Dry Reforming of Methane Using Cold Plasma; Kinetic Model Study

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ABSTRACT: *In this work, the dry reforming of methane was studied using a corona and gliding discharge plasma microreactors. A chemical kinetic model was developed to describe the experimental behavior observed. The kinetic model is proposed based on the assumption that the reactant molecules CH_4 or CO_2 are attacked by active species produced by the plasma discharges, and the production of this active species are a function of the plasma power. The modelization allowed the prediction of the conversion of the reactants (CH_4 and CO_2) according to the energy transfer to the gas ($P \times \tau$). The β value is characteristic of the energy cost; the lower β value indicated better efficiency. The β value of CH_4 was found to be 10.42 and 58.25 J and for CO_2 equal to 12.24 and 27.77 J for corona and gliding discharge plasma, respectively. The kinetic model also demonstrated that the methane and carbon dioxide conversion was an exponential function of the plasma energy, and were a linear function of the input energy for a CH_4 and CO_2 inlet concentration. Our Model also implied that a plasma reactor with a smaller input discharge power has better energy efficiency for CO_2 and CH_4 conversion.*

KEYWORDS: *Methane; Kinetic model; Plasma; Synthesis gas.*

INTRODUCTION

In recent years, about 85% of energy consumption is obtained from fossil fuels (such as coal, crude oil, and natural gas). Direct conversion of methane into Synthesis gas ($CO+H_2$) represents a great chemical and technological challenge for both the chemical engineering and petrochemical industry. Synthesis gas is used as a feedstock

in many chemical industries to produce hydrogen fuel, methanol and higher hydrocarbons. Many research has been done in Dry Reforming of Methane (DRM) is production of synthesis gas (syngas) from CH_4 and CO_2 by the following endothermic reaction:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H = 247 \ \text{kJ/mol} \qquad (1)$$

The advantage of this reaction is not only the use of two greenhouse gases (CH_4 and CO_2) but also the production of synthesis gas with a low H_2/CO molar ratio which is a preferable feedstock for the Fischer–Tropsch synthesis of liquid hydrocarbons [1].

Conversion of alkanes is a challenging problem due to the strong C–H and C–C bonds present (415 kJ/mol for methane) [2]. Alkane conversions at higher temperatures have inherent difficulties. (i) They lead to extensive endothermic C–C and C–H bond cleavage causing coke formation, (ii) if oxygen is present, they favor nonselective combustion, and (iii) they cause loss of catalyst activity. Thus, alkane activation at lower temperatures, even though challenging, is very interesting from a commercial point of view. Recently, non-thermal plasma reactors introduced one of the newest processes for DRM. In particular, plasmas can generate active species, i.e., electrons, ions, and radicals at lower temperature as compared to catalytic processes [3, 4]. Non-thermal plasma technology offers an attractive alternative to the conventional catalytic route for activating low value and inert molecules such as CH_4 and CO_2 into clean fuels and higher value chemicals at atmospheric pressure and low temperatures [5−8].

More specifically, corona discharges and dielectric barrier discharges (DBD) are two of the commonly used methods for producing nonequilibrium plasmas at atmospheric pressure. Generation of a corona at atmospheric pressure in a small and confined reactor space may imply a (i) more uniform and dense plasma, (ii) stronger electric field, (iii) higher concentration of electrons and radicals [9, 10]. CO_2 and CH_4 are often introduced into the plasma reactor with a dilution gas known as chemically inactive, like helium or argon [3, 11].

Although many experimental studies have been processed on this topic, the problems concerning plasma chemistry, kinetics of methane conversion, products yield and selectivity etc., are still not well understood. These researches aimed at plasma-assisted methane coupling reactions, CO_2 reforming and partial oxidation reactions and poorly referred to reaction mechanisms and kinetic model study for plasma-assisted DRM.

In this study, firstly, the DRM is studied for the in two types of cold plasma (corona and gliding discharge) and then the results of DRM are compared with other nonthermal plasmas. Also, the kinetic model is developed to estimate the real perspectives of DRM in the plasma field.

EXPERIMENTAL SECTION

In this study, corona and gliding discharge plasma were used to produce synthesis gas from methane and carbon dioxide at atmospheric pressure.

The corona plasma set-up

The quartz tubular reactor consists of a wire-plate tungsten electrode configuration. The reactor was oriented vertically, with the gas flow from top to bottom. The upper electrode was a tungsten wire suspended and centered axially within the reactor tube. A DC power supply with a high-voltage transformer of 0−12 kV was used to initiate corona discharges. Additionally, a positive corona discharge was applied, i.e. the plate electrode was grounded as the cathode (i.e., its potential is 0 V), and the wire electrode was at a positive potential as the anode. The typical breakdown voltage was about 5−6 kV, and the discharge power was measured by the product of the applied voltage on the reactor and the corona current through the reactor, monitored by an oscilloscope (Tektronix TDS2024B). The current of corona was in the range of 0.5−5 mA. The flow rates of the two ultra pure reactants, CH_4 (>99.99%) and CO_2 (>99.5%) in a molar ratio of CH_4/CO_2=0.5, with 60% argon as a diluting gas were regulated by mass flow controllers (Brooks 5850TR). The reactants were well-mixed and flowed through the reactor at room temperature and atmospheric pressure. The compositions of the feed gas mixture and the outlet gas were quantitatively measured by an online gas chromatograph (Agilent 6890N) equipped with a thermal conductivity (TCD) and a flame ionization detector (FID). The flow rates of the inlet and outlet gas were also measured by a soap bubble flow meter in order to carry out balance calculations of the elements. The outer diameter of the reactor is 30 mm, the length of the reactor is 50 mm. All of the experiments were repeated
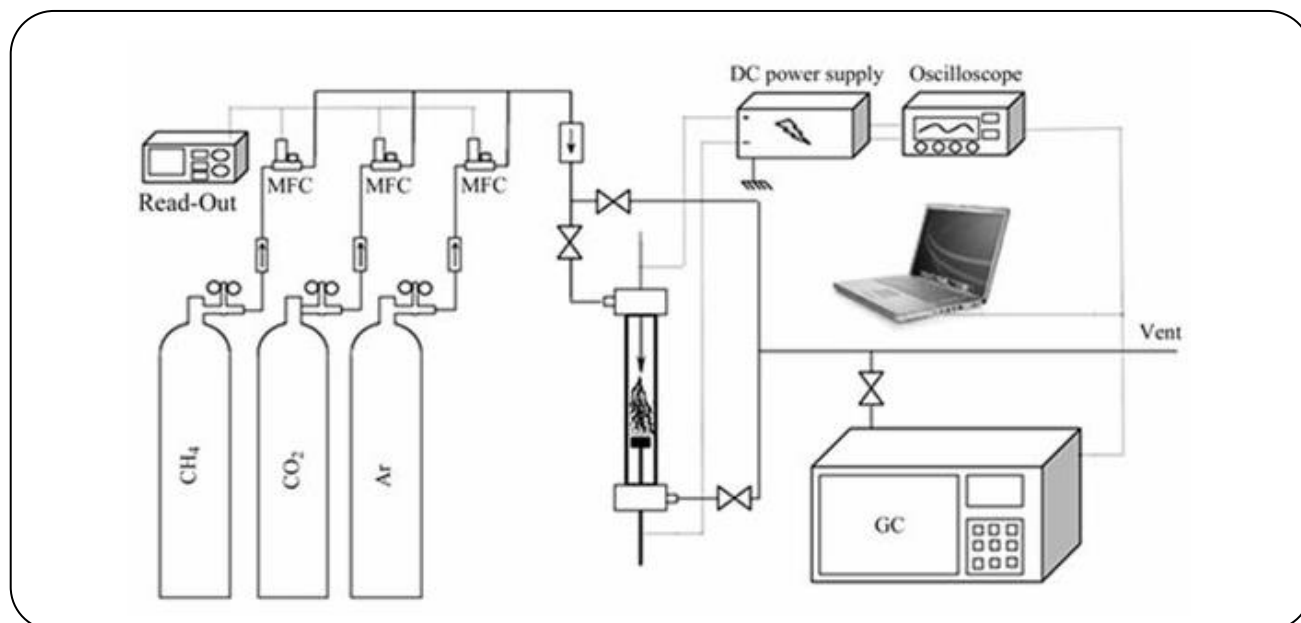
Fig. 1: Schematic diagram of the experimental set-up [12].

carefully several times. Fig. 1 depicts the experimental setups used in this work [12].

The gliding discharge plasma set-up

The reactor is a quartz tube containing a stainless steel rotating plate which acts as the ground electrode and a stainless steel high voltage needle electrode. The special design of plasma reactor permitted the crossing of all feed gases in the plasma region. The voltage was measured by a high voltage probe (Tektronix P6015). High-voltage (15 kV), high-current (200 mA) AC transformer was used as power supply.   The outer diameter of the reactor is 50 mm and the length of the reactor is 100 mm.

The mass flow controllers (Brooks 5850TR) controlled the flow rates of the two ultra pure reactants, CH_4 (>99.99%) and CO_2 (>99.5%) in a molar ratio of $CH_4/CO_2 = 0.5$, with 60% argon as a diluting gas, for gliding discharge plasma reactor set up. All gasses were controlled by Mass Flow Controllers (MFC Brooks 5850). The plasma reaction was obtained at near room temperature, and atmospheric pressure. The flow rates of inlet and outlet gas were measured by a bubble flow meter for more accuracy. The products lead to a GC that can analyze the composition of products on-line.

Methane and carbon dioxide conversion are defined as follows:

$$CH_{4\ Conversion(\%)} = x_{CH_4} = \tag{2}$$

$$\frac{\text{moles of } CH_4 \text{ converted}}{\text{moles of } CH_4 \text{ int roduced}} \times 100$$

$$CH_{4\ Conversion(\%)} = x_{CO_4} = \tag{3}$$

$$\frac{\text{moles of } CH_4 \text{ converted}}{\text{moles of } CH_4 \text{ int roduced}} \times 100$$

The following relation is applied for calculation of selectivity of products:

$$S_{H_2(\%)} = \frac{\text{moles of } H_2 \text{ produced}}{\text{moles of } CH_4 \text{ consumed}} \times 100 \tag{4}$$

$$S_{CO(\%)} = \tag{5}$$

$$\frac{\text{moles of CO produced}}{\text{moles of } CH_4 \text{ consumed} + \text{moles of } CO_2 \text{ cos umed}} \times 100$$

The specific energy input (SEI) is defined as the total input power (W) divided by the total feed flow rate (mL/min).

RESULTS AND DISCUSSION

The higher conversion of CH_4 in the presence of argon can be explained with the ''Penning dissociation'' phenomenon, which corresponds to an energy transfer from excited atom or molecule to other atom or molecule in ground state [13-15]. In our experiment the energy
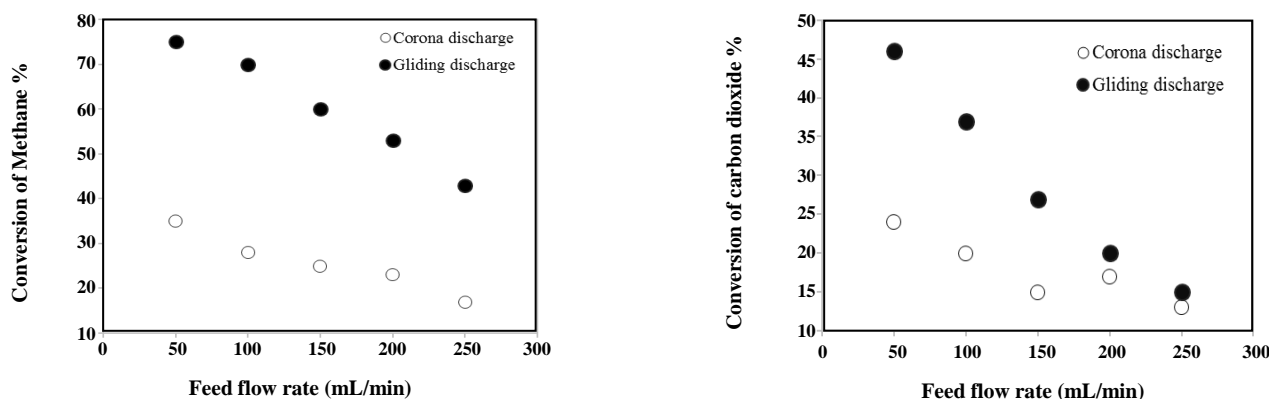
Fig. 2: Effect of feed flow rate on CH₄ (a) and CO₂ (b) conversion in corona and gliding discharge plasma
(Ar= 60 mol %, CH₄/CO₂= 0.5, 3 power=4, 10 W; respectively).

transfers proceed from metastable argon (Ar*) to the reactants molecules (CH_4 and CO_2). A decrease of the CH_4/Ar mole ratio factor favors the ''Penning dissociation'', and the conversion of CH_4 increases. The energy transfer resulted in the reactant dissociation can be shown as equations (6) and (7):

$$Ar^{\circ} + CH_4 \rightarrow Ar + CH_3 + H \tag{6}$$

$$Ar^{\circ} + CO_2 \rightarrow Ar + CO + O \tag{7}$$

Conversion and Selectivity

Interaction of electrons and free radicals in plasma non-equilibrium processes plays main mechanism [3]. The feed flow rate increased from 50 to 250 mL/min in the corona and gliding discharge plasma. The CH4 (XCH4) and CO2 (XCO2) conversion significantly decrease when the feed flow rate increases, which can be attributed to a decrease of the residence time of the methane and carbon dioxide in the discharge volume, resulting in a reduced chance for reactant molecules (CH4 and CO2) to collide with energetic electrons (e) and reactive species (Ar* and CH3) (Fig. 2).

The discharge power is found to be the most influential parameter for the plasma processing of methane in terms of the conversion of CH_4 and selectivity of H_2 (SH2) and CO (SCO).

In corona plasma, the conversion of CH_4 increases almost linearly with the increase of the plasma power (4-10 W), reaching a maximum value of 62% at a discharge power of 10 W. In addition, meanwhile, CO selectivity increase from 75 to 80%. The C2 hydrocarbons produced

from Eqs. (8) -(10) in plasma phase, these hydrocarbons broken again, so producing CO molecule probability increased. Meanwhile, hydrogen reacts with oxygen atoms (Eq. (11)) and H_2O is produced, thus H_2 selectivity decreases to 65% from 4 to 10 W. In gliding discharge plasma, input power increase from 10 to 30 W. Thus, the conversion of CH_4 increased from 65 to 74% (Fig. 3).

$$2CH_3 \rightarrow C_2H_6 \tag{8}$$

$$e + C_2H_6 \rightarrow C_2H_4 + H_2 \tag{9}$$

$$e + C_2H_4 \rightarrow C_2H_2 + H_2 \tag{10}$$

$$e + CO_2 \rightarrow CO + O \tag{11}$$

Overall range of the operating condition used in this study for developing the chemical kinetic models are summarized in Table 1.

Comparison of DRM among different non-thermal plasmas

Interesting results are presented in Table 2 when comparing the DRM by different typical non-thermal plasmas (our results are included). XCH_4, XCO_2, SH_2 and SCO appear to be good indicators for estimating the reforming performance of methane. It should be noted that some values claimed here may be slightly different from those reported by the authors. Our plasma (Gliding discharge) shows best SEI and good CH_4 and CO_2 conversion rates.

Table 1: Experimental data ranges used in this study for development of chemical kinetic model [12].

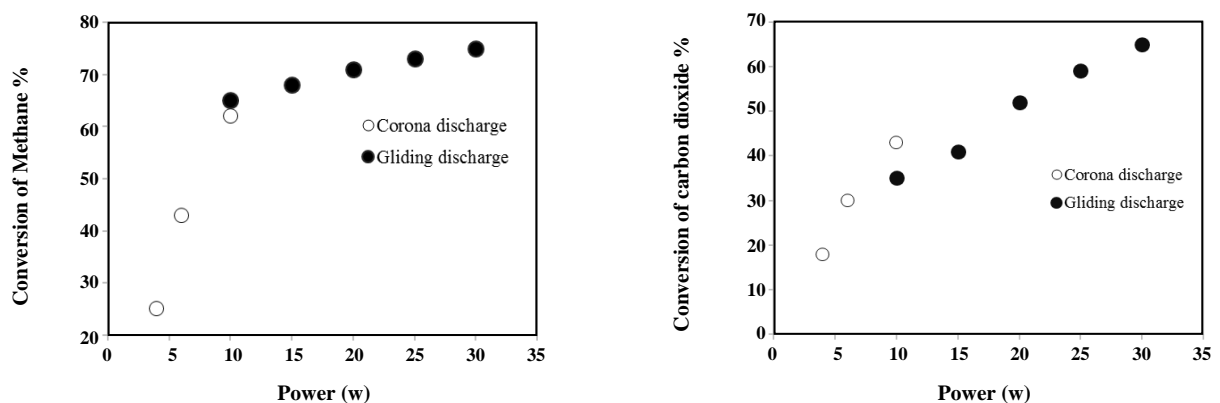| Types of plasma: Corona discharge					
Feed flow rate (ml/min) CO_2/CH_4 ratio= 0.5	Power (w)	XCH_4%	XCO_2%	SH_2%	SCO%
50	4	35	24	61	73
100	4	28	20	63	76
150	4	25	15	64	70
200	4	22	17	65	69
250	4	17	13	66	70
100	4	25	18	72	75
100	6	43	30	67	76
100	10	62	43	65	80
Types of plasma: Gliding discharge					
Feed flow rate (ml/min) CO_2/CH_4 ratio=0.5	XCH_4%	XCO_2%	SH_2%	SCO%	
50	75	46	42	65	
100	70	37	55	67	
150	60	27	56	57	
200	53	20	59	55	
250	43	15	62	52	
Power (w) Feed flow rate (ml/min)=100	XCH_4%	XCO_2%	SH_2%	SCO%	
10	65	35	77.8	65	
15	68	41	77.4	67	
20	71	52	76.5	69	
25	73	59	76	73	
30	74	65	75	76	

Fig. 3: Effect of input plasma power on CH_4 (a) and CO_2 (b) conversion rates in corona and gliding discharge plasmas (Ar= 60 mol %, CH_4/CO_2=0.5, feed flow rate=100 ml.min^{-1}).

Table 2: Comparison of conversion in different plasmas.

Plasma	Feed flow rate (ml/min)	CO_2/CH_4	P (W)	Conversion (%)		Selectivity (%)		SEI (kJ/L)	Refs
				CH_4	CO_2	H_2	CO		
Corona	95	1/1	46.3	62.4	47.8	70	66.8	29.2	[16]
DBD	150	2/1	50	64.3	55.4	-	33.3	20	[17]
Glow discharge	120	1/1	23	61	50	77.5	63	11.5	[18]
Gliding Arc discharge	1000	1/1	190	40	31	50	62	11.4	[14]
Corona	100	2/1	10	62	43	65	80	6	This paper
Gliding discharge	60	2/1	30	74	65	75	76	30	This paper

Chemical Kinetic Models

Simplified Global Chemical Kinetic Model

In order to compare the two reactors used in our experiment, a simplified global kinetic model was used to describe the DRM reaction behavior in different plasma reactor. This model was already used by authors [15, 19–21]. It is generally accepted that free radical processes are the main mechanisms in non-equilibrium plasma reaction [19, 22-23]. The chemical kinetics model was based on the following step process:

- The reactant molecules CH_4 or CO_2 (S) are attacked by active species R (radicals and Ar active species) produced by plasma discharges: S+R→products.

- The reaction rate would be: $r = k_1 R.S$, with k_1: reaction rate constant, R = radical concentration, S = (CH_4 + CO_2) concentration.

- The production rate of R is proportional to the plasma power supplied. We use the parameter $r_R \times P$ (r_R being the production rate of radicals per power supplied).

- The loss of R results from radicals recombination and from plasma chemical reactions with CH_4 + CO_2 and carbonaceous products.

The mass conservation equations for the molecules S and gas phase radicals R are given by:

$$\frac{dS}{dt} = -k_1 \cdot R \cdot S \tag{12}$$

$$\frac{dR}{dt} = r_R \times P - k_2 R - k_1 \cdot R \cdot S_0 \tag{13}$$

Where k_2 represents the reaction rate constant of the R loss, P the input power and S_0 the reactant (CH_4 + CO_2) initial concentration. By application of the stationary state principle and if we expect that the plasma discharges are reproducible, the concentration of radicals is constant along the reactor. Thus:

$$\frac{dR}{dt} = 0$$

And

$$R = \frac{r_R \times P}{k_2 + k_1 R \cdot S_0} \tag{14}$$

$$\frac{dS}{dt} = -k_1 S \frac{r_R \times P}{k_2 + k_1 R \cdot S_0} \tag{15}$$

After integration from reactor inlet (t = 0) to reactor outlet (τ = s), we obtain:

$$\frac{S}{S_0} = \exp\left(-\frac{k_1 r_R \times \tau \times P}{k_2 + k_1 S_0}\right) \tag{16}$$

Or X (reactant conversion)

$$X = 1 - \exp\left(-\frac{P \times \tau}{\beta(S_0)}\right) \text{ or } \ln(1-X) = \left(-\frac{P \times \tau}{\beta(S_0)}\right) \tag{17}$$

$$\beta(S_0) = \frac{1}{r_R}\left(\frac{k_2}{k_1} + S_0\right) = \frac{k_2}{k_1 r_R} + \frac{S_0}{r_R} \tag{18}$$

There is an exponential function of the CH_4 and CO_2 conversion and product. The β parameter is a linear function of the initial reactant concentration with a slope depending only on the production rate of radicals.

In order to obtain the β value for CH_4 and CO_2, the experimental data obtained were fitted to (13) (Fig. 4). In our experimental conditions, the β value for CH_4 and CO_2 equal to 10.42 and 12.24 J for corona discharge plasma, and to 58.25 and 27.77 J for gliding discharge plasma respectively.

         Research Article

Table 3: Kinetic modelization parameters.

Reactant	Linearity	K_2/k_1	r_R (ppm/J)
Corona			
CH_4	$\beta(S_0) = 14.29\ S_0 + 4.70$	0.33	69979
CO_2	$\beta(S_0) = 19.15\ S_0 + 4.58$	0.24	52219
Gliding discharge			
CH_4	$\beta(S_0) = 18.10\ S_0 + 5.29$	0.29	55249
CO_2	$\beta(S_0) = 35.60\ S_0 + 7.12$	0.20	28090

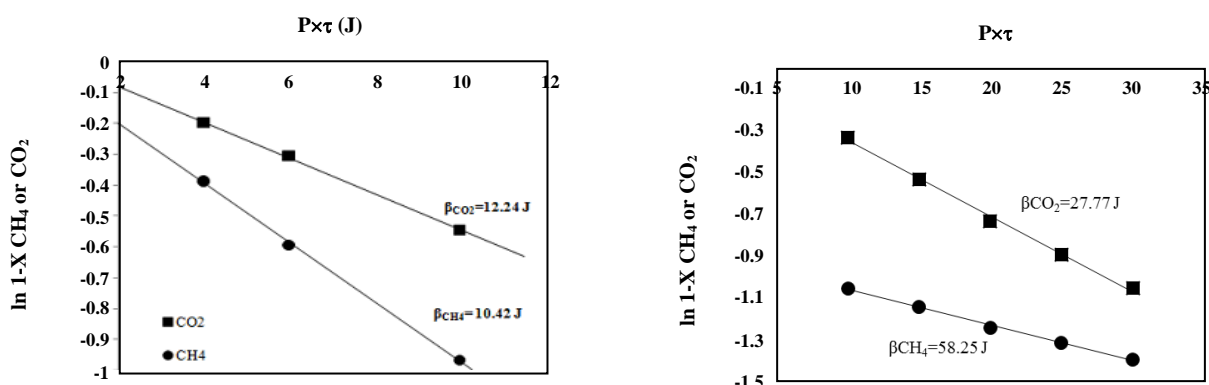*Fig. 4: Estimated β value for CH₄ and CO₂ with X₀ = 0.4 (Ar= 60 mol %) for corona (a) and gliding discharge (b) plasma according to the kinetic model.*

Linear increase of β with increasing the concentration of CH_4 and CO_2 are observed. The β value is characteristic of the energy cost, in the literature; it was often used to evaluate the efficiency of system using plasma for methane reaction [23-25]. A low value for β represents a better efficiency.

Table 3 reports the obtained values of r_R and k_2/k_1 for CH_4 and CO_2. It shows that the production rate of radicals depends strongly on the substance of reactant. The k2/k1 ratio value indicated the dominate reaction; the reaction between active species and reactant driving to product formation, or the actives species loss reaction by recombination or desexcitation [13].

In corona and gliding discharge plasma, for CO_2, the value of k_2/k_1 ratio (0.24, 0.20) respectively; indicates that the reaction of active species is favored compared to their loss. For CH_4 (k_2/k_1 ratio: 0.33, 0.29) respectively, the loss of active species is quite as considerable as the reaction, so the recombination of active species originated from methane occurs more immediate than

from carbon dioxide. The following equation calculated the β values:

$$X = 1 - \exp\left(\frac{P \times \tau}{\beta(S_0)}\right)$$

As shown in Fig. 5, this modeling is fitted well with the experimental data of CH4 and CO2 conversions in the presence of plasma discharges. This simple model based on a global kinetic approach gives an authentic prediction of the CH_4 and CO_2 conversions according to the argon dilution of the feed gas.

CONCLUSIONS

The DRM was investigated in the corona and gliding discharge reactors at atmospheric pressure and room temperature. A simplified global kinetic model was proposed. We have proposed a kinetic model based on the assumption that the reactant molecules CH_4 or CO_2 (S) are attacked by active species produced by the plasma discharges, and production of this active species are
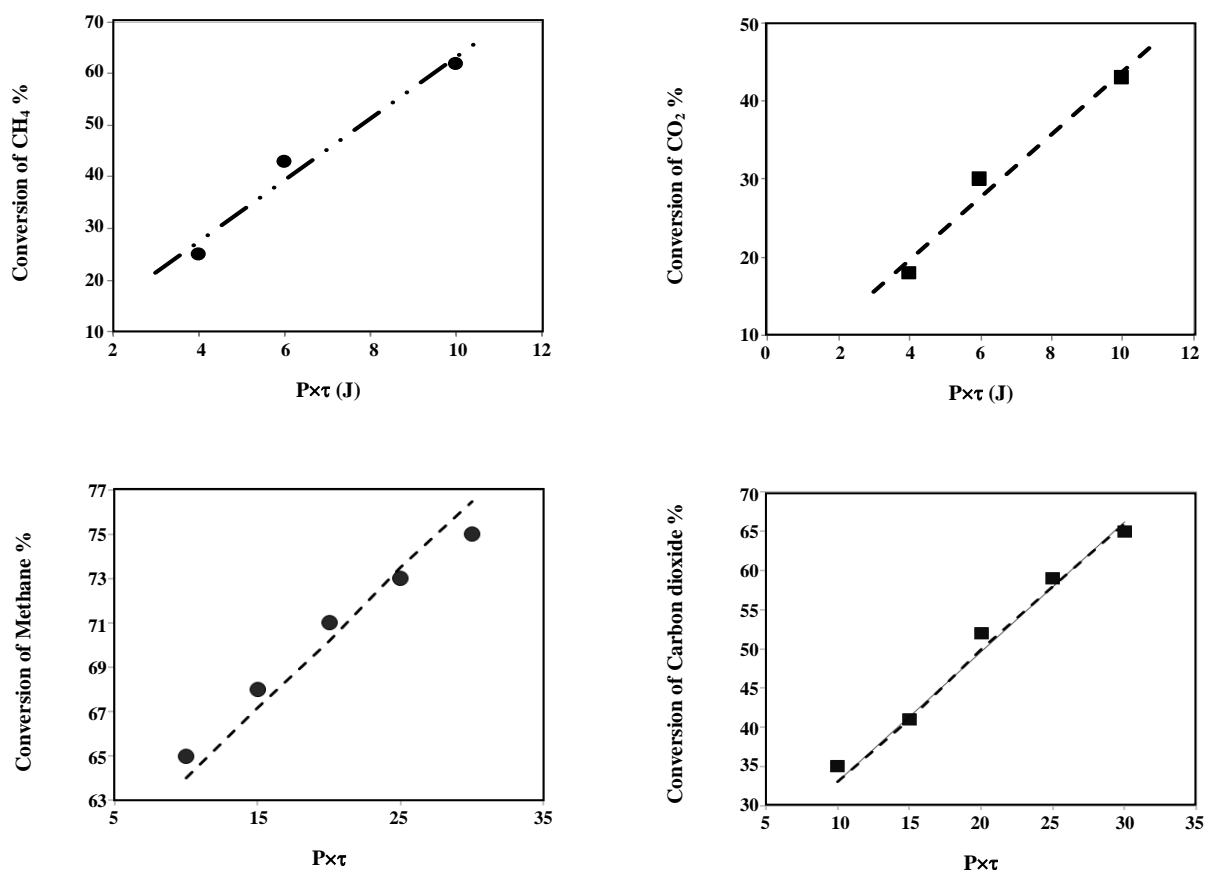
Fig. 5: Simulated behavior of CH4 conversion and CO2 conversion according energy transferred to the gas during plasma discharge: P*τ (J) for corona (a), (b) and gliding discharge (c), (d) plasma (●, ■: experimental and - - - calculated data).

function of the plasma power. The kinetic model demonstrated that there is an exponential function of the reactant conversion and plasma energy. The modelization allows prediction of the reactants conversion according to the energy transfer to the gas ($P \times \tau$). The experimental data (CH_4 and CO_2 conversion) fits very well with the proposed kinetic law. This model also represents that a plasma reactor with a smaller input discharge power (corona discharge plasma) has better energy efficiency for CO_2 and CH_4 conversion.

REFERENCES

[1] Bradford M.C.J., Vannice M.A., CO₂ Reforming of CH₄, *Catal. Rev. Sci. Eng*, **41**: 1-42 (1999).

[2] Choudary T.V., Aksoylu E., Wayne Goodman D., Nonoxidative Activation of Methane, *Catal. Rev*, **45**(1): 151-203 (2003).

[3] Huang A., Xia G., Wang J., Suib S.L., Hayashi Y., Matsumoto H., CO₂ Reforming of CH₄ by Atmospheric Pressure AC Discharge Plasmas, *J. Catal*, **189**: 349-359 (2000).

[4] Aghamir F.M., Jalili A.H., Esfarayeni M.H., Khodagholi M.A., Conversion of Methane to Methanol in an ac Dielectric Barrier Discharge, *Plasma Sources Sci T,* **13**: 707-714 (2004).

[5] Rueangjitt N., Sreethawong T., Chavadej S., Sekiguchic H., Plasma-Catalytic Reforming of Methane in AC Microsized Gliding Arc Discharge: Effects of Input Power, Reactor Thickness, and Catalyst Existence, *Chem. Eng. J, (Amsterdam, Neth.)* **155**: 874-880 (2009).

[6] Gallon H.J., Tu X., Whitehead J.C., Effects of Reactor Packing Materials on H₂ Production by CO₂ Reforming of CH₄ in a Dielectric Barrier Discharge, *Plasma Process Polym*, **9**, 90-97 (2012).

[7] Li X.S., Lin C.K., Shi C., Xu Y., Wang Y.N., Zhu A.M., Stable Kilohertz Spark Discharges for High-Efficiency Conversion of Methane to Hydrogen and Acetylene, *J. Phys. D. Appl. Phys*, **41**: 175203175210 (2008).

[8] Gallon H.J., Tu X., Twigg M.V., Whitehead J.C., Plasma-Aassisted Methane Reduction of a NiO Catalyst—Low Temperature Activation of Methane and Formation of Carbon Nanofibres, *Appl Catal B,* **106**: 616-620 (2011).

[9] Savinov S.Y., Lee H., Song H.K., Na B.K., Decomposition of Methane and Carbon Dioxide in a Radio-Frequency Discharge, *Ind. Eng. Chem. Res*, **38**(7): 2540-2547 (1999).

[10] Marafee A., Liu C., Xu G., Mallinson R., Lobban L., An Experimental Study on the Oxidative Coupling of Methane in a Direct Current Corona Discharge Reactor over Sr/La$_2$O$_3$ Catalyst, *Ind. Eng. Chem. Res*, **36**: 632-637 (1997).

[11] Liu C., Marafee A., Allinson R., Lobban L., Methane Conversion to Higher Hydrocarbons in a Corona Discharge over Metal Oxide Catalysts with OH Groups, *Appl Catal A: Gen*, **164**: 21-33 (1997).

[12] Aziznia A., Bozorgzadeh H.R., Seyed-Matin N., Baghalha M., Mohamadalizadeh A., Comparison of Dry Reforming of Methane in Low Temperature Hybrid Plasma-Catalytic Corona with Thermal Catalytic Reactor over Ni/γ-Al$_2$O$_3$, *J. Nat. Gas Chem.*, **21**: 466-475 (2012).

[13] Goujard V., Tatibouet J.M., Batiot-Dupeyrat C., Carbon Dioxide Reforming of Methane Using a Dielectric Barrier Discharge Reactor: Effect of Helium Dilution and Kinetic Model, *Plasma Chem. Plasma P*, **31**(2): 315-325 (2011)**.**

[14] Indarto A., Choi J-W., Lee H., Song H.K., Effect of Additive Gases on Methane Conversion Using Gliding Arc Discharge, *Energy*, **31**(14): 2986-2995 (2006).

[15] Wang B., Yan W., Ge W., Duan X.O., Kinetic Model of the Methane Conversion Into Higher Hydrocarbons with a Dielectric Barrier Discharge Microplasma Reactor, *Chem. Eng. J*, **234**: 354-360 (2013).

[16] Yang Y., Methane Conversion and Reforming by Nonthermal Plasma on Pins, *Ind. Eng. Chem. Res.*, **41**(24): 5918-5926 (2002).

[17] Jiang T., Li M., Li Y., Xu G., Liu C., Eliasson B., Comparative Investigation on the Conversion of Greenhouse Gas Using Dielectric Barrier Discharge and Corona Discharge, *Journal of Tianjin University*, **35**(1): 19-22 (2002).

[18] Ghorbanzadeh A., Lotfalipour R., Rezaei S., Carbon Dioxide Reforming of Methane at Near Room Temperature in Low Energy Pulsed Plasma, *Int J. Hydrogen Energy*, **34**(1): 293-298 (2009).

[19] Yan K., van Heesch E.J.M., Pemen A.J.M., Huijbrechts P.A.H.J., From Chemical Kinetics to Streamer Corona Reactor and Voltage Pulse Generator, *Plasma Chem. Plasma P*, **21**(1): 107-137 (2001).

[20] Rudolph R., Francke K.P., Miessner H., Concentration Dependence of VOC Decomposition by Dielectric Barrier Discharges, *Plasma Chem. Plasma P*, **22**(3):401-412 (2002).

[21] Redolfi M., PhD. Thesis of the University Paris XIII (2007).

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

[23] Reddy E.L., Karuppiah J., Renken A., Kiwi-Minsker L., Subrahmanyam C., Kinetics of the Decomposition of Hydrogen Sulfide in a Dielectric Barrier Discharge Reactor, *Chem. Eng. Technol*, **35**: 2030-2034 (2012).

[24] Chiper A.S., Blin-Simiand N., Heninger M., Mestdagh H., Boissel P., Jorand F., Lemaire J., Leprovost J., Pasquiers S., Popa G., Postel C., Detailed Characterization of 2-Heptanone Conversion by Dielectric Barrier Discharge in N$_2$ and N$_2$/O$_2$ Mixtures, *J. Phys. Chem. A,* **114**: 397-407 (2010).

[25] Rosacha L.A., Korzekwa R.A., Advanced Oxidation and Reduction Processes in the Gas Phase Using Non-Thermal Plasmas, *J. Adv. Oxid. Technol*, **4**: 247-264 (1999).