

Different Tools on Multi-Objective Optimization of a Hybrid Artificial Neural Network – Genetic Algorithm for Plasma Chemical Reactor Modelling

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1. Introduction

Simultaneous modeling and optimization allows a cost-effective alternative to cover large number of experiments. The model should be able to improve overall process performance particularly for the complex process. A hybrid Artificial Neural Network - Genetic Algorithm (ANN-GA) was developed to model, to simulate, and to optimize simultaneously a catalytic-plasma reactor. The present contribution is intended to develop an ANN-GA method to facilitate simultaneous modeling and multi-objective optimization for co-generation of synthesis gas, C₂ and higher hydrocarbons from methane and carbon dioxide in a dielectric-barrier discharge (DBD) plasma reactor. The hybrid approach simplifies the complexity in process modeling the DBD plasma reactor.

A hybrid of ANN-GA method has been used for integrated process modelling and multi-objectives optimization. The detail hybrid algorithm for simultaneous modelling and multi-objective optimization has been developed in previous publication which focused on plasma reactor application (Istadi & Amin, 2005, 2006, 2007). They reported that the hybrid ANN-GA technique is a powerful method for process modelling and multi-objectives optimization (Nandi *et al.*, 2002, 2004; Ahmad *et al.*, 2004; Stephanopoulos & Han, 1996; Huang *et al.*, 2003; Radhakrishnan & Suppiah, 2004; Fissore *et al.*, 2004; Nandi *et al.*, 2002, 2004; Ahmad *et al.*, 2004; Kundu *et al.*, 2009; Marzbanrad & Ebrahimi, 2011; Bhatti *et al.*, 2011). The method is better than other technique such as response surface methodology (RSM) (Istadi & Amin, 2006, 2007), particularly for complex process model. The RSM proposes a quadratic model as empirical model for representing the effect of independent variables toward the targeting response. Therefore, all models which may not follow the quadratic trend are forced to the

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quadratic model. Disadvantage of the RSM method is then improved by the hybrid ANN-GA. In the later method, an empirical mathematical modelling of catalytic cracking was conducted by ANN strategy, while the multi-objectives optimization of operating conditions to reach optimal responses was performed using GA method.

In terms of single-response optimization applications, the selection of optimization method is very important to design an optimal catalyst as well as the relations between process parameters and catalytic performances (Wu *et al.*, 2002). Pertaining to the catalyst design, some previous researchers introduced ANN to design the catalysts (Hattori & Kito, 1991, 1995; Hou *et al.*, 1997). The ANN is feasible for modeling and optimization, and consequently, large number experiments can be avoidable (Wu *et al.*, 2002). According to the complex interaction among the catalyst compositions, the process parameters and the metal-support interaction with no clear reaction mechanism as in CO₂ OCM process, the empirical models are more useful in the catalyst design especially in the optimization studies. The reason is that the phenomenological modeling of interactions in the catalyst design is very complex. Unfortunately, a single-response optimization is usually insufficient for the real CO₂ OCM process due to the fact that most responses, i.e. methane conversion, product selectivity and product yield, are dependent during the process. Therefore, simultaneous modeling and multi-objective optimization techniques in complex plasma reactor is worthy. A simultaneous multi-objective optimization is more realistic than a single-response from reliability point of view. Empirical and pseudo-phenomenological modeling approaches were employed by previous researchers (Wu *et al.*, 2002; Larentis *et al.*, 2001; Huang *et al.*, 2003) for optimizing the catalytic process. The empirical modeling is efficient for the complex process optimization, but the drawback is that the model has no fundamental theory or actual phenomena meaning.

Pertaining to multi-objective optimization, a graphical multi-responses optimization technique was implemented by previous researchers for xylitol crystallization from synthetic solution (de Faveri *et al.*, 2004), but it was not useful for more than two independent variables or highly nonlinear models. In another study, a generalized distance approach technique was developed to optimize process variables in the production of protoplast from mycelium (Muralidhar *et al.*, 2003). The optimization procedure was carried out by searching independent variables that minimize the distance function over the experimental region in the simultaneous optimal critical parameters. Recently, robust and efficient technique of elitist Non-dominated Sorting Genetic Algorithm (NSGA) was used to obtain solution of the complex multi-objective optimization problem (Huang *et al.*, 2003; Nandasana *et al.*, 2003; Zhao *et al.*, 2000; Nandi *et al.*, 2004). A hybrid GA with ANN was also developed (Huang *et al.*, 2003) to design optimal catalyst and operating conditions for O₂ OCM process. In addition, a comprehensive optimization study of simulated moving bed process was also reported using a robust GA optimization technique (Zhang *et al.*, 2002b).

Several methods are available for solving multi-objective optimization problem, for example, weighted sum strategy (The MathWorks, 2005; Youness, 2004; Istadi, 2006), ϵ -constraint method (Yu *et al.*, 2003; The MathWorks, 2005; Youness, 2004), goal attainment method (Yu *et al.*, 2003; The MathWorks, 2005), NSGA (Nandasana *et al.*, 2003; Zhang *et al.*, 2002b; Yu *et al.*, 2003), and weighted sum of squared objective function (WSSOF) (Istadi & Amin, 2006b, 2007; Istadi, 2006) to obtain the Pareto set. The NSGA method has several advantages (Zhang *et al.*, 2002b): (a) its efficiency is relatively insensitive to the shape of the

Pareto-optimal front; (b) problems with uncertainties, stochasticities, and discrete search space can be handled efficiently; (c) spread of the Pareto set obtained is excellent, and (d) involves a single application to obtain the entire Pareto set. Among the methods, the NSGA is the most powerful method for solving a complex multi-responses optimization problem. In the multi-objective optimization of the CO₂ OCM process, the goal attainment combined with hybrid ANN-GA method was used to solve the optimization of catalytic-plasma process parameters. The multi-objective optimization strategy was combined simultaneously with ANN modelling and GA optimization algorithm. The multi-objective optimization deals with generation and selection of non-inferior solution points or Pareto-optimal solutions of the responses / objectives corresponding to the optimal operating parameters. The DBD plasma-catalytic coupling of methane and carbon dioxide is an intricate process within the plasma-catalytic reactor application. A hybrid ANN-GA modelling and multi-objective optimization was developed to produce a process model that simulated the complex DBD plasma – catalytic process. There were no previous researchers focused on the simultaneous modelling and multi-objective optimization of DBD plasma – catalytic reactor using the hybrid ANN-GA.

The objective of this chapter is to model and to optimize the process performances simultaneously in the DBD plasma-catalytic conversion of methane to higher hydrocarbons such that the optimal process performances (CH₄ conversion and C₂ hydrocarbons yield) are obtained at the given process parameters. In this Chapter, multi-objective optimization of two cases, i.e. C₂ hydrocarbon yield and C₂ hydrocarbons selectivity, and C₂ hydrocarbons yield and CH₄ conversion, to produce a Pareto Optimal solution is considered. In the process modeling, a number of experimental data was needed to validate the model. The ANN-based model required more example data which were noise-free and statistically well-distributed. Therefore, design of experiment was performed using central composite design with full factorial design for designing the training and test data sets. The method was chosen in order to provide a wider covering region of parameter space and good consideration of variable interactions in the model. This chapter is organized according to sections 1, 2, 3 and 4. After Introduction in section 1, section 2 covers design of experiment and strategy for simultaneous modeling and optimization including hybrid ANN-GA algorithm. In section 3, multi-objective optimization of methane conversion to higher hydrocarbons process over plasma – catalytic reactor is applied. In this section, ANN simulation of the DBD plasma – catalytic reactor performance is also presented with respect to the two cases. The final section, section 4 offers conclusions about the chapter.

2. Design of experiment, modeling, and optimization strategies

2.1 Central composite design for design of experiment

Central Composite Design for four factors was employed for designing the experimental works in which variance of the predicted response Y at some point X is only a function of distance from the point to the design centre (Montgomery, 2001). Hence, the variance of Y remained unchanged when the design is rotated about the centre. In the design, standard error, which depends on the coordinates of the point on the response surface at which Y is evaluated and on the coefficients β , is the same for all points that are same distance from the central point. The value of a for star point with respect to design depends on the number of

points in the factorial portion of the design which is given in Equation (1) (Montgomery, 2001; Clarke & Kempson, 1997).

$$a = (n_c)^{1/4} \quad (1)$$

where n_c is number of points in the cube portion of the design ($n_c = 2^k$, k is number of factors). Since there are four parameters/factors in this experiment, the n_c number is equal to 2^4 (= 16) points, and $a=2$ according to Equation (1).

An experimental design matrix revealed in Table 1 consists of sets of coded conditions expressed in natural values (Istadi & Amin, 2006a) with a two-level full factorial design (n_c), star points (n_s) and centre points (n_0). Based on this table, the experiments for obtaining the responses of CH₄ conversion ($X(\text{CH}_4)$), C₂ hydrocarbons selectivity ($S(\text{C}_2)$) and C₂ hydrocarbons yield ($Y(\text{C}_2)$) were carried out at the corresponding independent variables. Number experimental data were used for validating the hybrid ANN-GA model of the catalytic-plasma CO₂ OCM process. Sequence of the experimental work was randomized in order to minimize the effects of uncontrolled factors. The experimental data from catalytic-plasma reactor operation with respect to combination of four factors including their respected responses (plasma-catalytic reactor performances: CH₄ conversion, C₂ hydrocarbons selectivity, C₂ hydrocarbons yield, and H₂ selectivity) are presented in Table 2.

Factors	Range and levels				
	$-a$	-1	0	$+1$	$+a$
CH ₄ /CO ₂ Ratio (X_1), [-]	0.8	1.5	2.5	3.5	4.2
Discharge voltage (X_2), kV	12.5	13.5	15.0	16.5	17.5
Total feed flow rate (X_3), cm ³ /min	18	25	35	45	52
Reactor temperature (X_4), °C	81	150	250	350	418

Note: -1 (low level value); +1 (high level value); 0 (centre point); $+a$ and $-a$ (star points)

Table 1. Central Composite Design with fractional factorial design for the catalytic DBD plasma reactor (Istadi, 2006)

2.2 Simultaneous modelling and multi-objective optimization

The integrated ANN-GA strategy meets the objective based on two steps: (a) development of an ANN-based process model which has inputs of process operating parameters of plasma - catalytic reactor, and output(s) of process output/response variable(s), i.e. yield of C₂hydrocarbons or hydrogen, or methane conversion; and (b) development of GA technique for multi-objective optimization of the ANN model. Input space of the ANN model is optimized using the GA technique such that the optimal response(s) or objective(s) are obtained corresponding to the optimal process parameters. The developed simultaneous algorithm is presented in a hybrid Algorithm of ANN-GA schematically for simultaneous modeling and optimization.

In the GA, a population of strings (called chromosomes), which encode individual solutions towards an optimization problem, adjusts toward better solutions. The solutions are represented in binary strings. The evolution begins from a population of randomly

generated individuals and grows to produce next generations. In each generation, the fitness of each individual in the new population is evaluated and scored (recombination and mutation) to form a new population. During the fitness evaluation, the resulted ANN model is used. The new population is then used in the next iteration. The algorithm terminates when either a maximum generations number has been reached, or a best fitness level has been approached for the population. The multi-objective optimization can be formulated by converting the problem into a scalar single-objective optimization problem which is solvable by unconstrained single-response optimization technique. Many methods can be used for converting the problems into scalar optimization problem, such as weighted sum of squared objective functions (WSSOF), goal attainment, weighted sum strategy, and ϵ -constraint method.

Schematic diagram of the feed-forward ANN used in this model development is depicted in Figure 1. Detail stepwise procedure used for the hybrid ANN-GA modelling and multi-objectives optimization is modified from the previous publications (Istadi, 2006; Istadi & Amin, 2007). The modified algorithm is described in this section and is depicted schematically in Figure 2. The fit quality of the ANN model was checked by a correlation coefficient (R) or a determination coefficient (R^2) and Mean Square Error (MSE). The ANN model generated was repeated until the R^2 reached higher than 0.90. The commonly employed error function to check the fit quality of the model is the MSE as defined in Equation (2).

$$MSE = \frac{1}{N_p K} \sum_{i=1}^{i=N_p} \sum_{k=1}^{k=K} (t_{i,k} - y_{i,k})^2 \quad (2)$$

where N_p and K denote the number of patterns and output nodes used in the training, i denotes the index of the input pattern (vector), and k denotes the index of the output node. Meanwhile, $t_{i,k}$ and $y_{i,k}$ express the desired (targeted or experimental) and predicted values of the k^{th} output node at i^{th} input pattern, respectively.

With respect to the ANN modelling, a feed-forward ANN model was used in this model development which was trained using back-propagation training function. In general, four steps are developed in the training process: assemble the training data, create the network object, train the network, and simulate the network response to new inputs. The schematic of the feed-forward neural network used in the model development is depicted in Figure 1. As shown, the network consists of three layers nodes, i.e. input, hidden, and output layers comprising four numbers of each processing nodes. Each node in the input layer is linked to all nodes in the hidden layer and simultaneously the node in the hidden layer is linked to all nodes in the output layer using weighting connections (W). The weights are adjusted in the learning process in which all the patterns of input-output are presented in the learning phase repeatedly. In addition, the feed-forward neural network architecture also addresses the bias nodes which are connected to all nodes in subsequent layer, and they provide additional adjustable parameters (weights) for the fitting.

From Figure 1, W^H and W^O denote the weights between input and hidden nodes and between hidden and output nodes, respectively. Meanwhile, y^H and y^O denote the outputs vector from hidden and output layers, respectively. In this system, b^H and b^O signify the

scalar bias corresponding to hidden and output layers, respectively. The weighted input (W) is the argument of the activation/transfer function f , which produces the scalar output y . The activation function net input is a summing function (n^H or n^O) which is the sum of the weighted input (W^H or W^O) and the bias b . In order that the ANN network accurately approximates the nonlinear relationship existing between the process inputs and outputs, it needs to be trained in a manner such that a pre-specified error function is minimized. There are many learning algorithms available and the most popular and successful learning algorithm used to train multilayer network is back-propagation scheme. Any output point can be obtained after this learning phase, and good results can be achieved.

Process variables				Responses/ Dependent variables (%)			
CH ₄ /CO ₂ ratio (X ₁)	Discharge voltage (X ₂)	Total feed flow rate (X ₃)	Reactor Temperature (X ₄)	X(CH ₄) (Y ₁)	S(C ₂₊) (Y ₂)	S(H ₂) (Y ₃)	Y(C ₂₊) (Y ₄)
3.5	16.5	45	150	21.45	26.13	13.24	5.61
3.5	16.5	25	150	23.48	33.41	12.13	7.85
* 3.5	13.5	45	350	18.76	28.43	13.16	5.33
1.5	16.5	25	350	27.55	27.47	8.11	7.57
3.5	13.5	25	350	20.22	35.21	12.87	7.12
1.5	13.5	45	150	23.11	26.98	8.01	6.24
1.5	16.5	45	350	28.03	24.45	7.48	6.85
* 1.5	13.5	25	150	30.02	24.15	8.54	7.25
0.8	15.0	35	250	32.14	12.54	5.17	4.03
4.2	15.0	35	250	21.12	34.77	13.99	7.34
2.5	12.5	35	250	18.55	29.76	10.22	5.52
2.5	17.5	35	250	41.32	28.01	10.12	11.57
2.5	15.0	18	250	38.65	31.77	11.32	12.28
* 2.5	15.0	52	250	20.88	30.00	11.56	6.26
2.5	15.0	35	81	25.49	28.04	9.87	7.15
2.5	15.0	35	418	26.74	32.55	10.41	8.70
2.5	15.0	35	250	25.77	31.33	11.55	8.07
2.5	15.0	35	250	23.41	30.74	9.87	7.20
2.5	15.0	35	250	25.14	29.65	10.44	7.45
* 2.5	15.0	35	250	26.11	28.14	9.54	7.35

Note: X, S, and Y denote conversion, selectivity and yield, respectively, and C₂₊ comprises C₂H₄, C₂H₆, C₂H₂, C₃H₈.

* These data were used as test set.

X₁ (CH₄/CO₂ feed ratio); X₂ (Discharge voltage, kV); X₃ (Total feed flow rate, cm³/min); X₄ (Reactor wall temperature, °C); Pressure: 1 atm; Catalyst loading: 5 gram; Frequency: 2 kHz (pulse)

Table 2. Experimental data of hybrid catalytic DBD plasma reactor at low temperature (Istadi, 2006)

Therefore, an input vector from the training set is applied to the network input nodes, and subsequently outputs of the hidden and output nodes are computed. The outputs are computed as follows: (a) the weighted sum of all the node-specific input is evaluated, which is then transformed using a nonlinear activation function (f), such as tangent-sigmoid (tansig) and linear (purelin) transfer functions for hidden and output layers, respectively; (b) the outputs from the output nodes $\{y_{i,k}\}$ are then compared with their target values $\{t_{i,k}\}$, and the difference is used to compute the MSE (Equation 2); (c) upon the MSE computation, the weight matrices W^H and W^O are updated using the corresponding method (Levenberg-Marquardt) (Hagan & Menhaj, 1994; Yao *et al.*, 2005).

In the back-propagation training method, the input x and target t values were normalized linearly to be within the range $[-1 \ 1]$. The normalization of inputs and outputs leads to avoidance of numerical overflows due to very large or very small weights (Razavi *et al.*, 2003; Bowen *et al.*, 1998; Yao *et al.*, 2005). This normalization was performed to prevent mismatch between the influence of some input values to the network weights and biases. Network training was performed using Levenberg-Marquardt algorithm due to its fast convergence and reliability in locating the global minimum of the mean-squared error (MSE) (Levenberg-Marquardt) (Hagan & Menhaj, 1994; Yao *et al.*, 2005). The transfer function at the hidden layer nodes is tangent sigmoid, which is nonlinear but differentiable. The output node utilizes the linear transfer function so that the input values n equal to the output values y . The normalized output values y_n are retransformed to its original range (Razavi *et al.*, 2003; Bowen *et al.*, 1998; Yao *et al.*, 2005).

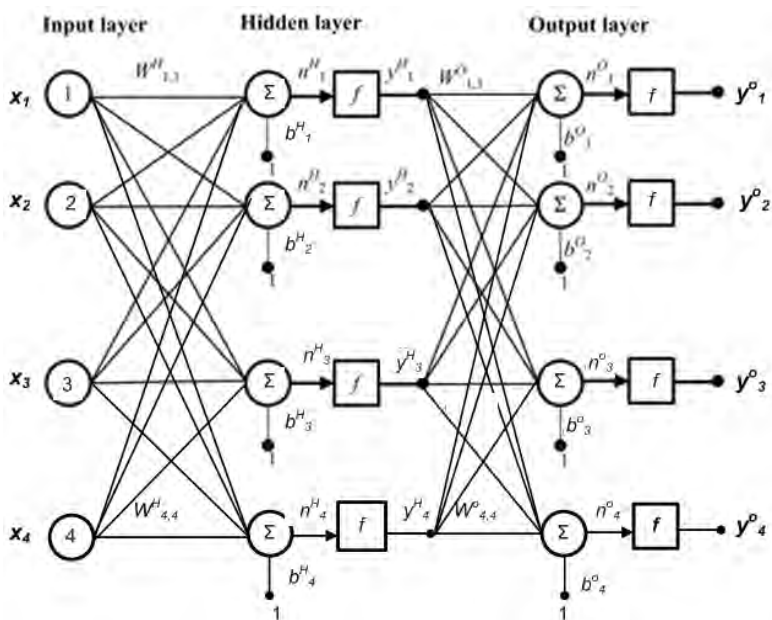


Fig. 1. A schematic diagram of the multi-layered perceptron (MLP) in feed-forward neural network with back-propagation training (X_1 : CH_4/CO_2 ratio; X_2 : discharge voltage; X_3 : total feed flow rate; X_4 : reactor temperature; y^o_1 : CH_4 conversion; y^o_2 : C_2 hydrocarbons selectivity; y^o_3 : Hydrogen selectivity; and y^o_4 : C_2 hydrocarbons yield)

In terms of multi-objective optimization, GA was used for solving the scalar optimization problem based on the principle of survival of the fittest during the evolution. The GA implements the “survival of the fittest” and “genetic propagation of characteristics” principles of biological evolution for searching the solution space of an optimization problem. In nature, individuals must adapt to the frequent changing environment in order to survive. The GA is one of the strategic randomized search techniques, which are well known for its robustness in finding the optimal or near-optimal solution since it does not depend on gradient information in its walk of life to find the best solution. Various kinds of algorithm were reported by previous researchers (Tarca *et al.*, 2002; Nandi *et al.*, 2002, 2004; Kundu *et al.*, 2009; Bhatti *et al.*, 2011).

The GA uses and manipulates a population of potential solutions to find optimal solutions. The generation is complete after each individual in the population has performed the genetic operators. The individuals in the population will be better adapted to the objective/fitness function, as they have to survive in the subsequent generations. At each step, the GA selects individuals at random from the current population to be parents and uses them to produce the children for the next generation. Over successive generation, the population evolves toward an optimal solution. The GA uses three main types of rules at each step to create the next generation from the current population: (a) *Selection rules* select the individuals, called parents, that contribute to the population at the next generation; (b) *Crossover rules* combine two parents to form children for the next generation; (c) *Mutation rules* apply random changes to individual parents to form children.

The detail stepwise procedures for the hybrid ANN-GA algorithm for simultaneous modelling and optimization are described below and are depicted schematically in Figure 2:

- Step 1. (Development of an ANN-based model):** Specify input and output experimental data of the system used for training and testing the ANN-based model. Create the network architecture involving input, hidden and output layers. Investigate the optimal network architecture (optimal number of hidden layer) and make sure that the network is not overfitted.
- Step 2. (Training of the ANN-based model):** Normalize the experimental input and output data to be within the range [-1 1]. The normalization is performed to prevent mismatch between the influence of some input values to the network weights and biases. Train the network using the normalized data by utilizing a robust training algorithm (Levenberg-Marquardt).
- Step 3. (Initialization of solution population):** Set the initial generation index (*Gen*) to zero and the number of population (N_{pop}). Set the number of independent variables (*nvars*). Generate a random initial population of N_{pop} individuals. Each individual possesses vector entries with certain length or called as *genes* which are divided into many segments based on the number of decision variables (*nvars*).
- Step 4. (Fitness computation):** In this step the performance (fitness) of the solution vector in the current population is computed by using a fitness function. Normalize the solution vector x_j to be within the range [-1 1]. Next, the vector x_j is entered as inputs vector to the trained ANN-based model to obtain the corresponding outputs y_j , $y_j=f(x_j, W, b)$. Re-transform the output vector y_j to the original values that are subsequently utilized to compute the fitness value/scores of the solution.

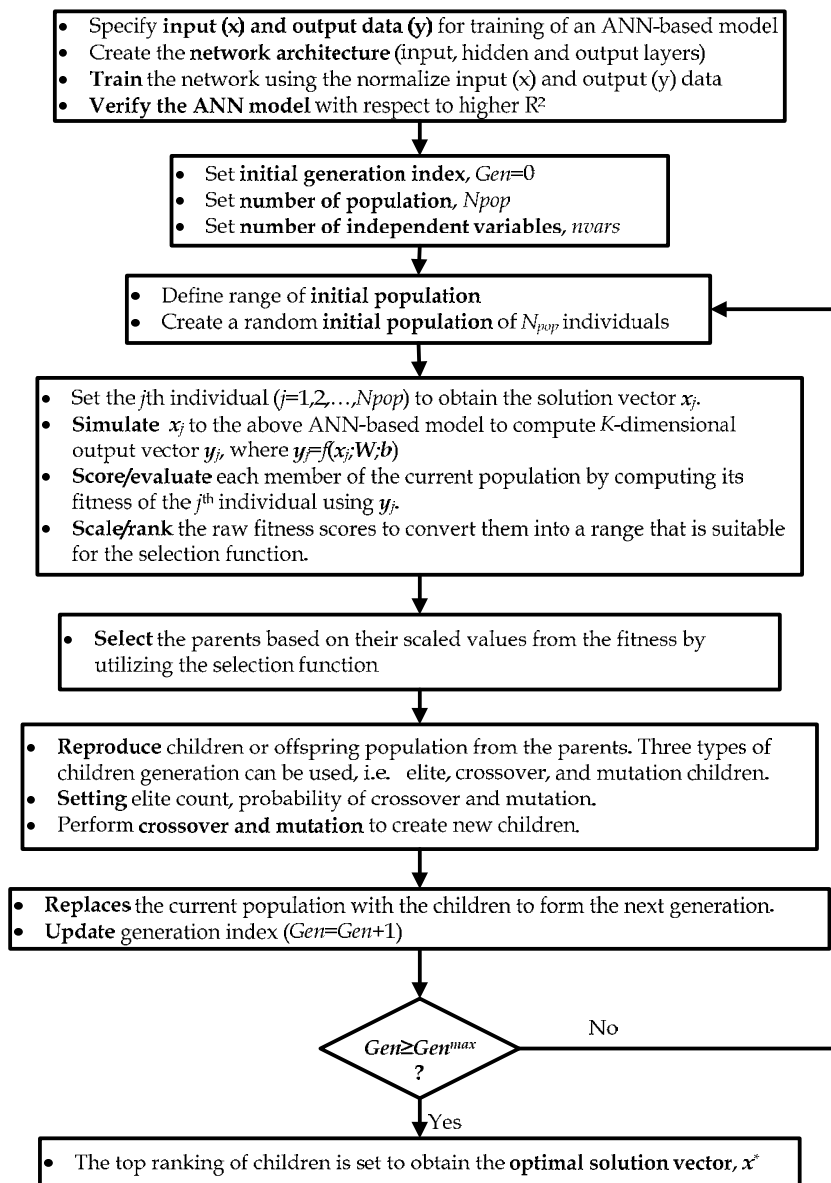


Fig. 2. Flowchart of the hybrid ANN-GA algorithms for modelling and optimization

Step 5. (Scaling the fitness scores): Scale/rank the raw fitness scores to values in a range that is suitable for the selection function. In the GA, the selection function uses the scaled fitness values to choose the parents for the next generation. The range of the scaled values influences performance of the GA. If the scaled values vary too widely, the individuals with the highest scaled values reproduce too rapidly, taking over the

population gene pool too quickly, and preventing the GA from searching other areas of the solution space. On the other hand, if the scaled values vary only a little, all individuals have approximately the same chance of reproduction and the search will progress slowly. The scaling function used in this algorithm scales the raw scores based on the rank of each individual instead of its score. Because the algorithm minimizes the fitness function, lower raw scores have higher scaled values.

- Step 6. (Parents selection):** Choose the parents based on their scaled values by utilizing the selection function. The selection function assigns a higher probability of selection to individuals with higher scaled values. An individual can be selected more than once as a parent.
- Step 7. (Reproduction of children):** Reproduction options determine how the GA creates children for the next generation from the parents. **Elite count** (E_{child}) specifies the number of individuals with the best fitness values that are guaranteed to survive to the next generation. Set elite count to be a positive integer within the range: $1 \leq E_{child} \leq N_{pop}$. These individuals are called elite children. **Crossover fraction** (P_{cross}) specifies the fraction of each population, other than elite children, that are produced by crossover. The remaining individuals in the next generation are produced by mutation. Set crossover fraction to be a fraction between 0 and 1.
- **Crossover:** Crossover enables the algorithm to extract the best genes from different individuals by selecting genes from a pair of individuals in the current generation and recombines them into potentially superior children for the next generation with the probability equal to *crossover fraction* (P_{cross}) from Step 7.
 - **Mutation:** Mutation function makes small random changes in the individuals, which provide genetic diversity and thereby increases the likelihood that the algorithm will generate individuals with better fitness values.
- Step 8. (Replaces the current population with the children):** After the reproduction is performed and the new children are obtained, the current populations are replaced with the children to form the next generation.
- Step 9. Update/increment the generation index):** Increment the generation index by 1: $Gen=Gen+1$.
- Step 10. (Repeat Steps 4-9 until convergence is achieved):** Repeat the steps 4-9 on the new generation until the convergences are met. The GA uses the following five criteria to determine when the algorithm stops:
- *Generations:* the algorithm stops when the number of generation reaches the maximum value (Gen_{max}).
 - *Fitness limit:* the algorithm stops when the value of the fitness function for the best point in the current population is less than or equal to *Fitness limit*.
 - *Time limit:* the algorithm stops after running for an amount of time in seconds equal to *Time limit*.
 - *Stall generations:* the algorithm stops if there is no improvement in the objective function for a sequence of consecutive generations of length *Stall generations*.
 - *Stall time limit:* the algorithm stops if there is no improvement in the objective function during an interval of time in seconds equal to *Stall time limit*. The algorithm stops if any one of these five conditions is met.
- Step 11. (Assign the top ranking of children to the optimal solution vector):** After the GA convergence criteria is achieved, the children possessing top ranking of fitness value is assigned to the optimized population or decision variable vector, x^* .

There is a vector of objectives, $F(\mathbf{X}) = \{F_1(\mathbf{X}), F_2(\mathbf{X}), \dots, F_M(\mathbf{X})\}$ where M denotes the number of objectives, that must be considered in chemical engineering process. The optimization techniques are developed to find a set of decision parameters, $\mathbf{X} = \{X_1, X_2, \dots, X_N\}$ where N is the number of independent variables. As the number of responses increases, the optimal solutions are likely to become complex and less easily quantified. Therefore, the development of multi-objectives optimization strategy enables a numerically solvable and realistic design problem (Wu *et al.*, 2002; Yu *et al.*, 2003). In this method, a set of design goals, $F^* = \{F_1^*, F_2^*, \dots, F_M^*\}$ is associated with a set of objectives, $F(\mathbf{X}) = \{F_1(\mathbf{X}), F_2(\mathbf{X}), \dots, F_M(\mathbf{X})\}$. The multi-objectives optimization formulation allows the objectives to be under- or over-achieved which is controlled by a vector of weighting coefficient, $w = \{w_1, w_2, \dots, w_M\}$. The optimization problem is formulated as follow:

$$\begin{aligned} \underset{\gamma, \mathbf{x} \in \Omega}{\text{minimize}} \quad & \gamma \quad \text{subject to} \quad F_1(\mathbf{x}) - w_1\gamma \leq F_1^* \\ & F_2(\mathbf{x}) - w_2\gamma \leq F_2^* \end{aligned} \quad (3)$$

Specification of the goals, (F_1^*, F_2^*) , defines the goal point. The weighting vector defines the direction of search from the goal point to the feasible function space. During the optimization, γ is varied which changes the size of the feasible region. The constraint boundaries converge to the unique solution point (F_{1s}, F_{2s}) .

3. Results and discussion

3.1 Development and testing of artificial neural network – Genetic algorithm model

In developing a phenomenological model, it is mandatory to consider detailed kinetics of stated multiple reactions in the conservation equations. However, due to the tedious procedures involved in obtaining the requisite kinetic information within phenomenological model, the empirical data-based ANN-GA model was chosen for maximizing the process performances. In this study, simultaneous modeling and multi-objectives optimization of catalytic-plasma reactor for methane and carbon dioxide conversions to higher hydrocarbons (C_2) and hydrogen was done. The purpose of multi-objectives optimization is to maximize the process performances simultaneously, i.e. CH_4 conversion (Y_1) and C_2 hydrocarbons yield (Y_4). Accordingly, four parameters namely CH_4/CO_2 ratio (X_1), discharge voltage (X_2), total feed flow rate (X_3), and reactor temperature (X_4), generate input space of the ANN model. In the ANN model, the four parameters and four targeted responses (CH_4 conversion (y^{o_1}), C_2 hydrocarbons selectivity (y^{o_2}), Hydrogen selectivity (y^{o_3}), and C_2 hydrocarbons yield (y^{o_4}) were developed and simulated.

Regarding the simultaneous modeling and optimization using the ANN-GA method (Figure 2), accuracy of the hybrid method was validated by a set of simple discrete data extracted from a simple quadratic equation (i.e. $y = -2x^2 + 15x + 5$). From the testing, the determination coefficient (R^2) of the method closes to 1 means the empirical method (ANN-GA) has a good fitting, while the relative error of the optimized results (comparison between GA results and analytical solution) are below 10%.

In this chapter, Multi Input and Multi Output (MIMO) system with 4 inputs and 4 outputs of the ANN model was developed. Prior to the network training, numbers of experimental data (Table 2) were supplied into the training. The data were obtained based on the

experimental design (central composite design) as revealed in Tables 1 and 2. In each network training, the training data set was utilized for adjusting the weight matrix set, W . The performance of the ANN model is considered as fitness tests of the model, i.e. MSE, R, and epoch number (epochs). Comparison of the ANN model performance for various topologies was performed. The MSE decreases and R increases with increasing number of nodes in the hidden layer. However, increasing number of hidden layer takes more time in computation due to more complexity of the model. Therefore, optimization of layer number structure is important step in ANN modeling.

The ANN model fitness in terms of comparison between targeted (t) and predicted (y) performances is shown in Figures 3 and 4. In the figures, the ANN models are fit well to the experimental data which is demonstrated by high determination coefficients (R^2) of 0.9975 and 0.9968 with respect to CH_4 conversion (y_1) and C_2 hydrocarbons yield (y_2) models, respectively. The high R^2 and low MSE value implies a good fitting between the targeted (experimental) and the predicted (calculated) values. Therefore, the ANN-based models are suitable for representing the plasma-catalytic conversion of methane and carbon dioxide to higher hydrocarbons. From the simulation, the hybrid ANN-GA algorithm is supposed to be powerful for simultaneous modeling and optimizing process conditions of the complex process as inline with the previous literatures (Istadi & Amin, 2006, 2007) with similar algorithm. The R^2 by this method is high enough (higher than 0.95). The ANN-GA model has advantageous on the fitted model which is a complex non linear model. This is to improve the weaknesses of the response surface methodology that is forced to quadratic model.

3.2. Multi-objective optimization of DBD plasma - Catalytic reactor performances

In this study, simultaneous modeling and multi-objective optimization of catalytic-plasma reactor for methane and carbon dioxide conversions to higher hydrocarbons (C_2) and hydrogen was performed. The multi-objective optimization is aimed to maximize the CH_4 conversion (Y_1) and C_2 hydrocarbons yield (Y_4) simultaneously. Accordingly, four respected parameters, namely CH_4/CO_2 ratio (X_1), discharge voltage (X_2), total feed flow rate (X_3), and reactor temperature (X_4) are optimized stated as input space of the ANN model. In the ANN model, the four parameters and four targeted responses (CH_4 conversion (y^{o_1}), C_2 hydrocarbons selectivity (y^{o_2}), hydrogen selectivity (y^{o_3}), and C_2 hydrocarbons yield (y^{o_4})) were developed and simulated. In this case, two responses or objectives can be optimized simultaneously to obtain optimum four respected process parameters, i.e. CH_4 conversion and C_2 hydrocarbons yield (y^{o_1} and y^{o_4}), CH_4 conversion and C_2 hydrocarbon selectivity (y^{o_1} and y^{o_2}), or CH_4 conversion and hydrogen selectivity (y^{o_1} and y^{o_3}). For maximizing F_1 and F_4 (CH_4 conversion and C_2 hydrocarbons yield, respectively), the actual objective functions are presented in Equation 4 which is one of the popular approaches for inversion (Deb, 2001; Tarafder *et al.*, 2005). The equation was used due to the default of the optimization function is minimization.

$$F_i = \frac{1}{1 + F_{i,o}} \quad (4)$$

where $F_{i,o}$ denotes the real objective functions, while F_i is the inverted objective functions for minimization problem.

For the multi-objectives optimization, the decision variables/operating parameters bound were chosen from the corresponding bounds in the training data as listed in Table 3. Meanwhile, Table 4 lists the numerical parameter values used in the GA for all optimization runs. In this optimization, rank method was used for fitness scaling, while stochastic tournament was used for selection method to specify how the GA chooses parents for the next generation. Meanwhile, scattered method was chosen for crossover function and uniform strategy was selected for mutation function. From the 40 numbers of population size, two of them are elite used in the next generation, while 80% of the rest population was used for crossover reproduction and 20% of them was used for mutation reproduction with 5% rate.

Operating Parameters	Bounds
CH ₄ /CO ₂ feed ratio	$1.5 \leq X_1 \leq 4.0$
Discharge voltage (kV)	$12 \leq X_2 \leq 17$
Total feed flow rate (cm ³ /min)	$20 \leq X_3 \leq 40$
Reactor temperature (°C)	$100 \leq X_4 \leq 350$

Table 3. Operating parameters bound used in multi-objectives optimization of DBD plasma reactor without catalyst

Computational Parameters	Values
Population size	40
Elite count	2
Crossover fraction	0.80
Number of generation	20
Fitness scaling function	fitscalingrank
Selection function	selectiontournament
Crossover function	crossoverscattered
Mutation function	mutationuniform
Mutation probability	0.05

Table 4. Computational parameters of GA used in the multi-objectives optimization

The Pareto optimal solutions owing to the simultaneous CH₄ conversion and C₂ hydrocarbons yield and the corresponding four process parameters are presented in Figure 5. The Pareto optimal solutions points are obtained by varying the weighting coefficient (w_k) in Equation (3) (goal attainment method) and performing the GA optimization corresponding to each w_k so that the γ reaches its minimum value ($F_k(x) - w_k \cdot \gamma \leq F_k$) (goal). From Figure 5, it was found in the Pareto optimal solution that if CH₄ conversion improves, C₂ hydrocarbons yield deteriorates or vice versa. Theoretically, all sets of non-inferior/Pareto optimal solutions are acceptable. The maximum CH₄ conversion and C₂ hydrocarbons yield of 48 % and 15 %, respectively are recommended at corresponding optimum process parameters of CH₄/CO₂ feed ratio 3.6, discharge voltage 15 kV, total feed flow rate 20 cm³/min, and reactor temperature of 147 °C. Larger CH₄ amount in the feed and higher feed flow rate enhance the C₂₊ hydrocarbons yield which is corroborated with the results of Eliasson *et al.* (2000). From the Pareto optimal solutions and the corresponding optimal operating parameters, the suitable operating conditions ranges for DBD plasma

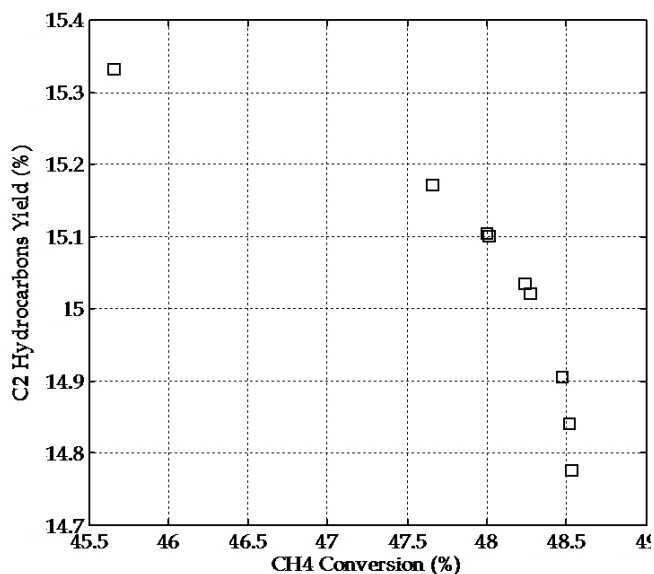


Fig. 5. Pareto optimal solutions with respect to multi-objectives optimization of CH₄ conversion (Y₁) and C₂hydrocarbons yield (Y₂).

3.3 Effect of hybrid catalytic-plasma DBD reactor for CH₄ and CO₂ conversions

When a gas phase consisting electrically neutral species, electrons, ions and other excited species flow through the catalyst bed, the catalyst particles become electrically charged. The charge on the catalyst surface, together with other effects of excited species in the gas discharge leads to the variations of electrostatic potential of the catalyst surface. The chemisorption and desorption performances of the catalyst therefore may be modified in the catalyst surface (Jung *et al.*, 2004; Kraus *et al.*, 2001). Effects of these modifications on methane conversion are dependent on the amount and concentration of surface charge and the species present at the catalyst surface (Kim *et al.*, 2004). The combining DBD plasma and a heterogeneous catalyst are possible to activate the reactants in the discharge prior to the catalytic reaction, which should have positive influences on the reaction conditions.

Comparison of the application of DBD plasma technology in CH₄ and CO₂ conversion with catalyst is studied in this research. Since most of the energetic electrons are required to activate the CH₄ and CO₂ gases in a discharge gap, special consideration must be taken in the designing a reactor that maximizes the contact time between the energetic electrons and the neutral feed gas species. The catalyst located in the discharge gap is an alternative way to increase the time and area of contact between gas molecules and energetic electrons in addition to other modification of electronic properties. The energetic electrons determine the chemistry of the conversions of both gases (Eliasson *et al.*, 2000; Yao *et al.*, 2000; Zhou *et al.*, 1998). The nature of dielectric and electrode surfaces is also an important factor for products distribution of CH₄ and CO₂ conversions using the DBD.

In the catalytic DBD plasma reactor system, the catalyst acts as a dielectric material. Most of the discharge energy is used to produce and to accelerate the electrons generating highly active species (metastable, radicals and ions). The combined action of catalysts and a non-equilibrium gas discharge leads to an alternative method for production of syngas and hydrocarbons from CH_4 and CO_2 . When an electric field is applied across the packed dielectric layer, the catalyst is polarized and the charge is accumulated on the dielectric surface. An intense electric field is generated around each catalyst pellet contact point resulting in microdischarges between the pellets. The microdischarges in the packed-bed of catalyst produced energetic electrons rather than ions. The microdischarges induced a significant enrichment of electrons that were essential for the sustainability of plasmas. Methane and carbon dioxide were chemically activated by electron collisions. Liu *et al.* (1997) concluded that the electronic properties of catalysts have an important role in oxidative coupling of methane using DBD plasma reactor. The electronic properties and catalytic properties can be expected to be changed if the catalyst is electrically charged.

From the non-catalytic DBD plasma reactor, it is shown that the plasma process seems to be less selective than conventional catalytic processes, but it has high conversion. The conventional catalytic reactions on the other hand can give high selectivity, but they require a certain gas composition, an active catalyst, and high temperature condition (endothermic reaction). In the hybrid catalysis-plasma, the catalyst has important roles such as increasing the reaction surface area, maintaining and probably increasing the non-equilibrium properties of gas discharge, acting as a dielectric-barrier material, and improving the selectivity and efficiency of plasma processes by surface reactions. The catalyst placed in the plasma zone can influence the plasma properties due to the presence of conductive surfaces in the case of metallic catalysts (Heintze & Pietruszka, 2004; Kizling & Järås, 1996). The catalyst can also change the reaction products due to surface reactions. The heating and electronic properties of the catalyst by the plasma induce chemisorption of surface species. A synergy between the catalyst and the plasma is important so that the interactions lead to improved reactant conversions and higher selectivity to the desired products. However until now, the exact role of the catalyst in the DBD plasma reactor is still not clear from the chemistry point of view. Even the kind of plasma reactor determines the product selectivity (Gordon *et al.*, 2001). The most significant influence of the plasma was observed at low temperatures (Liu *et al.*, 2001b) at which the catalysts were not active. At higher temperatures the catalysts became active; nonetheless, the plasma catalytic effect was still observed (Huang *et al.*, 2000).

3.4. Simulation of DBD plasma - Catalytic reactor performances

This section demonstrates ANN simulation for the effect of operating parameters (X_1 , X_2 , X_3 , X_4) in catalytic DBD plasma reactor on CH_4 conversion (y_1) and C_2 hydrocarbons yield (y_4). The simulation results were presented in three dimensional surface graphics (Figures 6 to 13). From the results, the CH_4 conversion and C_2 hydrocarbons yield are affected by CH_4/CO_2 feed ratio, discharge voltage, total feed flow rate, and reactor wall temperature from the ANN-based model simulation.

Figures 6, 7, 8, and 9 simulates the effect of discharge voltage, CH_4/CO_2 feed ratio, total feed flow rate, and reactor temperature on the methane conversion. Increasing the discharge voltage improves methane conversion significantly. That is true because energy of energetic

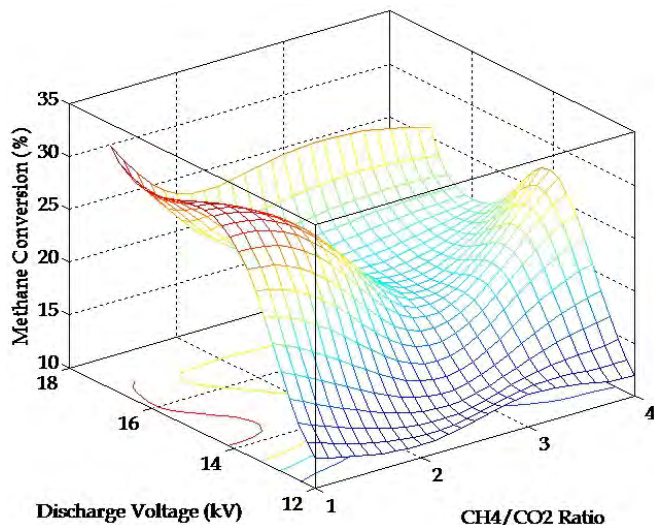


Fig. 6. Effect of discharge voltage (X_2) and CH_4/CO_2 ratio (X_1) toward methane conversion (y_1)

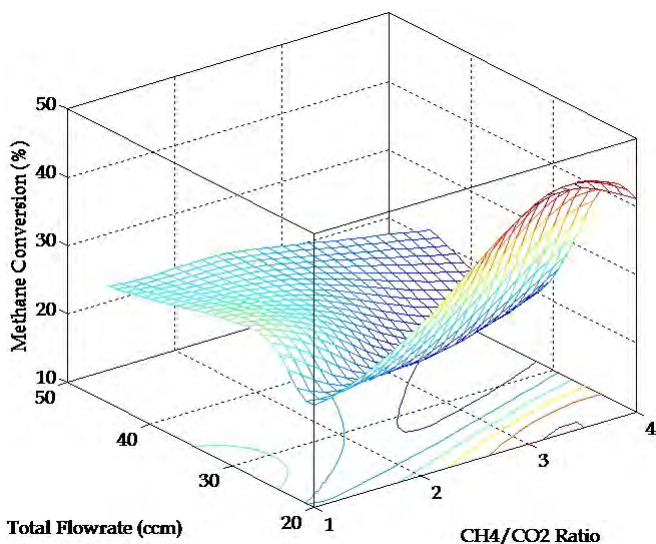


Fig. 7. Effect of total flow rate (X_3) and CH_4/CO_2 ratio (X_1) toward methane conversion (y_1)

electrons is dependent on the discharge voltage. Higher the discharge voltage, higher the energy of electrons flows from high voltage electrode to ground electrode. Increasing the CH_4 concentration in the feed favors the selectivity of C_2 hydrocarbons and hydrogen significantly, but the C_2 hydrocarbons yield is slightly affected due to the decrease of CH_4 conversion. It is suggested that the CH_4 concentration in the feed is an important factor for the total amount of hydrocarbons produced. However, increasing CH_4/CO_2 ratio to 4 reduces the methane conversion considerably and leads to enhanced C_2 hydrocarbons

selectivity and H_2/CO ratio. It is confirmed that CO_2 as co-feed has an important role in improving CH_4 conversion by contributing some oxygen active species from the CO_2 . This phenomenon is corroborated with the results of Zhang *et al.* (2001).

Effect of total feed flow rate on methane conversion is displayed in Figures 7 and 8. From the figures, total feed flow rate has significant effect on methane conversion. Higher the total feed flow rate, lower methane conversion. This is due to primarily from short collision of energetic electrons with feed gas during flow through the plasma reactor. Therefore, only a few reactant molecules that has been cracked by the energetic electrons.

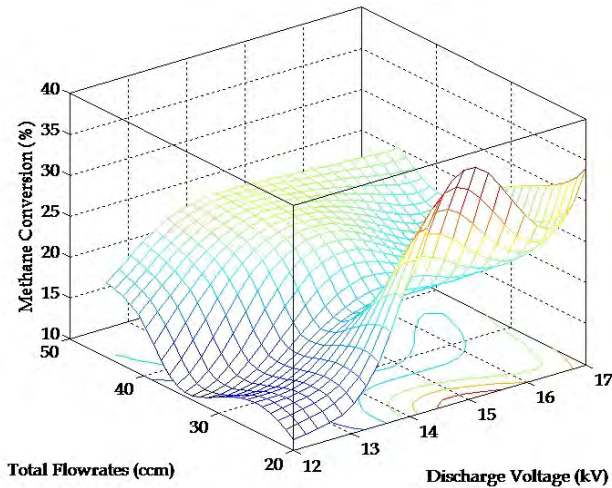


Fig. 8. Effect of total flow rate (X_3) and discharge voltage (X_2) toward methane conversion (y_1)

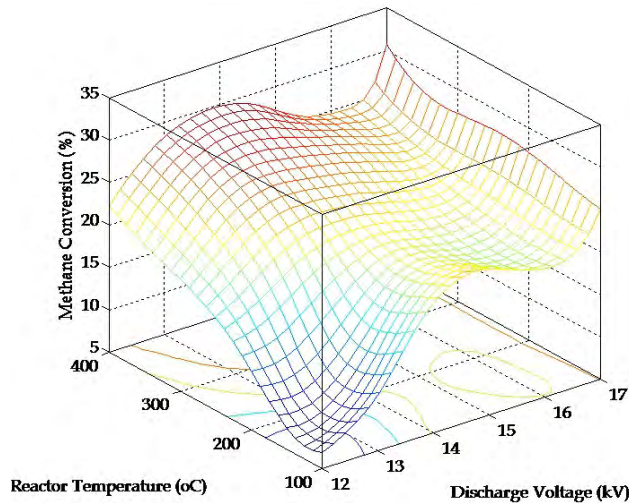


Fig. 9. Effect of reactor temperature (X_4) and discharge voltage (X_2) toward methane conversion (y_1)

Figures 10, 11, 12, and 13 presents the effect of discharge voltage, CH₄/CO₂ feed ratio, total feed flow rate, and reactor temperature on the C₂ hydrocarbons yield. The yield of gaseous hydrocarbons (C₂) increases with the CH₄/CO₂ feed ratio as exhibited in Figure. It is possible to control the composition of C₂ hydrocarbons and hydrogen products by adjusting the CH₄/CO₂ feed ratio. Increasing CH₄/CO₂ ratio above 2.5 exhibits dramatic enhancement of C₂ hydrocarbons yield and lowers CH₄ conversion slightly. In this work, the composition of the feed gas is an essential factor to influence the product distribution. Obviously, more methane in the feed will produce more light hydrocarbons.

In comparison with non-catalytic DBD plasma reactor, the enhancement of reactor performance is obtained when using the hybrid catalytic-DBD plasma reactor (Istadi, 2006). The CH₄ conversion, C₂ hydrocarbons selectivity, C₂ hydrocarbons yield and H₂ selectivity of catalytic DBD plasma reactor is higher than that without catalyst (Istadi, 2006). The catalyst located in the discharge gap can increase the time and area of contact in addition to other modification of electronic properties. Therefore, collision among the energetic electrons and the gas molecules is intensive. Through the hybrid system, the chemisorption and desorption performances of the catalyst may be modified in the catalyst surface (Jung *et al.*, 2004; Kraus *et al.*, 2001) which is dependent on the amount and concentration of surface charge and the species on the catalyst surface (Kim *et al.*, 2004). The results enhancement was also reported by Eliasson *et al.* (2000) over DBD plasma reactor with high input power 500 W (20 kV and 30 kHz) that the zeolite catalyst introduction significantly increased the selectivity of light hydrocarbons compared to that in the absence of zeolite.

Varying the discharge power/voltage affects predominantly on methane conversion and higher hydrocarbons (C₂) yield and selectivity. At high discharge voltage the CH₄ conversion becomes higher than that of CO₂ as presented in Table 2, since the dissociation energy of CO₂ (5.5 eV) is higher than that of CH₄ (4.5 eV) as reported by Liu *et al.* (1999a). More plasma species may be generated at higher discharge voltage. Previous researchers suggested that the conversions of CH₄ and CO₂ were enhanced with discharge power in a catalytic DBD plasma reactor (Caldwell *et al.*, 2001; Eliasson *et al.*, 2000; Zhang *et al.*, 2001) and non-catalytic DBD plasma reactor (Liu *et al.*, 2001b). From Figures 10 and 12, the yield of C₂ hydrocarbons decreases slightly with the discharge voltage which is corroborated with the results of Liu *et al.* (2001b). This means that increasing discharge power may destroy the light hydrocarbons (C₂-C₃). In this research, the lower range of discharge power (discharge voltage 12 - 17 kV and frequency 2 kHz) does not improve the H₂ selectivity over DBD plasma reactor although the catalyst and the heating was introduced in the discharge space as exhibited in Figures 9 and 13. Eliasson *et al.* (2000) reported that higher discharge power is necessary for generating higher selectivity to higher hydrocarbons (C₅₊) over DBD plasma reactor with the presence of zeolite catalysts. Higher discharge power is suggested to be efficient for methane conversion. As the discharge power increases, the bulk gas temperature in the reaction zone may also increase.

The total feed flow rate also affects predominantly on residence time of gases within the discharge zone in the catalytic DBD plasma reactor. Therefore, the residence time influences collisions among the gas molecules and the energetic electrons. Increasing the total feed flow rate reduces the residence time of gases and therefore decreases the C₂ hydrocarbons yield dramatically as demonstrated in Figures 11 and 12. A lower feed flow rate is beneficial for producing high yields light hydrocarbons (C₂₊) and synthesis gases with higher H₂/CO

ratio as reported by Li *et al.* (2004c). The hydrogen selectivity is also affected slightly by the total feed flow rate within the range of operating conditions. Indeed, the total feed flow rate affects significantly on the methane conversion rather than yield of C_2 hydrocarbons. Actually, the low total feed flow rate (high residence time) leads to high intimate collision among the gas molecules, the catalyst and high energetic electrons. The high intensive collisions favor the methane and carbon dioxide conversions to C_{2+} hydrocarbons.

From Figures 9 and 13, it is evident that the current range of reactor temperature only affects the catalytic - DBD plasma reactor slightly. The methane conversion and C_2 hydrocarbons yield is only affected slightly by reactor wall temperature over the CaO-MnO/CeO₂ catalyst. This may be due to the altering of the catalyst surface phenomena and the temperature of energetic electrons is quite higher than that of reactor temperature. The adsorption-desorption, heterogeneous catalytic and electronic properties of the catalysts may change the surface reaction activity when electrically charged. However, the chemistry and physical phenomena at the catalyst surface cannot be determined in the sense of traditional catalyst. Some previous researchers implied that the synergistic effect of catalysis-plasma only occurred at high temperature where the catalyst was active. Huang *et al.* (2000) and Heintze & Pietruszka (2004) pointed out that the product selectivity significantly improved only if the temperature was high enough for the catalytic material to become itself active. Zhang *et al.* (2001) also claimed that the reactor wall temperature did not significantly affect the reaction activity (selectivity) over zeolite NaY catalyst under DBD plasma conditions at the temperature range tested (323-423 K). Particularly, increasing the wall temperature at the low temperature range tested did not affect the reaction activity under plasma conditions. In contrast, some other researchers suggested that the synergistic effect of catalysis - plasma may occur at low temperature. Based on the ANN-based model simulation, it can be suggested that low total feed flow rate, high CH_4/CO_2 feed ratio, high discharge voltage and proper reactor temperature are suitable for producing C_{2+} hydrocarbons and synthesis gas over catalytic DBD plasma reactor.

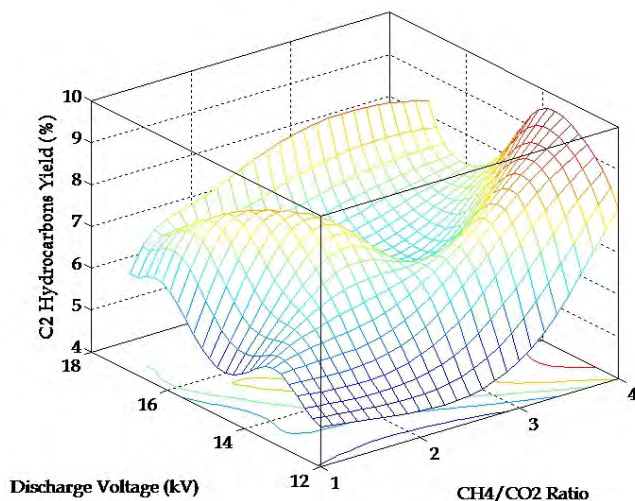


Fig. 10. Effect of discharge voltage (X_2) and CH_4/CO_2 ratio (X_1) toward C_2 hydrocarbons yield (y_4)

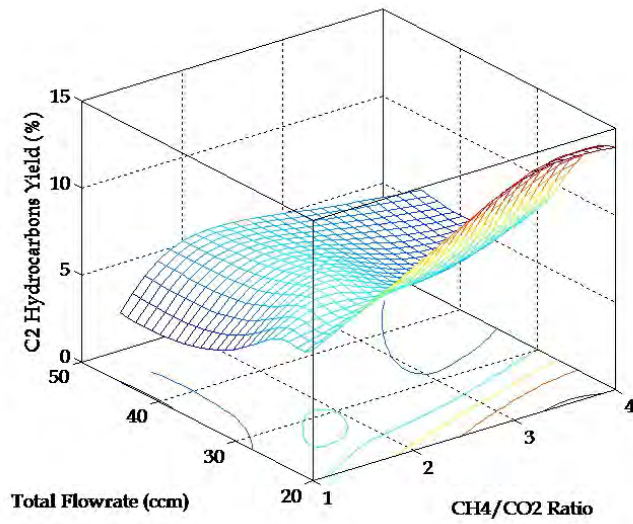


Fig. 11. Effect of total feed flowrate (X_3) and CH_4/CO_2 ratio (X_1) toward C_2 hydrocarbons yield (y_4)

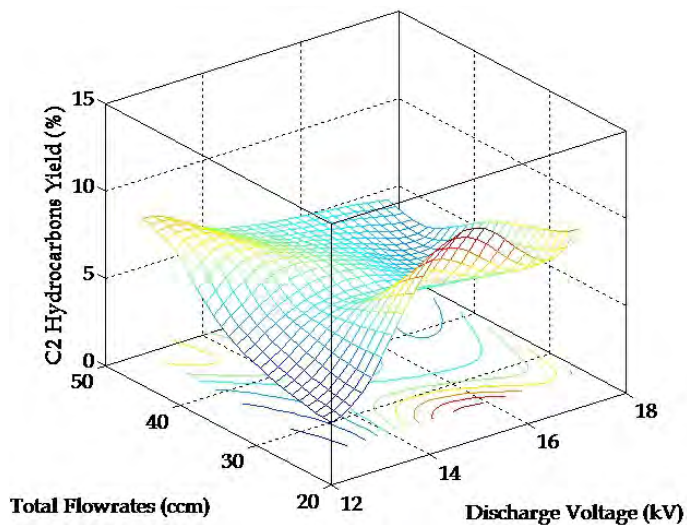


Fig. 12. Effect of total feed flowrate (X_3) and discharge voltage (X_2) toward C_2 hydrocarbons yield (y_4)

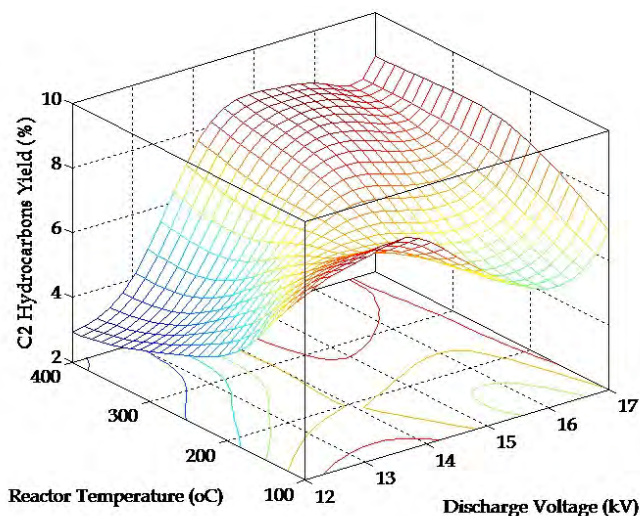


Fig. 13. Effect of reactor temperature (X_4) and discharge voltage (X_2) toward C_2 hydrocarbons yield (y_4)

4. Conclusions

A hybrid ANN-GA was successfully developed to model, to simulate and to optimize simultaneously a catalytic-DBD plasma reactor. The integrated ANN-GA method facilitates powerful modeling and multi-objective optimization for co-generation of synthesis gas, C_2 and higher hydrocarbons from methane and carbon dioxide in a DBD plasma reactor. The hybrid approach simplified the complexity in process modeling of the DBD plasma reactor. In the ANN model, the four parameters and four targeted responses (CH_4 conversion (y^o_1), C_2 hydrocarbons selectivity (y^o_2), hydrogen selectivity (y^o_3), and C_2 hydrocarbons yield (y^o_4)) were developed and simulated. In the multi-objectives optimization, two responses or objectives were optimized simultaneously for optimum process parameters, i.e. CH_4 conversion (y^o_1) and C_2 hydrocarbons yield (y^o_4). Pareto optimal solutions pertaining to simultaneous CH_4 conversion and C_2 hydrocarbons yield and the corresponding process parameters were attained. It was found that if CH_4 conversion improved, C_2 hydrocarbons yield deteriorated, or vice versa. Theoretically, all sets of non-inferior/Pareto optimal solutions were acceptable. From the Pareto optimal solutions and the corresponding optimal operating parameters, the suitable operating condition range for DBD plasma reactor for simultaneous maximization of CH_4 conversion and C_2 hydrocarbons yield could be recommended easily. The maximum CH_4 conversion and C_2 hydrocarbons yield of 48 % and 15 %, respectively were recommended at corresponding optimum process parameters of CH_4/CO_2 feed ratio 3.6, discharge voltage 15 kV, total feed flow rate 20 cm^3/min , and reactor temperature of 147 $^{\circ}C$.

5. Abbreviations

ANN : artificial neural network
 GA : genetic algorithm

ANN-GA	: artificial neural network – genetic algorithm
DBD	: dielectric-barrier discharge
NSGA	: non-dominated sorting genetic algorithm
CO ₂ OCM	: carbon dioxide oxidative coupling of methane
O ₂ OCM	: oxygen oxidative coupling of methane
CCD	: central composite design
MSE	: mean square error
MLP	: multi-layered perceptron
WSSOF	: weighted sum of square objective function
MIMO	: multi input multi output

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