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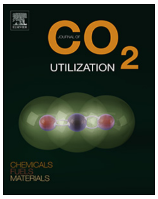

CO_2 conversion to syngas through the steam-biogas reforming process

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ABSTRACT

The steam-biogas reforming (SBR) process to convert biogas to a high hydrogen syngas was studied experimentally and using Aspen Plus simulations. An integrated renewable power generation system where the SBR process was coupled with a Solid Oxide Fuel Cell (SOFC) was studied using the Aspen Plus model. The experimental work was conducted over a metal-foam-coated [Pd(7)-Rh(1)]/[$CeZrO_2$(25)-Al_2O_3(75)] catalyst in a Heat Exchanger Platform (HEP) reactor. SBR simulations were conducted for biogas feeds with CH_4/CO_2 ratios of 40/60, 50/50 and 60/40 at S/C ratios of 1.00–2.00 over a temperature range of 873–1123 K. The experimental data show that positive CO_2 conversion was attainable only at temperatures higher than 1073 K, although the equilibrium based simulation predicts positive CO_2 conversion through most of the operating temperature range. Energy efficiency of the overall system was approximately 40% at temperatures of 948 K and above. Coke formation over the Pd-Rh catalyst was estimated to be 1.05–2.88% of the carbon input to the system. Fresh and used catalysts were characterized by BET adsorption, porosimetry, CO chemisorption and Scanning Electron Microscopy. The results show that the proposed system can provide a viable approach to utilizing distributed renewable methane resources for localized power generation.

1. Introduction

The distributed nature of renewable energy sources, particularly carbon based resources, is a major barrier to achieving economically viable utilization. Landfill gas (LFG) and biogas are the primary sources of renewable methane around the world. However, LFG sources are often not developed or are flared due to economic constraints. Of the facilities under operation, most achieve low thermal efficiencies, typically in the range of 20–40% with 25% being the most common value [1]. New technology options with improved efficiency but reduced costs are necessary to enable increased utilization.

LFG normally contains 40–60% CO_2 along with moisture and other contaminants. Although gas compositions from different sources vary widely, there are several contaminants and compounds that are commonly found in most LFG streams: sulfur compounds, halogenated compounds, ammonia, silicon compounds and siloxanes, and particulate matter [2]. The contaminants must be removed from the raw LFG during the upgrading process. Technologies for LFG cleanup include water scrubbing, cryogenic separation, physical absorption, chemical absorption, pressure swing adsorption, membrane separation, in-situ upgrading and biological upgrading methods [2]. Depending on the source of LFG, the energy consumption of the cleanup process is about 0.05–0.15 MJ/MJ LFG [2] which has a significant impact on the net process efficiency.

Converting the CO_2 in the LFG along with CH_4 into syngas (H_2 + CO), instead of separating and venting it, can offer multiple benefits that are discussed elsewhere [3]. The research team has experimentally evaluated the combined steam and CO_2 reforming of methane, referred to as ‘bi-reforming’ or Steam Biogas Reforming (SBR) [3–6]. The chemical reactions associated with methane reforming are listed below. Since both CH_4 and CO_2 are present in LFG, combined reforming with steam and CO_2 is particularly attractive. The product syngas can be converted into electricity in conventional systems or in a Solid Oxide Fuel Cell (SOFC), as proposed in this study.

$$\text{Steam Methane Reforming (SMR): } CH_4 + H_2O \rightarrow 3H_2 + CO \quad \Delta H^{\theta} = 206.1\ \text{kJ/mol} \tag{1}$$

$$\text{Water-gas Shift (WGS): } CO + H_2O \rightarrow H_2 + CO_2 \quad \Delta H^{\theta} = -41.2\ \text{kJ/mol} \tag{2}$$

$$\text{Dry Reforming (DR): } CH_4 + CO_2 \rightarrow 2H_2 + 2CO \quad \Delta H^{\theta} = 247.3\ \text{kJ/mol} \tag{3}$$

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$$\text{CH}_4\text{ Dehydrogenation: } CH_4 \rightarrow 2H_2 + C \qquad \Delta H^{\theta} = 74.82\text{ kJ/mol} \tag{4}$$

$$\text{SBR reaction: } 2CH_4 + H_2O + CO_2 \rightarrow 5H_2 + 3CO \qquad \Delta H^{\theta} = 453.4\text{ kJ/mol} \tag{5}$$

The dry reforming (DR) reaction is more energy intensive compared to the well-known steam reforming reaction (SMR) and is prone to coke formation through the CH_4 dehydrogenation reaction. Carbon deposition over the catalyst surface is rapid and inhibits catalyst activity. Steam addition to the dry reforming reaction leads to significant mitigation of coke deposition.

Once the CH_4 is converted to H_2, fuel cells offer an important technology option for power generation in small to medium scale localized projects that do not require expansive infrastructure. Fuel cells are commercially used in a wide range of applications, including but not limited to: medium to large power stations, distributed generation in buildings, small/portable power supply equipment, and auxiliary power units in vehicles [7]. The degree of hydrogen purity required by fuel cells is dependent on the type of fuel cell and the desired application. Systems with high hydrogen purity requirement are generally not suited for renewable energy projects due to the costs associated with high grade purification. Fuel cells that can tolerate other gas species, especially carbon monoxide, are highly desirable since natural gas reforming produces syngas (H_2 + CO) that must be upgraded to pure hydrogen. From this perspective, suitable candidates for such applications include Molten Carbonate Fuel Cells (MCFC) and Solid Oxide Fuel Cells (SOFC). These fuel cells are capable of using H_2 streams with higher CO concentrations and therefore offer the possibility of coupled reforming and fuel cell systems [8]. SOFCs are among the most studied fuel cell options due to their high conversion efficiencies and the potential ability to handle other fuels in addition to H_2 [7,9,10]. Here, we study the conversion of CH_4, CO_2, and steam into a high hydrogen syngas using the ‘bi-reforming’ reaction in a heat exchanger platform (HEP) reactor. This syngas is then used as the fuel in an SOFC. The energy required for the bi-reforming reaction is supplied by combustion of the SOFC flue gas in alternating compartments of the same HEP reactor.

Steam biogas reforming has been studied using a number of different systems. Galvagno et al., have reported syngas composition from biogas-steam reforming over a wide range of temperatures and pressures using Aspen Plus simulations and over a commercial Ni/Al_2O_3 catalyst [11]. The study also reported that the process thermal efficiency for syngas production through the steam biogas reforming process is between 85 and 95% (efficiency is defined as the ratio of energy out from the reformer to energy in to the reformer) which decreases with increasing temperature. The integration of reforming systems with fuel cells has also been reported in the literature before [11–14]. Chiodo et al., studied the integration of a reforming reaction process with a fuel cell system and found the fuel utilization rate (rate of conversion of fuel input to the fuel cell into electricity) to be approximately 60 to 85% for SOFCs [12]. They also show that for SOFC fuel utilization rates of 55% or less, the integrated reforming process can be sustained through the heat generated by the SOFC and flue gas combustion. Miyake et al., showed that the syngas produced from biogas reforming over Ni/$LaAl_2O_3$ catalyst is an effective feedstock for the SOFC process [15]. Biogas reforming processes coupled with fuel cell systems studied by Farhad et al., [16] and Trendewicz et al., [17] achieved 42.4% and 51.6% electricity generation efficiency, respectively. Van herle et al., showed that the integrated biogas to electricity process efficiency (for plants under operation in Switzerland) can be in the range of 18–36% with the electrical efficiency of the stack at 42% [18].

Angeli et al., used Ni(10)CeZrLa and Rh(1)CeZrLa steam biogas reforming catalysts to achieve 50% methane conversion at 823 K with a steam to methane ratio of 3.0 [19]. The study reports drops in catalyst performance with high deactivation rates when in use for longer time periods (5% after 55 h). The catalysts performance was poor compared to equilibrium predictions. Process parameters (steam to methane ratio, optimum operating condition) also play an important role in improving efficiency and optimization efforts in lab scale studies are reported in the literature [20–23].

Previously reported experimental data using Pd and Rh based catalysts show that bimetallic combination of catalysts perform better than monometallic catalysts by enhancing syngas selectivity, suppressing coke buildup, and mitigating active metal oxidation [6,24–26]. Also $CeZrO_2$-modification of Al_2O_3 as catalytic support material leads to improved catalyst activity, thermal stability and metal dispersion, and reduces coke formation resulting from methane reforming [6,27–29].

Performance analysis of the integrated reforming and end-use systems is a crucial step in selecting viable approaches and optimizing specific combinations. The steam biogas reforming process combined with a SOFC system represents a potentially viable approach and experimental work has been performed on the catalyst. However the process has not been studied in detail as an integrated system. There are no reports available in the literature that compare experimental data and simulation results for the proposed system over a range of conditions in order to identify the preferred operating parameters. This study investigates the performance of the steam-biogas reforming process coupled with SOFC system using a custom built Aspen Plus process model. The simulation results are presented and where relevant, are compared with experimental data obtained over a metal-foam-coated Pd-Rh based catalyst in a compact HEP reactor.

2. Simulation and experimental

2.1. Simulation model

Aspen Plus is a well-known simulation tool that has the ability to model complex chemical processes using built-in process units and physical/chemical property databases. An Aspen Plus model of the integrated system consisting of the fuel reformer, combustor and SOFC simulator process blocks was created for this study. The combustor burns the SOFC stack flue gas and provides heat to fuel reformer located in alternating compartments of the heat exchanger platform (HEP) reactor. Stoichiometric reactor blocks are used to simulate the individual components (SOFC, combustor and reformer). Fig. 1 depicts the process block diagram of the integrated system. Initially, CH_4, CO_2 and water are mixed and heated up before entering the fuel reformer. The feed stream is converted to reformate consisting of mostly syngas, which is directed to the fuel cell along with the air needed for the oxidation of H_2 and CO in the SOFC anode. Flue gas from the fuel cell stack is then fed to the combustor coupled with the fuel reformer. The reformer is modeled using a built in equilibrium reactor that uses the Peng-Robinson equation of state. The combustor coupled with the reformer is a stoichiometric reactor that completely burns the combustible components of the SOFC stack flue gas. The simulation model is used to determine all the material and energy stream rates and the compositions. Equilibrium reactant conversion and product distribution for the SBR process were evaluated for biogas feeds having CH_4/CO_2 ratios of 40/60, 50/50 and 60/40. The process was evaluated at steam/CH_4 (S/C) ratios (mole/mole ratio) of 1.00 to 2.00 with 0.25 increments over a temperature range of 873 K–1123 K. The major assumptions used in the model are:

- Equilibrium is determined through Gibbs free energy minimization.
- Elemental carbon formation is not considered.
- The SOFC converts 70% of H_2 and CO in the reformate gas into electricity.
- SOFC stack flue gas combustion in the HEP reactor uses 40% excess air.
- Additional fuel (CH_4) is supplied to the combustor if needed.