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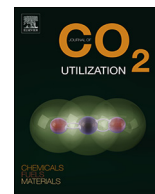


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## CO<sub>2</sub> conversion to syngas through the steam-biogas reforming process

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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<sub>2</sub>(25)-Al<sub>2</sub>O<sub>3</sub>(75)] catalyst in a Heat Exchanger Platform (HEP) reactor. SBR simulations were conducted for biogas feeds with CH<sub>4</sub>/CO<sub>2</sub> 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<sub>2</sub> conversion was attainable only at temperatures higher than 1073 K, although the equilibrium based simulation predicts positive CO<sub>2</sub> 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.

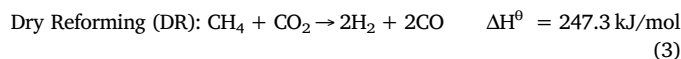
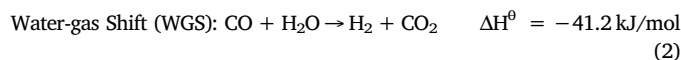
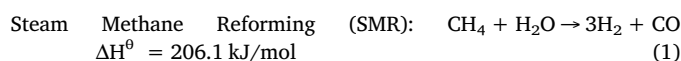
### 1. Introduction

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<sub>2</sub> 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

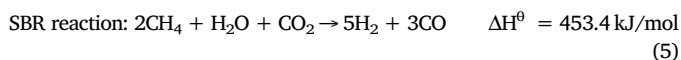
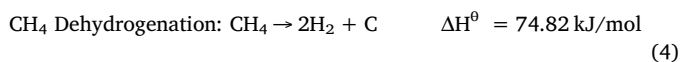
source of LFG, the energy consumption of the cleanup process is about 0.05–0.15 MJ/MJ LFG [2] which has a significant impact on the net process efficiency.

Converting the CO<sub>2</sub> in the LFG along with CH<sub>4</sub> into syngas (H<sub>2</sub> + 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<sub>2</sub> 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<sub>4</sub> and CO<sub>2</sub> are present in LFG, combined reforming with steam and CO<sub>2</sub> 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.



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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<sub>4</sub> 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<sub>4</sub> is converted to H<sub>2</sub>, 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<sub>2</sub> + 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<sub>2</sub> 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<sub>2</sub> [7,9,10]. Here, we study the conversion of CH<sub>4</sub>, CO<sub>2</sub>, 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<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>-modification of Al<sub>2</sub>O<sub>3</sub> 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<sub>4</sub>, CO<sub>2</sub> 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<sub>2</sub> 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<sub>4</sub>/CO<sub>2</sub> ratios of 40/60, 50/50 and 60/40. The process was evaluated at steam/CH<sub>4</sub> (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<sub>2</sub> and CO in the reformate gas into electricity.
- SOFC stack flue gas combustion in the HEP reactor uses 40% excess air.
- Additional fuel (CH<sub>4</sub>) is supplied to the combustor if needed.

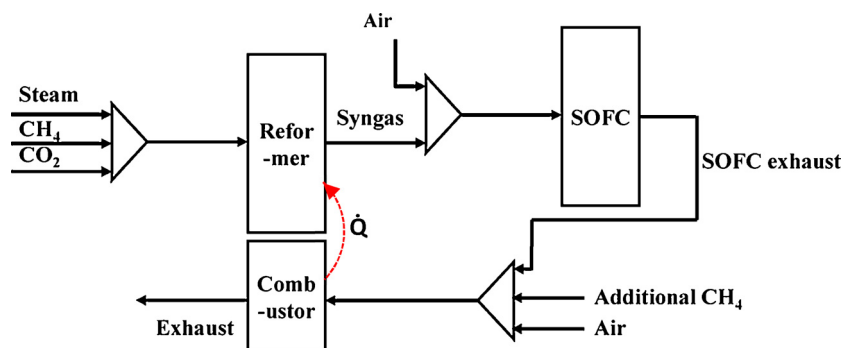


Fig. 1. Process block diagram for the SOFC-integrated steam-biogas reforming process.

## 2.2. Experimental

### 2.2.1. Catalyst

A supported Pd-Rh catalyst was prepared by coating the metal-oxide composites onto metal foam strips made of Ni-Cr-Al alloy. The catalytic composites were made by loading 1.31 wt% Pd(7)-Rh(1) clusters on CeZrO<sub>2</sub>-modified Al<sub>2</sub>O<sub>3</sub> powder having CeZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> wt. ratio of 25/75. Catalyst preparation procedure is described in detail elsewhere [5]. The Pd-Rh catalyst was characterized by nitrogen adsorption and porosimetry (Micromeritics, ASAP 2010), CO pulse chemisorption (BEL, BelCat Analyzer) and Scanning Electron Microscope (JEOL, JSM-5610). Physical properties and chemical composition of the Pd-Rh catalyst free of the metal foam substrate are respectively listed in Tables 1 and 2. Surface and cross-section SEM images of the metal-foam-coated Pd-Rh catalyst are presented in Fig. 2. The EDX data for fresh and used catalysts obtained by using a transmission electron spectroscopy (TEM, Hitachi Ltd., H-7600) is taken as an evidence for any coke deposition. Average metal particle size of the catalyst was less than 2.5 nm as calculated from metal dispersion data.

### 2.2.2. SBR reaction experiments

Reaction runs were conducted in the multichannel HEP reactor (Catacel/Johnson-Matthey), described in previous articles [5]. Metal-foam-coated Pd-Rh catalyst strips were inserted into the reforming side of the reactor through which the reformer feed stream was passed under atmospheric pressure at GHSV (Gas Hourly Space Velocity) of 1400 h<sup>-1</sup>. Several K-type thermocouples installed at different axial positions in the reactor were used to measure the catalyst bed temperature. Combustion side of the HEP reactor was packed with metal-foam-coated catalyst strips prepared by loading Pd-Pt clusters on CeZrO<sub>2</sub>-modified Al<sub>2</sub>O<sub>3</sub> powder. Thermocouples were also installed on the combustion side of the reactor in the same manner as described above. The HEP reactor was enclosed inside a temperature-

Table 1

Physical properties of the metal-foam-coated Pd-Rh/(CeZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) catalyst.

BET surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore size (nm)	Metal dispersion (%)
125.4	0.519	15.0	43.9

Table 2

Chemical composition of the catalytic Pd-Rh/(CeZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) composite wash-coat.

Catalyst	Active metal (wt%)	Oxide (wt%)
Pd-Rh/(CeZrO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> )	Pd-1.15, Rh-0.16	Al <sub>2</sub> O <sub>3</sub> 74.0, CeZrO <sub>2</sub> 24.7

programmed furnace interfaced with a personal computer. The biogas feeds used in the experimental work consisted of 60% CH<sub>4</sub> and 40% CO<sub>2</sub>. Product gas composition from the SBR reaction was analyzed on a dry basis by using a residual gas analyzer (Cirrus, MKS Technologies). Reaction runs were performed at S/C ratio of 1.50 in the range of 873 K–1123 K. SBR performances were evaluated using the following equations:

$$\text{CH}_4 \text{ conversion} = \left( \frac{(\text{CH}_4)_{\text{in}} - (\text{CH}_4)_{\text{out}}}{(\text{CH}_4)_{\text{in}}} \right)_{\text{reformer}}$$

$$\text{CO}_2 \text{ conversion} = \left( \frac{(\text{CO}_2)_{\text{in}} - (\text{CO}_2)_{\text{out}}}{(\text{CO}_2)_{\text{in}}} \right)_{\text{reformer}}$$

$$\text{H}_2/\text{CO} \text{ ratio of the product gas} = \left( \frac{(\text{H}_2)_{\text{out}}}{(\text{CO})_{\text{out}}} \right)_{\text{reformer}}$$

$$\text{Overall system efficiency} = \frac{\text{MW of SOFC}}{\text{MJ/s of CH}_{4\text{in}} + \text{MJ/s of additional fuel in}}$$

$$\text{Coke formation (\%)} = \left( \frac{\text{moles of carbon in the feed} - \text{moles of gaseous carbon in the product gas}}{\text{moles of carbon in the reforming feed}} \right)_{\text{reformer}}$$

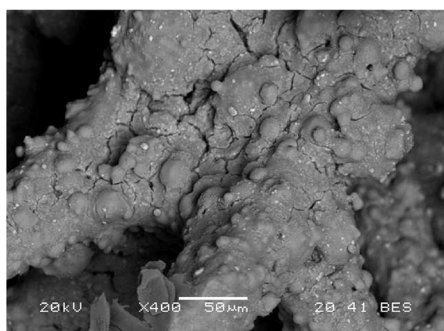
## 3. Results and discussion

### 3.1. Simulation

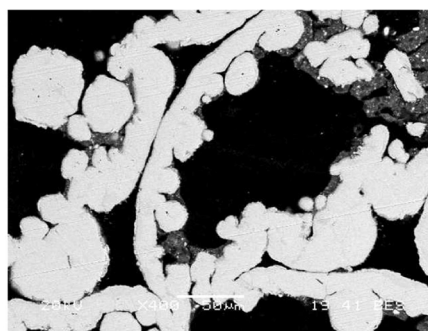
The SBR process evaluated over a wide range of S/C ratios, temperatures and CH<sub>4</sub>/CO<sub>2</sub> ratios using the Aspen Plus simulation model is shown in Fig. 1. The impact of temperature and S/C ratio on the feed conversion and other performance metrics was studied. Higher CH<sub>4</sub> conversion is expected for the SBR process compared to dry reforming of CH<sub>4</sub> alone. Equilibrium CH<sub>4</sub> conversion obtained were higher than 50% at 873 K for all the S/C ratio used in the study as shown in Fig. 3. CH<sub>4</sub> conversion increased by 15% when S/C ratio increased from 1.00 to 2.00, and the difference in CH<sub>4</sub> conversion due to S/C ratio attenuated with increase in temperature. For all the S/C ratios studied, CH<sub>4</sub> conversion reached a maximum of 95% at a temperature of 1023 K, and was steady above this temperature.

Equilibrium CO<sub>2</sub> conversion is negative at some temperatures as shown in Fig. 4. Negative CO<sub>2</sub> conversion indicates net CO<sub>2</sub> generation by the reforming process which decreases with increasing temperature and decreasing S/C ratio. At 950 K and above, CO<sub>2</sub> conversion becomes positive which implies net CO<sub>2</sub> consumption by the process. Reformer temperatures 1023 K or above represent attractive operating conditions with higher than 90% CH<sub>4</sub> conversion and 25% CO<sub>2</sub> conversion for S/C ratios of 1.50 or less.

The SBR reaction occurs inside the HEP reactor with CH<sub>4</sub> being the only energy containing species in the reformer feed. H<sub>2</sub> and CO from the reformer are sent to the SOFC whereas the unreacted CH<sub>4</sub> is



SEM image: catalyst surface



SEM image: catalyst cross-section

Fig. 2. SEM images of the metal-foam-coated Pd-Rh/(CeZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) catalyst.

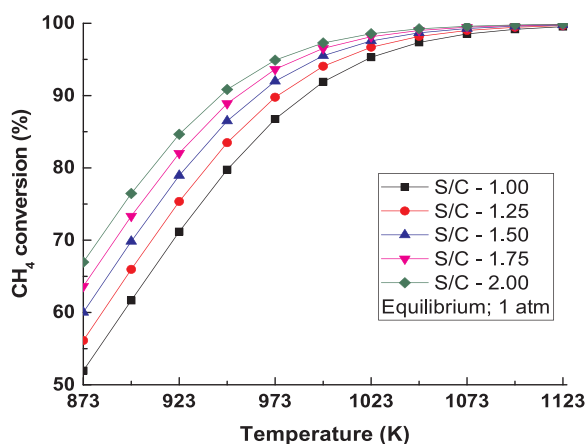


Fig. 3. SBR CH<sub>4</sub> conversion at equilibrium via simulation (CH<sub>4</sub>/CO<sub>2</sub> ratio of 60/40).

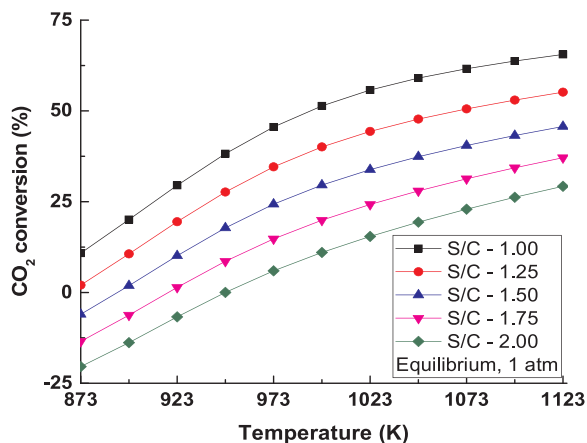


Fig. 4. SBR CO<sub>2</sub> conversion at equilibrium via simulation (CH<sub>4</sub>/CO<sub>2</sub> ratio of 60/40).

supplied back to the combustor located inside the HEP reactor. Heat supply is necessary for the SBR reactions, steam generation and feed pretreatment. All the heat required for the reformer is supplied by the combustion of the unreacted CH<sub>4</sub> from the reformer, H<sub>2</sub> and CO unused by the SOFC and additional fuel in form of CH<sub>4</sub> if needed. Fig. 5 shows the overall system efficiency for different S/C ratios as a function of temperature. The efficiency initially increases with temperature and stabilizes at approximately 1023 K. At lower temperatures, higher S/C ratio leads to higher CH<sub>4</sub> conversions as well as increased syngas production and SOFC output.

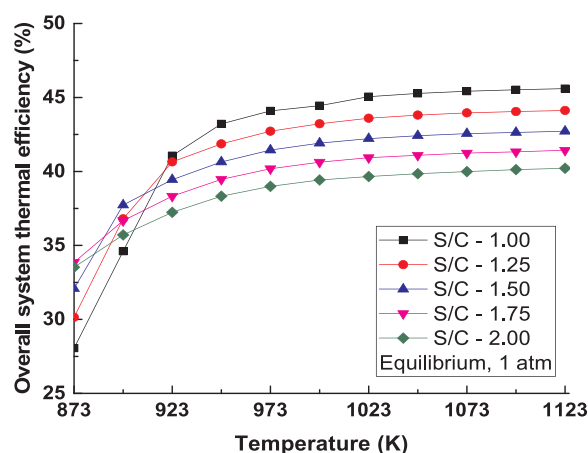


Fig. 5. Overall system efficiency (%) for the SBR equilibrium process integrated with SOFC for the biogas feed with CH<sub>4</sub>/CO<sub>2</sub> ratio of 60/40.

CH<sub>4</sub>/CO<sub>2</sub> ratio is often dependent on the biogas source and is also varied to check the process performance. S/C is maintained at 1.50 at atmospheric pressure while checking the effect of CH<sub>4</sub>/CO<sub>2</sub> ratio on process performance. CH<sub>4</sub> conversion increases with decreasing CH<sub>4</sub> concentration in the feed, and at temperatures above 1073 K CH<sub>4</sub> conversion is mostly independent of the feed composition as shown in Fig. 6(a). A similar trend can be observed for CO<sub>2</sub> conversion, as shown in Fig. 6(b). Overall system efficiency increases with increasing CH<sub>4</sub>/CO<sub>2</sub> ratio as shown in Fig. 6(c).

### 3.2. Catalytic SBR comparison with simulation results

The metal foam supported catalysts, Pd-Rh/Al<sub>2</sub>O<sub>3</sub> modified with CeZrO<sub>2</sub>, demonstrated better performance for steam biogas reforming process during earlier studies [6]. Based on the previously reported experimental results, [Pd(7)-Rh(1)/CeZrO<sub>2</sub>(25)-Al<sub>2</sub>O<sub>3</sub>(75)] was selected as the reforming catalyst for this study. The equilibrium data obtained by Aspen Plus process simulation is compared with the experimental data.

Experimental CH<sub>4</sub> conversion is lower than the equilibrium value over the entire temperature range studied as shown in Fig. 7. A similar trend for CH<sub>4</sub> conversion has been reported in the literature [30,31]. Above 1000 K, the conversion is independent of temperature and the gap between experimental and equilibrium data is also attenuated. The experimental CO<sub>2</sub> conversion data show significant deviation from the equilibrium values. CO<sub>2</sub> conversion also increases with temperature and the trend has been observed previously [31]. The CO<sub>2</sub> is produced by WGS reaction and consumed by both DR and Reverse WGS (RWGS). The WGS reaction thermodynamics is favored at relatively low

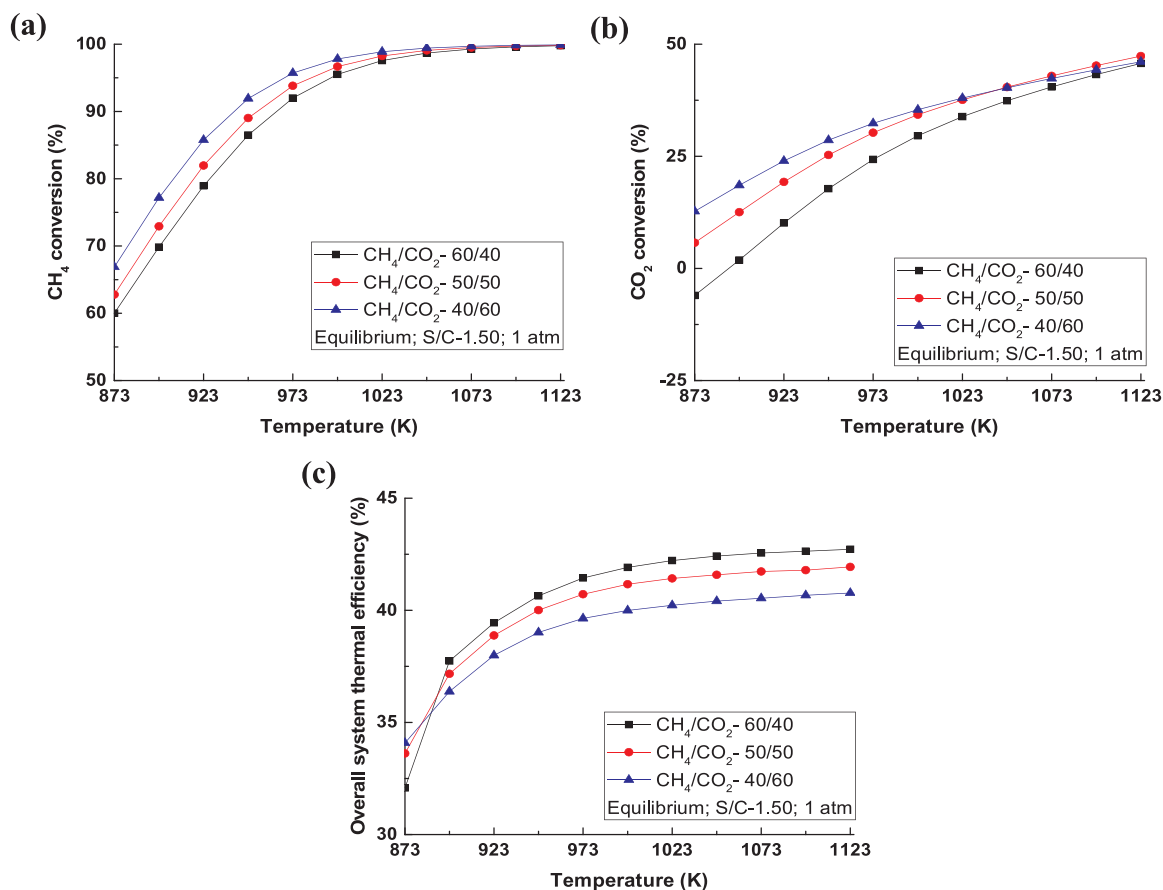


Fig. 6. SBR equilibrium performance for biogas feed with different CH<sub>4</sub>/CO<sub>2</sub> ratios: (a) CH<sub>4</sub> conversion; (b) CO<sub>2</sub> conversion; (c) overall system efficiency.

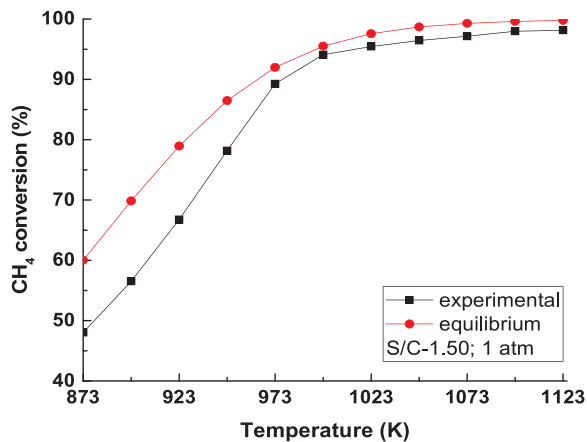


Fig. 7. CH<sub>4</sub> conversion (%) compared between SBR equilibrium simulation and experimental results for the biogas feed with CH<sub>4</sub>/CO<sub>2</sub> ratio of 60/40.

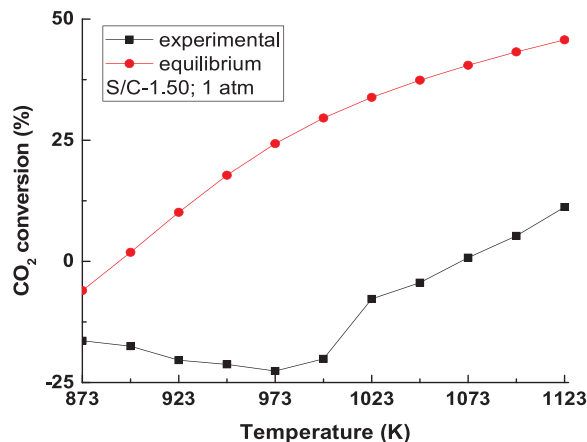


Fig. 8. CO<sub>2</sub> conversion (%) compared between SBR equilibrium simulation and experimental results for the biogas feed with CH<sub>4</sub>/CO<sub>2</sub> ratio of 60/40.

temperatures whereas RWGS is favored over a higher temperature range [32]. Moreover, CO<sub>2</sub> conversion by dry reforming also increases with an increase in temperature. In this experimental study, at temperatures below 1073 K, net CO<sub>2</sub> consumption is not attained due to the WGS reaction dominating; this changes at temperatures of 1073 K and above. The difference between equilibrium and experimental data for CO<sub>2</sub> consumption is shown in Fig. 8 and a similar trend was observed by Ashrafi et al., [30]. They reported that the equilibrium CO<sub>2</sub> conversion decreases with S/C ratio at S/C ratios of 2.00 or higher. Their reported equilibrium CO<sub>2</sub> conversion data at S/C ratio of 2.71 ranged from -37% to 5% in the temperature range of 873 K–1123 K whereas experimental CO<sub>2</sub> conversion ranged from about -27% to 10% in the

same temperature zone which is comparable with this study.

Fig. 9 compares the variation of experimental and equilibrium H<sub>2</sub> fractions in syngas (excluding steam in calculation) with temperature. The experimental values align well with the equilibrium predicted product gas hydrogen fraction. The experimental H<sub>2</sub>/CO ratios, however, are noticeably higher than the equilibrium predicted values (Fig. 10). Experimental CH<sub>4</sub> conversions and H<sub>2</sub> fractions are close to the equilibrium values whereas CO<sub>2</sub> conversions are significantly lower than the equilibrium values. This indicates that the steam reforming reaction dominates the dry reforming reaction in the experiments and also suggests water gas shift activity. The trend and the H<sub>2</sub>/CO ratio values obtained are similar to the values reported in earlier studies [30]. High H<sub>2</sub>/CO ratio (H<sub>2</sub> rich syngas) is preferred for the SOFC as H<sub>2</sub>

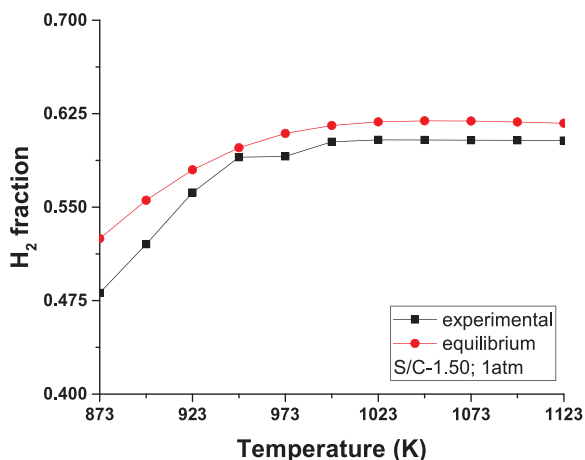


Fig. 9. H<sub>2</sub> fraction of product syngas compared between SBR equilibrium simulation and experimental results for the biogas feed with CH<sub>4</sub>/CO<sub>2</sub> ratio of 60/40.

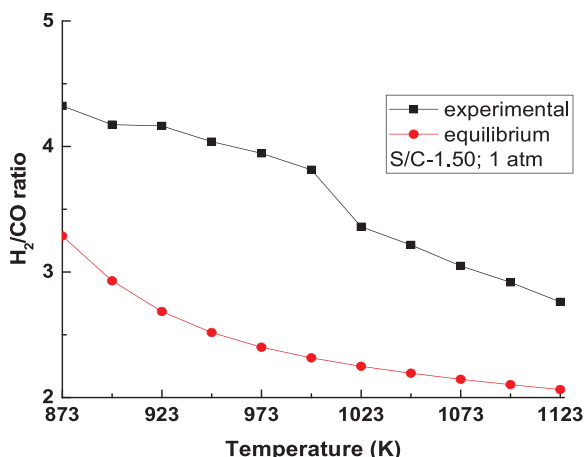


Fig. 10. H<sub>2</sub>/CO ratio of product syngas compared between SBR equilibrium simulation and experimental results for the biogas feed with CH<sub>4</sub>/CO<sub>2</sub> ratio of 60/40.

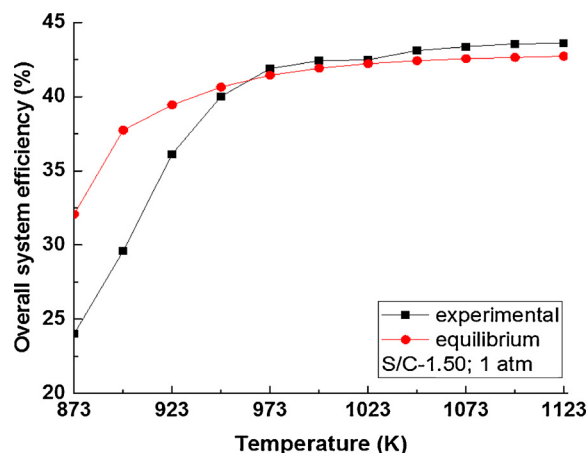


Fig. 12. Overall system efficiency (%) compared between SBR equilibrium simulation and experimental results for the biogas feed with CH<sub>4</sub>/CO<sub>2</sub> ratio of 60/40.

is the major feedstock for electrochemical processes.

Details of the HEP reactor system coupled with the SOFC as well as the overall system efficiency calculations are shown in Fig. 11. The sample calculation is based on SBR experimental results over the metal foam coated catalyst at 1023 K and 1 atm. with an S/C ratio of 1.50. The higher the CH<sub>4</sub> conversion the lower the CH<sub>4</sub> concentration in the SOFC exhaust and thus necessitates additional fuel supply to the combustor. Higher operating temperatures lead to higher CH<sub>4</sub> conversion and improved overall system efficiency as shown in Fig. 12. Once the overall system efficiency is above 40%, it does not increase significantly with increasing temperature. At temperatures above 973 K there are no significant differences between the equilibrium and experimentally predicted system efficiencies, making this the minimum preferable operating temperature.

Data shown in Table 3 presents the coke formation from steam-

Table 3

Coke formation (%) from the SBR reaction over the Pd-Rh catalyst. (Coke formation percentage was evaluated on the basis of carbon balance by subtracting the carbon in the product gases from the carbon in biogas feed.).

Temperature	923	948	973	998	1023	1048	1073	1098	1123
Coke formation (%)	1.05	1.24	1.63	1.98	2.16	2.44	2.88	2.31	2.20

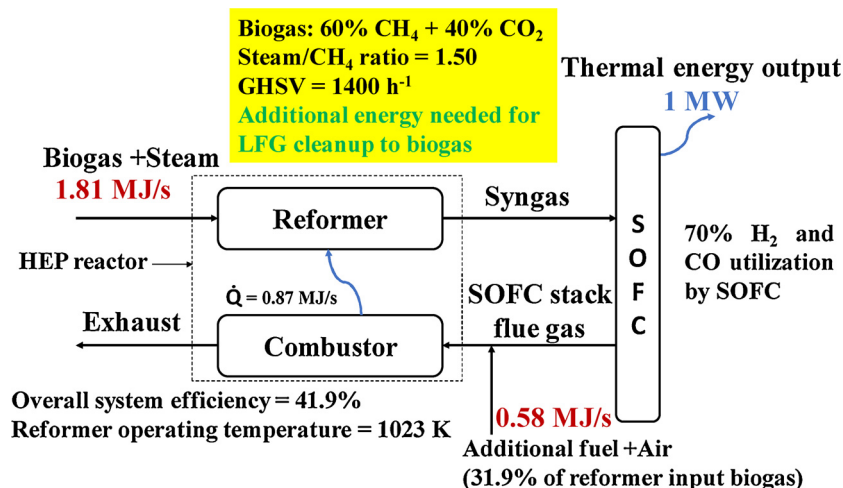


Fig. 11. A schematic process flow diagram for calculating the overall efficiency of the integrated SBR and SOFC system.



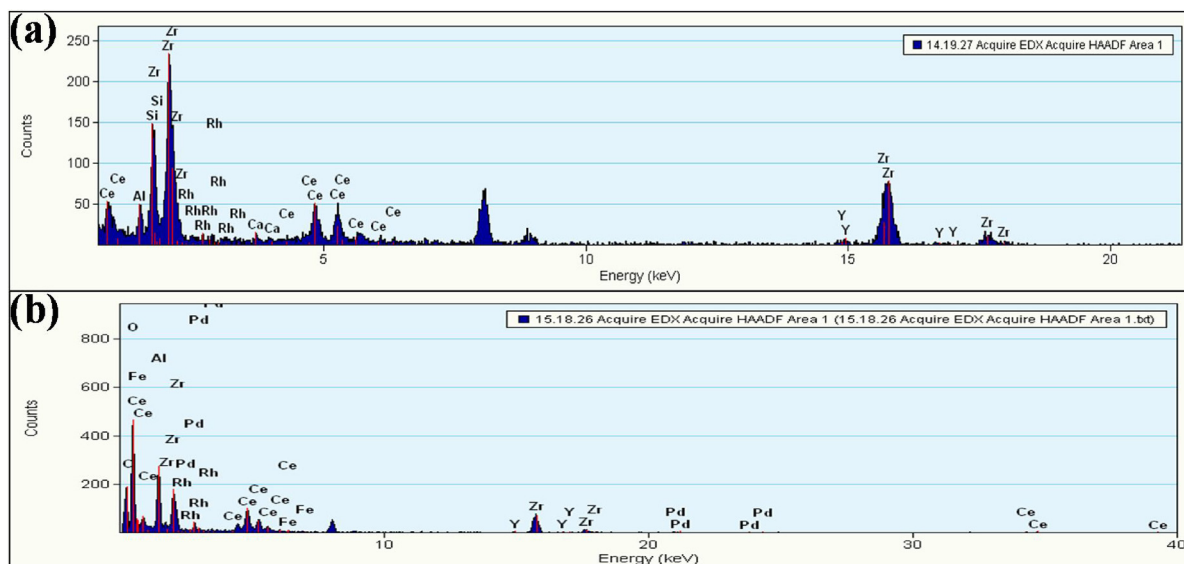
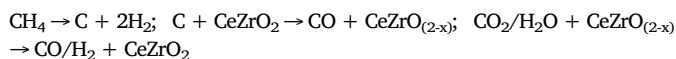


Fig. 13. EDX data for the fresh (a) and used (b) catalyst as an evidence for coke formation.

biogas reforming process. There are no comparable studies reported in the literature on coke formation during the SBR process. The observed coke deposition is significantly lower than during the dry reforming process, which is expected. Coke accumulation in this study increases with temperature until 1073 K and decreases at higher temperatures and comparable with our previous study [3]. The catalyst was checked with EDX data for coke formation evidence and the results are shown in Fig. 13. The EDX data shows no coke existence in the fresh catalyst and evidence of coke deposition in the used catalyst. The significantly reduced coke deposition compared to literature data can be attributed to CeZrO<sub>2</sub> modification of the catalyst by the following mechanism [33].



#### 4. Conclusions

A renewable energy system to produce electricity from biogas feed by integrating the SBR process with an SOFC was evaluated through experimental and modeling study. The system performance was evaluated using the Aspen Plus process simulation tool and through SBR experiments over a metal-foam-coated 1.31 wt% [Pd(7)-Rh(1)]/[CeZrO<sub>2</sub>(25)-Al<sub>2</sub>O<sub>3</sub>(75)] catalyst. The results of this study are summarized below:

- 1 For biogas feeds with CH<sub>4</sub>/CO<sub>2</sub> ratios of 40/60, 50/50 and 60/40, and S/C ratio of 1.00–2.00, higher than 90% CH<sub>4</sub> conversion and net positive CO<sub>2</sub> conversion were attainable at temperatures of 1073 K and above under atmospheric pressure. The overall system efficiency increased with decreasing S/C ratios at temperatures of 923 K and above.
- 2 For S/C ratio of 1.50, the overall system efficiency increased with increasing CH<sub>4</sub> concentration in biogas feed whereas CH<sub>4</sub> and CO<sub>2</sub> conversions increased with decreasing CH<sub>4</sub> concentration in biogas feed.
- 3 For the biogas feed with CH<sub>4</sub>/CO<sub>2</sub> ratio of 60/40 and at S/C ratio of 1.50, experimental CH<sub>4</sub> conversion was comparable with the equilibrium value at 973 K and above whereas experimental CO<sub>2</sub> conversion was much less than the equilibrium value throughout the temperature range tested: net positive CO<sub>2</sub> conversion was achieved only at 1073 K and above.
- 4 For the biogas feed composition and S/C ratio described above,

experimental H<sub>2</sub>/CO ratio of product syngas was greater than the equilibrium value throughout the temperature range tested due to WGS reaction effect. The integrated system can achieve energy efficiency values of 40% or higher at reformer temperatures of 948 K and above.

- 5 Coke formation (%) from the SBR process in this work is estimated to be 1.05–2.88% of the carbon input to the system and is comparable with our previous study.

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