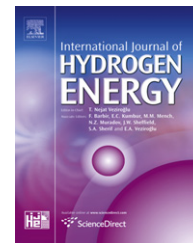


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Hydrogen production through partial oxidation of methane in a new reactor configuration

Amir Motamed Dashliborun^a, Shohreh Fatemi^{a,b,*}, Ali Taheri Najafabadi^a

^a School of Chemical Engineering, College of Engineering, University of Tehran, P.O. Box: 11365-4563, Tehran, Iran

^b Oil and Gas Processing Center of Excellence, University of Tehran, P.O. Box: 11155-4563, Tehran, Iran

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ABSTRACT

Performance of the side feeding (SF) air injection in the process of partial oxidation of methane (POM) has been investigated by means of developing a one-dimensional steady-state non-isothermal model. A fixed bed reactor (FBR), a one-side feeding reactor (One-SF), and a membrane reactor (MR) has been compared for the conversion of methane, selectivity of hydrogen and reactor temperature. The results of the model revealed that the One-SF can operate within FBR and MR, and increasing the number of air injections of SF could achieve to the performance of the MR. The performance of the two to five-SF was studied according to the hydrogen selectivity, methane conversion, temperature profile and H_2/CH_4 ratio. It was observed that increasing the number of injections up to the three, increased the selectivity of hydrogen from 0.496 to 0.530 and decreased the outlet temperature from 1269 K to 1078 K. These results lead to creating of a process with controllable operating temperature and enhancing the selectivity of hydrogen. Consequently, decreasing the problems of high operating temperature in FBR and reduction of the process cost compared with MR.

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1. Introduction

POM as a desirable process has been recently widely studied to produce syngas ($H_2 + CO$) from natural gas. Syngas is widely applicable in the process of methanol production, Fischer-Tropsch synthesis and ammonia synthesis after separation of hydrogen. The molar ratio of H_2/CO in syngas produced by POM is higher than this ratio in reforming reaction, therefore appropriate recycling CO_2 is necessary to achieve to the desired H_2/CO ratio. Unfortunately, CO_2 recycling may cause deactivation of the catalyst [1–7].

Recently, membrane reactors have been considerably attracting the interest of many researchers due to their ability to perform simultaneously reaction and separation in a single unit [8,9]. Furthermore, membrane reactors have high

selectivity and low operating temperature than fixed bed reactors due to controllability of oxygen permeation. However, membrane reactors have many deficiencies such as low conversion of methane due to limiting in the oxygen permeation, changing the properties of membrane due to high operating temperature, membrane fouling, and mechanical strength problem [10–12]. Moreover, high construction cost of the membrane reactor is another problem from an economical point of view. According to these restrictions, application of membrane reactors has not been completely scaled up for industrial applications.

Nowadays, fixed bed reactors are more common in industrial applications, although they have many deficiencies such as, high operating temperature and low selectivity for the syngas. Therefore, it is necessary to improve the performance

* Corresponding author. School of Chemical Engineering, University of Tehran, Tehran, Iran. Tel./fax: +98 21 61112229.

E-mail address: shfatemi@ut.ac.ir (S. Fatemi).

of POM process and incline to the performance of membrane reactors. Since oxygen has a large impact on the selectivity of the syngas product in POM [11,13–15], a new configuration is proposed in this work that inlet oxygen is divided into the side streams along the body of fixed bed reactor instead of completely feeding into the reactor at the entrance. As a result, the inlet oxygen could be better controlled in the reaction zone and the reactor performance would approach to a membrane reactor [16].

Many possible reaction pathways have been proposed for the kinetics of POM to syngas. One of the most common and applicable pathways for POM to syngas has been proposed by De Groot and Froment over Ni catalyst [6]. They considered four reactions containing complete combustion of methane, partial steam reforming of methane, water gas shift reaction and complete steam reforming of methane as the reaction pathway of this process (equations (1)–(4), respectively).

These reactions were used in one-dimensional heterogeneous non-isothermal reactor model at steady conditions for modeling the process in FBR, SF and MR.



A steady-state one-dimensional heterogeneous reactor model proposed for POM to syngas over Ni/Al₂O₃ catalyst in a dense membrane reactor by Jin et al. [16]. A steady-state one-dimensional non-isothermal model for catalytic perovskite type dense membrane reactor has been proposed by Rui et al. [17], and developed by Kumar et al. [18].

In this study, a steady-state non-isothermal one-dimensional model has been developed for a side feeding reactor. The reaction pathway (equations (1)–(4)) has been considered for nickel catalyst and perovskite type dense membrane. The performance of the three types of reactors, FBR, MR and SF has been compared in terms of conversion of methane, selectivity of hydrogen and temperature of the reaction zone. The sensitivity analysis has been carried out and the effect of increasing number of side streams has been studied by the numerical computation of the model in SF to achieve to the best performance.

2. Mathematical modeling

2.1. Kinetic model

The kinetic rate equations for combustion of methane, partial steam reforming of methane, the water gas shift reaction, and the complete steam reforming of methane are introduced and combined in the mole balance and energy balance equations of the reactors. For combustion of methane on a supported Pt catalyst, a Langmuir–Hinshelwood (LH) rate equation have been proposed by Trimm and Lam [19]. The corresponding adsorption parameters of this rate equation were adjusted for

a Ni catalyst by De Smet et al. [20]. Methane combustion rate equation is introduced by the following equation:

$$R_1 = \frac{k_{1a} p_{\text{CH}_4} p_{\text{O}_2}}{\left(1 + k_{\text{CH}_4}^0 p_{\text{CH}_4} + k_{\text{O}_2}^0 p_{\text{O}_2}\right)^2} + \frac{k_{1b} p_{\text{CH}_4} p_{\text{O}_2}}{\left(1 + k_{\text{CH}_4}^0 p_{\text{CH}_4} + k_{\text{O}_2}^0 p_{\text{O}_2}\right)} \quad (5)$$

The Langmuir–Hinshelwood rate equations for the partial steam reforming of methane, the water gas shift reaction, and the complete steam reforming of methane derived from the work of Xu and Froment [21] and have been introduced by the following equations, respectively:

$$R_2 = \frac{\frac{k_2}{p_{\text{H}_2}^{2.5}} \left(p_{\text{CH}_4} p_{\text{H}_2\text{O}} - \frac{p_{\text{H}_2}^3 p_{\text{CO}}}{K_{\text{eq},2}} \right)}{\left(1 + k_{\text{CO}} p_{\text{CO}} + k_{\text{H}_2} p_{\text{H}_2} + k_{\text{CH}_4} p_{\text{CH}_4} + \frac{k_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}}}{p_{\text{H}_2}} \right)^2} \quad (6)$$

$$R_3 = \frac{\frac{k_3}{p_{\text{H}_2}} \left(p_{\text{CO}} p_{\text{H}_2\text{O}} - \frac{p_{\text{H}_2} p_{\text{CO}_2}}{K_{\text{eq},3}} \right)}{\left(1 + k_{\text{CO}} p_{\text{CO}} + k_{\text{H}_2} p_{\text{H}_2} + k_{\text{CH}_4} p_{\text{CH}_4} + \frac{k_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}}}{p_{\text{H}_2}} \right)^2} \quad (7)$$

$$R_4 = \frac{\frac{k_4}{p_{\text{H}_2}^{3.5}} \left(p_{\text{CH}_4} p_{\text{H}_2\text{O}}^2 - \frac{p_{\text{H}_2}^4 p_{\text{CO}_2}}{K_{\text{eq},4}} \right)}{\left(1 + k_{\text{CO}} p_{\text{CO}} + k_{\text{H}_2} p_{\text{H}_2} + k_{\text{CH}_4} p_{\text{CH}_4} + \frac{k_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}}}{p_{\text{H}_2}} \right)^2} \quad (8)$$

To avoid the complexity of the analytic evaluation of effectiveness factors for reaction rates, the average values of effectiveness factor suggested by De Groot and Froment [6] have been used for the above reactions (equations (1)–(4)). The net rate of consumption of each reactant and formation of each product can be determined by multiplying the intrinsic kinetic rates and corresponding value of effectiveness factors and their stoichiometric coefficients. The corresponding kinetic parameter values have been listed in Table 1 and Table 2.

2.2. Oxygen permeation model in membrane reactor

In this study, the properties of perovskite type oxygen permeable dense membrane has been used [11]. The oxygen permeation flux is described as:

Table 1 – Arrhenius parameter, heat of reaction and effectiveness factor of reactions [6,22].

Reaction	A _j	E _j (J/mol)	ΔH _{Rj} (J/mol)	η _j
1	A(k _{1a}) = 8.11 × 10 ⁰⁵ (mol bar ⁻² Kg ⁻¹ s ⁻¹) A(k _{1b}) = 6.82 × 10 ⁰⁵ (mol bar ⁻² Kg ⁻¹ s ⁻¹)	86.0	–802 × 10 ³	0.05
2	A(k ₂) = 1.17 × 10 ¹⁵ (mol bar ^{0.5} Kg ⁻¹ s ⁻¹)	240.1 × 10 ³	206 × 10 ³	0.07
3	A(k ₃) = 5.43 × 10 ⁰⁵ (mol bar ⁻¹ Kg ⁻¹ s ⁻¹)	67.1 × 10 ³	–41 × 10 ³	0.7
4	A(k ₄) = 2.83 × 10 ¹⁴ (mol bar ^{0.5} Kg ⁻¹ s ⁻¹)	243.9 × 10 ³	165 × 10 ³	0.06

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