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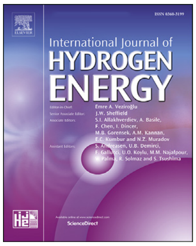

Thermodynamic study on the integrated supercritical water gasification with reforming process for hydrogen production: Effects of operating parameters

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ABSTRACT

In this paper, a conceptual process design of the integrated supercritical water gasification (SCWG) and reforming process for enhancing H_2 production has been developed. The influence of several operating parameters including SCWG temperature, SCWG pressure, reforming temperature, reforming pressure and feed concentration on the syngas composition and process efficiency was investigated. In addition, the thermodynamic equilibrium calculations have been carried out based on Gibbs free energy minimization by using Aspen Plus. The results showed that the higher H_2 production could be obtained at higher SCWG temperature, the H_2 concentration increased from 5.40% at 400 °C to 38.95% at 600 °C. The lower feed concentration was found to be favorable for achieving hydrogen-rich gas. However, pressure of SCWG had insignificant effect on the syngas composition. The addition of reformer to the SCWG system enhanced H_2 yield by converting high methane content in the syngas into H_2. The modified SCWG enhanced the productivity of syngas to 151.12 $kg/100kg_{feed}$ compared to 120.61 $kg/100kg_{feed}$ of the conventional SCWG system. Furthermore, H_2 yield and system efficiency increased significantly from 1.81 $kg/100kg_{feed}$ and 9.18% to 8.91 $kg/100kg_{feed}$, and 45.09%, respectively, after the modification.

Introduction

Sewage sludge is the by-product of wastewater treatment process which is considered to be a potential energy resource for the production of gaseous or liquid fuels. Nevertheless, after mechanical dewatering, sewage sludge still has high water content (typically 80–90%.wt) which is not suitable for conventional thermochemical processes such as; pyrolysis or gasification, and combustion. Furthermore, sewage sludge

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has many harmful substances such as heavy metals, pathogens, poorly biodegradable organic contaminants, viruses, which cause a difficulty in the disposal techniques [1]. Therefore, a proper technique conversion is necessary to be developed. With the gain of avoiding the drying pretreatment, supercritical water gasification is a guaranteeing technique to convert high moisture content solid fuels into gaseous fuels with rich hydrogen or methane that can be used for a varied range of downstream applications.

Supercritical water gasification (SCWG) seems to be one of the thermochemical conversion technologies for wet biomass and organic wastes without drying process [2]. It takes place at a temperature and pressure above its critical point (374.3 °C and 22.1 MPa) [3]. The organic matter (especially carbon, hydrogen, and oxygen) in the sewage sludge is converted into gases (mainly H_2 CH_4, CO, and CO_2) [4]. This conversion is made by the unique changes in the physiochemical properties of water in supercritical conditions [5]. The physiochemical characteristics such as ion product, density, viscosity, dielectric constant are greatly different at supercritical conditions. The water density in supercritical water is extremely lower than that normal condition, 166.54 kg/m^3 (at 400 °C, 25 MPa) and 997 kg/m^3 (at 25 °C, 0.1 MPa) [6]. The decreasing of water density may affect the drop of ion product, which indicates that free-radical mechanism is preferable. Also, the dielectric constant decreases significantly from approximately 80 (at 25 °C, 0.1 MPa) to 5 (at the critical point), which is typical of a nonpolar solvent for organic compounds. Since the unique properties, supercritical water has been regarded not only as an attractive reactant but also as a catalyst. It has both liquid-like and gas-like characteristics, high diffusivity, and good solubility [7]. Nowadays, the reliability and sustainability of technologies play a crucial role in the industrial market. In general, SCWG has a big challenge to be applied in the market. There are several challenges on the design and configuration of SCWG system such as; (1) the pump system could do with the high solids content, (2) the material of SCWG reactor still needs to be evaluated by considering harsh operating condition, corrosion-resistant, and safety risk, (3) the proper heat integration is needed to minimize the energy loss. Thus, a research on the continuous flow system is required to deal with the clogging, plugging, precipitation, and char formation problems as well as the selection of proper catalysts [8]. From economic point of view, the SCWG is considered to be too expensive, due to a high operating cost, only biomass with high disposal costs are attractive feedstock [9,10]. The study on the techno-economic of glycerol reforming for hydrogen and power production showed that the specific of capital investment cost of conventional steam reforming and auto-thermal reforming were around 1199 USD/kW_{net} and 1290 USD/kW_{net}, respectively [11]. For sewage sludge treatment, the SCWG process will be attracted when the sewage sludge revenues exceed 72 USD/ton dry-matter [10]. By an improvement of the configuration of SCWG process design, the economic value of SCWG could be further raised.

Despite most of the experimental studies in batch and continuous system, with and without catalysts have been done, modeling studies of SCWG are still need to be further developed. Various studies have performed thermodynamic equilibrium calculation of SCWG for estimating the equilibrium product gas compositions, gas yield and gasification efficiency. In the past, most of the studies used a model of biomass or feedstock such as glucose, methanol, glycerol, cellulose, and ethanol in order to simplify the process modeling [12–16]. The effect of parameter conditions including temperature, pressure, and water-to-feedstock ratio has been examined. Recently, several studies used a real biomass or solid feedstock as a material to closely match up to the real feedstock conditions. Yakaboylu et al. [17] investigated the partitioning of an element on the basic compounds and phases of mixed pig-cow manure in supercritical water. Castello and Fiori [18] studied the thermodynamic modeling of supercritical water gasification by using microalgae *Spirulina* as a pseudo-compounds. To our knowledge, the work of Yan et al. [19] was the first study aimed to briefly evaluate the effect of the elemental composition of the biomass in SCWG. The study was in-depth continued by Louw [6] on the comprehensive investigation of the effect of biomass composition (in terms of its carbon, hydrogen, and oxygen content) to aid in the selection of suitable biomass feedstock for SCWG at various operating conditions.

Thanks to Ortiz et al. [20] for the initial development of the proposed design of supercritical water reforming of glycerol for electrical production in an energy self-sufficient system. The proposed design was equipped with a heat exchanger for optimizing the whole process performance. The effect of the key operating parameters in the reforming process has been studied, as well as an energy and exergy analysis. Since high operating conditions and relatively high operating cost, the combination of SCWG with others process is necessary to be developed. Fiori et al. [21] proposed the conceptual process design of SCWG aimed at producing H_2 as a feedstock of fuel cells. The purpose of the study was to expect the possibility of the small-scale plant with an energetically self-sustained. A similar study was done by Wan [22] on the innovative system by combining the gasification unit with supercritical water unit to produce clean syngas for a solid oxide fuel cell.

Keeping the above into consideration, a new configuration of the integrated supercritical water gasification process in the process simulation using Aspen Plus has been developed. The process configuration was designed to be as simple and feasible as an actual pilot or industrial scale construction. The detailed flow sheet is illustrated in Section 2.3 showing the possible use of H_2 for feeding fuel cells and high purity CO_2 for other uses such as methanol synthesis [23]. The sewage sludge is considered as a feedstock for the process due to its abundant availability in recent years, especially in China [24]. We improved the process design proposed by Fiori et al. [21] with modifications i.e., the addition of reformer unit after SCWG reactor, the addition of turbine expander, and CO_2-absorber. The main function of the reformer unit is to enhance the H_2 yield by converting high methane in the syngas obtained from low temperature of SCWG (375–500 °C). Steam reforming of methane and dry reforming of methane reaction were involved in the reformer unit. The turbine expander was used to generate electricity for internal use by expanding the high pressure syngas existing in the SCWG reactor. The energy required to sustain the SCWG reactor and reformer supplies from combustor, as reported by Ortiz et al. [25]. In this study, the performance of SCWG reactor in term of the

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