Analysis of an Oxidative Coupling of Methane (OCM) Reactor: Multi Point Feeding Policy

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Abstract – A mathematical modeling of catalytic oxidative coupling of methane (OCM) is studied to improve overall performance. A multi-point feeding reactor is investigated to compare with fixed bed reactor in present of Mn/Na₂WO₄/SiO₂ catalyst. The model contains two set of governing equation which are momentum balance to determine velocity profile and pressure of the system and materials balance to calculate concentration of each involving species in the OCM reaction. The results clearly indicated that conversion is significantly increased when feeding with multi-point in reactor.

Keyword: Oxidative coupling of methane, Multipoint feed, Mn/Na₂WO₄/SiO₂

1. Introduction

Ethylene, a gaseous organic compound with the formula of C₂H₄, is an important unsaturated hydrocarbon. It produces and markets the basic petrochemical building blocks, known as olefins, which are used primarily as a raw material for producing other chemical products. Total ethylene worldwide consumption will return to 115 million tons by the end of 2010 [1]. Considering an olefins production, the major problems nowadays are not only the limitation of reactant conversion and product yield but also the need to concern about the energy required for separation processes. The sustainability of feedstock is another important issue. In general, the ethylene production involves the steam cracking of hydrocarbon feedstocks, e.g., LPG (propane + butane), NGL (ethane, propane and butane) and naphthas. The use of methane as feedstock is an alternative promising way. Methane is a major component in natural gas and biogas and can be used for ethylene production via an oxidative coupling of methane (OCM) process. In such a process, methane (CH₄) is reacted with oxygen over a catalyst to form water and methyl radical (CH₃). The methyl radical combines together to form alkenes, mostly ethane (C₂H₆). However, ethane can be further thermally dehydrogenated to produce ethylene (C₂H₄) but the selectivity of ethylene is always reduced due to the carbon dioxide obtained from the combustion reaction of methane and oxygen.

The main reactions of the OCM can be summarized as follows [1]:

Step 1: 2CH₄ + 0.5O₂ → C₂H₄ + H₂O (1)
Step 2: CH₄ + 2O → CO₂ + 2H₂O (2)
Step 3: CH₄ + O₂ → CO + H₂O + H₂ (3)
Step 4: CO + 0.5O₂ → CO₂ (4)
Step 5: C₂H₆ + 0.5O₂ → C₂H₄ + H₂O (5)
Step 6: C₂H₄ + 2O → 2CO + 2H₂O (6)
Step 7: C₂H₆ → C₂H₄ + H₂ (7)
Step 8: C₂H₄ + 2H₂O → 2CO + 2H₂ (8)
Step 9: CO + H₂O → CO₂ + H₂ (9)
Step 10: CO₂ + H₂ → CO + H₂O (10)

One of the effective OCM catalysts is Mn/Na₂WO₄/SiO₂, which shows a good stability along the reaction time and reaction temperature [2]. Several studies proposed to use the Mn/Na₂WO₄/SiO₂ catalyst in different types of reactor such as a fixed bed reactor and a membrane reactor. The reactor performance was considered in terms of methane conversion, selectivity
and yield of ethylene and CH\textsubscript{4}/O\textsubscript{2} ratio. Karimi et al. [3] performed the OCM reaction in a fixed bed reactor by using the CH\textsubscript{4}/O\textsubscript{2} ratio at 4:1, 840 °C, GHSV 1620 hr\textsuperscript{-1}. The experimental results showed that the C2 selectivity is 57.3 % and the methane conversion is 20.3%. Compared to the co-feed fixed bed reactor, an alumina-membrane reactor gave the yield increased 10% and C2 selectivity increased 30%. Lu et al. [4] proposed that introducing helium to oxygen feed gave higher C2 selectivity and yield.

From literatures [5], it was showed that a higher local CH\textsubscript{4}/O\textsubscript{2} ratio results in a higher selectivity. In addition, higher conversion can be obtained at lower overall CH\textsubscript{4}/O\textsubscript{2} ratio. As a membrane reactor can independently control the local CH\textsubscript{4}/O\textsubscript{2} ratio by permeability of the substance, the use of the membrane reactor tends to give higher selectivity than a conventional packed bed reactor. However, membrane reactors are sophisticated to be operated and manufactured. In contrast, a fixed bed reactor can overcome such difficulties. Thus, a combination of the advantages of both the reactors should be considered and this leads to a concept of a multipoint feeding fixed bed reactor. Lu et al. [6] studied a general cross-flow reactor with six different feeding strategies. It was found that the distributed reactor gives higher desired product yield than the conventional co-feed reactor.

In this study, a multipoint feeding fixed bed reactor for ethylene production from an oxidative coupling of methane reaction over Mn/Na\textsubscript{2}WO\textsubscript{4}/SiO\textsubscript{2} catalyst is investigated by using a two-dimensional mathematical model of a packed bed reactor. Two feeding scenarios of methane and oxygen at side inlets are studied and the results of methane conversion and C\textsubscript{2} yield of each feeding scenario are compared.

2. Mathematical Model

In this study, a two-dimensional axial symmetry model of a fixed bed oxidative coupling of methane reactor, as shown in Figure 1, is considered. The reactor consists of three points of side feeding and has length of 10 cm and 1 cm in diameter. Multipoint feed is proposed to distribute methane or oxygen to the reactor as design parameters. The side feed locations are at 0.25, 0.50 and 0.75 cm. To simplify the complexity of the reactor model, the reactor was assumed to be operated under isothermal condition and only two sets of transport phenomena equations consisting of momentum (Eq. 3) and mass (Eq. 4) conservations were considered. The reaction kinetics of the OCM over Mn/Na\textsubscript{2}WO\textsubscript{4}/SiO\textsubscript{2} catalysts were obtained from Daneshpayeh et al. [2].

Momentum balance (Brinkman equation):

\[
\nabla \cdot \left( \frac{-\eta}{\rho} \left( \nabla u + (\nabla u)^T \right) \right) + \rho l = \frac{\eta}{\epsilon} \nabla \cdot u = 0
\]

Mass balance:

\[
\nabla \cdot \left( \rho \omega - \rho_0 \sum_{j=1}^{n} D_j \left( \nabla x_j + (\nabla x_j)^T \right) \right) = R
\]

Table 2 shows operating parameters and conditions of the OCM reactor. The proposed reactor model was numerically solved by using COMSOL MULTIPHYSICS 3.4 software. Finite element method was selected to solve for the concentrations of CH\textsubscript{4}, O\textsubscript{2}, C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{2}, H\textsubscript{2}, H\textsubscript{2}O, CO and CO\textsubscript{2} including the velocity and partial pressure of all reaction species. To investigate the effect of the feeding policy, study cases are reported in Tables 3 and 4 are considered. The study cases can be grouped into 3 scenarios. The first one (“Base case”) represents a conventional packed bed reactor. In the second scenario (oxygen side feed, OS), methane is fed through the main inlet with some part of oxygen and the left amount of oxygen is fed into the reactor via the side inlet. The last scenario (methane side feed, MS) was vice versa to the second scenario. Overall space time is 30 kg.s/m\textsuperscript{3} for all of the study cases [1]. In all simulations, air is used as an oxygen source.

![Figure 1: Multi point feeding fixed bed reactor](image-url)
3. Results and discussion

Simulations of the oxidative coupling of methane in a multi-point feed reactor on Mn/Na2WO4/SiO2 catalyst are performed to investigate the reactor performance in terms of methane conversion and C2 yield. The reactor was operated at 850 °C, CH4/O2 ratio of 5 and space time of 30 kg.s/m3. Fig. 2 shows that for the base case, the methane concentration decreases along the reactor length and it tends to remain constant near the end of the reactor, which means the reactor length in this study is long enough to reach the steady state of the OCM reaction. It is also noticed that the methane concentrations in the MS cases are kept almost constant along the reactor length due to the addition of methane by side feeding. Considering the OS cases, the methane concentrations are more depleted than that in the base case. This indicates that the distribution of oxygen feed can enhance the methane conversion. It is noted that the CH4/O2 ratio in the conventional packed bed reactor (“base case”) cannot independently be controlled at a lower ratio, which favors the methane conversion.

In Fig. 3, the concentration profiles of oxygen are shown. The concentration profiles of oxygen stayed in opposite side of methane concentration in Fig. 2. The reason is same for methane an additional amount of oxygen is fed into reactor so concentration in the OS cases is remain almost the same all along reactor length. Then versa, when no additional oxygen in the MS cases, the oxygen concentrations is depleted when go deeper in the reactor region.

In Fig. 4, methane to oxygen ratios are shown to compare for all cases. All of the CH4/O2 ratios in the MS cases are higher than the base case and the OS cases. These results confirm that a multi-point feeding of oxygen can help to keep the CH4/O2 ratio at low value. As discussed above, maintaining the CH4/O2 ratio at low value as possible can enhance the methane conversion. In contrast, multi-point feeding of methane results in an increase in the CH4/O2 ratio, thereby lowering the methane conversion. The methane conversion and C2 yield are summarized in Table 5 for all study cases. It is note that the C2 yields seems to be constant for all cases.

### Table 5: Performances of the OCM reactors

<table>
<thead>
<tr>
<th>Case</th>
<th>Conversion CH4</th>
<th>C2 Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base case</td>
<td>15.185</td>
<td>12.20</td>
</tr>
<tr>
<td>OS 1</td>
<td>32.922</td>
<td>11.47</td>
</tr>
<tr>
<td>OS 2</td>
<td>36.416</td>
<td>11.33</td>
</tr>
<tr>
<td>MS 1</td>
<td>39.179</td>
<td>10.88</td>
</tr>
<tr>
<td>OS 3</td>
<td>4.069</td>
<td>11.32</td>
</tr>
<tr>
<td>MS 2</td>
<td>1.150</td>
<td>11.01</td>
</tr>
<tr>
<td>MS 3</td>
<td>1.071</td>
<td>10.67</td>
</tr>
</tbody>
</table>
4. Conclusions

A multi-point feeding of an OCM fixed bed reactor was proposed and analyzed with the aim to improve its performance. A two-dimensional model of the OCM reactor operated at isothermal condition was developed based on momentum and mass balance equations. In the study, feed policies are classified into two groups that are methane side feed and oxygen side feed. The simulation results showed that for the methane side feed case, the methane conversion is decreased, whereas for the oxygen side feed case, it is enhanced because the $\text{CH}_4/\text{O}_2$ ratio can be kept in a suitable range. Therefore the multi-point feeding OCM reactor is more promising.

Future Works

As the oxidative coupling of methane (OCM) is a highly exothermic reaction, a hot spot temperature would affect the operation of an OCM reactor. Thus, effect of temperature change on the OCM reactor will be further studied.

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