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Response Surface Methodology for Carbon Dioxide Reforming of Methane over Ni/5La-ZrO_2 Catalyst

Tahani Gendy, Radwa El-Salamony*, Seham El-Temtamy, Salwa Ghoneim, Dalia Abd El-Hafiza, Mohamed Ebiad, Ahmed El Naggar

Egyptian Petroleum Research Institute (EPRI), Cairo, Egypt

radwa2005@hotmail.com, tsgendy@yahoo.com, sehamtemtamy@yahoo.com, salwaghoneim70@yahoo.com, dalia_epri@yahoo.com, m_a_ebaad@yahoo.com, drmeto1979@yahoo.com

KEYWORDS

Dry reforming of methane, Box-Behnken experimental Design, Hourly space velocity, Reaction temperature, CO_2: CH_4 mole ratio.

SHORT SUMMARY

The performance of Ni/5La-ZrO_2 catalyst for the dry reforming of $\boldsymbol{CH_4}$ using carbon dioxide has been scrutinized employing Box-Behnken experimental Design. Moreover the Response Surface Methodology (RSM) has been performed to investigate the effect of the different operating parameters, namely the hourly space velocity, the reaction temperature and ($\boldsymbol{CO_2}$: $\boldsymbol{CH_4}$) mole ratio on the conversion and formation of different components involved in the reaction system and to evaluate the predictive capabilities of the methodology. Also, the RSM has been employed to elucidate such effects in the three and two dimensions and to display the location of the predicted maximum of the various components comprising the reaction system. This study revealed that the reaction temperature has a pronounced effect followed by the ($\boldsymbol{CO_2}$: $\boldsymbol{CH_4}$) mole ratio while the hourly space velocity has a weak effect.

EXTENDED ABSTRACT

Dry reforming of methane (DRM) has conventional importance from both industrial and environmental aspects. It has dual advantages of utilizing the two principal components of greenhouse gases CH_4 and CO_2 as feedstocks besides producing hydrogen and syngas can be used as fuel, or as a chemical intermediate for the synthesis of chemicals and synthetic fuel [1,2]. In this research *Ni/5La-ZrO_2* catalyst was used for reforming of methane using carbon dioxide. Catalyst preparation and characterizing as well as the reforming experiments are given in reference [1] Investigating the reaction system to get the optimal operating conditions for maximizing hydrogen and syngas could be accomplished either via performing experiments that study each operating variable at a time while keeping other variables constant but this method is time-, money-, and energy consuming or through employing experimental design [3]. Experimental design is an effective tool for maximizing the amount of information gained from a study while minimizing the amount of data to be collected. The central composite design and Box–Behnken design (BBD) methods are the mostly used methods for the optimization of processes in RSM [4]. Fewer experiments are needed when using the BBD method, making this a better choice than the central composite design method. Response Surface Method RSM involves: (1) selection of the process parameters, responses and the experimental design method, (2) performing of experiments and collection of results, (3) mathematical modeling of experimental data by polynomial equations, with the best fitting response through analysis of variance, (4) constructing response surface 2D and 3D plots, and (5) locating the optimal conditions. The experimental factors studied comprise the space velocity, temperature and ($\boldsymbol{CO_2}$: $\boldsymbol{CH_4}$) mole ratio (see table 1). In order to establish the proper experimental design to be performed; these natural values have been codified to be in the range of -1 and +1 to allow the parameters of different units and magnitude to be investigated more evenly employing the frequently used relation given below:

$$\boldsymbol{coded\ value} = \frac{\boldsymbol{actual\ value - mean}}{\boldsymbol{half\ of\ range}} \quad \textbf{(1)}$$

Table 1. Actual and coded values of the process parameters

Space velocity ($Cm^3g^{-1}h^{-1}$)		Temperature (°C)		CO2/CH4	
Actual	Coded	Actual	Coded	Actual	Coded
2000	-1	600	-1	1	-1
4000	0	700	0	1.5	0
6000	1	800	1	2	1

Functional relationships between the coded independent variables and dependent variables could be established using multiple regression technique by fitting second order equation of the following form:

$$\boldsymbol{Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i \ + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} \beta_{ij} X_i X_j \ + \sum_{i=1}^{k} \beta_i X_i^2 + \varepsilon} \quad \textbf{(2)}$$

where, Y is the response variable; X_i and X_j are the input coded values of the variables that affect the response variable and **ε** represents the random error or uncertainties between predicted and measured values, ***k*** is the number of variables, and β_0 , β_i, β_{ii} and β_{ij} are the regression constants of intercept, linear, quadratic and interaction terms, respectively [5]. Transformation of the response variables employing the Box-Cox method has been introduced as a method for stabilizing the variance of the response, normalizing the distribution of the response variable, and improving the data fitting of the model [6]. The resulting power transformations to represent the response Y in Eq. (2) for the various components of the reaction system are: $\boldsymbol{(CH_4)^3}$, $\boldsymbol{(CO_2)^3}$, $\boldsymbol{CO}$& $\boldsymbol{H_2}$. The regression has been performed by means of Microsoft Excel 2010 and Matlab 9.0 to determine the coefficients of the equation for the ***coded factors*** along with the statistical parameters. Preliminary application of RSM indicated that there is no direct effect of space velocity and there is only mutual effect of temperature and $\boldsymbol{(CO_2 : CH_4)}$ mole ratio for $\boldsymbol{CO_2}$ conversion and $\boldsymbol{H_2}$ formation so the term $\boldsymbol{(\sum_{\substack{i=1 \\ i<j}}^{k-1} \sum_{j=2}^{k} \beta_{ij} X_i X_j)}$ has been only considered for those two cases and the following equation (3) has been adopted to represent the response surface of conversion or formation of the various components as a function of the coded input variables.

$$\boldsymbol{Y = \beta_0 \ + \ \beta_T * X_T + \beta_{Rt} * X_{Rt} + \beta_{SV}^2 * X_{SV}^2 \ + \ \beta_T^2 * X_T^2 \ + \beta_{Rt}^2 * X_{Rt}^2 \ + \beta_{T*Rt} * X_T * X_{Rt}} \quad \textbf{(3)}$$

Where:

SV: space velocity, ***T***: reaction temperature, and ***Rt***: CO_2:CH_4 mole ratio.

The large F-values and small Significance **F** values implies that the equation models are significant for all terms in the polynomial equation within 95% confidence interval except that for ***CO*** (85% confidence interval). **adj-R^2** values of > 0.8 obtained for all components except that for ***CO*** 0.61. The agreement between the "$\boldsymbol{R_{pred}^2}$" values with the corresponding "$\boldsymbol{R_{adj}^2}$" implies the real and good relation between the independent and dependent variables. Adequate precision values of (> 4) show good models discrimination. The values of **CV** < 20 except that for ***CO*** are considered acceptable. Employing the values of the regression parameters for various components resulted in the following quadratic model of RSM equations:

For CH_4 conversion:

$$\boldsymbol{(CH_4)^3 = 837258.6 \ + 294386.4 * T - 87502.5 * Rt - 269584.4 * T^2 - 101379.3 * Rt^2} \quad \textbf{(4)}$$

For CO_2 conversion:

$$\boldsymbol{(CO_2)^3 \ = 811958.9 \ + 242485.6 * T - 121283.4 * Rt - 117013.3 * T^2 + 180757.7 * T * Rt} \quad \textbf{(5)}$$

For CO production:

$$\boldsymbol{CO = 54.08 \ + \ 5.47875 * T + 5.94 * Rt - 10.56625 * SV^2 \ - 8.92375 * Rt^2} \quad \textbf{(6)}$$

For H2 production:

$$\boldsymbol{H_2 \ = 45.48 \ + 11.36625 * T - 12.2575 * Rt + 11.32625 * SV^2 \ + 10.5525 * T * Rt} \quad \textbf{(7)}$$

With the aid of these equations, Matlab 9.0 has been employed to perform the Response Surface plots for the predicted conversion or formation of the various components comprising the reaction system versus two coded variables while keeping the third at zero value. The curvature natures of these plots indicate the interaction of their independent variables (Fig. 1).

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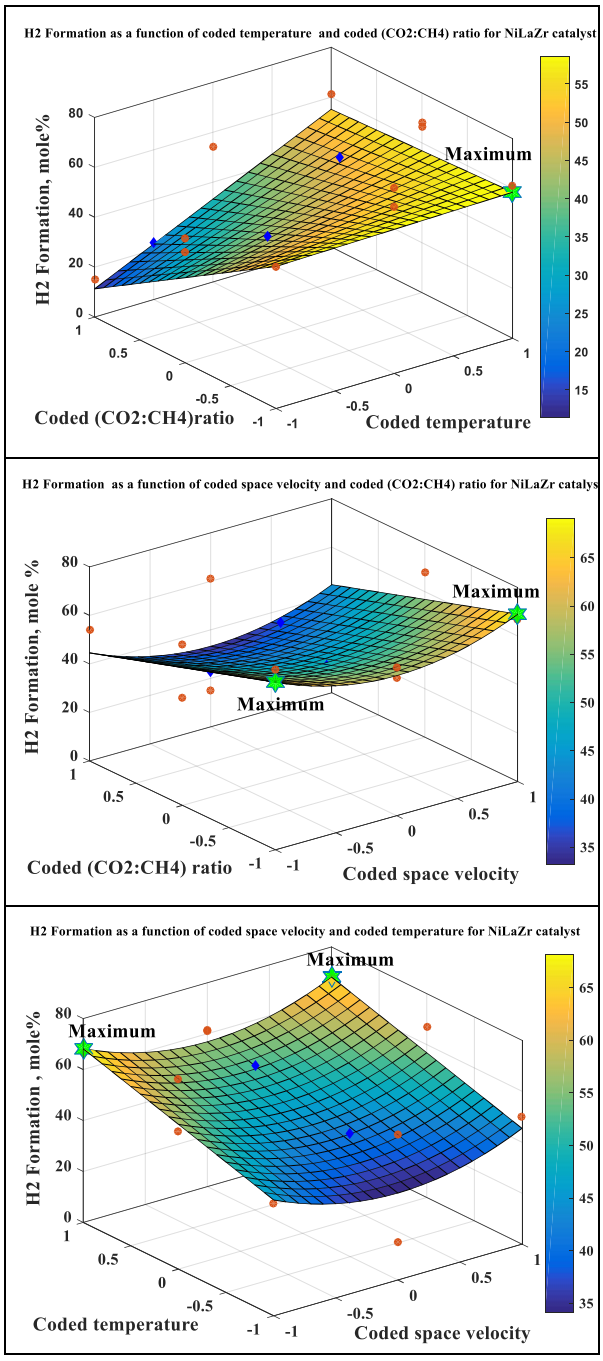

Figs (1) Surface plots for H_2 Formation over Ni/La-ZrO_2 catalyst

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