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Continuous hydrogen production by biomass gasification in supercritical water heated by molten salt flow: System development and reactor assessment

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ABSTRACT

Hydrogen production by biomass gasification using solar energy is a promising approach for overcoming the drawbacks of fossil fuel utilization, but the storage of discontinuous solar flux is a critical issue for continuous solar hydrogen production. A continuous hydrogen production system by biomass gasification in supercritical water using molten-salts-stored solar energy was proposed and constructed. A novel double tube helical heat exchanger was designed to be molten salts reactor for hydrogen production. Model compounds (glycerol/glucose) and real biomass (corn cob) were successfully gasified in this molten salts reactor for producing hydrogen-rich gas. The unique temperature profiles of biomass slurry in the reactor were observed and compared with that of conventional electrical heating and direct solar heating approaches. Product gases yield, gasification efficiency and exergy conversion efficiency of the reactor were analyzed. The results showed that the performances of reactor were determined by feedstock style, biomass concentration, residence time and biomass slurry temperature profiles.

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1. Introduction

The growing energy demand coupled with the depletion of fossil resources as well as the increasing environmental pollution has stimulated the growing interest in using hydrogen as a clean fuel. The hydrogen demand must be satisfied by clean, secure and renewable production approaches. Since solar thermal energy has many advantages, such as abundant reserves, non-polluting, high concentrated energy flux etc [1], solar hydrogen production technology is regarded as an ideal option.

A numerous of efforts have been made for hydrogen production using solar thermal energy, some of them are listed as

follows. The earliest and simplest method is one-step water splitting process, it is pointed by Kogan [2] that vapor could be heated to above 2500 K for dissociation to product hydrogen and oxygen gases, and more hydrogen yield need even higher temperature. For decreasing reaction temperature, multi-step water splitting processes are presented, including IS cycle proposed by GA [3], UT-3 proposed by Tokyo university [4] and metal-oxide redox pair cycle [5]. The reaction temperature for multi-step water splitting process is lower than that of one-step method, but still at a high level. For the case of metal-oxide redox pair cycle, the metal oxide must be heated up to 2000 K for reducing metal-oxide to metallic simple substance,

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which is needed for next-step hydrogen generation. Since hydrogen production using exclusive solar thermal energy requires extreme high temperature, the method of biomass/water gasification coupling with solar heating technique has gained many attention in recent decades.

Supercritical water gasification (SCWG) of biomass is one of these promising approaches, with an outstanding advantage in converting high moisture biomass to hydrogen-rich fuel gas [1]. Its reaction temperature is below 923 K, which can be achieved by concentrated solar power with a small mean flux concentration ratio. Since the solar energy is low-density before concentration, it is costly on high-temperature solar concentrating process, meanwhile the usage of high temperature material is also expensive. The method of SCWG by biomass could provide a solution to the issue of low-cost solar hydrogen production [6].

Another worldwide issue for solar hydrogen process is solar energy storage. The discontinuous solar energy flux is affected by seasons and other meteorological factors, for example, zero-power at night and low-power in cloudy weather. The discontinuous solar flux leads to a non-stop variation in reaction parameters of the hydrogen production process, especially the reaction temperature and pressure. It would bring about a deviation in reaction parameters from the optimal condition, even lead to a system breakdown. Therefore the solar energy storage is very important for continuous and high-efficiency solar chemical conversion for hydrogen production [7]. Unfortunately, most of the previous experimental studies were focused on the hydrogen production with fluctuant solar power, and the apparatuses were designed with the assumed steady and optimal solar flux. To the best of the author's knowledge, little information has been devoted to solving the problem of discontinuous solar heating in solar hydrogen cycles.

For solar energy storage and transfer, a variety of fluids was employed in high temperature heat storage and transfer, including water, air, and mineral oil, before molten salts were selected as the best for solar hydrogen technique, as it is shown in Fig. 1 [2,6,8–13]. The favorable thermal physical and chemical properties of nitrate molten salts, such as large specific heat, low vapor pressure, low corrosive and toxic, chemical stability at high temperature are appropriate for the SCWG process. Therefore a novel system of hydrogen production by biomass gasification in supercritical water using

molten salts as solar thermal storage and heat transfer media was constructed at the State Key Laboratory of Multiphase Flow in Power Engineering (SKLMFPE).

In this work, the approach of solar heat storage by molten salts for continuous hydrogen production was proposed and implemented. Since the hydrogen production reactor using molten salts fluid is the key component in this system, the gasification characteristics and the exergy conversion efficiency (based on second-law analysis) of the novel hydrogen production reactor were mainly concerned. The heating characteristics of the molten salts heating reactor were compared with that of electrical heating reactor [14] and concentrated solar heating reactor [15] in previous literature. Model compound (glycerol/glucose) and real biomass (corn cob) were chosen as feedstock to be gasified in the molten salts SCWG reactor. The gas yield, molar fraction and temperature profiles of both SCW and molten salts fluid were measured, and the effects of feedstock type, biomass concentration, reactor temperature distributions and feedstock flow rates on the performances of molten salts reactor were assessed.

2. Apparatus and experimental process

The schematic diagram of the hydrogen production system with SCWG using solar storage energy was presented in Fig. 2. Three main subsystems were comprised in this system: (i) The feedstock subsystem; (ii) heat storage subsystem; (iii) heat exchanger/reactor subsystem.

In the feedstock subsystem, deionized water and biomass slurry were separately transported and finally mixed together before being introduced into the molten salts reactor. For deionized water, it was pressured and transported to the regenerator by a high-pressure metering pump with a maximum flow rate of 12 kg/h, and the flow rate was measured by a mass flow meter (SIEMENS MASSFLO, Germany). The deionized water was preliminary heated by a regenerator up to 660 ± 10 K using the recycle-heat provided by the high temperature reaction effluent. Then, the fluid entered the molten salt preheater and was further heated to above critical temperature by discharged molten salt fluid from the molten salts reactor. In biomass slurry side, a feeder using movable piston was employed to continuously transport feedstock. The structure and working method of the feeder was reported in the previous literature [16]. Biomass feedstock was mixed with the former preheated deionized water and quickly be heated to supercritical temperature (>700 K) for the purpose of minimizing char and tar formation [17]. The ratio of feedstock to preheated supercritical water was about 1:5. After leaving the reactor, the reaction effluent passed through the shell side of the regenerator, and the energy efficiency was improved by this heat-recycle approach [18]. To separate product gas from the high-solubility supercritical water, the effluent was rapidly quenched by the cooler and decompressed by the back pressure valve to the ambient temperature and pressure, respectively. Finally, the product fuel gas was collected using separator, and the gas flow rate was measured by the wet test gas meter.

The heat storage subsystem was comprised of a molten salts storage vessel, a molten salts solar receiver, a molten

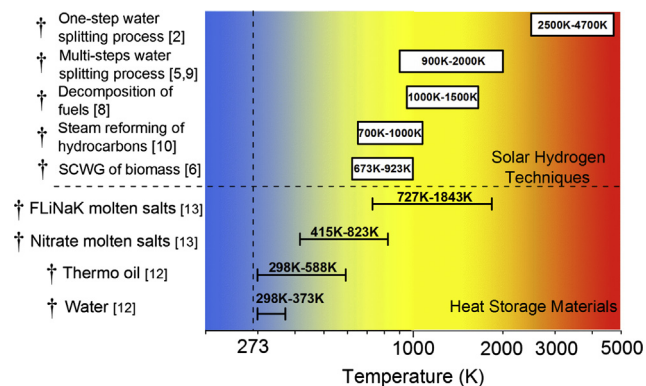


Fig. 1 – Reaction temperatures of various solar hydrogen techniques and heat storage temperatures of various materials.

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