Co-Generation of C_{2+} Hydrocarbons and Synthesis Gas from Methane and Carbon Dioxide using Dielectric-Barrier Discharge Plasma Reactor without Catalyst at Low Temperature

Istadi [1,2] and Nor Aishah Saidina Amin [1,*]

[1] Chemical Reaction Engineering Group (CREG), Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, UTM Skudai, Johor Bahru, 81310 Malaysia

[2] Permanent Address: Chemical Reaction Engineering & Catalysis (CREC) Group, Dept. of Chemical Engineering, Diponegoro University, Semarang, Indonesia
E-mail: istadi@tekim.ft.undip.ac.id

ABSTRACT

Co-generation of C_{2+} hydrocarbons and synthesis gas from methane and carbon dioxide has been an important issue in tackling the global warming effects from the two greenhouse gases. Dielectric-barrier discharge (DBD) plasma technology has been proposed to improve the process involving conversion and utilization of both methane and carbon dioxide. In this paper, a study on the effects of CH_4/CO_2 feed ratio, total feed flow rate, and discharge voltage on performance of DBD plasma reactor without catalyst at low temperature were addressed. The three factors in the DBD reactor showed significant effects on the reactor performances, i.e. methane conversion, synthesis gas and C_{2+} hydrocarbons selectivities. With the DBD plasma reactor without catalyst, the C_{2+} hydrocarbons (ethane, ethylene, acetylene, and propane) and synthesis gas (hydrogen and carbon monoxide), were produced from methane and carbon dioxide at low temperature with promising performances. Co-feeding carbon dioxide to the methane feed stream reduced coking and enhanced methane conversion. Methane and carbon dioxide conversions were influenced significantly by the discharge voltage. High discharge voltage, low CH_4/CO_2 feed ratio, and low total feed flow rate were suitable for the co-generation over DBD plasma reactor with potential performances.

Keywords: dielectric-barrier discharge, plasma discharge reactor, CH_4-CO_2 conversion, synthesis gas

1. INTRODUCTION

The studies on conversion and utilization of methane and carbon dioxide are widely researched in the field of C1 chemistry. Several technologies have been proposed to improve the efficiency and utilization of methane and carbon dioxide. Mitigation of CO_2, one of the most important greenhouse gases, is the crucial agenda in global warming issues. Meanwhile, the direct conversion of methane to C_{2+} hydrocarbons and synthesis gas has a large implication towards the utilization of natural gas in the gas-based petrochemical and liquid fuel. The CO_2 and CH_4 contents in Natuna's, Arun's and Terengganu's natural gases with CH_4/CO_2 ratio 28/71, 75/15 and 80/8, respectively should be strategically utilized for the production of synthesis gas, higher hydrocarbons, liquid fuels and other important chemicals [1,2].The potentials of non-conventional DBD plasma reactor for converting the two greenhouse gases, CH_4 and CO_2, to higher hydrocarbons and synthesis gas at low temperature and ambient pressure have also been reported [3]. A comprehensive review on recent development of plasma reactor technology for the co-generation of synthesis gas and C_{2+} hydrocarbons from methane and carbon dioxide has been reported to address the features, drawbacks, challenges, and feasibility of this technology [4].

The oxidative coupling of methane (OCM) is a promising and novel route for the conversion of natural gas to C_2 hydrocarbons in the presence of a basic catalyst within the temperature range of 923 to 1127 K. Recently, carbon dioxide was used to replace oxygen as an oxidant in oxidative coupling of methane by carbon dioxide (CO_2 OCM) to produce active oxygen species which promotes formation of

* **Corresponding Author**. E-mail: noraishah@fkkksa.utm.my. Tel. +607-5535588, Fax. +607-5581463

CH_3^* radicals from methane. Unlike O_2, CO_2 does not induce gas phase radical reactions. It is thus expected that the development of active catalysts achieves high selectivity to C_2 hydrocarbons. From the thermodynamic studies, production of C_2H_6 and C_2H_4 from CH_4 and CO_2 showed low performances due to thermodynamic limitation [5,6]. Pertaining to CO_2 OCM reaction, various binary metal oxides have been proposed, i.e. CaO-CeO_2 [5], SrO-MnO_2 [7], and MnO_2-$SrCO_3$ [8]. Almost all the catalysts achieved low methane conversion (up to 7%), high enough C_2 hydrocarbons selectivity (up to 85%), and low C_2 hydrocarbons yield (up to 4.5%). The CH_4 and CO_2 reactions over these catalysts only produce C_2H_6, C_2H_4 and CO without any other products such as H_2, C_2H_2, or C_3H_8. In addition with respect to ternary metal oxide system, CaO-MnO/CeO_2 catalyst attained C_2 selectivity of 76.6% and C_2 yield of 3.7% using an optimization strategy [9]. The low performance of the CO_2 OCM reaction is related to high ΔG_T^o at all temperature range which showed that the reactions are no favoured thermodynamically. The major intricacy for direct methane conversion to higher hydrocarbons and oxygenates involve the intensive energy consumption requirement and also activating the stable C-H bonds in the methane molecule using conventional catalysis.

Due to the thermodynamic constraints in obtaining high yield for the CO_2 OCM, further improvements are required including the exploitation of some non-conventional technologies such as plasma reactor. In this paper, a study on the effects of CH_4/CO_2 feed ratio, total feed flow rate, and discharge voltage on performance of DBD plasma reactor without catalyst at low temperature are addressed. The effect of the process variables on the CH_4 conversion, selectivity and yield of C_{2+} hydrocarbons, and H_2/CO ratio are considered.

2. EXPERIMENTAL METHOD

2.1. Experimental Rig Set-up of DBD Plasma Reactor

The schematic diagram of experimental rig set-up of DBD plasma reactor is depicted in Figure 1, while Figure 2 presents the schematic diagram of high voltage generator circuit. A high voltage pulse AC generator supplies a voltage in the ranges 0 - 17 kV with a pulsed waveform at a frequency of up to 10 kHz (Atama Tech Sdn Bhd). The voltage measurement was conducted using an oscilloscope (ISO-TECH ISR 622) equipped with a high voltage probe (Atama Tech Sdn Bhd). All experimental works were conducted at fixed pulse frequency (2 kHz).

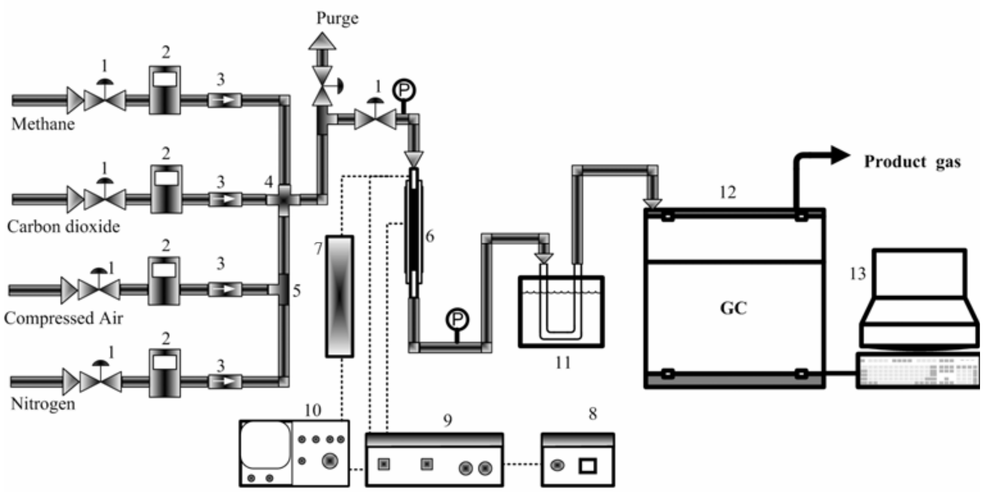


Figure 1. Schematic diagram of experimental rig set-up of DBD plasma reactor: (1). Ball valve; (2). Volumetric flow controller; (3). Check valve; (4,5). Four and three way valves; (6). DBD plasma reactor; (7). High voltage probe; (8). DC power supply; (9). High voltage generator; (10). Oscilloscope;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

The high voltage pulse AC generator circuit as depicted in Figure 2 can be divided to two main sections: the oscillator and the power drive. The oscillator is built around a CMOS 4093 (4-nand gates) and is 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 capacitor 10 nF. The on/off time control gives a very good regulation to fine-tune the output for maximum output voltage. In fact, once the frequency was increased, the voltage was decreased, and vice versa. The power drive is built around a power switching transistor (2N3055) which is driven by a 2N2222 transistor. The power transistor receives the command signal from the oscillator that opens and closes many times per second the primary coil of the transformer, thus inducing a high voltage in the transformer secondary coil. The output voltage is dependent on the transformer type, power transistor, and power supply.

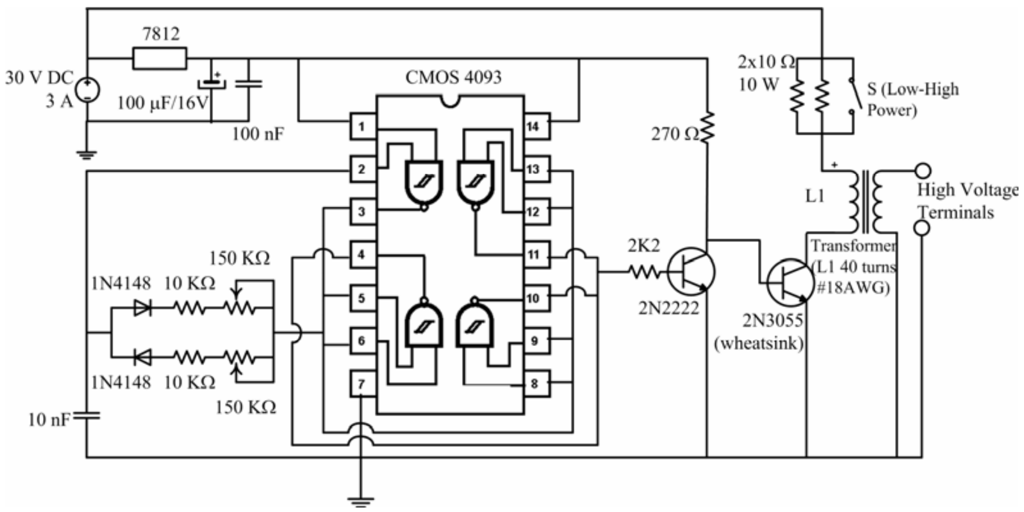


Figure 2. Schematic diagram of high voltage generator circuit

2.2. Design of Experiment (DOE)

A Central Composite Rotatable Design (CCRD) for three independent variables was employed to design the experiments [9]. The design is intended to reduce the number of experiments and to arrange the experiments with various combinations of independent variables. The ranges and levels used in the experiments are given in Table 1. The experimental design matrix resulted by the CCRD are revealed in Table 2 involves 19 sets of coded conditions expressed in natural values. The design consists of 8 cube points of two-level full factorial design, 6 star points and 5 centre points. In this paper, effect of three variables on the performances of plasma CH_4-CO_2 conversion is presented in three dimensional surface profiles. The surface profile was prepared based on the experimental results with respect to the CCRD design by utilizing Statistica software (Statsoft, Inc.). The profiles were produced in the software by implementing an empirical quadratic polynomial approach to the experimental data with reasonable determination coefficient.

Table 1. Ranges and levels of factors or independent variables used in experiments

Factors	Range and levels				
	-α (-1.68)	-1	0	+1	+α (+1.68)
CH_4/CO_2 Ratio, [-]	0.3	1	2	3	3.7
Discharge voltage, kV	12.6	13.4	14.6	15.8	16.6
Total feed flow rate, cm^3/min	26.4	40	60	80	93.6

Note: -1 (low level value); +1 (high level value); 0 (center point); +α and -α (star points)

3. RESULTS AND DISCUSSION

3.1. Principles of DBD Plasma Reactor

The principle is based on high energy electrons. Non-thermal plasma can be defined as gas consisting of electrons, highly excited atoms and molecules, ions, radicals, photons and neutral particles in which the electrons have a much higher energy than the neutral gas particles. Non-thermal plasma is also called non-equilibrium plasma due to the significant difference of temperature or kinetic energy between the electrons and the neutral particles [3]. 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 and maintained by electrical discharge [3] which is a direct way to produce non-thermal plasma by applying a high voltage to a gas space and incurring gas breakdowns. The gas breakdowns generate electrons that are accelerated by an electric field forming non-thermal plasma. 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 [3,10]. When the electric field in the discharge gap is high enough to cause breakdowns in most gases, a large number of microdischarges are observed. The active atoms and metastable compounds subsequently collide with molecules, and reactions may occur. For CO_2 reforming of methane, it is expected that CH_4 and CO_2 participate in the reactions and be converted into higher hydrocarbons and synthesis gases. The possible reactions occurred in the CH_4 and CO_2 conversions over the DBD plasma reactor without catalyst at low temperature can be described as follows [3]:

$$CH_4 + e \rightarrow CH_3^* + H^* + e \quad (1)$$
$$CO_2 + e \rightarrow CO + O^* + e \quad (2)$$
$$CH_3^* + CH_3^* \rightarrow C_2H_6 \quad (3)$$
$$C_2H_6 + e \rightarrow C_2H_5^* + H^* + e \quad (4)$$
$$C_2H_5^* + CH_3^* \rightarrow C_3H_8 \quad (5)$$
$$H^* + H^* \rightarrow H_2 \quad (6)$$
$$C_2H_5^* + e \rightarrow C_2H_4 + H^* + e \quad (7)$$
$$C_2H_4 + e \rightarrow C_2H_3^* + H^* + e \quad (8)$$
$$C_2H_3^* + e \rightarrow C_2H_2 + H^* + e \quad (9)$$
$$C_2H_5^* + C_2H_5^* \rightarrow C_4H_{10} \quad (10)$$
$$C_4H_{10} + e \rightarrow C_4H_9 + H^* + e \quad (11)$$
$$H_2 + e \rightarrow 2H^* + e \quad (12)$$
$$CH_3^* + e \rightarrow CH_2^* + H^* + e \quad (13)$$
$$CH_2^* + e \rightarrow CH^* + H^* + e \quad (14)$$
$$CH^* + CH^* \rightarrow C_2H_2 \quad (15)$$
$$CH_2^* + CH_2^* \rightarrow C_2H_4 \quad (16)$$
$$CH^* + e \rightarrow C + H^* + e \quad (17)$$

In the reactions, e denotes high energy electron, while * express radical species from dissociation reaction.

3.2. Experimental Data of DBD Plasma Reactor without Catalyst at low temperature

The experimental results of DBD plasma reactor without catalyst at low temperature are listed in Table 2. The experimental data is presented based on design of experiment (DOE) with three independent variables, CH_4/CO_2 ratio, discharge voltage, and total feed flow rate. The CCRD design is practical for addressing the effect of each independent variable as well as the interaction among the variables [9]. Gaseous hydrocarbons (C_2-C_3), hydrogen and CO are the main products in the gas phase. The CO is principally produced from the dissociation of carbon dioxide, while the light hydrocarbons and hydrogen are the primary products from methane conversion. Pertaining to the C_{2+} hydrocarbons products, the concentration of ethane (C_2H_6) is much higher than that of ethylene (C_2H_4), acetylene (C_2H_2) and propane (C_3H_8) in the gaseous products. The results are significantly different with the results using corona discharges [3,12] where acetylene (C_2H_2) is the primary product. Direct conversions of CH_4 and CO_2 to higher hydrocarbons and synthesis gases is promising over the DBD plasma reactor without catalyst at low temperature. In fact, the conversions using conventional catalytic fixed bed reactor at high temperature (about 850 ^oC) only produced C_2H_6, C_2H_4 and CO with very low CH_4 conversion, namely CO_2 OCM [9]. In other catalytic process (carbon dioxide reforming of methane), it only produced H_2 and CO at high temperature (about 850 ^oC) over suitable catalyst with considerable methane conversion.

Table 2. Experimental data of DBD plasma reactor without catalyst at low temperature

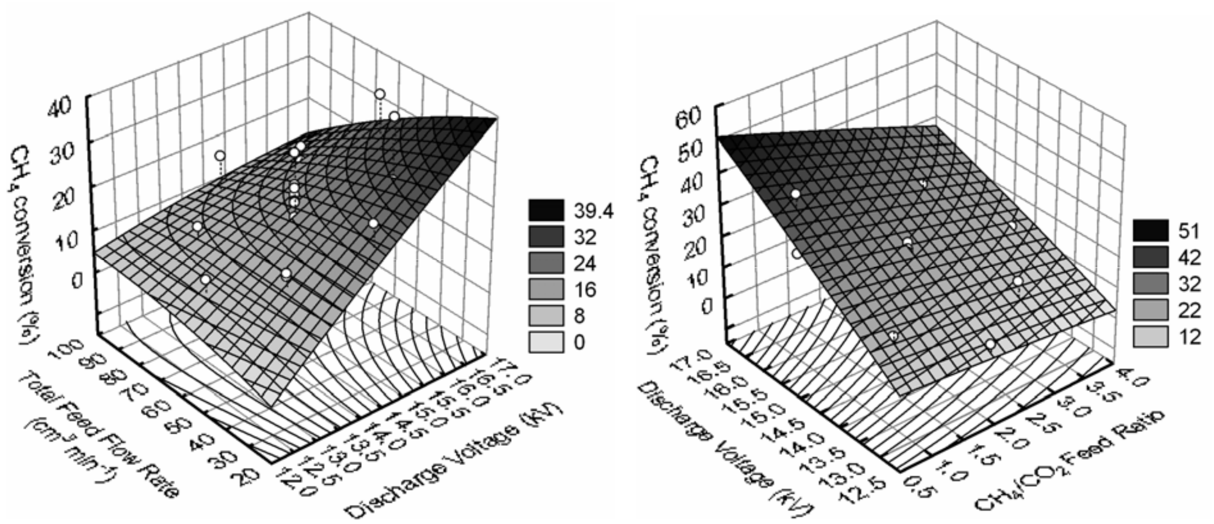
Process variables			Responses/Dependent variables								
CH_4/CO_2 ratio	Discharge voltage (kV)	Total feed flow rate (cm^3/min)	X CH_4 (%)	X CO_2 (%)	S C_{2+} (%)	S H_2 (%)	S CO (%)	Y C_{2+} (%)	Y H_2 (%)	Y CO (%)	H_2/CO Ratio
3.0	13.4	40.0	13.28	9.33	24.90	10.21	7.04	3.31	1.36	0.86	2.30
3.0	13.4	80.0	5.64	4.53	33.78	13.91	8.05	1.91	0.79	0.43	2.53
3.0	15.8	40.0	24.63	17.65	25.43	10.68	10.32	6.26	2.63	2.28	1.43
3.0	15.8	80.0	16.03	9.09	15.17	6.51	3.94	2.43	1.05	0.56	2.74
1.0	13.4	40.0	14.16	12.50	16.84	8.80	7.45	2.38	1.25	1.00	1.32
1.0	13.4	80.0	10.93	9.55	15.03	8.01	6.84	1.64	0.88	0.70	1.19
1.0	15.8	40.0	38.40	23.96	10.76	7.14	14.05	4.13	2.74	4.41	0.64
1.0	15.8	80.0	19.54	10.63	13.68	8.14	10.13	2.67	1.59	1.45	0.91
3.7	14.6	60.0	14.78	12.56	24.29	8.26	6.38	3.59	1.22	0.90	1.87
0.3	14.6	60.0	29.23	13.60	4.86	7.86	11.50	1.42	2.30	1.93	0.46
2.0	12.6	60.0	9.25	8.49	29.94	12.04	11.21	2.77	1.11	1.00	1.21
2.0	16.6	60.0	34.17	20.20	14.27	3.62	3.82	4.88	1.24	1.12	1.45
2.0	14.6	26.4	24.36	11.74	20.45	7.36	7.08	4.98	1.79	1.47	1.76
2.0	14.6	93.6	17.97	13.84	13.64	4.88	3.67	2.45	0.88	0.59	1.83
2.0	14.6	60.0	19.90	12.63	16.85	6.39	7.51	3.35	1.27	1.28	1.17
2.0	14.6	60.0	18.42	13.58	17.46	6.62	7.10	3.22	1.22	1.16	1.23
2.0	14.6	60.0	18.05	13.10	15.68	5.70	4.19	2.83	1.03	0.69	2.02
2.0	14.6	60.0	22.18	12.68	13.24	4.48	2.90	2.94	0.99	0.57	2.50
2.0	14.6	60.0	21.36	13.28	13.67	4.53	3.72	2.92	0.97	0.70	1.89

Note: - X, S, Y denote conversion, selectivity and yield, respectively
- C_{2+} comprises C_2H_4, C_2H_6, C_2H_2, C_3H_8.

3.3. Effect of Operating Conditions on CH_4 Conversion, C_{2+} Hydrocarbons Selectivity and Yield over DBD Plasma Reactor

CH_4 conversion, C_{2+} hydrocarbons selectivity and yield are significantly affected by discharge voltage, CH_4/CO_2 ratio and total feed flow rate as depicted in Figures 3 - 5. From Figure 3, the CH_4 conversion enhances with concentration of CO_2 in the feed. As an oxidant, CO_2 is first decomposed to CO and O^* by high energy electrons. The hot electrons collide with CO_2 molecules and excite them to higher energy levels to dissociate or initiate the reactions. The dissociation reaction of CO_2 generates some oxygen species. Some excited atomic species such as metastable oxygen species ($O(^1D)$) are active species for the generation of methyl radicals from CH_4 via dissociation reaction. The dissociation of CO_2 will generate oxygen active species that assist plasma catalytic methane conversion. With co-feed of CO_2, the reaction of methane species is deeply influenced by the new reactive oxygen species so that the conversion of methane is much higher than CO_2 conversion as exhibited in Table 2. The possible mechanism is that the reactive oxygen removes H atom in methane to generate the hydrocarbons radicals [3]. The excited species will react with the hydrocarbons radicals in the plasma zone. Indeed, the co-feed CH_4 and CO_2 promote the conversion each other. The distribution of hydrocarbon products changes significantly with the CH_4/CO_2 feed ratio [10]. It is suggested that the

CH_4 concentration in the feed is an important factor for the total amount of hydrocarbons produced. Lower amount of CO_2 in the feed favours the production of C_{2+} hydrocarbons as revealed in Figures 4 and 5. From Table 2, the larger the CO_2 amount in the feed, the higher the CO selectivity, whereas the selectivity of all higher hydrocarbons decreased. This phenomenon is corroborated with the results of Zhang et al. [10]. The yield of gaseous hydrocarbons (C_{2+}) increases considerably with the CH_4/CO_2 feed ratio as exhibited in Figure 5. It is possible to control the composition of C_{2+} hydrocarbons and hydrogen products by adjusting the CH_4/CO_2 feed ratio. It is recommended that the range of CH_4/CO_2 feed ratio 2 – 3 should be used to get a high selectivity of C_{2+} hydrocarbons and hydrogen with high methane conversion. Further increasing CH_4/CO_2 ratio above 3 favours lower CH_4 conversion and coking formation. In this work, the composition of feed gas is an important factor to influence the product distribution. Obviously, more methane in the feed will produce more hydrocarbons. The drawback of DBD plasma methane conversion with pure CH_4 feed is the formation of carbon deposits on the surface of electrode. The co-feed of CO_2 can inhibit the deposition of carbon and thus sustain the operations of DBD. The coke is mainly formed via CH_4 decomposition, not CO disproportionation. The dissociation energy of CO possessing of 11.1 eV is higher than that of dissociation energy of CH_x (x=1-4), which is lower than 5 eV [12]. The CO_2 is more difficult to be dissociated via the collisions of electrons than CH_x.



(a) (b)

Figure 3. Effect of operating conditions on CH_4 conversion: (a) discharge voltage and total feed flow rate vs CH_4 conversion presented at CH_4/CO_2 ratio of 3; (b) discharge voltage and CH_4/CO_2 ratio vs CH_4 conversion presented at total feed flow rate of 40 cm^3/min

Total feed flow rate affects the residence time within the discharge zone. Increasing the total feed flow rate reduces the conversion of methane and carbon dioxide quickly as demonstrated in Figure 3(a) [12]. In fact, increasing the total feed flow rate does not affect significantly on the C_{2+} hydrocarbons and hydrogen selectivity. Fincke et al. [13] concluded that an appropriate ratio of CH_4/CO_2 in the feed, a relatively low discharge voltage, and a relatively large total feed flow rate are benefit for higher energy efficiency. Actually, the low total feed flow rate with high residence time leads to the high intimate collision among the gas molecules and high energy electrons. The high intensive collisions favour the methane and carbon dioxide conversions to C_{2+} hydrocarbons.

The various kinds of electric sources were used in plasma reactor such as AC, DC, microwave, or pulse power supply operated at high voltage and high frequency AC power. Varying the discharge power/voltage affects predominantly on methane conversion and higher selectivity of higher hydrocarbons (C_2-C_3). The conversions of CH_4 and CO_2 increase with discharge voltage as exhibited in Figure 3. At high discharge power the CH_4 conversion becomes higher than that of CO_2 at higher discharge voltage since the dissociation energy of CO_2 (5.5 eV) is higher than that of CH_4 (4.5 eV) [3,14]. More plasma species are generated at higher discharge voltage. In addition to high energy electron, species such as H, OH, O radicals can attack CH_4 molecules to produce more methyl radicals. The selectivity of C_{2+} hydrocarbons decreases slightly with increasing the discharge voltage at fixed frequency as revealed in Figure 4 which is corroborated with the result of Liu et al. [15] and Song et al. [16]. This means that the increased discharge power may destroy light hydrocarbons (C_2-C_3). The low discharge power is beneficial to obtain higher selectivity to light hydrocarbons (C_2-C_3), but the CH_4 conversion is low. Eliasson et al. [17] reported that higher discharge power is necessary for generating higher selectivity to higher hydrocarbons (C_{5+}) over DBD reactor with the presence of zeolite catalysts. Higher discharge power is suggested for efficient methane conversion. As the discharge power increases, the bulk gas temperature in the reaction zone increases.

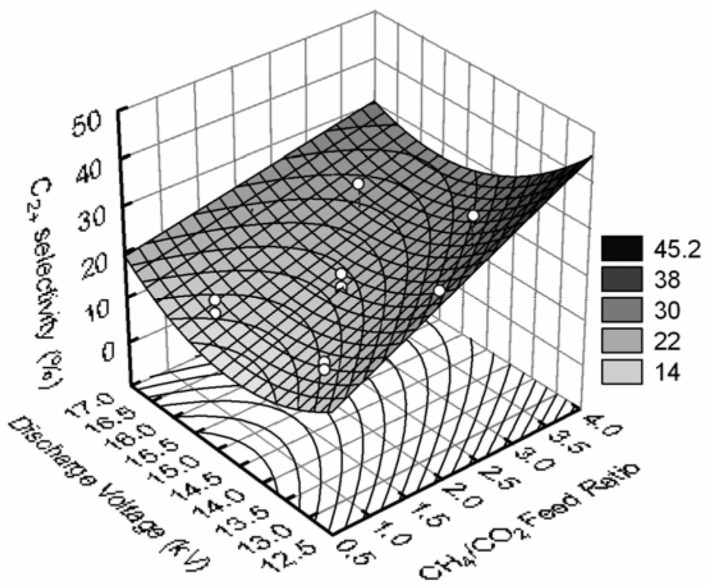


Figure 4. Effect of discharge voltage and CH_4/CO_2 feed ratio on C_{2+} selectivity presented at total flow rate of 40 cm^3/min

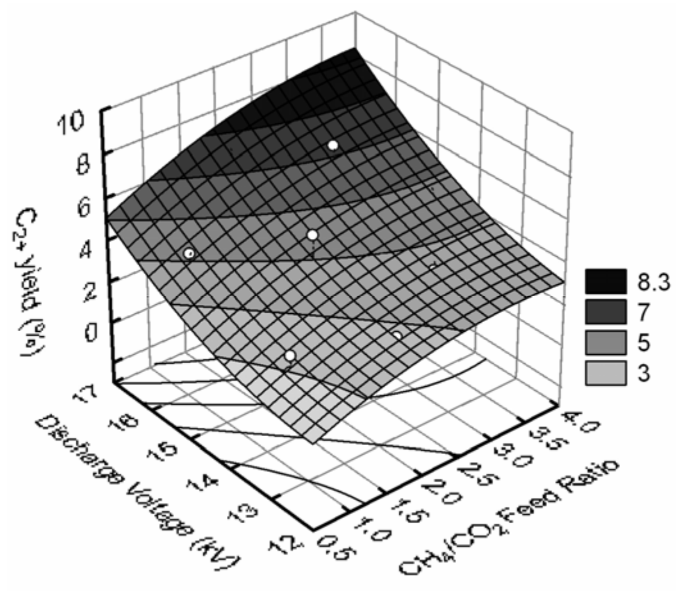


Figure 5. Effect of discharge voltage and CH_4/CO_2 feed ratio on C_{2+} hydrocarbons yield presented at total feed flow rate of 40 cm^3/min

Based on the effect of operating variables studies, it is recommended that low total feed flow rate, high CH_4/CO_2 feed ratio and high discharge voltage are suitable for producing C_{2+} hydrocarbons and synthesis gas. Table 3 shows the results of DBD plasma reactor at recommended conditions and their comparison with pure CH_4 as a feed. From the table, it is shown that CH_4/CO_2 ratio = 3 provides more promising results. However, increasing CH_4/CO_2 ratio to 4 reduces methane conversion considerably and leads to enhanced C_{2+} hydrocarbons selectivity and H_2/CO ratio slightly. It is confirmed that CO_2 as co-feed has an important role in improving CH_4 conversion by contributing oxygen active species from the CO_2. The coking formation was appeared obviously in the surface of electrode at CH_4/CO_2 ratio of 4. The significant decreasing CH_4 conversion from 21.95% to 15.23% is also reported for pure CH_4 as a feed with higher C_{2+} hydrocarbons selectivity. The coking formation is obvious distinctly in the surface of electrode. In this case, CO_2 also helps the reduction of coking formation. It can be concluded that too high CH_4/CO_2 ratio is not suggested in the operation of DBD plasma reactor due to decrement of CH_4 conversion and coking formation reasons.

Table 3. Results of DBD plasma reactor without catalyst at potential operating conditions and comparison with that at pure CH_4 as feed.

Process variables			Responses/Dependent variables								
CH_4/CO_2 Ratio	Discharge Voltage (kV)	Total Feed Flow Rate (cm^3/min)	X CH_4 (%)	X CO_2 (%)	S C_{2+} (%)	S H_2 (%)	S CO (%)	Y C_{2+} (%)	Y H_2 (%)	Y CO (%)	H_2/CO Ratio
3.0	17.2	30	25.38	17.09	27.04	9.52	5.58	6.88	2.42	1.32	2.92
4.0	17.2	30	21.95	18.45	30.79	9.52	4.29	6.76	2.09	0.92	3.85
Pure CH_4	17.2	30	15.23	-	34.88	9.78	-	5.32	1.45	-	-

3.4. Effect of DBD Plasma Conditions on H_2/CO Synthesis Gas Ratio

Figure 6 presents the effect of discharge voltage and CH_4/CO_2 feed ratio on H_2/CO synthesis gas ratio. From the figure, the H_2/CO product ratio is mainly controlled by the discharge voltage and CH_4/CO_2 feed ratio. Increasing the discharge voltage leads to an increase in the H_2/CO ratio slightly and achieves maximum at 13.5 kV. Next increasing the discharge voltage decreases the H_2/CO ratio slightly due to more CO is produced from CO_2 and CH_4 which is in agreement with the result of Song et al. [16] without catalyst. The H_2/CO ratio increases considerably with CH_4 concentration in the feed gas. This means that once CH_4 concentration in the feed gas increased more H_2 was produced and less CO in the product. It is possible to control the composition of the synthesis gas product by adjusting the molar ratio of feed gases. Zhang et al. [11] reported that lower feed flow rate and high discharge voltage is beneficial for producing synthesis gases with higher H_2/CO ratio and for obtaining high selectivity to higher hydrocarbons.

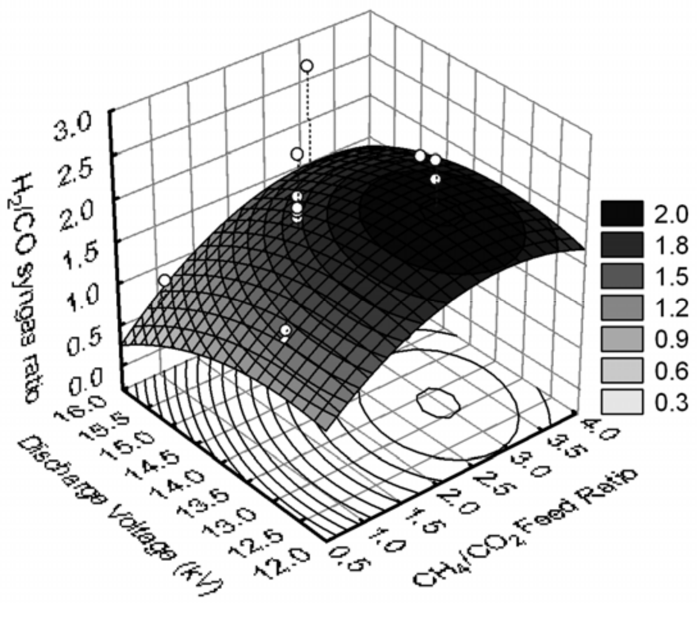


Figure 6. Effect of discharge voltage and CH_4/CO_2 feed ratio on H_2/CO synthesis gas ratio presented at total feed flow rate of 40 cm^3/min

4. Conclusions

A study on the effects of CH_4/CO_2 feed ratio, total feed flow rate, and discharge voltage on the performance of DBD plasma reactor without catalyst at low temperature were successfully addressed. The three factors in the DBD plasma reactor showed significant effects on the reactor performances, i.e. methane conversion, synthesis gas selectivity, C_{2+} hydrocarbons selectivity. A lower feed flow rate was appropriate for producing high selective C_{2+} hydrocarbons and higher H_2/CO ratio of synthesis gases, because of high residence time of the gases within the discharge zone. The range of CH_4/CO_2 feed ratio being 2 – 3 is suitable in the DBD reactor to obtain high selective C_{2+} hydrocarbons and hydrogen with high methane conversion. High discharge power/voltage is required to obtain high yield C_{2+} hydrocarbons. It is concluded that too high CH_4/CO_2 ratio is not suggested in the operation of DBD plasma reactor due to decrement of CH_4 conversion and coking formation. The application of the DBD plasma reactor is potential for the co-generation of C_{2+} hydrocarbons and synthesis gases from methane and carbon dioxide. Future development by introducing suitable catalysts is required in order to improve the C_{2+} hydrocarbons selectivity.

Acknowledgment

The authors would like to express their sincere gratitude to the Ministry of Science, Technology and Innovation, Malaysia for the financial support received under the IRPA Project No 02-02-06-0016 EA099. The authors thank Encik Suzaimi and Encik Yap (ATAMA Sdn Bhd) for fabrication of high voltage generator and high voltage probe, respectively.

References

[1] Suhartanto, T., York, A.P.E., Hanif, A., Al-Megren, H. and Green, M.L.H. (2001). Potential Utilisation of Indonesia's Natuna Natural Gas Field via Methane Dry Reforming to Synthesis Gas. *Catalysis Letters*. 71: 49-54.

[2] Centi, G., Cavani, F., Trifirò, F. (2001). *Selective Oxidation by Heterogeneous Catalysis*. New York: Kluwer Academic/Plenum Publishers

[3] Liu, C.J., Xu, G.H., and Wang, T. (1999). Non-Thermal Plasma Approaches in CO_2 Utilization. *Fuel Processing Technology*. 58:119-134.

[4] Istadi, and Amin, N.A.S. (2005). Co-Generation of Synthesis Gas and C_{2+} Hydrocarbons from Methane – Carbon Dioxide Reaction in A Hybrid Catalytic-Plasma Dielectric-Barrier Discharge Reactor: A Review. *Fuel*. Under Review.

[5] Wang,Y., Takahashi, Y., and Ohtsuka, Y. (1999). Carbon Dioxide as Oxidant for the Conversion of Methane to Ethane and Ethylene Using Modified CeO_2 Catalyst. *Journal of Catalysis*. 186:160-168.

[6] Istadi, and Amin, N.A.S. (2005). Co-generation of C_2 Hydrocarbons and Synthesis Gases from Methane and Carbon Dioxide: A Thermodynamic Analysis. Submitted to *Journal of Natural Gas Chemistry*.

[7] Wang, Y., and Ohtsuka, Y. (2001). Mn-based Binary Oxides as Catalyst for the Conversion of Methane to C_{2+} Hydrocarbon with Carbon Dioxide as an Oxidant. *Applied Catalysis A: General*. 219: 183-193.

[8] Cai, Y., Chou, L., Li, S., Zhang, B. and Zhao, J. (2003). Selective Conversion of Methane to C_2 Hydrocarbons Using Carbon Dioxide over Mn-$SrCO_3$ Catalysts. *Catalysis Letters*. 86(4): 191-195.

[9] Istadi and Amin, N.A.S. (2005). A Hybrid Numerical Approach for Multi-Responses Optimization of Process Parameters and Catalyst Compositions in CO_2 OCM Process over CaO-MnO/CeO_2 Catalyst. *Chemical Engineering Journal*. 106: 213-227.

[10] Zhang, K., Kogelschatz, U. and Eliasson, B. (2001). Conversion of Greenhouse Gases to Synthesis Gas and Higher Hydrocarbons. *Energy & Fuels*. 15: 395-402.

[11] Zhang, K., Eliasson, B. and Kogelschatz, U. (2002). Direct Conversion of Greenhouse Gases to Synthesis Gas and C_4 Hydrocarbons over Zeolite HY Promoted by a Dielectric-Barrier Discharge. *Industrial and Engineering Chemistry Research*. 41: 1462-1468.

[12] Li, M.W., Xu, G.H., Tian, Y.L., Chen, L., and Fu, H.F. (2004). Carbon Dioxide Reforming of Methane Using DC Corona Discharge Plasma Reaction. *Journal of Physical Chemistry A*. 108: 1687-1693.

[13] Fincke, J.R., Anderson, R.P., Hyde, T., Detering, B.A., Wright, R., Bewley, R.L., Haggard, D.C., and Swank, W.D. (2002). Plasma Thermal Conversion of Methane to Acetylene. *Plasma Chemistry and Plasma Processing*. 22: 105-136.

[14] Zou, J.J., Zhang, Y., Liu, C.J., Li, Y., and Eliasson, B. (2003). Starch-enhanced Synthesis of Oxygenates from Methane and Carbon Dioxide Using Dielectric-barrier Discharges. *Plasma Chemistry and Plasma Processing*. 23: 69-82

[15] Liu, C.J., Xue, B., Eliasson, B., He, F., Li, Y. and Xu, G.H. (2001). Methane Conversion to Higher Hydrocarbons in the Presence of Carbon Dioxide using Dielectric Barrier-Discharge Plasmas. *Plasma Chemistry and Plasma Processing*. 21: 301-309.

[16] Song, H.K., Lee, H., Choi, J.W., and Na, B.K. (2004). Effect of Electrical Pulse Forms on the CO_2 Reforming of Methane using Atmospheric Dielectric Barrier Discharge. *Plasma Chemistry and Plasma Processing*. 24: 57-72.

[17] Eliasson, B., Liu, C.J., and Kogelschatz, U. (2000). Direct Conversion of Methane and Carbon Dioxide to Higher Hydrocarbons using Catalytic Dielectric-Barrier Discharges with Zeolites. *Industrial and Engineering Chemistry Research*. 39: 1221-1227.