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Supercritical water gasification research and development in China

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ABSTRACT

Supercritical water gasification is a promising technology to convert coal/biomass/organic wastes to hydrogen cleanly and efficiently. Extensive investigations on supercritical water gasification were conducted in China. State Key Laboratory of Multiphase Flow in Power Engineering (SKLMFPE) together with other universities/institutes established experimental device with the reactor type of quartz tube reaction system, tubular reactor and fluidized bed reactor. The fluidized bed reactor system solved the blocking problems to guarantee continuous and stable gasification. Typically Hongliulin coal as a typical coal in China was completely gasified in supercritical water fluidized bed system and the hydrogen yield was 77.5 mol per kg of coal. A pilot scale demonstration plant for supercritical water gasification driven by solar concentration system was established with a handling capacity of 1 t/h and it proves the feasibility of the system scale up. A novel thermodynamics cycle power generation system based on coal gasification in supercritical water was proposed with the obvious advantages of high coal-electricity efficiency and zero pollutant emission. An Integrated Cooperative Innovation Center with the name of A New Type of High-efficient Coal Gasification Technology and its Large-scale Utilization was founded in order to vigorously enhance the industrialization of the technology.

1. Introduction

Supercritical water is water at a temperature and pressure above its critical point (temperature 374.3 °C and pressure 22.1 MPa). Supercritical water is a single phase that possesses the characteristics of both gas and liquid without surface tension and liquid/gas phase boundary. Supercritical water has sufficient density to give appreciable dissolving power, diffusivity higher than that in liquids and lower viscosity to enhance mass transport. It provides a homogeneous and rapid reaction environment for gasification [1–3].

Organic matter (especially carbon, hydrogen and oxygen) is converted into gases (mainly H_2 and CO_2), meanwhile other elements such as N, S, P, As and Hg deposit as inorganic salts in supercritical water. The separation of CO_2 from H_2 is easy because solubility can be a strong function of pressure and temperature near the critical region [4–7].

China depends heavily on coal for both energy production and energy consumption and China is suffering heavily from the pollutants by agricultural and industrial wastes. It is expected that supercritical water gasification of coal/biomass/organic wastes may hopefully provide a potential way for the energy industry of China. Researchers has paid much attention to supercritical water gasification and made much progress in China.

2. Gasification system

SKLMFPE has constructed many types of experimental device including quartz tube reaction system, autoclave system, tubular flow system, supercritical water fluidized bed reactor system and pilot scale demonstration system since 1997. The quartz tube reactor system is constructed to investigate the gasification characteristics in extreme reaction condition (up to temperature of 1000 °C, pressure of 35 MPa) to obtain the complete gasification condition of each feedstock [8]. The quartz tube reaction system provides a cheap and fast gasification experiment for the non-catalytic gasification reaction kinetic to eliminate the catalytic effect caused by stainless steel reaction wall. The quartz tube reaction has the potential function to carry out the visualization research for the gasification mechanism study.

A high throughput autoclave gasification system with 6 channels was established. The autoclaves are made of stainless steel 316, Hastelloy C276 or Inconel 625. The autoclave reaction system is helpful for the gasification kinetics study, catalyst screening and novel supercritical water hydrothermal nano-material synthesis [9]. The preliminary catalyst screening experiment results show

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that: (1) as for homogeneous catalyst, basic catalyst is proved to lead to micro holes in the coal matrix to accelerate the gasification reaction and increase the carbon gasification efficiency; (2) as for heterogeneous catalyst, SKLMFPE has done extensive experiments in screening the active, stable Ni-based heterogeneous catalyst to decrease the operating temperature. We have also obtained experience and method in catalyst preparation, screening and evaluation. Ni–Mg–Al catalyst is proved to be a promising catalyst for biomass/coal/organic wastes and its model compounds gasification in supercritical water [10–16].

The first continuous supercritical water gasification device in China was established in SKLMFPE and the experimental results shows that more hydrogen in gas product is obtained than that in feedstock, which proves that the hydrogen in water is released to gas [17]. Another continuous supercritical water gasification device was developed [7,18,19] and synergistic effect was found during the co-gasification process of coal and biomass/black liquid, and the synergistic effect may be explained by the hydrogen match mechanism [20]. Funded together with Griffith University by Australian Research Council (ARC), the author's research team constructed an experimental device of biomass gasification in supercritical water with the handling capacity of 1 kg/h. The experimental device has been transported to Australian and put into operation. In continuous reaction system, homogenous catalyst is easy to handle and can form a uniform slurry, but homogenous catalyst is difficult to be recovered. Heterogeneous catalyst may have strong activity, however, the catalyst particle is difficult to be dispersed well in the reaction medium and the phase resistance between feedstock particle and catalyst particle may not guarantee a rapid reaction rate. What's more, the heterogeneous catalyst may also cause blocking problems in tubular reactor [21].

The first supercritical water fluidized bed in the world was established to enhance heat and mass transfer during supercritical water gasification so that coke plugging problems was solved. Fluidized bed reactor provides an easier way for ash discharge due to the limited solubility of inorganic matter. Fluidized bed reactor also favors catalyst loading as bed material. Coal, biomass and organic wastes were used as feedstock [22–26]. Several kinds of coals in China have been used for the experiments of supercritical water gasification and complete gasification results were obtained. The detailed comparison and the analyses will be published elsewhere. Thereinto, Hongliulin Coal is selected as typical Chinese coal due to its huge reserves. The elemental and proximate analysis data are seen as Table 1 and the carbon content is almost 75%. The supercritical water gasification result of Hongliulin coal is seen in Table 2. YH_2 means hydrogen yield, equals the mass of certain gas product divided by the mass of dry matter in feedstock; CE means carbon gasification efficiency, equals mass of carbon element in gas product divided by the mass of carbon in dry matter in the water-coal-slurry. It can be observed that Hongliulin coal

Table 1
Elemental and proximate analysis data of the different coals.

Elemental analysis (wt%)					Proximate analysis (wt%)				Qb, ad(MJ/kg)
C	H	N	S	O[a]	M	A	V	FC	
74.29	4.69	1.00	1.12	9.26	2.79	6.84	33.19	57.18	29.61

[a] By difference.

Table 2
Gasification characteristic of Hongliulin Coal in supercritical water in fluidized bed reaction system (pressure 23–25 MPa; K_2CO_3:Coal = 0.1:1).

Concentration of slurry (wt%)	Gas fraction (%)						YH_2 (mol kg^{-1})	CE (%)
	H_2	CO	CH_4	CO_2	C_2H_4	C_2H_6		
10[a]	56.2	1.68	9.3	31.69	0.05	1.07	77.5	100.2
20[b]	56.2	1.88	9.31	31.39	0.04	1.2	77.5	100.5

[a] Coal slurry flow rate: 20.38 g/min; flow rate of preheated water:coal slurry = 3.88:1; reaction zone temperature: 640–670 °C.
[b] Coal slurry flow rate: 20.2 g/min; flow rate of preheated water:coal slurry = 4.27:1; reaction zone temperature: 640–690 °C.

Table 3
Main organizations in supercritical water gasification of organic wastes.

	Reactor type	Feedstock	Key parameters	Main contributions
SKLMFPE	Quartz tube, autoclave, fluidized bed	Landfill leachater, sewage sludge, Black liquid	380–540 °C	Renewable resources Recovery and harmless treatment [15,24,25,31,35]
South China University of Technology	Tubular reactor	PVA-contained waste water, polyethylene glycol	20–36 MPa, 20–60 s.	Ni/ZrO_2 is a promising heterogeneous catalyst for hydrogen production by SCWG [44]
Hohai University	Batch	Dewatered sewage sludge	400–455 °C, 0–60 min	The PAHs in the solid residue are mainly composed of 4-ring PAHs [46–48]
Shangdong University	Transpiring wall reactor	Methanol	8–17 kg/h	A transpiring wall reactor is used to treat organic and recover energy [51,52]
Tianjin University	Simulation	Coal	–	A MD insight into SCWG of coal [53,54]
Coal Chemistry in Shanxi	Coiled tubular reactor	Cotton printing and dyeing wastewater	400–600 °C	A salt separator was applied to prevent the reactor block [57]
Tongji University	Batch reactor	Sebacic and azelaic acids	300–400 °C	Intermediate products in the oxidation of high molecular weight carboxylic acids were identified [55]