Synergetic Effects of Plasma, Temperature and Diluant on Nonoxidative Conversion of Methane to C_{2+} Hydrocarbons in a Dielectric Barrier Discharge Reactor

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ABSTRACT: *Noncatalytic and nonoxidative conversion of methane in a dielectric barrier discharge (DBD) reactor is examined at different temperatures, gas residence times and input powers. In addition, the ratio of methane to helium as a diluant, is changed in the range of 0.6 to 1.8. Results show significant synergetic effects of plasma, temperature and helium on the methane conversion and C_{2+} selectivities. C_2 hydrocarbons are the main products (more than 70%) of the process, however, minor amounts of heavier hydrocarbons up to C_8 are formed. At an input power of 230W and gas residence time of 6 sec, when the temperature increases from 100 to 200°C, the methane conversion enhances by 33%. In the temperature of 100-350°C, the methane conversion passes through a maximum at CH_4/He ratio of 1.0, at which the highest effect of the temperature is observed. In addition, at 350°C, when the input power increases from 140 to 230W, the CH_4 conversion enhances from 20.3 to 27.0%. As the temperature increases from 100 to 350°C, the selectivity of ethane decreases from 81.5 to 73.0%, while the selectivities of ethylene and acetylene enhances by about 40% and 270%, respectively. The frequency of effective collisions among the reactants, excited helium (He*), and free electrons (e-) seems to increase with temperature, that in turn leads to higher methane conversions and changes in products selectivities.*

KEY WORDS: *Dielectric barrier discharge, Synergy, Plasma conversion, Nonoxidative, Methane, C_{2+} hydrocarbons, Diluant.*

INTRODUCTION

Due to the existence of abundant reserves of natural gas in the world, direct conversion of natural gas, predominantly methane, into higher molecular weight hydrocarbons represents a great chemical and techno-

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1021-9986/05/4/63 9/$/2.90

logical challenges for both chemical engineers and petrochemical industries. Nonoxidative conversion of methane could be an interesting alternative to the oxidative conversion (e.g. oxidative coupling of methane, OCM) due to its higher selectivity towards heavier hydrocarbons [1-3]. However, due to the high stability of C-H bond in methane, its direct conversion needs a strong source of energy for breaking the C-H bond in methane and generating active species of electrons, ions, and radicals. One of the most important types of plasma for chemical processes is nonequilibrium plasma, characterized by low gas and high electrons temperatures. In other words, the nonequilibrium plasma consists of electrons that have a much higher energy than the bulk gas species. These electrons could have energies ranging from 1 to 10 eV corresponding to temperatures ranged from 10,000 to 100,000K. Dielectric barrier discharge (DBD), is a nonequilibrium plasma reactor, which at atmospheric pressures, offers high reactor volumes, and is commonly used for chemical processes.

In a dielectric barrier discharge (DBD) reactor, when the amplitude of the applied ac electric field reaches a certain critical value, the so-called breakdown is initiated in the gas. When breakdown is initiated at any location within the discharge gap, the charge accumulates on the dielectric resulting in an opposite electric field. This opposite electric field locally reduces the external electric field in the gap and interrupts the current flow within a few nanoseconds. By this mechanism, individual current filaments called micro discharges are formed. The duration of micro discharges depends on the reactor pressure, gas composition, and the dielectric used. A large number of such micro discharges will be formed when a stable DBD operation is established [4].

Research has been conducted on methane conversion using plasma environment to initiate the reaction in an oxidative environment [5-8]. Most of the products in oxidative conversion of methane using corona, pulsed discharge and microwave discharge are low molecular weight hydrocarbons, as well as carbon oxides. This means that due to high exothermicity of the oxidative conversion, most of the higher molecular weight hydrocarbons are susceptible to the secondary conversion to carbon oxides, which in turn lead to lower selectivity to these products. However, the only products of the nonoxidative conversion of methane in nonequilibrium plasma are C_{2+} hydrocarbons, although minor amounts of carbon are deposited on the reactor walls.

The principal advantages of the DBD are that, nonequilibrium conditions can be easily established at atmospheric pressure and that the entire electrode area is effectively used for discharge reactions. In the DBD reactor, a wide range of the hydrocarbons could be produced due to its large volume of discharges. This makes direct production of liquid fuel formation feasible [9-19]. Such products contain a large amount of branched hydrocarbons, which have higher octane number when used as a blend in the gasoline pool. However, a problem with the direct fuel production from methane using DBD is the formation of carbon species and the plasma polymerized carbon film [9]. Up to now direct and nonoxidative methane conversion using high frequency pulsed plasma [20, 21], catalytic and microwave plasma [22], dinitrogen microwave plasma [23], RF plasma reactor [24], and pulsed plasma [25] in low pressure, have been investigated by different research groups. But simultaneous effects of heat, diluant gas and non-equilibrium plasma was not investigated.

In the present study, the synergetic effect of DBD plasma and temperature on the conversion and product selectivities of noncatalytic and nonoxidative methane conversion in a DBD reactor is investigated. Along with the effects of different CH_4/He ratios and feed flow rates are examined.

EXPERIMENTAL

Fig. 1 presents the DBD reactor and the experimental set up used for this study. The DBD reactor consists of a quartz tube containing an inner cylindrical stainless steel rod and an outer stainless steel foil as its electrodes. The annular gap between the quartz tube and the rod is 1.2 mm and the DBD reactor length is 120 mm. The feed flows in the annular gap. A function generator (Pintek FG-32) with 0.5-3 MHz frequency capable of generating six types of output waveforms and up to 10V was used to generate the sinusoidal wave. A high voltage amplifier (Trek 10/40 A) working at about 3 kHz and 10-20 kV (pick to pick) was used to amplify the voltage. The power delivered to the dielectric barrier discharge reactor was calculated by the following formula;

$P = ½ Vm Am \cos(\varphi)$

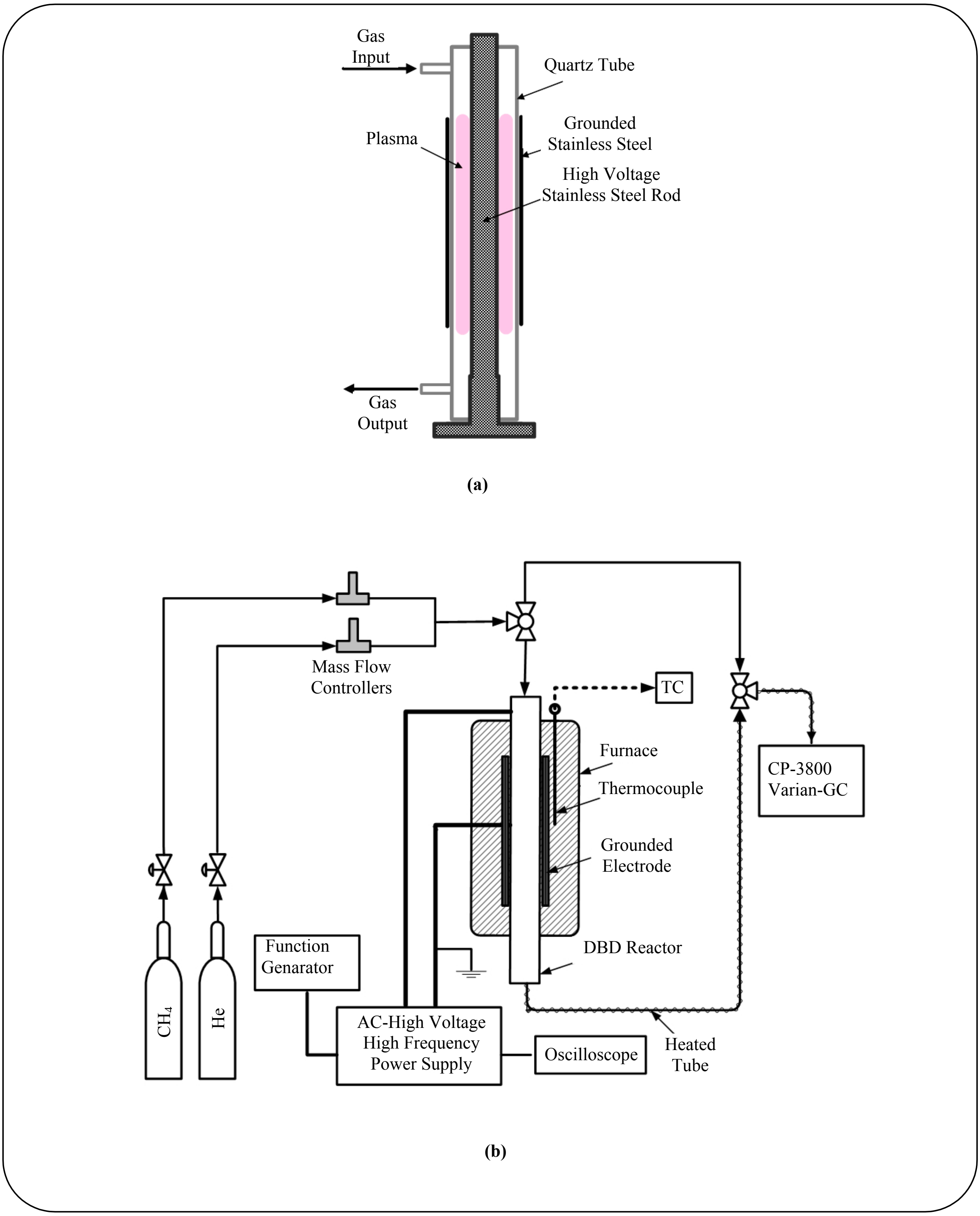

Fig.1: DBD reactor (a) and experimental set up (b).

Where;

P = power in W

Vm = maximum voltage in kV

Am = maximum current in mA

φ = phase lag between voltage and current waves in degree

Voltage, current, and the phase lag were measured by an oscilloscope (HAMEG HM 203.7). As is seen in Fig. 1, the feed gases, CH_4 and He are introduced into the reactor via mass flow controllers. The effluent from the reactor contains un-reacted CH_4 and low and high molecular weight hydrocarbons. The effluent was transferred through a 1/8″ OD stainless steel tube, the temperature of which was adjusted at a few degrees higher than the reactor temperature, to prevent the possible condensation of the heavy hydrocarbons. A modified multi-valve, multicolumn Varian CP-3800 refinery gas analyzer (RGA) from Varian-Chrompack was used for analyses of the effluent from the reactor. The RGA was equipped with an FID and a TCD. The signals from the detectors were conditioned, digitized, and processed by a software (Star Chromatography Workstation Software). Using the hydrocarbon standards, RGA peaks were identified and calibrated so that we could calculate the molar flow rate of different products.

In order to raise the reactor temperature to the desired temperature, an electrical heating system around the reactor was employed. The temperature of the heating system was controlled via a PID temperature controller. Precaution were taken to avoid the disturbance of the high voltage and high frequency power supply of the plasma on the electrical heating system and its controller.

RESULTS AND DISCUSSION

In this research, each run of experiments lasted for about 40 minutes and the effluent concentration of individual species was monitored by the gas chromatograph (RGA). Analyses of the reactor effluent were performed when the stable performance of the reactor system was established.

Stability of plasma, methane conversion and products selectivities

Fig. 2 demonstrates the stability of nonoxidative conversion of methane in the DBD reactor. This set of experiments was conducted at constant temperature of 200°C, while keeping a constant 16-sccm total flow rate of 50 mole% methane in helium at ambient pressure of 660 mmHg. A frequency of 3kHz and a voltage of 14kV, corresponding to a power of 230 watts, were applied to the DBD reactor. It takes about 40 min for the DBD reactor to reach 100±2°C, just by the energy of the plasma. Then the DBD reactor was externally heated in the furnace to raise the temperature to 200±4°C. The performance of the DBD reactor in regards to methane conversion and different products selectivities is quite stable within the time interval of 40-240 min used for this experiment. As reported by other groups [19, 24], minor amounts of soot deposits were found on the inner wall of quartz reactor and the outer surface of the stainless steel rod (high voltage electrode). However, the deposits did not affect the stability of the DBD reactor.

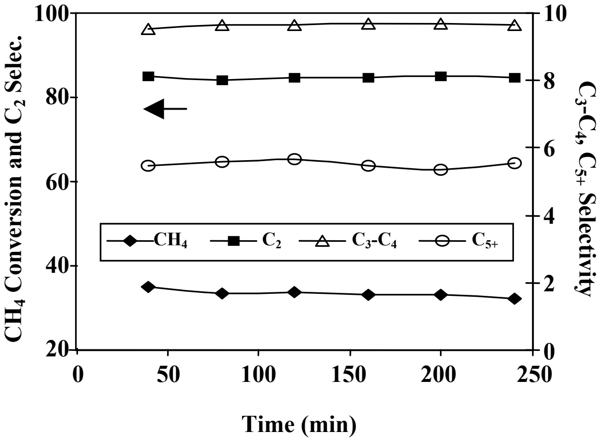

Fig. 2: Stability of DBD reactor at 200 °C. (Conditions: 14 kV and 3 kHz (power = 230 W), feed flow rate =16 sccm with 50 mole% CH_4 in helium).

In the DBD reactor, the CH_4 conversion was primarily affected by three factors:

1) methane mole fraction in its mixture with helium,

2) total gas flow rate,

3) input power (W) determined by voltage (kV) and frequency (kHz). The effects of these factors on the methane conversion and products selectivities of nonoxidative conversion of methane in the DBD reactor are investigated and the results are presented in the following sections.

Effect of helium concentration and temperature on methane conversion and C_{2+} selectivities

Experiments were conducted by varying the CH_4/He while keeping a constant total flow rate of 32 sccm, corresponding to a residence time of 12 sec, at ambient pressure of 660 mmHg. Fig. 3 illustrates the effect of CH_4/He ratio on the methane conversion and product selectivities at different temperatures. For all of the temperatures examined, the methane conversion passes through a maximum at CH_4/He ratio of 1. Fig. 3 shows that the highest effects of the temperature on the methane conversion maxima at CH_4/He of 1 occurs in the range of 100-200°C. At higher temperatures range, minor effects of the temperature are observed. Lower effects of temperature at other CH_4/He ratios are detected.

The C_2 selectivity, the main product of the non-oxidative conversion of methane in the DBD reactor, passes through a minimum at CH_4/He ratio of 1. The C_2 selectivity monotonously decreases with the temperature at different CH_4/He ratios. However, the C_3, C_4, and C_{5+} selectivities show maxima at CH_4/He ratio of 1 and, in most cases, increase with temperature.

The diluent gases are not passive components in the plasma atmosphere; they are used to control the reactivity of the plasma. It has been established that helium in its excited state is a much better charge and energy transfer body compared to other diluent gases such as argon and nitrogen [26].

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Previous investigations on oxidative coupling of methane, in corona discharge reactor show that the formation of methyl radical is the rate-controlling step [27]. Presence of oxygen increases the concentration of methyl radicals, which in turn result in higher methane conversion. In general, methyl radical formation is thought to be responsible for the initiation of radical reactions leading to higher molecular weight hydro-carbons. There is a consensus among majority of the researchers that methyl radicals are formed by a homolytic hydrogen abstraction either catalytically or by action of a third body such as electron(e-) or excited state of a gas like helium [24] which are present in the plasma reactions.

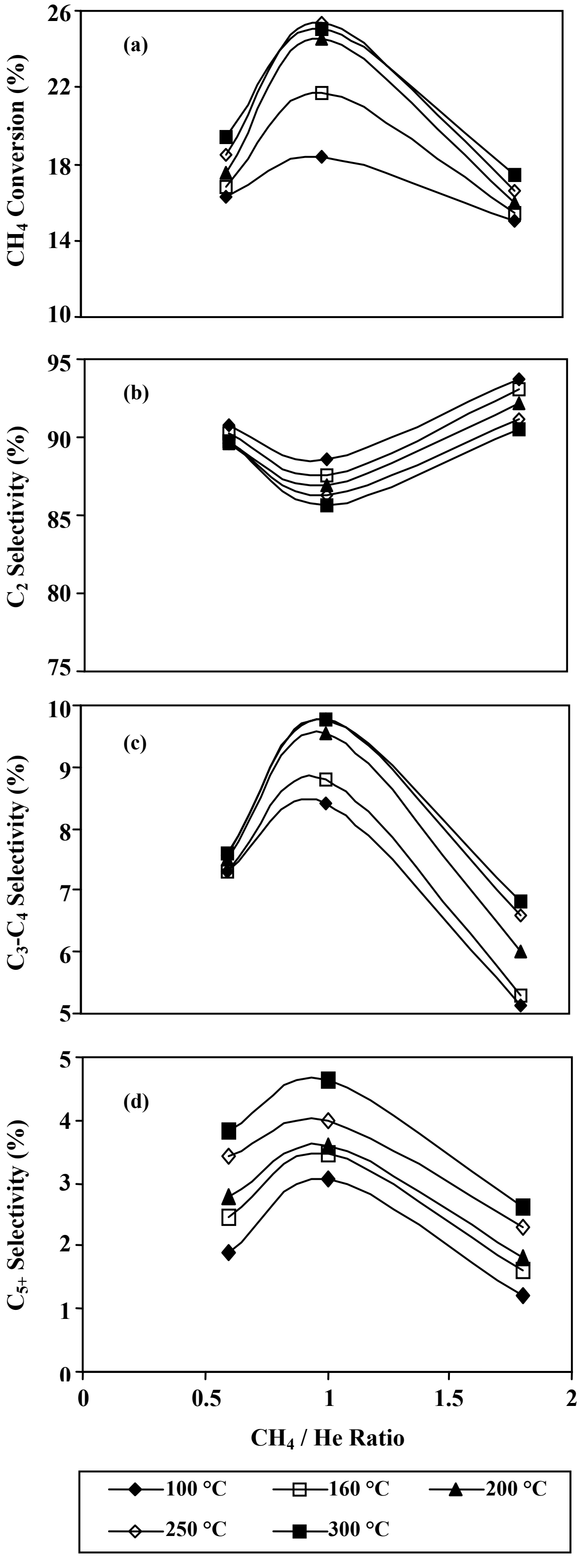

Fig. 3: Effects of CH_4/He ratio and temperature on methane conversion and C_{2+} selectivities of nonoxidative conversion of methane in a DBD reactor.(Conditions: 660 mmHg, 230 W, 14 kV and 32 sccm or 12 sec residence time).

$$CH_4 + e^- \longrightarrow CH_3^{\cdot} + H^{\cdot} + e^-$$
$$CH_4 + He^* \longrightarrow CH_3^{\cdot} + H^{\cdot} + He$$

Different hydrocarbons are formed via the following reactions:

$$CH_3^{\cdot} + e^- \text{ (or } He^*) \longrightarrow CH_2^{\cdot} + H^{\cdot} + e^- \text{ (or He)}$$
$$CH_2^{\cdot} + e^- \text{ (or } He^*) \longrightarrow CH^{\cdot} + H^{\cdot} + e^- \text{ (or He)}$$
$$2\, CH^{\cdot} \longrightarrow C_2H_2$$
$$2\, CH_3^{\cdot} \longrightarrow C_2H_6$$
$$C_2H_6 + e^- \text{ (or } He^*) \longrightarrow C_2H_5^{\cdot} + H^{\cdot} + e^- \text{ (or He)}$$
$$2\, C_2H_5^{\cdot} \longrightarrow C_2H_6 + C_2H_4$$
$$2\, C_2H_5^{\cdot} \longrightarrow C_4H_{10}$$
$$C_2H_5^{\cdot} + CH_3^{\cdot} \longrightarrow C_3H_8$$

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Fig. 3a indicates that methane conversion increases with CH_4/He ratio to a maximum at 1.0 and then decreases at higher CH_4/He ratios. It appears that there are two effects involved in this behavior [26]. At lower values of CH_4/He or in fact lower methane partial pressures, methane conversion is low, and increases with an increase in methane concentration. However, at higher methane partial pressures i.e. lower helium partial pressures, the positive effects of helium start to diminish. This results in a decrease in the methane conversion. Therefore, there is an optimum CH_4/He ratio, which leads to a maximum methane conversion for each set of operating conditions of plasma power, temperature, etc.

Fig. 3a also demonstrates that at higher temperatures, methane conversion is improved for all CH_4/He ratios. This may be attributed to the synergetic effects of temperature and plasma; the concentration of charged and excited particles increases with temperature in the plasma atmosphere leading to higher methane conversions.

Synergetic effects of plasma power and temperature

In this set of experiments, helium was used as a diluent gas, other conditions were as follows: frequency was kept constant at 3 kHz, input voltage used were 11 and 17.5 kV, pressure was 660 mmHg, and total gas flow rate was 32 sccm.

Table 1 presents the carbon atom products selectivities for the reaction at 140W and 100-350°C. The selectivities are based on the carbon atoms in the products; e.g., the molar formation rate of C_4, in calculation of selectivities, is multiplied by 4. In addition, it should be noted that for products heavier than C_3 all of the isomers of the product have been considered collectively. The products consist of a wide rang of hydrocarbons mainly from C_2 to C_8.

Table 1: Effect of temperature on product selectivities in percentage. (Conditions: 11 kV and 3 kHz (input power of 140 W), feed flow rate of 32 sccm with 50% CH_4 in helium, C_4 to C_8 include all isomers).

Temp. (°C) / Comp.	100	160	200	250	350
C_2H_6	81.47	78.22	76.51	74.81	73.01
C_2H_4	7.93	8.68	9.22	10.17	11.18
C_2H_2	0.93	1.72	2.22	2.70	3.41
C_3H_8	4.68	4.88	4.86	4.72	4.70
C_4	2.53	3.34	3.75	3.75	4.15
C_5	1.38	1.68	1.84	1.97	2.22
C_6	0.68	0.87	0.97	1.07	0.95
C_7	0.24	0.34	0.38	0.44	0.27
C_8	0.16	0.26	0.25	0.37	0.10

Fig. 4 presents the changes of carbon atom selectivity of the products with their carbon number in the range of C_2 to C_6 at two temperatures of 100 and 350°C. It shows that the most selective product of nonoxidative conversion of methane in the DBD reactor is C_2 hydrocarbons (C_2H_6, C_2H_4 and C_2H_2). There is a sharp decrease in C_3 selectivity, and then the higher hydrocarbon selectivities decrease with a nearly constant logarithmic slope. Fig. 4 shows that the collective C_{3+} selectivities slightly are increased with temperature.

Figs. 5a and 5b present methane conversion and product selectivities at two powers of 140 and 230W. For reactor temperatures higher than 100°C, the DBD reactor was externally heated. Fig. 4a shows that when the input power increases from 140 to 230W, the CH_4 conversion enhances from 16.5 to 17.5% at 100°C and from 20.3 to 27.0% at 350°C, respectively. The results reveal that, higher input power and higher temperature provide more energy for the ionization of gas molecules. In addition, the frequency of effective collisions among the reactants, excited helium (He*), and free electrons (e-) increases with temperature. Both phenomena enhance the methane conversion.

Figs. 5a and 5b show the effect of temperature on the C_{2+} selectivities at the two powers of 140 and 230W. For

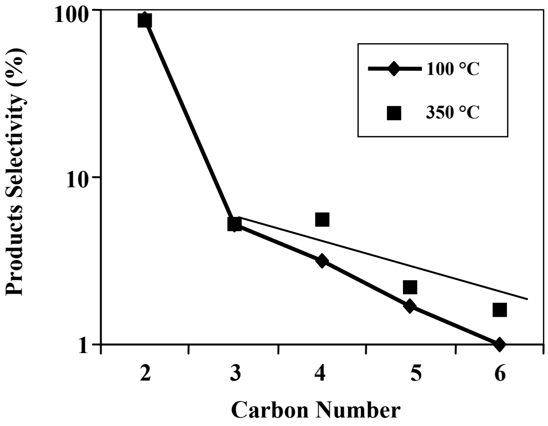

Fig. 4: The carbon atom selectivity via carbon number at different reactor temperatures of 100 and 300^{o}C. (Conditions:230 W, 14kV, 3 kHz, 32 sccm of 50% CH_4 in Helium, 660 mmHg, methane conversion: 16-26%).

both figures the C_2 selectivity decreases with temperature, whereas the C_{3+} selectivities is slightly improved. Table 1 demonstrates that at 140W input power, when the temperature increases from 100 to 350 °C, the selectivity of ethane decrease from 81.5 to 73.0, while the 73.0, while the selectivities of ethylene and acetylene enhances by about 40% and 270%, respectively. In addition, the selectivities for C_{6+} pass through maxima at 250^{o}C. It seems that the dehydrogenation of ethane, which results in formation of more ethylene and acetylene, is enhanced at higher temperatures. This may be explained based the chain reactions described in section 3.2, i.e., the reactions which lead to ethylene and acetylene are enhanced at higher temperatures. However, in the absence of plasma, ethane dehydrogenation reactions could not occur at the low temperatures examined in this study.

Effect of residence time on methane conversion and C_{2+} selectivities of the DBD reactor

In these experiments two different gas flow rates of 16 and 32 sccm, respectively corresponding to 24 and 12 sec gas residence times, were tested at different temperatures. Other conditions were as follows: pressure of 660 mmHg, CH_4/He ratio of 1.0, and input power of 230W.

Table 2 presents the methane conversion and C_{2+} selectivities at the two gas residence times and different temperatures. The results indicate that, at the three temperatures of 100, 200, and 300^{o}C tested, the methane conversion enhances with the gas residence time. As the gas residence time increases from 12 to 24 sec, the methane conversion increases by about 25% and 20% at 100^{o}C and 300^{o}C, respectively. The same effect of temperature on the enhancement of methane conversion is observed at the two gas residence times.

Table 2: Methane conversion and C_{2+} selectivities in percentage at two residence times of 12 and 24 sec and different temperatures.(Conditions: 660 mmHg, CH4/He ratio of 1.0, and input power of 230W).

	Gas Residence Time (sec)	12	24	12	24	12	24
	Temperature (°C)	100		200		300	
	CH_4 Conversion	18.4	23.2	24.5	28.1	25.1	30.1
Selectivity	C_2H_6	80.7	79.2	77.4	75.6	74.4	72.4
	C_2H_4	6.3	5.5	6.7	6.7	8.1	7.8
	C_2H_2	1.3	1.4	2.1	2.5	2.8	3.2
	C_3H_8	5.3	5.8	5.3	5.6	5.1	5.5
	C_4	3.2	3.8	4.5	4.1	5.1	4.6
	C_{5+}	3.3	4.4	4.5	6.5	4.0	5.6

Table 2 also shows that the C_{5+} selectivity slightly increases with gas residence time, while the C_3-C_4 selectivities does not change significantly. In addition, the ethane selectivity decreases with gas residence time to minor amounts, while the enhancement of ethylene and acetylene selectivities is not consistent.

CONCLUSIONS

Methane is converted to predominantly C_2 and heavier hydrocarbons up to C_8 in a dielectric barrier discharge reactor without use of oxygen. The temperature, input power, helium concentration, and gas residence time is changed and their effects on the methane conversion and C_{2+} selectivities is investigated. Significant synergetic effects among the plasma, temperature and helium concentration is observed. The methane conversion increases with temperature, input power and gas residence time. The C_2 products selectivities decrease and C_{3+} products selectivities increase with temperature, power input, and gas residence time. However, the methane conversion shows maxima at CH_4/He ratio of 1.0, at which the temperature exhibits the most significant effects. At the same ratio, C_2 products

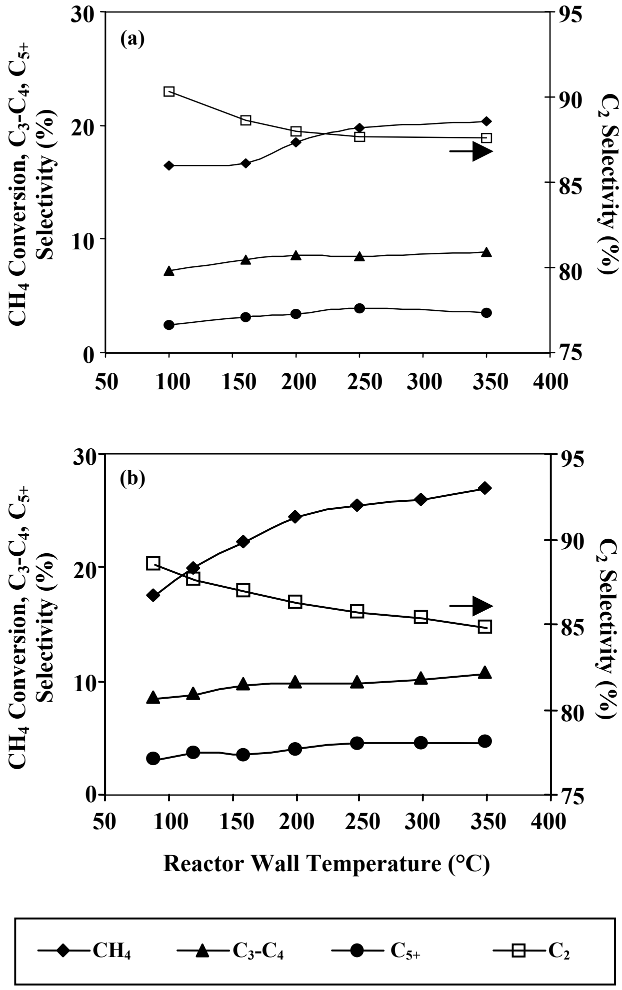

Fig. 5: Effect of temperature and input power on methane conversion and product selectivities.(Conditions: Feed flow rate = 32 sccm with 50% CH_4 in helium) a)Voltage =11kV and 3 kHz (Power =140 W), b) Voltage =14kV and 3kHz (Power =230 W).

selectivities show minima and C_{3+} ones show maxima, which considerably change with temperature. The use of active catalysts and their synergetic effects with temperature and diluents is under investigation.

Acknowledgments

The authors wish to acknowledge the Iranian Academic Center for Education, Culture and Research for a fellowship to M.S. Haji Tarverdi and Arak Petrochemical Company for partial support of the project (Contract Number PAT-50860).

Received : 14th February 2005 ; Accepted: 10th September 2005

REFERENCES

[1] Lunsford, J.H., Catalytic conversion of methane to more useful chemicals and fuels: a challenge for the 21st century, *Catal. Today*, **63**, 165 (2000).

[2] Fox, J.M., *Catal. Rev. Sci. Eng.*, **35**, 169, (1993).

[3] Parkyns, N.D., Warburton, C.I. and Wilson, J.D., Natural gas conversion to liquid fuels and chemicals: Where does it stand?, *Catal. Today*, **18**, 385 (1993).

[4] Liu, C.J., Eliasson, B., Xue, B., Li, Y. and Wang, Y., *React. Kinet. Catal. Lett.*, **74**, 71 (2001).

[5] Mallinson, R. G., Sliepcevich, C. M., and Rusek, S., ''Methane Partial Oxidation in Alternating Electric Fields,'' Division of Fuel Chemsitry,Proc. Amer. Chem. Soc. Meeting, Vol. 32, No. 3, American. Chemical Society, San Francisco (1987).

[6] Bhatnager, R., and Mallinson, R. G., ''The Partial Oxidation of Methane Under the Influence of an AC Electric Discharge,'' Methane and Alkane Conversion Chemistry, Bhasin, M. M. and Slocum, D. N., eds., Plenum, New York, 249 (1995).

[7] Larkin, D. W., Caldwell, T. A., Lobban, L. L. and Mallinson, R. G., Oxygen Pathways and Carbon Dioxide Utilization in Methane Partial Oxidation in Ambient Temperature Electric Discharges, *Energy & Fuels*, **124**, 740 (1998).

[8] Rosacha, L. A., Anderson, G. K., Bechtold, L. A., Coogan, J. J., Heck, H. G., Kang, M., McCulla, W.H., Tennant, R.A. and Watnuck, P.J., "Treatment of Hazardous Wastes Using Silent Discharge Plasmas", Non-Thermal Plasma Technique for Pollution Control, Penetrante, B.M. and Schultheis, S.E., eds., NATO ASI Ser., Vol. G 34, Part B, Springer-Verlag, Berlin, Heidelberg (1993).

[9] Eliasson, B., Liu, C.J. and Kogelschatz, U., Direct Conversion of Methane and Carbon Dioxide to Higher Hydrocarbons Using Catalytic Dielectric-Barrier Discharges with Zeolites, *Ind. Eng. Chem. Res.*, **39**, 1221 (2000).

[10] Yao, S.L., Nakayama, A. and Suzuki, E., Methane conversion using a high-frequency pulsed plasma: Discharge features, *AIChE J.*, **47**, 419 (2001).

[11] Suib, S.L. and Zerger, R.P., A Direct, Continuous, Low-Power Catalytic Conversion of Methane to Higher Hydrocarbons via Microwave Plasmas, *J. Catal.*, **139**, 383 (1993).

[12] Liu, C. J., Mallinson, R. and Lobban, L.,

Comparative investigations on plasma catalytic methane conversion to higher hydrocarbons over zeolites, *Appl. Catal. A,* **178**, 17 (1999).

[13] Yao, S.L., Ouyang, F., Nakayama, A., Suzuki, E., Okumoto, M. and Mizuno, A., Oxidative Coupling and Reforming of Methane with Carbon Dioxide Using a High-Frequency Pulsed Plasma, *Energy & Fuels*, **14**, 910 (2000).

[14] Jeong, H.K., Kim, S.C., Han, C., Lee, H., Song, H.K. and Na, B.K., Conversion of Methane to Higher Hydrocarbons in Pulsed DC Barrier Discharge at Atmospheric Pressure, *Korean J. Chem. Eng.*, **18**, 196 (2001).

[15] Kado, S., Sekine, Y. and Fujimoto, K., Direct synthesis of acetylene from methane by direct current pulse discharge, *Chem. Commun.*, 2485 (1999).

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

[17] Tao Jiang , Yang Li , Chang-jun Liu , Gen-hui Xu, Baldur Eliasson , Bingzhang Xue, Plasma methane conversion using dielectric-barrier discharges with zeolite A, *Catalysis Today*, **72**, 229 (2002).

[18] Thanyachotpaiboon, K., Chavadej, S., Caldwell, T. A., Lobban, L.L. and Mallinson, R.G., Conversion of Methane to Higher Hydrocarbons in AC Nonequilibrium Plasmas, *AIChE Journal*, **44** (10), 2252, October (1998).

[19] Shuiliang, Y., Nakayama, A. and Suzuki, E., Methane conversion using a high-frequency pulsed plasma: Important factors, *AIChE Journal*, **47** (2), 413 (2001).

[20] Shuiliang, Y., Nakayama, A. and Suzuki, E., Methane conversion using a high-frequency pulsed plasma: Discharge factors, *AIChE Journal*, **47** (2), 419 (2001).

[21] Yang, Y., Direct Non-oxidative methane conversion by non-thermal plasma: Experimental study, *Plasma Chemistry and Plasma Processing*, **23** (2), 283 (2003).

[22] Huang, J. and Suib, S.L., Dimerization of methane through microwave plasma, *J. Phys. Chem.*, **97**, 9403 (1993).

[23] Oumghar, A., Lerand, J.C., Diamy, A.M., Turillon, N. and Ben-Aim., A Kinetic of Methane Conversion By A Dinitrogen Microwave Plasma, *Plasma Chemistry and Plasma Processing*, **14** (3), p. 229 (1994).

[24] Hsieh, L. T., Lee, W. j., Chen, C.Y., Chang, M.B. and Chang, H.C., Converting Methane By Using An RF Plasma Reactor, *Plasma Chemistry and Plasma processing*, **18** (2), p. 215 (1998).

[25] Yao, S., Nakayama, A. and Suzuki, E., Acetylene and hydrogen from pulsed plasma conversion of methane, *Catalysis Today*, **71**, 219 (2001).

[26] Stephanie L. Brock, Manuel Marquez, z Steven L. Suib, y,1 Yuji Hayashi, and Hiroshige Matsumoto, Plasma Decomposition of CO_2 in the Presence of Metal Catalysts, *Journal of Catalysis*, **180**, 225 (1998).

[27] Bagheri-Tar, F., Khodadadi, A.A., Malekzadeh A. and Mohajerzadeh, S.S., Oxidative Coupling of Methane in a Negative DC Corona Reactor at Low Temperature, *Can. J. Chem. Eng.*, **81** (1), 37 (2003).