Comprehensive Thermodynamic Analysis and Simulation of Electrified Modular Reactors for Bi-reforming of Methane

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Highlights

- Comprehensive thermodynamic analysis of bi-reforming methane (BRM) is presented.
- Boundary of no carbon formation is identified in feed composition, temperature and pressure.
- Scale-up feasibility of BRM in electrified modular wire reactors is assessed.
- Sensitivity analysis of BRM with feed composition, space time, power supply is presented.

1. Introduction

Growing concerns about the level of greenhouse gases (GHGs) in the atmosphere and their impact on climate change has led to the drive to develop carbon-free technologies. These GHGs, mainly due to burning and production of fossil fuels, are now being recovered and converted into useful products [1]. Among them, carbon dioxide and methane are of greater concern since they are the most emitted (79.4% and 11.5%, respectively in the U.S.) and contribute significantly to global warming [2]. Some known processes for simultaneous conversion of both methane and CO_2 in a single reactor are steam and dry reforming, partial oxidation, bi- and tri-reforming. While these processes show promise for industrial use (with a few of them already being commercial), due to the need for very high temperatures, they all face unique challenges such as catalyst deactivation, low conversions, and complex product formation [3]. Additionally, these processes are endothermic and require heat supply that is traditionally achieved via burning fossil fuels, again leading to significant CO_2 emissions. The last challenge can be resolved by utilizing electrified reactors where the source of heat can come from renewable power [4].

In this work, we focus on electrified bi-reforming of methane (eBRM) that simultaneously converts methane and CO_2 (the two major greenhouse gases) into syngas and to higher value products using renewable power. We note that as compared to other reforming processes, bi-reforming of methane (BRM) leads to H_2 to CO ratio at higher methane conversion, which is favorable for Fisher-Tropsch and methanol synthesis processes. However, it may face the challenge of carbon deposition depending on the feed composition and operating pressure and temperature. Therefore, first we perform a comprehensive thermodynamic analysis of carbon formation in BRM and identify the boundary of the regions of no carbon deposition. These results serve as a guide to experimental validation, catalyst and reactor design for eBRM. In the second part, we use a single site kinetic model to examine the scale-up feasibility of the BRM process in electrified modular reactors [5] and present a preliminary assessment of the impact of various design and operating variables.

2. Methods

The overall BRM reaction ($3CH_4 + CO_2 + 2H_2O \rightarrow 4CO + 8H_2$) with possible carbon deposition can be represented by three independent reactions, namely (i) steam reforming: $CH_4 + H_2O \rightarrow CO + 3H_2$, (ii) dry reforming: $CH_4 + CO_2 \rightarrow 2CO + 2H_2$, and (iii) carbon deposition: $CO_2 + 2H_2 \rightarrow 2H_2O + C$. The thermodynamic analysis to determine equilibrium composition (given the feed composition, pressure, and temperature) is based on minimizing Gibbs free energy. The zero-carbon line is obtained by solving the three equilibrium relations corresponding to the three independent reactions as follows:

$$K_{eq,j} = \prod_{i=1}^{N_s} \left(\frac{y_i P}{P_{ref}}\right)^{\nu_{ji}} = \exp\left(-\frac{\Delta G_j}{R_g T}\right), \qquad (1)$$

coupled with imposing the constraint of zero extent of the carbon deposition reaction. Here $K_{eq,j}$, ν_{ji} and ΔG_j are equilibrium constants, stoichiometric coefficient of i^{th} species and change in Gibbs free energy, respectively for j^{th} reaction; P, P_{ref} and T are pressure, reference pressure and temperature; N_s is the number of species; and y_i is the mole fraction of i^{th} species. Newton's method with arc-length continuation is used to determine the exact boundary of the zero-carbon line/surface. The reaction pathway analysis and scale-up simulations of the bi-reforming process in electrified reactors followed a procedure that is similar to the steam reforming process presented in [5].

3. Selected Results

It is found that carbon deposition has a non-monotonic dependence on temperature as shown in Figure 1a. Here, feed composition is represented by the molar ratios of total reforming agent to methane, i.e. $\alpha = (CO_2 + H_2O){:}\,CH_4$ and $\beta = CO_2{:}\,H_2O$. Similarly, the zero-carbon line is shown in P-T space for various compositions in Figure 1b. It can be seen from this figure that zero-carbon line for a given feed composition may also be non-monotonic in pressure (in addition to temperature), which is non-intuitive. The full article presents a comprehensive analysis of carbon deposition, methane and CO_2 conversions along the zero-carbon line, reaction path analysis, and simulation results of the BRM process in electrified wire reactors.

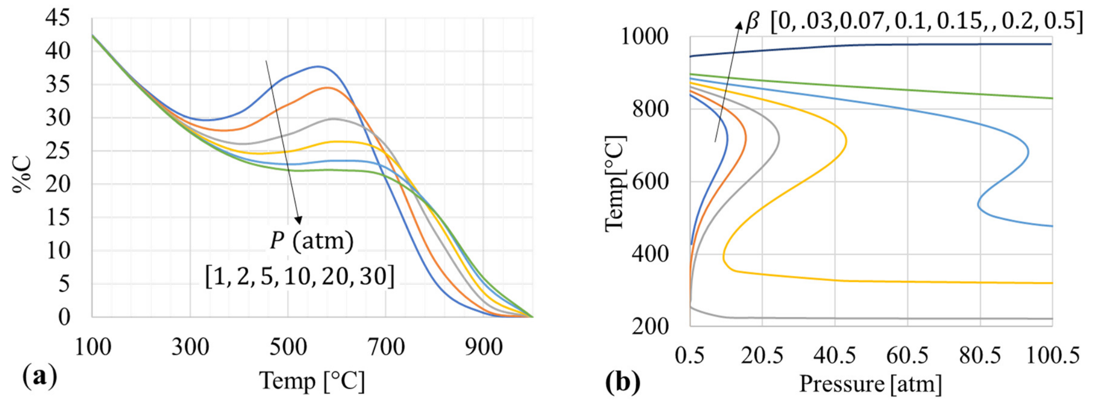

Figure 1. (a) carbon deposition at $\alpha = 1, \beta = 0.5$, and (b) zero carbon line for $\alpha = 1$ and $0 \leq \beta \leq 0.2$.

4. Key Conclusions

(i) Bi-reforming with slightly excess stoichiometric reformer to methane ratio (i.e., $1 \leq \alpha \leq 1.2$) and more steam than CO_2 (i.e., $0.3 \leq \beta \leq 0.5$) was found to be the optimal range for no carbon deposition and 80% or higher equilibrium conversion of both methane and CO_2 at 10 bar and at operating temperatures of 950 °C. (ii) Reactor simulation results for bi-reforming (similar to those shown in [5] for steam reforming) indicate the feasibility of the BRM process in electrified reactors with high methane and CO_2 conversion and a possible commercial pathway for producing syngas and liquid hydrocarbons.

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References

[1] D. Pakhare, J. Spivey. Chemical Society Reviews 43.22 (2014) 7813-7837.
[2] US Environmental Protection Agency, https://www.epa.gov/ghgemissions/overview-greenhouse-gases.
[3] U. Oemar, K. Hidajat, S. Kawi. Applied Catalysis A: General 402.1-2 (2011) 176-187.
[4] V. Balakotaiah, R.R. Ratnakar. AIChE Journal 68.2 (2022): e17542.
[5] R.R. Ratnakar, V. Balakotaiah. International Journal of Hydrogen Energy 49 (2024): 916-926.

Keywords

Electrified reactors; bi-reforming of methane; carbon deposition; scale-up