Determination of optimal temperature profile in an OCM plug flow reactor for the maximizing of ethylene production

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ABSTRACT

An optimal temperature profile for achieving the highest amount of ethylene production in a fixed bed plug flow reactor of oxidative coupling of methane (OCM) was determined and analyzed from chemical reactions point of view. A performance index was defined to solve the problem and the optimal temperature profile was found by means of “piecewise linear continuous optimal control by dynamic programming” (PLCOCIDP) algorithm. The performance obtained from the optimal temperature profile was compared with the best isothermal performance of the reactor, gained from optimization calculations. It was concluded that the quantity of ethylene production by applying the optimal temperature profile is about 42% greater than that of the best isothermal performance of the reactor at 1096.3 K. It was also observed that maximization of ethylene production and minimization of carbon dioxide production are interrelated in this system. The effects of total pressure and initial oxygen concentration were studied as well. The optimal temperature profile spread out and its minimum point rose a little with increasing the concentration of oxygen and/or decreasing the total pressure. Moreover, when the total pressure or initial oxygen mole fraction was elevated, the ethylene molar flux increased, however the selectivity of ethylene reduced in case of increasing the oxygen molar flux.

Keywords: OCM, Optimal control, Performance index, Optimization, Dynamic programming, Temperature profile

1. Introduction

Ethylene is one of the most important productions of petrochemical industries which can be produced by different processes. One of which is oxidative coupling of methane (OCM). The main purpose of OCM is to produce some valuable materials including ethylene by coupling of methane. It was discovered by Keller and Behasin [1] for the first time and now has got a great practical importance for many of countries all over the world. It is generally accepted in the present century, that natural gas (methane) will be known as an important source of energy (gaseous fuels), transportable liquid fuels and chemicals (petrochemicals) increasingly [2,3]. In spite of present attractions, there are still serious problems to use OCM widely in the petrochemical industries such as complex oxidation and heterogeneous reactions which lead to the shortage of ethylene and ethane yield. With the aim of improving ethane and ethylene’s yield, many researches have been focused on the catalysts used in the OCM process, their properties and influential factors on their performance [4–6]. Malekzadeh and co-workers measured and correlated the electrical conductivity and catalytic performance of MoO3/Na2WO4/SiO2 catalysts in OCM [7]. Wang et al. prepared Na2WO4–Mn/SiO2 catalysts by three different methods and compared their performances, stabilities and structures [8]. Choudhary et al. studied different effective factors such as catalyst calcinations temperature and gas atmosphere used in catalyst calcinations on activity and selectivity of La-promoted MgO [9]. They reported that the parameters had strong influences on the activity and selectivity of catalyst at only lower reaction temperatures (T<700 °C). The relationship between the structure and the performance of Na2W–Mn/SiO2...
catalysts for OCM was investigated by Ji et al. [10]. It was found in their study that the reactions proceed best with the contents of Na–W and Mn in the catalyst between 0.4–2.3%, 2.2–8.9% and 0.5–3%, respectively. It was also concluded that tetrahedral WO₄ is more active and selective for the OCM reaction. Yu Lio et al. examined the effects of pressure on OCM process and the catalyst stability over MgO/BarCO₃ [11]. Some researches have been also conducted on the modeling and simulation of the OCM reactors. Kiatkitipong et al. compared the performance of different reactors in oxidative coupling of methane by the use of modeling [12]. In another work, he has simulated the production of C₂ hydrocarbons and electricity through the OCM process in a solid oxide fuel cell type reactor (SOFC) [13]. Tye and co-workers developed a one-dimensional model for the oxidative coupling of methane over La₂O₃/CaO catalyst in a packed fixed bed reactor [14]. They studied the effects of parameters such as methane to oxygen ratio, temperature, space velocity and dilution effects of N₂ or H₂O in feed. They observed that the conversion and selectivity and the yield increased with temperature and the maximum value of yield was obtained at 1098 K. In an independent study, Tye developed a heterogeneous fixed bed modeling for OCM over La₂O₃/CaO catalyst, considering the importance of pore diffusion resistance [15]. Makri et al. performed a successful 100 folds scale-up for a gas-recycle reactor separator by simulation [16]. The application of membrane to control oxygen concentration along the reactor can offer a possibility to achieve much higher C₂ selectivity and yield for OCM. Line et al. studied the reaction using a reactor equipped with a catalytically active membrane [17–19]. Lu and co-workers investigated methane oxidative coupling in a porous γ-alumina membrane reactor and compared its performance with a packed reactor operated at similar conditions. They reported that the methane conversion in the membrane reactor was lower than co-feed reactor at the same reaction conditions, but C₂ yield and selectivity were higher at similar methane conversions [20]. Kao et al. studied an OCM packed porous membrane reactor (PMR) on Li/MgO catalyst and showed that at fixed methane feed rate there was an optimum oxygen feed pressure that would achieve the highest C₂ yield [21].

There has been some works on optimization of the conditions in order to improve performance. Istadi et al. optimized process parameters (CO₂/CH₄ ratio and reactor temperature) and catalyst compositions for CO₂ oxidative coupling of methane reaction over CaO–MnO/CoO₂ catalyst in order to maximize methane conversion, C₂ yield and selectivity. It was found that the CH₄ conversion was a saddle function and did not show a unique optimum as revealed by the canonical analysis [22]. In another work, the ratio of molar flow of feed to weight of catalyst applied in the reactor (contact time) and the temperature of reactor on Li/MgO catalyst was simultaneously optimized at isothermal conditions by Norashah et al. [23]. However, there have been only few researches addressing the optimal control in an OCM process. Rojnuckarin et al. applied an optimal control strategy to the problem of finding the flux profiles for the conversion of methane to ethylene and acetylene in a plug flow reactor. They used chlorine-catalyzed oxidative pyrolysis mechanism for their calculations [24].

The present study deals with the optimal control in an OCM reactor in which temperature is considered as the control variable. The optimal temperature profile along a fixed bed plug flow reactor is determined over La₂O₃/CaO as the catalyst to maximize the ethylene production. The degree of performance improvement under mentioned conditions is compared with the best isothermal performance of the reactor. In addition, the effects of pressure and initial oxygen ratio on the optimal temperature profile are pointed out. The algorithm of piecewise linear continuous optimal control by iterative dynamic programming (PLCCODIP) is employed in this research [25].

2. The reaction scheme

A molecular mechanism is applied in order to predict the present reactor behavior. In this regard, the reaction scheme, proposed by Stansch et al., which consists of a ten-step network of reactions, is used [26]. The reaction steps have been presented as follows:

\[
\begin{align*}
\text{CH}_4 + 2\text{O}_2 & \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \\
2\text{CH}_4 + 0.5\text{SO}_2 & \rightarrow \text{C}_2\text{H}_6 + \text{H}_2\text{O} \\
\text{CH}_4 + \text{O}_2 & \rightarrow \text{CO} + \text{H}_2\text{O} + \text{H}_2 \\
\text{CO} + 0.5\text{SO}_2 & \rightarrow \text{CO}_2 \\
\text{C}_2\text{H}_6 + 0.5\text{SO}_2 & \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} \\
\text{C}_2\text{H}_4 + 2\text{O}_2 & \rightarrow 2\text{CO} + 2\text{H}_2\text{O} \\
\text{C}_2\text{H}_6 & \rightarrow \text{C}_2\text{H}_4 + \text{H}_2 \\
\text{C}_2\text{H}_4 + 2\text{H}_2\text{O} & \rightarrow 2\text{CO} + 4\text{H}_2 \\
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + \text{H}_2 \\
\text{CO}_2 + \text{H}_2 & \rightarrow \text{CO} + \text{H}_2\text{O}
\end{align*}
\]

Beside the above reactive components, nitrogen is added to the gas flow as a temperature regulator in the reactor in order to avoid the formation of hot spots. The estimated rates for the above reactions can be given in Eqs. (11–16) as shown by Stansch et al. [26]. Moreover, the kinetic parameters used in the reaction scheme and the conditions suitable for use of Eqs. (1–16) are presented as in Tables 1 and 2, respectively.

\[
r_j = \frac{k_{0j}e^{-E_{aj}/RT}p_{C0j}p_{P0j}}{\left[1 + K_{CO2}e^{-\Delta H_{CO2}/RT}p_{CO2}\right]^j} \quad j = 1, 3 - 6
\]

\[
r_2 = \frac{k_{02}e^{-E_{aj2}/RT}(K_{O2}e^{-\Delta H_{O2}/RT}p_{O2})^{y_2}p_{C1H4}}{\left[1 + K_{CO2}e^{-\Delta H_{CO2}/RT}p_{CO2}\right]^2}
\]

\[
r_7 = k_0e^{-E_{aj7}/RT}p_{C1H6}
\]

\[
r_8 = k_0e^{-E_{aj8}/RT}p_{CO}p_{H2O}
\]

\[
r_9 = k_0e^{-E_{aj9}/RT}p_{CO}p_{H2O}
\]

\[
r_{10} = k_{10}e^{-E_{aj10}/RT}p_{CO}p_{H2O}^2
\]
3. **Theory**

3.1. **Modeling equations**

Modeling is the basis of solving any optimal control problem. This investigation benefits from a modeling performed by Ching Thian Tye et al. [14]. They have developed a one-dimensional model to simulate the reactions. Also, the system was assumed to work at steady state conditions. The modeling had been carried out for a plug flow reactor, packed with La2O3/CaO catalyst. The kinetic model involved both catalytic and non-catalytic reactions. It has been assumed that the gas flow behavior inside the reactor could be described by the ideal gas law.

The differential equations set of the reactor consisted of eight mass balance equations, an energy balance equation and a relationship for momentum balance. These equations for each element were presented by Ching Thian Tye et al. [14] as follows:

### 3.1.1. Mass balance

\[
\frac{d(C_i)}{d(Z)} = \frac{1}{u_s} \left( \bar{\rho}_b \sum j \dot{f}_{g,j} + \rho_b \sum j \dot{f}_{c,j} \right)
\]

Where:
- \( C_i \) molar concentration of component (mol/m³)
- \( u_s \) superficial velocity (m/s)
- \( r_{g,j} \) rate of formation of gas-phase reaction \( j \) (mol/(m² s))
- \( Z \) length (m)
- \( r_{c,j} \) rate of formation of catalytic reaction \( j \) (mol/(m² s))
- \( \alpha_{i,j} \) stoichiometric coefficient of component \( i \) in reaction \( j \)
- \( \rho_b \) density of catalyst in the bed (g/m³).

### 3.1.2. Energy balance

\[
\frac{dT}{d(Z)} = \frac{1}{\bar{C}_p} \left( \bar{\rho}_b \sum j (-\Delta H_j) + \rho_b \sum j (-\Delta H_j) + 4q^* \right)
\]

Where:
- \( T \) temperature (K)
- \( \Delta H_j \) heat of reaction \( j \) (kJ/(kg,K))
- \( \bar{C}_p \) specific heat (kJ/(kg,K))
- \( q^* \) heat of flux (kJ/(m² s))
- \( \rho_b \) density of gas flow (kg/m³).

### 3.1.3. Momentum balance (Ergun’s equation)

\[
\frac{dP}{d(Z)} = -\frac{\bar{\rho}_b U_e^2}{\psi \bar{P}} \left( 1 - \frac{\bar{\rho}_b}{\bar{\rho}_b} \right) \left[ \frac{150(1 - \bar{\rho}_b)}{\psi \bar{P}} + 1.75 \right]
\]

Where:
- \( \bar{P} \) total pressure of the system (kPa)
- \( \bar{P} \) average porosity of bed
- \( \psi \) shape factor
- \( d_p \) packing diameter (m)
- \( \bar{P} \) average reactor catalyst size of 0.3 mm and a reactor diameter of 6 mm.

The results of the present solution were found to fit the experimental data plausibly. Table 3 shows a set of simulated results and experimental data compared under same space velocity. All these runs were operated at a feed flow rate of 4 cm³ s⁻¹ over 14.8 mg of La2O3/CaO catalyst, a total pressure of 110 kPa, and reactor diameter of 6 mm. Other experimental conditions have been reported by Stansch [27].

To convert the partial pressure of each component to concentration, the relationship for ideal gas law, \( P_i = \frac{C_i}{RT} \) was used. In present research, the set of differential equations was solved by Rung–Kutta–Merson method. MATLAB 7.0.1 software was applied for the computations.

### 3.2. Validation of solving the model equations

Before solving any optimal control problem, we should ensure about the accuracy of the model equations’ results. The validity of the solution was tested in two ways. First, by comparing with the simulated results presented by Ching Thian Tye et al. [14] and second, by comparison with the experimental data, reported by Stansch [27]. The results of solving the set of equations which form the basis of this work and the results reported by Ching Thian Tye et al. at the same conditions are illustrated in Fig. 1. In this figure, the yield and the selectivity profiles of C₂ (ethane and ethylene) at isothermal, adiabatic and non-isothermal–non-adiabatic modes, obtained by solving Eqs. (17–19) (curves a), have been compared with C₂ yield and selectivity profiles calculated by Ching Thian Tye et al. [14] (curves b). It can be seen that the profiles in these two cases agree with each other satisfactorily.

The results of the present solution were found to fit the experimental data satisfactorily. Table 3 shows a set of simulated results and experimental data compared under same space velocity. All these runs were operated at a feed flow rate of 4 cm³ s⁻¹ over 14.8 mg of La2O3/CaO catalyst, a total pressure of 110 kPa, average reactor catalyst size of 0.3 mm and a reactor diameter of 6 mm. Other experimental conditions have been reported by Stansch [27].

It was found that the results of the solution procedure, applied in this research, fitted the experimental data fairly.

### Table 1 – The kinetic parameters [26]

<table>
<thead>
<tr>
<th>Step</th>
<th>( K_{0,j} ) (mol g⁻¹ s⁻¹ Pa⁻⁶ m⁻³)</th>
<th>( E_{a,j} ) (kJ mol⁻¹)</th>
<th>( m_j )</th>
<th>( n_j )</th>
<th>( K_{j,CO_2} ) (Pa⁻¹)</th>
<th>( \Delta H_{ad,CO_2} ) (kJ mol⁻¹)</th>
<th>( K_{j,CO} ) (Pa⁻¹)</th>
<th>( \Delta H_{ad,CO} ) (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20 × 10⁻³</td>
<td>48</td>
<td>0.24</td>
<td>0.76</td>
<td>0.25 × 10⁻¹²</td>
<td>175</td>
<td>-</td>
<td>124</td>
</tr>
<tr>
<td>2</td>
<td>23.2</td>
<td>182</td>
<td>1.0</td>
<td>0.40</td>
<td>0.83 × 10⁻¹³</td>
<td>186</td>
<td>-</td>
<td>168</td>
</tr>
<tr>
<td>3</td>
<td>0.52 × 10⁻⁶</td>
<td>68</td>
<td>0.57</td>
<td>0.85</td>
<td>0.36 × 10⁻¹²</td>
<td>187</td>
<td>-</td>
<td>166</td>
</tr>
<tr>
<td>4</td>
<td>0.11 × 10⁻³</td>
<td>104</td>
<td>1.0</td>
<td>0.55</td>
<td>0.40 × 10⁻¹²</td>
<td>168</td>
<td>-</td>
<td>211</td>
</tr>
<tr>
<td>5</td>
<td>0.17</td>
<td>157</td>
<td>0.95</td>
<td>0.37</td>
<td>0.45 × 10⁻¹²</td>
<td>166</td>
<td>-</td>
<td>211</td>
</tr>
<tr>
<td>6</td>
<td>0.06</td>
<td>166</td>
<td>1.0</td>
<td>0.96</td>
<td>0.16 × 10⁻¹²</td>
<td>211</td>
<td>-</td>
<td>211</td>
</tr>
<tr>
<td>7</td>
<td>1.2 × 10⁻⁶</td>
<td>226</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>9.3 × 10⁰</td>
<td>300</td>
<td>0.97</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0.19 × 10⁻³</td>
<td>173</td>
<td>1.0</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.26 × 10⁻¹</td>
<td>220</td>
<td>1.0</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Units are mol s⁻¹ m⁻³ Pa⁻¹.
well. In Table 3 it is observed that when the temperature increases, the maximum error between simulated and experimental results is within 9.3%. The error differences between the simulated and experimental data can be caused due to several reasons. The reactions of pre and post-catalytic zone were not considered into account in the model and the simulations [14,26]. The gas-phase reaction considered in the model is interstitial gas-phase reaction within the catalytic bed. There could be reactions in gas phase that occur before reactants enter to the catalytic bed, such as gas-phase oxidation of methane; this makes a deviation from the initial conditions assumed in the simulations. The same holds for the post-catalytic zone of the reactor. The gas-phase reaction like thermal decomposition and combustion contribute somehow different to the catalytic bed performance, which were not considered in the simulation; this resulted in some differences between the simulated and experimental data.

3.3. Configuration of problem

In this investigation the optimal temperature profile for maximizing ethylene production in a reactor of oxidative coupling of methane is inspected. Each optimal control problem consists of two parts, equations and system restrictions, and performance index.

3.3.1. System restrictions

System equations which are defined as Eqs. (11–16) are the first group of system restrictions. The second are the permitted ranges for the state variables and the control variable (i.e. temperature) which are listed in Table 2. The second group of restrictions is due to operational conditions necessitated by the applied reaction scheme conformation.

Fig. 1 – $C_2$ yield and selectivity profiles along the reactor at isothermal (.....), adiabatic (▁) and non-adiabatic–non-adiabatic (▁▁) conditions ($T^* = 973$ K, $CH_4/O_2 = 10$, $C_{O_2} = 25\%$, $m_{cat}/V_{STP} = 3.75$ kg s m$^{-3}$, $U=140$ W m$^{-2}$ K) (a) presented in this research by solving Eqs. (17), (18) and (19), (b) reported by Ching Thian Tye et al. [14].
3.3.2. Performance index

The main purpose of this work is to maximize the ethylene production. The related objective function is introduced as Eq. 20.

\[
P.I.: \frac{\dot{u}_s \cdot C_{C_2H_4}}{A_C} \bigg|_{Z=Z_t} = (\frac{U_{Cs} \cdot C_{C_2H_4}}{Z=0} \cdot A_C) \quad (20)
\]

P.I. Performance index
A_C Cross-sectional area of the reactor (m²)
Z_f Length of the reactor (m)

Since the cross-sectional area is constant along the reactor and the ethylene flow rate at the entrance is not supposed to change in time, one can eliminate them from Eq. (20), without making any alteration on the optimal temperature profile. As a result, the objective function can be simplified as follows:

\[
P.I. = (\frac{u_s \cdot C_{C_2H_4}}{Z=Z_t}) \quad (21)
\]

As can be seen from Eq. (21), the performance index in the present problem is the molar flux of ethylene at the reactor outlet.

The algorithm of piecewise linear continuous optimal control by iterative dynamic programming (PLCOCIDP) [25], was applied to obtain the optimal temperature policy. The parameters of this algorithm used in this investigation, have been presented in Table 4. It was decided to use a multi-pass method where the number of stages is doubled after every pass, each consisting of 30 iterations, and the best temperature policy obtained thereof was used as an initial temperature trajectory for the next pass. The initial uniform temperature of \( T = 1150 \) K was selected as the initial guess for the optimal temperature.

Fig. 2 shows the performance index, calculated by Eq. (21), at each iteration in the last pass, at \( P_t = 130 \) kPa and \( \gamma_{O_2} = 0.15 \). As can be observed, the performance index rapidly increases from the initial value of 2.3469 mol/(m² s) to 2.3485 mol/(m² s) at the end. On the other hand, the quantity of the performance index, i.e. the ethylene production, at the best constant temperature (1096.3 K) only reaches 1.66 mol/(m² s) that means a 42% improvement by applying the optimal control policy compared to that of the optimized constant temperature.

4. Results and discussions

The reactor, investigated in this research, was a fixed bed with \( \text{La}_2\text{O}_3/\text{CaO} \) as catalyst. The operating pressure at the entrance of the reactor was set equal to 130 kPa. Other structural characteristics and flow conditions at the entrance of the reactor (i.e. boundary conditions for solving Eqs. (17–19)) have been given in Table 5.

Fig. 3 shows the optimal temperature profile in the reactor. As observed, the optimal temperature profile can be divided into three parts. In the first part, the reactor temperature decreases from 1228 K to 1100 K; in the second part, it gradually reaches 1140 K, and finally in the third part, the reactor temperature increases sharply to 1228 K (maximum allowable temperature) and remains unchanged, up to the end of the reactor.

Since only methane and oxygen exist as reactants at the entrance of the reactor, only reactions (1–3) are likely to occur. In Table 1, it is observed that the activation energies in reactions (1, 3) are considerably lower than the sum of the oxygen adsorption enthalpy and the activation energy of reaction (1). Considering the terms in the denominators of Eqs. (11, 12), it can be inferred that the temperature at the entrance of the reactor should be maximized, in order for the rate of reaction (2) to increase more than reactions (1, 3). Accounting
The best isothermal performance of the reactor at the conditions given in Table 5 can be achieved at 1096.3 K. Figs. 4 and 5 show the results obtained at the constant temperature 1096.3 K (curves b) in comparison with those of applying the optimal temperature profile (curves a). In Fig. 4 it is observed that oxygen disappears sooner when the optimal temperature profile is applied, compared to the best isothermal performance. This happens because, all parts of the optimal temperature profile (Fig. 3) are higher than 1096.3 K, and hence the rate of reactions in case of applying the optimal temperature profile is greater. In Fig. 5, it can be seen that applying the optimal temperature profile results in an increase of ethylene production from 1.66 mol/(m² s) at isothermal mode to 2.35 mol/(m² s). Furthermore, there is no sudden increase for the best isothermal performance (see Fig. 5). It has its origin in the constant temperature in this case and then no abrupt intensification of ethene thermal cracking reaction occurs.

4.1. Effect of initial oxygen concentration

The initial oxygen concentration is one of the most influencing factors in OCM processes. In this work the effects of initial oxygen mole fraction on the optimal temperature profile and the performance of the reactor were also evaluated. Fig. 6 shows the optimal temperature profiles for three different oxygen mole fractions in feed. As illustrated here, if the oxygen concentration reduces, the valleys in the optimal temperature profiles become more slender and their minimum points appear at lower temperatures. Since the rate of reaction (6) lessens as the initial oxygen mole fraction decreases, the ethylene reforming reaction plays a more important role in the ethylene consumption at lower oxygen mole fractions. The last reaction is very sensitive to temperature variations, and subsequently the minimum point of the temperature profile should decline with decreasing oxygen. In addition, if less amount of oxygen had been used at the entrance of the reactor, it would vanish sooner. As a result, we would have a delay in the sharp increasing of temperature profile which is quite obvious in the light of Figs. 6 and 7. Figs. 8 and 9 respectively show molar flux and selectivity of ethylene along the reactor. If the amount of oxygen increases, more ethane is produced via methane coupling reaction (i.e.
Fig. 6 – Effects of initial oxygen mole fraction on optimal temperature profile at \( P_t = 130 \) kPa.

Fig. 7 – Effects of initial oxygen mole fraction on conversion of oxygen at \( P_t = 130 \) kPa.

Fig. 8 – Effects of initial oxygen mole fraction on ethylene molar flux at \( P_t = 130 \) kPa.
Fig. 9 – Effects of initial oxygen mole fraction on selectivity of ethylene at $P_t = 130$ kPa.

Fig. 10 – Effects of total pressure on optimal temperature profile at $\gamma_{O_2} = 0.15$.

Fig. 11 – Effects of total pressure on conversion of oxygen at $\gamma_{O_2} = 0.15$. 
reaction (2)). This causes the ethylene molar flux to rise from 2 mol/(m² s) at \( \gamma_{O2} = 0.1 \) to 2.35 mol/(m² s) at \( \gamma_{O2} = 0.15 \), however, it intensifies the CO₂ producing reactions more than those of ethylene producing. Therefore, the ethylene selectivity declines from 52.95% at \( \gamma_{O2} = 0.1 \) to 46.77% at \( \gamma_{O2} = 0.15 \) in Fig. 9. This is more pronounced when oxygen is completely disappeared.

As a conclusion, taking into account the selectivity profiles (Fig. 9), molar fluxes (Fig. 8) and sensitivity of reactions (2, 5, 6) to oxygen partial pressure, there may be an optimum initial oxygen molar flux which is out of the acceptable range in Table 2 for verification of basic kinetic model equations [26].

4.2. Total pressure effects

The effects of total pressure on the performance of the reactor at allowable conditions (given in Table 2) were also investigated. Fig. 10 shows the optimal temperature profiles at 110 kPa and 130 kPa with the initial oxygen mole fraction of 0.15. As described previously, the falling slope of the temperature profile at the beginning of the reactor allows the effects of undesirable reactions (6, 8) to be depressed. On the other hand, a reduction of the total pressure from 130 kPa to 110 kPa can lessen the rate of undesirable and desirable reactions. Therefore on a trade-off, the minimum point of the temperature profile can shift up about 10 K and its beginning slope becomes slightly milder. Also the optimal temperature profile becomes more stretched in horizontal direction on decreasing the total pressure (see Fig. 10). As shown in Fig. 11, the lower reaction rates at lower pressures cause the oxygen conversion to reach the maximum limit (100%) after a longer period of time. Therefore, in case of decreasing the total pressure, the temperature profile arrives at 1228 K more slowly. It is shown in Fig. 12 that when the total pressure reaches 130 kPa (from 110 kPa) the ethylene molar flux improves from 2.21 mol/(m² s) to 2.35 mol/(m² s). This happens due to the promotion of ethylene producing reactions rates, especially of that of ethane thermal cracking. This also causes the selectivity of ethylene to grow from 44.76% at 110 kPa to 46.77% at 130 kPa (shown in Fig. 13).

5. Conclusions

The optimal temperature profile in a fixed bed plug flow reactor of OCM process for maximizing ethylene production...
was considered in this article. Since the terms of carbon dioxide partial pressure appear in denominators of $C_F$ producing reaction rate equations, an increase in carbon dioxide leads to decrease of ethane producing rate and also decreasing the production rate of ethylene. Therefore the evolution of the optimal temperature profile along the reactor has to be in such a way that minimizes the carbon dioxide production. It was also observed that applying the optimal profile of temperature caused oxygen to be eliminated sooner than that of the best isothermal performance of the reactor. This was due to an increase in reaction rates in the case of using the optimal temperature strategy. Furthermore, the ethylene molar flux increased from 1.66 mol/(m$^2$ s) to 2.35 mol/(m$^2$ s) by applying the optimal temperature distribution along the reactor. Thus, an increase of 42% was achieved in the ethylene production. The effects of initial oxygen mole fraction on the optimal temperature profile and the performance of the reactor were explained. It was observed that when higher amount of oxygen is used at the entrance of the reactor, it would vanish earlier which in turn leads to a delayed rise of temperature. Also, when initial mole fraction of oxygen increased from $y_0=0.1$ to $y_0=0.15$, more ethylene was produced, but its selectivity declined from 52.95% to 46.77%. The effects of total pressure on the performance of the reactor at allowable conditions were also investigated. It was shown that in the case of increasing total pressure, the temperature profile and the oxygen conversions approach the maximal points more quickly. Moreover, when the total pressure reached up to 130 kPa (from 110 kPa), the ethylene molar flux had a change from 2.21 mol/(m$^2$ s) to 2.35 mol/(m$^2$ s) and selectivity of ethylene improved from 44.76% to 46.77%.

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