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# Simulation of a Catalytic Membrane Reactor for Oxidative Coupling of Methane –A Comparative Study for Isothermal and Non-isothermal Conditions

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## ABSTRACT

*Oxidative coupling of methane (OCM) is comparatively an advantageous route for the production of ethylene by utilizing methane, the main component of natural gas. However, this technology is hindered by problems associated with the selectivity and yield of C<sub>2</sub> product due to an excess oxidation reaction. Using a membrane reactor for oxidative coupling of methane has the advantage of precisely controlling the rate of delivery of oxygen to the catalyst. The sensitivity of the model system towards changes in inlet conditions is analyzed. Classical reactor control parameters like flow rates, inlet concentrations and temperature are also varied to investigate parametric sensitivity and the response of the membrane reactor. Simulation results show the effect of parameters such as temperature, CH<sub>4</sub> flow rate on the operating conditions, and membrane parameters on the yield, selectivity and methane conversion. The reaction scheme used in this work includes all possible reactions for OCM. Relative feasibility of OCM performance for isothermal and non-isothermal conditions is also investigated.*

## KEYWORDS

*Oxidative coupling of methane (OCM), Kinetic modeling*

## INTRODUCTION

The oxidative coupling of methane (OCM) to C<sub>2</sub> and higher hydrocarbons has been seen as a promising way to upgrade natural gas and continues to attract both industrial and academic interest. OCM produces ethylene as desired product with the reversible reaction involving homogeneous as well as heterogeneous reaction steps. Simultaneously, methane produces carbon oxides and higher chain length hydrocarbons which are considered as undesirable products. Methane interacts with oxygen species in the gas phase as well as on the catalyst surface. A great deal of effort has recently been put on OCM to ethylene or ethane (C<sub>2</sub> products) using conventional reactors. However, the inherent limit to the yield of the C<sub>2</sub> products achieved in a conventional packed-bed reactor is about 25%. This is because of complete oxidation reactions occurring in the gas phase and partially on the catalyst surface, which lower substantially the C<sub>2</sub> selectivity especially under the conditions of high temperature and pressure. A membrane reactor using a dense, oxygen semi permeable ceramic membrane offers a possibility to achieve a much higher C<sub>2</sub> selectivity and yield for OCM. In addition, the membrane reactor is safer in operation and may separate simultaneously oxygen from air in one device. The membrane is typically made of a fast oxygen ionic conducting ceramic material. Such a membrane reactor consists of a dense oxide membrane layer of which one side is exposed to methane and the other to oxygen. Different from the catalyst operated in the conventional mode such as in a packed-bed reactor, direct

contact between methane and oxygen in the gas phase is avoided in the membrane reactor as it leads to low conversion of methane [5].

Oxidative coupling of methane (OCM) is a widely researched pathway to convert natural gas to useful chemicals. Careful reactor design is needed owing to the high operating temperature of around 1000 K and the substantial heat production of the reaction, which reaches the practical limit of application of tubular reactors [1,2]. This necessitates cautious reaction control and detailed knowledge about the systems dynamics. To perform the oxidative coupling of methane reaction, Mixed-conducting oxide membranes such as pervoskite-type membranes are a promising alternative. Oxygen is gradually dosed from the surrounding shell side of the reactor into the catalyst-filled reaction zone to achieve a low local oxygen concentration which enhances reaction selectivity [3,4]. Due to the increasing demand of ethylene over the global market and the rising price of ethylene feedstock, researchers have devoted considerable effort over the past 30 years in finding economic process route such as OCM for the production of ethylene from methane. However, the production of C<sub>2</sub> hydrocarbons (i.e. ethylene + ethane) through OCM has been prohibited from commercial practice due to low overall yield [5].

Extensive studies on the OCM process have been conducted since the pioneer work of Keller and Bhasin [3] in 1982. There are many different reactor concepts proposed for use in this process. A fixed-bed reactor (FBR) has been used widely for OCM process due to its technological simplicity. Hong and Yoon studied the OCM process using the calcium chloride (CaCl<sub>2</sub>)-promoted calcium chlorophosphate catalysts, whereas Ji et al. [6] and Liu et al.[7] used the sodium tungsten oxide-Manganese/ Silicon dioxide (Na<sub>2</sub>WO<sub>4</sub>-Mn/SiO<sub>2</sub>) catalysts. However, this type of the 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 run-away, 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 [9]. Daneshpayeh et al. [8] 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 Zarrinepashne et al. [10] 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.

This study focuses on the isothermal operation of OCM and its advantage over adiabatic one, considering a dense tubular membrane reactor, to enhance the performance of OCM. Study is based on a mixed-conducting oxide membrane of pervoskite-type, which is popularly known for its ability 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</sub>- (BSCFO) is one such membrane with high oxygen permeability and an efficient oxygen distributor in the OCM reactor (Shao et al.)[11].

## MODEL DESCRIPTION FOR OCM CATALYTIC MEMBRANE REACTOR

Majority of kinetic models of OCM reaction which produces C<sub>2+</sub> hydrocarbons (ethane and ethylene) have been studied extensively based on following reaction mechanisms. All the researches have proved that the kinetics of OCM reaction is very complicated in terms of the proposed mechanisms as they involved several chemical species. Based on the previous research, kinetics mechanisms of OCM are broadly classified as [12 - 18]:

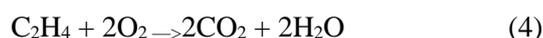
- i) Spectroscopic studies of O<sup>-</sup> species and the reaction with methane
- ii) Kinetic simulations of gaseous phase reactions
- iii) Simultaneous kinetic simulation of gaseous phase and surface reactions
- iv) Integrating kinetics of many radical reactions of single or several reactions
- v) Surface kinetics of methane consumption
- vi) Power rate law expression of C<sub>2+</sub> (ethane and ethylene) and CO<sub>x</sub> (CO and CO<sub>2</sub>) formation

Good approximation of experimental results have been achieved by the kinetic mechanisms proposed by Stansch et al. [13], Cheng and Shuai [19], Yaghobi and Ghoreishy [20], and Santamaria et al. [21].

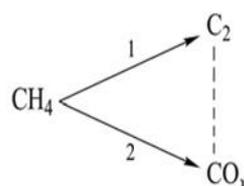
One of the best reaction mechanisms for OCM was suggested by Stansch et al. [13] who proposed a comprehensive ten-step kinetic model of OCM on the basis of kinetic measurements in over a wide range of reaction conditions. The reaction scheme contains three primary and seven consecutive steps. The conversion of hydrocarbons and of carbon monoxide with oxygen were described by applying Hougen-Watson type rate equations while for the other reactions power law rate equations were used. With this kinetic model, the experimentally determined conversions of methane and oxygen, as well as the yields of C<sub>2+</sub> hydro carbons and carbon oxides, could be predicted with an average accuracy of 20%.

A simplified reaction kinetic scheme was proposed by Yaghobi and Ghoreishy [20] for OCM over titanate pervoskite (SnBaTiO<sub>3</sub>) considering methane was converted in two parallel reactions by coupling reaction to C<sub>2+</sub> as a selective channel and by complete or partial oxidation to CO<sub>x</sub> as a non-selective step. Power law model was used to describe the reaction rates of methane and the products. The parameters in the power law model were estimated using linear regression.

A four lump kinetic scheme was suggested by Cheng and Shuai [19] which considered the catalytic reactions of methane, ethane and ethylene with oxygen as follows:



Another kinetic scheme was proposed by Santamaria et al. [21] considered both the gas phase and catalytic reactions shown by the following triangle reaction network:



Few other kinetic expressions available in the literature use power law for the description of reaction rates [22,26]. This category appears to be simple and practical. For this category, the use of intermediates is avoided and the rate of any product formation can only be expressed as a function of the reactant concentrations. This method has its own advantages and disadvantages. The form of kinetics adopted in this study is also power law, as this type of kinetics can be used for reactor simulations and it gives accurate results for reactor output. However, the detailed reaction mechanism, and components and radicals interactions cannot be described by this kind of equation.

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> (BSCFO) 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 (equations (5)-(10)) is developed based on the following assumptions:

- ) Steady-state operation
- ) No radial distribution of concentration in the tube or on the shell side of the reactor
- ) Axial diffusion dispersion is neglected
- ) Ideal gas law is assumed

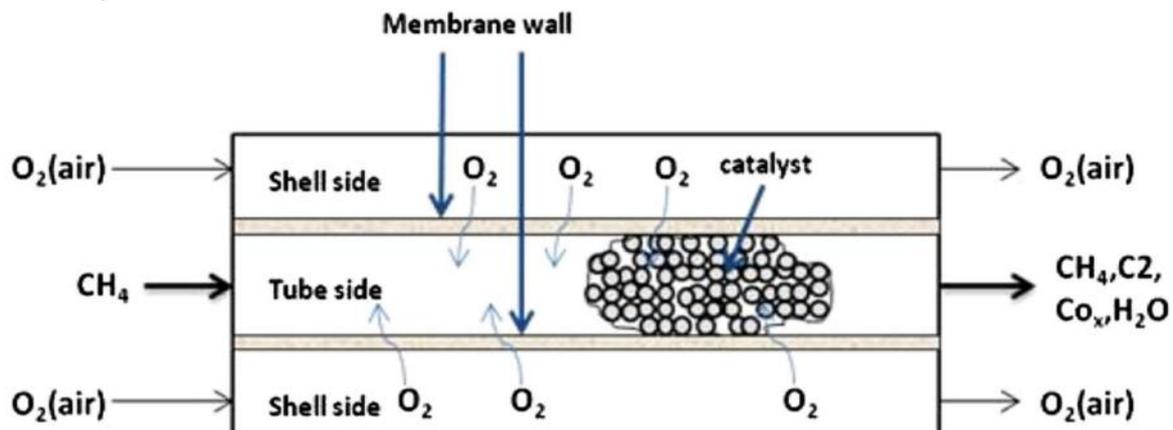


Fig1. Schematic representation of membrane reactor model for OCM

### Mass Balances

Tube side:

$$\frac{dF_t^t}{d} = \frac{W}{V} A_c \sum_{j=1}^n v_{i,j} r_j + \pi d_2 J_{O_2} \quad (5)$$

Shell side:

$$\frac{dF_{O_2}^s}{d} = -\pi d_1 d_2 \quad (6)$$

### Energy balances (for adiabatic operation)

Tube side:

$$\frac{dT^t}{d} = \frac{\frac{W}{V} A_c \sum_i (-\Delta H_i r_i) - q + \pi d_2 J_{O_2} C_{pO_2} \Delta T}{\sum_j F_j C_{p_j}} \quad (7)$$

Shell side:

$$\frac{dT^s}{d} = \frac{q}{F_{O_2}^s C_{pO_2}} \quad (8)$$

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

$$q = \frac{A_c K_m (T^t - T^s)}{M} \quad (9)$$

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 overall oxidative coupling process is highly exothermic and isothermal operation would be difficult to be achieved. Adiabatic operation is easier to bring into practice because of the simplicity of construction of the reactor. In the reactor model for adiabatic operation, an energy balance equation (Eq. (9)) is considered besides mass balance equations.

The oxygen permeation through the tubular BSCFO membrane can be explained by the oxygen flux (Equation (10)), which developed by Kim et al. [23].

$$J_{O_2} = \frac{\pi C_i D_a}{2S (d_1/d_2)} l \left( \frac{P_1}{P_2} \right) \quad (10)$$

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.

### KINETIC MODEL:

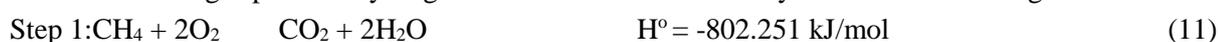
This is a comprehensive kinetic model to predict behavior of this catalyst. The Lanthanum oxide/calcium oxide ( $\text{La}_2\text{O}_3/\text{CaO}$ ) catalyst which is necessary for modeling and simulation of the OCM reactors. Since the OCM is a complex reaction network of parallel and consecutive, heterogeneous as well as homogeneous reaction steps, numerous reaction models have been presented to describe the performance of the OCM process. The models proposed in literature differ in the reaction schemes applied and in the number of product compounds considered.

Reaction network of Stansch et al. [13] consists of nine heterogeneous and one homogeneous reaction steps. According to this model, methane is converted in three parallel reactions - formation of ethane by oxidative coupling of methane, nonselective total oxidation of methane to carbon dioxide and partial oxidation of methane to carbon monoxide. Carbon monoxide is oxidized to carbon dioxide. In consecutive steps, the conversion of ethane can proceed by two parallel routes, i.e. by heterogeneous catalytic oxidative dehydrogenation of ethane and thermal gas-phase dehydrogenation of ethane to ethylene. Ethylene can be converted to carbon monoxide in two parallel ways; i.e. partial oxidation and steam reforming. Also carbon monoxide to carbon dioxide ratio is influenced by the water-gas-shift reaction which proceeds in both directions. In this reaction network model direct oxidation of ethane to carbon oxides was neglected. In the oxidation of methane to carbon monoxide, two fast steps, i.e. formation and consecutive decomposition of formaldehyde, were lumped. Reactions of ethane and ethylene to higher hydrocarbons ( $\text{C}_{3+}$ ) with less than 5% selectivity are neglected [24]. Parallel reactions in the gas-phase are mostly lumped with the heterogeneous steps and their contribution is accounted during the estimation of kinetic parameters. This model was first developed based on OCM over  $\text{La}_2\text{O}_3/\text{CaO}$  in the range of 760–780 °C.

In order to choose the best OCM reaction network for developing a comprehensive kinetic model for OCM reaction, Daneshpayeh et al [8] compared five networks using Genetic algorithms. After parameter estimation of all network models with appropriate rate equations, the models were discriminated based on experimental data and a statistical method. Their experimental results showed that oxidative and thermal dehydrogenation of ethane and total oxidation of hydrocarbons have significant effects on OCM reaction. Therefore, these reactions must take into the account in reaction network. Both experimental and statistical analysis confirms that the reaction network of Stansch et al. [13] has the best accuracy compared to other models. This model considers almost all reaction steps of other models, including heterogeneous and homogeneous, primary and consecutive reactions. Taking into account the inhibiting effects of oxygen and carbon dioxide, kinetics of ethane formation was described with a Hougen-Watson type equation and other reaction steps were described by applying the power-law rate equations.

#### Kinetic details of OCM:

A comprehensive kinetic model of the OCM reaction used in this study was developed by Stansch et al.[13] 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:

$$r_j = \frac{K_{0j} e^{-E_{a,j}/R} P_C^{m_j} P_{O_2}^{n_j}}{(1 + K_{j,C} e^{-\Delta H_{a,j,C}/R} P_{CO_2})^2} \quad j = 1, 3-6 \quad (21)$$

$$r_2 = \frac{k_{0,2} e^{-E_{a,2}/R} (K_{0,O_2} e^{-\Delta H_{a,O_2}/R} P_{O_2})^{n_2} P_{CH_4}}{[1 + (K_{0,O_2} e^{-\Delta H_{a,O_2}/R} P_{O_2})^{n_2} + (K_{j,C} e^{-\Delta H_{a,j,C}/R} P_{CO_2})^2]} \quad (22)$$

$$r_7 = k_{0,7} e^{-E_{a,7}/R} P_{C_2H_6} \quad (23)$$

$$r_8 = k_{0,8} e^{-E_{a,8}/R} P_{C_2H_4}^{m_8} P_{H_2O}^{n_8} \quad (24)$$

$$r_9 = k_{0,9} e^{-E_{a,9}/R} P_C^{m_9} P_{H_2O}^{n_9} \quad (25)$$

$$r_{10} = k_{0,10} e^{-E_{a,10}/R} P_{CO_2}^{m_{10}} P_{H_2}^{n_{10}} \quad (26)$$

Investigating OCM performance:

The set of differential and algebraic equations considered under model equations and kinetics of OCM are solved using Euler integration method in MATLAB. Performance of OCM reaction is evaluated by considering conversion ( $X_{C_4}$ ), selectivity ( $S_{C_2}$ ) and  $C_2$  Yield ( $Y_{C_2}$ ). Table 1 lists the kinetic parameters used for the above reaction scheme.

$$X_{C_4} (\%) = \frac{m_{O_2} C_{4i} v_e}{(m_{O_2} C_{4f})} \times 100 \quad (27)$$

$$S_{C_2} (\%) = \frac{2x(m_{O_2} C_{2hy})_p}{m_{O_2} C_{4c}} \times 100 \quad (28)$$

$$Y_{C_2} (\%) = \frac{2x(m_{O_2} C_{2hy})_p}{(m_{O_2} C_{4f})} \times 100 \quad (29)$$

**Table1: OCM kinetic parameters Stansch et al. [7]**

Step	$K_{0,j}$ ( $\text{mol g}^{-1}\text{s}^{-1}$ $\text{Pa}^{-(m+n)}$ )	$E_{a,j}$ ( $\text{kJ mol}^{-1}$ )	$m_j$	$n_j$	$K_{j,\text{CO}_2}$ ( $\text{Pa}^{-1}$ )	$\Delta H_{\text{ad},\text{CO}_2}$ ( $\text{kJ mol}^{-1}$ )	$K_{j,\text{O}_2}$ ( $\text{Pa}^{-1}$ )	$\Delta H_{\text{ad},\text{O}_2}$ ( $\text{kJ mol}^{-1}$ )
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				

<sup>a</sup> units are  $\text{mol s}^{-1}\text{m}^{-3}\text{Pa}^{-1}$

**Table 2: Operating conditions and reactor configuration**

<u>Operating conditions</u>	
Temperature ( $^{\circ}\text{C}$ )	800 (Range: 700 - 900)
Methane/Oxygen feed ratio	2(Range: 0.5 – 3)
Methane feed flow rate ( $10^{-3}\text{mol/s}$ )	1.6(Range: 1.2 - 2.8)
<u>Reactor configuration</u>	
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

**Table 3: Heat capacity of gas species involved in the reactions ( $C_{p,j}$ ) J/mol-K**

CH <sub>4</sub>	35.618
O <sub>2</sub>	29.407
CO <sub>2</sub>	37.144
H <sub>2</sub> O	35.499
CO	28.517
C <sub>2</sub> H <sub>4</sub>	42.923
C <sub>2</sub> H <sub>6</sub>	52.623
H <sub>2</sub>	28.869

**Table 4: The ambipolar diffusion coefficients ( $D_a$ ) at different temperature (700- 900 $^{\circ}\text{C}$ )(Lu et al.,[25])**

T ( $^{\circ}\text{C}$ )	$D_a$ ( $\text{m}^2\text{s}^{-1}$ )
700	$0.77 \times 10^{-10}$
750	$1.16 \times 10^{-10}$
800	$1.68 \times 10^{-10}$
850	$2.34 \times 10^{-10}$
900	$3.31 \times 10^{-10}$

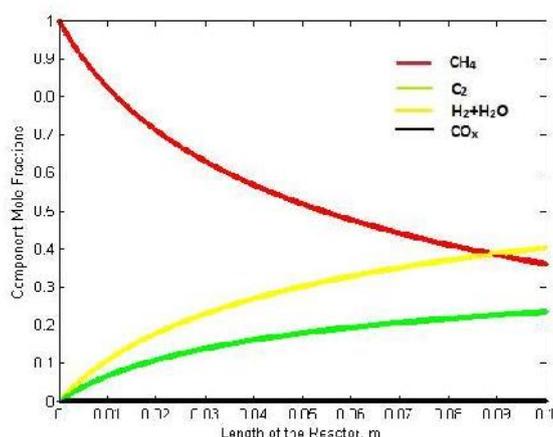
## RESULTS AND DISCUSSION

The primary advantage of using the membrane reactor was to facilitate combustion of methane throughout the reactor length, not letting it to occur solely at the beginning of the reactor which would otherwise damage the reactor due to temperature build up caused by exothermic nature of the reaction.

The sensitivity of Stansch et al. [13] model towards the changes in inlet conditions was analyzed. The simulation model was studied for various inlet conditions like reactor temperature and methane flow rate, methane to oxygen ratio.

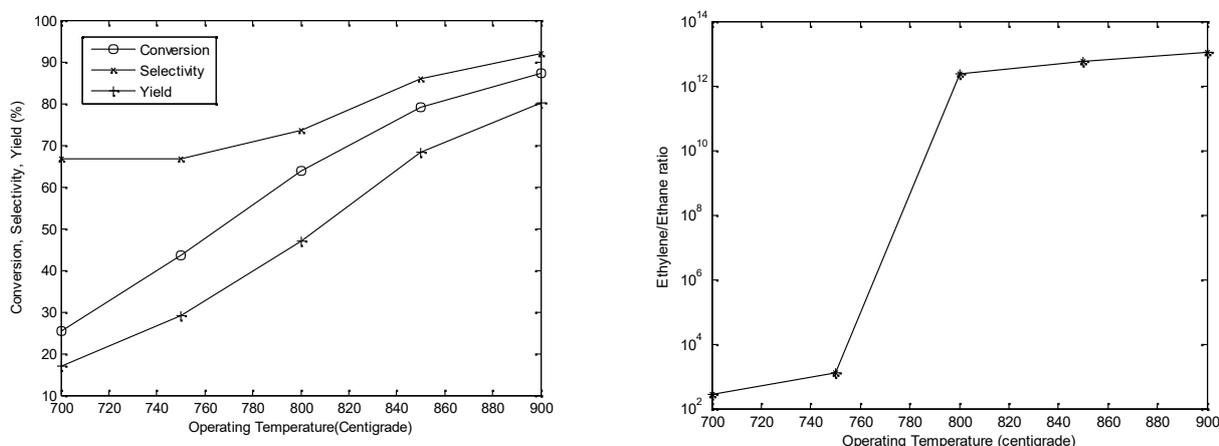
### Concentration profiles along the length of the reactor:

The simulation was run at reactor temperature of 800°C, for a methane flow rate of  $1.6 \cdot 10^{-3}$  mol/s and reactor length of 0.1 meter. The changes of component mole fractions predicted by the model (for isothermal conditions) along the length of the reactor are given in Fig.2. From model predictions, it was observed that methane conversion followed a steep linear decline towards the end of the reactor. It shows the concentration profiles of  $C_2$ ,  $CO_x$ ,  $(H_2 + H_2O)$ , and  $H_2O$  along the reaction side of the reactor. It is found that as the methane concentration decreases along the reactor length, the other gaseous components increase due to the increased reaction rates after oxygen is permeated from the shell side. Oxygen can be consumed not only by the oxidative reactions but also by the dehydrogenation of ethane and ethylene.



**Fig2: Concentration profiles on the tube side of membrane reactor**

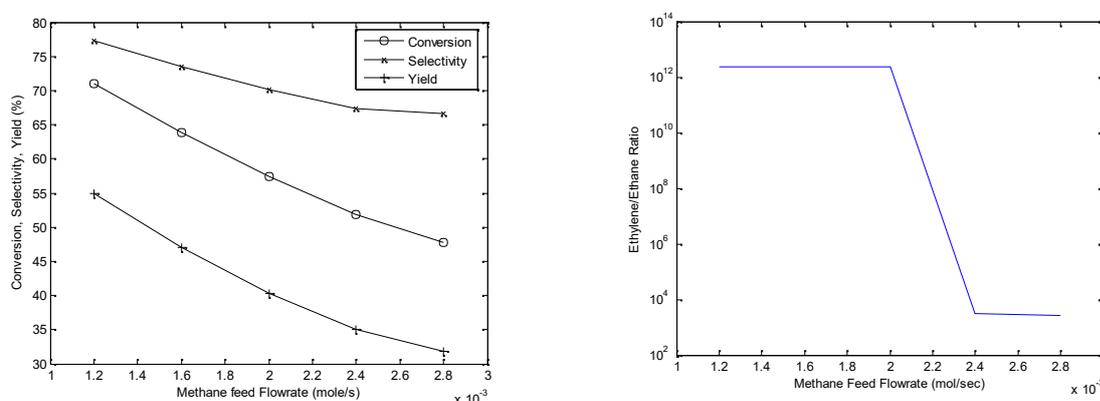
### Effect of operating temperature



**Fig3: Effect of operating temperature on a)  $CH_4$  Conversion, Selectivity and Yield of  $C_2$  products and b)  $C_2H_4/C_2H_6$  product ratio**

The effect of operating temperatures on the performance of an OCM membrane reactor has been investigated by varying the inlet temperature from 700°C to 900°C as shown in Fig.3, for a methane flow rate of  $1.6 \times 10^{-3}$  mol/s, reactor length of 0.1 meter and methane/oxygen ratio at 2. When the operating temperature is changed from 700 to 900 °C, initially, the CH<sub>4</sub> conversion and C<sub>2</sub> product yield are increased with increasing operating temperature, as seen in Fig. 3a. This is because the reaction rate and oxygen flux through the membrane are increased at higher temperatures Shao et al.[11]. 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 leads to more undesired side reaction and causes a slow rise in C<sub>2</sub>selectivity and C<sub>2</sub> yield. The increments of H<sub>2</sub>, H<sub>2</sub>O, and CO<sub>x</sub> products indicate that the rate of hydrocarbons oxidation over La<sub>2</sub>O<sub>3</sub>/CaO catalyst is favored at high temperatures. As a result, the C2 selectivity increases at a flatter profile with higher operating temperature. The simulation result also shows that an increase in temperature can improve the C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> product ratio (Fig. 3b). It can be observed that the dehydrogenation (thermal cracking) of ethane to ethylene is more pronounced at 800°C and for temperatures beyond that the ratio does not increase much.

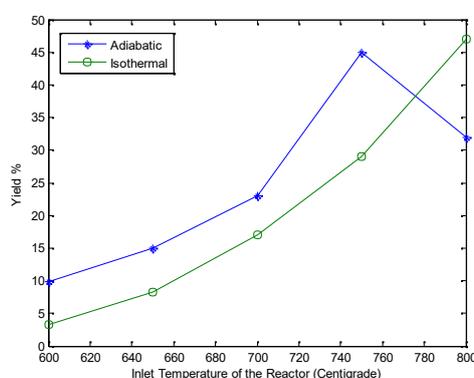
#### Effect of methane feed flow rate



**Fig4: Effect of methane feed flow rate on a) CH<sub>4</sub> Conversion, Selectivity and Yield of C<sub>2</sub> products and b) C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> product ratio**

Fig. 4a shows CH<sub>4</sub> conversion, selectivity and yield of C<sub>2</sub> products for different methane feed flow rates varying from 1.2 to 2.8 mole-s<sup>-1</sup>, at a temperature of 800°C and methane to oxygen ratio at 2. When the flow rate of methane is higher than that required, as seen above in fig. 4a and fig. 4b, oxygen availability in the tube side decreases and hence efficiency of OCM performance decreases, leading to a steep fall in C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> for feed flow rate beyond 2 mole-s<sup>-1</sup>

#### Adiabatic operation



**Fig5: Comparison of C<sub>2</sub> yield under isothermal and adiabatic conditions**

Many previous studies on the OCM process assumed isothermal condition in the membrane reactor. But this led to the formation of hotspot in the reactor, particularly in the fixed-bed type. This problem was overcome by using a catalytic membrane reactor, by virtue of which oxygen supply was distributed along the reactor length, and thus the reactor was maintained at an approximate isothermal condition. But, due to the highly exothermic nature of OCM reactions, the assumption that the reactor is operated under the isothermal condition might lead to the unrealistic prediction of the reactor performance. Hence the OCM reactor was run under an adiabatic operation, where heat released during the oxidation coupling process increased the reactor temperature. Compared with the isothermal operation, as seen in Fig. 5, the adiabatic operation provides a higher  $C_2$  yield at the inlet temperature range of 600–800 °C.

## CONCLUSIONS

Simulations were done using isothermal and also adiabatic conditions for the ten step reaction mechanism used in the model. The model predictions indicated that the reaction temperature, reactor length and  $CH_4$  feed flow rates played vital role in determining the extent of reactions. The kinetic models in literature suffered a setback as they considered only the primary reactions leading to the desired products. But the kinetic model considered in the above study is a comprehensive model which considered all the possible kinetics that impacts the reactions. It is suggested that this kinetic model can be used for estimating the methane conversion, and  $C_{2+}$  selectivity and yield under the similar conditions. This kinetic model may be used as a generic one for membrane reactors with OCM catalysts, with similar properties for studying the reaction parameters and sensitivity. The trends depicting the OCM performance (of methane conversion,  $C_{2+}$  selectivity and yield) were investigated for varying temperatures and methane feed flow rates. The results showed that this model can be used for kinetic modeling of OCM with its own limitations. It was also observed that applicable range of temperature to obtain maximum yield is between 600– 800°C by carefully controlling the oxygen flow rate and thereby minimizing the side effects of high temperatures. The study shows that an adiabatic operation would yield better performance of an OCM reactor over isothermal operation.

## LIST OF SYMBOLS

<b>Variables</b>			
$A_{cs}$	Cross-sectional area of the tube side ( $m^2$ )	$q$	Heat flux between the tube side and shell side ( $J m^{-1} s^{-1}$ )
$C_i$	Density of oxygen ions ( $mol m^{-3}$ )	$r_j$	Rate of reaction $j$ ( $mol g^{-1} s^{-1}$ )
$C_{p_i}$	Heat capacity of specie $i$ ( $J mol^{-1} K^{-1}$ )	$S$	Effective area of the membrane tube ( $m^2$ )
$D_a$	Ambipolar diffusion coefficients ( $m^2 s^{-1}$ )	$V$	Reactor volume ( $m^3$ )
$d_1$	Outer diameter of the membrane tube (m)	$T$	Temperature ( $^{\circ}C$ )
$d_2$	Inner diameter of the membrane tube (m)	$W$	Catalyst weight (g)
$E_{a, j}$	Activation energy in reaction $j$ ( $kJ mol^{-1}$ )	$Z$	Reactor length (m)
$F_i$	Molar flow rate of specie $i$ ( $mol s^{-1}$ )		
$H_i$	Heat of reaction $i$ ( $J mol^{-1}$ )	$v_i$	<b>Greek symbols</b>
$J_{O_2}$	Oxygen flux through the membrane ( $mol cm^{-2} s^{-1}$ )	$j$	Stoichiometric coefficient of component $j$ of reaction $i$
$K_m$			
$K_0$	Average thermal conductivity ( $J s^{-1} m^{-1} K^{-1}$ )	$t$	
$L$	Kinetic parameter ( $mol g^{-1} s^{-1} Pa^{-(m+n)}$ )	$s$	<b>Superscripts</b>
$M$	Length of the membrane tube (m)		Tube side
$P_i$	Membrane thickness (m)		Shell side
	Partial pressure of component $i$ (Pa)		

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