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Optimization of OCM reactions over Na–W–Mn/SiO_2 catalyst at elevated pressure using artificial neural network and response surface methodology

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Hybrid genetic algorithm.

Abstract In this study, Response Surface Methodology (RSM) and Artificial Neural Network (ANN) predictive models are developed, based on experimental data of the Oxidative Coupling of Methane (OCM) over Na–W–Mn/SiO_2 at 0.4 MPa, which was obtained in an isothermal fixed bed reactor. Results show that the simulation and prediction accuracy of ANN was apparently higher compared to RSM. Thus, the Hybrid Genetic Algorithm (HGA), based on developed ANN models, was used for simultaneous maximization of CH_4 conversion and C_{2+} selectivity. The pareto optimal solutions show that at a reaction temperature of 987 K, feed GHSV of 15790 h^{-1}, diluents amounts of 20 mole%, and methane to oxygen molar ratio of 3.5, the maximum C_{2+} yield obtained from ANN-HGA was 23.91% (CH_4 conversion of 34.6% and C_{2+} selectivity of 69%), as compared to 22.81% from the experimental measurements (CH_4 conversion of 34.0% and C_{2+} selectivity of 67.1%). The predicted error in optimum yield by ANN-HGA was 4.81%, suggesting that the combination of ANN models with the hybrid genetic algorithm could be used to find a suitable operating condition for the OCM process at elevated pressures.

1. Introduction

The catalytic Oxidative Coupling of Methane (OCM) to higher hydrocarbons (especially ethane and ethylene) has been the subject of challenging research in utilizing natural gas as a chemical feedstock. Among various catalysts explored for methane coupling, the Mn/Na_2WO_4/SiO_2 catalyst, first studied by Fang et al. [1,2], is considered to be one of the most promising. Therefore, it has been extensively studied by several researchers [3–10]. Most work on this catalyst was conducted under pressures below one atmosphere. However, for commercial applications and in order to reduce the size of the reactor, it is required to perform oxidative coupling of methane at higher pressures. Also, performing the OCM reaction at elevated pressures economically favors product separation and energy saving [11]. On the other hand, higher pressure will lead to a drop in C_{2+} selectivity and yield, i.e. higher pressures will facilitate undesired total oxidation reactions.

Among the earliest economic studies on commercialization of OCM based processes by Union Carbide in 1992 [12], it had been assumed that the reactor pressure could increase up to 0.44 MPa without a major impact on C_{2+} yield of the reaction per pass. In a more recent feasibility study by RIPI (Research Institute of Petroleum Industry) and JOGMEC (Japan Oil, Gas and Metal Company) [13], it has been found that the plant cost index reaches its minimum value if the reactor operates at 0.4 MPa pressure, assuming the catalyst performance does not change by increasing the pressure to 0.4 MPa.

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So, it is important to determine reaction conditions that optimize the performance of this process at an elevated pressure. For this purpose, an appropriate kinetic model is required. In the case of the Na–W–Mn/SiO_2 catalyst, most reported kinetic models in the literature [14,15] are based on gathered reaction data at atmospheric total pressure. On the other hand, experimental results at higher pressures for this catalyst [16] show that as a result of several secondary and crossing reactions that may occur, the OCM reactions at elevated pressures are more complex than those at atmospheric pressure.

Application of the conventional modeling approach is not well suited for OCM reactions at elevated pressures because of the lack of a suitable kinetic model. However, this problem can be overcome by using empirical methods. In empirical methods, two approaches are possible; statistical based, and artificial intelligence-based black box.

In statistical-based approaches, Response Surface Methodology (RSM) has been extensively used in various processes [17–20]. However, its application in OCM processes is very rare [4,21,22].

Artificial Neural Networks (ANNs) are now successfully used in many areas of science and engineering [23–27]. Application of ANN for the modeling of OCM process has been the subject of some articles. Abdolahi et al. [28] used a neural network for prediction of CH_4 conversion, ethylene and C_{2+} selectivity on the periodic operation of the OCM process over the Ce/Li/MgO catalyst. A hybrid Genetic Algorithm (GA) with ANN was also used by Haung et al. [29] to design optimal catalyst and operating conditions in the OCM process. Recently, Istadi and Amin [30] used this technique for modeling and optimization of the catalytic dielectric barrier discharge plasma reactor for CO_2-OCM processes.

With the aforementioned background, there is no report addressing the modeling and optimization of OCM reactions at elevated pressures. Therefore, in this study, we report experimental data obtained for OCM reactions over a Na–W–Mn/SiO_2 catalyst at 0.4 MPa in an isothermal fixed bed reactor. Next, two RSM and ANNs modeling approaches were used to recognize the relationship between input variables, such as feed methane to oxygen molar ratio, feed GHSV (Gas Hourly Space Velocity), feed diluents amounts, reaction temperature and output variable. Finally, the modeling capabilities of RSM and ANNs were compared and the GA multi-objective optimization algorithm, based on the best mentioned methods, is applied for simultaneous maximization of CH_4, conversion, and C_{2+} selectivity, to obtain the Pareto optimal solutions.

2. The experimental work

2.1. Catalyst preparation

The SiO_2 was first prepared by the co precipitation method. Calculated amounts of sodium silicate (Na_2SiO_4) and sulfuric acid (H_2SO_4) were added to 400 ml distilled water at 353 K, with a pH equal to 8, at constant stirring to produce a thick paste. The paste was spread and dried for 24 h at 373 K. Thereafter, it was calcined in air for 5 h at 723 K.

The Na–W–Mn/SiO_2 catalyst was prepared by a two-step incipient wetness impregnation method. An aqueous solution with an appropriate concentration of $Mn(NO_3)_2 \cdot 6H_2O$ was added to prepare SiO_2 support, evaporated to dryness, and dried in air at ambient temperature for 24 h and then 373 K for one day. After that, the $Na_2WO_4 \cdot 2H_2O$ solution, having appropriate concentration, was added to the prepared material, followed by drying, similar to the previous step. The catalyst was then calcined at 1123 K for 15 h and the resulting powder was pelletized, crushed and sieved to 30–35 mesh.

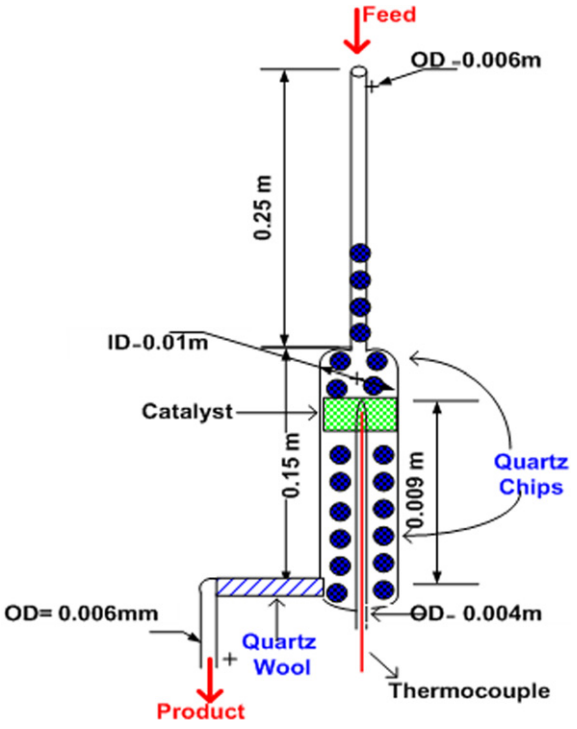

Figure 1: Schematic of the quartz fixed bed reactor.

The Atomic Absorption Spectrophotometry (AAS) (A- Analyst 200) and inductively coupled plasma (ICP) (Wear Metal Analyzer—Plasma 400) analyses, show that the components wt% in the prepared catalyst are 1.4 wt% Na–2.1 wt% W–1.5 wt% Mn/SiO_2. The details of the catalyst characterizations are given in our previous article [31].

2.2. Experimental set up

A micro catalytic fixed bed reactor, made of quartz, with 0.01 m inner diameter, located in a vertical furnace with two electric heaters, was used to measure the performance of the catalyst under various conditions (Figure 1). The diameter of the pre-catalytic and post-catalytic zone was reduced to 6 mm and filled with quartz chips (mesh 20/25), in order to minimize the contribution of any gas-phase reactions. An amount of 4 gr catalyst was placed at the hottest part of the reactor. The reaction temperature was measured using the Ni/Cr–Ni/Al thermocouple within the quartz thermo-well, which was inserted into the center of the catalyst bed. In all experiments, the reactant gases, CH_4, O_2 and N_2, were co-fed into the reactor and their flow rates were controlled with mass flow controllers. The reactor effluent gases, after removing water by condensation at 268 K, were analyzed by an online gas chromatograph (CHROMPACK CP-9000) with a thermal conductivity detector for detecting O_2, N_2, CH_4, CO, CO_2, C_2H_4 and C_2H_6. A flame ionization detector was used for detecting the higher hydrocarbons. The pressure of the system was controlled using a pressure controller.

The CH_4 conversion (X_{CH_4}), selectivity ($S_{C_{2+}}$) and yield ($Y_{C_{2+}}$) of the product hydrocarbons are calculated using the following equations: see Eqs. (1)–(3) is given in Box I.

Table 1 presents the experimental data which are used in this work for development of ANN and RSM models.

$$X_{CH_4}\% = \frac{\text{moles of } CH_4 \text{ converted}}{\text{moles of } CH_4 \text{ in feed}} * 100, \quad (1)$$

$$S_{C_{2+}}\% = \frac{\sum n(\text{moles of } C_n \text{ hydrocarbons in products})}{(\text{moles of CO} + \text{moles of } CO_2 + \sum n(\text{moles of } C_n \text{ hydrocarbons})) \text{ in products}} * 100 \quad n \geq 2, \quad (2)$$

$$Y_{C_{2+}}\% = X_{CH_4} * S_{C_{2+}} * 100. \quad (3)$$

Box I

Table 1: Experimental data at 0.4 MPa used in this study for development of ANN and RSM models.

T(K)	Feed's GHSV(h^{-1})	Feed's CH_4/O_2 molar ratio	Feed's N_2 mole%	X_{CH_4}%	$S_{C_{2+}}$%
983.00[a]	14285.00	5.97	0.07	22.41	75.25
973.00[a]	12766.00	5.99	0.03	8.18	66.42
998.00[a]	15790.00	3.97	10.17	32.32	72.68
948.00[a]	14285.00	5.97	0.07	3.93	52.22
948.00[a]	15790.00	3.96	19.63	30.62	70.97
958.00[a]	12766.00	3.12	20.41	34.77	61.85
973.00[a]	12766.00	4.09	0.12	29.24	69.79
1023.00[a]	14285.50	3.03	19.39	35.74	62.32
998.00[a]	14285.00	3.94	0.19	28.82	65.54
998.00[a]	14285.50	3.09	10.38	35.99	63.31
963.00[a]	14285.50	4.08	10.47	31.67	72.51
998.00[a]	12766.00	3.13	9.42	34.62	61.55
948.00[a]	12766.00	3.13	9.42	34.62	61.55
973.00[a]	15790.00	3.97	10.17	32.32	72.68
948.00[a]	15790.00	3.13	10.33	36.11	63.93
998.00[a]	14285.50	3.03	19.39	35.74	62.32
998.00[a]	14285.00	3.15	0.02	35.27	62.53
973.00[a]	14285.00	5.97	0.07	17.04	70.12
998.00[a]	12766.00	5.99	0.03	22.57	75.18
963.00[a]	14285.00	3.15	0.02	35.27	62.53
973.00[a]	15790.00	3.15	18.86	35.79	65.90
973.00	15790.00	3.96	19.63	31.74	72.41
948.00	12766.00	5.99	0.03	3.42	53.48
948.00	12766.00	4.09	0.12	27.06	68.78
1023.00	14285.50	3.09	10.38	35.99	63.31
998.00	15790.00	3.13	10.33	36.11	63.93
998.00	15790.00	3.96	19.63	31.74	72.41
953.00	12766.00	4.09	10.43	30.62	71.06
998.00	14285.00	5.97	0.07	22.41	75.25
1023.00	15790.00	6.12	0.03	22.00	75.39
948.00	15790.00	3.20	0.00	35.14	63.86
948.00	15790.00	3.97	0.16	27.91	68.67
1023.00	15790.00	3.97	0.16	29.99	67.71
1023.00	14285.50	4.08	10.47	31.67	72.51
1023.00	15790.00	3.96	19.63	31.74	72.41
998.00	15790.00	3.15	18.86	35.79	65.90
998.00	15790.00	3.97	0.16	29.99	67.71
948.00	12766.00	3.19	0.00	33.80	61.01
1023.00	15790.00	3.20	0.00	35.14	63.86
998.00	15790.00	6.12	0.03	22.00	75.39
998.00	12766.00	3.19	0.00	33.80	61.01
1023.00	12766.00	3.12	20.41	34.77	61.85
1023.00	15790.00	3.13	10.33	36.11	63.93
1023.00	12766.00	4.09	10.43	30.62	71.06
973.00	14285.00	3.94	0.19	28.82	65.54
1023.00	14285.00	5.97	0.07	22.41	75.25
1023.00	14285.00	3.15	0.02	35.27	62.53
943.00	14285.50	4.08	10.47	23.73	67.31
973.00	15790.00	6.12	0.03	22.00	75.39
998.00	12766.00	4.09	0.12	29.24	69.79
988.00	12766.00	5.99	0.03	21.71	74.56
1023.00	15790.00	3.97	10.17	32.32	72.68
1023.00	12766.00	5.99	0.03	22.57	75.18
948.00	15790.00	3.97	10.17	31.33	71.99
948.00	14285.50	3.03	19.39	35.74	62.32
1023.00	14285.00	3.94	0.19	28.82	65.54
998.00	14285.50	4.08	10.47	31.67	72.51
1023.00	12766.00	3.19	0.00	33.80	61.01

Table 1 (*continued*)

T(K)	Feed's GHSV(h^{-1})	Feed's CH_4/O_2 molar ratio	Feed's N_2 mole%	X_{CH_4}%	$S_{C_{2+}}$%
943.00	12766.00	4.09	10.43	6.38	48.87
1023.00	12766.00	3.13	9.42	34.62	61.55
973.00	15790.00	3.97	0.16	29.99	67.71
1023.00	15790.00	3.15	18.86	35.79	65.90
1023.00	12766.00	4.09	0.12	29.24	69.79
948.00	12766.00	3.12	20.41	4.98	42.55
998.00	12766.00	3.12	20.41	34.77	61.85
948.00	14285.50	3.09	10.38	35.99	63.31
948.00	14285.00	3.94	0.19	27.98	66.55
998.00	15790.00	3.20	0.00	35.14	63.86
998.00	12766.00	4.09	10.43	30.62	71.06
948.00	15790.00	6.12	0.03	3.43	55.68
948.00	15790.00	3.96	19.63	19.00	79.00
973.00	15790.00	3.96	19.63	24.00	81.30
1023.00	15790.00	3.96	19.63	24.00	81.30

[a] These data were used as test set.

3. Artificial Neural Network (ANN)

ANNs are widely accepted as an approach offering an alternative way to tackle complex and ill-defined problems. The Back-Propagation (BP) neural network is a widely used supervised neural network modeling. A typical BP neural network is a single direction multilayer neural network. It contains one input layer and one or more hidden layers. Each layer comprises one or more nodes, called neurons. A neuron in a certain layer receives information from all the neurons of the preceding layer. It sums the information, weighted by the factor corresponding to the connection and the bias of the network, and transmits this sum to all the neurons of the next layer using an activation function (e.g. the sigmod function). The number of nodes in the input and output layers represent, effectively, the number of variables used in the prediction and the number of variables to be predicted. However, the appropriate number of hidden layers and nodes on these hidden layers cannot be known in advance and are normally set through trial and error. Two steps are required to build a back-propagation neural network:

Step 1: Network architecture selection including:

(a) Determination of the type of transfer function (sigmoid, hyperbolical tangent or linear) in each layer.

(b) Determination of the number of hidden layers and nodes.

Step 2: Validation of the model.

The network architecture is determined by trial and error during the training phase, while validation of the model is performed via evaluating model performance using the test data.

4. Response surface methodology

RSM is a collection of mathematical and statistical techniques useful for the modeling and analysis of problems. So, it

can be used for cases in which complex relations are involved. The method involves relating a single output variable to a number of input variables. Adequacy of the proposed model is revealed using the diagnostic checking tests provided by analysis of variance (ANOVA). In this study, the full quadratic model (Eq. (4)) was used to correlate the dependent and independent variables:

$$Y = b_0 + \sum_{i=1}^{n} b_i X_i + \sum_{i=1}^{n} b_{ii} {X_i}^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} X_i X_j, \quad (4)$$

where Y is the response variable (methane conversion or C_{2+} selectivity), b_0 is the offset term (constant), b_i are regression coefficient for linear effects, b_{ii} are the quadratic coefficients, b_{ij} are the interaction coefficients, n is the number of independent variables and X_i are the actual values of the independent variables.

5. Multi objective optimization

The quadratic model of RSM can be easily optimized using conventional gradient-based methods. These optimization methods require the objective function to be continuous, differentiable and more importantly smooth, so, they cannot be used efficiently for optimizing the input space of an ANN model.

One of the Global Optimization Algorithms (GOA) is the Genetic Algorithm (GA). GA is an intelligent stochastic optimization technique based on the mechanism of natural selection and genetics. It starts with a set of trial solutions (called populations) and then the final solution evolves iteratively by applying some genetic operators (e.g., selection, cross over and mutation). Based on the GA ability, it can be used to optimize the input space ANN models. A notable characteristic of this algorithm is that it can find the region of the optimal values, quickly; however, the ability of an accurate search in this region is not satisfactory for complex systems. Therefore, GA is often hybridized with a Local Optimization Algorithm (LOA) to improve its performance as a global optimization technique.

In the present work, the Pareto optimal solutions are obtained from multi objective optimization using the post-hybridization of GA with a LOA. MATLAB GA optimization toolbox (Version 7.6.0324) using the function "fgoalattain" is used as the hybrid local search method [32]. That uses the final solution from GA as its initial point.

The optimal problem could be expressed in the following formula:

$$f(x_i) = \max(X_{CH_4}\%), \quad (5)$$
$$g(x_i) = \max(S_{C_{2+}}\%),$$

where:

$x_i = T(\mathrm{K}), CH_4/O_2, \mathrm{GHSV}(h^{-1})$ and N_2 mole%.

For the mentioned multi objective optimization problem, the decision variables (operating parameters) are chosen from the corresponding bounds that are already listed in Table 1.

6. Results and discussion

6.1. Predictive modeling with ANN

In order to reduce the time consuming trial and error steps for suitable numbers of hidden layers and nodes, and to increase the accuracy of the models, separate networks for the prediction of methane conversion (X_{CH_4}) and C_{2+} selectivity ($S_{C_{2+}}$) are developed. The networks were built with the neural network toolbox, MATLAB software. The back-propagation training was achieved using the Levenberg–Marquadt algorithm (function 'trainlm'), principally because of its fast convergence rate for moderately sized networks.

Table 2: Statistical results and details of the neural network models used for prediction of $X_{CH_4}\%$ and $S_{C_{2+}}\%$.

	Model	
	$S_{C_{2+}}\%$	$X_{CH_4}\%$
No. of hidden layer	1	2
No. of nodes	4-6-1	4-6-2-1
Type of transfer function	logsig–purelin	tansig–tansig–purelin
R^2 (train)	0.994	1.00
MSE (train)	0.272	0.006
AARE%(train)	0.612	0.237
R^2 (test)	0.976	0.998
MSE (test)	0.861	0.209
AARE% (test)	1.05	1.479

Note: Total number of weights and bias adjusted during the training period is 37 and 47 for the C_{2+} selectivity and methane conversion networks, respectively.

For the data set considered in the present study, the input variables, as well as the target variables, are first normalized into the range of −1 to 1, using the following formula:

$$X_n = \frac{2(X - X_{\min})}{X_{\max} - X_{\min}} - 1, \quad (6)$$

where $X_{\min}$ and $X_{\max}$ are the minimum and maximum values of the raw data. After normalization of experimental data (73 data points), they are randomly divided into two subsets: training set (70% of total data) and test set (30% of total data). The training set is used to estimate the neural network parameters (weight and biases) and the test set is used to validate the networks.

The performance of each network is evaluated by statistical criteria. The statistical criteria consist of correlation coefficient (R^2), Mean Square Error (MSE) and Average Absolute Relative Error (AARE). The R^2 statistic measures the linear correlation between actual and predicted parameter values. The MSE and AARE values are used to quantify the error between the observed and predicted values. The optimal value for R^2 is 1.0, and for MSE and AARE is 0.0. These statistical measures are defined as:

$$R^2 = 1 - \frac{\sum_{i=1}^{n} (X_{obs} - X_{cal})^2}{\sum_{i=1}^{n} (X_{obs} - \overline{X}_{cal})^2}, \quad (7)$$

$$\mathrm{MSE} = \frac{1}{n} \sum_{h=1}^{n} (X_{obs} - X_{cal})^2, \quad (8)$$

$$\mathrm{AARE} = \frac{1}{n} \sum \left| \frac{X_{obs} - X_{cal}}{X_{obs}} \right| * 100, \quad (9)$$

where, n is the number of data points, $\overline{X}$ the average of X over the n samples, and X_{obs} and X_{cal} are the actual and predicted values.

The final networks were selected on the basis of the lowest errors (MSE and AARE) and highest R^2 value on the training and test sets of data. The results are presented in Table 2.

According to the obtained results, the final network for prediction of C_{2+} selectivity consists of four neuron input layers, six neurons in the hidden layer and one neuron in the output

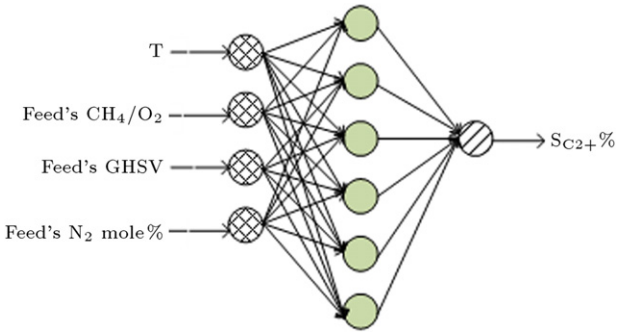

Figure 2: Architecture of the neural network model used in this study for prediction of SC_{2+}%.

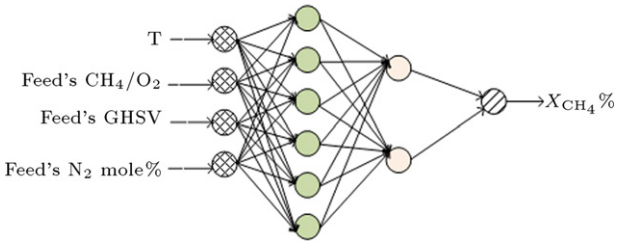

Figure 3: Architecture of the neural network model used in this study for prediction of X_{CH_4}%.

layer, as shown in Figure 2. The activation function between the input and the hidden layer was 'logsig', as given by:

$$f(x) = \frac{1}{1+e^{-x}}. \tag{10}$$

And the one between the hidden layer and the output layer was 'pureline', given by:

$$f(x) = x. \tag{11}$$

The final network for prediction of CH_4 conversion consists of one input layer with four neurons, two hidden layers with six and two neurons, respectively, and one output layer with one node, as shown in Figure 3. The activation function used for the hidden layers is 'tansig', given by:

$$f(x) = \frac{1-e^{-x}}{1+e^{-x}}, \tag{12}$$

and 'pureline' for the output layer.

The inputs of the selected neural networks were feed methane to oxygen molar ratio, feed GHSV, feed diluents amounts and reaction temperature, and output of the developed networks were C_{2+} selectivity and CH_4 conversion, respectively.

The weight and bias values of each layer for final models are shown in Tables 3 and 4.

6.2. Predictive modeling with RSM

MATLAB software version 7.6.0324 was used for regression analysis of the experimental data to calculate the model coefficients and also for evaluation of the statistical significance of the models. The RSM models were trained and tested with the same data used for development of the neural network models. However, here, no normalization was done.

Table 3: Bias and weights of the methane conversion network.

j	b_j	k	b_k	l	b_l
1	1.9581	1	−1.7045	1	−1.1107
2	−0.5607	2	0.7044		
3	−1.2972				
4	0.2590				
5	−5.7948				
6	3.0097				

w_{ij}	**1**	**2**	**3**	**4**
1	−2.2272	−2.1889	0.1811	−0.0188
2	−2.2244	1.5241	1.1355	0.1244
3	−3.8495	1.7432	−0.5784	−0.0096
4	0.4493	−1.0740	1.5847	6.1249
5	−0.7259	0.6185	−0.5221	−5.0198
6	1.2996	2.6913	0.1885	0.1610

w_{ij}	**1**	**2**	**3**	**4**	**5**	**6**
1	0.9905	0.1447	0.1438	0.0037	0.0322	−0.0970
2	−0.0301	0.1179	2.8829	0.4337	−4.3413	−1.1219

w_{ij}	**1**	**2**
1	1 6211	2 9295

Table 4: Bias and weights of the C_{2+} selectivity network.

j	b_j	k	b_k
1	5.6548	1	−2.2249
2	8.7851		
3	−0.4085		
4	−5.3775		
5	18.2831		
6	0.2401		

w_{ij}	**1**	**2**	**3**	**4**
1	−5.6623	1.3756	7.2411	0.1046
2	−13.0869	0.3800	−0.9592	−9.6449
3	−5.7371	−3.9534	−3.5057	6.7477
4	5.0728	−4.7809	0.3336	0.1757
5	−2.2146	−3.2239	2.0586	15.4472
6	−0.9206	−0.0618	−0.1198	−0.0191

w_{ij}	**1**	**2**	**3**	**4**	**5**	**6**
1	−0.2970	−1.2498	−0.0551	−2.2587	7.0653	−4.0093

The final models are as follows:

$$\begin{aligned} X_{CH_4}\% = {} & -1844.57 + 4.72X_1 + 0.05X_2 - 73.28X_3 - 6.75X_4 \\ & - 3.69 \times 10^{-5}X_1X_2 + 0.08X_1X_3 + 0.01X_1X_4 \\ & + 7.17 \times 10^{-5}X_2X_3 + 1.13 \times 10^{-4}X_2X_4 - 0.07X_3X_4 \\ & - 3.16 \times 10^{-3}{X_1}^2 - 7.54 \times 10^{-7}{X_2}^2 \\ & + 0.59{X_3}^2 - 0.04{X_4}^2, \end{aligned} \tag{13}$$

$$\begin{aligned} S_{C_{2+}}\% = {} & -1273.78 + 3.16X_1 + 0.04X_2 - 47.99X_3 - 5.88X_4 \\ & - 4.18 \times 10^{-5}X_1X_2 + 0.09X_1X_3 + 4.06 \times 10^{-3}X_1X_4 \\ & + 1.53 \times 10^{-4}X_2X_3 + 1.66 \times 10^{-4}X_2X_4 + 0.24X_3X_4 \\ & - 2.202 \times 10^{-3}{X_1}^2 - 3.63 \times 10^{-7}{X_2}^2 \\ & - 1.65{X_3}^2 - 0.01{X_4}^2, \end{aligned} \tag{14}$$

where X_1, X_2, X_3 and X_4 are the reaction temperature (°C), feed GHSV(h^{-1}), feed methane to oxygen molar ratio and feed diluents (N_2) amounts (mole%), respectively.

Table 5: Analysis of variance results for RSM model of methane conversion.

Source	Degree of Freedom (DF)	Sum of Square (SS)	Mean Square (MS)	F-value	p-value
Regression	14	2826.29	201.88	9.52	<0.0001
Residual	37	766.05	20.7		
Total	51	3592.34			
$R^2 = 0.79$					

Table 6: Analysis of variance results for RSM model of hydrocarbons selectivity.

Source	Degree of Freedom (DF)	Sum of Square (SS)	Mean Square (MS)	F-value	p-value
Regression	14	2144.59	153.19	8.07	<0.0001
Residual	37	702.53	18.99		
Total	51	2847.12			
$R^2 = 0.75$					

The significance of each model was assessed from determination coefficient (R^2), which was found to be 0.79 and 0.75 for X_{CH_4}% and $S_{C_{2+}}$% models, respectively. These values imply that 79% and 75% of the total variation in methane conversion and C_{2+} selectivity can be explained by the developed models. In addition, the correlation coefficient (R), 0.89 and 0.87, for the models (X_{CH_4}% and $S_{C_{2+}}$%), signifies an acceptable correlation between the experimental and predicted values.

The ANOVA technique is used to check the adequacy of the developed models. First, the F-ratio of the model is calculated as a ratio of mean square regression error and mean square residual error. Then, the calculated F-ratio of the model is compared with the corresponding tabulated value (F-table) for a specified level of confidence. If the calculated value of the F-ratio is greater than the F-table (i.e.: $f(P-1, N-P, \alpha)$), then, a statistically significant regression model is obtained. In the F-table, $P-1$ and $N-P$ are degrees of freedom for regression and residual, respectively, and α is specified level of significance. Also, P is the number of regression model parameters and N is the number of experimental data used for development of the model.

Results obtained by the ANOVA technique are shown in Tables 5 and 6. As can be seen, the computed F-ratios are 9.52 (X_{CH_4}%) and 8.07 ($S_{C_{2+}}$%) and both of these values exceed the F-table (f (14, 37, 0.95) =1.97) based on 95% confidence level. Also, the calculated probability values (p-value) from the analysis of two models are <0.0001. Therefore, regarding the F-ratios and p-values of the developed models, it can be concluded that the developed models give almost good prediction, and were significant at a high confidence level.

In the multiple regression analysis, the p-value and t-value are used to check the significance of each parameter of the model. The smaller the p-value, or the greater the magnitude of t-value, indicates that the model terms are significant. If the p-value of a parameter is larger than 0.05, the confidence level of this parameter is below 95%, and if the p-value is equal to 1, the parameters do not affect the response variable. In usual cases, the term with a p-value > 0.05 can be eliminated from the model. However, in this study, the insignificant terms are still maintained to support the hierarchical nature of the developed models.

From the above discussion, the results in Table 7 can be considered the examination basis of the effect of the operating parameters on the OCM reaction performance at 0.4 MPa.

Table 7: t-value and p-value of each variable in the developed RSM models.

Model term	RSM model for prediction of X_{CH_4}%		RSM model for prediction of of $S_{C_{2+}}$%	
	t-value	p-value	t-value	p-value
Constant	−3.16	0.003	−2.28	0.029
X_1	3.10	0.004	2.17	0.037
X_2	2.06	0.046	1.80	0.080
X_3	−3.29	0.002	−2.25	0.031
X_4	−2.78	0.008	−2.53	0.016
X_1X_2	−2.28	0.028	2.70	0.010
X_1X_3	3.47	0.001	3.79	0.001
X_1X_4	2.78	0.009	1.44	0.158
X_2X_3	0.13	0.898	0.29	0.776
X_2X_4	1.52	0.138	2.31	0.026
X_3X_4	−0.30	0.764	1.00	0.322
X_1^2	−2.94	0.006	−1.96	0.057
X_2^2	−1.07	0.293	0.54	0.595
X_3^2	0.51	0.612	−1.50	0.142
X_4^2	−2.09	0.043	−0.50	0.617

From Table 7, the linear term of feed methane to oxygen molar ratio (X_3) and its interaction with reaction temperature (X_1X_3) have the largest effect on methane conversion, at 99.95% confidence level of significance, as indicated by the lowest p-value (<0.005) and the highest absolute t-value (3.29 and 3.47). Next, the linear and quadratic terms of the reaction temperature (X_1 and X_1^2) show a substantial significant effect at 99% confidence level (p-value < 0.01). The linear term of feed GHSV (X_2) and its interaction term of reaction temperature with feed GHSV (X_1X_2), the quadratic and linear terms of feed diluents amounts (X_4^2 and X_4) and its interaction term with reaction temperature (X_1X_4) are at 95% confidence level (p-value < 0.05). Next, in order of significance, is the interaction term of feed GHSV with feed diluents amounts (X_2X_4), which is statistically significant at 80% confidence level.

As illustrated, interaction terms of the reaction temperature with feed methane to oxygen molar ratio (X_1X_3) has the largest effect on C_{2+} selectivity, because it has the lowest p-value (0.001) and the highest t-value (3.79). Also, in this case, X_2, X_1X_4, X_2X_3, X_3X_4, X_1^2, X_2^2, X_3^2 and X_4^2 could be considered less significant in affecting C_{2+} selectivity, as their p-values are greater than 0.05.

7. Comparison of regression analysis and ANN models

The developed ANN and regression models were compared for all experimental data sets. The R^2, R^2_{adj}, MSE, AARE% and variance for the developed models were calculated and listed in Table 8. As shown in Table 8, the developed ANN models have the lowest errors (MSE, AARE% and variance) and highest determination coefficients (R^2 and R^2_{adj}), with respect to the developed RSM models. Figure 4 shows the predictive values by ANN and RSM models versus the experimental values (test data set) for methane conversion and C_{2+} selectivity, respectively. As can be seen, the predicted values by ANN models were close to the experimental values. Thus, the comparison between the developed models shows that ANN models have a much better prediction than the regression models. This higher predictive accuracy of ANN models can be attributed to their universal ability to capture the non-linearity of the system, whereas the developed RSM models non-linearity is limited to its quadratic terms.

Table 8: Comparison of predictive ability of RSM and ANN.

Parameters	Train data				Test data			
	ANN		RSM		ANN		RSM	
	X_{CH_4}	$S_{C_{2+}}$	X_{CH_4}	$S_{C_{2+}}$	X_{CH_4}	$S_{C_{2+}}$	X_{CH_4}	$S_{C_{2+}}$
R^2	1.00	0.99	0.79	0.75	1.00	0.98	0.73	0.62
R^2_{adj}	1.00	0.98	0.71	0.66	*1.00*	1.03	0.10	−0.27
MSE	0.01	0.27	14.73	13.51	0.21	0.86	24.11	13.34
AARE%	0.24	0.61	18.61	4.31	1.48	1.05	19.67	4.53
Variance	0.06	0.94	20.70	18.99	−0.17	−1.13	84.39	46.69

Table 9: Pareto optimal solutions.

Operating conditions				Performance		
X_{N_2} (mole%)	CH_4/O_2	GHSV(h^{-1})	T (°K)	X_{CH_4}%	$S_{C_{2+}}$%	$Y_{C_{2+}}$%
20.00	3.52	15790.00	989.00	34.54	69.22	23.91
20.00	3.15	15790.00	948.00	35.75	65.52	23.42
20.00	3.33	15790.00	982.40	35.20	67.51	23.76
20.00	3.38	15790.00	986.79	35.06	67.99	23.84
20.00	3.27	15790.00	949.36	35.45	66.59	23.60
20.00	3.45	15790.00	988.63	34.85	68.55	23.89
20.00	3.49	15790.00	987.53	34.70	68.90	23.90
20.00	3.24	15790.00	986.70	34.43	66.78	23.66
20.00	3.16	15790.00	987.05	35.58	66.09	23.52
20.00	3.31	15790.00	985.15	35.27	67.35	23.75
20.00	3.50	15790.00	986.78	34.64	69.02	23.91
20.00	3.47	15790.00	987.63	34.78	68.72	23.90
20.00	3.35	15790.00	983.03	35.14	67.73	23.80
20.00	3.42	15790.00	988.86	34.94	68.33	23.87
20.00	3.27	15790.00	988.07	35.37	67.00	23.70
20.00	3.20	15790.00	948.00	35.66	65.88	23.49
20.00	3.18	15790.00	948.00	35.69	65.76	23.47
20.00	3.25	15790.00	948.34	35.54	66.29	23.56
20.00	3.40	15790.00	988.43	35.00	68.16	23.86
20.00	3.52	15790.00	989.06	34.54	69.22	23.91

8. Optimization

In this work, ANN models with a hybrid genetic algorithm were used to obtain the Pareto optimal set for simultaneous maximization of CH_4 conversion and C_{2+} selectivity of the OCM process. The optimal operating set derived using the developed ANN models is presented in Table 9. Table 9 shows the optimal results for simultaneous maximization of CH_4 conversion and C_{2+} selectivity when the C_{2+} yield is greater than 23%. It shows that optimal results can be achieved by changing the operating parameters of feed methane to oxygen molar ratio and reaction temperature from 3.15 and 948 K to 3.52 and 989 K, respectively, while the feed N_2 mole% and feed GHSV have constant values (20 mole% and 15790 h^{-1}). Enhancement of C_{2+} yield is necessary for the OCM process to be commercialized. Table 9 shows that the maximum C_{2+} yield of 23.91% was estimated at the feed diluents amounts of 20 mole%, the methane to oxygen molar ratio of 3.5, GHSV of 15 790 h^{-1}, and reaction temperature of 987 K. Therefore, an additional experiment was carried out in order to validate the optimum yield result.

A comparison of maximum predicted C_{2+} yield with the developed ANN models and relevant experimental result is given in Table 10. The comparison shows that the predicted and experimental C_{2+} yields for the developed ANN models were 23.9% and 22.8%, respectively, and the predicted error in optimum yield by ANN models was 4.8%. The low errors between the predicted and observed values confirm that the ANN modeling, combined with hybrid genetic algorithm optimization, is a useful tool for optimization of the OCM process at elevated pressures.

Table 10: Comparison of optimized values and experimental results.

Estimated results[a](%)			Experimental results[a](%)			Relative error (%)		
X_{CH_4}	$S_{C_{2+}}$	$Y_{C_{2+}}$	X_{CH_4}	$S_{C_{2+}}$	$Y_{C_{2+}}$	X_{CH_4}	$S_{C_{2+}}$	$Y_{C_{2+}}$
34.6	69.0	23.9	34.0	67.1	22.8	1.9	2.8	4.8

[a] Operating conditions: N_2 = 20 mole%, CH_4/O_2 = 3.5, GHSV = 15790.0 h^{-1} and T = 987 K.

9. Conclusions

This study reveals that the oxidative coupling of methane (OCM) operated at 0.4 MPa has a commercial potential. Therefore, optimal operating conditions under this pressure must be determined for industrial purposes. However, it is difficult to establish a mathematical model based on the fundamental laws of chemical kinetics due to the complexity of its homogeneous–heterogeneous kinetics. In this work, the experimental data for OCM reactions over the Na–W–Mn/SiO_2 catalyst was obtained at 0.4 Mpa and used to develop predictive models based on RSM and ANN techniques.

These study results show that the mean square error and average absolute relative error for the developed neural network models for predicting methane conversion and C_{2+} selectivity were much smaller than those for the developed RSM models. This indicated that the ANN models have a much higher modeling ability than the RSM based models. A combination of developed ANN models with the hybrid genetic algorithm has been used to obtain the optimal values of operating conditions for simultaneous maximization of CH_4

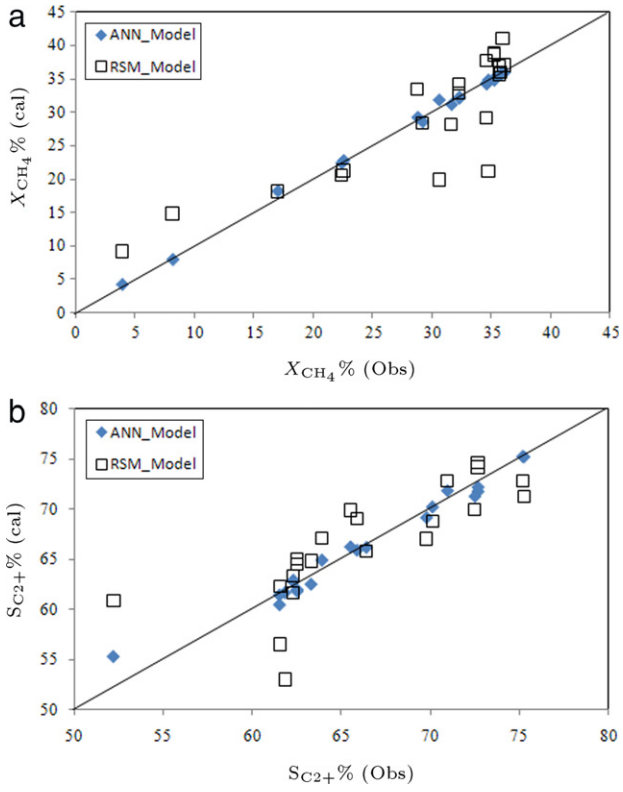

Figure 4: Comparison of RSM and ANN model for prediction of test data set (a) CH_4 conversion, (b) C_{2+} selectivity.

conversion and C_{2+} selectivity of the OCM process at 0.4 MPa. The predicted operating conditions were experimentally tested to get actual CH_4 conversion and C_{2+} selectivity. The good agreement between the predicted and observed values, demonstrates the power and reliability of the ANN models and hybrid genetic algorithm for optimization of OCM reaction conditions. It was found that the C_{2+} yield of 22.8% can be obtained at 0.4 MPa, which is the highest reported performance for an OCM catalyst at high pressures. This result may encourage other research and development groups to intensify their efforts toward commercialization of OCM based processes.

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