Oxidative Coupling of Methane: Reactor Performance and Operating Conditions

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Abstract
In this work, the achievable performance in case of desired-product selectivity, yield and conversion are evaluated systematically for different reactors in order to find the optimum range of operation for the OCM process. This approach is applied to a nonisothermal plug flow reactor and a nonisothermal porous packed bed membrane reactor using different types of catalysts in the wide range of operating conditions. Moreover, a fluidized bed reactor is also considered. The results show that tracking the optimum area of operation has a monotonic direction under some range of operating conditions, whereas it reflects a qualitative trade-offs under some other ranges of operating conditions. For all investigated reactor concepts the likelihood of optimal operating conditions are found, and the best corresponding performance for all of them are reported.

Keywords: Oxidative coupling of methane, reactor design, membrane reactor, fluidized bed reactor

1. Introduction
The production of C₂ hydrocarbons (i.e. ethylene + ethane) through the oxidative coupling of methane (OCM) has been prohibited from commercial practice due to low overall yield. In particular, today's catalysts exhibit either high selectivity (>70%) coupled with low conversion (<5%) or high conversion (>75%) with low selectivity (<15%) [1]. This implies that an optimum ratio of conversion - selectivity exist, in order to achieve the highest possible yield of C₂ hydrocarbons.

Many different reactor concepts were proposed for the oxidative coupling of methane, for instance: counter current simulated moving bed reactor [2], solid oxide fuel cell reactor [3], catalytic dense membrane reactor [3,4], fluidized bed reactor [5,6], porous membrane reactor [7,8], fixed bed reactor [5]. All of those reactor concepts are having their advantages and drawbacks. However, only the last three reactor types have the potential to be exploited industrially. Therefore only those three reactor types will be investigated in this study.

Fixed bed reactor represents a state of the art in the industry, and has to be examined in detail. Several studies on this reactor type were done, and the biggest drawback are severe hot spots, formed as a consequence of the poor heat removal from the highly exothermal reaction. Feed dilution is necessary if any application is expected. Fluidized bed reactor has been investigated only briefly [5,6,9], and it showed similar performance like the fixed bed reactor. The biggest advantage of the fluidized bed reactor is the isothermal operation and a possibility to operate using undiluted feeds [6,9]. This option is very attractive for industry (even in the case of lower selectivity) because costly separation of nitrogen and methane is prevented, and the downstreaming process is simplified.
Membrane reactor concept allows fine distribution of one reactant into the reactor, using a porous membrane as a gas distributor. Fine oxygen distribution has been proven to give enhanced selectivity even with significant methane conversion. However, feed dilution and reactor size are main drawbacks of this reactor type. Feed dilution is necessary because of the safety reasons as well as for low heat transfer rates. Reaction rates are approximately one order of magnitude smaller compared to fixed and fluidized bed reactor, therefore much bigger reactor is needed to achieve same conversion level. In this work three reactor concepts are compared using a same graphical approach for obtaining information about their optimal performance. Moreover same kinetic model for catalyst La$_2$O$_3$/CaO is used in order to give comprehensive comparison of these reactor concepts.

2. Modeling

2.1. Fixed bed reactor

Fixed bed reactor was simulated using a standard pseudo homogeneous plug flow reactor model:

$$\frac{dF_i}{dt} = r_{i,e} A$$  \hspace{1cm} (1)

Where $F_i$ (mol/s) is the molar flow-rate for component $i$ and $A$ (m$^2$) is the cross sectional area of the tubular reactor. Both isothermal and nonisothermal simulations were performed with a typical 2:1 methane to oxygen feed ratio and a reactor of 7 mm diameter, with a flow rate of 10 cm$^3$/s. Additionally, nonisothermal simulation was done adding a differential reactor heat balance into the system of equations.

2.2. Membrane reactor

Membrane reactor model is based on pseudo-homogeneous one dimensional flow. No radial and axial diffusion was taken into account. This was possible only due to the small reactor diameter of 7 mm used in the simulation. The reactor model equations are:

$$\frac{dF_{i,t}}{dt} = r_{i,t} A_t - N_i \pi d'$$ \hspace{1cm} (2a)

$$\frac{dF_{i,s}}{dt} = N_i \pi d' + r_{i,s} A_s$$ \hspace{1cm} (2b)

Where $F_i$ (mol/s) is the molar flow-rate for component $i$ in the tube and the shell side of the membrane reactor, and $A$ (m$^2$) is the cross sectional area of the tubular reactor. $N_i$ represents the mass transport of the components through the membrane. Reaction occurs in both tube and shell side of the reactor. More details of this model can be found in [11]. In case of membrane reactor, heat balance equations similar to Eq. (2) were added in order to simulate nonisothermal reactor behavior similarly like for the plug flow reactor.

2.3. Fluidized bed reactor

Fluidized bed reactor was simulated using a modified two phase model suggested by Werther et al.[12] :

$$\left[u - u_{mf} (1 - \varepsilon_s)\right] \frac{dC_{b,t}}{dh} + k_{b,t} \alpha (C_{b,t} - C_{e,t}) = \varepsilon_b r (C_{b,t}, T, \varepsilon_m)$$ \hspace{1cm} (3a)

$$\left[u_{mf} (1 - \varepsilon_b)\right] \frac{dC_{e,t}}{dh} = k_{e,t} \alpha (C_{b,t} - C_{e,t}) + (1 - \varepsilon_b) r (C_{e,t}, T, \varepsilon_e)$$ \hspace{1cm} (3b)
Here $C_i$ (mol/m$^3$) represents the concentration of component $i$ in bubbles and emulsion, $\varepsilon$ represents porosity, $k_{gi}$ is the mass transfer between bubbles and emulsion and $r_i$ is reaction rate. Diameter of the simulated fluidized bed reactor is 40 mm, for the Geldart A group of particles of 110 µm diameter. The range of operation of the fluidized bed reactor lies between fluidization numbers of 3-15, therefore in the bubbling regime. More details about the reactor model applied in this study can be found in [12].

3. Results and discussion

Fixed bed reactor has been simulated for the isothermal and nonisothermal case in order to investigate the achievable performance of this reactor type. Only two variables are influencing the performance of this reactor type: inlet composition which can be represented as inlet ratio of methane to oxygen, and temperature of the feed. For the isothermal case temperature in the reactor was kept constant and equal to the inlet temperature. For the nonisothermal simulation this temperature was only an inlet boundary condition, and the heat balance determined temperature at other points in the reactor. The simulation results for the isothermal case are represented in the figure 1.

As can be seen from the Fig. 1, there is a range of optimal operating conditions for this reactor type. These operating conditions are temperature of 810°C and inlet methane to oxygen ratio of 1.2. The maximum yield of higher hydrocarbons obtained by simulation accounts for 20% as reported by experiments as well [5].

Nonisothermal simulation shows the necessity to use diluted feeds in order to efficiently remove heat from the reactor. Wall heat transfer coefficient was calculated by correlation of Li and Finlayson (1977), (260 W/mK) with environment temperature of fixed to 600 K. When environment temperature was kept same like the inlet temperature (like for the oven), temperature runaway was inevitable for any applied condition. It can be concluded that significant dilution of the catalyst bed and dilution with nitrogen is required in order to avoid hot-spot formation in the fixed bed reactor. On the other hand where dilution of the feed or the catalyst surpasses certain critical value, hot spots do not appear and temperature in the reactor drops monotonously. Here we can emphasize that controlling the temperature in the fixed bed is almost an impossible task. Reason for this is very fast and exothermal reaction, which is self-accelerating when heat balance is disturbed. Consequently hot spots of more than 300K are observed.
Similar investigations were conducted for the membrane reactor. Several variables such as flow of the feed in the tube side and in the shell side were manipulated, as well as oxygen concentration in the shell, temperature and the membrane thickness. We concluded that the thickest membrane investigated (0.1 mm) provided the best overall reactor performance. Moreover, equal flow rate of the tube and the shell stream allowed higher yield in comparison to other investigated flow rates. Influence of the shell oxygen fraction and the inlet temperature on the yield can be seen on the figure 3.

Porous membrane reactor gave remarkably high yields of over 50%. It should be noted that there are no experimental investigations for use of undiluted feeds and such high membrane thickness to testify whether simulated results are reasonable or not. Highest yield achieved so far in a porous membrane reactor is 27.5 % obtained by Lu et al [8]. Nonisothermal simulation for the porous membrane reactor showed some disadvantages for membrane reactor application. In most cases temperature runaway was observed, similarly like for the fixed bed reactor. However, because of the slower reaction rate in the membrane tube, it was possible to maintain hot spot formation below desirable level.
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by manipulating the feed dilution and membrane thickness (fig. 4). During this investigation, tube and shell flow rate were kept constant – 4 cm$^3$/s with a stoichiometrical ratio of methane/oxygen and inlet temperature of 750°C. It can be noticed that membrane reactor has to be operated with significant feed dilution and with a thick membrane in order to provide isothermal operation. This leads to a significant increase in reactor size required for necessary conversion level.

Finally, fluidized bed reactor was investigated under different operating conditions. Manipulation of the reaction temperature, feed composition and the fluidization velocity showed influence of these variables on the reactor performance. Increase in fluidization velocity showed monotonous increase in yield and selectivity, most probably because “reaction front” was moved away from the distributor zone to the bulk, and allowed bubble mass transfer to play an important role. For further simulation only the highest flow rate of 15 u$_{mf}$ was applied. Results are shown on the figure 5.

Fig. 4 Nonisothermal simulation of the membrane reactor: influence of the feed dilution (left, δ = 0.1 mm) and membrane thickness (right, 75% dilution) on the hot spot formation

Fig. 5 Influence of the reaction temperature and feed composition on the performance of the fluidized bed reactor
The highest yield in the fluidized bed of 26% is in reasonable agreement with experiments [6,9]. Nonisothermal simulation for the fluidized bed was not applied, because most of the authors of experimental studies on the OCM in the fluidized bed reactor have reported isothermal behavior, even when they used undiluted feed [6,9]. We can therefore adopt the fact that the fluidized bed reactor provides the possibility to operate under isothermal operation under all simulated conditions.

4. Conclusions
A model-based performance analysis of fixed bed, fluidized bed, and porous membrane reactor were conducted. Simulation results undoubtedly show that fixed bed reactor can not be used industrially, even when high heat transfer rates are applied. This reactor type has no control over the reaction heat in case of small dilution, and behaves almost ideally adiabatically. \( \text{C}_2\) yields of 20% are not satisfactory for an industrial application. In contrast to this, the membrane reactor offers the possibility to increase the yield by fine oxygen distribution through the membrane. However, application of undiluted feeds and thin membranes result in hot spots of over 100 K. Even though a yield of over 50% yield is achievable for such conditions, these are only theoretical results. For an isothermal operation thick membranes and over 80% feed dilution are necessary. The fluidized bed reactor shows an improved performance in comparison to the fixed bed reactor. Although yields of 26% are still below industrial requirements, the use of undiluted feeds and an isothermal operation are the main advantages of this reactor type. A further economical analysis of the membrane reactor and/or the fluidized bed reactor including the downstreaming process is however necessary in order to answer definitively the question which is the most suitable OCM reactor concept. For this purpose, a mini-plant is currently being built at the Berlin Institute of Technology.

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References