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Hydrogen production from heavy fraction of bio-oil using iron-based chemical looping process: Thermodynamic simulation and performance analysis

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ABSTRACT

The purpose of this work is to investigate the overall performance of the iron-based chemical looping hydrogen (CLH) production from the heavy fraction of bio-oil (HFB). The multiple ASPEN models are employed to simulate a two-stage fluidized bed reduction reactor considering the thermodynamic equilibrium limit. Several important factors are discussed to determine the suitable reactor operation conditions for the process simulation of two operation modes. The results show HFB CLH process has a maximum hydrogen efficiency of 73.1% (LHV) and a total thermal efficiency of 59.2% (LHV) at the cost of decreasing the CO_2 capture efficiency under the condition of supplementary firing. Within the complete self-sustaining operation range, the highest hydrogen thermal efficiency is 57.8% (LHV) corresponding to a total thermal efficiency of 58.3% (LHV) and a CO_2 capture efficiency of nearly 100%. This study indicates the CLH process has significant advantages over the conventional coal gasification (CG) for hydrogen production owing to its high energy conversion efficiency and high-efficient CO_2 capture with low cost.

Introduction

Hydrogen (H_2) is an important feedstock of petroleum chemical industry. It has been widely utilized for various processes including crude oil refining, methanol and ammonia synthesis, hydrogenation and hydrocracking [1]. H_2 is a clean and environmental-friendly energy carrier suitable to be used not only for power generation but also for transport sector in hydrogen fuel cells [2], which can alleviate the environmental problems resulting from current massive fossil fuel consumption. However, H_2 is a secondary fuel derived from primary energy sources like fossil fuels [3–5]. H_2 can be produced from a wide variety of feedstock available anywhere through various methods [6]. Currently H_2 is mostly produced from fossil fuels (accounting for 96%) through the most mature CG and steam methane reforming (SMR) followed by water gas shift (WGS) and a pressure swing adsorption (PSA) processes [7]. The natural gas steam reforming technology has provided

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about 48% of the world's total hydrogen consumption [8]. The SMR technology has afforded more than 90% of all the H_2 produced in the USA [9].

The above-mentioned conventional technologies for H_2 production are comparatively complicated in process configuration, including an acid gas removal process and a PSA process for 99.99% pure H_2. These processes are energy-intensive and high-cost with large amounts of carbon dioxide (CO_2) emissions [10]. The post-purification process produced 13.7 kg of CO_2 per 1 kg of H_2. The post-purification process of SMR technology accounted for approximately 30% of the total capital cost and it expended 50–60 € per tonne CO_2 captured at the technical level of the day [11–13]. With the increase of hydrogen demand, it is eagerly expected that hydrogen production process is high-efficiency, environment-friendly and cost-effective. Cormos et al. proposed and systematically investigated the innovative hydrogen and power co-generation process based on the co-gasification of coal with or without addition of various alternative fuels with carbon capture and storage (CCS) and attained a flexible ratio of power and hydrogen in the range of 400 MW electricity and 0–200 MW hydrogen with 90% carbon capture rate [1,7,14,15]. In recent years, there have been many significant developments in hydrogen production using renewable resources such as biomass to decrease the dependence on fossil fuels. The chemical looping (CL) strategy is considered as a promising alternative option for hydrogen production.

The CL strategy was exploited by Lewis and Gilliland to produce CO_2 utilizing carbonaceous fuels early in the 1950s [16]. It has been proposed to achieve high efficient combustion or gasification of carbonaceous fuels with inherent CO_2 capture [17]. Chemical looping combustion (CLC) is a novel and flameless combustion mode mainly comprised of a fuel reactor (FR), an air combustion reactor (AR), and oxygen carrier (OC). The oxygen in air is indirectly transmitted to the fuel in FR by virtue of the redox reaction of OC circulating between two reactors. One of the greatest advantages of CLC is that CO_2 produced is easily separated for sequestration. In CLC, the oxygen from air required for fuel oxidation reaction is transmitted to fuel by means of oxygen carriers. The direct contact between air and fuel is avoided, which essentially prevents the product CO_2 from being mixed with a large amount of nitrogen from combustion air. A concentrated stream of CO_2 free from dilution with nitrogen can be obtained only through condensing the water vapor. For decades, extensive research has been carried out focusing on CLC utilizing various carbonaceous fuels available, including the development of OC, the reactor design and the process synthesis [18–20]. With the growing demand of hydrogen and increasingly stringent CO_2 emission limits, the CL strategy for hydrogen production shows potential advantages. A novel hydrogen production process based on the cyclic redox reaction was proposed and referred as chemical looping hydrogen (CLH) [21], which was a three-reactor CL process using iron oxides as OC, as shown in Fig. 1.

Compared with the CLC process, the CLH process adds a steam oxidation reactor (SR) to produce high-concentrated hydrogen. The CLH process is actually an integration of the mature steam-iron process and the innovative chemical looping combustion process [22]. The hydrocarbon feedstock is fully oxidized to CO_2 and H_2O by the hematite (Fe_2O_3) and

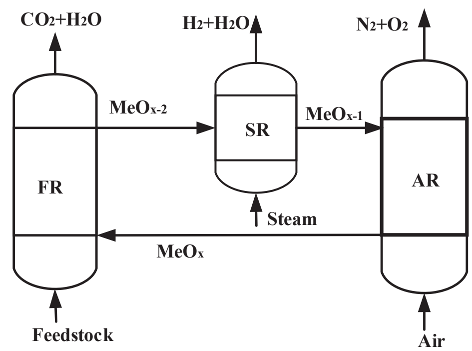

Fig. 1 – Schematic diagram of CLH process with three reactors.

Fe_2O_3 is reduced to a lower valent state simultaneously in FR. Then the partially or fully reduced OC from FR reacts with steam to produce hydrogen and is partially oxidized to the magnetite (Fe_3O_4) in SR. Lastly Fe_3O_4 from SR is further oxidized by oxygen from air to its original oxidation state in AR. Hence the separation of H_2 from CO_2 is completed spontaneously. Currently, Fe_2O_3 is considered as the most suitable OC for the CLH process on the basis of thermodynamic analysis [23–25]. Furthermore, Fe_2O_3 abundant in the nature is low-cost and environmentally friendly.

The CLH technology is in development and has attracted great attention by virtue of inherent separation of CO_2 and H_2O at a low-cost way. The CLH process needs to satisfy the demand of complete conversion of hydrocarbon feedstock and hydrogen production simultaneously. Many researchers have performed experimental investigation including the suitable oxygen carrier, the feasible reactor structure and the optimum operating conditions [20,26–28]. Meanwhile several researchers have carried out the study on the energy utilization system integration based on the CLH process for H_2 and power co-generation and its performance evaluation. Xiang et al. investigated the iron-based CL process for co-production of hydrogen and electricity using coal-based syngas as feedstock by means of ASPEN Plus software, and confirmed it feasible and promising [29]. Fan LS research group studied the iron-based CLH process using coal, natural gas and biomass as feedstock respectively and validated it was more efficient than the conventional energy conversion processes [9,19,30]. Cormos et al. carried out continuous research on the various chemical looping systems for hydrogen and power co-generation with CCS using coal and various alternative fuels through process flow modeling and process integration techniques, and confirmed the iron-based direct chemical looping option was the most efficient design with net electrical efficiency higher than 41%, carbon capture efficiency greater than 99%, and a carbon capture energy penalty in the range of 3.2 net electricity percentage points [31–34]. The above-mentioned researches greatly contribute to further insight into the CLH technology.

Nowadays much attention has been paid to the application of biomass and its derivatives in order to reduce the fossil CO_2 emissions. Bio-oil derived from biomass fast pyrolysis is a renewable liquid fuel comprising of aqueous phase and organic phase. The aqueous phase contains many kinds of