Hydrogen Production via Methane Steam Reforming Process

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Abstract

Renewable energy is generally defined as energy that is collected from renewable resources such as wind, sunlight, rain, waves, and geothermal heat. Hydrogen is produced using a number of non-renewable and renewable resources such as fossil fuels and biomass. The other feedstock for hydrogen is water in electrolysis process. Microorganisms such as bacteria and algae can produce hydrogen through biological processes.

Hydrogen is produced in some processes as a byproduct. In some processes, the produced hydrogen along with other by-products is sent to flare; however, it can be processed as an energy resource. In this paper, hydrogen production via Methane steam reforming process is investigated. The simulation results show that separation of produced hydrogen provides a significant energy source for mentioned chemical reaction.

Keywords: Renewable Energy, Hydrogen production, Methane steam reforming

1- INTRODUCTION

The main part of energy demand in the world is provided by fossil fuels. The main challenge of fossil fuels is reducing the oil and gas reservoirs along with increasing the carbon dioxide in the environment. Hydrogen as a green energy with high efficiency is one of the best alternatives for fossil fuels [1]. Hydrogen is a carbon free fuel with higher energy content than hydrocarbons which is extensively used in fuel cells [2]. The main advantage of hydrogen is its flexibility for using in automotive engines and power plants [3]. The main part of required hydrogen in the world is produced by hydrocarbons reforming. The other method for hydrogen production is water electrolysis [4]. Hydrogen is produced during some chemical reactions as a byproduct. One these reactions is Methane steam reforming process. This process is performed over cooper based catalyst such as Cu/Cr_2O_3 [5,6,7], Cu/SiO_2 [8,9], and $Cu/ZnO/Al_2O_3$ [10]. In addition carbide and tungsten based catalysts also are used in this process.
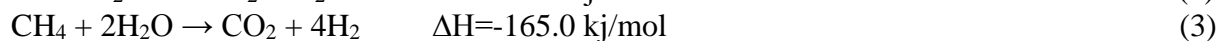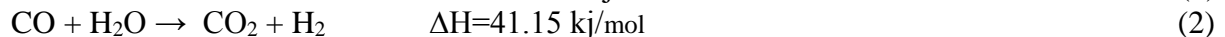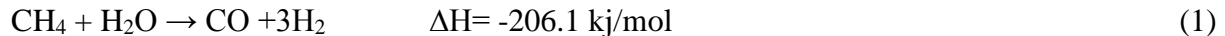
In this paper feasibility of Hydrogen production in Methane steam reforming process is investigated.

2- PROCESS DESCRIPTION

Steam reforming of methane [1] is an important industrial process for hydrogen production. Despite its effectiveness for meeting current hydrogen demands, the energy intensive nature of SRM deviates from current awareness and efforts in improvingthe sustainability of industrial processes. One possible approachto overcome the high energy consumption would be to lower theoperating temperatures of the SRM process while maintaining rea-sonable conversions [11]. The higher degree of endothermicity of the process makes it operate at high temperature conditions. In industrial SMR processes, water gas shift reactors are needed downstream of the reformer to convert the undesired CO into CO_2 and H_2 product. Later on, amine scrubbing or pressure swing adsorption [2] process is required to achieve the higher purity of H_2 [12]. To address the issue of global warming, researchers developed the concept of combining the reforming process with in-situ CO_2 separation. This process was named sorption enhanced steam methane reforming [3] process [13-15]. The addition of sorbent (CO_2 acceptor) along with the catalyst promotes the performance of the reforming process not only by shifting the reactions towards more H_2 production but also in terms of purity of H_2 (CO_2 free product), as well as suppressing equilibrium solid carbon by-product and permitting both lower temperatures of operations and steam demand [16].   The system Methane Steam Reforming / Water Gas Shift appears as a simple model. Few species are involved as reactants – Steam and Methane – and the products are only Carbon Monoxide (which can react with steam), Carbon Dioxide and Hydrogen.

However, multiple side reactions are in fact involved in the whole process and the kinetic associated to the system becomes difficult to use. The reactions impose a complexity of the system representation such as adsorption, carbon formation, and side reactions. From these different reactions, multiple species should be added in the process model.

These three reactions represent the methane steam reforming, the water-gas shift and the methanation:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H = -206.1 \text{ kj/mol} \qquad (1)$$
$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H = 41.15 \text{ kj/mol} \qquad (2)$$
$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \qquad \Delta H = -165.0 \text{ kj/mol} \qquad (3)$$

We can see how the third reaction is the direct sum of the two previous one. This would be pushing us to eliminate it from our model. However, this set of reaction has been found from an intensive research from Xu and Froment (1989), and we will keep the reactions as they have been exposed. A schematic of Methane steam reforming process is illustrated in Figure 1. The simulation is performed by Aspen-HYSYS 7.3. The Peng-Robinson equation of state is used for determination of thermodymic properties of materials.

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[1]. SRM
[2]. PSA
[3]. SE-SMR

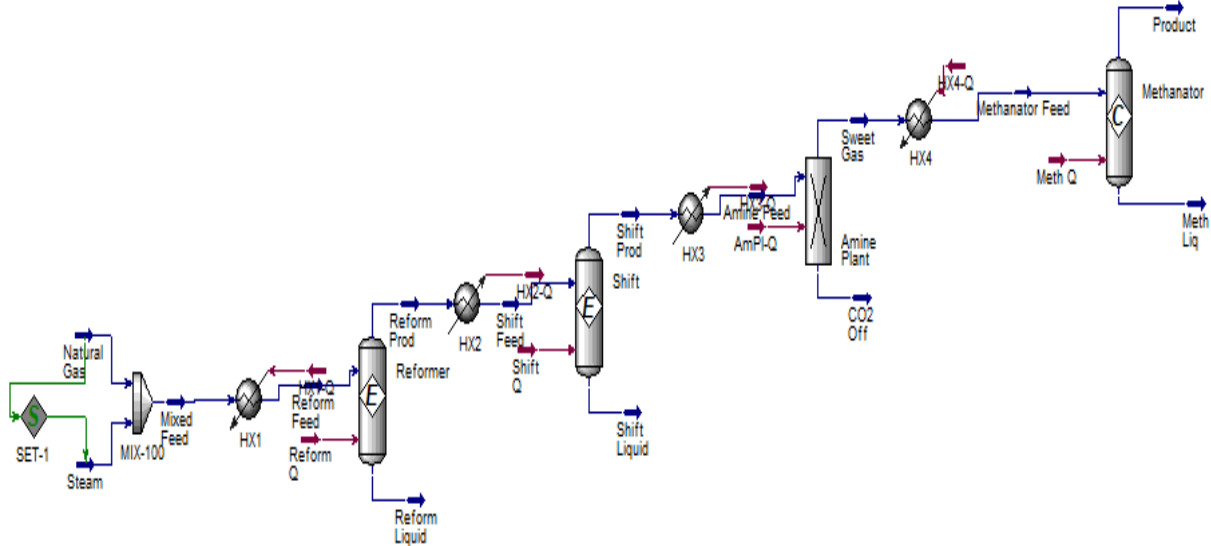**Figure 1- Schematic of Methane steam reforming process**

3- KINETIC MODEL

Kinetic of methane steam reforming process in presence of Cu/ Al_2O_3 catalyst is presented as following [17]:

$$K = K_{CO}.P_{CO} + K_{H_2}.P_{H_2} + K_{CH_4}.P_{CH_4} + K_{H_2O}.\frac{P_{H_2O}}{P_{H_2}} \tag{4}$$

$$r_1 = \frac{k_1}{P_{H_2}^{2.5}}\left(P_{CH_4}.P_{H_2O} - \frac{P_{H_2}^3.P_{CO}}{K_1}\right)/K^2 \tag{5}$$

$$r_2 = \frac{k_1}{P_{H_2}}\left(P_{CO}.P_{H_2O} - \frac{P_{H_2}.P_{CO_2}}{K_2}\right)/K^2 \tag{6}$$

$$r_3 = \frac{k_1}{P_{H_2}^{3.5}}\left(P_{CH_4}.P_{H_2O}^2 - \frac{P_{H_2}^4.P_{CO_2}}{K_3}\right)/K^2 \tag{7}$$

Where, P_{H2}, P_{H2O}, P_{CH4} and P_{CO2} are partial pressure of Hydrogen, Water, Methane and Carbon dioxide, respectively. Furthermore, K_1, K_2 and K_3 are Arrhenius constants that for these reactions are given as following:

$$k_1 = k_1,0 . \exp\left(\frac{E_1}{R}.\left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right) \tag{8}$$

$$k_2 = k_2,0 . \exp\left(\frac{E_2}{R}.\left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right) \tag{9}$$

$$k_3 = k_3,0 . \exp\left(\frac{E_3}{R}.\left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right) \tag{10}$$

Where, $k_{1,0}$, $k_{2,0}$ and $k_3,0$ pre-exponential factor and E_1, E_2 and E_3 activation energy are presented in Table 1.

Table 1- Reactions constants in methane steam reforming

Reaction 1	$K_{1,0}$	1.8e-4	$[kmol.bar^{0.5}/(kg_{cat}.h)]$
	E	240.1	$[KJ/mol]$
Reaction2	$K_{2,0}$	7.6	$[kmol/(bar.kg_{cat}.h)]$
	E	67.1	$[KJ/mol]$
Reaction3	$K_{3,0}$	2.2e-5	$[kmol.bar^{0.5}/(kg_{cat}.h)]$
	E	243.9	$[KJ/mol]$

4- RESULTS AND DISCUSSION

Figure 2 illustrated Reform and Hydrogen production as a function of pressure of natural gas. It is shown that by increasing the pressure, Reform and hydrogen production decreases to pressure of 140 kPa. After pressure of 140 kPa, Reform and Hydrogen production is independent of pressure, thus the optimum pressure of natural gas is selected as 67 kPa.
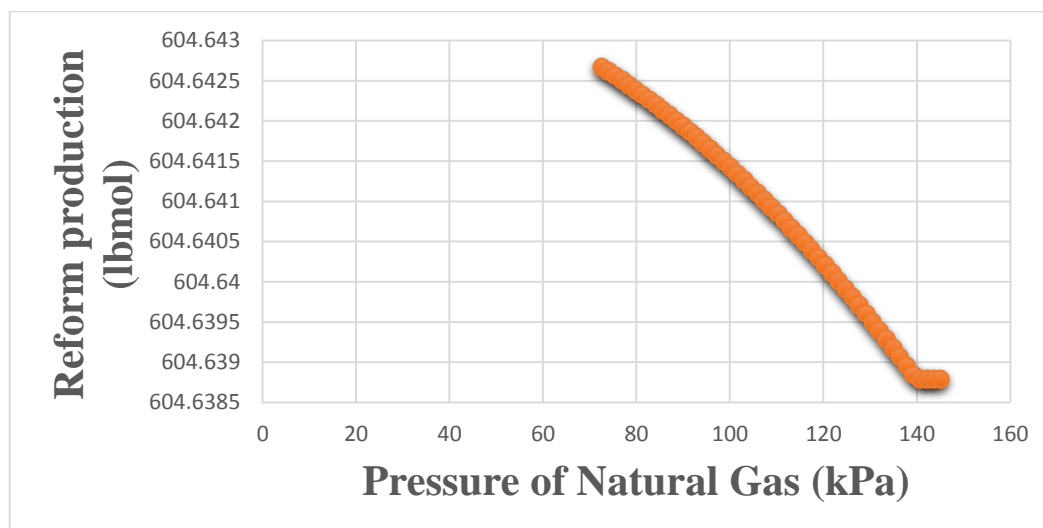

Figure2- Pressure of Natural Gas effect on the Reform and Hydrogen production

Figure 3 illustrated Reform and Hydrogen production as a function of temperature of natural gas. It is shown that by increasing the temperature, Reform and hydrogen production does not change. Therefore, it can be concluded reform and hydrogen production is independent of temperature.
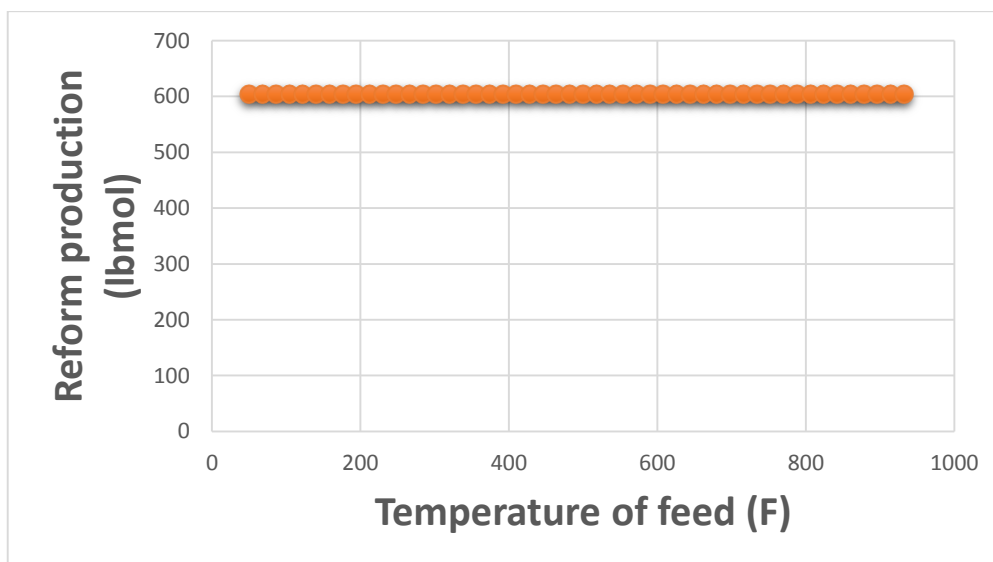

Figure 3- Temperature of Natural Gas effect on the Reform and Hydrogen production

5- CONCLUSIONS

In this paper the hydrogen production during methane steam reforming is investigated. It is shown that the hydrogen value is significant as a byproduct. In practice, the produced hydrogen after separation from mixture is sent to flare; however, it is shown that it can be recovered and processed as a renewable and very clean energy.

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