Simulation of a Catalytic Membrane Reactor for Oxidative Coupling of Methane

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Methane is the most abundant component of natural gas. There is considerable interest in direct and indirect conversion of methane to more valuable products such as basic feedstock and liquid fuel (Anderson, 1989; Poirier et al., 1991; Fox, 1993). The work of Keller and Bhasin (1982) has drawn worldwide attention to oxidative coupling of methane by a catalytic process to produce ethane and ethylene (C_2 products). However, total oxidation of methane leading to useless carbon dioxide and water is thermodynamically favored over the formation of ethane and ethylene, and in addition the desired C_2 products tend to undergo further oxidation.

Considerable efforts screening a large number of mainly metal oxide-based catalysts have been made to obtain a suitable one active and especially selective toward the desired C_2 products, and the C_2 yield of up to 30% has been reported (Amenomiya et al., 1990; Fox, 1993). Currently, the oxidative coupling of methane is mostly carried out in either redox or cofeed mode, an assessment of which may be found in the review article by Poirier et al. (1991). There are few studies regarding the potential advantages of using membrane reactors in the conversion of methane. Lund (1992) reported a simulation study of a membrane reactor for the partial oxidation of methane to formaldehyde, with the role of the membrane being to remove formaldehyde from the reaction system to prevent its further oxidation. An overview regarding the use of catalytic membrane reactors was given by Noble (1992) for the partial oxidation of methane to methanol. As far as the oxidative coupling of methane is concerned, Omata et al. (1989) conducted an investigation in a ceramic membrane reactor and used the membrane to minimize the contact of C_2 products with oxygen and to prevent nitrogen buildup in the recycled methane stream. We report here a simulation study showing that using a catalytic membrane reactor would greatly improve the selectivity and yield to C_2 compounds, compared with the conventional cofeed operation.

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Modeling

There is considerable literature that deals with reaction kinetics of oxidative coupling of methane (van der Wiele et al., 1992; McCarty, 1992; Hutchings et al., 1992). We use the kinetic data obtained experimentally by Hinsen et al. (1984) with 34 wt. % lead oxide catalyst impregnated on γ-alumina, to demonstrate the potentials of using a catalytic membrane reactor. They found that the following reactions took place when methane and oxygen were passed over the catalyst:

$$CH_4 + 2O_2 = CO_2 + 2H_2O \quad (1)$$

$$2CH_4 + 1/2O_2 = C_2H_6 + H_2O \quad (2)$$

$$C_2H_6 + 1/2O_2 = C_2H_4 + H_2O \quad (3)$$

$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O \quad (4)$$

The intensive kinetic rate expression determined for each of the above reactions is given, respectively, by

$$r_1 = 0.015 \exp(-6{,}134/T) C_{CH_4}^{0.4} C_{O_2}^{1.5} \quad (5)$$

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

$$r_3 = 1.0 \times 10^{-4} \exp(-722/T) C_{C_2H_6}^{0.8} C_{O_2}^{1.0} \quad (7)$$

$$r_4 = 1.0 \times 10^{-16} \exp(26461/T) C_{C_2H_4}^{0.8} C_{O_2}^{1.6} \quad (8)$$

These expressions were obtained simply by experimental data fittings and no reaction mechanisms were involved.

Let us consider two types of reactor. The first one is a conventional plug-flow tubular reactor coated with a layer of catalyst on the inside wall; both reactants methane and oxygen enter at one end, and exit at the other after having reacted with each other over the catalyst layer. The second consists of a tubular porous section (membrane) coated with the same catalyst and in addition, surrounded by a tube with a larger diameter. This allows oxygen introduced in the annulus to permeate through the membrane into the reactor in a

well controlled way; methane enters into the reactor and reacts with permeated oxygen along the membrane.

We assume for both reactors: plug flow of gaseous reactants and products, negligible mass-transfer resistance, isothermal, ideal gas behavior, constant pressure and steady-state operation. We also assume for the membrane reactor that the oxygen flux through the membrane is independent of the oxygen partial pressure inside the reactor (which is true when $P_{O_2}^{out} \gg P_{O_2}^{in}$) and that no other reactants and products permeate through the membrane.

The equations governing the cofeed reactor are given by

$$dF_i/dx - \pi d_r f_c R_i = 0 \tag{9}$$

where F_i is molar flow rate of component i, d_r is the reactor diameter and f_c is defined as the quantity of catalyst per unit of reactor wall surface. R_i is the generation rate of component i given by

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

with ν_{ij} the stoichiometric coefficient of component i in reaction j and r_j the intensive reaction rate of reaction j given by Eqs. 5 to 8. The inlet conditions (at $x = 0$) are: $F_{CH_4} = F_{CH_4}^i$, $F_{O_2} = F_{O_2}^i$ and $F_i = 0$ where i represents the components other than methane and oxygen.

For the membrane reactor, the governing equations and inlet conditions are the same for all the components except oxygen. We have regarding this material

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

where f_{O_2} is oxygen flux through the membrane. The oxygen molar flow at inlet is null but the same amount of oxygen as $F_{O_2}^i$ permeates through the membrane uniformly along the length of the reactor.

With the assumption of ideal gas behavior, the concentration of component i is related to its molar flow rate by

$$C_i = (P/RT)(F_i/\Sigma F_i) \tag{12}$$

The molar flow rate of component i at any position in both reactors can be determined by solution of Eq. 9 or by solution of Eqs. 9 and 11 with the help of a numerical procedure such as the fourth-order Runge-Kutta method.

Results and Discussion

In this simulation study, we compare the performance of these two types of reactor by evaluating the influence of operation conditions such as temperature, pressure and flow ratio of methane to oxygen on selectivity and yield to C_2 products and to CO_2. Methane conversion is defined as:

$$X_m = \left(F_{CH_4}^i - F_{CH_4}^0\right)/F_{CH_4}^i \tag{13}$$

The selectivity and yield to products i are as follows:

$$S_i = \kappa F_i^0 / \left(F_{CH_4}^i - F_{CH_4}^0\right) \tag{14}$$

$$Y_i = S_i X_m \tag{15}$$

where κ equals 2 for ethane and ethylene, and 1 for carbon dioxide.

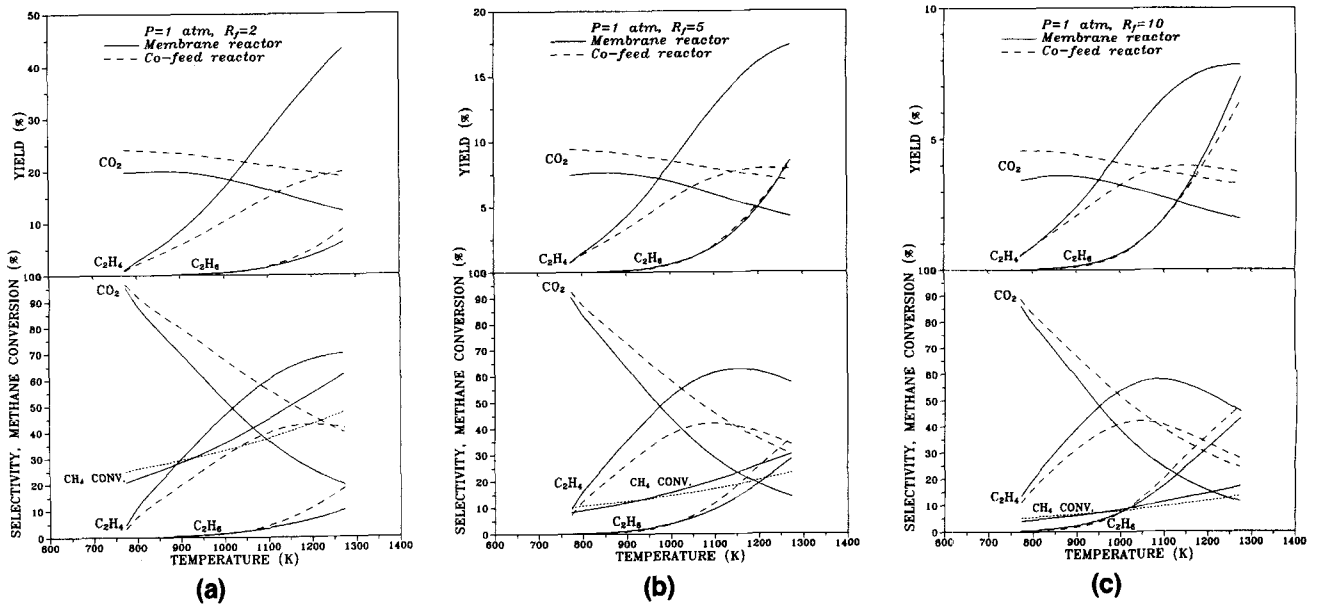

Figure 1. Methane conversion, selectivity and yield to ethane, ethylene, and carbon dioxide as a function of temperature in both reactors.

Inlet molar flow rate ratio of methane to oxygen $R_f = 2$ (a), $R_f = 5$ (b) and $R_f = 10$ (c), and operating pressure $P = 1$ atm.

The simulation was conducted for tubular reactors of 0.08 m in length and 0.014 m in diameter with a total reactants (methane and oxygen) molar flow rate of 9.6×10^{-5} mol/s; the weight of coated catalyst was assumed to be 1 g. The methane conversion and the selectivity and yield to ethane, ethylene and carbon dioxide as a function of temperature for both reactors are shown in Figures 1a, 1b, and 1c, with the inlet molar flow rate ratio of methane to oxygen (R_f) varying from 2 to 10 and the operating pressure equal to 1 atm. For comparison purpose, the total molar flow rate has been maintained constant for these flow rate ratios in order to have the same reaction time (about 2 s at 773 K). We observe that for the temperature range simulated (773 to 1,273 K) the membrane reactor gives always better performance than the conventional cofeed reactor in terms of producing more C_2 compounds and less CO_2. Moreover, the improvement by using the membrane reactor is more significant at higher temperature, especially for the production of ethylene which is our preferred compound. For a flow rate ratio of 5 and a temperature of 1,273 K (Figure 1b), for example, the yield to C_2 products and CO_2 is 26 % and 4 % respectively, in the membrane reactor; comparing with the corresponding values of 16% and 7% in the cofeed reactor, the improvement is 60% for the C_2 compounds and 40% for CO_2. Generally speaking, the increase of temperature favors the formation of C_2 compounds and inhibits that of CO_2. Nevertheless, there exists an optimal temperature for the selectivity of ethylene when the flow rate ratio is higher than 5 and this optimal point shifts downward as the flow rate ratio increases; this fact may serve as a guideline in the future reactor design. Regarding the effect of the flow rate ratio, increasing the ratio lowers the CO_2 selectivity, and enhances significantly the selectivity to ethane while the selectivity to ethylene does not always have an increasing trend. On the other hand, the yields decrease without exception due to lower methane conversions. The above observations may be explained well in a qualitative manner by analyzing the rate expressions of the C_2 compounds generating (consuming) reactions and CO_2 producing reactions. For instance, the fact that the CO_2 selectivity is lower in the membrane reactor is consistent with the fact that the reaction order with respect to oxygen in CO_2 producing reactions is higher; as the oxygen concentration at the reactor inlet is much lower in the membrane reactor than in the cofeed reactor, the CO_2 producing reactions are suppressed much more than the C_2 compounds generating reactions, resulting in the decrease of the CO_2 selectivity.

Influence of the operating pressure inside the reactors on the selectivity and yield is shown in Figure 2 for temperature equal to 1,023 K and the flow rate ratio equal to 2. In the conventional reactor, the methane conversion and the selectivities and yields to all the products are practically independent of the operating pressure; whereas for the membrane operation the pressure increase improves significantly the methane conversion, favors the ethylene formation and reduces the CO_2 production. These observations are valid for other flow rate ratios between 2 and 50. So, at methane to oxygen flow rate ratio equal to 2, the methane conversion increases from 38 to 51%, the ethylene selectivity goes from 50 to 67% and CO_2 selectivity decreases from 48 to 32% in the membrane reactor when the operating pressure varies from 1 to 4 atm, which corresponds to an improvement of the

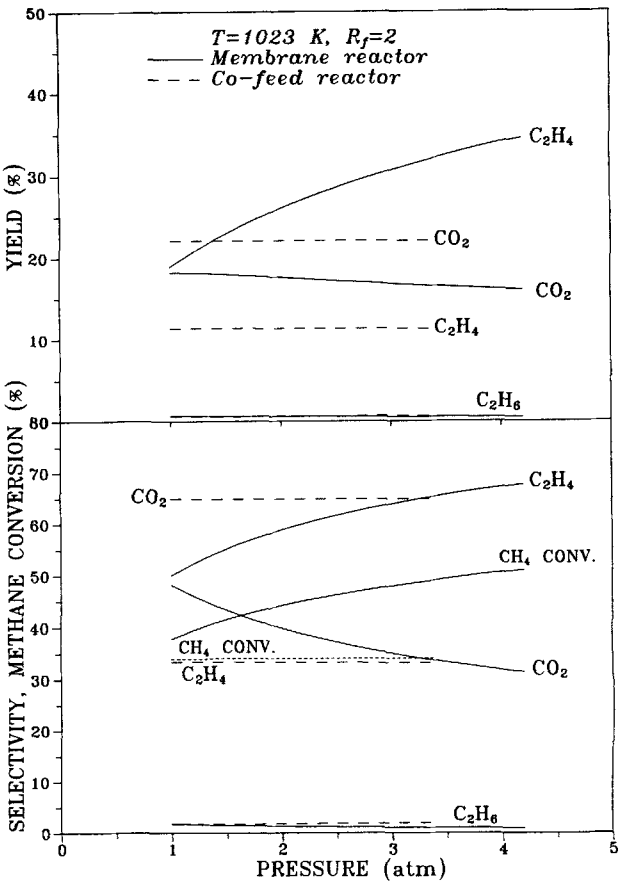

Figure 2. Influence of operating pressure on selectivity and yield: $T=1{,}023$ K and $R_f=2$.

ethylene yield of about 300% (from 11 to 34%) and a reduction of CO_2 yield of 27% (from 22 and 16%) in comparison with the performance of the conventional cofeed reactor.

With a scale-up factor of 40, we observe that there is little change in membrane reactor performance in terms of the methane conversion, the yields towards C_2 products and carbon dioxide, though the production of ethane is favored in the larger reactor over ethylene.

Conclusions

The essential difficulty for economical production of ethylene and ethane from the oxidative coupling of methane is to inhibit the thermodynamically favored deep oxidation of methane and C_2 products and to enhance the selectivity and yield to C_2 products, especially ethylene. The simulation results show clearly the achievements by carefully controlling the oxygen supply to the reacting system through a membrane reactor. Since the oxygen molecules are smaller than the other reactants and products, the proposed operating mode allowing solo transport of oxygen into the reactor may be realized without difficulty by proper selection of a membrane such as porous ceramics or Vycor glass which are commercially available. Although the simulation was conducted using relatively simple kinetic expressions obtained with lead oxide catalyst, there is little doubt that the membrane reactor

will show similar advantages with a better catalyst. As a result, the use of a catalytic membrane reactor with the proposed configuration is complementary, in addition to the catalyst investigation, to making the oxidative coupling of methane an economically viable process.

Notation

C_i = concentration of component i, mol/m^3
d_r = reactor diameter, m
f_c = quantity of catalyst per unit of reactor wall surface, g cat/m^2
f_{O_2} = oxgyen flux through the membrane, mol/m^2
F_i = molar flow rate of component i, mol/s
L_r = reactor length, m
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)
S_i = selectivity to product i, %
T = temperature, K
X_m = methane conversion, %
Y_i = yield to product i, %
κ = coefficient in Eq. 14, equal to 2 for ethane and ethylene, and 1 for carbon dioxide

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