 g/min) and alkali catalysts (K_2CO_3, KOH, Na_2CO_3 and NaOH) were systematically investigated in this study. The results showed that semicoke-water slurry of 30 wt% was continuously transported into the reactor and stably gasified without plugging problems. Hydrogen yield of 85.90 mol/kg was obtained with the hydrogen molar fraction of 61.02%. In particular, carbon gasification efficiency of more than 95% was obtained under the conditions of 660 °C, 60 g/min flow rate of preheated water and 10 wt% feedstock concentration with 5 wt% K_2CO_3.

Introduction

Semicoke industry has become a characteristic industry to link coal production and coal chemical industry in China in recent 20 years. Semicoke powders with particle size less than 6 mm account for about 10% of the total amount of semicoke. Early, a lot of semicoke powders were thrown into rivers and farmlands due to lack of market demand, causing water and fertile farmlands to be contaminated. At present, in consideration of the constraints of rising energy prices as well as national environmental protection policies, the majority of semicoke powders are incinerated as the fuel of boiler [1,2]. However, direct combustion of semicoke powders is difficult because of the low volatile content and the high ignition point [3]. Thus it is extremely important to explore a new way to use semicoke powders reasonably.

Supercritical water can dissolve organic compounds because of its special physical and chemical properties such as very low dielectric constant, and reduced number and durability of hydrogen bonds [4,5]. In addition, gases are also miscible in supercritical water, so supercritical water provides a single fluid phase for chemical reaction process as reaction medium, which has the advantages of achieving higher concentrations of typical reactants, and omits the interphase heat/mass transfer [5]. Furthermore, the solubility and the diffusion coefficients of supercritical water can be easily controlled by adjusting the reaction temperature and pressure. Therefore, gasification of organic matters in supercritical water is considered to be a promising technology, which can not only use the supercritical water as the reaction medium, but also separate gas and/or liquid by simply reducing the reaction temperature and/or pressure [6]. Today, hydrogen

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has become an important kind of raw materials in petrochemical and chemical industry, and there is a growing interest in the use of hydrogen as fuel [7]. Hydrogen is defined as a green attractive energy source and has attracted extensive attention worldwidely due to its potential higher energy efficiency and less generation pollutants, which may replace conventional fossil fuels in the future [8]. Due to the above advantages of supercritical water, many researches have conducted in the application of supercritical water to gasify waste [9,10], biomass [11–15] and coal [16–19] for hydrogen production.

Vostrikov [9] studied municipal sewage sludge gasification in supercritical water conditions ($T \leq 750\ ^{\circ}C$; $P \leq 30$ MPa). The predominant gaseous products among volatile conversion included CO_2, H_2, CH_4 and NH_3 according to the mass-spectrometric data. They found that the rate of the conversion increased with temperature and mainly depended on the interaction of water molecules with sewage sludge carbon ($T > 600\ ^{\circ}C$).

The influences of pressure, temperature, residence time, and alkali addition on the gasification of corn starch, clover grass and corn silage in supercritical water were studied by Pedro [11]. The results showed that increasing the temperature and residence time could improve the gas yield, but the changes in pressure had no effect on the gasification yield. Potassium addition affected the gasification yield of corn starch, but had no obvious influence on the gas yield of the potassium-containing natural products of clover grass and corn silage.

Hui Jin [16] investigated the gasification of coal in supercritical water with a fluidized bed reactor. The coal-water slurry of 24 wt% could be continuously transported in the reactor and stably gasified without plugging problems; hydrogen yield of 32.26 mol/kg was obtained with the hydrogen fraction of 69.78%. Furthermore, the recycle of the liquid residual from the gasification system was also studied.

Supercritical water gasification of waste, biomass or coal had been widely studied, however, there were limited studies on supercritical water gasification of semicoke. Semicoke gasification in supercritical water can not only achieve high-efficiency utilization of semicoke powders but also obtain hydrogen. Gasification of semicoke by supercritical water gasification technology has many advantages. When semicoke is made into slurry with water as reaction materials, the reaction materials are not easy to coke and block the pipeline due to the low tar content of semicoke. In this case, slurry with high concentration can realize continuous transmission. Besides, the surface of semicoke particle has abundant pore structure [20], which can adsorb catalysts easily and accelerate the gasification reaction. Additionally, the carbon content of semicoke powders is high, but its price is cheap [21], so using semicoke to produce hydrogen and carbon dioxide will bring immeasurable economic benefits.

In order to make a better research of supercritical water gasification technology, our laboratory (State key Laboratory of Multiphase Flow in Power Engineering) developed the supercritical water fluidized bed reactor system independently [14]. Comparing to the plasma gasification and entrained gasification, the supercritical water fluidized bed gasification has many advantages. Firstly, in the supercritical water fluidized bed reactor, semicoke particles form a fluidization state, which ensures residence time of semicoke particles in the reactor long enough. Secondly, because of the special physical and chemical properties of supercritical water [5], the gaseous products can be diffused effectively, which benefits further gasification reactions. Thirdly, the plasma gasification and entrained gasification need relatively high temperature (about 1200 °C or higher) in the gasification reactions [22–26], however, the supercritical water fluidized bed gasification can obtain good results at relatively low temperature (about from 500 to 700 °C) [16]. Finally, the residues deposit in the bottom of the reactor during the gasification reactions, rather than carried away from the reactor top, which can reduce the investments of the fly ash capture equipment.

In this study, a novel utilizing method for semicoke powders was proposed. This was the first time supercritical water was applied to gasify semicoke. The influences of the main operating parameters including temperature, feedstock concentration, flow rate of preheated water and alkali catalysts were systematically investigated in order to determine the optimum condition of gasification of semicoke with the supercritical water fluidized bed reactor. What's more, the higher feedstock concentration of slurry than the literature [16] was continuously transported in the reactor.

Experiments

Materials

The semicoke used in the experiments was obtained from Yulin, Shaanxi, China. The elemental and proximate analysis of it was listed in Table 1. K_2CO_3, KOH, Na_2CO_3 and NaOH were all anhydrous reagents and were supplied by the Tianli Chemical Reagent Co., Ltd. All these alkaline catalysts were analytical pure reagents. Xanthan gum was purchased from the Shandong Fufeng Fermentation Co., Ltd.

Experimental set up

The experiments were carried out with the supercritical water fluidized bed reactor system, and the schematic

Table 1 – Elemental and proximate analysis of the semicoke.

	Elemental analysis [wt%]					Proximate analysis [wt%]			
Species	C	H	N	S	O[a]	Moisture	Ash	Volatiles	Fixed carbon
Semicoke	69.12	1.35	0.89	0.711	10.329	0.7	16.9	15.74	67.36

[a] By difference.

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