Jurnal Teknologi, 39(F) Dis. 2003: 35–52
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OPTIMIZATION OF OXIDATIVE COUPLING OF METHANE USING RESPONSE SURFACE METHODOLOGY

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Abstract. Oxidative Coupling of Methane (OCM) reaction over Li/MgO catalyst was optimized using experimental design from 'Statsoft Statistica' version 6.0 software. The manipulated variables chosen in this study were operating temperature, total flow rate per weight of catalyst (F/W), and weight percent of Li doped into MgO catalyst, whilst methane conversion, C_2 product selectivity, and C_2 product yield were the responses. The equation model was tested with Anova analysis with 99% degree confidence. The Response Surface Methodology (RSM) was employed to determine the optimum responses. By means of variance analysis and additional experiments, the adequacy of this model was confirmed.

Keywords: OCM, optimization, experimental design, response surface methodology

Abstrak. Tindak balas penggandingan beroksida metana (OCM) terhadap mangkin Li/MgO dioptimumkan menggunakan reka bentuk eksperimen daripada perisian 'Statsoft Statistica' versi 6.0. Pemboleh ubah yang dipilih dalam kajian ialah suhu operasi, total kadar aliran suapan per berat mangkin (F/W), dan peratus berat Li yang dimasukkan ke dalam mangkin MgO, manakala penukaran metana, kememilihan C_2, dan keberhasilan C_2 merupakan sambutannya. Model persamaan diuji menggunakan analisis Anova dengan 99% darjah keyakinan. Metodologi sambutan permukaan (RSM) digunakan bagi menentukan sambutan optimum. Dengan menggunakan analisis varians dan eksperimen tambahan, kejituan model dapat disahkan.

Kata kunci: OCM, pengoptimuman, reka bentuk eksperimen, metodologi sambutan permukaan

1.0 INTRODUCTION

Following the oil crisis in the 1970s, concerted effort was focused on synthetic fuel production [1]. The development of a simple and commercially advantageous process for direct conversion of natural gas to more easily transportable products was desired. Keller and Bhassin [2] suggested that catalytic reaction for the direct conversion of natural gas to ethane and ethylene offered a new route for ethylene production. Moreover, the expansive reforming step used in the conventional natural gas conversion processes is eliminated in the direct conversion, and thus, increases the energy efficiency of the process [3]. The research impetus has then been directed at the utilization of

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natural gas which seems to be the best alternative to replace petroleum for higher oxygenates production [1,4,5].

The research activities on oxidative coupling of methane (OCM) have mainly focused on the formation of higher hydrocarbons, particularly ethane and ethylene, abbreviated as C_2 products [6]. Numerous types of catalyst have been tested for OCM and Li/MgO catalyst has been given considerable attention in the past few years. For example, Ito and co-workers [7] reported that methane conversion of 38% and C_2 selectivity of 50% were achieved over Li/MgO catalyst. In another study, using similar catalyst, Choudhary *et al.,* [8] obtained methane conversion and C_2 selectivity of 29% and 66%, respectively. Unfortunately, due to low product yield, commercialization is still not feasible. Therefore, numerous studies are directed at obtaining higher methane conversion and C_2 selectivity that could eventually lead to the OCM process being commercialized. One possible way to improve the results is via process optimization.

The Response Surface Methodology (RSM), introduced by Box and Wilson [9], is an effective and successful technique used to obtain the optimum value and the most influencing variable among a few set of variables that affects the value of any responses [10]. With this method, it is more convenient to study the relation between variables compared to the traditional method employed by earlier researchers. Traditional optimization methods, which are single dimensional search, are usually cumbersome. The methods involve extended experimental periods and interactions among variables especially if several variables are involved [11]. Optimization experiments via central composite design are suitable to account for the interactions. A combination of factors generating a certain optimum response could be identified through central composite design and RSM. RSM, an experimental strategy for seeking the optimum conditions for a multivariable system, is a more efficient technique for optimization. The experimental design utilizes RSM which is a collection of statistical technique for designing experiments, building models, and determining optimum conditions for the desired response [12].

The objective of this paper is to optimize the processing parameters (independent variables) such as operating temperature, total flow rate per weight of catalyst (F/W), and weight percent of lithium doped into the MgO catalysts. Product quality analysis (response) involving methane conversion, C_2 selectivity, and C_2 yield were analyzed for the OCM process. The parameters are chosen based on the most influential variables affecting the responses [13]. The results from this study will provide information on the optimum conditions for high C_2^+ yield.

2.0 METHODOLOGY

2.1 Preparation of Catalysts

The experimental study involved set of different weight percent of Li doped into Li/MgO catalysts. The weight percent of Li doped into the MgO catalysts were 0.02,

0.05, 0.1, 0.15 and 0.23. The preparation method for the Li promoted MgO catalysts was based on previous literature [13]. Powdered magnesium carbonate (GCE Laboratory Chemicals (MgO 40-43.5%)) was impregnated with the lithium carbonate (BDH Laboratory Supplies (99%)) solution at the desired weight percent of Li doped and dried at 120°C for six hours. The dried sample was calcined at 750°C for another six hours in static air prior to crushing to 75 mesh particles (100 microns).

2.2 Catalytic Testing and Experimental Set-up

The OCM reaction over the catalyst was carried out in a continuous flow quartz reactor (ID = 9 mm). Figure 1 shows the set-up of the experimental rig. The catalysts were pretreated *in situ* in a flow of nitrogen at the catalyst calcination temperature for an hour. The gas feed was a mixture of pure methane and oxygen. In this research, we have opted to use pure oxygen instead of air in the feed to ensure that the oxygen concentration was maintained high in achieving the maximum product yield. The reaction was performed at the following conditions: amount of catalyst, 0.1 g; F/W at

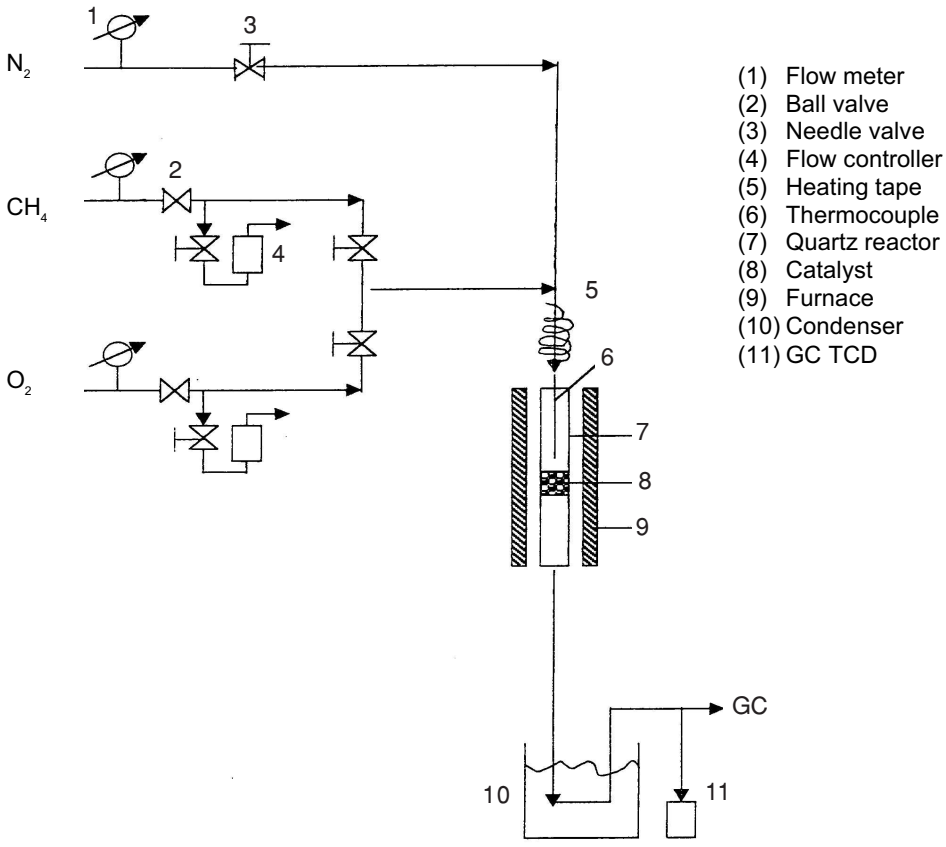

Figure 1 Experimental rig set-up

STP: 2520-14620 $cm^3g^{-1}h^{-1}$; CH_4/O_2 ratio in feed = 8.0, and reaction temperature: 593 – 857°C. The reaction conditions were based on the previous literatures [13, 14]. The effluent gases from the reactor were analyzed by an on-line Hewlett Packard Agilent 2000 gas chromatograph using Porapak-N columns.

2.3 Experimental Design

Table 1 tabulates the low, middle, and high levels for all the independent variables: temperature, X_1; F/W, X_2; and weight percent of Li doped, X_3 were all based on the literature review [13]. Accordingly, 650, 725, and 800°C were chosen for variable X_1; 5140, 8570, 12000 $cm^3g^{-1}h^{-1}$ for X_2 and 0.05, 0.1 and 0.15 wt % for X_3. The allowances for extreme measures were designated as $-\alpha$ and $+\alpha$ in the central composite design.

Table 1 Levels of variables chosen for trials

	$-\alpha$	−1	0	+1	$+\alpha$
Temperature, X_1 (°C)	592.7	650.0	725.0	800.0	857.3
F/W, X_2 ($cm^3g^{-1}h^{-1}$)	2520.0	5140.0	8570.0	12000.0	14620.0
% Li Loaded, X_3	0.02	0.05	0.10	0.15	0.23

The optimization method using RSM comprised three major steps, namely design of experiment using statistical approach, coefficient estimation based on mathematical model and response prediction, and finally model adequacy check. The equation model was tested with ANOVA analysis with 99% degree of confidence.

The RSM output such as contour and 3-D graphic surface plots provide the optimum and most influential variable for methane conversion, C_2 selectivity and C_2 yield. According to the central composite design, the total number of experiment combinations is $2^k + 2k + n_o$, where k is the number of independent variables and n_o is the number of experiments repeated at the center point. In this case, $n_o = 2$.

The variables X_i were coded as x_i according to Equation (1). The basis to form a polynomial equation is given in Equation (2).

$$x_i = (X_i - X_o)/\Delta X; \quad i = 1,2,3\ldots k \qquad \ldots (1)$$

$$Y_u = \beta_o + \sum_{i=1}^{k} \beta_i X_{ui} + \sum_{i=1}^{k} \beta_{ii} X^2{}_{ui} + \sum \sum_{i<j}^{k} \beta_{ij} X_{ui} X_{uj} \qquad \ldots (2)$$

where

Y_u = predicted response u
β_o = offset term
β_i = linear term
β_{ii} = squared term

β_{ij} = interaction term
x_i = dimensionless value of an independent variable
X_i = real value of an independent variable
X_o = real value of an independent variable at center point
X = step change, and
u = 1, 2...n.

In this work, there were three independent variables and after substituting $k = 3$, Equation (2) was expressed as Equation (3).

$$Y_u = \beta_o + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 \quad \ldots (3)$$

The actual experimental design for optimization is shown in Table 2. From Equation (3), a total of 16 runs were needed to optimize the methane conversion, C_2 selectivity and C_2 yield. The result for the design was obtained using the Design Expert Statsoft software "Statistica" version 6.0, 2001.

Table 2 Independent variables used in process optimization

Trial no.	Independent Variables		
	Temperature	F/W	% Li doped
1	650.0	5140.0	0.05
2	650.0	5140.0	0.15
3	650.0	12000.0	0.05
4	650.0	12000.0	0.15
5	800.0	5140.0	0.05
6	800.0	5140.0	0.15
7	800.0	12000.0	0.05
8	800.0	12000.0	0.15
9	725.0	8570.0	0.10
10	592.7	8570.0	0.10
11	857.3	8570.0	0.10
12	725.0	2520.0	0.10
13	725.0	14620.0	0.10
14	725.0	8570.0	0.03
15	725.0	8570.0	0.23
16	725.0	8570.0	0.10

3.0 RESULTS AND DISCUSSION

3.1 Optimization

The RSM results indicated that the conversion of methane, C_2 selectivity and C_2 yield depend on the operating temperature, F/W, and weight percent of Li doped into the

MgO catalysts. For each experiment, the conversion of methane, selectivity of C_2,and yield of C_2 products were calculated using Equation (4) to (6).

$$\text{Conversion of methane} = \frac{\text{Mole methan input} - \text{Mole methane output}}{\text{Mole methane input}} \times 100\% \quad \ldots (4)$$

$$\text{Selectivity of } C_2 \text{ product} = \frac{\text{Mole of carbon in } C_2 \text{ produced}}{\text{Mole of carbon in methane reacted}} \times 100\% \quad \ldots (5)$$

$$\text{Yeild of } C_2 \text{ product} = \text{conversion} \times \text{selectivity} \quad \ldots (6)$$

The three independent variables were combined using the RSM design to optimize the response within the region of the 3-D observation space. The optimization approach allows one to design a minimal number of experimental runs. The model also evaluated the effect of each independent variable to a response, singly, and in combination with other variables, which is not otherwise feasible. The experimental values and the predicted responses for the 16 trial runs are presented in Table 3.

Table 3 Experimental and predicted values for methane conversion, C_2 selectivity, and C_2 yield

Trial no.	% Methane Conversion		% C_2 Selectivity		% C_2 Yield	
	Experimental	Predicted	Experimental	Predicted	Experimental	Predicted
1	25.9	26.4	51.9	56.4	13.4	14.9
2	27.6	29.7	50.2	49.2	13.9	14.6
3	18.3	23.6	47.1	49.6	8.6	11.7
4	21.8	24.2	39.7	41.6	8.7	10.1
5	28.6	29.7	67.7	63.2	19.4	18.8
6	38.9	37.1	66.5	65.1	25.9	24.2
7	32.3	33.8	40.6	54.7	13.1	18.5
8	35.5	38.5	47.1	55.8	16.7	21.5
9	41.7	41.5	77.4	76.5	32.3	31.7
10	26.9	22.8	49.3	35.0	13.3	8.0
11	39.0	38.4	56.6	53.5	22.1	20.5
12	30.3	31.0	58.2	65.9	17.6	20.4
13	35.0	30.0	50.2	51.7	17.6	15.5
14	28.4	25.4	70.4	60.6	20.0	15.4
15	34.0	32.4	62.4	55.2	21.2	17.9
16	41.4	41.5	77.2	76.5	32.0	31.7

In the present investigation, it was observed that the responses changed significantly when the independent variables were varied. From the experimental data, the highest methane conversion of 41.7% and highest C_2 selectivity of 77.4% were achieved at run number 9. Consequently, the maximum yield of C_2 was 32.3 %.

Using multiple regression analysis of the experimental data, the following second order polynomial equations provided the empirical model for the three dependent variables [Equations (7) to (9)]:

$$Y_1 = -310 + 0.872X_1 + 6.24 \times 10^{-4}X_2 + 198X_3 - 6.19 \times 10^{-4}X_1^2 - 3.06 \times 10^{-7}X_2^2 - 1.61 \times 10^{3}X_3^2 + 6.69 \times 10^{-6}X_1X_2 + 0.272X_1X_3 - 3.87 \times 10^{-3}X_2X_3 \ldots (7)$$

$$Y_2 = -915 + 2.46X_1 - 2.19 \times 10^{-2}X_2 - 5.14X_3 - 1.61 \times 10^{-3}X_1^2 - 7.35 \times 10^{-7}X_2^2 - 1.89 \times 10^{3}X_3^2 - 1.52 \times 10^{-5}X_1X_2 + 0.476X_1X_3 + 1.53 \times 10^{-3}X_2X_3 \ldots (8)$$

$$Y_3 = -540 + 1.41X_1 - 9.40 \text{ x } 10^{-2}X_2 - 155X_3 - 9.47 \times 10^{-4}X_1^2 - 4.54 \times 10^{-7}X_2^2 - 1.75 \times 10^{3}X_3^2 - 2.61 \times 10^{-6}X_1X_2 + 0.322X_1X_3 + 2.40 \times 10^{-3}X_2X_3 \ldots (9)$$

where Y_1 is the predicted methane conversion, Y_2 is the predicted C_2 selectivity, and Y_3 is the predicted C_2 yield. The analysis of variance (ANOVA) for three responses displaying the total, regression, and error of sum of square are shown in Tables 4 to 6.

The F value in Tables 4 to 6 is a ratio of the mean square due to error. The value of F is compared to the table value $F_{(p-1, N-p, \alpha)}$ or $(F_{0.01})$. If the value of F is smaller than $F_{(0.01)}$, then the null hypothesis is accepted at the a level of significance. If the null hypothesis is true, it means that the model is a good predictor of the experimental data. From the ANOVA table, the value of F for methane conversion, C_2 selectivity and C_2 yield are 3.598, 3.668 and 4.033, respectively. These F values are smaller compared to the tabulated value $F_{(0.01)}$, = 7.980 suggesting that the null hypothesis is true.

Table 4 ANOVA for methane conversion (quadratic response surface model fitting)

Source	Sum of squares	Degree of freedom	Mean Square	F_{Value}	$F_{0.01}$	R_2
S.S. Regression	599.433	9	66.604	3.598	7.980	0.844
S.S. Error	111.079	6	18.513			
S.S. Total	710.513	15				

Table 5 ANOVA for C_2 selectivity (quadratic response surface model fitting)

Source	Sum of squares	Degree of freedom	Mean Square	F_{Value}	$F_{0.01}$	R_2
S.S. Regression	1854.60	9	206.066	3.668	7.980	0.846
S.S. Error	337.113	6	56.186			
S.S. Total	2191.71	15				

Table 6 ANOVA for C_2 yield (quadratic response surface model fitting)

Source	Sum of squares	Degree of freedom	Mean Square	F_{Value}	$F_{0.01}$	R_2
S.S. Regression	644.9389	9	71.660	4.033	7.980	0.858
S.S. Error	106.6015	6	17.767			
S.S. Total	751.5404	15				

The coefficient of determination R-squared (R^2) (Tables 4 to 6) for methane conversion, C_2 selectivity, and C_2 yield are 0.844, 0.846, and 0.858, respectively. The value of R^2 is a measure of total variation of observed values about the mean described by the fitted model. The value is always between zero and unity. When $R^2 = 1$, it indicates that the statistical model considers the variability in the data. In contrast, when $R^2 = 0$, the result indicate that none of the variability in the response can be described by the experimental factor. Hence, the R^2 values in this study signify a good agreement between the experimental and predicted values.

The fitted model in Equation (7) to (9) can be used to map empirically the response function over the experimental region. The contour plot helps in assessing the effect of any two independent variables combined on the response. Each contour curve represents an infinite number of responses of two test variables. The maximum predicted response is indicated by the surface confined in the smallest ellipse in the contour diagram. The 3-D graphical surface plots illustrate the responses of the dependent variables. The main goal of response surface is to efficiently hunt for the optimum values of the variables such that the response is maximized [15].

It is evident from the plots that CH_4 conversion reached its maximum at a combination of coded level 690-860°C and 5000-13000 $cm^3g^{-1}h^{-1}$. The model predicted a maximum CH_4 conversion of 38% in this range (Figure 2). Similar operating parameters between 670-820°C and 3500 – 11000 $cm^3g^{-1}h^{-1}$ produced C_2 selectivity above 67% (Figure 5) and at operating parameters between 680-810°C and 5000 – 10000 $cm^3g^{-1}h^{-1}$ produced maximum C_2 yield above 25 % (Figure 8). These observations are consistent with the work by Hutchings [1] who reported that temperature in excess of 600°C were required in order to observe selective methane activation, whereas at lower temperature CO_x was observed as the only carbon containing products.

Figure 3 exhibits the relationship between weight percent of Li doped and temperature. Methane conversion above 38.5% could be obtained when temperature is in the range of 690-850°C and weight percent of Li doped is in the range of 0.065-0.17. The same factors led to C_2 selectivity above 68% at 670-810°C and 0.03-0.16% (Figure 6) while at operating parameters between 690-800°C and weight percent of Li doped between 0.06 and 0.14% produced optimum C_2 yield above 28% (Figure 9).

The interaction of weight percent of Li doped and F/W could be observed in Figures 4, 7, and 10. The F/W and weight percent Li doped should be in the range of 3000-

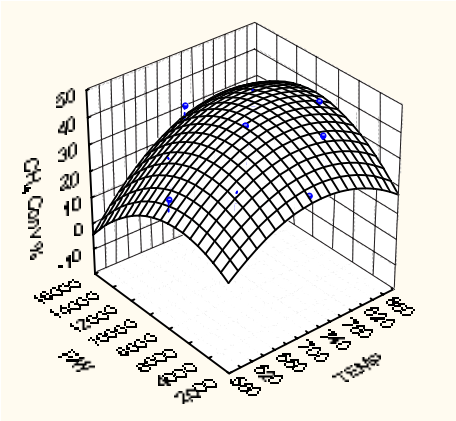

Figure 2 3-D graphic surface optimization of methane conversion versus F/W and temperature

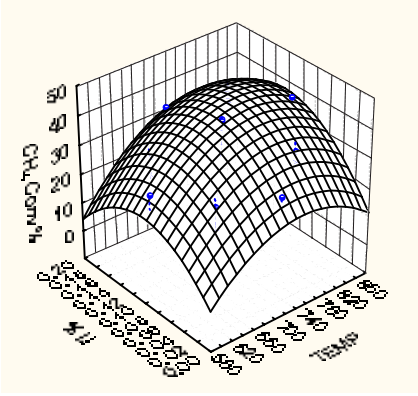

Figure 3 3-D graphic surface optimization of methane conversion versus wt % Li and temperature

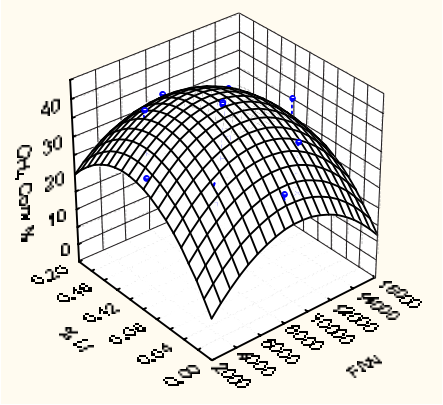

Figure 4 3-D graphic surface optimization of methane conversion versus wt % Li and F/W

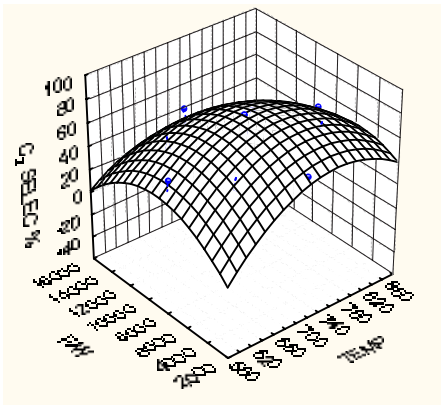

Figure 5 3-D graphic surface optimization of C_2 selectivity versus F/W and temperature

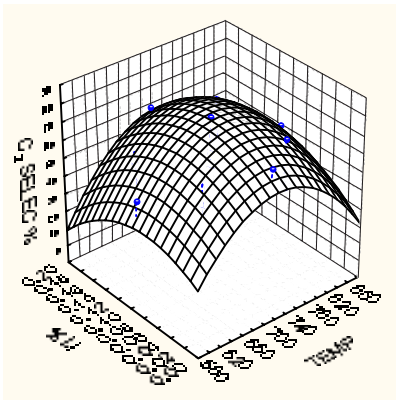

Figure 6 3-D graphic surface optimization of C_2 selectivity versus wt % Li and temperature

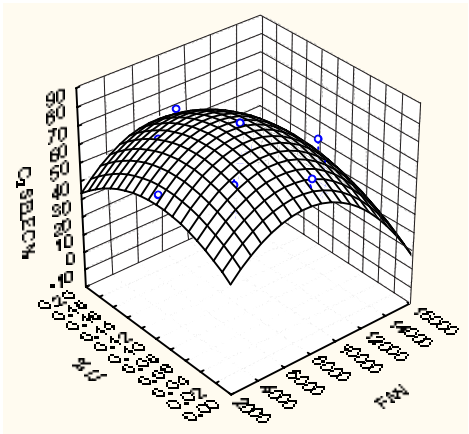

Figure 7 3-D graphic surface optimization of C_2 selectivity versus wt % Li and F/W

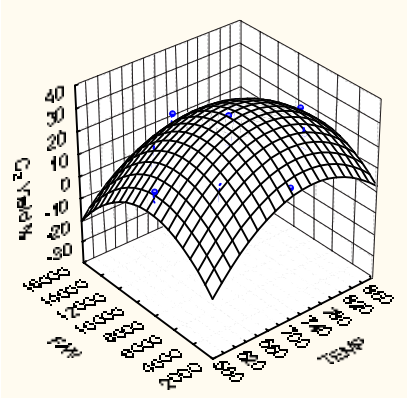

Figure 8 3-D graphic surface optimization of C_2 yield versus F/W and temperature

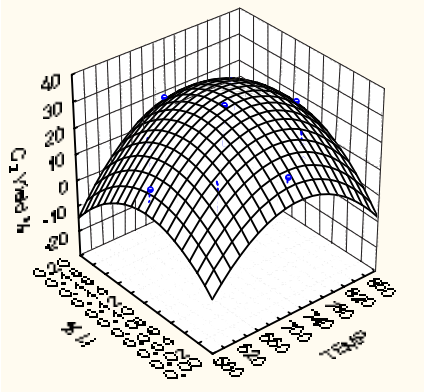

Figure 9 3-D graphic surface optimization of C_2 yield versus wt % Li and temperature

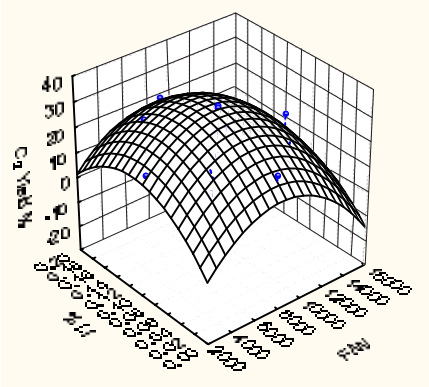

Figure 10 3-D graphic surface optimization of C_2 yield versus wt % Li and F/W

12200 $cm^3g^{-1}h^{-1}$ and 0.06-0.16 respectively to reach CH_4 conversion above 37%. The C_2 selectivity above 70% is expected when F/W is 4500-10500$cm^3g^{-1}h^{-1}$ and weight percent Li doped is 0.03-0.15. C_2 yield above 20% is expected when F/W is 5000-10500 $cm^3g^{-1}h^{-1}$ and weight percent of Li doped is 0.06-0.14.

The significance of each coefficient for CH_4 conversion, C_2 selectivity, and C_2 yield were determined using the student t-test distribution value and p-value tabulated in Tables 7 to 9, respectively. The larger the t-test value and the smaller the p-value are the more significant is the corresponding coefficient. The results in Table 7 indicate that the variable with the largest effect on CH_4 conversion is linear temperature (with β_1=0.87164) having a t-test value of 3.885 and a p-value = 0.008124. This is followed by weight percent of Li doped (quadratic) flow rate (quadratic), and temperature (quadratic) with t-test values of 3.028, 2.674 and 2.613, and p-values of 0.023165, 0.036847 and 0.039951 respectively. The F/W (linear) between 2520 to 14620 $cm^3g^{-1}h^{-1}$ could be considered not to affect the methane conversion as the t-test value is 0.304 (p-value = 0.77123). Although the linear effect of weight percent Li is insignificant, its impact to the OCM process is still significant due to the quadratic effect towards methane conversion.

Table 7 Significance of regression coefficients for CH_4 conversion

Term	Regression coefficient	CH_4 t-test value	Conversion p-value
Constant	–310.11 (β_0)	13.640	0.000010
Temperature	0.87164 (β_1)	3.885	0.008124
F/W	6.2400×10^{-4} (β_2)	–0.304	0.771230
Wt % Li doped	198.40 (β_3)	1.759	0.129039
(Temperature)(F/W)	6.6882×10^{-6} (β_{12})	1.131	0.301216
(Temperature)(wt % Li doped)	0.27237 (β_{13})	0.671	0.526944
(F/W)(wt % Li doped)	3.8675×10^{-3} (β_{23})	–0.436	0.678045
(Temperature)(Temperature)	6.1869×10^{-4} (β_{11})	–2.613	0.039951
(F/W)(F/W)	30266×10^{-7} (β_{22})	–2.673	0.036847
(wt % Li doped)(wt % Li doped)	1612.9 (β_{33})	–3.028	0.023165

Likewise, the results in Table 8, indicate that temperature (quadratic) is the most significant in determining the optimum C_2 selectivity with t-value of 3.897 (p-value= 0.006865). This is followed by F/W (quadratic) and F/W (linear) with t-values of 3.726 (p-value = 0.008008) and 2.689 (p-value = 0.009788), respectively. The coefficient of interaction between F/W (linear) and weight percent Li doped was found to be insignificant with t-value = 0.099.

Next, the results in Table 9 indicate that the variable with the largest effect on CH_4 yield is linear temperature (with β_1=1.4061) having a t-test value of 4.104 and a p-value

Table 8 Significance of regression coefficients for C_2 selectivity

Term	Regression coefficient	C_2 t-test value	Selectivity p-value
Constant	–914.71 (β_0)	-3.811	0.008849
Temperature	2.4564 (β_1)	1.627	0.154847
F/W	2.1884×10^{-2} (β_2)	2.617	0.039749
Wt % Li doped	5.1400 (β_3)	–0.009	0.992997
(Temperature)(F/W)	1.5175×10^{-5} (β_{12})	–1.473	0.191177
(Temperature) (wt % Li doped)	0.47590 (β_{13})	0.673	0.525759
(F/W)(wt % Li doped)	1.5265×10^{-3} (β_{23})	0.099	0.924523
(Temperature)(Temperature)	1.6075×10^{-3} (β_{11})	–3.897	0.008008
(F/W)(F/W)	7.3469×10^{-7} (β_{22})	–3.726	0.009788
(wt % Li doped)(wt % Li doped)	1890.0 (β_{33})	–2.037	0.087858

= 0.006327. This is followed by flow rate (quadratic), temperature (quadratic) and weight percent Li doped (quadratic) with t-test values of 4.098, 4.082 and 3.358, and p-values of 0.006371, 0.006487 and 0.0152731 respectively. The coefficient of interaction between flow rate (linear) and weight percent of Li doped was found to be insignificant with t-value = 0.276. The results in Tables 7 to 9 indicate temperature is extremely vital in the process of determining the C_2 yield.

Table 9 Significance of regression coefficients for C_2 yield

Term	Regression coefficient	C_2 yield	
		t-test value	p-value
Constant	–540.18 (β_0)	–4.003	0.007098
Temperature	1.4061 (β_1)	4.104	0.006327
F/W	9.3973×10^{-2} (β_2)	1.998	0.092637
Wt % Li doped	155.2221 (β_3)	0.491	0.640881
(Temperature)(F/W)	2.6093×10^{-6} (β_{12})	–0.450	0.668222
(Temperature)(wt % Li doped)	0.32233 (β_{13})	0.811	0.448278
(F/W)(wt % Li doped)	2.3980×10^{-3} (β_{23})	–0.276	0.791838
(Temperature)(Temperature)	9.4677×10^{-4} (β_{11})	–4.082	0.006487
(F/W)(F/W)	4.5444×10^{-7} (β_{22})	–4.098	0.006371
(wt % Li doped)(wt % Li doped)	1752.20 (β_{33})	–3.358	0.015273

The RSM responses using the Statistica software indicated that the maximum methane conversion is 43.3%, which occurred at the following optimum conditions: temperature = 778.1°C, F/W = 8883.8 $cm^3g^{-1}h^{-1}$ and weight percent of Li doped is 0.117. The highest C_2 selectivity is 78.4% when temperature = 743.6°C, F/W = 7312.6

$cm^3g^{-1}h^{-1}$, and weight percent Li doped = 0.095. Furthermore, at the corresponding optimum temperature = 750.1°C, F/W = 7901.4 $cm^3g^{-1}h^{-1}$, and weight percent Li doped = 0.108%, the highest C_2 yield is 32.6%.

Additional optimization experiments were performed to validate the results obtained by empirical modeling. In Table 10, the difference between the predicted and observed results are 3.2%, 2.8%, and 0.9% for CH_4 conversion, C_2 selectivity, and C_2 yield respectively. The results in Table 10 demonstrate that statistical model is useful in the accurate prediction of the process.

Table 10 Comparison between predicted and observed responses at optimized conditions

	Temperature (°C)	**F/W ($cm^3g^{-1}hr^{-1}$)**	**Wt % Li doped**	**Predicted value**	**Observed value**	**Predicted error (%)**
% CH_4 conversion	778.1	8883.8	0.117	43.3	41.9	3.2
% C_2 selectivity	743.6	7312.6	0.095	78.4	76.8	2.0
% C_2 yield	750.1	7901.4	0.108	32.6	32.3	0.9

Based on both the experimental and predicted results, methane conversion, C_2 selectivity, and C_2 yield have maximum values at different optimum conditions. For maximum methane conversion, it is observed that the values for operating temperature, F/W, and weight percent Li doped are higher than the corresponding values to obtain the maximum C_2 selectivity. High temperature up to ≈ 778°C is vital because its combination with F/W of 8883.8 $cm^3g^{-1}h^{-1}$, weight percent Li of ≈ 0.1, and CH_4/O_2 ratio of 8 allows the breakage of CH_4 bond to its respective methyl radicals, thus it initiates further elementary reactions to take place [16].

The importance of high temperature for methane conversion tally with the t-test and p-value (Table 7) which shows temperature is the most significant among the three independent variables studied. A sufficient amount of Li (≈ 0.1%) doped into MgO catalyst had formed active sites on the catalyst surface, and assisted the formation of methyl radicals on a reduced surface site [17]. High concentration of Li^+O^- active sites initiated the reaction by abstracting a hydrogen atom from CH_4 [18]. When certain amount of methyl radicals exists in void space, it is possible that coupling of methyl radicals proceeded without the required high temperature needed to form the methyl radicals. This can be correlated with the t-test and p-value where weight percent of Li doped (Table 8) has significant influence for methane conversion (Table 7), but minute influence on the C_2 selectivity (Table 8), implying that addition of lithium species is not very important for C_2 selectivity but detrimental for methane conversion.

CH_3 radicals formed on the catalysts surface active sites should be swept away immediately from the catalyst bed [19]. Sufficient F/W will create suitable residence time and push the methyl radicals out of the reaction zone, allowing them to couple in

gas phase [19] to form C_2 products. The effect of F/W is therefore very important in encouraging C_2 product formation and its significance is proven from the t-test and p-value in Table 8.

Table 11 indicates the results achieved in this study were improved via the optimization process. When compared with the work in the literature [8,14], the optimum F/W may be lower, but it provides the best residence time for the desired gas-phase reaction as discussed earlier. At the optimum conditions, the maximum yield achieved increased up to 84.2% compared to the same temperature and weight percent of Li doped in the work reported by Choudhary *et al.*, [14].

Table 11 Comparison of OCM results between present work at optimized conditions and Choudhary *et al.*, [8, 14]

	Temperature (°C)	**F/W ($cm^3g^{-1}hr^{-1}$)**	**Wt % Li doped**	**C_4 Conversion**	**C_2 Solectivity (%)**	**C_2 Yield (%)**
This work	778.1	8883.8	0.117	43.3		
	743.6	7312.6	0.095		78.4	
	750.0	7901.4	0.108			32.6
Choudhary[8]	750.0	12400.0	0.1	28.9	66.2	
Choudhary[20]	700.0	10320.0	0.1	21.2	75.0	15.9
	750.0	10320.0	0.1	27.6	64.0	17.7

From the catalytic reaction point of view, OCM process involves both the heterogeneous (surface catalyzed) and homogeneous (gas phase) reactions steps for obtaining the final product. The proposed mechanism for OCM process demonstrated that the initial step for activation of methane occurred on the catalyst surface and abstraction of H from methane formed methyl radicals CH_3. as shown in the reaction steps below [7]. In the next step, coupling of methyl radicals yielded ethane, which is then dehydrogenated to ethylene.

$$CH_4 + s \rightarrow H_s + CH_3. \quad \text{(surface heterogeneous reaction)}$$

$$2CH_3^{\cdot} \rightarrow C_2H_6 \quad \text{(gas phase homogeneous reaction)}$$

4.0 CONCLUSIONS

The Response Surface Methodology involving an experimental design and regression analysis is an effective method to find the optimum conditions of the independent variables, and also in assessing their effects on the two responses considered. The maximum methane conversion, C_2 selectivity, and C_2 yield are determined by the operating temperature, F/W, and weight percent of Li doped. The second order

polynomial equation model estimation is derived using ANOVA statistical testing and yields 99% degree of confidence of response behaviors to variables. Among the three variables, temperature and weight percent of Li doped were found to be more important for achieving maximum methane conversion. F/W is detrimental in achieving high selectivity of C_2 products. Consequently, to achieve the maximum C_2 yield, combination of temperature and F/W are the two main factors to be considered for process optimization. The adequacy of this model is confirmed by means of variance analysis and additional experiments.

ACKNOWLEDGMENT

The authors gratefully acknowledge the financial support received in the form of a research grant (Project 02-02-06-0101) from the Ministry of Science, Technology and Environment, Malaysia and Universiti Teknologi Malaysia.

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