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Catalytic-Dielectric Barrier Discharge Plasma Reactor For Methane And Carbon Dioxide Conversion

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Abstract

A catalytic - DBD plasma reactor was designed and developed for co-generation of synthesis gas and C_{2+} hydrocarbons from methane. A hybrid Artificial Neural Network - Genetic Algorithm (ANN-GA) was developed to model, simulate and optimize the reactor. Effects of CH_4/CO_2 feed ratio, total feed flow rate, discharge voltage and reactor wall temperature on the performance of catalytic DBD plasma reactor was explored. The Pareto optimal solutions and corresponding optimal operating parameters ranges based on multi-objectives can be suggested for catalytic DBD plasma reactor owing to two cases, i.e. simultaneous maximization of CH_4 conversion and C_{2+} selectivity, and H_2 selectivity and H_2/CO ratio. It can be concluded that the hybrid catalytic DBD plasma reactor is potential for co-generation of synthesis gas and higher hydrocarbons from methane and carbon dioxide and showed better than the conventional fixed bed reactor with respect to CH_4 conversion, C_{2+} yield and H_2 selectivity for CO_2 OCM process.

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Keywords: Plasma chemical reactors; Optimization; hybrid ANN-GA; Dielectric-barrier discharge; Pareto Optimal Solution

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_4 and CO_2, greenhouse gas contributors, 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; Istadi & Amin, 2006a). The energetic electrons collide 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 is high enough to cause breakdown in most gases, a large number of microdischarges are observed. The active atoms and metastable compounds subsequently collide with molecules and reactions may occur.

Up to recently, only few researchers focused on modeling studies of DBD plasma reactor, but not modeled comprehensively (Eliasson and Kogelschatz, 1991; Kang et al., 2003) However, litera-

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tures on comprehensive plasma modeling in DBD reactor in relation with optimization of process parameters are limited. The comprehensive plasma reactor model should take into account the various fields, 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 the complex and nonlinear problems, the Artificial Neural Network (ANN) was chosen to model the complex behavior between input and output in the catalytic-DBD plasma process. ANN has been widely used in chemical engineering applications for complex process modeling, 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 modeling and optimization (Nandi et al., 2002, 2004; Ahmad et al., 2004). The hybrid ANN-GA technique is a powerful method for modeling and optimization of complex processes which is better than other technique such as response surface methodology.

The present contribution is intended to introduce potential of Dielectric Barrier Discharge (DBD) Plasma Reactor for methane and carbon dioxide conversion to synthesis gas and higher hydrocarbons. The multi-objective optimization (combined ANN-GA) is developed to obtain the range of optimal operating variables.

Experimental and Numerical Methods

Apparatus of DBD Plasma Reactor

The experimental apparatus of DBD plasma reactor is schematically depicted in Figure 1, while the configuration or design of the DBD plasma reactor was presented elsewhere (Istadi & Amin, 2006b). A high voltage AC generator supplied a voltage from 0 kV 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.) (Istadi, 2006). The Atama's high voltage probe was calibrated using Tektronix P6015 High Voltage Probe.

The variables involve are discharge gap width, discharge voltage and frequency, reactant (CH_4/CO_2) ratio, and total feed flow rate. The DBD plasma reactor was operated without heating and catalyst. The reactor temperature may increase to about 60 °C due to electron heating on the surface of electrode. During the process, the gas temperature can be within the range of room temperature, while the electrons can reach temperatures of $10^4 - 10^5$ K in a dielectric-barrier discharge. The non-thermal plasma can be generated by applying a high voltage to a gas space and incurring gas breakdowns. The gas breakdowns

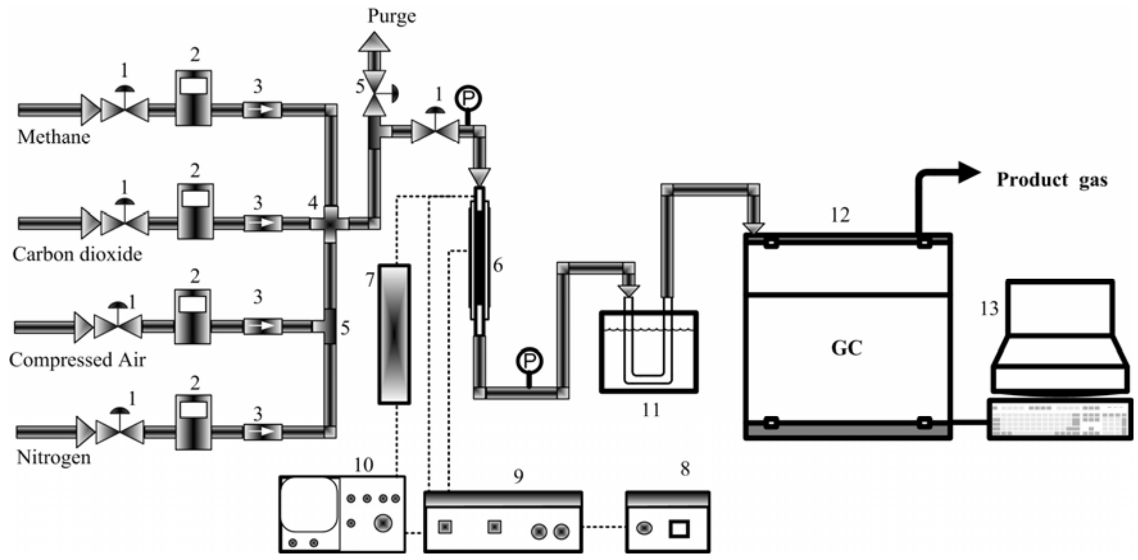

Figure 1. Schematic diagram of apparatus of DBD plasma reactor: (1). Ball valve; (2). Volumetric flow controller; (3). Check valve; (4,5). Four and three way valves; (6). DBD plasma reactor; (7). High voltage probe; (8). DC power supply; (9). High voltage AC generator; (10). Oscilloscope; (11). Condensor; (12). Online GC; (13). Computer for GC; (P). Pressure gage

generate electrons that are accelerated by electric field. The electrical discharges can be realized in several ways depending on the types of voltage applied and reactor specification. In the plasma reactor, the energetic electrons collide with molecules in the gas, resulting in excitation, ionization, electron multiplication, and the formation of atoms and metastable compounds.

Hybrid Artificial Neural Network – Genetic Algorithm (ANN-GA) Approach for Modeling and Optimization

In this research, the MATLAB environment was used for developing computer codes of genetic algorithm optimization (The Mathworks, 2005). The important think is on how to combine the ANN and the GA algorithms in a hybrid algorithm to support simultaneous modeling and multi-objective optimization (Zhao et al., 2000). 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. The detail stepwise procedure for the hybrid ANN-GA algorithm for modeling and optimization was presented elsewhere (Istadi & Amin, 2006b, 2007).

Design of Experiment

The ANN-based model requires more example data which are noise-free and statistically well-distributed. However, the ANN-based model is not good at extrapolation. This weakness can be solved by collecting more example data in the regions where extrapolation is required. The design of the experiment was performed using central composite design (CCD) with full factorial design for designing 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 1 with respect to the catalytic DBD plasma reactor, while the experimental design matrix and the experimental results for validating or training the ANN model are described elsewhere (Istadi & Amin, 2007).

Results and Discussion

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 Figures 2-5 from the ANN-based model simulation.

Figure 2 presents the simulation of CH_4/CO_2 feed ratio effect on the catalytic DBD plasma process performance. Increasing CH_4 concentration in the feed favors 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 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 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. 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

Table 1. Central Composite Design with fractional factorial design for the catalytic DBD plasma reactor

Factors	Range and levels				
	-α	-1	0	+1	+α
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), K	355	423	523	623	691

Note: -1 (low level value); +1 (high level value); 0 (center point); +a and -a (star points) 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 Figure 2 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 Figure 2, 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.

The catalyst located in the discharge gap can increase the time and area of contact in addition to other modification of electronic properties. Through the hybrid system, the chemisorption and desorption performances of the catalyst may be modified in the catalyst surface 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 of 500 W (20 kV and 30 kHz) where the zeolite catalyst introduction significantly increased the selectivity of light hydrocarbons compared to that in the absence of the zeolite, i.e. C_2H_6 selectivity from 8.5 to 11.1% and decreased selectivities of C_{5+} and other oxygenates from 41.2 to 34.2%. The CO selectivity slightly decreased when using the zeolite, but the formations of carbon and plasma polymerization were inhibited.

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 Figure 3. 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 Figure 2, the selectivities of C_{2+} hydrocarbons and hydrogen decrease slightly with the discharge voltage corroborated with the results of Liu et al. (2001). This means that increasing discharge power may destroy the light hydrocarbons (C_2-C_3). In comparison, high C_2 and C_3 hydrocarbons selectivities (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 were 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.

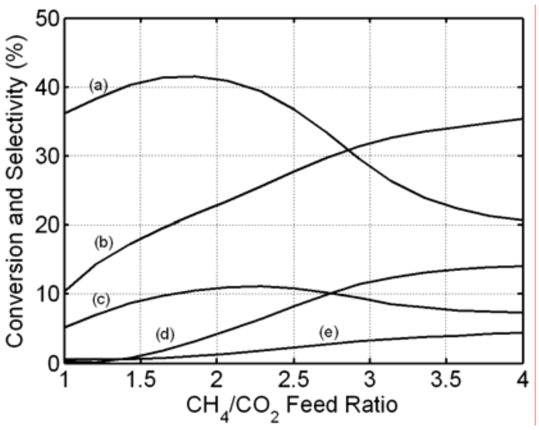

Figure 2. Effect of CH_4/CO_2 feed ratio on catalytic DBD plasma reactor performance at discharge voltage 15 kV, 30 cm^3/min total feed flow rate and reactor temperature 473 K: (a) CH_4 conversion, (b) C_{2+} selectivity, (c) H_2 selectivity, (d) C_{2+} yield, (e) H_2/CO ratio

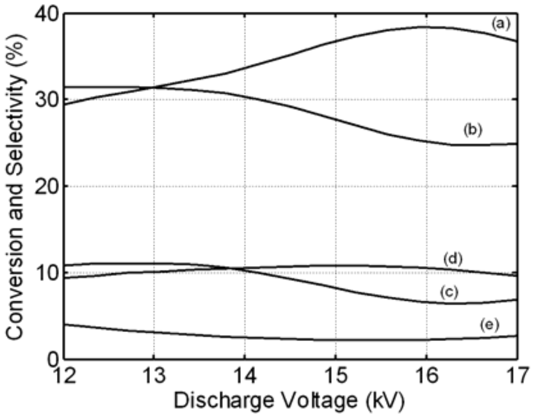

Figure 3. Effect of discharge voltage on catalytic DBD plasma reactor performance at CH_4/CO_2 feed ratio 2.5, 30 cm^3/min total feed flow rate and reactor temperature 473 K: (a) CH_4 conversion, (b) C_{2+} selectivity, (c) H_2 selectivity, (d) C_{2+} yield, (e) H_2/CO ratio

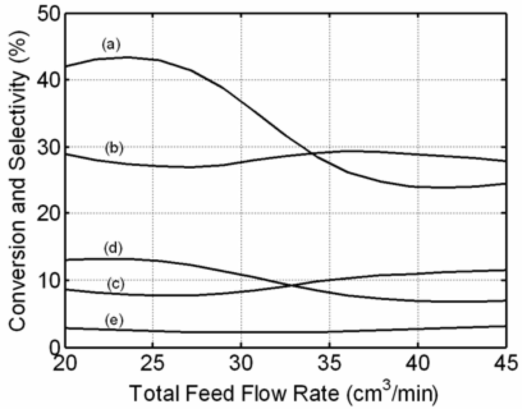

Figure 4. Effect of total feed flow rate on catalytic DBD plasma reactor performance at CH_4/CO_2 feed ratio 2.5, discharge voltage 15 kV and reactor temperature 473 K: (a) CH_4 conversion, (b) C_{2+} selectivity, (c) H_2 selectivity, (d) C_{2+} yield, (e) H_2/CO ratio

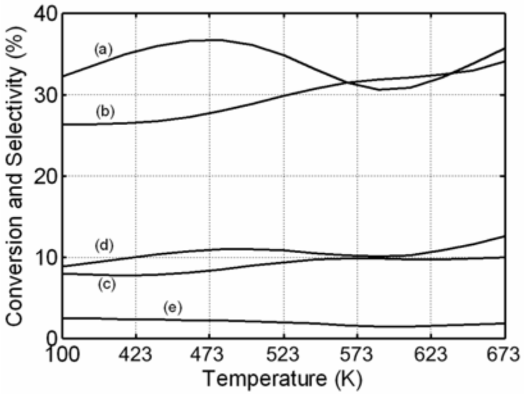

Figure 5. Effect of reactor wall temperature on catalytic DBD plasma reactor performance at CH_4/CO_2 feed ratio 2.5, discharge voltage 15 kV and total feed flow rate 30 cm^3/min: (a) CH_4 conversion, (b) C_{2+} selectivity, (c) H_2 selectivity, (d) C_{2+} yield, (e) H_2/CO ratio

The 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 quickly as demonstrated in Figure 4. 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 Figure 4, 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 significantly on the methane conversion rather than selectivity of C_{2+} hydrocarbons and hydrogen. 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.

Pertaining to the reactor wall temperature, Figure 5 presents the effect of reactor temperature variation 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, 2005). In endothermic reactions, normally high temperatures are required to add enthalpy. In this research, the methane and carbon dioxide reaction over CaO-MnO/CeO_2 catalyst in the DBD plasma reactor is influenced significantly by energetic electrons. The carbon was also formed at the entire surface of electrode during the reaction. A good plasma catalytic activity was achieved only when streamer discharges were present. At higher temperatures, the streamer discharge may turn to an arc-like discharge and thermal effects dominate the reactions. The non-equilibrium streamer discharge at lower temperatures favored the formation of the higher hydrocarbons. From Figure 5, it is evident that the current range of reactor temperature (373-673 K) only affects the catalytic DBD plasma reactor slightly. The methane conversion is slightly affected by reactor wall temperature over the CaO-MnO/CeO_2 catalyst. The C_{2+} hydrocarbons selectivity is enhanced slightly by the reactor temperature which may be due to the altering 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 can not be determined in the sense of traditional catalyst.

Pareto-Optimal Solutions of Multi-objectives Optimization using Hybrid ANN-GA Strategy

Five objectives should be maximized simultaneously corresponding to four operating parameters. The simultaneous maximization is intended to come close to the real conditions of the process, but huge number of objectives to be optimized simultaneously, the more difficult the optimization process is. To simplify the optimization problem, the optimization of noncatalytic DBD plasma reactor is 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.

The Pareto optimal solutions of catalytic DBD plasma reactor for CH_4 and CO_2 conversions process are depicted in Figure 6 with respect to simultaneous maximization of CH_4 conversion and C_{2+} hydrocarbons selectivity. The Pareto optimal solutions points are obtained by varying the weighting factor ($\boldsymbol{w_k}$) and performing the GA optimization corresponding to each $\boldsymbol{w_k}$ ($0 \leq \boldsymbol{w_k} \leq 1$). 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. CH_4 conversion can achieve as high as 23.5% with C_{2+} selectivity equal to 39.6%, while the C_{2+} selectivity can be obtained as high as 29.9% with CH_4 conversion equal to 47.0%. The results can be achieved by altering the operating parameters of CH_4/CO_2 feed ratio, discharge voltage, total feed flow rate and reactor wall temperature from 4.0, 12.8 kV, 25.2 cm^3/min and 423 K to 2.2, 12.8 kV, 20 cm^3/min and 423 K, respectively. CH_4 conversion improves at lower CH_4/CO_2 ratio, since high CO_2 concentration in the feed improves the decomposition of methane. The C_{2+} selectivity increases with CH_4/CO_2 ratio. Increasing the total feed flow rate decreases the CH_4 conversion and enhances the C_{2+} selectivity slightly which is in agreement with the results of Eliasson et al. (2000) and Liu et al. (1998). However, CH_4 conversion and C_{2+} selectivity are only slightly affected by the discharge voltage and the reactor temperature within the range of Pareto optimal solutions.

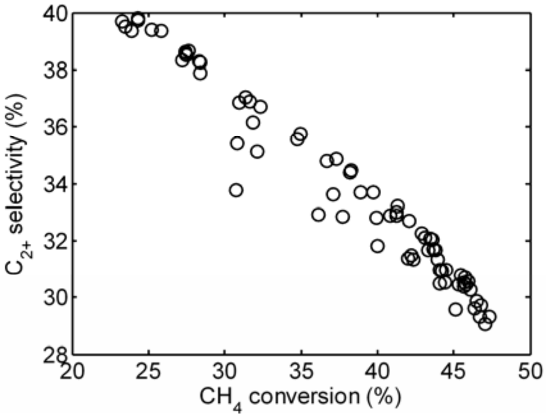

Figure 6. Pareto optimal solutions obtained from simultaneous maximization of CH_4 conversion and C_{2+} selectivity for catalytic DBD plasma reactor

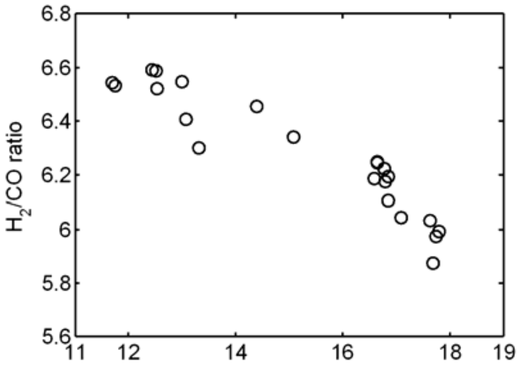

Figure 7. Pareto optimal solutions obtained from simultaneous maximization of H_2 selectivity and H_2/CO ratio for catalytic DBD plasma reactor

Pertaining to simultaneous maximization of H_2 selectivity and H_2/CO ratio (Case 2), the Pareto optimal solution is presented in Figures 7. From the figure, it was found that the Pareto optimal solution shows non inferior feature where H_2 selectivity increases at decreasing H_2/CO ratio within the Pareto zone. H_2 selectivity can achieve as high as 17.8% with H_2/CO ratio equal to 5.9, while the H_2 selectivity can be obtained as high as 11.7% with H_2/CO ratio equal to 6.6%. The optimal operating parameters suitable for simultaneous optimization of H2 selectivity and H_2/CO ratio can be recommended where CH_4/CO_2 ratio being 3.9-4.0, discharge voltage about 14.0 kV, total feed flow rate being about 20-40 cm^3/min, and reactor temperature being 373-453 K. Higher CH_4 concentration enhances the H_2 selectivity, but not for discharge voltage. The discharge voltage does not influence the H_2 selectivity. It is shown that the H_2 selectivity is influenced slightly by reactor wall temperature in the catalytic DBD plasma reactor.

Comparison between DBD Plasma and Conventional Fixed Bed Reactors at the Same Feed Flow Rate and Catalyst

Table 2 presents the comparison between catalytic DBD plasma reactor and conventional fixed bed reactor at the same total feed flow rate and catalyst (Istadi, 2006). From the table, it is shown that the catalytic DBD plasma reactor is better than the conventional fixed bed reactor with respect to CH_4 conversion, C_{2+} yield and H_2 selectivity. In addition, the C_{2+} hydrocarbons resulted from catalytic DBD plasma reactor include ethane (C_2H_6), ethylene (C_2H_4), acetylene (C_2H_2), and propane (C_3H_8), while those of conventional fixed bed reactor include only ethane and ethylene. The DBD plasma reactor produces some hydrogen, while the conventional fixed bed reactor does not produce hydrogen. However, the C_{2+} se-

Table 2. Comparison between plasma and conventional fixed bed reactors at the same catalyst (12.8CaO-6.4MnO/CeO_2) and total feed flow rate

Parameters	Reactor Performance		
	Catalytic Plasma Reactor		Conventional Fixed Bed Reactor [3]
	Total Feed flow rate = 30 cm^3/min [1]	Total Feed flow rate = 50 cm^3/min [2]	
CH_4 conversion	36.7%	25.1%	5.1%
C_{2+} selectivity	29.3%	26.0%	75.6% *)
H_2 selectivity	9.8%	8.3%	No H_2 product
C_{2+} yield	11.1%	6.6%	3.9% *)
CO selectivity	14.5%	13.6%	37.8%
H_2/CO ratio	4.4	2.0	No H_2 product

*) comprises only C_2H_6 and C_2H_4

[1] From ANN model simulation: Discharge voltage = 16 kV, Frequency = 2 kHz, T= 473 K, CH_4/CO_2 ratio = 3, Total feed flow rate = 30 cm^3/min

[2] From ANN model simulation: Discharge voltage = 16 kV, Frequency = 2 kHz, T= 473 K, CH_4/CO_2 ratio = 3, Total feed flow rate = 50 cm^3/min

[3] CO_2/CH_4 = 2, T = 1127 K, total feed flow rate = 50 cm^3/min

lectivity of DBD plasma reactor is still lower than that of conventional reactor. Pertaining to DBD plasma reactor, lower total feed flow rate (30 cm^3/min) shows better performance than higher feed flow rate (50 cm^3/min). Another benefit of catalytic DBD plasma reactor is that only very low temperature of the reactor is required to do the process, because in fact the high energetic electrons are produced in the discharge zone (achieve 10^4-10^5 K). Indeed, the hybrid catalytic DBD plasma reactor is effective for co-generation of C_{2+} hydrocarbons and synthesis gas from methane and carbon dioxide.

Conclusions

The hybrid catalytic DBD plasma reactor is potential for co-generation of C_{2+} 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 CH_4/CO_2 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 good fitting. It can be concluded that three factors, i.e. CH_4/CO_2 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 C_{2+} 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 owing to simultaneous maximization of CH_4 conversion and C_{2+} selectivity, and/or H_2 selectivity and H_2/CO ratio. It can be concluded that the hybrid catalytic DBD plasma reactor is more suitable for CO_2 OCM process than the conventional catalytic reactor over CaO-MnO/CeO_2 catalyst. The synergism of the catalyst and the plasma affects the products distribution, particularly C_{2+} hydrocarbons selectivity.

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