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CARBON DIOXIDE REFORMING OF METHANE TO SYNGAS: MODELING USING RESPONSE SURFACE METHODOLOGY AND ARTIFICIAL NEURAL NETWORK

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Abstract. 1wt% of Rhodium (Rh) on Magnesium Oxide (MgO) catalyst have been investigated for carbon dioxide reforming of methane (CORM) with the effect of oxygen. The effect of temperature, O_2/CH_4 ratio and catalyst weight on the methane conversion, synthesis gas selectivity and H_2/CO ratio were studied. With the help of experimental design, two mathematical approaches: empirical polynomial and artificial neural network were developed. Empirical polynomial models correlation coefficient, r, was above 85%. However, the feed forward neural network correlation coefficient was more than 95%. The feed forward neural network modeling approach was found to be more efficient than the empirical model approach. The condition for maximum methane conversion was obtained at 850°C with O_2/CH_4 ratio of 0.14 and 141 mg of catalyst resulting in 95% methane conversion. A maximum of 40% hydrogen selectivity was achieved at 909°C, 0.23 of O_2/CH_4 ratio and 309 mg catalyst. The maximum H_2/CO ratio of 1.6 was attained at 758°C, 0.19 of O_2/CH_4 and 360 mg catalyst.

Keywords: Synthesis gas, carbon dioxide reforming of methane, rhodium, MgO, experimental design, feed forward neural network

Abstrak. Kesan oksigen terhadap mangkin 1% berat Rhodium di dalam Magnesium Oksida (MgO) dikaji untuk proses pembentukan semula metana dengan menggunakan gas karbon dioksida (CORM). Kesan tiga parameter utama: suhu, nisbah reaktan (O_2/CH_4) dan berat mangkin terhadap penukaran metana, kememilihan gas sintesis dan nisbah H_2/CO diselidiki. Dengan bantuan reka bentuk eksperimen, dua pendekatan matematik: polinomial empirik dan rangkaian saraf buatan diterbitkan. Pekali kolerasi model polinomial empirik yang diterbitkan, r, adalah melebihi 85%. Walau bagaimanapun, pekali kolerasi untuk suapan hadapan rangkaian saraf pula melebihi 95%. Oleh itu, suapan hadapan rangkaian saraf adalah lebih efisen dari pada model polinomial empirik. Penukaran metana tertinggi sebanyak 95% dihasilkan pada suhu 850°C dengan nisbah O_2/CH_4 sebanyak 0.14 dan 141 mg mangkin. Kememilihan hidrogen secara maksima sebanyak 40% boleh dicapai pada suhu 909°C, nisbah O_2/CH_4 sebanyak 0.23 dan 309 mg mangkin. Nisbah maksima H_2/CO sebanyak 1.6 dihasilkan pada suhu 758°C dengan nisbah O_2/CH_4 sebanyak 0.19 dan 360 mg mangkin digunakan.

Kata kunci: Gas sintesis, pembentukan semula metana menggunakan gas karbon dioksida, rhodium, MgO, reka bentuk eksperimen, suapan hadapan rangkaian saraf

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1.0 INTRODUCTION

Synthesis gas, a composition of carbon monoxide and hydrogen, can be used to produce high purity hydrogen streams and chemical products with higher added values such as hydrocarbons, oxygenated compounds and polycarbonates. Several processes can be applied to produce synthesis gas such as partial oxidation (POM), steam reforming (SRM) and carbon dioxide reforming of methane (CORM). The commercial process to produce synthesis gas is via steam reforming of natural gas, although this process is very expensive due to high heat demand [1]. Many researchers such as Choudhary *et al.* [2] studied the alternative routes to convert natural gas to synthesis gas by combining POM, SRM and CORM reaction routes. The reaction network in all cases is very complex. The reaction steps are described in Equations (1) - (6). The overall reaction of Partial Oxidation and CORM process is described in Equation (7).

$$CH_4 + CO_2 \leftrightarrows 2CO + 2H_2 \qquad \text{(}CO_2\text{ reforming)} \qquad \Delta H^o_{R,298K}(\text{kJ/mol})=247 \quad (1)$$

$$CH_4 + \tfrac{1}{2}O_2 \leftrightarrows CO + 2H_2 \qquad \text{(Partial oxidation)} \qquad \Delta H^o_{R,298K}(\text{kJ/mol})=-36 \quad (2)$$

$$CH_4 + 2O_2 \leftrightarrows CO_2 + 2H_2O \qquad \text{(Combustion)} \qquad \Delta H^o_{R,298K}(\text{kJ/mol})=-802 \quad (3)$$

$$CO_2 + H_2 \leftrightarrows CO + H_2O \qquad \text{(Water-gas shift)} \qquad \Delta H^o_{R,298K}(\text{kJ/mol})= 41 \quad (4)$$

$$2CO \leftrightarrows C + CO_2 \qquad \text{(Boudouard reaction)} \qquad \Delta H^o_{R,298K}(\text{kJ/mol})=-172 \quad (5)$$

$$CH_4 \leftrightarrows C + 2H_2 \qquad \text{(}CH_4\text{ decomposition)} \qquad \Delta H^o_{R,298K}(\text{kJ/mol})= 75 \quad (6)$$

$$2CH_4 + CO_2 + \tfrac{1}{2}O_2 \rightarrow 3CO + 4H_2 \qquad \Delta H^o_{R,298K}(\text{kJ/mol})=211 \quad (7)$$

The main objective for combining the reforming reaction is to produce varied H_2/CO ratios, which are appropriate for the production of oxygenated compounds, heavy hydrocarbons by Fisher Tropsch synthesis and carbon monoxide for synthesis of polycarbonates [3]. Furthermore, the combinations of natural gas reforming reactions are energetically favorable. For example, POM is highly exothermic, the temperature control may be difficult at certain condition, leading to hot spot formation particularly in large scale process. Thus, the addition of carbon dioxide can significantly improve the reactor temperature control and reduce the risk of hot spot development since CORM is an endothermic process. In addition, the oxygen feed to CORM can reduce the carbon deposition and increase methane conversion [2]. With addition of oxygen, a small amount of carbon deposition occurred on the oxygen unexposed part of Pt/ZrO_2 catalyst as reported by O'Connor *et al.* [3]. Besides, this combined process may also reduce the cost of production because CO_2 is cheap, abundant and a greenhouse gas [4].

The catalysts commonly used for synthesis gas production are based on the VIII metal transition group including Rh, Ru, Pt, Pd, Ni and Co, supported on metalic oxides such as TiO_2, ZrO_2, Al_2O_3, SiO_2 and MgO. Rh on MgO support shows remarkable catalyst performance and stability compared to other Rh catalyst on other support [5]. In addition, Liao and Zhang [6] proved that Rh metal on support catalyst is the most efficient catalyst for methane dissociation in the reaction of methane and oxygen. Therefore, Rh on MgO support catalyst was chosen in this report.

The application of experimental design and a mathematical modeling technique as a mathematical tool to represent the reaction is essential. Experimental design is a proven technique that continues to show increasing use in chemical industries. Response surface methodology (RSM) is a method to determine the optimum condition of a process. RSM is a set of technique designed to find the optimum value of the response and the influencing factors. It has similarity with regression analysis. In regression analysis, empirical mathematical model is derived from the experiment data. RSM method of optimization of a medium composition is efficient, relatively simple, and time and material saving in their studies of optimization [7-9]. However, there is increasing interest in the artificial neural network modeling in different field of materials science recently. Artificial neural network (ANN) modeling is a relatively new non-linear statistical technique. It can be used to solve problems that are not eligible for conventional statistical methods. ANN can be used to model properly the kinetics of different catalytic reactions under different reaction conditions, being an alternative for mechanism-based kinetics models. The modeling of catalytic reaction by neural networks (*black box* models) has been proven and the influence of experimental dispersion in fitting data has been also estimated, tolerating reasonable degrees of error [10].

The purpose of this study is to utilize statistical technique, RSM, and ANN in CORM process with the addition of oxygen using 1wt% of Rh/MgO catalyst in order to obtain an optimum condition for maximum methane conversion, maximum hydrogen yield and H_2/CO ratio near to one. Two models were developed and analyzed; polynomial empirical model and feed forward neural network model.

2.0 EXPERIMENTS

2.1 Catalyst Preparation

Magnesium Oxide (MgO) with minimum 97% purity supplied by Merck was used as a support. For impregnating rhodium into the supports, a dilute solution of Rhodium (III) nitrate (0.003M) was slowly added to the MgO slurries (3g/l, 353K) over a period of 12 hours. Subsequently, the slurry was stirred for an additional 60 hours in order to achieve homogeneous distribution of Rh throughout the support. The samples were dried in the oven at 120°C and calcined for 5 hours at 800°C. Additional pretreatment of the catalyst was performed by heating the catalyst to 550°C over a period of one hour in the flow of pure nitrogen (100 ml/min) before testing the catalyst.

2.2 Apparatus

The experimental rig was set up as shown in Figure 1. The fixed-bed vertical quartz tube reactor (ID of 9.1 cm and length of 30 cm) and catalyst (above 65 mesh size) were preheated with N_2 gas for one hour at 550°C. The gaseous products were analyzed by a GC (Agilent 6890 series) with Thermal Conductivity Detector (TCD) that was equipped with molecular sieve and PORAPAK Q column. Calibration of the GC using Scott gas standard (cat-89779) resulted in a mole/area ratio for each gas. Chemstation software was used to calculate the integration of the peak area. GC samples were analysed every 30 minutes with the GC operating condition: 21.0 ml/min He as carrier gas, TCD detector at T_{Det} = 200°C, t_1 = 5 minutes for T_1 = 40°C, heating rate, r_1 = 12°C/min to T_2 = 200°C and finally cooled to T_3 = 40°C. The sample was injected to the GC every 30 minutes. The injection was automatically controlled by programmed sequence provided by Chemstation.

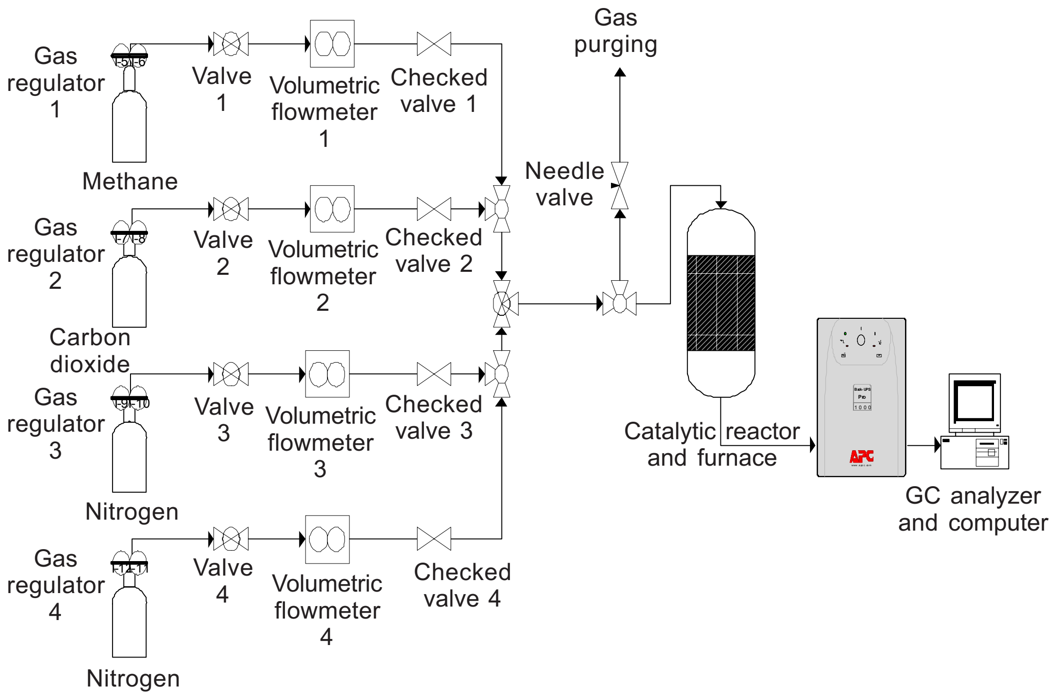

Figure 1 Experimental rig

2.3 Experimental Design

The experimental conditions were defined using central composite design techniques, one of the tools in RSM. The experimental plan was proposed in order to detect the possible existence of minimum points on the response factor surfaces. Three independent experimental variables, namely, operation temperature (x_1), O_2/CH_4 ratio (x_2) and catalyst weight in 100 ml/min total flow rate (x_3) were selected as controlled factors. Their experimental range and levels used in this work are given in the Table 1. The upper, center and lower point of the design were coded as +1, 0 and -1 while α is called star point resulting a total of 16 experiments.

Table 1 The levels of variables chosen for trials

	-α	-1	0	+1	+α
Temperature (x_1), °C	581.82	650.00	750.00	850.00	918.18
O_2/CH_4 ratio (x_2), mol/mol	0.07	0.10	0.15	0.20	0.23
Catalyst weight (x_3), mg	31.82	100.00	200.00	300.00	368.18

The CH_4 and CO_2 conversion and H_2 and CO yield were calculated, based on Equations (8) - (10).

$$\text{Methane conversion, } X_{CH4} = \frac{\text{mole of reacted reactant}}{\text{mole of reactant inlet}} \times 100\% \tag{8}$$

$$H_2 \text{ selectivity, } S_{H_2} = \frac{\text{mole of hydrogen atom in produced } H_2}{\text{mole of hydrogen atom reacted from } CH_4} \times 100\% \tag{9}$$

and

$$H_2/CO \text{ product ratio} = \frac{\%\text{ mole } H_2 \text{ in effluent gases}}{\%\text{ mole CO in effluent gases}} \tag{10}$$

The polynomial empirical models were used to analyze the influence of the process variables on the response factors. Second order polynomial models were used to verify the linear and quadratic effects of the process variables and their linear and quadratic interactions. Response surface methodology was applied to the methane conversion and hydrogen yield using a commercial stat software version 6. Each response Y can be represented by a quadratic model of the response surface, here with three independent variables is given as follows:

$$Y_i = \beta_o + \sum_{j=1}^{3} \beta_j x_j + \sum_{i<j} \beta_{ij} x_i x_j + \sum_{j=1}^{3} \beta_{ij} x_j^2 \tag{11}$$

where Y_i is the predicted response, β_o is the offset term, β_j is the linear effect, β_{ij} is the interaction effect and β_{jj} is the squared effect.

A feed forward 'black box' neural network models were developed using 16 experiments data planned by central composite design as training data and 6 other experiments data as generalized data. The independent experimental variables were operation temperature (x_1), O_2/CH_4 ratio (x_2) and catalyst weight in 100 ml/min total flow rate (x_3). The outputs were CH_4 conversion, H_2 yield and H_2/CO ratio. Process inputs for neural network models were inconsistent in term of their magnitudes. Thus, these input data were scaled within a consistent range (e.g. 0 to 1) before introducing them to the input layer of the network to ensure that each data is given fair contribution in determining the network output.

The data scaling method employed in this research is shown as followed:

$$X_{is} = \frac{X_i X_{i\min}}{X_{i\max} X_{i\min}} \tag{12}$$

where, X_{is} is the scaled input and X_i is the actual input before scaling whereas $X_{i_{\min}}$ and $X_{i_{\max}}$ are the minimum and maximum values of the inputs respectively. The maximum and minimum values of the input are selected based on data set available for training.

The structure of feed forward neural network process estimator consisted of a set of Multi-Input Single-Output (MISO) network as shown in Figure 2. Log-sigmoid transfer

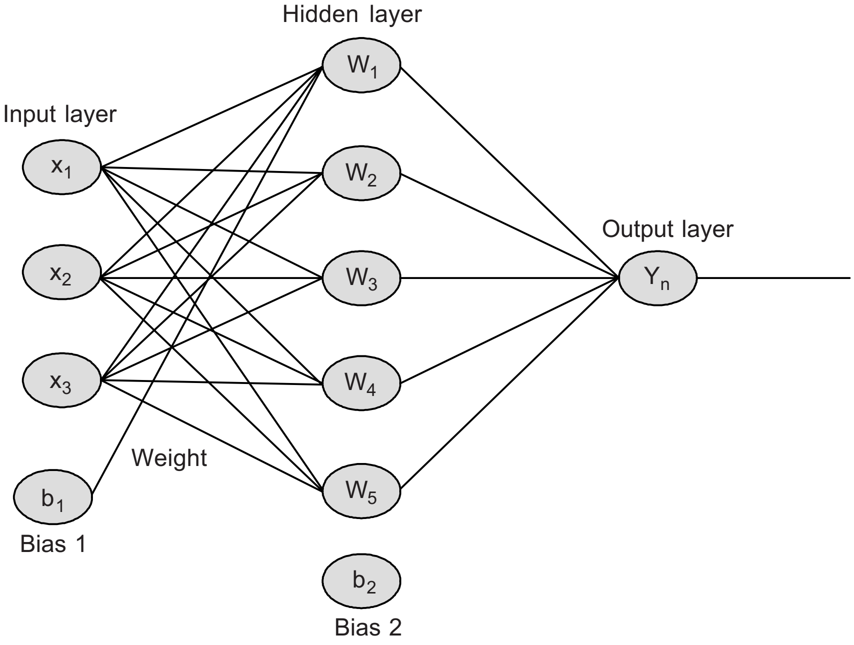

Figure 2 Feed forward hierarchical neural network architecture

function and purelin transfer function were used in the network. Neural network package in Matlab 6.1 was used to design and simulate the network. The networks were trained using Levenberg Marquardt Learning Algorithm. Trial and error search method was applied to select the optimum topology of the classifiers. The information was propagated forward to the output layer where the output variable was calculated and compared to the actual value in order to generate a prediction error. When the structure of the neural network is selected, the values of weights associated to each connection between neurons of adjacent layers were obtained so that the root mean sum of squares errors (RMSE) was minimized. The RMSE is defined as:

$$RMSE = \sqrt{\left(\frac{\sum(\text{Predicted} - \text{Observed})^2}{\text{No. of data}}\right)} \tag{13}$$

3.0 RESULT AND DISCUSSION

3.1 Experimental result

The process of carbon dioxide reforming of methane with the effect of oxygen led to methane conversions ranging from 56 to 94%, hydrogen selectivity ranging from 13.31 to 35.55% and H_2/CO mole ratio of 0.6 to 1.46, as shown in Table 2.

It was verified that the Rh/MgO catalyst has an outstanding catalyst reactivity and stability when was tested for 16 hours at 900°C with O_2/CH_4 ratio equal to 0.17 and catalyst weight at 261mg in 100ml/min of total flow rate. As shown in Figure 3, constant performance of 94% methane conversion and 1.43 H_2/CO ratio were obtained after 60 minutes. Not only methane conversion and H_2/CO ratio constant, the hydrogen and carbon monoxide yields were unchanged through out the study. It can be deduced that Rh/MgO catalyst was stable with excellent catalyst reactivity at high temperature for 16 hours. This catalyst characteristic was important for commercial catalyst that can be used in Fisher-Tropsch process. The stability of Rh/MgO was due to strong interaction between Rh and MgO that formed magnesium rhodium oxide ($MgRh_2O_4$) after a high temperature calcinations, which was reduced with higher difficulty than rhodium oxide (Rh_2O_3) [5].

3.2 Polynomial Empirical Model

The polynomial empirical model obtained to describe the experimental methane conversion (%) data in term of variables was:

$$\begin{aligned} Y_1 = {} & 88.16 + 9.61x_1 - 3.77x_1^2 + 3.23x_2 - 3.47x_2^2 + 2.04x_3 - 2.79x_3^2 \\ & -0.11x_1x_2 - 1.91x_1x_3 + 0.41x_2x_3 \end{aligned} \tag{14}$$

Table 2 Factorial central composite design with observed and predicted value

No.	Variables			Y_1		Y_2		Y_3	
	X_1	X_2	X_3	Observed	Predicted	Observed	Predicted	Observed	Predicted
1	650	0.10	100	56.70781	61.21027	13.31	13.64	0.78	0.63
2	650	0.20	100	65.35150	69.04179	18.70	17.80	1.04	0.92
3	650	0.10	300	64.97570	68.28542	20.63	21.39	0.68	0.72
4	650	0.20	300	76.89498	77.77107	21.93	22.15	1.21	1.11
5	850	0.10	100	80.92184	84.48946	25.70	25.00	1.18	1.15
6	850	0.20	100	90.73479	91.86879	33.70	32.45	1.46	1.28
7	850	0.10	300	83.15977	83.91320	30.28	30.69	1.24	1.24
8	850	0.20	300	93.00541	92.94667	35.55	34.74	1.45	1.48
9	582	0.15	200	65.73237	60.51436	16.05	15.57	0.60	0.73
10	918	0.15	200	93.91720	92.85085	34.55	35.71	1.42	1.48
11	750	0.15	32	81.58118	76.05646	23.54	24.79	0.85	1.09
12	750	0.15	368	83.67197	82.91232	33.80	33.23	1.37	1.33
13	750	0.07	200	79.53462	74.46247	17.78	17.07	0.67	0.71
14	750	0.23	200	89.85640	88.64418	22.58	23.97	0.99	1.15
15	750	0.15	200	88.20754	88.29504	30.89	30.38	1.31	1.29
16	750	0.15	200	87.30430	88.29504	29.98	30.38	1.30	1.29

X_1 = Temperature (°C)
X_2 = O_2/CH_4 ratio
X_3 = Catalyst weight (mg)

Y_1 = Methane conversion
Y_2 = H_2 selectivity
Y_3 = H_2/CO ratio

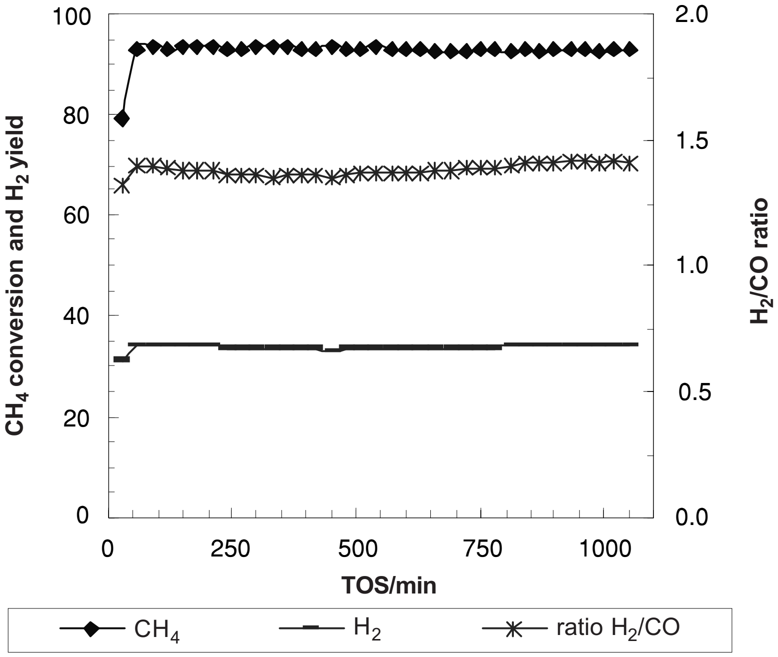

Figure 3 Rh/MgO catalytic reactivity at 900°C for more than 16 hours. (Total flow rate = 100 ml/min, CO_2/CH_4 = 1.0, O_2/CH_4 = 0.17 and catalyst weight of 261mg

which led to a linear correlation coefficient of 0.922. The temperature and O_2/CH_4 ratio were the main variables affecting the methane conversion. The methane conversion increases with increasing operating temperature and oxygen in the reaction system. This could be already as expected due to the increase of combustion efficiency as reported by Souza and Schmal (2003) [11].

However, the empirical model representing the experimental hydrogen (H_2) selectivity (%) data is as follows:

$$\begin{aligned} Y_2 = 30.38 + 5.99x_1 - 1.67x_1^2 + 2.05x_2 - 3.49x_2^2 + 2.51x_3 - 0.48x_3^2 \\ + 0.82x_1x_2 - 1.51x_1x_3 - 0.85x_2x_3 \end{aligned} \tag{15}$$

The linear correlation coefficient achieved is 0.987. The temperature shows the highest influence on hydrogen selectivity, followed by the O_2/CH_4 ratio and the catalyst weight. Higher hydrogen selectivity was obtained at higher temperature and catalyst weight. However, when O_2/CH_4 ratio in a range of 0.15 to 0.23 and temperature >900°C, lower selectivity of hydrogen was observed. This is probably due to the existence of secondary parallel reactions in which the hydrogen probably reacts with oxygen in carbon dioxide to form water.

$$CO_2 + H_2 \leftrightarrows CO + H_2O \qquad \Delta H° = 41 \text{ kJ/mol} \tag{16}$$

In addition, the experimental H_2/CO ratio was described by the polynomial empirical model with a linear correlation coefficient of 0.860 was as follow:

$$\begin{aligned} Y_3 = 1.29 + 0.22x_1 - 0.07x_1^2 + 0.13x_2 - 0.13x_2^2 + 0.08x_3 - 0.03x_3^2 \\ -0.04x_1x_2 + 0.03x_2x_3 \end{aligned} \tag{17}$$

The temperature and O_2/CH_4 ratio are the most influential process variables. The H_2/CO ratio increase from 0.6 to 1.46 with increasing of temperature and O_2/CH_4. Like hydrogen selectivity result, the ratio of H_2/CO decrease from 1.46 to 1.42 at higher temperature (>900°C). The same observation was also attained when O_2/CH_4 increase from 0.15 to 0.23. This was influenced by carbon dioxide reforming and partial oxidation of methane reaction. Mo *et al.* (2003) [12] also reported the same result for $Pt/CoAl_2O_4/Al_2O_3$ and the H_2/CO ratio varies from 1.05 to 1.68 as O_2/CH_4 ratio increased from 0.08 to 0.67.

3.3 Feed Forward Neural Network Model

In this work, all ANN models were developed in MATLAB environment. A designed training data sets are more desirable than random experimental sets, due to their higher orthogonality [13,14]. Central composite design is applied to design the training data set.

Three neural network models have been developed with three input nodes, one hidden layer and one output. The models were trained using back propogation algorithm with the Levenberg Marquardt method to optimize the weight and biases. The process of ANN modeling includes following steps:

(1) database collection,
(2) analysis and pre-processing of the data,
(3) design and training of the neural network,
(4) test of the trained network, and
(5) use of the trained NN for simulations and predictions.

The neural network model was able to predict the methane conversion, hydrogen selectivity and H_2/CO ratio precisely. Three neural network models have been developed with each models consists of three input nodes, a four nodes hidden layer with sigmoid function as activation function and one output with purelin function as activation function. The value of predicted and experimental values, for all reaction conditions, is shown in Table 3.

Table 3 Experimental results and predicted result from neural network model for training data

No.	**Variables**			**Y_1**		**Y_2**		**Y_3**	
	X_1	**X_2**	**X_3**	**Observed**	**Predicted**	**Observed**	**Predicted**	**Observed**	**Predicted**
1	650	0.10	100	56.71	56.71	13.31	13.31	0.78	0.79
2	650	0.20	100	65.35	65.27	18.70	18.69	1.04	1.01
3	650	0.10	300	64.98	64.89	20.63	20.63	0.68	0.67
4	650	0.20	300	76.89	76.80	21.93	21.94	1.21	1.21
5	850	0.10	100	80.92	80.89	25.70	25.70	1.18	1.18
6	850	0.20	100	90.73	90.57	33.70	33.69	1.46	1.46
7	850	0.10	300	83.16	83.13	30.28	30.28	1.24	1.25
8	850	0.20	300	93.01	93.17	35.55	35.55	1.45	1.45
9	582	0.15	200	65.73	65.64	16.05	16.04	0.60	0.60
10	918	0.15	200	93.92	93.92	34.55	34.55	1.42	1.03
11	750	0.15	32	81.58	81.64	23.54	23.54	0.85	0.85
12	750	0.15	368	83.67	83.50	33.80	33.80	1.37	1.37
13	750	0.07	200	79.53	79.41	17.78	17.78	0.67	0.67
14	750	0.23	200	89.86	89.82	22.58	22.58	0.99	1.02
15	750	0.15	200	88.21	87.78	30.89	30.44	1.31	1.31
16	750	0.15	200	87.30	87.78	29.98	30.44	1.30	1,31

X_1 = Temperature (°C)
X_2 = O_2/CH_4 ratio
X_3 = Catalyst weight (mg)

Y_1 = Methane conversion
Y_2 = H_2 selectivity
Y_3 = H_2/CO ratio

A model equation of a single neuron can be written as follow:

$$y_{pi}^{l} = \sum_{i=1}^{n}\left(w_{ij}a_{ij}\right) + b_j \qquad (18)$$

where w_{ij}, a_{ij} and b_j represent weight, input and bias of i row in j layer. Once the node is calculated, it passes the result to the transfer function, $f(y)$. The functions used in this study were sigmoidal function and purelin function. Thus, the complete node calculation for a sigmoidal function is:

$$f(y) = \frac{1}{1+e^{-y}} \qquad (19)$$

and for purelin function is:

$$f(y) = y \qquad (20)$$

3.4 Evaluation of Models Fitness

The quality of models fitness (polynomial empirical and ANN) can be checked by several criteria. In this study, the coefficient of correlation, r and Analysis of Variance, ANOVA are considered to verify the fitness of the model.

The polynomial empirical model coefficients of correlation value, r, for the methane conversion (Y_1), H_2 selectivity (Y_2) and H_2/CO ratio (Y_3) were 0.960, 0.993 and 0.927 respectively indicating fairly good agreement between the experimental and predicted values from the models. The values of r^2 for Y_1, Y_2 and Y_3 are 0.922, 0.986 and 0.860 respectively indicating that 92.2%, 98.6% and 86.0% of the total variation in the three responses are attributed to the experimental variables.

Nevertheless, the r value for neural network models is higher than polynomial empirical models. The r value for methane conversion (Y_1) and H_2 selectivity (Y_2) were 0.9998 and 0.9997 respectively, while the r value of H_2/CO ratio (Y_3) was 0.8950. The values indicate good agreement between the experimental and predicted values of each feed forward neural network models. As a result, the values of r^2 for Y_1, Y_2 and Y_3 were 0.9997, 0.99995 and 0.9987 respectively. It denoted that 99.97%, 99.95% and 99.87% of the total variation in the three responses are attributed to the experimental variables. By comparing the r and r^2 values of each models developed, it clearly shows that feed forward neural network model fitness were greater than the polynomial empirical model.

Figures 4 and 5 show the observed value versus predicted value from polynomial empirical model and neural network model developed. It is clearly shown that both developed models can represent the process quite satisfactorily because both model approaches, correlations coefficients were above 85% accuracy. However, the neural network coefficient of correlation, r_{nn}, for neural network was higher than coefficient

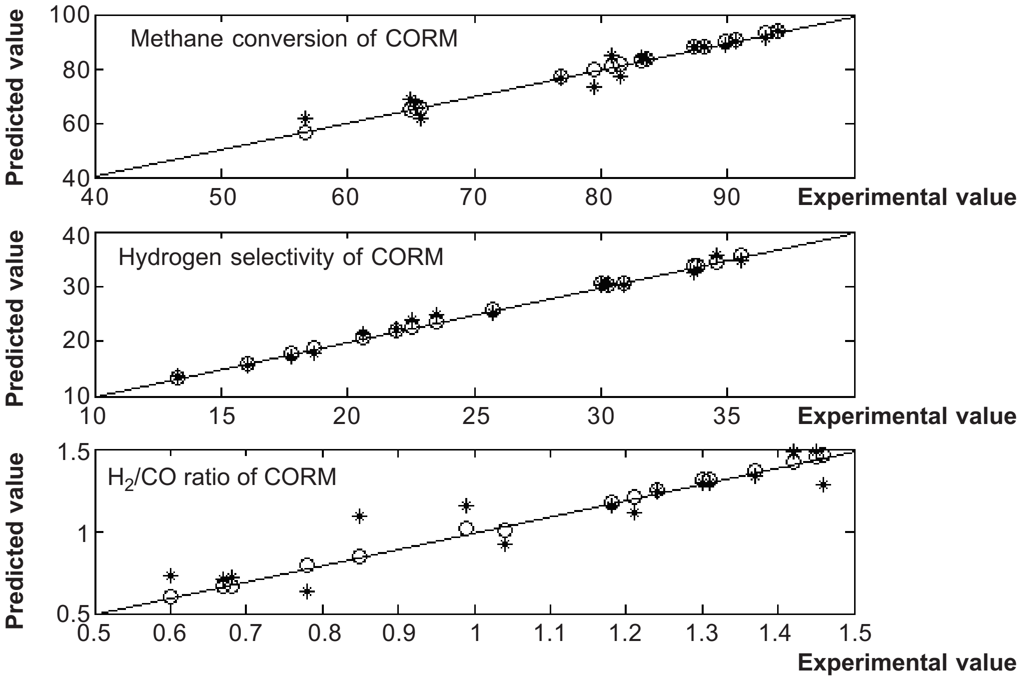

Figure 4 Comparison of predicted and experimental value for training data. (✳ Polynomial Empirical model, ○ Neural Network model)

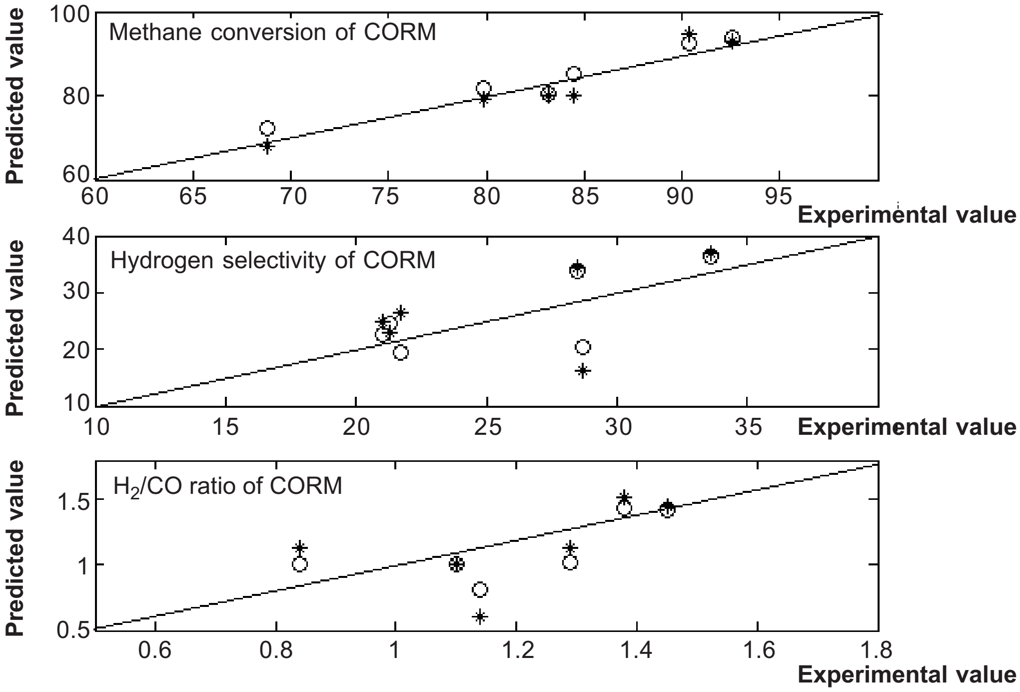

Figure 5 Comparison of predicted and experimental value for validation data. (✳ Polynomial Empirical model, ○ Neural Network model)

correlations of polynomial empirical model, r_{em}. Improving this, unlike predicted and observed values of polynomial empirical models, the predicted value for feed forward neural network models are placed almost equal to the observed value for both training and validation data. Thus, it can be deduced that feed forward neural network do have better performance compared to polynomial empirical model even though there were limited data available.

Each fitted model was further checked with the analysis of variance (ANOVA) as shown in Table 4. In this case, the adequacy of fitted model was tested using static F value. The F-value for the regression is defined as Mean Squares regression divided by Mean squares residual. The F-value is compared to the Statistical Table value $F_{(p-1,\ N-p,\ \alpha)}$. If F-value is greater than F-value $_{(p-1,\ N-p,\ \alpha)}$ from Statistical Table, the hypothesis is accepted and null hypothesis is rejected at the α level of significance. So, the F-value $_{(p-1,\ N-p,\ \alpha)}$ from Statistical Table for 95% confidence level or the a value of 0.05 is 3.37. The hypothesis of this work is the developed model is a good predictor of the experimental data to represent the process.

From the ANOVA analysis in Table 4 for polynomial empirical model, the F value of Y_1, Y_2 and Y_3 are 7.98, 47.98 and 4.30 respectively and greater than $F_{(p-1,\ N-p,\ \alpha)}$ value. This indicates that the hypothesis is true with high significant at 95% confidence level ($\alpha = 0.05$).

The capabilities of feed forward neural networks models representing the process were also checked with the analysis of variance (ANOVA) as shown in Table 4. In this case, same hypothesis as polynomial empirical model analysis was assumed. As presented in Table 4, the ANOVA values for feed forward neural network model, the F value for Y_1, Y_2 and Y_3 are 2477, 1243.43 and 40 respectively and tremendously greater than $F_{(p-1,\ N-p,\ \alpha)}$ value of Statistical Table. This clearly shows that the hypothesis is true with high significant at 95% confidence level ($\alpha = 0.05$).

By comparing the F values for polynomial empirical model with ANN model, it is clearly shown that the F values for neural networks models were larger than the F values for polynomial empirical model. It is suggested that modelling via neural network is more precise and reliable in predicting the value compared to polynomial empirical model. We can conclude that the ANN based model with the help of design of experiments shows high correlation between observed and predicted value for training even though being developed using fewer number of input variables. The same observation was also reported by Lanouette *et al.* (1999)[15].

3.5 Optimization

Since it had been demonstrated that the neural network was able to effectively predict the methane conversion, hydrogen yield and H_2/CO ratio of the experiments, a final network with the optimum architecture was used for the optimisation purpose. The optimisation was performed by a grid search algorithm, exploring the region defined by the experimental design extremes, dividing each factor in 40 intervals. Therefore, a total of 40^3 situations were evaluated, simulating the corresponding response factors of the neural network. A similar method was also approached by Marengo *et al.* [14].

The optimum conditions were obtained with the maximum response factors. The results from Multiple Input Single Output (MISO) Feed forward neural network optimisation result are tabulated in Table 5.

From Table 5, the optimum point for methane conversion is 95.06% when 0.1416 of O_2/CH_4 ratio and 141.07 mg catalyst used in the reaction at 850°C. However, optimum hydrogen selectivity achieved at 39.56% when the reaction temperature performed at 909.6° with 0.2298 of O_2/CH_4 ratio and 309.17 mg catalyst used. In order to get the optimum H_2/CO ratio of 1.72, with 0.1878 O_2/CH_4 ratio and 359.6 mg catalyst is needed to react at 758°C.

4.0 CONCLUSION

Central Composite Design tool in RSM is a powerful tool to plan the experiments. With the help of experimental design, empirical modeling and ANN modeling are developed for CORM with a presence of oxygen. Empirical modeling and ANN modeling can be used to represent this reaction. However, ANN modeling is more appropriate in predicting the output than empirical modeling although a small number of training data available. It was definitely observed that the operating temperature, O_2/CH_4 ratio and catalyst weight in 100 ml/min of total flow rate are significant effect on the response factors.

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