

Investigation of Hydrogen Production Process by Partial Oxidation of Natural Gas in a Large Non-Catalytic Reformer and Comparison with Methane Steam Reforming Process in a Small Catalytic Reformer

Seyed Behzad Haghi^a, Gholamreza Salehi^b, Masoud Torabi Azad^{c*}, Ali Lohrasbi Nichkoohi^d

^a Energy System Group, Faculty of Marine Science, Islamic Azad University, North Tehran Branch, Tehran Iran

^b Department of Mechanical Engineering, Islamic Azad University, Central Tehran Branch, Tehran Iran

^c Department of Physical Oceanography, Faculty of Marine Science, Islamic Azad University, North Tehran Branch, Tehran Iran

^d Department of Mechanical Engineering, Islamic Azad University, Nowshahr Branch, Nowshahr, Iran

ABSTRACT

In the first part of the research, non-catalytic natural gas reformer is investigated numerically. The governing equations include the mass equation, the species equation with Eddy Dissipation Concept modeling using GRI-1.2 mechanism, the momentum and energy equation with RANS turbulence model. The results show that increasing the pressure promotes conversion of CH₄ into hydrogen, but from pressure 3 MPa and above, hydrogen production remains almost constant. Also, if the ratio of oxygen to natural gas increases to 0.66, the temperature increases and the concentration of CH₄ in the exhaust gas decreases. In addition, as the ratio of water vapor to natural gas increases, the temperature in the reformer decreases and the H₂/CO (synthetic gas) ratio in the output increases. In the next section, methane steam reforming is examined to overcome the hot spot problem in these reformers. The mass, Brinkman, component and energy transport equation are used for the multi-tube catalytic reformer. The effects of inlet temperature of heating tubes, CH₄/H₂O ratio and configuration of heating tubes have been investigated. The results show that increasing the inlet temperature of the heating tubes, the CH₄/H₂O ratio up to 0.25 and the number of heating tubes, increase methane reforming.

Keywords Natural Gas Reformer, Hydrogen, Numerical Method, Partial Oxidation, Porous Media

* Corresponding Author: Email: M_Azad@iau-tnb.ac.ir

1. Introduction

The main method of producing hydrogen gas is its extraction from synthetic gas, which is very important from an economic point of view. Steam reforming, non-catalytic partial oxidation and auto thermal reforming are the three main methods for converting natural gas to synthesized gas. [1] The non-catalytic partial oxidation method has been successfully commercialized and used on a large scale. This method, similar to the automatic temperature reforming method, causes technical problems such as the formation of high temperature points (up to 2000 K) which cause damage to the reformers due to the appearance of hot spots.

Numerical modeling and simulation of laboratory models in these reformers play an important role in the design, optimization and also increase the size of these chemical reactors. Zero-dimensional rotating reactor models [2] and one-dimensional premixed models [3] have been reported to simulate medium-sized reactors. In previous studies, Zhou et al. simulated a partial non-catalytic oxidation of natural gas in high-pressure reformer [4].

Another method that is currently used as the main method of hydrogen production is natural gas reforming, in which approximately 95% of the hydrogen produced on an industrial scale in the United States is done by the Methane Steam Reforming process (MSR) in the catalytic bed. In the MSR process, methane to hydrogen is converted using two reforming and water-gas shift (WGS) reactions [5]. Research shows that reforming large converters with capacities of 0.5 to 500 MW to produce hydrogen in small-scale fuel cells (500 kW) is not cheap [6]. Therefore, more attention has been focused on small-scale technologies to provide efficient, compact and flexible systems for converting methane to hydrogen.

2. Mathematical modeling of the problem.

1.2. The first part of the research: Modeling the natural gas oxidation process

The industrial reformer used in the first part of this research has a height of 11.58 meters and a diameter of 1.8 meters. Natural gas (98.57% methane, 0.95% ethane and 0.48% propane based on molar fraction), oxygen and water vapor are injected through a multi-channel chamber which is demonstrated in figure 1.

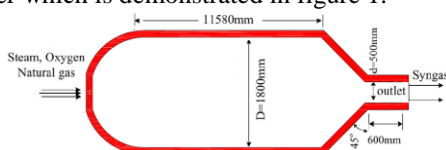


Fig. 1. Schematic of modeled non-catalytic reformer

The governing equations [7] include the conservation of mass, species, momentum, and energy equation with RANS approach. The GRI-1.2 mechanism, based on EDC model, which includes 177 basic chemical reactions for 32 species, is used to calculate the reaction rate in oxidation processes.

2.2 The second part of the research- Methane Steam Reforming Modeling

To model the methane steam reforming, a reactor with nickel as catalysts is investigated. The reformer consists of a porous cylinder with a diameter of 60 mm and a height of 150 mm, which is covered with 3 mm thick foam. Inside the cylinder, copper heating tubes (8 or 12) with a diameter of 8 mm and 150 mm length are used to provide the heat for the chemical reaction which is demonstrated in figure 2.

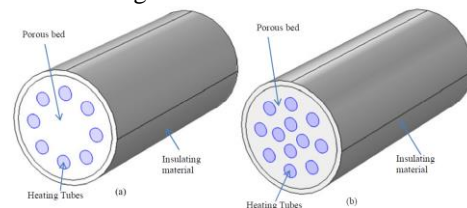


Fig. 2. Schematic of modeled catalytic bed reformer

Hot air enters the heating tubes from one side and water vapor and natural gas from the other side enters the reformer. The conservation of mass equation, Brinkman, and Stefan Maxwell transport equations for a multi-channel catalytic reformer have been studied more details is demonstrated in references [8].

3. Results and Discussion

1.3 First part results

Table 1 Comparison of this study and experimental approach

	This study	Experimental Data[4]
H ₂ mole fraction (%)	52.14	61.08
CH ₄ mole fraction (%)	0.48	0.93
CO mole fraction (%)	30	34.62
Output gas temperature (K)	1750	1610

As described above the methane consumption in output boundary is lower than experimental data so it is shown that the reactions have been terminated because the syngas cannot reach to chemical equilibrium with reactant in the reforming condition.

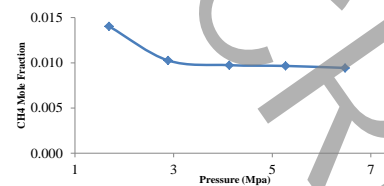


Fig. 3. The effects of pressure on outlet CH₄ concentration.

The effect of pressure on outlet syngas concentration is shown in Figures 3. The result indicates that an increase in pressure promotes natural gas conversion.

1.3 Second part results

As shown in Fig. 4, the conversion of methane for $T = 1200\text{K}$ in the 12-tube configuration is 1.7 times higher than that in the 8-tube configuration. With this configuration, the required temperature for the reforming process decreases, which is ideal for the reformer design and operations. Furthermore, by comparing the 8-tube reforming at 1200K and the 12-tube reforming at 1000K , it is shown that it is more effective to increase temperature than to increase heating tubes.

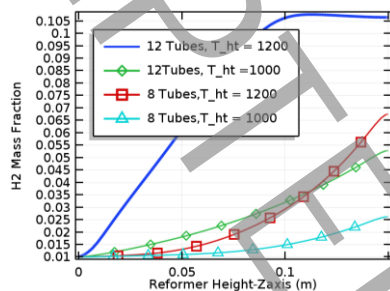


Fig. 4. H2 Mass fraction along reformer centerline for different heating tube configuration

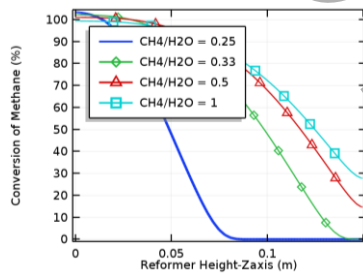


Fig. 5. Conversion of Methane along the reformer bed centerline for different ratios of CH_4/Steam

As demonstrated in Fig. 5, when ratios are higher than stoichiometric ratios (0.25), reforming process raises although for $0.25 < \text{CH}_4/\text{Steam} < 0.33$, the conversion of methane is the same as that at the outlet of the catalytic bed (about 98% of reforming can be achieved). But for fewer ratios, its efficiency is decreased down to 70%. Also, it shows that when the ratio is 0.25, the reforming can be achieved on half of the reformer, so it can be in the best condition to be designed for the reformer length and it also reduces the reformer dimension with higher efficiency.

4. Conclusions

Due to the limitations of the experimental method for studying hydrogen production reformers, CFD has been used in this research. The findings of this study in the first part show that increasing the ratio of oxygen to natural gas, increasing the ratio of water vapor to natural

gas and increasing the chamber pressure increases the production of hydrogen gas. To overcome this hot spot and compare two described method, the numerical study of MSR in a catalytic bed with two different configurations have been investigated using Comsol software. The simulation results show that increasing the inlet air temperature in the heating tubes increases the performance of the reformer but also increases the percentage of carbon monoxide in the reformer outlet, which is considered a challenge. To solve this problem, instead of increasing the inlet air temperature, we increase the number of tubes in the catalytic bed. This design eliminates the need to increase the temperature as well as increase the efficiency of the reformer. Although the effect of increasing the temperature at the inlet of heat tubes is still better than increasing the number of tubes, but with a 12-pipe converter, the conversion takes place at a shorter distance from the converter, which in turn makes the converter shorter and it becomes economic savings.

5. References

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