MULTI-RESPONSE OPTIMIZATION STRATEGY FOR CATALYST COMPOSITIONS AND PROCESS PARAMETERS DESIGN FOR CO_2-OCM PROCESS OVER CaO-MnO/CeO_2 CATALYST

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ABSTRACT

The catalytic CO_2-OCM (Carbon Dioxide Oxidative Coupling of Methane) reaction to produce C_{2+} hydrocarbons is considered to be one of the most effective uses of natural gas in the gas-based petrochemical industries. A new hybrid numerical approach, using Weighted Sum of Squared Objective Functions (WSSOF) algorithm, was developed for multi-response optimization of CO_2-OCM. The hybrid approach combined the response surface methodology (RSM) and MATLAB optimization tools to produce a set of Pareto-optimal solutions. An additional criterion was proposed over the Pareto-optimal solutions to obtain a final unique solution. Maximum responses of any two combinations of C_{2+} selectivity, C_{2+} yield, and CH_4 conversion were obtained simultaneously at the corresponding optimal conditions of CO_2/CH_4 ratio, reactor temperature, as well as wt% CaO and wt% MnO in the CeO_2-supported catalyst.

Keywords: CO_2-OCM Process, Multi-Response Optimization, Response Surface Methodology, Weighted Sum of Squared Objective Functions.

1 INTRODUCTION

Recently, the conversion of methane into C_{2+} hydrocarbons (ethane and ethylene) using carbon dioxide as an oxidant has received considerable attention (Asami et al., 1995; Wang and Ohtsuka, 2000, 2001; Wang et al., 1999; Cai et al., 2003; Istadi and Amin, 2004a). The high CO_2/CH_4 ratio in Natuna's natural gas compositions, comprising of up to 71 % carbon dioxide and 28 % methane (Suhartanto et al., 2001), should be strategically utilized for the production of higher hydrocarbons, liquid fuels and other important chemicals. Equations (1) and (2) are the two main CO_2-OCM reaction schemes which produce C_{2+} hydrocarbons, while carbon monoxide and water are the by-products.

$$2CH_4 + CO_2 \Leftrightarrow C_2H_6 + CO + H_2O \quad \Delta H^{o}_{298} = +106 \text{ kJ/mol} \qquad (1)$$
$$2CH_4 + 2CO_2 \Leftrightarrow C_2H_4 + 2CO + 2H_2O \quad \Delta H^{o}_{298} = +284 \text{ kJ/mol} \qquad (2)$$

The relationship between catalyst compositions and catalytic performances is crucial for a successful commercially viable CO_2-OCM process. The optimal operating parameters, such as the CO_2/CH_4 ratio and reactor temperature, and the catalyst compositions in the CeO_2-supported catalyst, provide essential information for scaling-up the CO_2-OCM process. Unfortunately, only a few researchers have utilized the optimization tool for designing an optimal catalyst composition (Huang et al., 2003). However, individual response optimization is usually insufficient for the design of complex CO_2-OCM process. Simultaneous multi-response optimization is more realistic and may be one of the preceding steps before the CO_2-OCM process can be commercialized. Compared to simultaneous multi-response technique, the individual response optimization does not portrait real conditions of a chemical process.

The 15 wt% CaO-5 wt% MnO/CeO_2 catalyst was found as the most potential for CO_2-OCM from the screening of CeO_2-based binary and ternary metal oxides catalysts (Istadi and Amin, 2004a). Interestingly, the stability test showed that the 15 wt% CaO-5 wt% MnO/CeO_2 catalyst was stable with no obvious coking during 20 h of reaction time on stream. However, the process parameters and the catalyst compositions of the CO_2-OCM process were not optimized.

The main objective of this paper is to develop a hybrid numerical approach for the simultaneous multi-response optimization of CH_4 conversion, C_{2+} hydrocarbon selectivity and/or C_{2+} hydrocarbon yield for the CO_2-OCM process. A key feature of the hybrid numerical approach is the application of Weighted Sum of Squared Objective Functions (WSSOF) algorithm to the simultaneous maximization of two responses, i.e. CH_4 conversion and C_{2+} selectivity, CH_4 conversion and C_{2+} yield, or C_{2+} selectivity and C_{2+} yield, as the following task after the development of empirical single-response models.

2 EXPERIMENTAL AND NUMERICAL METHOD

2.1 TECHNIQUE FOR INDIVIDUAL-RESPONSE MODELING

A Central Composite Rotatable Design (CCRD) for four factors was employed for experimental design (Montgomery, 2001; Cornell, 1990) using regression analysis software (STATISTICA version 6 software). Four independent variables, namely CO_2/CH_4 ratio (X_1), reactor temperature (X_2), wt% CaO (X_3) and wt% MnO (X_4) in the CeO_2-supported catalyst, were selected as the controlled factors. The design consists of a two-level full factorial design (2^4=16), eight star points and two center points. The sequence of experiment was randomized in order to minimize the effects of uncontrolled factors. The detailed description of the single-response optimization was described elsewhere (Istadi and Amin, 2004b). A quadratic polynomial equation was developed to predict the responses as a function of independent variables involving their interactions.

2.2 TECHNIQUE FOR MULTI-RESPONSE OPTIMIZATION

The optimization techniques are developed to find a set of optimal independent variables, $\mathbf{X}=\{X_1,X_2,\ldots,X_N\}$, that maximizes or minimizes a vector of objectives, $\mathbf{F(X)} = \{F_1(\mathbf{X}), F_2(\mathbf{X}),\ldots, F_M(\mathbf{X})\}$, where N is the number of independent variables and M is the number of objectives. The detail algorithm using the WSSOF technique is revealed in Table 1.

TABLE 1. Hybrid algorithm of multi-response optimization using WSSOF technique

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Step 1
Obtain individual response models ($F_1(\mathbf{X})$ and $F_2(\mathbf{X})$) using RSM.
Step 2
Formulate a multi-response optimization problem from the individual response models
Step 3
Convert the multi-response optimization ($\mathbf{F(X)}$ into a single-response optimization ($f(\mathbf{X})$)
problem by introducing weighting factors, $W_i$, using Equation (3).
Step 4
Solve the single response problem using unconstrained optimization technique.
Use the Nelder-Mead Simplex technique for the multi-variable unconstrained optimization using
MATLAB optimization toolbox.
Find the $\mathbf{X}$ and $\mathbf{F(X)}$ values corresponding to the various $W_i$, in which $\Sigma W_i=1$, and $W_i \geq 0$.
    Step 4a
    Put a starting point $\mathbf{X}_0$. Set initial $W_i=[0\ 1]^T$.
    Step 4b
    Calculate right hand side of Equation (3) and set as a function file.
    Step 4c
    Solve a single-response unconstrained optimization problem according to Step 3
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Step 4d

Calculate $F_1(\mathbf{X})$ and $F_2(\mathbf{X})$ based on **X** at each W_i combination.

Calculate sum of both functions. Save the values of **X**, W_i, $\mathbf{F(X)}$ and sum of $\mathbf{F(X)}$

Step 4e

Is $W_i \leq 1$? If yes, update W_i values as the initial guess and go to **Step 4a**. If no, terminate.

Step 5

Choose maximum of $\sum \mathbf{F(X)}$. Find the corresponding **X** values by interpolation technique.

The common task in multi-response optimization is to create a non-inferior solution or Pareto-optimal solution to a set of problems and then select among its members a solution that satisfies the objectives (Zhang et al., 2002). Particularly, the multi-response optimization can be formulated by converting the problem into a scalar single-response optimization problem, $f(\mathbf{X})$, as expressed in Equation (3) (Nandi et al., 2004; MathWorks, 2001; Edgar et al., 2001; Warsito and Fan, 2003) which takes into account the simultaneous two responses.

$$\begin{aligned} &\underset{\mathbf{X} \in \Omega}{\text{maximize}} \quad f(\mathbf{X}) = \sum_{i=1}^{2} W_i \,.\, F_i(\mathbf{X})^2 \\ &\text{subject to}: \ \sum_{i=1}^{2} W_i = 1 \text{ and } 0 \leq W_i \leq 1 \end{aligned} \tag{3}$$

In Equation 3, W_1 and W_2 denote the weighting factors with respect to the objective functions, $F_1(\mathbf{X})$ and $F_2(\mathbf{X})$ 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, is assigned to the objective functions, $\mathbf{F(X)}$. The underlying problem is that there are many combinations of W_1 and W_2 values to convince the non-inferior solution point which are not the final solution of the problem. The final optimal criterion requires an additional knowledge that depends on the system. In this paper, the sum of the objective functions, $\sum \mathbf{F(X)}$, is proposed as the final optimal criterion.

3 RESULTS AND DISCUSSION

3.1 INDIVIDUAL-RESPONSE MODEL OF CO_2-OCM PROCESS

The individual response models for the CH_4 conversion, C_{2+} hydrocarbon selectivity and yield were developed using RSM as a function of the process parameters and the catalyst compositions as described in Equations (4)-(6), respectively (Istadi and Amin, 2004b). The individual response optimization deals with determining the optimal CO_2/CH_4 ratio, reactor temperature, wt% CaO and wt% MnO in the CaO-MnO/CeO_2 catalyst to achieve the maximum CH_4 conversion, C_{2+} selectivity and C_{2+} yield as described elsewhere (Istadi and Amin, 2004b). The subsequent task of the optimization is focused on finding the simultaneous maximum values of two responses.

$$\begin{aligned} F_{CH_4\,\text{Conversion}}(\mathbf{X}) = {} & 129.1997 - 1.1842\,X_1 - 0.3204\,X_2 - 1.5961\,X_3 + 1.0048\,X_4 \\ & - 1.8843\,X_1^2 + 0.0002\,X_2^2 - 0.0024\,X_3^2 + 0.0232\,X_4^2 + 0.0107\,X_1X_2 \\ & + 0.0995\,X_1X_3 - 0.2087\,X_1X_4 + 0.0019\,X_2X_3 - 0.0008\,X_2X_4 - 0.0204\,X_3X_4 \end{aligned} \tag{4}$$

$$\begin{aligned} F_{C_{2+}\,\text{Selectivity}}(\mathbf{X}) = {} & -1963.6145 + 142.4914\,X_1 + 4.7758\,X_2 - 12.6837\,X_3 + 10.249\,X_4 \\ & - 15.6574\,X_1^2 - 0.0029\,X_2^2 - 0.1304\,X_3^2 - 0.5532\,X_4^2 - 0.1286\,X_1X_2 \\ & + 1.5858\,X_1X_3 + 1.172\,X_1X_4 + 0.0144\,X_2X_3 - 0.0063\,X_2X_4 + 0.0202\,X_3X_4 \end{aligned} \tag{5}$$

$$\begin{aligned} F_{C_{2+}\,\text{Yield}}(\mathbf{X}) = {} & -85.0825 + 11.4363\,X_1 + 0.1874\,X_2 - 0.4972\,X_3 - 0.9347\,X_4 \\ & - 2.178\,X_1^2 - 0.0001\,X_2^2 - 0.0088\,X_3^2 - 0.0277\,X_4^2 - 0.0045\,X_1X_2 \\ & + 0.0534\,X_1X_3 + 0.0695\,X_1X_4 + 0.0007\,X_2X_3 + 0.0014\,X_2X_4 - 0.0022\,X_3X_4 \end{aligned} \tag{6}$$

3.2. MULTI-RESPONSE OPTIMIZATION OF CO_2-OCM PROCESS

3.2.1. Simultaneous Optimization of C_{2+} Selectivity and Yield, CH_4 Conversion and C_{2+} Selectivity, and CH_4 Conversion and C_{2+} Yield

The simultaneous multi-response optimization of C_{2+} hydrocarbons selectivity and yield are revealed in Table 2. It is shown that the simultaneous optimal multi-responses are achieved at values of 76.17 % and 3.66 % for C_{2+} hydrocarbons selectivity and yield, respectively. In fact, the results are lower than those obtained from the individual response optimization (Istadi and Amin, 2004b). The corresponding optimal process parameters and catalyst composition are achieved at the CO_2/CH_4 ratio and reactor temperature of 1.99 and 856 °C, respectively and the wt% CaO and wt% MnO of 12.74 % and 6.37 %, respectively. 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 individual-response, while the wt% MnO has the lowest effect.

The interaction between reactor temperature and wt% CaO has also significantly affected the responses (Istadi and Amin, 2004b). Pertaining to the relationship between reactor temperature and wt% CaO, the results also indicate that high C_{2+} selectivity is achieved at lower reactor temperature and wt% CaO in the catalyst, while high C_{2+} yield is achieved at higher reactor temperature and wt% CaO in the catalyst. The considerable C_{2+} hydrocarbons yield at high reactor temperature is related to a high methane conversion. Increasing CaO content in the catalyst enhances the CO_2 adsorption on the catalyst surface due to increasing catalyst basicity and improved the methane conversion, C_{2+} hydrocarbons selectivity and C_{2+} yield. In fact, higher reactor temperature is not selective to C_{2+} hydrocarbons means that methane may be largely converted into carbon monoxide rather than C_{2+} hydrocarbons. The catalyst plays an important role in promoting the product selectivity to C_{2+} hydrocarbon and in inhibiting the reaction to CO and water.

TABLE 2. Multi-responses optimization result of C_{2+} selectivity and yield

Simultaneous multi-responses		Corresponding
Response	Maximum value	Weighting Coefficient (W_i)
C_{2+} Selectivity ($F_1(\mathbf{X})$)	76.17 %	$W_1 = 0.0016$
C_{2+}Yield ($F_2(\mathbf{X})$)	3.66 %	$W_2 = 0.9984$

Factors location for simultaneous optimal multi-responses	
Factor	Optimum Value
CO_2/CH_4 ratio (X_1)	1.99
Reactor Temperature (X_2)	856 °C
wt% CaO in the catalyst (X_3)	12.74 %
wt% MnO in the catalyst (X_4)	6.37 %

TABLE 3. Multi-responses optimization result of CH_4 conversion and C_{2+} selectivity

Simultaneous multi-responses		Corresponding
Responses	Maximum value	Weighting Coefficient (W_i)
CH_4 conversion ($F_1(\mathbf{X})$)	3.58 %	$W_1 = 0.98$
C_{2+} Selectivity ($F_2(\mathbf{X})$)	82.41 %	$W_2 = 0.02$

Factors location for simultaneous optimal multi-responses	
Factor	Optimum Value
CO_2/CH_4 ratio (X_1)	1.86
Reactor Temperature (X_2)	816 °C
wt% CaO in the catalyst (X_3)	8.07 %
wt% MnO in the catalyst (X_4)	6.96 %

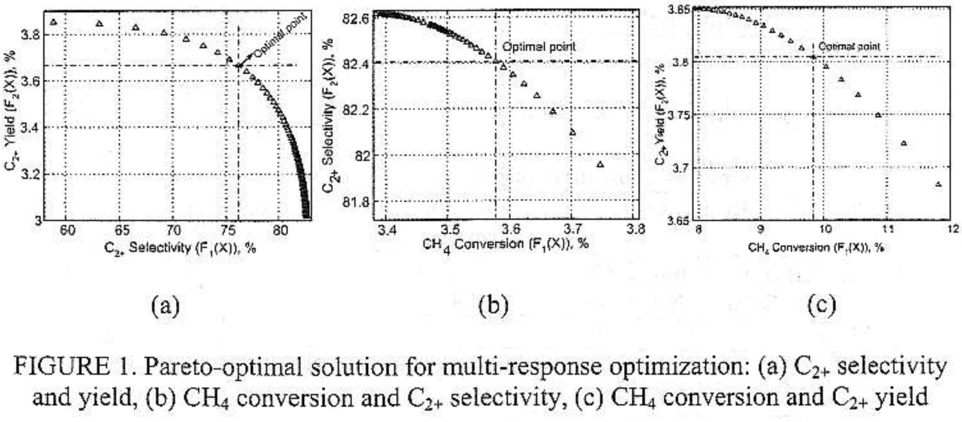
TABLE 4. Multi-responses optimization result of CH_4 conversion and C_{2+} yield

Simultaneous multi-responses		Corresponding
Responses	Maximum value	Weighting Coefficient (W_i)
CH_4 conversion ($F_1(\mathbf{X})$)	9.83 %	$W_1 = 0.017$
C_{2+} yield ($F_2(\mathbf{X})$)	3.80 %	$W_2 = 0.983$
Factors location for simultaneous optimal multi-responses		
Factor		Optimum Value
CO_2/CH_4 ratio (X_1)		2.01
Reactor Temperature (X_2)		927 °C
wt% CaO in the catalyst (X_3)		16.67 %
wt% MnO in the catalyst (X_4)		7.65 %

Table 3 reveals the simultaneous CH_4 conversion and C_{2+} hydrocarbons selectivity optimization together with the corresponding optimal independent variables. In this table, the simultaneous optimal CH_4 conversion and C_{2+} hydrocarbons selectivity are achieved at values of 3.58 % and 82.41 %, respectively at the corresponding CO_2/CH_4 ratio and reactor temperature of 1.86 and 816 °C, respectively and the wt% CaO and wt% MnO of 8.07 % and 6.96 %, respectively. In fact in the individual response optimization, the C_{2+} selectivity has a maximum performance at low reactor temperature, while high CH_4 conversion is achieved at high reactor temperature. However, the simultaneous optimization of both responses is significantly affected on lowering the optimal reactor temperature. The simultaneous optimal CH_4 conversion and C_{2+} hydrocarbons yield responses are obtained at 9.83 % and 3.80 %, respectively as revealed in Table 4 at corresponding CO_2/CH_4 ratio and reactor temperature of 2.01 and 927 °C, respectively and the wt% CaO and wt% MnO of 16.67 % and 7.65 %, respectively. Indeed, both CH_4 conversion and C_{2+} hydrocarbons yield are enhanced at a high reactor temperature, but C_{2+} hydrocarbons selectivity is improved at a low reactor temperature.

3.3. GENERATION OF PARETO-OPTIMAL SOLUTIONS

The present optimization problem involves two objective functions which are influenced in the opposite direction by changing the decision variables. The WSSOF technique allows a simpler algorithm, but unfortunately, the solution obtained depends largely on the values assigned to the weighting factors chosen. 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, well-known as Pareto-optimal solutions (Zhang et al., 2002; Silva and Biscaia, 2003). The Pareto-optimal solutions have the characteristic of moving from one point to another on the set results that improves one objective function, but worsens another.



(a) (b) (c)

FIGURE 1. Pareto-optimal solution for multi-response optimization: (a) C_{2+} selectivity and yield, (b) CH_4 conversion and C_{2+} selectivity, (c) CH_4 conversion and C_{2+} yield

Figures 1(a)-(c) depict the Pareto-optimal solution of the CO_2-OCM process optimization over CaO-MnO/CeO_2 catalyst corresponding to the simultaneous optimization of C_{2+} hydrocarbons selectivity and yield, CH_4 conversion and C_{2+} hydrocarbons selectivity, and CH_4 conversion and C_{2+} hydrocarbons yield, respectively. It can be seen from the figures that if the value of $F_1(X)$ is increased, the value of $F_2(X)$ are worsened. Thus, it cannot be deduced that any of these non-dominated solutions in the Pareto set is an acceptable solution. The final unique optimum is chosen at the maximum sum of objective functions corresponds to the highest C_{2+} selectivity and yield, CH_4 conversion and C_{2+} selectivity, or CH_4 conversion and C_{2+} yield simultaneously. The Pareto set is useful, however, since it narrows the choices and facilitates to guide the decision maker in selecting the preferred solution among the set of Pareto-optimal points.

4 CONCLUSION

A new multi-response optimization algorithm using weighted sum of squared objective functions technique (WSSOF) to obtain Pareto-optimal solutions was developed. A unique optimal among the Pareto set of solutions was produced by considering an additional optimal criterion. The algorithm was utilized to optimize four independent variables of the CO_2-OCM process which comprise of CO_2/CH_4 ratio, reactor temperature, wt% CaO and wt% MnO in the catalyst in order to maximize two simultaneous responses, 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 individual-response modeling using RSM with MATLAB Optimization toolbox. Based on the Pareto-optimal solutions developed, the optimal conditions, catalyst compositions and process parameters, for the maximum simultaneous responses were obtained. The results of the multi-response optimization could facilitate in recommending the suitable operating conditions and catalyst compositions for the CO_2-OCM process.

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