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Using glycerol for hydrogen production via sorption-enhanced chemical looping reforming: Thermodynamic analysis

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ABSTRACT

Sorption enhanced-chemical looping reforming (SECLR), which combines a chemical looping reforming method (CLR) and a sorption-enhanced reforming method (SER) in a single-stage process, is proposed for the hydrogen production from glycerol. The model of the SECLR process using a solid oxygen carrier and CO_2 absorbent is developed using a flowsheet simulator. The comparison between chemical looping reforming (CLR) with/without CaO sorbent is investigated. The results show that the addition of CaO sorbent provides an increase in a hydrogen concentration. The SECLR process is then deeply analyzed by considering the effect of the primary parameters on its performance in terms of hydrogen production, carbon formation and net energy requirements. The parametric analysis indicates that operating the SECLR at a steam-to-glycerol molar ratio higher than two and a sufficient calcium oxide-to-glycerol molar ratio of three can inhibit the formation of carbon. The hydrogen yield increases significantly upon increasing the reforming temperature. The required energy of the process varies with the amount of nickel oxide used as a solid oxygen carrier. The exergy analysis is considered to identify the optimal operation for self-sufficient energy and the results show that the operation of the SECLR at the nickel oxide-to-glycerol molar ratio of 1.87 is sufficient to be the most optimal condition with regard to both energy and exergy considerations.

1. Introduction

The ever-increasing energy demand and the limited amount of conventional fossil fuels coupled with the growing concerns of global warming have stimulated a number of researchers to search for alternative energy. Among the various alternative energy forms, hydrogen is considered an important energy carrier in the future [1]. It is also an important raw material in the chemical and petrochemical industries and can be used as a fuel in fuel cells to produce electrical energy. For reasons of sustainability, the use of renewable fuel sources for hydrogen production has received considerable attention [2].

Glycerol is an important renewable fuel that can be reformed into hydrogen by different methods, e.g., the steam reforming process [3], partial oxidation process [4], auto-thermal reforming process [5], aqueous-phase reforming process [6] and supercritical water reforming process [7]. Moreover, the use of glycerol as a hydrogen source can reduce a glut of glycerol from biodiesel production and consequently reduce its operating cost [8,9]. Presently, although many studies show that the catalytic steam reforming of glycerol is feasible for hydrogen production [10–13], the demand for high-purity hydrogen production is rapidly growing in the electronic, ceramic, and chemical industries. Hence, an improved process for high-purity hydrogen production is needed in terms of the better energy usage and control CO_2 emissions [14].

To enhance the performance of a hydrogen production process, the use of the concept of a multi-functional unit operation is interesting. Recently, a sorption-enhanced chemical looping reforming (SECLR) that combines a chemical looping reforming method (CLR) and a sorption-enhanced reforming method (SER) in one process stage was proposed by Rydén and Ramos [15]. The chemical looping reforming method is used for the production of hydrogen via the cyclic reduction and oxidation of a solid oxygen carrier [16–18], whereas the sorption-enhanced reforming method with in situ CO_2 removal is employed for the production and enhancement of the hydrogen purity. The sorption-enhanced chemical looping reforming process uses three interconnected fluidized bed reactors (i.e., reforming reactor, calcination reactor and air

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reactor) to produce high-purity hydrogen, carbon dioxide and nitrogen without the need for an additional gas separation unit.

In recent years, most studies on the sorption-enhanced chemical looping reforming have focused heavily on using methane as a fuel [19–22], whereas a few works have been done on glycerol. Dou et al. [23] showed that the continuous sorption-enhanced steam reforming of glycerol using two moving-bed reactors with a Ni-based catalyst and CaO sorbent can produce hydrogen with 93.9% purity. Dou et al. [24] designed the moving bed reactors to achieve that the catalyst oxidation and sorbent regeneration was taken place under the same conditions in the reactor. By combining different units in one stage, this process has a great potential for low cost hydrogen production and high efficiency. Recently, they have succeeded in studying the sorption-enhanced steam reforming of glycerol in a fixed-bed reactor [25]. The literatures also revealed the benefits of using NiO as a solid oxygen carrier for SECLR because of its high reactivity and strong catalytic properties. Once NiO is reduced, some metallic Ni obtained has the excellent catalytic properties for steam reforming and water gas shift reaction [24,26]. In general, transition metals have been used as oxygen carriers in chemical looping processes, such as iron, copper, nickel, cobalt and manganese. Zafar et al. [27] examined different solid oxygen carriers in a fluidized bed reactor and concluded that NiO appeared the most promising active metal. Fernandez et al. [28] reported that Ca/Cu chemical looping process is feasible for hydrogen production but it is only favored to operate under conditions of moderate temperature, low pressure and high steam/carbon molar ratio. To determine the optimal operating conditions, the theoretical and experimental study by Wang [29] was presented by considering the effects of reforming temperatures and reactants ratios; however, this work did not describe the energy management in each unit in details and completed thermodynamic analysis is not included.

In this work, the sorption enhanced-chemical looping reforming process (SECLR) of glycerol is studied. A thermodynamic approach is used to investigate the effects of the operating parameters on the SECLR under steady-state condition. The effects of the primary operating parameters, i.e., temperature (*T*), calcium oxide-to-glycerol ratio (CaO/G), nickel oxide-to-glycerol ratio (NiO/G) and steam-to-glycerol ratio (S/G), on the performance of the SECLR process are analyzed in terms of the hydrogen production, carbon formation, energy demand of each unit and the overall process. To determine the thermally self-sufficient condition, the result is discussed based on energy and exergy considerations.

2. Description of the sorption-enhanced chemical looping glycerol steam reforming (SECLR)

The flow diagram of the sorption-enhanced chemical looping reforming process (SECLR) for hydrogen production from glycerol is shown in Fig. 1. The process consists of three reactors: reforming reactor, calcination reactor and air reactor, three cyclones and two heaters. The reactant feed stream consists of glycerol ($C_3H_8O_3$) and water (H_2O) at 25 °C and 1 atm. Before feeding to the reforming reactor, the reactant stream is preheated in order to vaporize into vapor phase at 1 atm. The reactant stream in vapor phase and the solids (NiO + CaO) stream from Cyclone3 are sent to the reforming reactor. The feed flow rates of the glycerol and water streams, and the NiO + CaO stream are tested to assess the condition which gives the optimum hydrogen production. In the reforming reactor, glycerol is oxidized with NiO and H_2O together with CO_2, which is adsorbed by CaO. The product stream contains hydrogen as a major product and other gases and solids is sent to Cyclone1 to separate the solids from the gases. The solid product stream which consists of nickle (Ni) and calcium carbonate ($CaCO_3$) is sent to the calcination reactor operated at 900 °C and 1 atm in order to regenerate calcium oxide (CaO) and release pure CO_2 gas. The product stream from the calcination reactor is sent to Cyclone2 where CO_2 is separated gas from solid particles (Ni and CaO). Without separation of CaO, the CaO, Ni and air at temperature of 900 °C and 1 atm can be sent to the air reactor [24] in order to regenerate Ni to NiO via the oxidation reaction. The gases and solids produced from the air reactor are fed to Cyclone3 where N_2 and O_2 off-gas is separated from NiO and CaO solid. Finally, both NiO and CaO solids are recycled to the reforming reactor. In this study, the air flow rate is specified at 17 mol/s to regenerate the NiO completely. Dashed-line boxes represented in Fig. 1 are referred to the heat requirement inside reforming process (evaporator and reforming reactor), calcination reactor, and air reactor (heater and air reactor). All product streams released at high temperatures are cooled down to 150 °C, therefore the heat from hot gaseous products can be used as useful heat for the heat requiring units such as heaters and reactors. To compare with CLR process, hydrogen production by chemical looping reforming is operated without carbon dioxide sorption. The process flowsheet is similar to Fig. 1 but there is no CaO and $CaCO_3$ as the components Therefore, calcination reactor and its heat duty are also absent. The CLR process only uses two interconnected reactors: reforming reactor and air reactor, two cyclones and two heaters.

3. Thermodynamic analysis

Thermodynamic analysis is performed by using Aspen Plus simulator in which unit operations including reactors, cyclones and heaters in the process are modelled with equilibrium RGIBBS reactors, HEATERs, and SSPLIT, respectively. The minimization of Gibbs free energy can calculate the equilibrium compositions of gaseous and solid products without specification of the possible reactions. However, the potential of this approach is limited if the concern compositions are not completely added. In this study, pure glycerol and water are the main reactants for hydrogen production via the SECLR process or CLR process using NiO as the oxygen carrier and CaO as the CO_2 adsorbent. Therefore, the possible components in the process consist of gaseous components (H_2, H_2O, CO, CO_2, CH_4 and unreacted $C_3H_8O_3$) and solid components (NiO, Ni, CaO, $CaCO_3$, $Ca(OH)_2$ and C) [29]. The reactors are analyzed at a steady state operation with isothermal and isobaric conditions. The Aspen Plus simulation is set up with a stream class of MIXCIPSD, to allow for the perfect separation between solids and gases in the cyclones. The physical property method for thermodynamic calculation is based on the SOLIDS property. Other assumptions made are (1) kinetic effects are not considered in the simulation and thermodynamic assessments, (2) the deactivation of solid materials is not taken into account, (3) pressure drops are neglected during operation in all units, (4) all gaseous components behave as an ideal gas, and (5) heat transfer between the unit operation ideally occurs.

The sensitivity analysis in Aspen Plus is used to examine the effects of the operating conditions. The simulation is run by varying the reforming temperature (*T*), CaO/G ratio, S/G ratio and NiO/G ratio, with the objective of studying these parameters' effects on the gas production yield, hydrogen purity, carbon formation, and heat duty. The possible reactions in the SECLR process are shown in Table 1 [24,29]. The performance of the process is expressed in terms of yield of product *i* (Eq. (1)), purity of product *i* on dry basis (Eq. (2)), carbon formation (Eq. (3)), and net heat duty (Eq. (4)) which can be positive (endothermic process), negative (exothermic process), or zero (self-sufficient process), depending on the operating conditions. In all simulations the glycerol feed rate and operating pressure are kept at 1 mol/s and 1 atm, respectively. The key operating parameters for investigation are reforming temperatures (*T*), CaO/G ratio (Eq. (5)), S/G ratio (Eq. (6)) and NiO/G ratio (Eq. (7)).