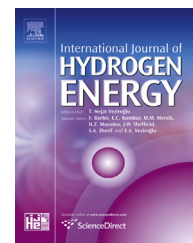




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Use of heavy fraction of bio-oil as fuel for hydrogen production in iron-based chemical looping process

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ABSTRACT

Chemical looping hydrogen (CLH) process with renewable energy sources as fuel shows the potential of producing pure hydrogen with inherent capture of CO₂ in a low-cost and sustainable way. The heavy fraction (HF) of bio-oil, derived from the fast pyrolysis of biomass and characterized as an energy carrier with difficulty in upgrading itself to bio-fuel or chemicals, was used in this study to generate H₂. Four low-cost iron-based oxygen carriers including an ilmenite and three iron ores were initially evaluated with respect to their reducibility and the ability to minimize carbon or iron carbide (Fe₃C) formation in a thermogravimetric analyzer (TGA). The reactivity and cyclic performance of the selected best candidate was then assessed in a laboratory scale fixed-bed reactor with HF bio-oil as fuel. The screening test in TGA showed that ilmenite was superior over the three iron ores in terms of promoting CO conversion and minimizing carbon or Fe₃C formation. Ilmenite could maintain its increasing reducibility with the increase of surrounding CO concentration, in contrast with the iron ores that were deactivated seriously by the formed carbon or Fe₃C. Subsequent CLH test with ilmenite and HF bio-oil showed that the reducibility and H₂ production capacity of ilmenite were strongly dependent on the operating temperature. The steam oxidation step at 950 °C yielded H₂ concentration and hydrogen yield exceeding all of those observed at the other investigated temperatures because of the deepest reduction degree of ilmenite at 950 °C. The decrease in the reducibility and H₂ production capacity of ilmenite in the cyclic test could be ascribed to the poorer physical structure of ilmenite with cycles.

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Introduction

Hydrogen, as a versatile energy carrier, holds great promises to secure the energy supply and help address the

environmental problems that confront with today's fossil fuel-based energy system. Currently, hydrogen is predominantly derived from the fossil fuels. Among the developed and immature hydrogen production technologies [1,2], steam-methane reforming (SMR) is the major well established and

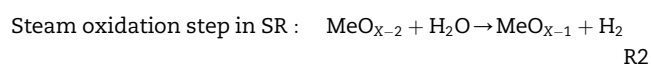
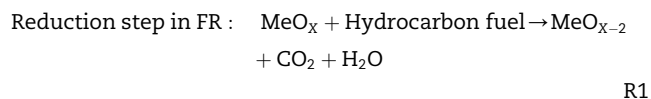
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more economically competitive technology which offers about 48% of the world's total hydrogen [3]. However, the primary drawbacks associated with SMR are: the large amount of methane burnt to maintain the high reformer temperature [4], the energy intensive post-purification of hydrogen [5] and the operating complexity with a lot of units involved in the operation process. In response to the growing demand on the hydrogen energy and the heightening concerns on the environmental problems, a cyclic redox hydrogen production process, referred as chemical looping hydrogen (CLH) [6], was developed and has attracted great concern by virtue of its high energy efficiency and the inherent separation of CO₂ at a low-cost.

The operating concept behind the CLH process is an upgrade of the existing steam-iron process by combining the chemical-looping combustion (CLC) process. The CLH process requires a third reactor equipped in the steam-iron reactor system to maintain the overall system heat balance and regenerate the oxygen carrier [6]. The schematic diagram of the CLH process is shown in Fig. 1. A typical CLH unit consists of a fuel reactor (FR), a steam reactor (SR) and an air reactor (AR). The CLH process is achieved by the oxygen carrier particles circulating among these three reactors to produce pure CO₂ in FR and high-purity H₂ in SR. In FR, the oxygen carrier is reduced by the hydrocarbon fuel to a lower valent state as shown in Reaction R1. Then the partially or fully reduced oxygen carrier is transferred to SR where the oxygen carrier is partially oxidized to an intermediate product and the hydrogen is generated by the water splitting reaction (Reaction R2). The partially oxidized oxygen carrier from SR is further oxidized by air to its original oxidation state in AR (Reaction R3).



Oxygen carrier is one of the most important parameters to determine the overall efficiency of a CL process. Extensive study on the oxygen carrier selection confirms the following

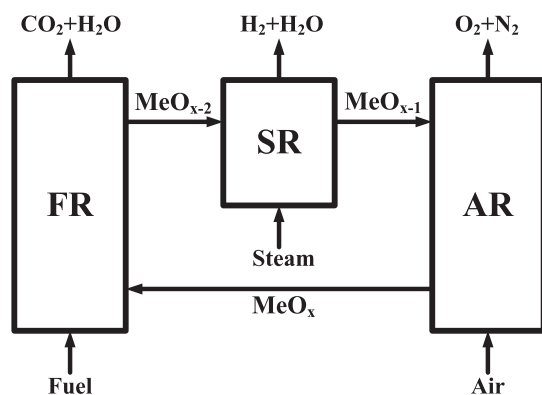


Fig. 1 – Schematic diagram of CLH process.

general criteria that the oxygen carrier should meet: thermodynamically capable to complete conversion of fuel to CO₂ and H₂O, high reactivity and regenerability during successive redox cycles, good resistance to avoid agglomeration, high mechanical strength to minimize attrition, minimum carbon formation, low manufacturing cost and environmental benign. Different redox pairs of transition metal oxides are proposed as oxygen carrier candidates in CLC, such as NiO/Ni, CuO/Cu, Fe₂O₃/Fe, Mn₂O₃/Mn and CoO/Co. However, the above mentioned oxygen carriers suitable for CLC process may not be appropriate for the CLH process, as the additional steam oxidation step in CLH requires the oxygen carrier having an extra important property to react with water to produce H₂. Thermodynamically analysis on the proposed oxygen carriers and other possible metal oxides by Gupta et al. [7] confirmed that iron-based oxygen carrier was the most appealing candidate with the best conversion of syngas to CO₂ and H₂O along with a high steam conversion to hydrogen in CLH process. Up to now, most of the iron-based oxygen carriers applied in CLH process have been synthetically prepared, in which extensive research on the oxygen carrier development has been done in Fan's group at Ohio State University in the past few years [8]. Over 600 oxygen carriers prepared by varying the support/metal oxides composition and synthesis method have been tested in different prototype units and confirmed to be still under excellent condition after sustaining over 100 redox reaction cycles [9]. Recently, a 25 kWth sub-pilot CLH reactor has been designed, constructed and operated in Fan's group [10,11] using synthetic oxygen carriers. The H₂ purity higher than 99.99% with 100% carbon capture has been achieved in this sub-pilot unit. However, as the synthetic oxygen carrier is associated with high manufacturing cost and high raw material price, low-cost natural ores and industrial wastes have attracted great attention and been extensively applied in chemical looping process for fuel conversion [12–14] as oxygen carrier and for tar cleaning as catalyst during biomass gasification [15–17], due to their moderate reactivity, high recyclability, low-cost and minimum environmental impact, but the study on the CLH process with the application of low-cost iron-based oxygen carriers is rare.

Application of various types of fuels (gaseous, solid and liquid fuels) as the feedstock helps to deepen our understanding on the CL technology. Previous research in CLH and steam-iron process mainly concentrated on the assessment of methane and coal in different prototype units [18–20]. In comparison with coal resources, methane is a more efficient feedstock, as methane requires no solid handling due to its gaseous form and the H₂ production efficiency is higher than the efficiency obtained with coal as feedstock [21]. However, methane could only get its comparative advantage when the methane price is low. In viewing of the massive amount of CO₂ released with hydrocarbon fuels as feedstock, the use of biomass or its derivatives enables a carbon neutral means of making H₂ and offers the possibility to minimize the dependence on the non-renewable fossil fuels. However, the decentralized nature of biomass distribution determines that H₂ could only be produced in huge amount of small plants, thermal decomposition of the low-grade biomass to high density liquids, commonly referred as bio-oil, and collecting the produced liquid bio-oil from small plants to a big

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