

# Optimization of a Membrane-based Oxidative Coupling of Methane Reactor Using Surface Response Methodology

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An oxidative coupling of methane (OCM) is a promising process to convert methane into ethylene and ethane; however, it suffers from the relatively low selectivity and yield of ethylene at high methane conversion. In this study, a membrane reactor is applied to the OCM process in order to prevent the deep oxidation of a desirable ethylene product. First, simulations of the OCM reactor based on mass and energy balances coupled with detailed OCM kinetic model are performed and effects of key operating parameters, such as temperature, methane-to-oxygen feed ratio and methane flow rate, on the OCM reactor performance in terms of CH<sub>4</sub> conversion, C<sub>2</sub> selectivity and yield are analyzed. To determine its optimal operating conditions, an optimization of the OCM membrane reactor using a surface response methodology is carried out in the second part. The central composite design (CCD) is used to study the interaction of process variables (i.e., temperature, feed flowrate and CH<sub>4</sub>/O<sub>2</sub> ratio) and to find the optimum process operation to maximize the C<sub>2</sub> products yield.

## 1. Introduction

Methane is the main component of natural gas (NG) and biogas, and a by-product from oil refining and chemical industries. Conversion of methane to more useful chemicals and fuels is recognized as the next step to sustain economic growth and maintain fuel supplies (Bouwmeester, 2003). In addition, it could also reduce the severe greenhouse effect caused by methane. Different methodologies have been proposed to convert methane into olefins, higher hydrocarbons and gasoline via indirect and direct conversion processes. The indirect approach involves the production of synthesis gas (syngas), an intermediate, from methane (Arpornwichanop et al., 2011) and then transforms it into other chemicals via Fischer-Tropsch process, which causes a substantial energy loss. In contrast, the direct conversion process converts methane into higher hydrocarbons in a single step. Among the various direct processes, the oxidative coupling of methane (OCM) is a promising technology to convert methane into ethylene and ethane. Extensive studies on the OCM process have been conducted since the pioneer work of Keller and Bhasin in 1982. Many different reactor concepts, therefore, have been proposed for this process. Due to its technological simplicity, a fixed-bed reactor (FBR) is widely investigated. The operation of this reactor is accident prone because of the large amount of heat released during the course of the reaction. Furthermore, a poor heat removal from the highly exothermic reaction results in the occurrence of hot spots, affecting the reactor operation, such as temperature runaway, catalyst deactivation, undesired side reactions and thermal decomposition of products. Use of a fluidized-bed reactor, which has high heat transfer capacity, shows better heat management and temperature control than the fixed bed reactor system. Daneshpayeh et al. (2009) studied the OCM over Mn/Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalyst in a two-zone fluidized-bed reactor (TZFBR) and its performance was compared with the conventional fluidized-bed

reactor. Although the TZFBR gave the C<sub>2</sub> selectivity larger than the fluidized-bed reactor does, the C<sub>2</sub> yield was still relatively low (< 20%).

The difficulty in operation of the OCM process lies in the fact that intermediates and target products are more reactive than the reactant and therefore, are prone to deeply oxidize to CO<sub>x</sub>. Thus, the oxidation of methane and C<sub>2+</sub> products seems to be unavoidable when high oxygen content is present in the feed stream. The concept of using an oxygen distribution in a fixed-bed reactor was studied by Zarrinpashne et al. (2003) in order to improve the OCM performance. However, the proposed reactor concept cannot achieve the high yield of ethylene due to the incomplete gas mixing at the oxygen feeding points. This causes high oxygen concentration zones at which the C<sub>2+</sub> product is easily combusted and its selectivity falls significantly. Omata et al. (1989) initially applied a membrane reactor for the OCM process. The use of the membrane reactor to control oxygen concentration offers a possibility to achieve much higher C<sub>2</sub> hydrocarbons selectivity and yield. Mixed-conducting oxide membranes, such as perovskite-type membranes, are well known for their abilities to separate oxygen from air. Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3-δ</sub> (BSCFO), is an example of the promising mixed conducting membrane with high oxygen permeability and has proven to be a good candidate for use as an oxygen distributor in the OCM reactor (Shao et al., 2000). In this study, a dense tubular membrane reactor is investigated to improve the performance of the OCM. The mathematic model of the membrane reactor based on conservative equations and detailed OCM kinetic model is employed to analyze the effect of key operating parameters, such as temperature, methane-to-oxygen feed ratio and methane feed flow rate, on the efficiency of the OCM process in terms of CH<sub>4</sub> conversion, C<sub>2</sub> selectivity and C<sub>2</sub> yield. The simulated data obtained are used for the optimization of the process conditions using the central composite design (CCD) of response surface methodology (RSM).

## 2. Model of OCM membrane reactor

Figure 1 shows the configuration of a tubular membrane reactor for OCM. The membrane reactor considered consists of two concentric tubes; the inner tube is the dense Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3-δ</sub> membrane. Methane is fed into the tube side of the reactor while oxygen is fed into the shell side. The oxygen in the shell side permeates into the tube side through the membrane, which acts as an oxygen distributor, and reacts with methane via the OCM reaction in the presence of La<sub>2</sub>O<sub>3</sub>/CaO catalysts, which are packed in the tube side.

The mathematical model of the membrane reactor Eq (1)-Eq (5) is developed based on the following assumptions; the reactor is operated under steady-state operation, there is no radial concentration distributions in the tube or on the shell side of the reactor, axial diffusion dispersion is neglected and ideal gas law is assumed.

Mass balances

*Tube side:*

$$\frac{dF_i^t}{dz} = \frac{W}{V} A_{CS} \sum_{j=1}^n v_{i,j} r_j + \pi d_2 J_{O_2} \quad (1)$$

*Shell side:*

$$\frac{dF_{O_2}^s}{dz} = -\pi d_1 J_{O_2} \quad (2)$$

Energy balances

*Tube side:*

$$\frac{dT^t}{dz} = \frac{\left[ \frac{W}{V} A_{cs} \sum_i (-\Delta H_i r_i) - q + \pi d_2 J_{O_2} C_{p,O_2} \Delta T \right]}{\sum_j F_j C_{p_j}} \quad (3)$$

*Shell side:*

$$\frac{dT^s}{dz} = \frac{q}{F_{O_2}^s C_{p_{O_2}}} \quad (4)$$

where  $q$  is the heat flux between the tube side and shell side, which can be expressed by the following equation:

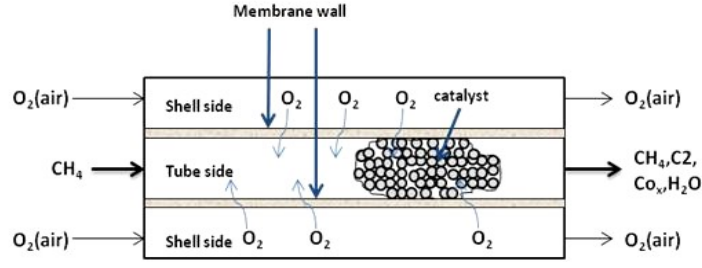


Figure 1: Schematic diagram of the OCM membrane reactor.

$$q = \frac{A_{cs} K_m (T^l - T^s)}{ML} \quad (5)$$

where  $A_{cs}$  is the cross section area of the tube side,  $K_m$  is the average thermal conductivity,  $M$  is the membrane thickness and  $L$  is the effective length of the tube.

The oxygen permeation through the tubular BSCFO membrane can be explained by the oxygen flux (Equation (6)), which was developed by Kim et al. (1998).

$$J_{O_2} = \frac{\pi L C_i D_a}{2S \ln(d_1 / d_2)} \ln\left(\frac{P_1}{P_2}\right) \quad (6)$$

where  $d_1$  and  $d_2$  are the outer and inner diameter of the membrane tube,  $L$ ,  $S$ ,  $C_i$  and  $D_a$  are the effective length of the tube, the effective area of the membrane tube, the density of oxygen ions and the ambipolar diffusion coefficients, respectively,  $P_1$  is the oxygen partial pressure in the shell side and  $P_2$  is the oxygen partial pressure in the tube side.

### 3. Kinetics of OCM

A comprehensive kinetic model of the OCM reaction used in this study was developed by Stansch et al. (1997) for the  $\text{La}_2\text{O}_3/\text{CaO}$  catalyst. The OCM consists of three primary and seven consecutive reaction steps taking into account the gas phase dehydrogenation of ethane and the ethylene steam reforming as:



The reaction rates for each reaction step are given below:

$$r_j = \frac{k_{0,j} e^{-E_{a,j}/RT} P_C^{m_j} P_{O_2}^{n_j}}{(1 + K_{j,\text{CO}_2} e^{-\Delta H_{ad,\text{CO}_2}/RT} P_{\text{CO}_2})^2} \quad j = 1, 3 - 6 \quad (17)$$

$$r_2 = \frac{k_{0,2} e^{-E_{a,2}/RT} (K_{0,\text{O}_2} e^{-\Delta H_{ad,\text{O}_2}/RT} P_{\text{O}_2})^{n_2} P_{\text{CH}_4}}{[1 + (K_{0,\text{O}_2} e^{-\Delta H_{ad,\text{O}_2}/RT} P_{\text{O}_2})^{n_2} + K_{j,\text{CO}_2} e^{-\Delta H_{ad,\text{CO}_2}/RT} P_{\text{CO}_2}]^2} \quad (18)$$

Table 1: Kinetic parameters of the OCM reactions

Step	$K_{0,j}$ ( $\text{mol g}^{-1} \text{s}^{-1} \text{Pa}^{-(m+n)}$ )	$E_{a,j}$ ( $\text{kJ mol}^{-1}$ )	$m_j$	$n_j$	$K_{j,\text{CO}_2}$ ( $\text{Pa}^{-1}$ )	$\Delta H_{\text{ad,CO}_2}$ ( $\text{kJ mol}^{-1}$ )	$K_{j,\text{O}_2}$ ( $\text{Pa}^{-1}$ )	$\Delta H_{\text{ad,O}_2}$ ( $\text{kJ mol}^{-1}$ )
1	$0.20 \times 10^{-5}$	48	0.24	0.76	$0.25 \times 10^{-12}$	-175		
2	23.2	182	1.00	0.40	$0.83 \times 10^{-13}$	-186	$0.23 \times 10^{-11}$	-124
3	$0.52 \times 10^{-6}$	68	0.57	0.85	$0.36 \times 10^{-13}$	-187		
4	$0.11 \times 10^{-3}$	104	1.00	0.55	$0.40 \times 10^{-12}$	-168		
5	0.17	157	0.95	0.37	$0.45 \times 10^{-12}$	-166		
6	0.06	166	1.00	0.96	$0.16 \times 10^{-12}$	-211		
7	$1.2 \times 10^7$ <sup>a</sup>	226						
8	$9.3 \times 10^3$	300	0.97	0				
9	$0.19 \times 10^{-3}$	173	1.00	1.00				
10	$0.26 \times 10^{-1}$	220	1.00	1.00				

Table 2: Range and levels of independent process variables for the OCM reactor

Independent variable		Coded levels		
		-1	0	1
CH <sub>4</sub> /O <sub>2</sub> feed ratio	X <sub>1</sub>	1	2	3
Operating temperature (°C)	X <sub>2</sub>	700	800	900
CH <sub>4</sub> feed flow rate (10 <sup>-3</sup> mol/s)	X <sub>3</sub>	1.2	2.0	2.8

$$r_7 = k_{0,7} e^{-E_{a,7}/RT} P_{\text{C}_2\text{H}_6} \quad (19)$$

$$r_8 = k_{0,8} e^{-E_{a,8}/RT} P_{\text{C}_2\text{H}_4}^{m_8} P_{\text{H}_2\text{O}}^{n_8} \quad (20)$$

$$r_9 = k_{0,9} e^{-E_{a,9}/RT} P_{\text{CO}}^{m_9} P_{\text{H}_2\text{O}}^{n_9} \quad (21)$$

$$r_{10} = k_{0,10} e^{-E_{a,10}/RT} P_{\text{CO}_2}^{m_{10}} P_{\text{H}_2}^{n_{10}} \quad (22)$$

where  $P_i$  stands for the partial pressure of component  $i$ ,  $K_0$  and  $E_{a,j}$  represent the kinetic parameter and the activation energy in reaction  $j$ . The kinetic parameters used for the above reaction scheme are presented in Table 1.

#### 4. Optimization of OCM reactor

In this study, a statistical analysis of the OCM process performance in term of C<sub>2</sub> yield is performed. The central composite design (CCD) is used to study the interaction of process variables and to predict the optimum process conditions maximizing the C<sub>2</sub> yield. The independent variables, i.e., CH<sub>4</sub>/O<sub>2</sub> feed ratio (X<sub>1</sub>), operating temperature (X<sub>2</sub>) and CH<sub>4</sub> feed flow rate (X<sub>3</sub>), with their operational range are given in Table 2. The response (Y) of the OCM process, the C<sub>2</sub> yield, is used to develop the quadratic polynomial equation that correlates the process response as a function of the independent variables and their interactions as shown in the Equation (23).

$$Y = \beta_0 + \sum_{i=1}^3 \beta_i X_i + \sum_{i=1}^3 \beta_{ii} X_i^2 + \sum_{i=1}^2 \sum_{j=i+1}^3 \beta_{ij} X_i X_j \quad (23)$$

where  $Y$  is the predicted response (dependent variables),  $\beta_0$  is the offset term,  $\beta_i$ ,  $\beta_{ii}$  and  $\beta_{ij}$  are the coefficients for the linear, squared and interaction effects and  $X_i$  and  $X_j$  are the factors (independent variables).

### 5. Results and discussion

#### 5.1 Parametric analysis of the OCM membrane reactor

In this section, the performance analysis of the dense tubular membrane reactor for the OCM process with respect to key operating parameters is presented. Table 3 shows the reactor configuration and

Table 3: Operating conditions and reactor configuration

Operating conditions	
Temperature (°C)	800
Methane/Oxygen feed ratio	2
Methane feed flow rate ( $10^{-3}$ mol/s)	1.6
Reactor configuration	
Length (cm)	10
Inner diameter of membrane tube (mm)	5
External diameter of membrane tube (mm)	8
Mass of catalyst (g)	0.45
Pressure for both tube and shell sides (atm)	1
Bulk bed porosity	0.36

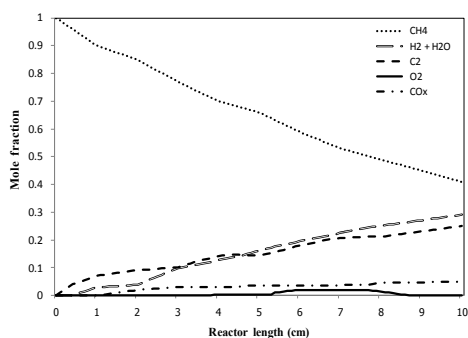


Figure 2: Concentration profiles along the reaction side of the OCM membrane reactor.

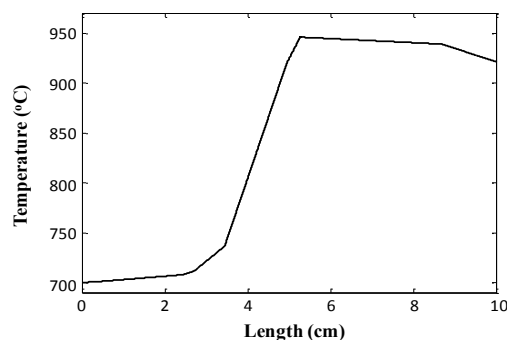


Figure 3: Temperature profile along the OCM reactor.

operational parameters used for the reactor simulation. Figure 2 shows the concentration profiles of  $\text{CH}_4$ ,  $\text{C}_2$ ,  $\text{O}_2$ ,  $\text{CO}_x$ ,  $\text{H}_2$  and  $\text{H}_2\text{O}$  along the tube side of the reactor when pure methane is fed to the tube side at the flow rate of  $1.6 \times 10^{-3}$  mol/s and the methane-to-oxygen ( $\text{CH}_4/\text{O}_2$ ) ratio of 2 and the operating temperature is kept constant at 800 °C. It is found that the methane concentration decreases along the reactor length and the other gaseous components increase due to the increased reaction rates after oxygen is permeated from the shell side. At the early stage of the reactions, the formation rate of  $\text{C}_2$  product by the OCM reactions is higher than the rate of methane deep oxidation (side reaction).

When the  $\text{CH}_4/\text{O}_2$  ratio is varied from 0.5 to 3, the results show that the  $\text{CH}_4$  conversion and  $\text{C}_2$  yield decrease from their highest value at the  $\text{CH}_4/\text{O}_2$  ratio of 0.5 due to the lower oxygen concentration at the reaction side. However, the undesired oxidation reaction of methane,  $\text{C}_2$  products and other intermediate products are intensely induced at higher oxygen concentration, as a result, the  $\text{C}_2$  selectivity decreases at higher  $\text{CH}_4$  conversion as well. Because the reaction of ethane to ethylene requires oxygen to react with ethane, higher  $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$  ratio is obtained at a lower  $\text{CH}_4/\text{O}_2$  ratio operation.

The effect of operating temperatures on the performance of the OCM membrane reactor is also studied in a range of 700–900 °C. Initially, the  $\text{CH}_4$  conversion and  $\text{C}_2$  product yield increase with increasing operating temperatures due to the higher reaction rate and oxygen flux through the membrane at higher temperatures. At the temperature above 850 °C, however, the amount of methane in the tube side decreases, while the permeation of oxygen into the tube side increases. This effect leads to more undesired side reaction and causes a decrease in  $\text{C}_2$  selectivity and  $\text{C}_2$  yield.

Regarding the effect of methane feed flow rate, the results show that the methane conversion,  $\text{C}_2$  selectivity and  $\text{C}_2$  yield are improved and reach their maximum values at the methane feed flow rate of  $2 \times 10^{-3}$  mol/s. At the methane feed flow rate below  $2 \times 10^{-3}$  mol/s, the performance of the OCM process increases because more methane can react with oxygen. However, when the flow rate of methane is higher than  $2 \times 10^{-3}$  mol/s, it is found that there is less oxygen concentration in the tube side and thus, the efficiency of the OCM process decreases.

Due to the highly exothermic nature of OCM reaction, the assumption that the reactor is operated under the isothermal condition might lead to the unrealistic prediction of the reactor performance. When the OCM reactor is run under an adiabatic operation, heat released during the oxidation coupling process increases the reactor temperature. Figure 3 shows the temperature profile along the reactor length when the inlet feed temperature is 700 °C. The reactor temperature increases and reaches its highest temperature of

945°C. Compared with the isothermal operation, the adiabatic operation provides a higher C<sub>2</sub> yield at the inlet temperature range of 700–800 °C.

## 5.2 Optimization of the OCM membrane reactor

Simulations of the OCM membrane reactor are performed based on the central composite design (CCD). The results show that the C<sub>2</sub> yield obtained is varied from 11.59 % to 34.12 %, depending on the operating conditions. These simulated data can be fitted by a second order quadratic model as given below:

$$Y = -330.594 + 19.779X_1 + 0.773X_2 + 20.031X_3 - 0.020X_1X_2 + 1.220X_1X_3 - (5.391 \times 10^{-3})X_2X_3 - 2.941X_1^2 - (4.260 \times 10^{-4})X_2^2 - 3.891X_3^2 \quad (24)$$

The validation of the model obtained is shown by the R<sup>2</sup> error of 0.9888; 98.88 % of the response variability could be explained by this regression model. The statistical analysis based on ANOVA for the quadratic model shows that the model F-value is 49.00, indicating the significance of the model and the P-value is less than 0.0500, indicating the significance of the model terms, i.e., X<sub>1</sub>, X<sub>2</sub>, X<sub>3</sub>, X<sub>1</sub>X<sub>2</sub>, X<sub>1</sub><sup>2</sup>, X<sub>2</sub><sup>2</sup> and X<sub>3</sub><sup>2</sup>.

In order to optimize the C<sub>2</sub> yield of the OCM reactor, the regressive model Eq(24) is used as an objective function. The optimization results show that the OCM reactor should be operated at the CH<sub>4</sub>/O<sub>2</sub> ratio of 0.83, the temperature of 847 °C and CH<sub>4</sub> flow rate of 2.1×10<sup>-3</sup> mol/s and the maximum C<sub>2</sub> yield of 36.49 % is obtained.

## 6. Conclusions

In this study, the analysis and optimization of a dense tubular membrane reactor for oxidative coupling of methane (OCM) is performed. The performance of the OCM reactor in terms of CH<sub>4</sub> conversion, C<sub>2</sub> selectivity and C<sub>2</sub> yield is considered and the results show that the reactor temperature, methane to oxygen feed ratio and methane feed flow rate are key parameters affecting the OCM reactor. The central composite design and the response surface method are employed to determine the optimum C<sub>2</sub> yield. It is found that the optimum conditions to maximize the C<sub>2</sub> production are at the temperature of 847°C, the CH<sub>4</sub> flow rate of 2.10 × 10<sup>-3</sup> mol/s and the CH<sub>4</sub>/O<sub>2</sub> ratio of 0.83. This data is beneficial for the optimal design of the OCM reactor for C<sub>2</sub> production.

## Acknowledgement

Support from the Ratchadaphiseksomphot Endowment Fund (CU-CLUSTER-FUND), Chulalongkorn University is gratefully acknowledged.

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