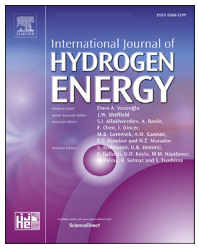
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–9

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



The evaluation of methane mixed reforming reaction in an industrial membrane reformer for hydrogen production

Seyyed Mohammad Jokar [a,*], *Payam Parvasi* [a], *Angelo Basile* [b]

[a] *Department of Chemical, Petroleum and Gas Engineering, Shiraz University of Technology, Shiraz, Iran*
[b] *CNR-ITM, C/o University of Calabria, Via Pietro Bucci, Cubo 17/C, 87030 Rende CS, Italy*

ARTICLE INFO

Article history:
Received 18 April 2018
Received in revised form
21 June 2018
Accepted 25 June 2018
Available online xxx

Keywords:
Mixed reforming
Industrial membrane reformer
Hydrogen production
CO_2 consumption

ABSTRACT

In this work, the performance of an industrial dense Pd–Ag membrane reformer for hydrogen production with methane mixed reforming reaction was evaluated. The rate parameters of mixed reforming reaction on a Ni based catalyst optimized by using the experimental results. One-dimensional models have been considered to model the steam reforming industrial membrane reformer (SRIMR) and mixed reforming industrial membrane reformer (MRIMR). The models are validated by experimental data.

The proficiency of MRIMR and SRIMR at similar conditions used as a basis of comparison in terms of temperature, methane conversion, hydrogen yield, syngas production rate and CO_2 flow rate. Results revealed that the methane conversion, hydrogen yield and syngas production rate in MRIMR is considerably higher than SRIMR. Furthermore, the operation temperature of MRIMR could be 195 °C lower than that for SRIMR. This would contribute to a major decrease in process costs as well as a reduction in catalyst sintering. On the other hand, although MRIMR consumes CO_2, the exited CO_2 flow rate at the SRIMR is three times more than that of at the MRIMR, which is a main advantage of MRIMR from the environmental issues point of view.

Introduction

Methane Steam reforming (MSR) is a common industrial process in which methane is converted into useful products, such as hydrogen and synthesis gas (syngas). In this process, Ni-based catalysts are mostly employed to produce syngas at high temperatures (800–1,000 °C) [1,2]. The AL_2O_3 is mainly used as a support in industrial methane reformers. There have been many researches dedicated to MSR reactions on Ni/AL_2O_3 catalysts [3–9].

The conventional reformers including a number of reforming tubes loaded by the catalyst and placed in a furnace. The following two endothermic reactions, namely steam reforming, are taken place in the reformer [3]:

$$CH_4 + H_2O \Leftrightarrow CO + 3H_2 \quad \Delta H = +206\ kJ/mol \tag{1}$$

$$CH_4 + 2H_2O \Leftrightarrow CO^2 + 4H_2 \quad \Delta H = +165\ kJ/mol \tag{2}$$

Furthermore, the following reaction known as the water gas shift reaction should be considered in the MSR reaction system.

* *Corresponding author.*
E-mail address: jokar@sutech.ac.ir (S.M. Jokar).

https://doi.org/10.1016/j.ijhydene.2018.06.142
0360-3199/

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \quad \Delta H = -41.7\ kJ/mol \tag{3}$$

Dry reforming of methane (equation (4)) is an alternative process for syngas production. The carbon dioxide could provide from waste products [10].

$$CH_4 + CO_2 \Leftrightarrow 2CO + 2H_2 \quad \Delta H = +247.9\ kJ/mol \tag{4}$$

The dry reforming reaction is an appropriate method for consuming CO_2 and methane simultaneously. Therefore, it has been taken into consideration from environmental aspects [2]. However, there are two disadvantages for dry reforming reaction:

1- The carbon deposits causing deactivation of the catalyst during the reaction [11–13].
2- At the same operating conditions, steam reforming provides higher methane conversion than dry reforming [14].

One alternative to overcome the mentioned problems would be to combine the dry and steam reforming (mixed reforming). The methane mixed reforming (MMR) process could decrease catalyst deactivation via oxidation of the carbonaceous products [15,16]. The MMR reactions are as follows [17]:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \text{ (steam reforming)} \tag{5}$$

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \text{ (steam reforming)} \tag{6}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \text{ (water} - \text{gas shift)} \tag{7}$$

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \text{ (dry reforming)} \tag{8}$$

Choudhary and Rajput [18] indicated that methane could be totally converted to syngas with high selectivity for carbon monoxide and hydrogen by MMR. Furthermore, the enhancing effect of combined steam and carbon dioxide reforming process on methane activity and hydrogen to carbon monoxide ratio was proved by Hegarty et al. [19].

Metal support catalysts are commonly used for MMR due to their high thermal conductivity [20]. The application of Ni based catalysts for MMR reaction was studied by some researchers [18,19,21–24].

The MMR reaction was performed on Ni/Y–Al_2O_3 catalyst at high temperatures by the work by Sona et al. [25]. By applying this catalyst the methane conversion of 98.3% achieved and also a low amount of carbon coke deposit formation observed in this process (3.6% after 200 h).

The application of membrane reactors in methane reforming has recently drawn particular attention. By using membrane reactor the full conversion could occur at low temperatures for methane reforming with Ni based catalysts [26].

Different techniques recently used to make supported Pd based membranes with elevated selectivity and permeability [27–31]. Unfortunately, such membranes exhibit high permeability and low selectivity or vice versa. Therefore, supported Pd based membranes are unsuitable to produce pure hydrogen because of their low hydrogen selectivity [32].

Dense Pd-based membranes have high hydrogen selectivity and good permeability. Furthermore, in comparison with supported membranes, dense membranes have the following two advantages:

1- They can operate at high pressure and temperature.
2- They have a considerable mechanical strength and could be easily acquired [33].

There are few studies investigating the industrial production of hydrogen by methane reforming in membrane reformers. Basile et al. [34] experimentally studied the methane steam reforming reaction in a dense Pd–Ag membrane reformer.

The methane conversion of 65% was achieved at the moderate temperature of 450 °C and the pressure of 5 bar. In the other work, their team modeled an industrial membrane reformer based on the experimental tests [35]. They indicated that at the optimum conditions (550 °C, P = 25 bar and S/C = 2.5), 98.9% of the methane conversion could be obtained in an industrial membrane reformer with the membrane thickness of 20 μm and 6 m length [35].

Jokar et al. [36] investigated the MMR in an experimental membrane reactor. They used Ni/CeO_2 as a catalyst and a membrane reactor with 150 μm thickness and 10 cm length. The best experimental results were observed at T = 450 °C and p = 350 kPa. At these conditions, 64% of conversion and 52% of hydrogen yield was achieved in the reactor.

As mentioned, all the previous works focused on modeling of industrial MSR reformers. Unfortunately, there is no investigation on the application of MMR for an industrial membrane reformer. Consequently, there is no exact rate for MMR reactions in a membrane reformer which normally operates at low temperatures (<550 °C). The objective of this work is to predict the performance of this kind of reformer, based on the experimental results obtained from Jokar et al. [36]. In this regard, the reaction rate constants are estimated and the industrial reformer is modeled. The results are then compared with common industrial membrane reformer with steam reforming reaction at optimal conditions given in De Falco et al.'s work [35].

Membrane reforming reactor model

A detailed kinetic model has been developed to evaluate the performance of an industrial membrane reactor.

Description of membrane reforming reactor

Fig. 1 shows the schematic diagram of an industrial membrane reformer. Syngas is produced in the shell side by passing gas mixture comprising methane, steam, inert gas (such as nitrogen) and steam and/or carbon oxide over Ni-based catalysts. The pure hydrogen is permeated to the tube side, from where it is removed by sweep gas, such as nitrogen or steam. The reactions take place in the shell side to give a higher heat-transfer rate due to the direct contact of reactants with the hot wall.

Please cite this article in press as: Jokar SM, et al., The evaluation of methane mixed reforming reaction in an industrial membrane reformer for hydrogen production, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.06.142