A hybrid numerical approach for multi-responses optimization of process parameters and catalyst compositions in CO2 OCM process over CaO-MnO/CeO2 catalyst

Istadi Istadi, Diponegoro University
A hybrid numerical approach for multi-responses optimization of process parameters and catalyst compositions in CO₂ OCM process over CaO-MnO/CeO₂ catalyst

Istadi 1, Nor Aishah Saidina Amin*  
Chemical Reaction Engineering Group (CREG), Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, UTM Skudai, Johor Bahru 81310, Malaysia  
Received 21 July 2004; received in revised form 24 November 2004; accepted 2 December 2004

Abstract

A new hybrid numerical approach, using Weighted Sum of Squared Objective Functions (WSSOF) algorithm, was developed for multi-responses optimization of carbon dioxide oxidative coupling of methane (CO₂ OCM). The optimization was aimed to obtain optimal process parameters and catalyst compositions with high catalytic performances. The hybrid numerical approach combined the single-response modeling and optimization using Response Surface Methodology (RSM) and WSSOF technique of multi-responses optimization. The hybrid algorithm resulted in Pareto-optimal solutions and an additional criterion was proposed over the solutions to obtain a final unique optimal solution. The simultaneous maximum responses of C₂ selectivity and yield were obtained at the corresponding optimal independent variables. The results of the multi-response optimization could be used to facilitate in recommending the suitable operating conditions and catalyst compositions for the CO₂ OCM process.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Weighted Sum of Squared Objective Functions; CO₂ OCM process; Multi-responses optimization; Pareto-optimal solutions

1. Introduction

The high CO₂/CH₄ ratio in Natuna’s natural gas compositions, comprising of up to 71% carbon dioxide and 28% methane [1], should be strategically utilized for the production of higher hydrocarbons, liquid fuels and other important chemicals. Recently, the conversion of methane to C₂ hydrocarbons (ethane and ethylene) using carbon dioxide as an oxidant (carbon dioxide oxidative coupling of methane (CO₂ OCM)) has received considerable attention [2–9]. Eqs. (1) and (2) are the two main CO₂ OCM reaction schemes to produce C₂ hydrocarbons, while carbon monoxide and water are the by-products.

\[
\begin{align*}
2\text{CH}_4 + \text{CO}_2 & \rightleftharpoons \text{C}_2\text{H}_6 + \text{CO} + \text{H}_2\text{O} \\
\Delta H_{298}^\circ & = +106 \text{ kJ/mol} \quad (1) \\
2\text{CH}_4 + 2\text{CO}_2 & \rightleftharpoons \text{C}_2\text{H}_4 + 2\text{CO} + 2\text{H}_2\text{O} \\
\Delta H_{298}^\circ & = +284 \text{ kJ/mol} \quad (2)
\end{align*}
\]

Catalyst screening of CeO₂-based catalysts for CO₂ OCM process over binary and ternary metal oxides [9] determined that the 15 wt.% CaO-5 wt.% MnO/CeO₂ catalyst as the most potential. Interestingly, the stability test showed that the 15 wt.% CaO-5 wt.% MnO/CeO₂ catalyst was stable with no obvious coking during 20h of reaction time on stream. However, the process parameters and the catalyst compositions of the CO₂ OCM process have not been optimized.

---

* Corresponding author. Tel.: +607 5535588; fax: +607 5581463.  
E-mail address: r-naishah@utm.my (N.A.S. Amin).

Present address: Department of Chemical Engineering, Diponegoro University, Semarang 50239, Indonesia.

1385-8947/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
The development of a highly efficient catalyst is important and the key to obtain a highly efficient catalyst is the catalyst design [10–13]. The relationships among catalyst compositions, process parameters and catalyst compositions toward the catalytic performances are very complex from the engineering and chemistry points of view, but the determination of a suitable catalyst is crucial for the CO2 OCM process. Preferably, the very complex relation should be modeled at a molecular level in the catalyst design to obtain a suitable catalyst compositions and optimal operating conditions. The optimal operating parameters, such as the CO2/CH4 ratio and reactor temperature, and the catalyst compositions in the CeO2-supported catalyst, provide essential information for industrial CO2 OCM process.

Pertaining to the catalyst design, some previous researchers introduced artificial neural network (ANN) to design the catalysts [10–13]. The selection of optimization method is very important to design an optimal catalyst as well as the relations between process parameters and catalytic performances [14]. The previous researchers suggested that artificial neural network is feasible and many experiments can be avoidable [14]. According to the complex interaction among the catalyst compositions, the process parameters and the metal-support with no clear reaction mechanism in the CO2 OCM process, it is more useful for the catalyst design using empirical models especially in the optimization studies. A single-response optimization is usually insufficient for the real CO2 OCM process due to the fact that most responses, i.e. methane conversion, products selectivity and yield, are dependent. Therefore, simultaneous multi-responses technique combined with the statistical single-response modeling using RSM is superior. Empirical and pseudo-phenomenological modeling approaches have been employed by researchers [14–16] for optimizing the catalytic process. The empirical modeling is efficient for the catalytic process optimization, but the drawback is that the model does not describe the fundamental theory or actual phenomena. The empirical model may be more appropriate for process optimization when the kinetic mechanism is not well known.

Concerning the multi-responses optimization, a graphical multi-responses optimization technique was implemented for xylitol crystallization from synthetic solution [17], but it is not useful for more than two independent variables or highly non-linear models. In another study, a generalized distance approach technique was developed to optimize process variables in the production of propanol from mycelium [18]. The optimization procedure was carried out by searching independent variables that minimize the distance function over the experimental region in the simultaneous optimal critical parameters. Recently, the robust and efficient technique of the elitist Non-dominated Sorting Genetic Algorithm (NSGA) was used to obtain the solution of the complex multi-objectives optimization problem [16,19–21]. A hybrid genetic algorithm (GA) with artificial neural network was also developed [16] to design optimal catalyst and operating conditions in the O2 OCM process. In addition, a comprehensive optimization study of simulated moving bed process was also reported using a robust genetic algorithm optimization technique [22].

The main objective of this paper is to develop a new hybrid numerical approach for the simultaneous multi-responses optimization in the CO2 OCM process. A key feature of the hybrid numerical approach is the development of the Weighting Sum of Squared Objective Functions (WSSOF) algorithm to the simultaneous maximization of two responses, i.e. CH4 conversion and C2 selectivity, CH4 conversion and C2 yield, or C2 selectivity and C2 yield, as the following task after the development of single-response models. In this hybrid numerical approach, the Nelder–Mead Simplex method was utilized in the algorithm for solving the unconstrained optimization problem.

2. Numerical methods and experimental design

2.1. Technique for single-response optimization

It is necessary to obtain the optimal single-response models and the corresponding independent variables before multi-responses optimization is carried out. The optimal single-responses are used for obtaining information of the optimization boundary ranges. For example, in multi-responses optimization, the simultaneous optimal C2 selectivity and yield is resulted in the entire range between both individual optimal values. In addition, reactor temperature and CO2/CH4 ratio (process parameters) and wt.% CaO and wt.% MnO in the CeO2 catalyst (catalyst compositions) are searched in the range between those of single-response optimization. It is supposed that the simultaneous optimum is located within the ranges of single-responses optimization. In this section, the single-response modeling and optimization are presented.

2.1.1. Design of experiment using central composite design

A Central Composite Rotatable Design (CCRD) for four independent variables was employed to design the experiments [26] in which the variance of the predicted response, Y, at some points of independent variables, X, is only a function of the distance from the point to the design center [23–25]. The design of experiment is intended to reduce the number of experiments and to arrange the experiments with various combinations of independent variables. In the rotatable design, the standard error, which depends on the coordinates of the point on the response surface at which Y is evaluated and on the coefficients β, is the same for all points that are the same distance from the central point. The value of α for rotatability depends on the number of points in the factorial portion of the design, which is given in Eq. (3) [23–25]:

\[ a = (F)^{1/4} \]  

(3)

where F is the number of points in the cube portion of the design \((F=2^k, k \) is the number of factors). Since there are
Table 1
Experimental ranges and levels of factors or independent variables

<table>
<thead>
<tr>
<th>Factors (X)</th>
<th>Range and levels (x_i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO_2/CH_4 ratio (X_1)</td>
<td>(−2) 1, 1.5, 2, 2.5, 3</td>
</tr>
<tr>
<td>Reactor temperature (X_2) (K)</td>
<td>973, 1048, 1123, 1198, 1273</td>
</tr>
<tr>
<td>wt.% CaO (X_3) (%)</td>
<td>5, 10, 15, 20, 25</td>
</tr>
<tr>
<td>wt.% MnO (X_4) (%)</td>
<td>1, 3, 5, 7, 9</td>
</tr>
</tbody>
</table>

For four factors, the \( F \) number is equal to \( 2^4 = 16 \) points, while \( a \) is equal to \( (16)^{1/4} = 2 \) according to Eq. (3).

Process parameters of CO_2/CH_4 ratio and reactor temperature, and catalyst compositions of wt.% CaO and wt.% MnO in the CeO_2-supported catalyst were selected as the independent variables. The ranges of the independent variables are based on the conditions screened prior to optimization and are often used in the literatures [4, 5, 7]. Pertaining to space velocity, gas hourly space velocity (GHSV) was fixed during the reaction. The fixed space velocity value was chosen based on the variables screening prior to optimization such that performance of the catalyst is not influenced significantly by the variable in the tested range. The ranges and levels used in the experiments are given in Table 1 in which \( X_1 \) denotes CO_2/CH_4 ratio, \( X_2 \) denotes reactor temperature, while \( X_3 \) and \( X_4 \) denote wt.% CaO and wt.% MnO in the CeO_2-supported catalyst, respectively [26]. In the experimental design, all variables are coded for statistical calculation according to Eq. (4) [23–25].

\[
x_i = \frac{a}{2}[X_i - (X_{\text{max}} + X_{\text{min}})]/(X_{\text{max}} - X_{\text{min}}) \quad (4)
\]

where \( x_i \) is the dimensionless coded value of the \( i \)th variable, \( X_i \) the natural value of the \( i \)th variable, \( X_{\text{max}} \) and \( X_{\text{min}} \) are the highest and the lowest limits of the \( i \)th variable, respectively.

The experimental design matrix resulted by the CCD revealed in Table 2 [26] consists of 26 sets of coded conditions expressed in natural values. The design consists of a two-level full factorial design \( (2^4 = 16) \), eight star points and two center points. Based on this table, the experiments for obtaining the responses, i.e. CH_4 conversion \( (X_{\text{CH}_4}) \), C_2 hydrocarbons selectivity \( (S_{\text{C}_2}) \) and C_2 hydrocarbons yield \( (Y_{\text{C}_2}) \) are carried out at the corresponding independent variables addressed in the experimental design matrix. These experimental data
are used for validating the single-response model of the catalytic CO$_2$ OCM process. The sequence of experiment was randomized in order to minimize the effects of uncontrolled factors. Detail description of the single-response modeling, the catalyst preparation and the catalyst testing were reported elsewhere [26].

### 2.1.2. Single-response modeling using Response Surface Methodology (RSM)

The central composite design results revealed in Table 2 were analyzed using Response Surface Methodology. All single-responses were modeled using the RSM corresponded to independent variables [23–25]. In general, pertaining to the second order considerations, the optimal value of the independent variables that produces a maximum or minimum response. In this paper, the design of experiment and the Response Surface Methodology were employed using STATISTICA, version 6, software (StatSoft Inc., Tulsa, USA).

By the RSM, a quadratic polynomial equation was developed to predict the responses as a function of independent variables involving their interactions [23–25]. In general, the model can be expressed in matrix notation as written in Eq. (6).

\[
Y = \beta_0 + X'\beta + X'BX
\]  

where

\[
X = \begin{bmatrix} X_1 \\ X_2 \\ X_3 \\ X_4 \\ X_5 \end{bmatrix}, \quad b = \begin{bmatrix} \beta_1 \\ \beta_2 \\ \beta_3 \\ \beta_4 \\ \beta_5 \end{bmatrix} \text{ and } B = \begin{bmatrix} 1 & \beta_{11} & \beta_{12} & \beta_{13} & \beta_{14} \\ \beta_{12} & \beta_{22} & \beta_{23} & \beta_{24} & \beta_{34} \\ \beta_{13} & \beta_{23} & \beta_{33} & \beta_{34} & \beta_{44} \\ \beta_{14} & \beta_{24} & \beta_{34} & \beta_{44} & \beta_{44} \end{bmatrix}
\]

The predicted response at the stationary point is approximated in Eq. (8).

\[
Y_0 = \hat{\beta}_0 + \frac{1}{2}X_0'b
\]  

The characteristic of the stationary point at the critical response is determined from the sign and magnitude of the eigenvalues ($\lambda_i$) [23,25,27]. The eigenvalues are obtained from the roots of the determinant relation as given in Eq. (9).

\[
|B - \lambda I| = 0
\]

If the $\lambda_i$ are all positive, then $X_0$ is a point of minimum response; if the $\lambda_i$ are all negative, then $X_0$ is a point of maximum response [25,27]. However, if the $\lambda_i$ have different signs, $X_0$ is a saddle point. Transformation of the fitted model into a new coordinate system with the origin at the stationary point $X_0$ and thus rotation of the axes until they are parallel to the principal axes help to characterize the stationary point of the fitted models [23–25]. An equation developed by the transformation is called the canonical form of the model, which is given in Eq. (10).

\[
Y = Y_0 + \lambda_1w_1^2 + \lambda_2w_2^2 + \lambda_3w_3^2 + \lambda_4w_4^2
\]

2.2. Theory for multi-responses optimization

In fact, there is a vector of objectives, $F(X) = \{F_1(X), F_2(X), \ldots, F_M(X)\}$ where $M$ denotes the number of objectives, that must be considered in chemical engineering process. The optimization techniques are developed to
find a set of decision parameters, \( X = \{X_1, X_2, \ldots, X_N\} \) where \( N \) is the number of independent variables, defined as the optimal independent variables. As the number of responses increases, the optimal solutions are likely to become complex and less easily quantified. Therefore, the development of multi-responses optimization strategy enables a numerically solvable and realistic design problem [14,28].

The task in multi-responses optimization is to create a non-inferior solution to a set of problems and then select among its members a solution that satisfies the objectives [22,29]. Generally, the mathematical description of multi-responses optimization is concerned with the minimization or maximization of a vector of objective functions, \( F(X) \), subject to a number of constraints and/or bounds as defined in Eq. (11) [27,29–30].

\[
\begin{align*}
\text{minimize} & \quad F(X) = [F_1(X), F_2(X), \ldots, F_M(X)]^T \\
\text{subject to} & \quad G_i(X) = 0, \quad i = 1, \ldots, I \\
& \quad H_j(X) \leq 0, \quad j = 1, \ldots, J \\
& \quad X_k^1 \leq X_k \leq X_k^L, \quad k = 1, \ldots, N \\
& \quad M \geq 2
\end{align*}
\]

In this problem there are \( N \) variables with \( J \) inequality constraints and \( I \) equality constraints. The function vector \( F(X) \) is the objective functions, \( G_i(X) \) is the \( i \)th inequality constraints and \( H_j(X) \) is the \( j \)th inequality constraints. The \( I \)th variable is varied in the bounds of \([X_k^1, X_k^L]\). The objective space means the space to which the objective vector belongs. The set of all feasible points \( \Lambda \) is called the feasible region \( F \), but in fact, there is no unique solution to this problem if any of the components of \( F(X) \) are competing. The multi-responses optimization concept is subsequently defined more precisely by considering a feasible region \( \Omega \) for the parameter space \( (X \in \mathbb{R}^N) \) that satisfies all the constraints as written in Eq. (12) [27,30].

\[
\begin{align*}
\Omega &= \{X \in \mathbb{R}^N\} \\
\text{subject to} & \quad G_i(X) = 0, \quad i = 1, \ldots, I \\
& \quad H_j(X) \leq 0, \quad j = 1, \ldots, J \\
& \quad X_k^1 \leq X_k \leq X_k^L, \quad k = 1, \ldots, N 
\end{align*}
\]

The formulation allows us to define the corresponding feasible region \( \Omega \) of the objective function space \( (F \in \mathbb{R}^M) \) as formulated in Eq. (13).

\[
\Lambda = \{F \in \mathbb{R}^M\} \quad \text{where} \quad F = F(X) \\
\text{subject to} & \quad X \in \Omega
\]

The mapping of the parameter space \( \Omega \) into the objective function space \( \Lambda \) represented for a two-dimensional case is depicted in Fig. 1(a) [30]. Therefore, a non-inferior solution is defined from the feasible region of objective function space \( \Lambda \) within the parameter space of individual objective functions of \( F(X) \). The solutions are known as Pareto-optimal or non-dominated solutions. A vector \( X' \in \Omega \) is said to be a Pareto-optimal point or a non-inferior solution point for multi-responses optimization if and only if there is no \( X \in \Omega \) such that \( F_M(X) \leq F_M(X') \) for all \( M \in \{1, 2, \ldots, M\} \) for minimization. A Pareto set is defined such that when we move from one point to another, at least one objective function improves and at least one other worsens. In the two-dimensional illustration, the set of non-inferior solution is depicted in Fig. 1(b) in which the Pareto-optimal solution points lie on the curve between points C and D. Points A and B represent a specific non-inferior solution points because an improvement in one objective, \( F_1 \), requires an increment in the other objective, \( F_2 \), such that \( F_{1B} > F_{1A} \) and \( F_{2B} > F_{2A} \).

Several methods are available for solving multi-responses optimization problem, for example, weighted sum strategy [30–32], \( \epsilon \)-constraint method [28,30,31,33], goal attainment algorithm [19,22,28] to obtain the Pareto set. Among the methods, the NSGA is the most powerful method for solving a complex multi-responses optimization problem. In the optimization of CO\(_2\) OCM process, the WSSOF method is proposed to solve the optimization of process parameters and catalyst composition in combination with the Response Surface Methodology.

Particularly, the multi-responses optimization problem, described in Eq. (11), can be formulated by converting the problem into a scalar single-response optimization problem, \( f(X) \), which is easy to be solved using unconstrained single-response optimization technique. The WSSOF technique allows a simpler algorithm, but unfortunately, the solution obtained depends largely on the values assigned to the weighting factors chosen. The scalar single-response equation converted from multi-responses optimization problem is expressed in Eq. (14) [21,27,30–31,34], which con-
siders the Weighted Sum of Squared Objective Functions method [32]:

\[
\maximize \mathbf{X} \in \Omega \quad f(F_i, W_i) = \sum_{i=1}^{2} W_i \cdot F_i(X)^2
\]  

subject to : \[\sum_{i=1}^{2} W_i = 1 \text{ and } 0 \leq W_i \leq 1\]  

(14)

where \(f(F_i, W_i)\) is called the utility function and the parametric weighting factors \((W_i)\) are under the constraint set \((\Omega)\). Generally, multi-responses optimization studies try to find the best tradeoff among more than one objective or to calculate all non-inferior solutions. The underlying problem is that there are many combinations of \(W_1\) and \(W_2\) values to convince the non-inferior solution.

In the equations, \(W_1\) and \(W_2\) denote weighting factors with respect to the objective functions, \(F_1(X)\) and \(F_2(X)\), respectively. The coupled responses, i.e. \(C_2\) selectivity and \(C_2\) yield, \(CH_4\) conversion and \(C_2\) selectivity, or \(CH_4\) conversion and \(C_2\) yield, are assigned to the objective functions, \(F(X)\), and the problem lies in attaching the weighting factors to each objective function. The weighting factors do not necessarily correspond directly to the relative importance of the objective functions. The maximization of Eq. (14) is interpreted as selection of \(W_1\) and \(W_2\) weighting factors for which the slope of the line comprising the weighting factors leads to the solution point where the line touches the boundary of \(X\).

The underlying problem is that there are many combinations of \(W_1\) and \(W_2\) values to convince the non-inferior solution point.

### 2.3. Additional criterion for determination of final optimal responses

Theoretically, all sets of non-inferior solutions at corresponding weighting factors are acceptable. In a real process, it is recommended to choose a set of operating conditions that will be adjusted to get high catalytic performances. In fact, the sets of solutions are not the final solution of the process optimization problem. The subsequent task of the non-inferior solutions is the selection of final optimal criterion, which requires an additional knowledge about the system. In this case, the sum of the objective functions, \(\sum F(X)\), is proposed as the final optimal criterion in single-response optimization. The detail single-response optimization can be stated as follows:

Step 1. Develop the independent response models \(F_1(X)\) and \(F_2(X)\) using Response Surface Methodology supported by the number of experimental data.

Step 2. Get values of maximum of the responses by minimizing the models independently of each other using Nelder–Mead Simplex algorithm. This step is aimed to obtain the boundary limits of multi-responses optimization.

Step 3. Formulate a multi-responses optimization problem by utilizing the single-response models according to Eq. (11):
Step 4. Convert the multi-responses optimization problem in Step 3 into a single-response optimization problem by introducing weighting factors, \(W_i\), according to Eq. (14).

\[
\text{maximize } f(\hat{W}_i) = \sum_{i=1}^{N} W_i \cdot F_i(x)\]

subject to \(\sum_{i=1}^{N} W_i = 1\) and \(0 \leq W_i \leq 1\).

Step 5. Solve the generated scalar single-response optimization problems using unconstrained optimization technique with respect to the variation of the weighting factor \((W_i)\). Boundary limits of the searching are based on the results of Step 2. Use the Nelder–Mead Simplex technique for multi-variable unconstrained optimization to solve the scalar single-response optimization. Find the solution of \(X^*\) and \(F(X)\) values corresponding to each combination of \(W_i\) subject to \(\sum W_i = 1\), and \(W_i \geq 0\). The detail sub-algorithm for this step can be written as follows:

Step 5a. Pick a starting point \(X_0\). Set initial \(W_i = [0\ 1]^T\) means that the searching is started from the boundaries \(F_2(X^*) = F_2^0(X^*)\) and \(F_1(X^*) = F_1^0(X^*)\).

Step 5b. Put the scalar single-response model of Eq. (14) as a function file.

Step 5c. Solve the scalar single-response unconstrained optimization problem (Eq. (14)) in Step 5b using Nelder–Mead Simplex technique. This step produces the optimal values of \(X^*\), \(F_1(X^*)\) dan \(F_2(X^*)\) with respect to the variation of weighting factor \(W_i\).

Step 5d. Calculate the normalized optimal responses values \((\hat{F}_1(X^*)\) and \(\hat{F}_2(X^*)\)) according to Eq. (15). Calculate sum of both normalized responses values \((\Sigma \hat{F}(X^*) = \hat{F}_1(X^*) + \hat{F}_2(X^*))\).

Step 5e. Is \(W_i \leq 1\)? If yes, update \(W_i\) values and go to Step 5b. If no, terminate.

Step 6. Select a maximum value of the sum of normalized responses at each \(W_i\) variations.

Step 7. Get the corresponding values of \(X^*\), \(F_1(X^*)\) and \(F_2(X^*)\) using interpolation method.

In this algorithm, the single-response optimization problem can be solved using a standard unconstrained optimization algorithm of Nelder–Mead Simplex technique [35], which is a robust algorithm for problems that are very nonlinear or have a number of discontinuities.

3. Results and discussions

3.1. Single-response optimization of CO₂ OCM process

The empirical single-response modeling of CO₂ OCM process over CaO-MnO/CoO₂ catalyst was developed by RSM based on design of experiment using CCRD. The models of CH₄ conversion, C₂ hydrocarbons selectivity and yield were developed as a function of the process parameters, i.e. CO₂/CH₄ ratio \((X_1)\), reactor temperature \((X_2)\), and the catalyst compositions, i.e. wt.% CaO \((X_3)\) and wt.% MnO \((X_4)\). The models of CH₄ conversion, C₂ hydrocarbons selectivity and yield were described in Eqs. (16–18), respectively [26].

\[
F_{	ext{CH}_4\text{conversion}}(X) = 230.9662 - 4.1100X_1 - 0.4251X_2 \\
+ 2.1151X_3 + 1.2208X_4 - 1.8843X_5^2 \\
+ 0.0002X_6^2 - 0.0024X_7^2 + 0.0232X_8^2 \\
+ 0.0107X_1X_2 + 0.0995X_1X_3 \\
- 0.2087X_1X_4 + 0.0019X_2X_3 \\
- 0.0008X_2X_4 - 0.0204X_3X_4 \tag{16}
\]

\[
F_{	ext{C}_2\text{selectivity}}(X) = -3480.035 + 177.6118X_1 + 6.3335X_2 \\
- 16.6266X_3 + 11.9748X_4 \\
- 15.6574X_5^2 - 0.0029X_6^2 - 0.1304X_7^2 \\
- 0.5532X_8^2 - 0.1286X_1X_2 \\
+ 1.5858X_1X_3 + 1.172X_1X_4 \\
+ 0.0144X_3X_3 - 0.0063X_2X_4 \\
+ 0.0202X_1X_4 \tag{17}
\]

\[
F_{	ext{C}_2\text{yield}}(X) = -150.0778 + 12.7327X_1 + 0.2579X_2 \\
- 0.6948X_3 - 1.3511X_4 - 2.2464X_5^2 \\
- 0.0001X_7^2 - 0.0101X_8^2 - 0.0250X_6^2 \\
- 0.0044X_1X_2 + 0.0536X_1X_3 \\
+ 0.0754X_1X_4 + 0.0008X_2X_3 \\
+ 0.0014X_1X_4 - 0.0021X_1X_4 \tag{18}
\]
The canonical analysis based on the stationary point of the CH$_4$ conversion, C$_2$ hydrocarbons selectivity and yield model are revealed in Eqs. (19)–(21), respectively.

$$Y_1 = 2.756 - 1.8913w_1^2 + 0.006w_1^3 + 0.0003w_1^4$$

$$Y_2 = 82.6022 - 15.7206w_1^2 - 0.3341w_1^3 - 0.0866w_1^4$$

$$Y_3 = 11.8116 - 2.2474w_1^2 - 0.0244w_1^3 - 0.0098w_1^4$$

where $Y_1$, $Y_2$, and $Y_3$ stand for the canonical form of the CH$_4$ conversion, C$_2$ selectivity and yield models, respectively. The mixed or different eigenvalues signs in Eq. (19) indicate that the CH$_4$ conversion model has a shape like a saddle at the stationary point [26,27], which consequently does not present a unique optimum point. The different trend is shown by C$_2$ selectivity and yield models in Eqs. (20) and (21), respectively. Both models show all negative eigenvalues indicate a unique maximum C$_2$ selectivity at the stationary point. The different magnitudes of eigenvalues reveal an elliptical contour shape, which means the effect of interaction among the independent variables is important [27].

The multi-variables single-response optimization was performed using the Nelder–Mead Simplex technique. Tables 3 and 4 reveal the independent optimal values of C$_2$ hydrocarbons selectivity and yield responses, respectively, together with their optimal independent variables. From Table 3, the C$_2$ hydrocarbons selectivity achieves a maximum value of 82.62% at the corresponding optimal factors of CO$_2$/CH$_4$ ratio, reactor temperature, wt.% CaO and wt.% MnO being 1.9, 1080 K, 8.2% and 6.8%, respectively. The results of the single-response optimization [26] is closed to the result by Wang et al. [5,7] and Cai et al. [8] in which a high C$_2$ hydrocarbons yield is attained at 3.93% with respect to CO$_2$/CH$_4$ ratio, reactor temperature, wt.% CaO and wt.% MnO of 2.0, 1175 K, 15.3% and 7.3%, respectively, as revealed in Table 4. The optimal C$_2$ yield was achieved at higher reactor temperature (1123–1148 K) and high CO$_2$/CH$_4$ ratio (about 2), which is in agreement with other researchers results [5,7,8]. The subsequent task of this work is focused on finding the simultaneous maximum values of both responses.

### Table 3

<table>
<thead>
<tr>
<th>Independent variables ($X$)</th>
<th>Location of optimum</th>
<th>Maximum C$_2$ selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$/CH$_4$ ratio ($X_1$)</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>Reactor temperature ($X_2$) (K)</td>
<td>1080</td>
<td>82.62</td>
</tr>
<tr>
<td>wt. % CaO in the catalyst ($X_3$) (%)</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>wt. % MnO in the catalyst ($X_4$) (%)</td>
<td>6.8</td>
<td></td>
</tr>
</tbody>
</table>

### Table 4

<table>
<thead>
<tr>
<th>Independent variables ($X$)</th>
<th>Location of optimum</th>
<th>Maximum C$_2$ yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$/CH$_4$ ratio ($X_1$)</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>Reactor temperature ($X_2$) (K)</td>
<td>1175</td>
<td>3.93</td>
</tr>
<tr>
<td>wt. % CaO in the catalyst ($X_3$) (%)</td>
<td>15.3</td>
<td></td>
</tr>
<tr>
<td>wt. % MnO in the catalyst ($X_4$) (%)</td>
<td>7.3</td>
<td></td>
</tr>
</tbody>
</table>

3.2. Interpretation of multi-responses optimization technique

#### 3.2.1. A hybrid numerical approach of WSSOF technique

Basically, the relation between catalysts compositions, process parameters and the catalytic reaction performances cannot be described in a simple empirical mathematical model. The mathematical models for CH$_4$ conversion, C$_2$ selectivity and yield are complex that depend on the catalyst composition and operating conditions, etc. The empirical modeling using RSM combined with multi-responses optimization is useful for optimizing the CO$_2$ OCM process in certain ranges of independent variables before the kinetic studies are carried out, but the models may be meaningless physically and phenomenologically. The hybrid method is also useful for exploring the interaction between the variables towards the process performances. The empirical modeling and the multi-responses optimization method are useful for designing a catalyst composition in relation with the process parameters and validated with some experimental data. The results of the hybrid multi-responses optimization can be used to recommend the operating conditions and catalyst compositions for further experimental works in CO$_2$ OCM process especially in the kinetic studies.

A numerical approach is implemented in this paper to optimize the simultaneous responses over the independent variables. The single-response modeling and optimization were conducted prior to multi-responses optimization using the Response Surface Methodology and the Nelder–Mead Simplex technique, respectively. The hybrid numerical approach combines the single-response modeling using RSM and solving the multi-responses optimization using WSSOF technique. Meanwhile, an additional criterion was proposed to obtain a final unique solution. In the multi-responses optimization, the numerical WSSOF technique is proposed by converting the multi-responses optimization into a scalar single-response problem as aforementioned in Eq. (14).

The detail numerical algorithm for the multi-responses optimization using the WSSOF technique was described clearly in the previous section. The numerical technique can be treated by introducing the weighting factors, $W_1$ and $W_2$, corresponding to $F_1(X)$ and $F_2(X)$, respectively. The two weighting factors do not necessarily correspond directly to the relative importance of the objectives. Sets of non-inferior solution points or Pareto-optimal solutions are obtained. In a
non-inferior solution set, no decrease can be made in any of the objectives without causing a simultaneous increase in one or more of the other objectives. One of the weighting factors ($W_1$) corresponding to $F_1(X)$ is varied in the range of 0–1, while another ($W_2$) with respect to $F_2(X)$ is varied conversely between 1 and 0 according to the constrain that sum of $W_1$ and $W_2$ equal to 1 [32]. Each weighting factor variation produces a scalar single-response optimization problem, which resulted in an optimal response corresponding with optimal decision variables ($X$). These treatments give a set of solution points or Pareto-optimal solution after whole weighting factor was varied.

In fact, the non-inferior solution points at corresponding weighting factors variation are not the final solution of the problem. It is still difficult to recommend a set of operating conditions and catalyst compositions that are suitable to achieve a high $C_2$ selectivity and yield simultaneously. The subsequent selection of those non-inferior solution points for a unique optimal solution requires a final decision criterion, which needs additional knowledge about the system. In this case, sum of the objective functions, $\sum F(X)$, is proposed as the final optimal criterion in the CO$_2$ OCM process optimization. As a result, the final optimal values of the responses corresponding to the optimal independent variables are generated.

3.2.2. Effect of weighting factors variation to the Pareto-optimal solution points

Generally, the multi-response optimization attempts to find the best tradeoff among more than one objective or to calculate all non-inferior solutions. In this case, the effect of weighting factors variations are shown in Figs. 2–4 pertaining to the simultaneous optimization of $C_2$ selectivity and yield, CH$_4$ conversion and $C_2$ selectivity, and CH$_4$ conversion and $C_2$ yield, respectively.

Fig. 2 takes into account the variation effect of $W_1$ and $W_2$ to the objective functions ($F(X)$) of $C_2$ selectivity and yield at which $W_1$ is varied in the range of 0.01–0, while consequently $W_2$ is varied in the range of 0.99–1. It is shown that increasing $W_1$ from 0 to 0.01 at decreased $W_2$ from 1 to 0.99 leads to increased objective function value of $C_2$ selectivity, $F_1(X)$, and simultaneously decreases $C_2$ yield, $F_2(X)$. The zero value of $W_1$ and the unity value of $W_2$ resulting the multi-responses optimization mean a single-response optimization of $F_2(X)$ as revealed in the algorithm of Step 2. Meanwhile on the contrary, the unity value of $W_1$ and the zero value of $W_2$ during the multi-response optimization mean an individual response optimization of $F_1(X)$. This phenomenon is formulated in Step 2 of WSSOF algorithm to obtain the boundary limits of multi-responses optimization.

In term of simultaneous $C_2$ selectivity and yield optimization, the $C_2$ hydrocarbons selectivity achieves 82.62% ($F_1^2(X^*)$) when the $C_2$ yield is 2.98% ($F_2^2(X^*)$) at the same independent variables. In the contrary, the optimal $C_2$ hydrocarbons yield is achieved at 3.93% ($F_2^1(X^*)$), while the corresponding $C_2$ hydrocarbons selectivity is 59.63% ($F_1^1(X^*)$) at the same independent variables. The correlations indicate an opposing trend between the two responses where the increment of one response lowers the other one and vice versa.

Moreover, variation effect of $W_1$ and $W_2$ to the objective functions of CH$_4$ conversion ($F_1(X)$) and $C_2$ selectivity ($F_2(X)$) is depicted in Fig. 3, where $W_1$ is varied in the range of 0.6–0.99, while consequently $W_2$ is varied in the range of 0.4–0.01. Increasing $W_1$ from 0.6 to 0.99 at decreased $W_2$ from 0.4 to 0.01 leads to increased objective function of CH$_4$ conversion and simultaneously decreases $C_2$ selectivity. In addition, Fig. 4 takes into account the variation effect of weighting coefficients to the objective functions of CH$_4$ conversion ($F_1(X)$) and $C_2$ yield ($F_2(X)$). It is shown that decreasing $W_1$ from 0.0236 to 0 at increased $W_2$ from 0.9764 to 1 leads to decreased objective function value of CH$_4$ conversion and simultaneously increases $C_2$ yield.
3.2.3. Generation of Pareto-optimal solution in multi-responses optimization

It is worth noting that single- and multi-responses optimizations problems are conceptually different. In the multi-responses optimization, there may not be a best solution (global optimum) with respect to both objectives. Instead, there are an entire set of optimal solutions that are evenly good which leads to a situation wherein a set of non-inferior solutions is obtained rather than a unique solution [22,36–37].

Figs. 5–7 depict the Pareto-optimal solutions of the CO\textsubscript{2} OCM process optimization over CaO-MnO/CeO\textsubscript{2} catalyst corresponding to the simultaneous optimization of C\textsubscript{2} selectivity and yield, CH\textsubscript{4} conversion and C\textsubscript{2} selectivity, and CH\textsubscript{4} conversion and C\textsubscript{2} yield, respectively. The trend of the Pareto-optimal solutions shown in the figures coincides with that of the weighting factors variation as depicted in Figs. 2–4. From the figures, it can be shown that if the $F_1(X)$ increases, consequently the $F_2(X)$ is worsened. Thus, it could not be deduced that any of these non-dominated solutions in the Pareto set is an acceptable final solution. The next task is how to choose a unique final solution. The final solution is important in recommending the suitable operating conditions and catalyst compositions of the process. The selection of the final solution over the entire non-inferior solution requires an additional knowledge of the system, and often, this knowledge is intuitive and non-quantifiable. In this paper, the choice of the final solution is based on the sum of both objective functions, $\sum F(X)$. As mentioned before, the unique optimum is chosen at maximum of the sum of objective functions. The final criterion means that the unique optimal solution corresponds to the highest C\textsubscript{2} selectivity and yield, CH\textsubscript{4} conversion and C\textsubscript{2} selectivity, or CH\textsubscript{4} conversion and C\textsubscript{2} yield simultaneously. The Pareto set is useful, however, since it narrows the choices and helps to guide the decision maker in selecting the desired operating variables or preferred solution from among the set of Pareto-optimal points.

3.2.4. Location of optimal process parameters and catalyst compositions in multi-responses optimization of CO\textsubscript{2} OCM

Location of the optimal process parameters and the catalyst compositions for the multi-responses optimization of CO\textsubscript{2} OCM.
Fig. 9. Location of final optimal conditions for simultaneous CH₄ conversion and C₂ selectivity optimization using maximum normalized $\Sigma \hat{F}(\mathbf{X})$ as criterion from Pareto-optimal solution.

CO₂ OCM are depicted in Figs. 8–10 for C₂ selectivity and yield, CH₄ conversion and C₂ selectivity and CH₄ conversion and C₂ yield, respectively. The objective functions in this section are presented as the normalized objective functions formulated in Eq. (15). Pertaining to simultaneous optimization of C₂ selectivity and yield, the optimal process parameters results depicted in Fig. 8 are 1.99 and 1127 K for CO₂/CH₄ ratio and reactor temperature, respectively. The simultaneous optimal C₂ selectivity and yield in this optimization is in accordance with the result by Wang et al. [5,7] and Cai et al. [8] at which a high C₂ yield was achieved at higher reactor temperature and high CO₂/CH₄ ratio (about 2). However, the high C₂ selectivity was attained at lower reactor temperature. In addition, the final optimal compositions of CaO-MnO/CeO₂ catalyst are 12.78% and 6.39% for wt.% CaO and wt.% MnO, respectively. Particularly, the unique final maximum C₂ selectivity and yield are included as one of the Pareto-optimal solutions set as revealed in Fig. 5. In fact, the optimal values of decision variables are located within the range of the individual response optimization using RSM except for the wt.% MnO.

Fig. 9 takes into account the location of simultaneous maximum CH₄ conversion and C₂ selectivity in which the final optimal conditions are shown at CO₂/CH₄ ratio 1.88 and reactor temperature 1084 K, respectively. Meanwhile, the final optimal catalyst compositions are obtained at 8.04 wt.% CaO and 6.88 wt.% MnO in the CeO₂-supported catalyst. The optimal decision factors of multi-responses optimization of CH₄ conversion and C₂ yield as depicted in Fig. 10 resulted in the final optimal conditions of 2.01 and 1191 K for CO₂/CH₄ ratio and reactor temperature, respectively. The corresponding optimal catalyst compositions are 16.09 wt.% CaO and 7.67 wt.% MnO in the CeO₂-supported catalyst.

3.3. Multi-responses optimization results of CO₂ OCM

3.3.1. Simultaneous optimization of C₂ selectivity and yield

The simultaneous multi-responses optimization results are revealed in Table 5 together with the corresponding optimal independent variables. It is shown that the simultaneous optimal multi-responses are achieved at values of 76.56% and 3.74% for C₂ hydrocarbons selectivity and yield, respectively. The optimal process parameters and catalyst compositions from the multi-responses optimization are achieved at CO₂/CH₄ ratio and reactor temperature of 1.99 and 1127 K, respectively, and the wt.% CaO and wt.% MnO of 12.78% and 6.39%, respectively. According to the results, the optimal independent variables are located within the range between those from the single-response optimization except for the wt.% MnO in the catalyst as revealed in Fig. 8. The distinct trend of wt.% MnO may be due to the complexity of the optimization problem of the CO₂ OCM process in the numerical computation. It implies that there exist different factors influencing both responses. The reactor temperature has the highest effect indicated by a high diversity in the optimal reactor temperature between multi- and single-responses, while the wt.% MnO has the lowest effect. The interaction between reactor temperature and wt.% CaO has also significantly affected the responses [26].

Pertaining to the relationship between reactor temperature and wt.% CaO, the previous results also indicate that a high C₂ selectivity is achieved at lower reactor temperature and wt.% CaO in the catalyst, while a high C₂ yield is achieved at higher reactor temperature and wt.% CaO in the catalyst. The considerable C₂ hydrocarbons yield at high reactor temperature is related to a high methane conversion. Increasing CaO content in the catalyst enhances the CO₂ adsorption on the catalyst surface due to increasing catalyst basicity and improved methane conversion. C₂ selectivity and C₂ yield. Interaction of reactor temperature and wt.% CaO in the catalyst ($X_2(X_1)$) gives a considerable significant effect towards
Table 5
Simultaneous optimal multi-responses of C2 selectivity and yield and its corresponding factors location

<table>
<thead>
<tr>
<th>Simultaneous optimal multi-responses</th>
<th>Corresponding weighting coefficient ((W_i))</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2 selectivity ((f_1(X)))</td>
<td>76.56</td>
</tr>
<tr>
<td>C2 yield ((f_2(X)))</td>
<td>3.74</td>
</tr>
</tbody>
</table>

Location of factors for simultaneous optimal multi-responses

<table>
<thead>
<tr>
<th>Factor/independent variable</th>
<th>Optimum value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)/CH(_4) ratio (X(_1))</td>
<td>1.88</td>
</tr>
<tr>
<td>Reactor temperature (X(_2)) (K)</td>
<td>1127</td>
</tr>
<tr>
<td>wt.% CaO in the catalyst (X(_3)) (%)</td>
<td>12.78</td>
</tr>
<tr>
<td>wt.% MnO in the catalyst (X(_4)) (%)</td>
<td>6.39</td>
</tr>
</tbody>
</table>

C\(_2\) hydrocarbons yield as reported in the previous paper [26]. In fact, a higher reactor temperature leads to enhancement of methane conversion and C\(_2\) hydrocarbons yield but diminished the C\(_2\) hydrocarbons selectivity [26]. Unfortunately, high reactor temperature is not selective to C\(_2\) hydrocarbons. In the case of the high reactor temperature, methane may be largely converted into carbon monoxide rather than C\(_2\) hydrocarbons. Based on this observation, the catalyst plays an important role in promoting the product selectivity to C\(_2\) hydrocarbon and in inhibiting the reaction to CO and water. According to thermodynamics equilibrium calculations, the equilibrium constant increases with the reactor temperature for an endothermic reaction such as CO\(_2\) OCM. The larger equilibrium constant shifts the reaction to the right and increases the equilibrium conversion.

3.3.2. Simultaneous optimization of CH\(_4\) conversion and C\(_2\) selectivity

The simultaneous CH\(_4\) conversion and C\(_2\) selectivity optimization results are revealed in Table 6. In this table, the simultaneous optimal CH\(_4\) conversion and C\(_2\) hydrocarbons selectivity are achieved at values of 3.48% and 82.56%, respectively. The corresponding optimal process parameters and catalyst compositions are achieved at the CO\(_2\)/CH\(_4\) ratio and reactor temperature of 1.88 and 1084 K, respectively, and the wt.% CaO and wt.% MnO of 8.04% and 6.88%, respectively. The operating conditions results can also be shown in Fig. 9. In fact, the simultaneous optimal C\(_2\) selectivity is closed to that of the optimal single-response. In the single-response optimization, the C\(_2\) selectivity has a maximum performance at low reactor temperature, while a high CH\(_4\) conversion is achieved at high reactor temperature. However, the simultaneous optimization of CH\(_4\) conversion and C\(_2\) selectivity is significantly affected on lowering the optimal reactor temperature. It is implied that a lower reactor temperature leads to a higher C\(_2\) selectivity, while a higher reactor temperature leads to a high C\(_2\) yield.

3.3.3. Simultaneous optimization of CH\(_4\) conversion and C\(_2\) yield

Table 7 demonstrates the multi-responses optimization of simultaneous CH\(_4\) conversion and C\(_2\) yield including its corresponding optimal conditions. It is shown that the simultaneous optimal CH\(_4\) conversion and C\(_2\) yield responses are obtained at 9.07% and 3.91%, respectively. From Table 7 it is revealed that the simultaneous optimal CH\(_4\) conversion and C\(_2\) hydrocarbons yield are achieved at CO\(_2\)/CH\(_4\) ratio and reactor temperature of 2.01 and 1191 K, respectively, and the wt.% CaO and wt.% MnO of 16.09% and 7.67%, respectively. In fact, the simultaneous optimal CH\(_4\) conversion and C\(_2\) yield are attained at high reactor temperature (1191 K). It is suggested that both CH\(_4\) conversion and C\(_2\) yield are en-

Table 6
Simultaneous optimal multi-responses of CH\(_4\) conversion and C\(_2\) selectivity and its corresponding factors location

<table>
<thead>
<tr>
<th>Simultaneous optimal multi-responses</th>
<th>Corresponding weighting coefficient ((W_i))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4) conversion ((f_1(X)))</td>
<td>3.48</td>
</tr>
<tr>
<td>C2 selectivity ((f_2(X)))</td>
<td>82.56</td>
</tr>
</tbody>
</table>

Location of factors for simultaneous optimal multi-responses

<table>
<thead>
<tr>
<th>Factor/independent variable</th>
<th>Optimum value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)/CH(_4) ratio (X(_1))</td>
<td>1.88</td>
</tr>
<tr>
<td>Reactor temperature (X(_2)) (K)</td>
<td>1084</td>
</tr>
<tr>
<td>wt.% CaO in the catalyst (X(_3)) (%)</td>
<td>8.04</td>
</tr>
<tr>
<td>wt.% MnO in the catalyst (X(_4)) (%)</td>
<td>6.88</td>
</tr>
</tbody>
</table>
Table 7
Simultaneous optimal multi-responses of CH$_4$ conversion and C$_2$ yield and its corresponding factors location

<table>
<thead>
<tr>
<th>Responses optimal multi-responses</th>
<th>Corresponding weighting coefficient ($W_i$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$ conversion ($F_1(X)$)</td>
<td>$W_1 = 0.015$</td>
</tr>
<tr>
<td>C$_2$ yield ($F_2(X)$)</td>
<td>$W_2 = 0.985$</td>
</tr>
</tbody>
</table>

Location of factors for simultaneous optimal multi-responses

<table>
<thead>
<tr>
<th>Factor</th>
<th>Optimum value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$/CH$_4$ ratio ($X_1$)</td>
<td>2.01</td>
</tr>
<tr>
<td>Reactor temperature ($X_2$) (K)</td>
<td>1191</td>
</tr>
<tr>
<td>wt.% CaO in the catalyst ($X_3$) (%)</td>
<td>16.09</td>
</tr>
<tr>
<td>wt.% MnO in the catalyst ($X_4$) (%)</td>
<td>7.67</td>
</tr>
</tbody>
</table>

Table 8
Result validations of the final optimal point in the multi-responses optimization of C$_2$ selectivity and yield

<table>
<thead>
<tr>
<th>C$_2$ yield (%)</th>
<th>C$_2$ selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_{multi-responses}$</td>
<td>$F_{experimental}$</td>
</tr>
<tr>
<td>3.74</td>
<td>3.76</td>
</tr>
<tr>
<td>3.74</td>
<td>3.39</td>
</tr>
<tr>
<td>3.74</td>
<td>3.49</td>
</tr>
<tr>
<td>3.74</td>
<td>3.35</td>
</tr>
<tr>
<td>Average relative error</td>
<td></td>
</tr>
<tr>
<td>$F_{multi-responses}$</td>
<td>$F_{experimental}$</td>
</tr>
<tr>
<td>76.56</td>
<td>65.27</td>
</tr>
<tr>
<td>76.56</td>
<td>63.56</td>
</tr>
<tr>
<td>76.56</td>
<td>67.92</td>
</tr>
<tr>
<td>76.56</td>
<td>67.21</td>
</tr>
<tr>
<td>Average relative error</td>
<td></td>
</tr>
</tbody>
</table>

Note: Operating conditions: CO$_2$/CH$_4$ ratio, 1.99; reactor temperature, 1127 K; catalyst, 12.78 wt.% CaO-6.39 wt.% MnO/CeO$_2$.

* % Relative error = ($F_{experimental} - F_{multi-responses}$) / $F_{multi-responses}$ x 100%.

hanced at a high reactor temperature as described elsewhere [26].

3.4. Results validation and benefit of multi-responses optimization in CO$_2$ OCM process

In this optimization, there are three multi-responses optimization combinations where two responses are simultaneously applied for each combination, i.e. C$_2$ selectivity and yield, CH$_4$ conversion and C$_2$ selectivity, and CH$_4$ conversion and C$_2$ yield. In this case, the optimization of C$_2$ selectivity and yield is chosen for the recommendation in order to suggest the operating conditions and the catalyst compositions. The reason for this choice is that C$_2$ yield involves CH$_4$ conversion and C$_2$ selectivity as mentioned in the previous section. It is expected that the simultaneous optimization of C$_2$ selectivity and yield takes into account the high performance of CH$_4$ conversion, C$_2$ selectivity and C$_2$ yield simultaneously.

Moreover, the experimental validations of CO$_2$ OCM process with respect to the multi-responses optimization of C$_2$ selectivity and yield are revealed in Table 8. In this validation, the C$_2$ selectivity and yield at the final optimal point are compared with those from experimental data at the similar conditions. From the table, it is shown that the average relative error for C$_2$ selectivity and yield are 16.10% and 7.47%, respectively. However, it is shown that the performances of the experimental works are still lower than that from the multi-responses optimization.

Indeed, the empirical modeling using RSM combined with multi-responses optimization is useful for optimizing the CO$_2$ OCM process in certain ranges of independent variables before kinetic studies are implemented. The empirical modeling and the multi-responses optimization method is useful for designing a catalyst as well as exploring the interaction among the variables towards the process performances. The results of the hybrid multi-responses optimization can be used to recommend the operating conditions and catalyst compositions for further experimental works in CO$_2$ OCM process especially in the kinetic studies.

4. Conclusions

A new multi-responses optimization algorithm using Weighted Sum of Squared Objective Functions technique to obtain Pareto-optimal solutions was developed. A unique optimal point among the Pareto set was resulted by considering an additional optimal criterion. The algorithm successfully optimized CO$_2$/CH$_4$ ratio, reactor temperature, wt.% CaO and wt.% MnO in the catalyst in order to maximize two responses simultaneously, i.e. C$_2$ hydrocarbons selectivity and yield, CH$_4$ conversion and C$_2$ selectivity, as well as CH$_4$ conversion and C$_2$ yield. The hybrid numerical approach
combined single-response modeling using Response Surface Methodology with the WSSOF technique for solving multi-responses optimization. In this paper, the WSSOF technique was successfully implemented to solve the multi-responses optimization in CO2 OCM process.

The operating conditions and catalyst compositions from multiple optimizations of C2 selectivity and yield within the Pareto-optimal solutions were chosen as recommendation for the CO2 OCM process. This choice was based on the fact that the C2 yield was taken into account both CH4 conversion and C2 selectivity. The values of 76.56% and 3.74% for C2 hydrocarbons selectivity and yield, respectively, were achieved with respect to the optimal independent variables: CO2/CH4 ratio = 1.99, reactor temperature = 1127 K, wt.% CaO = 12.78% and wt.% MnO = 6.39%.

The optimal C2 selectivity and yield from the validation results closed to those from multi-responses optimization with small relative errors. The results of the multi-response optimization could be used to facilitate in recommending suitable operating conditions and catalyst compositions for the CO2 OCM process.

Acknowledgment

The authors would like to express their sincere gratitude to the Ministry of Science, Technology and Innovation (MOSTI), Malaysia, for the financial support received under the Project No. 02-02-06-0016 EA/099.

References


