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Modelling and optimization of catalytic–dielectric barrier discharge plasma reactor for methane and carbon dioxide conversion using hybrid artificial neural network—genetic algorithm technique

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Abstract

A hybrid artificial neural network-genetic algorithm (ANN-GA) was developed to model, simulate and optimize the catalytic–dielectric barrier discharge plasma reactor. Effects of CH\textsubscript{4}/CO\textsubscript{2} feed ratio, total feed flow rate, discharge voltage and reactor wall temperature on the performance of the reactor was investigated by the ANN-based model simulation. Pareto optimal solutions and the corresponding optimal operating parameter range based on multi-objectives can be suggested for two cases, i.e., simultaneous maximization of CH\textsubscript{4} conversion and C\textsubscript{2+} selectivity (Case 1), and H\textsubscript{2} selectivity and H\textsubscript{2}/CO ratio (Case 2). It can be concluded that the hybrid catalytic–dielectric barrier discharge plasma reactor is potential for co-generation of synthesis gas and higher hydrocarbons from methane and carbon dioxide and performed better than the conventional fixed-bed reactor with respect to CH\textsubscript{4} conversion, C\textsubscript{2+} yield and H\textsubscript{2} selectivity.

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Keywords: Chemical reactors; Optimization; Reaction engineering; Numerical analysis; ANN-GA; Pareto optimal solution; Plasma reactor

1. Introduction

High energetic electrons in the plasma reactor are potential for development of efficient chemical reactors with low energy requirement. Non-conventional dielectric barrier discharge (DBD) plasma reactor is an efficient tool for converting CH\textsubscript{4} and CO\textsubscript{2} to synthesis gas and higher hydrocarbons at low temperature and ambient pressure (Caldwell et al., 2001; Larkin et al., 2001; Liu et al., 1999; Zou et al., 2003). The energetic electrons collided with molecules in the gas, resulting in excitation, ionization, electrons multiplication, and formation of atoms and metastable compounds (Caldwell et al., 2001; Larkin et al., 2001; Kogelschatz, 2003). When the electric field in the discharge gap was high enough to cause breakdown in most gases a large number of microdischarges were observed. The active atoms and metastable compounds subsequently collided with molecules and reactions may occur.

Up to recently, only few researchers focussed on modelling studies of DBD plasma reactor. Eliasson and Kogelschatz (1991) showed information on single microdischarge combined with reaction chemistry in a single barrier reactor. Another study, Kang et al. (2003) presented a numerical study for understanding the influences of barrier arrangements on the evolution and characteristics of discharges in DBD. The motions of electrons, positive ions, and negative ions in DBD were described by a set of continuity equations. The model included the direct interactions of electrons and photons with neutral gas particles, such as electron impact ionization, electron attachment, and photon impact ionization. However, literatures on comprehensive plasma modelling in DBD reactor pertaining to optimization of process parameters are limited. The comprehensive plasma reactor model should take into account the various subjects, such as chemistry, chemical reaction and...
kinetics, catalysis, and physics which consequently become very complex. The comprehensive plasma reactor model needs a robust numerical solver and time consuming to solve, which is not suitable for rapid prediction in optimization and process control. Due to its ability to model complex and nonlinear problems, the artificial neural network (ANN) was chosen to model the complex behaviour between input and output in the catalytic-DBD plasma process.

ANN has been widely used in chemical engineering applications for complex process modelling, process control, and fault detection and diagnosis (Stephanopoulos and Han, 1996; Huang et al., 2003; Radhakrishnan and Suppiah, 2004; Fissore et al., 2004). The combination of ANN and genetic algorithm (GA) has been used for integrated process modelling and optimization (Nandi et al., 2002, 2004; Ahmad et al., 2004). The hybrid ANN-GA technique is a powerful modelling and optimization method for complex processes and maybe better than other techniques such as the response surface methodology.

The present contribution is intended to develop an ANN-based DBD plasma reactor model and to optimize the process parameters by introducing integrated ANN-GA technique. Multi-objective optimization is utilized in order to obtain the optimal operating variable range and the Pareto optimal solution. Integrated modelling and optimization are planned to simplify the complex process modelling in catalytic DBD plasma reactor.

2. Numerical approach of hybrid ANN-genetic algorithm

In the last decade, ANN has emerged as an attractive tool for nonlinear modelling especially in situations where the development of phenomenological or conventional regression models becomes impractical. The most widely utilized ANN concept is the multi-layered perceptron (MLP) that approximates nonlinear relationship existing between a set of input data (causal process variable) and the corresponding output (dependent variables) data set. The ANN or MLP consists of an input, hidden, and an output layers. In recent years, the GA, members of the stochastic optimization group, have been used with great success in solving problems involving very large search spaces. The GA is originally developed as the genetic algorithm models duplicating population evolution in natural systems (Edgar et al., 2001). Several researchers employed the ANN-GA in their applications to get optimal operating conditions or parameter set up for the input variables in order to gain maximum performances or output variables such as in fluidized controlling catalytic cracker (Zhao et al., 2000), in chiller system (Chow et al., 2002), and in coal combustion (Hou et al., 2001).

2.1. Technique for ANN-based modelling

The ANN modelling has been widely used in chemical engineering applications such as steady state and dynamic process modelling, process identification, yield maximization, nonlinear control, and fault detection and diagnosis (Stephanopoulos and Han, 1996; Huang et al., 2003; Radhakrishnan and Suppiah, 2004; Fissore et al., 2004). The advantages of ANN-based model were reported by Nandi et al. (2002), i.e. (a) it can be generated only from the historic process input–output data (example data set), (b) knowledge of the process phenomenology is not necessary for the model development, (c) a properly trained model possesses generalization ability since it can accurately predict outputs for a new input data set, and (d) even multiple input-multiple output relationships can be simultaneously approximated.

In this research, an algorithm of hybrid ANN-GA for modelling and optimization of DBD plasma reactor was developed by utilizing neural network and genetic algorithm Toolboxes (MATLAB). The feedforward ANN model used in the model development was trained using backpropagation training function. In general, four steps were developed in the training process: (a) assemble the training data, (b) create the network object, (c) train the network, and (d) simulate the network response for new inputs. The feedforward neural network as shown in Fig. 1 consists of three layers nodes, i.e., input, hidden, and output layers comprising of $R$, $S$, and $K$ numbers of processing nodes, respectively. Each node in the input layer is linked to all the nodes in the hidden layer and simultaneously the node in the hidden layer is linked to all the nodes in the output layer using weighting connections. 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 feedforward neural network architecture also addresses the bias nodes which are connected to all the nodes in the subsequent layer, and they provide additional adjustable parameters (weights) for the fitting. The number of nodes in the feedforward neural network input layer ($R$) is equal to the number of inputs in the process, whereas the number of output nodes ($K$) is equal to the number of process outputs. The usage of bias nodes helps the ANN model to be positioned anywhere in the $R$-dimensional input space. In the absence of the bias nodes, the function is forced to pass through the origin of the $R$-dimensional space. From Fig. 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 the backpropagation scheme. Any output point can be obtained after this learning phase, and good results can be achieved.

Basically, the backpropagation training procedure is intended to obtain an optimal set ($W$) of the network weight matrices $W^H$ and $W^O$, which minimize an error function. The
commonly employed error function is mean-squared error (MSE) as defined by

\[
\text{MSE} = \frac{1}{N_{p} K} \sum_{i=1}^{N_{p}} \sum_{k=1}^{K} (t_{i,k} - y_{i,k})^2
\]

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 (target) and predicted values of the \(k\)th output node at \(i\)th input pattern, respectively.

Therefore, an input vector from the training set is applied to the network input nodes, and subsequently the 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, 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 mean-squared error (Eq. (1)), (c) upon the MSE computation, the weight matrices \(W^{H}\) and \(W^{O}\) are updated using the corresponding method (Hagan and Menhaj, 1994; Yao et al., 2005). Network training was performed using Levenberg–Marquardt algorithm due to its fast convergence and reliability in locating the global minimum of the MSE. The procedure completes one network training iteration (1 epoch) when repeated with the remaining input patterns in the training set. For the MSE minimization, several training iterations are usually necessary.

2.2. Algorithm for hybrid artificial neural network-genetic algorithm (ANN-GA) for modelling and optimization

In general, GA is a method for solving optimization problems 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 (Nandi et al., 2002, 2004; Tarca et al., 2002).

The computer code for hybrid ANN-GA calculation was developed by using the Neural Network and Genetic Algorithm Toolboxes in the MATLAB software (The Mathworks, 2005) combining the ANN and GA algorithms to model and to optimize the process simultaneously. The principal features of the GA are as follows: (a) it requires only scalar values and not the second- and/or first-order derivatives of the objective functions, (b) it is capable of handling nonlinear and noisy objective functions, (c) it performs global searches and thus is more likely to arrive at or near the global optimum, (d) it does not impose preconditions, such as smoothness, differentiability, and continuity, on the form of the objective function. Due these attractive features, the GA is perceived to being practical in solving diverse optimization problems in chemical engineering.

GA uses and manipulates a population of potential solutions to find optimal solutions. A generation was completed 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, which 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 numerical parameter values for the GA optimization in this research are listed in Table 1 for two cases. Initial populations are set randomly where the number of population \((N_{\text{pop}})\) used in this case is presented in Table 1. With respect to the population, conventional genetic algorithms are normally binary coded. After attempting with both binary and floating-point coded implementations, it is found that floating-point coding is more suitable than the binary one. Fitness scaling converts the raw fitness scores that are returned by the fitness function to the values in a range that is suitable for the selection function. The rank method scales the raw scores based on the rank of each individual instead of its score where the rank of an individual is its position in the sorted scores. Stochastic uniform selection specifies how the genetic algorithm chooses parents for the next generation where each parent corresponds to a section of the line of length proportional to its scaled value. The algorithm moves along the line in steps of equal size. Reproduction options determine how the genetic algorithm creates children for the next generation from the parents including elite count, crossover, and mutation. Elite count \((E_{\text{child}})\) specifies the number of individuals with the best fitness values that are guaranteed to survive to the next generation which count to be a positive integer \((1 \leq E_{\text{child}} \leq N_{\text{pop}})\). Crossover fraction \((P_{\text{cross}})\) with scattered option as presented in Table 1 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 (uniform option). The mutation with certain probability specifies how the genetic algorithm makes small random changes in the individuals in the population to create mutation children. The mutation also provides genetic diversity and enable the genetic algorithm to search a broader space. Therefore, the current populations are replaced with the children to form the next generation.

Having developed an ANN-based DBD plasma reactor model, a GA is used to optimize the \(R\)-dimensional input space \((x)\) of the ANN model. The corresponding optimization objective can be defined as finding the \(R\)-dimensional optimal decision factor, \(x^* = [x^*_1, x^*_2, \ldots, x^*_K]^T\), such that it maximizes the \(K\)-dimensional objective function vector \(f\), which is defined as:

\[
 f(x^*, W, b) = \sum_{k=1}^{K} f_k(x^*, W, b),
\]

where \(W = \{W^H, W^O\}\) and \(b = \{b^H, b^O\}\) are weights and biases parameters, respectively, for hidden and output layers of the network. It can be remarked in the above formulation that the problems belongs to multi-objectives optimization, which is simultaneously maximization of \(f_k(x^*, W, b)\) where \(k\) represents the number of objective functions. A simple approach to solve the multi-objectives optimization problem is by aggregating the objectives into a single-objective function namely weighted sum of squared objective function (WSSOF) algorithm (Istadi and Amin, 2005a). In the WSSOF method, each objective function is multiplied by a weighting coefficient \((w_k)\) and combined to form a single scalar objective function to be maximized. The maximization of a single objective function can be expressed as:

\[
 \text{maximize } f(x, W) = \sum_{k=1}^{K} w_k f_k(x, W)
\]

\[
 0 \leq w_k \leq 1 \quad \text{and} \quad \sum_{k=1}^{K} w_k = 1
\]

Pareto optimal solution or non-inferior optimal solution or non-dominated solutions is defined as an entire set of optimal solutions that are evenly good which leads to a situation wherein the solution is obtained rather than a unique solution. A Pareto set is defined such that when we move from one point to another, at least one objective function improves and at least one other worsens. Detail theory about Pareto optimal solution is available elsewhere (Istadi and Amin, 2005a).

The detail stepwise procedure for the hybrid ANN-GA algorithm for modelling and optimization is depicted schematically in Fig. 2. Normalization of the experimental input and output data was performed to be within the range \([-1,1]\), while training of the network of the normalized data uses the Levenberg–Marquardt algorithm. The algorithm stops if any one of the following five conditions is met. The genetic algorithm uses the following five criteria to determine when the algorithm stops:

- **Generations**: the algorithm stops when the number of generation reaches the maximum value \((\text{Gen}_{\text{max}})\).
- **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.
However, all the above criteria do not always guarantee global optimization. All possible combinations of input variables (from random initial population in genetic algorithm) are given to the trained ANN model to obtain the global optimization. The hybrid algorithm was verified for minimizing a simple problem as presented in Fig. 3. In the figure, the discrete data to be minimized are presented as circle symbols, while the simulated target data by the ANN model are displayed as a solid line curve. After optimization process using the hybrid ANN-GA algorithm, a set of minimum target variables with respect to independent variables with 10 replications are presented as triangle symbols in Fig. 3. The results show that the hybrid algorithm is suitable for simultaneous simulation and optimization of the simple problem. Ten replications of optimization with the similar minimum location also shows that the hybrid algorithm can be used for simulation and optimization of some problems with reproducible results.

### 3. Experimental

#### 3.1. Design of experiment

In the process modelling, the numbers of experimental data are needed to validate the model. The ANN-based model requires more example data which are noise-free and statistically well-distributed. Design of the experiment is performed using central composite design (CCD) with full factorial design for designing the training and test data sets. The CCD method is chosen since the method provides a wider covering region of parameter space and good consideration of variable interactions in the model (Istadi and Amin, 2006b). The CCD considers low, centre, and high levels of each independent variable. Another advantage of central composite design is to reduce the number of experimental works, but the experimental design includes a wider region of parameter space. The variable range and levels of the CCD are presented in Table 2 with respect to the catalytic DBD plasma reactor. The variable range and level of the CCD are presented in Table 2 for the catalytic-DBD plasma reactor.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Range and levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)/CO(_2) ratio (X(_1), –)</td>
<td>0.8 1.5 2.5 3.5 4.2</td>
</tr>
<tr>
<td>Discharge voltage (X(_2), kV)</td>
<td>12.5 13.5 15.0 16.5 17.5</td>
</tr>
<tr>
<td>Total feed flow rate (X(_3), cm(^3)/min)</td>
<td>18 25 35 45 52</td>
</tr>
<tr>
<td>Reactor temperature (X(_4), K)</td>
<td>355 423 523 623 691</td>
</tr>
</tbody>
</table>

*Note: –1 (low level value); +1 (high level value); 0 (center point); +\(\alpha\) and –\(\alpha\) (star points).*
Table 3
Experimental design matrix of catalytic DBD plasma reactor

<table>
<thead>
<tr>
<th>Process variables in real values</th>
<th>Process variables in coded values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_1$</td>
<td>$X_2$</td>
</tr>
<tr>
<td>3.5</td>
<td>16.5</td>
</tr>
<tr>
<td>3.5</td>
<td>16.5</td>
</tr>
<tr>
<td>3.5</td>
<td>13.5</td>
</tr>
<tr>
<td>1.5</td>
<td>16.5</td>
</tr>
<tr>
<td>3.5</td>
<td>13.5</td>
</tr>
<tr>
<td>1.5</td>
<td>16.5</td>
</tr>
<tr>
<td>1.5</td>
<td>13.5</td>
</tr>
<tr>
<td>0.8</td>
<td>15.0</td>
</tr>
<tr>
<td>4.2</td>
<td>15.0</td>
</tr>
<tr>
<td>2.5</td>
<td>12.5</td>
</tr>
<tr>
<td>2.5</td>
<td>17.5</td>
</tr>
<tr>
<td>2.5</td>
<td>15.0</td>
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<tr>
<td>2.5</td>
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<td>2.5</td>
<td>15.0</td>
</tr>
<tr>
<td>2.5</td>
<td>15.0</td>
</tr>
<tr>
<td>Note: −1 (low level value); +1 (high level value); 0 (centre point); +$\pi$ and −$\pi$ (star points) $X_1$ (CH$_4$/CO$_2$ feed ratio); $X_2$ (discharge voltage, kV); $X_3$ (total feed flow rate, cm$^3$/min); $X_4$ (reactor wall temperature, K).</td>
<td></td>
</tr>
</tbody>
</table>

The multi input and multi output (MIMO) system with four inputs and five outputs of the artificial neural network model was used; it can cover a wider range and interactions of variables.

3.2. Configuration of dielectric-barrier discharge (DBD) plasma reactor

The catalyst composition (12.8 wt.% CaO–6.4 wt.% MnO/ CeO$_2$) used in this plasma DBD reactor is based on the optimization results as described elsewhere (Istadi and Amin, 2005a). The catalyst was prepared by simultaneous impregnation method. Fig. 4 presents the detail schematic diagram of DBD plasma reactor configuration. A high voltage AC generator supplying a voltage from 0 to 17.5 kV with a pulsed waveform at a frequency of up to 10 kHz was used. The voltage measurement was conducted using an oscilloscope (ISO-TECH ISR 622) equipped with a high voltage probe (manufactured by Atama Tech Sdn. Bhd.) calibrated using a Tektronix P6015 high-voltage probe.

The circuit, as depicted in Fig. 5, can be divided into two main sections: the oscillator and the power drive. The oscillator was built around a CMOS 4093 (4-nand gates) and was configured as a pulse generator (duty cycle controlled). Either on or off time may be set by using the 150 kΩ potentiometer (high and low potentiometers). The main working frequency band can be set by proper selection of the 10 nF capacitor. The on/off time control gives very good regulation of the maximum output voltage. In this case, when the frequency increased the voltage decreased and vice versa. The power drive was built around a power switching transistor (2N3055) which was driven by a 2N2222 transistor. The power transistor received the command signal from the oscillator that opened and closed many times per second the primary coil of the transformer, thus inducing a high voltage in the transformer secondary coil. The power transistor needed a good heat-sink because it performed heavy currents. In order to limit this high current, a current limiting resistor (ballast resistor), one or two 10 Ω/10 watt resistor was applied. The output voltage was dependent on the transformer type, the power transistor, and the power supply.

The variables involved in the operation of a DBD plasma reactor were discharge gap width, discharge power (voltage and frequency), reactant (CH$_4$/CO$_2$) ratio, reactor wall temperature, catalyst type, and total feed flow rate. The DBD plasma reactor was operated without heating or catalyst. The reactor temperature may increased to about 60 °C due to electron heating on the surface of the electrode. During the process, the gas temperature could be within the range of room temperature, while the electrons could reach temperatures between 104 and 105 K in a dielectric barrier discharge. The non-thermal plasma could be generated by applying high voltage to a gas space to incur gas breakdowns. The gas breakdowns generated electrons that were accelerated by an electric field forming a non-thermal plasma. The electrical discharges could be realized in several ways depending on the types of voltage applied and reactor specification. In the plasma reactor, the energetic electrons collided with molecules in the gas, resulting in excitation, ionization, electron multiplication, and the formation of atoms and metastable compounds. When the electric field in the discharge gap was high enough to cause breakdowns in most gases a large number of microdischarges were observed. The active atoms and metastable compounds subsequently collided with molecules, and reactions may occur.

4. Results and discussion

4.1. Artificial neural network model development for MIMO system

The multi input and multi output (MIMO) system with four inputs and five outputs of the artificial neural network model...
Table 4
Experimental data of hybrid catalytic DBD plasma reactor at low temperature

<table>
<thead>
<tr>
<th>Process variables</th>
<th>Responses/dependent variables (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH&lt;sub&gt;4&lt;/sub&gt;/CO&lt;sub&gt;2&lt;/sub&gt; ratio (X&lt;sub&gt;1&lt;/sub&gt;)</td>
<td>Total feed flow rate (X&lt;sub&gt;2&lt;/sub&gt;)</td>
</tr>
<tr>
<td>3.5</td>
<td>16.5</td>
</tr>
<tr>
<td>3.5</td>
<td>16.5</td>
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<tr>
<td>3.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td>13.5</td>
</tr>
<tr>
<td>1.5</td>
<td>16.5</td>
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<tr>
<td>3.5</td>
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<td>1.5</td>
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<tr>
<td>1.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td>16.5</td>
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<tr>
<td>1.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td>13.5</td>
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<tr>
<td>0.8</td>
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<td>4.2</td>
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<td>2.5</td>
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<td>2.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td>17.5</td>
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<td>2.5&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>2.5 &lt;sup&gt;a&lt;/sup&gt;</td>
<td>15.0</td>
</tr>
<tr>
<td>2.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td>15.0</td>
</tr>
</tbody>
</table>

Note: X, S, Y denote conversion, selectivity and yield, respectively, and C<sub>2</sub>≡ comprises C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>3</sub>H<sub>8</sub>, X<sub>1</sub> (CH<sub>4</sub>/CO<sub>2</sub> feed ratio); X<sub>2</sub> (discharge voltage, kV); X<sub>3</sub> (total feed flow rate, cm<sup>3</sup>/min); X<sub>4</sub> (reactor wall temperature, K); Pressure: 1 atm; catalyst loading: 5 g; frequency: 2 kHz (pulse).

<sup>a</sup>These data were used as test set.
was developed for CH$_4$ and CO$_2$ conversion in catalytic DBD plasma reactor. The 4-9-11-5 ANN structure was trained to simulate the effect of each independent variable on the performance of the process. In this section, four independent variables, i.e., CH$_4$/CO$_2$ feed ratio ($X_1$), discharge voltage ($X_2$), total feed flow rate ($X_3$), and reactor wall temperature ($X_4$), are used as inputs of the MIMO network, while five dependent variables, i.e., CH$_4$ conversion ($Y_1$), C$_2$+$+$ selectivity ($Y_2$), H$_2$ selectivity ($Y_3$), C$_2$+$+$ yield ($Y_4$), and H$_2$/CO ratio ($Y_5$) are selected as outputs of the network as described in Tables 2 and 3. Twenty experimental data are partitioned into training (16 patterns) and test (four patterns) sets as presented in Table 4 where the data for test pattern are marked clearly. The experimental data were collected based on the experimental design matrix in Table 3.

The performance of the ANN model is considered as fitness tests of the model, i.e., mean square error, correlation coefficient ($R$), and epoch number (epochs). Comparison of the ANN model performance for various structures with one and two hidden layers is performed in the first step of the ANN-based model development. The ANN structure investigation implies that the mean square error decreases and correlation coefficient ($R$) increases with increasing number of nodes in the hidden layer. The epoch number also decreases with increasing number of nodes in the hidden layer. From the comparison, the 4-9-11-5 structure of ANN model is chosen for the next simulation. Comparison of the predicted and observed values of the five responses (CH$_4$ conversion ($Y_1$), C$_2$+$+$ selectivity ($Y_2$), H$_2$ selectivity ($Y_3$), C$_2$+$+$ yield ($Y_4$), and H$_2$/CO ratio ($Y_5$)) are depicted in Figs. 6(a)–(e), respectively, for all data including the test data. From the figure, it is shown that high value of correlation coefficients ($R$) of the ANN model, i.e., 0.997, 0.998, 0.991, 0.997, and 1, are obtained corresponding to the five responses.

In Fig. 6, the relative errors of the test set data with respect to Eq. (4) are also presented which vary between 8% and 21%. The high $R$ value implies a good fitting between the observed (experimental) and the predicted values, which means that the ANN-based model is suitable for representing the real process.

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Fig. 6. Comparison of predicted and observed values of the 4-9-11-5 ANN model of catalytic DBD plasma process for the following outputs: (a) CH$_4$ conversion ($Y_1$), (b) C$_2$+ selectivity ($Y_2$), (c) H$_2$ selectivity ($Y_3$), (d) C$_2$+ yield ($Y_5$), (e) H$_2$/CO ratio ($Y_5$). Note: Star symbol (*) represents the test data, while % error is average relative error of test set data.

4.2. Effect of operating parameters in catalytic DBD plasma reactor

This section presents the ANN simulation on the effect of operating parameters in catalytic DBD plasma reactor for CH$_4$ and CO$_2$ conversions. The simulations were carried out by varying one operating parameter, while the remaining parameters were kept constant. CH$_4$ conversion, C$_2$+ hydrocarbons selectivity and yield, H$_2$ selectivity, and H$_2$/CO ratio are affected by CH$_4$/CO$_2$ feed ratio, discharge voltage, total feed flow rate and reactor wall temperature as depicted in Figs. 7–10.

Fig. 7 presents the simulation of CH$_4$/CO$_2$ feed ratio effect on the catalytic DBD plasma process performance. Increasing the CH$_4$ concentration in the feed favours the selectivity of C$_2$+ hydrocarbons and hydrogen significantly, but the C$_2$+ hydrocarbons yield is only slightly affected by decreasing CH$_4$ conversion. It is suggested that the CH$_4$ concentration in the feed is an essential factor for the total amount of hydrocarbons produced. However, increasing CH$_4$/CO$_2$ ratio to four reduces...
Fig. 7. Effect of CH$_4$/CO$_2$ feed ratio on catalytic DBD plasma reactor performance at discharge voltage 15 kV, 30 cm$^3$/min total feed flow rate and reactor temperature 473 K: (a) CH$_4$ conversion, (b) C$_{2+}$ selectivity, (c) H$_2$ selectivity, (d) C$_{2+}$ yield, (e) H$_2$/CO ratio.

Fig. 8. Effect of discharge voltage on catalytic DBD plasma reactor performance at CH$_4$/CO$_2$ feed ratio 2.5, 30 cm$^3$/min total feed flow rate and reactor temperature 473 K: (a) CH$_4$ conversion, (b) C$_{2+}$ selectivity, (c) H$_2$ selectivity, (d) C$_{2+}$ yield, (e) H$_2$/CO ratio.

Fig. 9. Effect of total feed flow rate on catalytic DBD plasma reactor performance at CH$_4$/CO$_2$ feed ratio 2.5, discharge voltage 15 kV and reactor temperature 473 K: (a) CH$_4$ conversion, (b) C$_{2+}$ selectivity, (c) H$_2$ selectivity, (d) C$_{2+}$ yield, (e) H$_2$/CO ratio.

Fig. 10. Effect of reactor wall temperature on catalytic DBD plasma reactor performance at CH$_4$/CO$_2$ feed ratio 2.5, discharge voltage 15 kV and total feed flow rate 30 cm$^3$/min: (a) CH$_4$ conversion, (b) C$_{2+}$ selectivity, (c) H$_2$ selectivity, (d) C$_{2+}$ yield, (e) H$_2$/CO ratio.

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$_2$. Increasing CO$_2$ concentration in the feed improves the CH$_4$ conversion and CO selectivity which may be due to promoting the CH$_4$ conversion by oxygen from CO$_2$ decomposition. This phenomenon is corroborated with the results of Zhang et al. (2001). The yield of gaseous hydrocarbons (C$_{2+}$) increases slightly with the CH$_4$/CO$_2$ feed ratio as exhibited in Fig. 7 and consequently lowers at higher ratio. It is possible to control the composition of C$_{2+}$ hydrocarbons and hydrogen products by adjusting the CH$_4$/CO$_2$ feed ratio. From the ANN simulation result in Fig. 7, it can be shown that increasing CH$_4$/CO$_2$ ratio above 2.5 exhibits low enhancement of C$_{2+}$ yield and lower CH$_4$ conversion. In this work, the composition of the feed gas (CH$_4$/CO$_2$ ratio) is an important factor to adjust the product distribution. Obviously, more methane in the feed will produce more light hydrocarbons.

Varying the discharge power/voltage affects predominantly on methane conversion and higher hydrocarbons (C$_2$–C$_3$) selectivity. The methane conversion increases with discharge voltage as exhibited in Fig. 8. More plasma species may be generated at higher discharge voltage. Previous researchers suggested that the conversions of CH$_4$ and CO$_2$ were enhanced mainly with...
discharge power in a catalytic DBD plasma reactor (Caldwell et al., 2001; Eliasson et al., 2000; Zhang et al., 2001, 2002). From Fig. 7, the selectivities of C_{2+} hydrocarbons and hydrogen decrease slightly with the discharge voltage corroborated with the results of Liu et al. (2001) suggesting that increasing discharge power may destroy the light hydrocarbons (C_{2}-C_{3}). In comparison, high C_{2} and C_{3} hydrocarbons selectivities of 36.4% and 18%, respectively, were reported by Eliasson et al. (2000) at discharge power of 200 W (30 kHz) using DBD plasma reactor with zeolite catalyst. In this research, the lower range of discharge power (discharge voltage of 12–17 kV and frequency being 2 kHz) does not improve the H_{2} selectivity over DBD plasma reactor although the catalyst and the heating was introduced in the discharge space. Higher discharge voltage is suggested to be efficient for methane conversion. As the discharge voltage increases, the bulk gas temperature in the reaction zone may also increases.

The total feed flow rate also influences predominantly the residence time of gases within the discharge zone in the catalytic DBD plasma reactor which consequently affects collisions between the gas molecules and the energetic electrons. Increasing the total feed flow rate reduces the residence time of gases and therefore decreases the methane conversion swiftly as demonstrated in Fig. 9. A lower feed flow rate is beneficial for producing high yields light hydrocarbons (C_{2+}) and synthesis gases with higher H_{2}/CO ratio as reported by Li et al. (2004). From Fig. 9, it is shown that increasing the total feed flow rate decreases the CH_{4} conversion markedly and affects the C_{2+} hydrocarbons selectivity slightly. 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 on the methane conversion significantly rather than the selectivity of C_{2+} hydrocarbons and hydrogen. Essentially, low total feed flow rate (high residence time) leads to high intimate collision among the gas molecules, the catalyst and high energetic electrons. Consequently, high intensive collisions favour methane and carbon dioxide conversions to C_{2+} hydrocarbons.

Pertaining to the reactor wall temperature, Fig. 10 presents the effect of reactor temperature on the performance of catalytic DBD plasma reactor. Thermodynamic equilibrium calculations demonstrated that normal chemical reactions between CH_{4} and CO_{2} cannot be expected at temperatures lower than 523 K (Istadi and Amin, 2005b). In endothermic reactions, normally high temperatures are required to add enthalpy. In this research, methane and carbon dioxide reaction over CaO-MnO/CeO_{2} catalyst is slightly affected by reactor wall temperature. The C_{2+} hydrocarbons selectivity is enhanced slightly by the reactor temperature which may be influenced by the catalyst surface phenomena. 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.

### 4.3. Multi-objectives optimization of catalytic DBD plasma reactor using hybrid ANN-GA strategy

Five responses/objectives corresponding to four operating parameters should be maximized simultaneously. The simultaneous maximization is intended to come close to the real conditions of the process, but the higher number of objectives to be optimized simultaneously, the more difficult the optimization process is. To simplify the optimization problem, the multi-objectives optimization of the catalytic DBD plasma reactor are divided into two separate cases, i.e.: (a) simultaneous maximization of CH_{4} conversion and C_{2+} selectivity (Case 1), and (b) simultaneous maximization of H_{2} selectivity and H_{2}/CO ratio (Case 2). The choice of two objective functions for each case enables the simultaneous maximization of the real process performances and simplifies the optimization problems. It is noted that all cases (cases 1–2) are not related to each other where the grouping into two cases (with two objective functions each) is intended for simplicity. For the multiresponses optimization, the decision variables/operating parameters bounds are chosen from the corresponding bounds in the training data as listed in Table 5. The Pareto optimal solutions are obtained from multiobjectives optimization using the genetic algorithm (GA) tool.

Pertaining to Case 1, the optimal operating parameters of catalytic DBD plasma reactor for CH_{4} and CO_{2} conversions process are determined corresponding to simultaneous maximization of CH_{4} conversion and C_{2+} hydrocarbons selectivity as depicted in Fig. 11. The Pareto optimal solutions points are obtained by varying the weighting factor (w_{1}) in Eq. (3) and performing the GA optimization corresponding to each w_{1} (0 \leq w_{1} \leq 1). From the figure, it is found that if the CH_{4} conversion increases, the C_{2+} selectivity decreases, where all sets of non-inferior/Pareto optimal solutions are acceptable. The optimal operating parameters corresponding to the Pareto solutions are shown in Fig. 12. For example, CH_{4} conversion can achieve as high as 23.5% with C_{2+} selectivity equal to 39.6%.

<table>
<thead>
<tr>
<th>Operating parameters</th>
<th>Bounds</th>
</tr>
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<tbody>
<tr>
<td>CH_{4}/CO_{2} feed ratio</td>
<td>1.5 \leq X_{1} \leq 4.0</td>
</tr>
<tr>
<td>Discharge voltage (kV)</td>
<td>12 \leq X_{2} \leq 17</td>
</tr>
<tr>
<td>Total feed flow rate (cm^{3}/min)</td>
<td>20 \leq X_{3} \leq 40</td>
</tr>
<tr>
<td>Reactor wall temperature (K)</td>
<td>373 \leq X_{4} \leq 623</td>
</tr>
</tbody>
</table>

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while the C2+ selectivity can be obtained as high as 29.9% with CH4 conversion equal to 47.0%. The results can be achieved by altering the operating parameters CH4/CO2 feed ratio (X1), discharge voltage (X2), total feed flow rate (X3) and reactor wall temperature (X4) from 4.0, 12.8 kV, 25.2 cm³/min and 423 K to 2.2, 12.8 kV, 20 cm³/min and 423 K, respectively. In this optimization, it is obvious that effects of discharge voltage and reactor wall temperature are not significant. From the Pareto optimal solutions of catalytic DBD plasma reactor (Figs. 11 and 12) the CH4 conversion improves at lower CH4/CO2 ratio, since high CO2 concentration in the feed improves the decomposition of methane. It appeared in Fig. 12 that the C2+ selectivity increases with CH4/CO2 ratio. Increasing the total feed flow rate decreases the CH4 conversion and enhances the C2+ selectivity slightly which is in agreement with the results of Eliasson et al. (2000) and Liu et al. (1998). However, the CH4 conversion and C2+ selectivity are only slightly affected by the discharge voltage and the reactor temperature within the range of Pareto optimal solutions.

With respect to simultaneous maximization of H2 selectivity and H2/CO ratio (Case 2), the Pareto optimal solution and the corresponding optimal operating parameters are presented in Figs. 13 and 14, respectively. From Fig. 13, the Pareto
Table 6:
Comparison between plasma and conventional fixed bed reactors at the same catalyst (12.8CaO–6.4MnO/CeO₂) and total feed flow rate

| Parameters | Performance | Catalytic plasma reactor | Conventional fixed bed reactor
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>CH₄ conversion</td>
<td>Total feed flow rate = 30 cm³/min</td>
<td>36.7%</td>
<td>25.1%</td>
</tr>
<tr>
<td>C₂⁺ selectivity</td>
<td></td>
<td>29.3%</td>
<td>26.6%</td>
</tr>
<tr>
<td>H₂ selectivity</td>
<td></td>
<td>9.8%</td>
<td>8.3%</td>
</tr>
<tr>
<td>C₂⁺ yield</td>
<td></td>
<td>11.1%</td>
<td>6.6%</td>
</tr>
<tr>
<td>CO selectivity</td>
<td></td>
<td>14.5%</td>
<td>13.6%</td>
</tr>
<tr>
<td>H₂/CO ratio</td>
<td></td>
<td>4.4</td>
<td>2.0</td>
</tr>
</tbody>
</table>

*From ANN model simulation: discharge voltage = 16 kV, frequency = 2 kHz, T = 473 K, CH₄/CO₂ ratio = 3, total feed flow rate = 30 cm³/min.
*From ANN model simulation: discharge voltage = 16 kV, frequency = 2 kHz, T = 473 K, CH₄/CO₂ ratio = 3, total feed flow rate = 50 cm³/min.

Indeed, the hybrid catalytic DBD plasma reactor is effective for co-generation of C₂⁺ hydrocarbons and synthesis gas from methane and carbon dioxide.

5. Conclusions

The hybrid catalytic DBD plasma reactor is potential for co-generation of C₂⁺ hydrocarbons and synthesis gases from methane and carbon dioxide. A hybrid artificial neural network—genetic algorithm was developed to model, to simulate and to optimize the catalytic DBD plasma reactor. A study on the effects of CH₄/CO₂ feed ratio, total feed flow rate, discharge voltage and reactor temperature on the performance of hybrid catalytic DBD plasma reactor at low temperature was addressed by the ANN-based model simulation with very good fitting. It can be concluded that three factors, i.e., CH₄/CO₂ feed ratio, total feed flow rate, and discharge voltage, showed significant effects on the reactor performances. However, increasing the reactor wall temperature has no apparent influence on the selectivity to C₂⁺ hydrocarbons and hydrogen within the investigated range. The Pareto optimal solutions and corresponding optimal operating parameters ranges produced by multi-objectives optimization can be suggested for simultaneous maximization of CH₄ conversion and C₂⁺ selectivity, and/or H₂ selectivity and H₂/CO ratio. It can be concluded that the hybrid catalytic DBD plasma reactor is more suitable for CO₂ OCM process than the conventional catalytic reactor over CaO–MnO/CeO₂ catalyst with respect to CH₄ conversion, C₂⁺ yield and H₂ selectivity. The synergism of the catalyst (CaO–MnO/CeO₂) and the plasma affects the products distribution, particularly C₂⁺ hydrocarbons selectivity.

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References


