Oxidative Coupling of Methane in Membrane Reactor Reactor Simulation Studies and Multi Objective Optimization

M Kalyani, Bhadri Srinivas, V Ramesh Kumar, S V Satyanarayana

Abstract: *Oxidative coupling of methane (OCM) is the most efficient process pathway for ethylene manufacture from abundantly sourced methane. Fixed bed and fluidized bed reactors have been in use for OCM. However the difficulty in controlling the temperature during the exothermic reaction and deep oxidation of methane to produce less useful oxides of carbon, lead the focus onto membrane reactors for OCM. This work intends to compare the performance of OCM in a membrane reactor with a co-feed reactor for OCM and optimize the operating conditions. Based on the reaction kinetics in a conventional co-feed fixed bed reactor, a model is developed for membrane reactor and simulated to study the effect of various parameters on the performance of OCM to maximize ethylene selectivity and yield. Genetic algorithm is used for optimization of reactor temperature to maximize the selectivity and yield of C_2 products. To maximize selectivity to around 27- 30 %, lower conversion is preferred and temperature is to be maintained at 1150 K.*

Keywords: Oxidative coupling of methane (OCM), Co-feed, Membrane reactor

I. INTRODUCTION

OCM to C_2 and higher hydrocarbons is viewed as a most favorable pathway to produce more useful products from natural gas and continued to gather the attention of industrial and academic researchers. OCM comprises of homogeneous as well as heterogeneous reaction steps in a reversible reaction, to produce ethylene as a target product. Simultaneously, carbon oxides (CO_x) and higher hydrocarbons are also produced from methane as undesirable products in side reactions. Methane undergoes gas phase reaction with oxygen and also on the catalyst surface in lattice form. A good amount of research has been done on OCM to produce ethylene or ethane (C_2 products) using conventional reactors in the past ten years. However a conventional fixed bed reactor could only result in yield 25% C_2 products (ethane and ethylene). This is attributed to the complete oxidation

reactions occurring partially in the gaseous phase and on the catalyst surface, which tend to decrease C_2 selectivity to a very large extent, specifically under high temperature and pressure conditions. A membrane reactor was investigated for OCM to obtain a much higher C_2 selectivity and yield by minimizing the contact between C_2 products and oxygen [1]. In addition, the membrane reactor is a promising alternate for its safe operation and can also be simultaneously used to separate oxygen from air in one device. Thus eliminating the costs incurred in oxygen separation from air. Inorganic membranes are like glass, metal and ceramic materials and their oxides are suitable for high temperature options. Such type of membrane reactor is made up of a dense oxide membrane layer or a porous one. One side of it is exposed to catalytic material and the other to oxygen. Unlike the conventional co-feed mode as in a fixed bed reactor, distributed supply of oxygen through the membrane allows to maintain considerably low oxygen concentration in the reaction side, thereby increasing C_2 selectivity [2]. Careful reactor design is the need of the hour to counterfeit the high reactor temperature (more than 1000 K and the enormous heat generation by the exothermic nature of the reactions, which practically limits the use of conventional co-feed reactors [3], [4]. Hence careful reaction control and system dynamics are necessary. Factors like rising prices of ethylene feedstock and greater demand for ethylene in global markets have driven investigators in the past thirty years to make significant efforts in finding economically feasible processes like OCM, for obtaining C_2 hydrocarbons from methane. Due to comparatively low yields in OCM, the production of C_2 hydrocarbons via this route is still not upgraded for industrial production [5]. Pervoskite-type mixed-conducting oxide membranes are an efficient choice for OCM. As low local oxygen concentration enhances reaction selectivity [6], [7] oxygen is supplied from the reactor shell side into the catalyst filled tube side of the reactor (reaction zone). Extensive research on the OCM process has been conducted since the initial pioneering work of Keller and Bhasin [6] in 1982. Various reactor concepts have been proposed for OCM process. A fixed bed reactor has been the first option which was widely used due to its simplicity in operation. Choice of catalyst is also very crucial for OCM process as the surface of catalyst affects the reaction mechanism. A wide range of catalysts have been proposed, developed and tested for OCM process [8], [9] and [10] .

Catalyst selectivity and stability affect the performance of OCM.

Most of the OCM catalysts have failed either because of lack of stability or poor selectivity. However, fixed bed reactors suffered a setback from practical usability due to temperature runaway caused by large amount of heat released during the reaction. Furthermore, a poor heat management of the highly exothermic reaction results in the hot spots, causing deleterious effect on the reactor operation, such as uncontrollable temperature, deactivation of catalyst, unwanted side reactions, and thermal deterioration of products. A fluidized-bed reactor offer better heat transfer capacity and heat management to control temperature, over a fixed-bed reactor system [11]. Daneshpayeh et al. [12] studied OCM over $Mn/Na_2WO_4/SiO_2$ catalyst in a two zone fluidized bed reactor (TZFBR), and its performance was compared with the conventional fluidized bed reactor. Although the TZFBR achieved larger C_2 selectivity than the fluidized bed reactor, it ws was relatively less (20 %).

The operational difficulty in OCM process is that, the target products and intermediates are more reactive than the reactant itself and thereby results in deep oxidation to CO_x. Hence there should be a way out to avoid non-selective oxidation of methane and C_2 products due to the presence of high oxygen concentration in the reaction stream. Zarrinepashne et al. [13] proposed the concept of distributed oxygen feed in fixed bed reactors, to avoid the deleterious effect caused by high concentrations of oxygen, thereby improving OCM performance. But this reactor concept could not achieve predicted high C_2 yield, due to the incomplete mixing of gas at the oxygen feeding locations. This resulted high oxygen concentration spots where C_2 products are easily oxidised leading to a significant fall in selectivity.

The following kinetic mechanisms are used extensively for the study of a variety of kinetic models of OCM to produce C_2 hydrocarbons. Since the proposed mechanisms involve many chemical species, the kinetics of OCM reaction becomes complicated. Kinetic mechanisms of this reaction are mainly classified as [14], [15], [16], [17], [18], [19], [20], and [23]:

i. gaseous phase reactions – kinetic simulation
ii. gaseous phase and surface reactions – simultaneous simulation
iii. kinetics of several radical reactions of single or many reactions
iv. methane consumption surface kinetics
v. power law model rate expressions of C_{2+} and CO_X
vi. spectroscopic studies involving O^- species and the reaction with methane

Kinetic mechanisms proposed by Stansch et al. [14], Cheng et al. [23], Yaghobi et al. [20], and Santamaria et al. [21] are in good consistency with experimental results.

One of the mechanisms proposed by Stansch et al. [14] is a comprehensive multistep mechanism consisting of ten steps. This model was proposed on the basis of kinetic measurements over a wide range of reaction conditions. The scheme of reaction has three primary and seven consecutive steps. Hougen-Watson (HW) type of rate expressions were used to describe conversion of hydrocarbons and carbon monoxide with oxygen. The other reaction rates were described by power law rate model. The conversions of methane and oxygen were determined experimentally with this kinetic model. Also the yields of C_{2+} hydro carbons and carbon oxides could be predicted with an average accuracy of 20% [24].
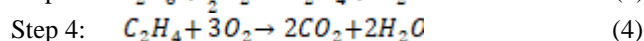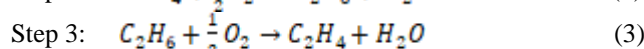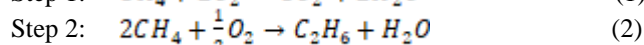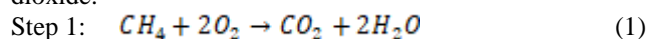
Another simplified kinetic scheme of reaction for OCM was proposed by Yaghobi et al. [20] over titaniate perovskite ($SnBaTiO_3$). Methane was considered to be converted in two parallel reactions by coupling reaction to C_2, as a selective channel and by complete or partial oxidation to CO_x as a non-selective step. The reaction rates of methane and the products are described by power law model. Linear regression was used to determine the parameters in the model.

This study focuses on the isothermal operation of OCM in a dense oxide membrane reactor, to achieve better performance of OCM. The simulation study proves that a membrane reactor acts as an efficient oxygen distributor and greatly improves the selectivity and yield of C_2 products over the co-feed reactor. To investigate the OCM performance, methane conversion, product selectivity and yield (for C_2H_4, C_2H_6 and CO_2) are evaluated by varying the reaction temperature between 900 and 1400 K over a reactor length of 0.8 meters for a methane to oxygen feed ratio of one at a pressure of 4 atm. Subsequently the effect of feed ratio (range = 1 to 5) and pressure (1 to 5 atm) are also studied for OCM membrane reactor. Operation of membrane reactors requires the minimization or maximization of several conflicting objectives. Hence multi objective optimization of a membrane reactor is much needed. Single variable multi objective optimization is performed for OCM to make an optimum choice of the operating conditions in the presence of trade-offs between the objectives. The results show that it is a nontrivial multi objective optimization problem, where no single solution exists that simultaneously optimizes chosen objective and the objective functions are said to be conflicting with each other, thus resulting in a finite number of pareto optimal solutions.

II. MODELLING OF OCM REACTOR

A. Reaction Scheme for OCM

The kinetic equations for OCM used in this study were experimentally developed by Hinsen et al. [22] with 34 wt. % ($PbO/ \gamma-Al_2O_3$) lead oxide catalyst impregnated on γ-alumina. To demonstrate the performance of the reactors, the kinetic model considered here comprises four simple reactions. Step 1 is non-selective oxidation of methane to carbon dioxide. Selective step 2 results in formation of ethane by OCM. In the consecutive step 3, ethylene is formed by heterogeneous catalytic dehydrogenation. Ethylene so formed can be deteriorated by further reaction with oxygen to form carbon dioxide.

Step 1: $$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{1}$$

Step 2: $$2CH_4 + \tfrac{1}{2}O_2 \rightarrow C_2H_6 + H_2O \tag{2}$$

Step 3: $$C_2H_6 + \tfrac{1}{2}O_2 \rightarrow C_2H_4 + H_2O \tag{3}$$

Step 4: $$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \tag{4}$$

B. Rate Equations

For the above considered reaction mechanism, the rate expressions have been derived by fitting expressions for the experimental data [22].

$$r_1 = 0.015\exp(-6134/T)C_{CH_4}^{0.4}C_{O_2}^{1.5} \tag{5}$$

$$r_2 = 0.6\exp(-11908/T)C_{CH_4}^{0.8}C_{O_2}^{1.1} \tag{6}$$

$$r_3 = 1.0x10^{-4}\exp(-722/T)C_{C_2H_6}^{0.8}C_{O_2}^{1.0} \tag{7}$$

$$r_4 = 1.0x10^{-16}\exp(26461/T)C_{C_2H_4}^{0.8}C_{O_2}^{1.6} \tag{8}$$

C. Reactor Configuration

The performance of OCM is considered in two modes of reactor operation – one is a co-feed operation in a tubular plug-flow reactor (experimental) and the other is membrane reactor (simulated). A dense oxide membrane tube separates the membrane tubular reactor into shell side and tube side. Oxygen permeates through the membrane in the shell side in a well-controlled way and reacts with methane in the catalyst coated tube side as in Fig.1. As the catalyst is packed in the tube side, only the tube side gases are in direct contact with it, thus causing the OCM reaction to occur along the membrane.
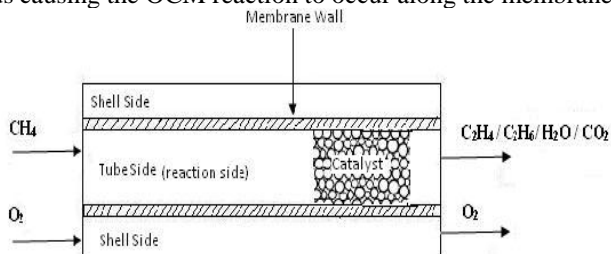

Fig. 1 Schematic Illustration of Tubular Membrane Reactor for OCM

D. Model Description

The simulation of OCM reactors is based on the mathematical model developed from the component mass balance equations written for each component 'i' as published in Cheng and Shuai [23].

Tube side and shell side component mass balance based on the following assumptions:

$$\frac{dF}{dL} - \pi d_R w_c R_i = 0 \tag{9}$$

$$R_i = \sum_{j=1}^{4} \vartheta_{ij} r_j \tag{10}$$

1. plug flow of gaseous components
2. no mass-transfer resistance
3. steady state, isothermal and isobaric conditions are maintained
4. ideal gas behavior
5. only length wise concentration distribution on both shell and tube side
6. no axial diffusion dispersion
7. the oxygen flux across the membrane is independent of the its partial pressure on the tube side of the reactor
8. membrane is impermeable to other reactants and products

At the inlet (x=0), except for methane and oxygen, molar flow rates of all other components are zero. For the membrane reactor, the tube side mass balance equations and inlet conditions are the same for all reactants and products, except oxygen. Hence for a membrane reactor,

$$\frac{dF_{O_2}}{dx} - \pi d_r \left(f_{o_2} + f_c R_{O_2} \right) = 0 \tag{11}$$

Based on the ideal gas equation, the concentration and molar flow rate of a component 'i' are related as:

$$C_i = \left(\frac{P}{RT}\right)\left(\frac{F_i}{\sum F_i}\right) \tag{12}$$

E. Investigating OCM Performance

The governing differential equations for co-feed reactor (equation - 9) and for membrane reactor (equation - 9 and 11) are each solved separately in MATLAB by using an implicit Runge-Kutta formula with a trapezoidal rule step as its first and a backward differentiation formula of order two as its second step.

Performance of OCM reaction is evaluated by considering methane conversion (X_{CH_4}), C_2 selectivity (S_{C_2}) and C_2 Yield (Y_{C_2}).

$$X_{CH_4}(\%) = \frac{moles\ of\ CH_4\ converted}{(moles\ of\ CH_4)_{feed}} x100 \tag{13}$$

$$S_{C_2}(\%) = \frac{2x(moles\ of\ C_2\ hydrocarbons)_{products}}{moles\ of\ CH_4\ converted} x100 \tag{14}$$

$$S_{CO_2}(\%) = \frac{(moles\ of\ C_2\ hydrocarbons)_{products}}{moles\ of\ CH_4\ converted} x100 \tag{15}$$

$$Y_{C_2}(\%) = \frac{2x(moles\ of\ C_2\ hydrocarbons)_{products}}{(moles\ of\ CH_4)_{feed}} x100 \tag{16}$$

Table. 1 Operating conditions and reactor specifications

Temperature range	900 – 1400 K
Feed (CH_4/O_2) ratio (R_f)	1 – 5
Total feed flow rate	9.6×10^{-5} mol/s
Length	0.8 m
diameter	0.014 m
Mass of catalyst	1.0 g
Pressure	Range: 1 to 5 atm
Flux across the membrane reactor	10^{-5} mol/m^2

III. RESULTS AND DISCUSSION

Adopting the kinetic model for OCM developed by Hinsen et al. [22], and the one-dimensional mathematical model developed by Cheng & Shuai [23], for an isothermal operation in a steady state catalytic tubular membrane reactor, OCM performance is analyzed by assuming ideal gas behavior, no diffusion dispersion along the axis for plug flow of gaseous reactants and products, with negligible mass-transfer resistance. Membrane reactor is simulated to study the effect of reaction temperature, ratio of methane to oxygen (feed ratio = R_f), and reactor pressure.

Methane conversion, selectivity of ethane, ethylene and carbon dioxide, yield of ethane, ethylene and carbon dioxide are the various aspects evaluated to analyze OCM performance in membrane reactor. Concentration profiles (Fig.2) are generated to compare the performance of co-feed reactor with membrane reactor.

Simulated results are compared with experimental co-feed results, to test and validate the model. Deviation and or percentage improvements in the OCM performance are reported (Table 2). Single variable multi objective optimization is performed for OCM in membrane reactors, using Genetic Algorithm technique to find optimum value of operating temperature for a fixed value of feed ratio.

A catalytic membrane reactor of length 0.8 m and radius 0.007 m is simulated with methane being fed from the tube side with a flow rate of 9.6×10^{-5} mol/s and oxygen evenly distributed along the length and diffusing through the membrane. One gram catalyst is coated on the reaction side of the reactor. Table1 shows the reactor configuration and the reactor operating conditions. Fig.2a and 2b illustrates the concentration profiles of CH_4, O_2, CO_2, H_2O and C_2 products across the length of the reactor. It is noticed that in fig.2a, for a cofeed reactor, methane and oxygen concentration decrease as the reaction occurs, causing an increase in concentration profile of other gaseous components. But in dense oxide membrane reactor (Fig.2b), only methane decreases as reaction progresses. Oxygen is not only consumed by selective and non-selective oxidation, but also by dehydrogenation of C_2 products. At the beginning of the reaction, selective oxidation of methane is greater than non-selective and hence the formation of C_2 products is more than CO_2. In the later stages, when oxygen concentration depletes, OCM reaction and also non-selective oxidation become slow and constant. It is observed that the concentration of C_2 products obtained is 40% higher in a membrane reactor than in a conventional reactor.
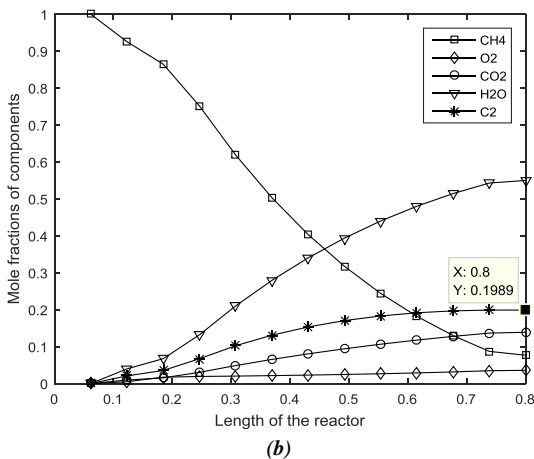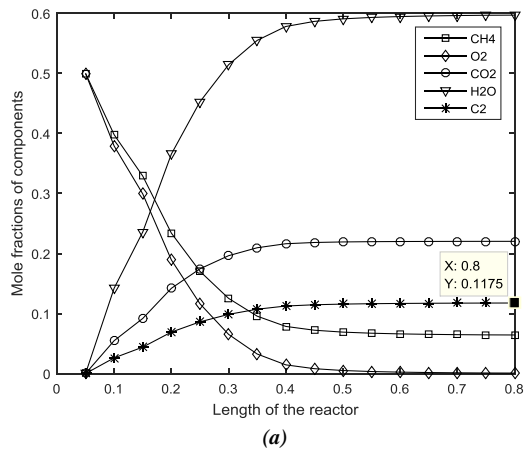
Fig. 2 Concentration profiles for: a) Co-feed Reactor b) Membrane Reactor (R_f = 1, Pressure = 4 atm, Temperature = 1300 K)

A. Effect of Operating Temperature

For CH_4/O_2 ratio (R_f) of 1 and 4 atm of operating pressure, the membrane reactor model is simulated at different operating temperatures ranging from 900 to 1400K. Fig 3a and 3b show methane conversion, selectivity and yield of products as functions of temperature. C_2H_6 selectivity increases with temperature even beyond T=1400 K though C_2H_4 selectivity significantly decreases beyond 1200 K from 29% to 27% at 1300 K and even less further. Though methane conversion, selectivity and yield of C_2H_6 are consistently on rise with temperature, temperatures beyond 1250 K are not favorable for ethylene selectivity. Selectivity and yield of CO_2, which is an unwanted product, decreased with the temperature.

(a)

(b)
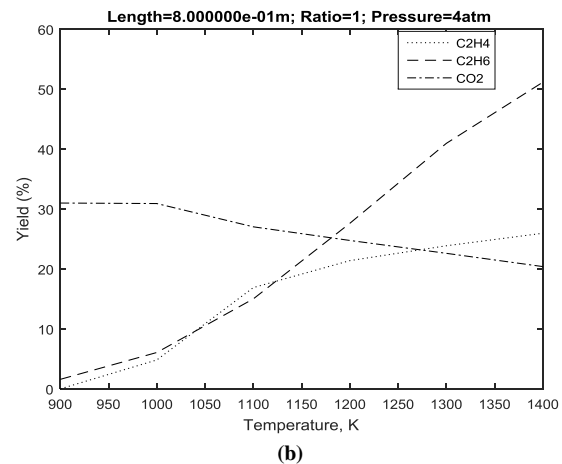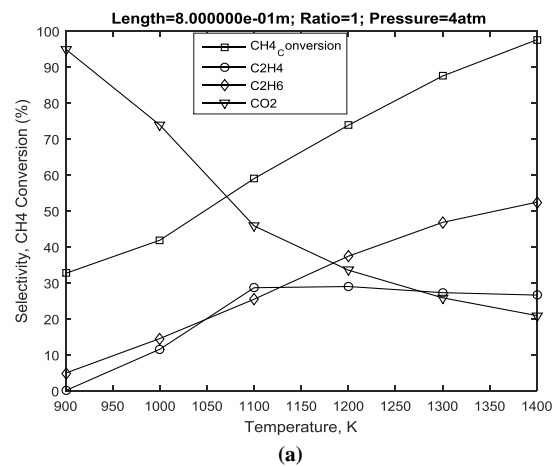
Fig. 3 Effect of reactor temperature on product selectivity and yield

B. Effect of CH_4/O_2 ratio

Membrane reactor simulated at 1200 K temperature, 4 atm pressure and R_f ranging from 1 to 5, selectivity of C_2 products decreases with increasing ratios. For all the excess oxygen supplied has no significant effect on the product selectivity and yield beyond a value of 2, as is from Fig. 4a and 4b.

(a)

(b)
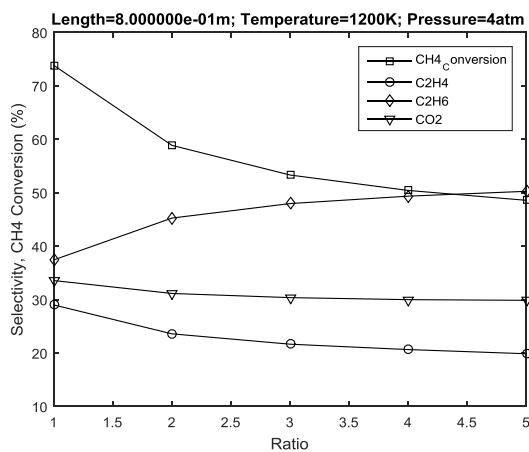
(a)

(b)

Fig. 4 Effect of CH_4/O_2 ratio on selectivity and yield

C. Effect of Operating Pressure

As illustrated in Fig. 5a and 5b, high operating pressure favors selectivity and yield of ethylene in a membrane reactor, there by suppressing the formation of CO_2. But based on the observations for a reactor simulated at 1200K and $R_f = 1$, optimal value of pressure can be considered as 4 atm. As the operating pressure varies from 1 to 5 atm, ethylene yield increases fivefold (5% to 25%).Ethane selectivity plunged from 43% to 31% whereas for CO_2, from 46% to 35%. Higher pressures in membrane reactor favor methane conversion. Thereby significantly improves C_2H_4 formation and substantially reduces the production of CO_2 and C_2H_6.

(a)

(b)

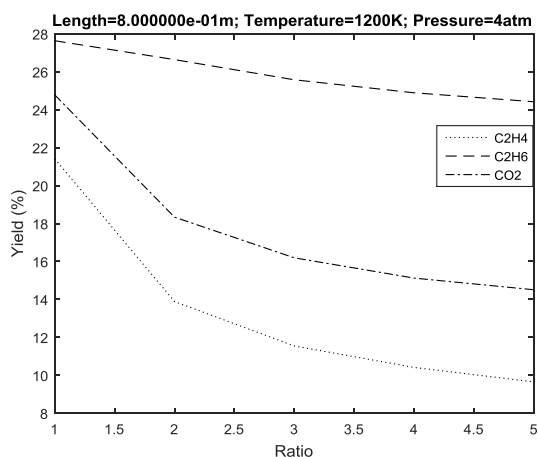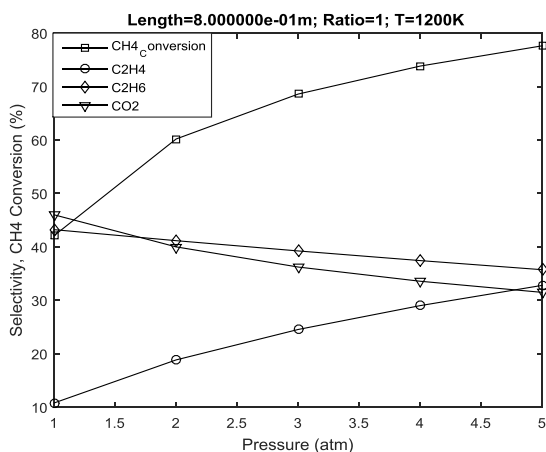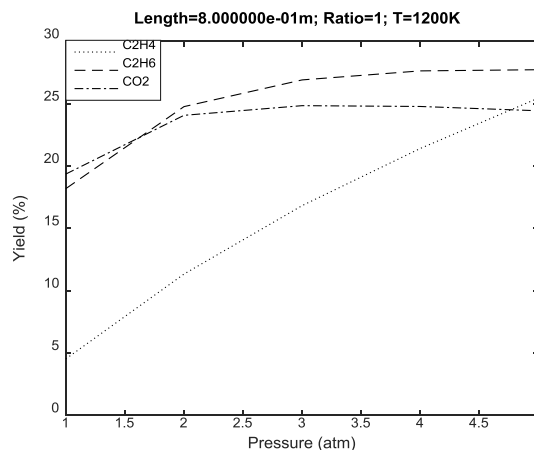**Fig. 5 Effect of reactor pressure on selectivity and yield**

IV. CO-FEED REACTOR VS MEMBRANE REACTOR FOR OCM

Model predictions for OCM in membrane reactor are compared with the experimental data obtained for co-feed reactor [22]. Table 2 shows that the performance of membrane reactor is well in line with the co-feed data but with a relative improvement in selectivity and yield of ethylene. Lesser conversion of methane and greater yield of ethylene prove the membrane reactor to be a better choice over the conventional co-feed reactor.

It is evident from Table 2 that for temperatures above 1200 K, there is not much change in the performance of membrane reactor over co-feed reactor. At 1200 K in membrane reactor, ethylene selectivity is 59% higher than that in a co-feed reactor and, ethylene yield is higher by 51% for a 5% less conversion.

Table 2: Comparison of co-feed and membrane reactor simulation results for OCM

Temperature (K)	1000	1100	1200	1300	1400
Methane Conversion					
Cofeed	56.3	68.1	78.1	87.6	96.2
Membrane	41.9	59	73.8	87.5	97.6
% Decrease	25	13	5	0.11	0.51
Ethylene Selectivity					
Cofeed	6.1	16.9	18.2	17.1	16.8
Membrane	11.6	28.7	29	27.3	26.6
% Improvement	90	69	59	60	60
Ethylene Yield					
Cofeed	3.5	11.5	14.2	15	16.2
Membrane	4.9	16.9	21.4	23.9	26
% Improvement	40	47	51	59	60

V. MULTI OBJECTIVE OPTIMIZATION (MOO) OF OCM IN MEMBRANE REACTOR

Process optimizations usually have objectives that conflict each other. For such cases, MOO provides several optimum solutions which satisfy the given objectives.

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These solutions referred to as Pareto-optimal front and are non-dominated solutions, offer deeper insight into the trade-offs involved among the chosen objectives and offer a wide range of choice for implementation. The goal of any MOO problem is to identify the Pareto front. The pareto front is generated by applying genetic algorithm for the mathematical model used for the membrane reactor (equations 9 to 11). The two objective functions are chosen as a combination of CH_4 conversion (%), C_2H_4 selectivity (%) or C_2H_4 yield (%) (Table 3). The preliminary investigation is done by setting the constraint for initial reactor temperature (Lower bound = 1000 K and Upper bound = 1300 K) and fixing the decision variables CH_4/O_2 ratio and pressure at 1 and 4 atm. Optimization of the objectives is done with respect to the temperature constraint. The pareto optimal solution is obtained in MATLAB using the genetic algorithm routine. The pareto optimal solution obtained after 40 generations for a population size of 10 is shown in the Table 3.

Table 3: Summary of Multi Objective Optimization of OCM in Membrane Reactor

Pareto Front	Objective Functions	Decision Variables
Fig 6a	X_{CH_4}, $S_{C_2H_4}$,	$1 = R_t = 5$
Fig 6b	$S_{C_2H_4}$, $Y_{C_2H_4}$	$1 = P = 5$

Constraints	Fixed Variables	Computational Parameters
$1000 = T = 1300$	L = 0.8 m $d_R = 0.014$ m	Generations = 40 Population size = 10 Pareto fraction = 0.9
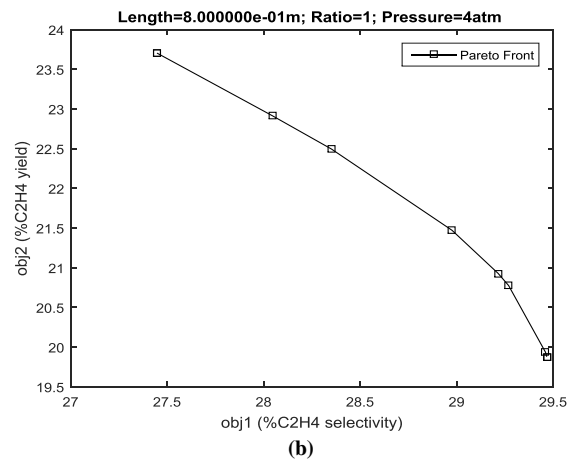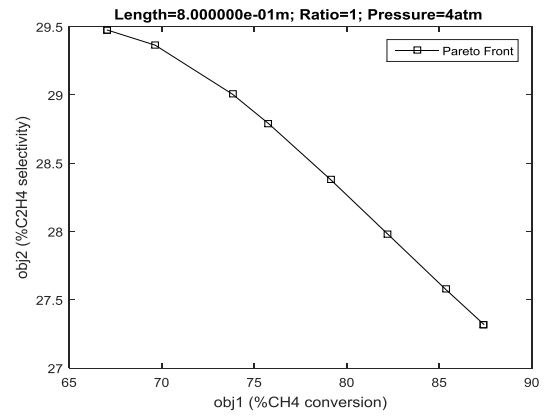
Table 4: Pareto optimal solutions after 40 generations

No	Temperature	X_{CH_4}(%)	$S_{C_2H_4}$(%)
1	1299.1	87.4	27.3
2	1153.5	67.0	29.5
3	1199.9	73.8	29.0
4	1299.1	87.4	27.3
5	1153.5	67.0	29.5
6	1259.3	82.2	28.0
7	1213.4	75.8	28.8
8	1237.0	79.1	28.4
9	1171.3	69.6	29.4
10	1282.9	85.3	27.6

No	Temperature	$S_{C_2H_4}$(%)	$Y_{C_2H_4}$(%)
1	1290.8	27.4	23.7
2	1156.5	29.5	19.9
3	1238.6	28.4	22.5
4	1201.9	29.0	21.5
5	1255.7	28.0	22.9
6	1184.9	29.2	20.9
7	1157.9	29.5	19.9
8	1180.4	29.3	20.8
9	1156.5	29.5	19.9
10	1290.8	27.4	23.7

(a)

(b)

Fig. 6 Pareto optimal front after 40 generations- for different combinations of objective functions

Optimization is performed to maximize the objective functions. Fig 6a, 6b are the pareto optimal front after 40 generations, for different combinations of objective functions (ethylene selectivity and methane conversion – Fig.6a, ethylene selectivity and ethylene yield – Fig.6b). Methane conversion projects a maximum of around 87.4% (Fig 6a). Selectivity varies between 27 to 30%. To maximize selectivity, lower conversion is preferred and temperature to be maintained at around 1153 K. (Table 3), due to the conflicting nature of the objective functions (conversion and selectivity, selectivity and yield).Maximum ethylene yield of 23.7 is achieved by keeping ethylene selectivity low at 27.4%. Further for methane conversion and ethylene yield as objective functions, the solution converges to a single point optimum at T = 1289.7 K with 86.21 % conversion and 23.68% yield. Hence methane conversion and ethylene yield are two non-conflicting objectives for the chosen set of operating conditions. Hence the choice of operating conditions must be made based on the a priori knowledge of the process, ease of operation and other factors crucial to the process.

VI. CONCLUSIONS

A dense oxide tubular membrane reactor is simulated to investigate the effect operating conditions - temperature, feed ratio and pressure. This study shows that OCM in oxygen-transport dense membrane tubular catalytic reactors are an efficient alternative over conventional co-feed reactor. Controlled supply of oxygen enables to suppress non-selective oxidation of methane and ethylene. This work proves that the model based on simple kinetics obtained from experimental data can be used to simulate the reactor close to the conventional but with substantial improvement in selectivity and yield of ethylene and inhibiting the formation of unwanted products. OCM reactor performance is measured in terms of CH_4 conversion, C_2 products and CO_2 selectivity and yield. The simulation results show that methane to oxygen feed ratio and operating temperature are the prime factors which affect the OCM performance for the selected catalyst and membrane. Though pressure does not considerably affect OCM performance in a co-feed reactor, higher pressures up to 5 atm considerably improves methane conversion, selectivity and yield of C_2 products whereas decreasing the same for CO_2. Single variable MOO technique is performed using genetic algorithm technique and it recommends an optimum temperature of about 1289 K with 86.21 % methane conversion and a maximum ethylene yield of 23.68%., for a fixed methane to oxygen feed ratio of one. Conflicting nature of conversion and selectivity suggests that it is acceptable to keep the conversion slightly low but maximize the selectivity. This leads to a temperature setting of 1153 K for a maximum selectivity of 29.5 at a low methane conversion of 67%. Ensuring perfect isothermal conditions with the aid of heat removal systems and careful selection of catalyst and membrane can make the OCM process in membrane reactors. These simulation and optimization results can be used for optimal design of a membrane reactor for C_2 production.

NOMENCLATURE

C_i = concentration of reactants and products, i, mol/m^3

d_R = reactor diameter, m

w_c = catalyst weight per unit surface of reactor wall, g cat/m^2

f_{O_2} = flux of oxygen through the membrane, mol/m^2

L = length of the reactor

F_i = molar flow rate of reactants and products, i, mol/s

P = operating pressure, atm

r_j = intensive reaction rate given by Eqs. 5 to 8, mol/(g cat-s)

R_i = generation rate of component i, mol/(g cat-s)

R_f = Feed ratio, CH_4/O_2

S_i = selectivity to product, i, %

T = temperature, K

X_i = methane conversion, %

Y_i = yield of product, i, %

ϑ_{iJ} = stoichiometric coefficient of reactants and products

Subscripts

$C_2 = C_2H_6$ and C_2H_4

CO_x = CO and CO_2

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