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Hydrogen production from natural gas using an iron-based chemical looping technology: Thermodynamic simulations and process system analysis

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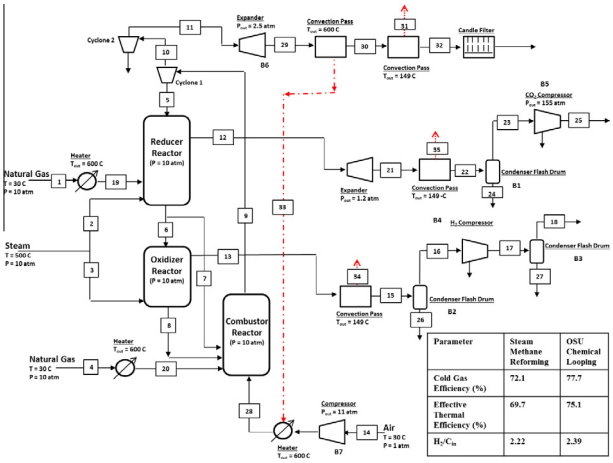
HIGHLIGHTS

- Design of iron-based chemical looping process using moving bed for H_2 from CH_4.
- Auto-thermal operation design using thermodynamic rationale for 90% carbon capture.
- Cold gas efficiency: 5% points higher than Steam Methane Reforming baseline case.
- Net thermal efficiency: 6% points higher than Steam Methane Reforming baseline case.
- Sensitivity analysis: Energy recovery scheme, operating pressure, no carbon capture.

GRAPHICAL ABSTRACT



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ABSTRACT

Hydrogen (H_2) is a secondary fuel derived from natural gas. Currently, H_2 serves as an important component in refining operations, fertilizer production, and is experiencing increased utilization in the transportation industry as a clean combustion fuel. In recent years, industry and academia have focused on developing technology that reduces carbon emissions. As a result, there has been an increase in the technological developments for producing H_2 from natural gas. These technologies aim to minimize the cost increment associated with clean energy production. The natural gas processing chemical looping technology, developed at The Ohio State University (OSU), employs an iron-based oxygen carrier and a novel gas–solid counter-current moving bed reactor for H_2 production. Specifically, this study examines the theoretical thermodynamic limits for full conversion of natural gas through iron-based oxygen carrier reactions with methane (CH_4), by utilizing simulations generated with ASPEN modeling software. This study initially investigates the reducer and the oxidizer thermodynamic phase diagrams then derives an optimal auto-thermal operating condition for the complete loop simulation. This complete loop simulation is initially normalized for analysis on the basis of one mole of carbon input from natural gas. The H_2 production rate is then scaled to match that of the baseline study, using a full-scale ASPEN simulation for computing cooling loads, water requirements and net parasitic energy consumption. The full scale ASPEN simulation is used to analyze the thermal efficiency of multiple energy recovery schemes, for

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Nomenclature

x_1	fraction of solids exiting the reducer and going to the combustor (kg/kg)
x_2	fraction of solids exiting the reducer and going to the oxidizer (kg/kg)
ΔH^{o}_{298}	enthalpy of the specified reaction at 298 K (kJ/mol)
$\Delta H_{reducer}$	enthalpy of the net reaction of the reducer reactor at a specified temperature
$\Delta H_{oxidizer}$	enthalpy of the net reaction of the reducer reactor at a specified temperature
$\Delta H_{combustor}$	enthalpy of the net reaction of the reducer reactor at a specified temperature
gpm	gallons per minute
HHV	higher heating value
ppm	parts per million
ppmv	parts per million by volume
% w/w	percentage weight fraction of the specific component in a mixture of components
kW_e	kilo Watts electric
kW_{th}	kilo Watts thermal
MJ/kg	megajoule per kilograms
kmol/h	kilomole per hour
kg/h	kilogram per hour
% v/v	volume fraction of the specified component in a mixture of components
J/kmol	Joule per kilomole
CGE	cold gas efficiency (ratio of HHV of products to HHV of reactants)
ETE	effective thermal efficiency (ratio of HHV of products plus parasitic energy consumption to the HHV of reactants)
OSU	The Ohio State University
DOE/USDOE	The United States department of energy
SMR	steam methane reforming technology
AGR	acid gas removal technology
mmBtu/h	million british thermal units per hour
PSA	pressure swing adsorption
CL	chemical looping
BOP	balance of plant

further validation of the chemical looping process. Resulting from this study, the chemical looping technology is found to produce a cold gas efficiency improvement of more than 5 percentage points and an effective thermal efficiency of more than 6 percentage points over the conventional steam methane reforming process, while producing H_2 from natural gas with greater than 90% carbon capture.

1. Introduction

Hydrogen (H_2) is an emission-free energy carrier which can potentially be used to satisfy all the energy needs of the human population. Industry and academia recognize the potential of H_2 and have made considerable investments in research that focuses on de-risking parameters that are critical to wide-spread utilization [1–3]. Currently H_2 is used mainly in ammonia synthesizing facilities for urea (fertilizer production), in the refining of crude oil for use in the transportation sector and in methanol production facilities. Technologies that propose to utilize H_2 as transportation fuel are able to efficiently address the challenge of curbing emissions resulting from non-point, non-stationary sources like vehicles, as H_2 combustion does not produce carbon emissions [4]. While the combustion of H_2 is emission free, its production is not. H_2 is a secondary fuel derived from primary sources of energy like fossil fuels [5–7]. Despite a considerable volume of research on developing non-fossil fuel based technologies, natural gas based technologies continue to dominate the H_2 production market [8–10]. More than 95% of the world's H_2 production comes from natural-gas. Wide-spread development of technologies utilizing H_2 can help increase the energy security of a country with rich natural gas reserves, such as the USA, by reducing dependence on imported oil [11–14]. Currently, greater than 90% of all the H_2 produced in the USA utilizes steam–methane reforming (SMR) technology. During SMR a natural gas feed is reacted with steam in reformer tubes lined with a Nickel based catalyst to produce syngas [15–17]. Fig. 1 shows the SMR case for H_2 production with >90% carbon capture as analyzed in Case 1-1, in the U.S. Department of Energy (DOE) report titled Assessment of Hydrogen Production with CO_2 Capture Volume 1: Baseline State-of-the-Art Plants [18].

Reactions shown in Eqs. (1) and (2) constitute the primary reactions in the reformer tubes. Reaction (1) is the dominant of the two under high temperature reactor conditions ($T \sim 900\ ^{\circ}C$).

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H^{o}_{298} = +206\ kJ/mol \tag{1}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H^{o}_{298} = -41\ kJ/mol \tag{2}$$

The overall reaction in SMR is endothermic in nature. The energy required to maintain high heat demand is supplied by combusting a fraction of the recycled fuel gas and a small split of the natural gas feed (~10% v/v). The syngas produced is subjected to a two-stage water–gas shift reactor to produce more H_2 by way of reaction in Eq. (2). H_2 is separated from the syngas using a pressure swing adsorption (PSA) unit. In a carbon constrained scenario, two separate acid gas removal (AGR) CO_2 separation units are required to produce a sequester-ready CO_2 stream as shown in Fig. 1. One AGR unit is used on the syngas clean-up stream while the other is used to separate CO_2 from the combustion product outside of the reformer tubes. The typical SMR cold-gas efficiency (CGE) with $\geqslant$90% CO_2 capture is ~72% (HHV basis) [18]. The benefits associated with eliminating downstream clean-up costs are a major motivation driving the development of technologies, like chemical looping, that have the potential for significant improvement over the baseline SMR process [19,20].

Chemical looping technologies are being investigated to reduce the cost of H_2 production from CH_4 with controlled carbon emissions [19–21]. There have been several chemical looping based research approaches directed toward reducing the energy consumption and improving efficiency for generating H_2 from natural gas with CO_2 capture. These can be conceptually classified into three general areas based on the technology focus.

The first set of approaches deals with intensifying the conventional SMR process with CO_2 capture by supplying the endothermic