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Iron oxide looping for natural gas conversion in a countercurrent moving bed reactor

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HIGHLIGHTS

- Countercurrent moving bed studied for chemical looping conversion of natural gas.
- Thermodynamic criteria developed using Ellingham diagram and ASPEN Plus Gibbs model.
- Critical Fe_2O_3/CH_4 molar ratio is determined for complete CH_4 conversion.
- The advantages of the proposed moving bed reactor design are proofed with both the modeling and bench scale experimental results.

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ABSTRACT

Chemical looping technologies have the potential to reduce the natural-gas conversion cost in a carbon-constrained scenario. Given the increasing importance of natural gas to global energy supply, this work investigates the application of an iron oxide based chemical looping technology for natural gas conversion. A thermodynamic criterion for selecting iron oxide based oxygen carrier material and designing the reaction system is developed using an adapted Ellingham diagram. Equilibrium modeling for detailed thermodynamic analysis is conducted for verifying the Ellingham diagram analysis. The thermodynamic equilibrium model also establishes a system baseline performance, and experimental proof of concept bench-scale demonstration is investigated. The bench-scale testing is used to characterize the effect of parameters like solids to gas ratio and temperature of the reactor on system performance. An optimal set of operating conditions is identified for further testing on a larger scale.

1. Introduction

The evolving natural gas consumption could significantly alter the energy infrastructure for the next few decades [1]. Technology advancements such as hydraulic fracturing enable the vast reserves of unconventional gas such as shale gas to be retrieved in a safe and cost-effective manner. The U.S. Energy Information Administration predicts a rapid increase in shale gas supply from 5.0 trillion cubic feet in 2010 to 19.6 trillion cubic feet in 2040, switching the U.S. from a natural gas importer to a net exporter [2]. Natural gas is mainly composed of methane (CH_4), which is an important fuel and chemical feedstock. Methane combustion with air (Reaction (1)) is generally used in a boiler and/or a gas turbine for heat and electricity generation.

$$0.5CH_4 + O_2 = 0.5CO_2 + H_2O \quad (1)$$

Natural gas is also a dominant source for hydrogen (H_2) production, usually involving the steam methane reforming (Reaction (2)) and water gas shift reactions (Reaction (3)).

$$CH_4 + H_2O = CO + 3H_2 \quad (2)$$

$$CO + H_2O = CO_2 + H_2 \quad (3)$$

Natural gas conversion processes for electricity or hydrogen production generate carbon dioxide (CO_2) as a by-product, which is considered to be the largest contributor to global warming. Newer technology development in electricity and hydrogen production is focused on reducing these emissions via carbon capture and storage [3]. In conventional natural gas processing technologies, CO_2 separation results in a significant energy and cost penalty. For example, CO_2 capture with amine based adsorption will decrease a natural gas combined cycle (NGCC) process efficiency

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by ~8% and increase the cost of electricity by ~44% [4]. For the conventional natural-gas to H_2 production process, CO_2 removal units take up to 50% of the total capital cost [5]. Novel technologies, such as chemical looping processes, have been developed to improve the efficiency and reduce the cost for natural gas conversion with CO_2 capture [6–8].

The chemical looping scheme prevents the direct mixing between natural gas and the oxidizing gas. Oxygen carrier particles (typically metal oxide based materials) are used to transfer the oxygen from air (Reaction (4)) and/or steam (Reaction (5)) to methane (Reaction (6)).

$$O_2 + 2Me = 2MeO \quad (4)$$

$$H_2O + Me = H_2 + MeO \quad (5)$$

$$CH_4 + 4MeO = CO_2 + 2H_2O + 4Me \quad (6)$$

Here, Me and MeO refer to lower and higher oxidation state metal oxides, respectively. The summation of Reactions (4) and (6) equates to Reaction (1) for heat and electricity production. Similarly, the combination of Reactions (5) and (6) can equivalently replace the combination of Reactions (2) and (3) for hydrogen generation. The reactors used to perform Reactions (4)–(6) are named the combustor (or air reactor), oxidizer (or hydrogen reactor), and reducer (or fuel reactor), respectively. The salient feature of the chemical looping approach is its capability of *in-situ* CO_2 capture. In the traditional processes, CH_4 conversion and CO_2 separation usually take place in multiple individual unit operations. The chemical looping approach can integrate the CH_4 conversion and CO_2 separation in one step via Reaction (6), and serves to intensify the overall natural gas processing technology.

Significant research efforts have been completed for investigating chemical looping combustion for natural gas to electricity application [8–16]. Some recent developments have been directed toward hydrogen production [9,10,17]. The selection of an oxygen carrier material determines the reactor design and limits of the overall process performance [18]. Nickel oxide based materials have been widely developed and applied for methane conversion because of its fast kinetics for methane conversion [17,18]. The thermodynamics of NiO/Ni, however, restrict the steam to H_2 conversion in Reaction (5) and CH_4 conversion in Reaction (6) [19,20]. In addition, the high cost of nickel-based materials inhibits its further scale up for commercial application. In comparison, iron oxide based materials are considered to be affordable and functional in chemical looping conversion of natural gas [21,22].

Ohio State's iron-based chemical looping process with hydrogen generation consists of three reactors as shown in Fig. 1: a reducer, an oxidizer, and a combustor. The reducer reactor converts the natural gas to CO_2/H_2O while reducing the oxygen carrier (Fe_2O_3) to a lower oxidation state (Fe/FeO). The oxidizer partially re-oxidizes the oxygen carrier from Fe/FeO to Fe_3O_4 oxidation state with steam while generating H_2 in the gas product stream. The combustor then fully re-oxidizes the oxygen carrier particles to Fe_2O_3 while producing heat and oxygen-depleted air. The exothermic reaction is controlled by in-bed heat exchange and excess air flow in the combustor such that the temperature of the regenerated particle is high enough to drive the endothermic reactions in the reducer yet not excessively high to melt the particle. Heat can be also recovered in the combustor spent air. Above the combustor, the riser pneumatically conveys the oxygen carrier to the top of the process through a separation device such as a cyclone, which separates the oxygen-depleted air stream from the solid particles. The oxygen carrier in OSU's chemical looping process is several mm for circulating moving bed applications as compared to several hundred micron for circulating fluidized bed. The larger size particle

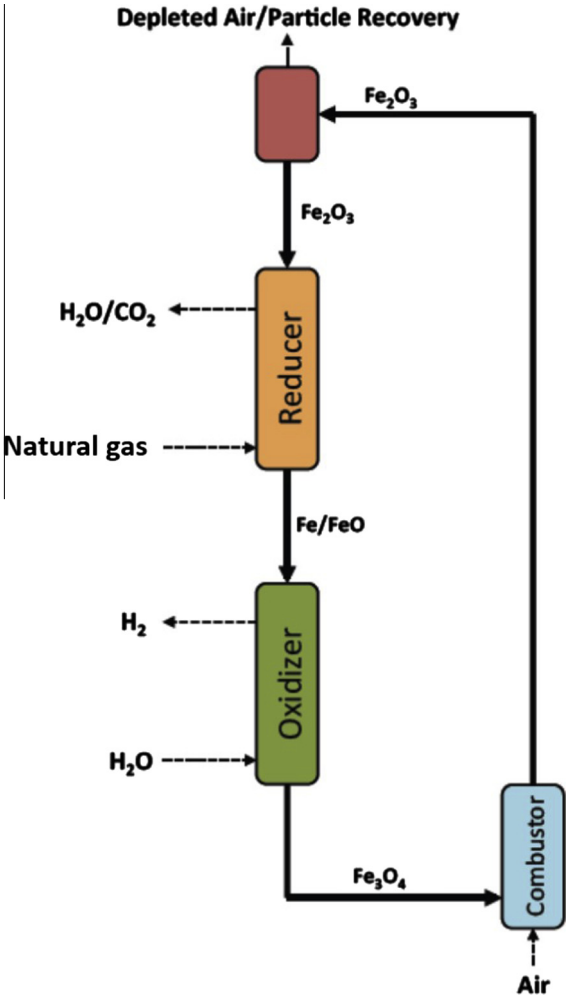

Fig. 1. Chemical looping process for hydrogen production and carbon capture.

has been tested under many reduction oxidation cycles and is straightforward to fluidize as shown in previous studies [9,10].

An important portion of a chemical looping reactor system is the reducer reactor, as its main role is to reduce the oxygen carrier properly and efficiently while producing a pure stream of sequestration-ready carbon dioxide. There exist a great number of publications studying fluidized bed chemical looping combustion using methane [23–27], yet there are few that study moving bed. A prototype countercurrent moving bed bench scale unit was initially studied by Li et al. using iron oxide to convert syngas and methane [28,29]. The system ran for 15 h with syngas conversions higher than 99.5% and an iron oxide conversion of 50% (mol O consumed per total mol O in Fe_2O_3) [28]. Similarly, Tong et al. have performed parametric studies on a 25 kW_{th} moving-bed reducer reactor by changing the gas hourly space velocity of the natural gas injected [30]. Their results show that high conversion of methane (~98%) can be achieved at a number of conditions within reducer temperatures of 930 and 975 °C, methane flows from 2 to 5 slpm, and oxygen carrier flow rate of 150 g/min. These results showed high conversion of oxygen carrier, with the maximum oxygen carrier conversion being 43.6% at 98.9% methane conversion [30]. The Korean Institute of Energy Research has also considered using a moving bed for its Three Reactor Chemical Looping (TRCL) system [31]. Countercurrent moving beds have also been studied by Wu et al. [32] and Chiu [33,34] at The National Taiwan University of Science and Technology to determine the proper conditions for complete methane conversion in a moving bed consisting of iron and aluminum oxide. They have tested

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