Synthesis of oxygenated compounds from methane, carbon dioxide and liquid water using non-thermal plasma

J.F Gelves, L. Dorkis, E. Fourré, C. Batiot-Dupeyrat

Abstract— **Oxygenated compounds were obtained from methane and carbon dioxide using the unconventional activation by dielectric barrier discharge plasma. The process was performed using a multiphase feed composed of methane, liquid water and carbon dioxide as oxidizing agent. The effect of the CH4/CO2 ratio as well as the flow of liquid water were investigated. The results show that the presence of liquid water in the reactor favors the formation of oxygenated compounds. A direct proportional relation between the flow of water, concentration of methane in the gaseous feed (in the presence of water) and the amount of the produced oxygenates was observed. The highest value of selectivity towards oxygenated compounds was 21.2%, with methanol and formic acid being the main products formed.**

Index Terms— **Non-thermal plasma, dielectric barrier discharge, biogas, methane oxidation, oxygenated products.**

I. INTRODUCTION

Oxygenated compounds play an important role in the contemporary chemical industry: Methanol, acetic acid, formaldehyde or acetone can be considered as sources of energy or as raw materials for the synthesis of a large number of value-added products [1-5]. The main route for obtaining oxygenates (especially methanol) today is through a two-stage process, where natural gas is the main raw material in the process. The first stage consists in obtaining synthesis gas $(CO + H_2)$ through methane reforming route, process that is carried out at high temperature, requiring robust equipment. The second step is the synthesis process, which operates at lower temperature (200-300 °C) but requires high working pressures (> 50 bar). The complete process is not only costly but it presents also thermodynamic limitations, resulting in low methanol yields (<6%) [6]. For that reason there has been an interest in finding a direct route for the synthesis of oxygenated compounds, that proved its feasibility. However the results obtained have not managed to overcome yet the efficiency of the two-stage process [7, 8]. The chemical activation by non-thermal plasma (NTP) has been known for more than 100 years, but only a few decades ago this technique has attracted the attention of researchers as a possible alternative for the direct synthesis of oxygenated compounds [9-11]. The main advantage of non-thermal plasma is that it allows the activation of reactants at atmospheric pressure and low temperature (room

J.F. Gelves, **L. Dorkis** Universidad Nacional de Colombia, Facultad de Minas, Departamento de Materiales y Minerales, Grupo de Investigación en Catálisis y Nanomateriales, Medellín, Colombia

E. Fourré, C. Batiot-Dupeyrat, Université de Poitiers, CNRS UMR7285, Institut de Chimie des Milieux et Matériaux de Poitiers, ENSIP, Bat B1, TSA 41105, 1 rue Marcel Doré, 86073 Poitiers CEDEX 9, France

temperature), through the formation of highly active species such as radicals, excited atoms, ions and molecules. The generated reactive species play important roles in the initiation and propagation of many physical and chemical reactions [12].

Many studies were reported on the use of NTP to perform the reaction of dry reforming of methane. Apart from syngas, the formation of oxygenated compounds, but in trace amounts, was reported [13-15]. The partial oxidation of methane, in order to increase the selectivity towards oxygenated compounds such as methanol and formaldehyde, was also developed by various authors [16-18].

Different works have been carried out in order to increase the selectivity towards oxygenated compounds using non-thermal plasma. Radiofrequency, corona type and dielectric barrier discharge plasma have been developed for this purpose [19-21]. In the same way different oxidizing agents such as oxygen, air and carbon dioxide have been used [22-24]. The best results have been obtained with oxygen, however, the reaction presents the disadvantage that a significant part of the reacted carbon is converted into carbon dioxide.

The use of carbon dioxide as an oxidizing agent presents different advantages, because this compound often accompanies methane in many sources of supply, especially natural gas (for example, Kapuni natural gas in New Zealand has approximately 40% of CO_2 in its composition), it is also one of the two main constituent of biogas sources [25-26]. The direct use of CO_2 would not only avoid methane purification treatments, but would contribute to the reduction of carbon dioxide expelled to the atmosphere, which is known to be one of the main responsible for global warming [27].

The difficulty of working with CO_2 in the reaction (both conventional and non-thermal plasma) is the high stability of the molecule (strong intramolecular bonds that make the molecule chemically quite inert and thermodynamically stable) [28], requiring high energy input to achieve high conversion. An important drawback associated with the use of NTP to produce oxygenates, is the low stability of organic molecules, in gas phase, under the plasma discharge. Indeed, oxygenated molecules such as methanol or formaldehyde are rapidly oxidized into CO_2 under the conventional experimental conditions used. However Nozaki et al. [29-30] succeeded in the improvement of oxygenates formation by developing microreactors in which condensation of liquid products is favored. The injection of a liquid film of water in order to trap the oxygenated product was also developed by the authors using oxygen as oxidant [31].

Therefore, it is an even greater challenge to obtain a direct route to oxygenated product that is economically viable. This last aspect highlights the importance of the present study. The

present work has focused on evaluating the effects of the concentration of the reactant gases (CH_4 and CO_2) in order to increase the conversion rate and to improve the selectivity towards oxygenated compounds. Likewise, the research was aimed at evaluating the effect of liquid water in the feed on the two variables mentioned above.

II. EXPERIMENTAL SECTION

The reaction was performed at room temperature and atmospheric pressure in a coaxial dielectric barrier discharges (DBD) reactor (figure 1). The non-thermal plasma reactor (dielectric barrier discharge) was composed of a quartz tube (ID: 4mm; ED: 6mm), a stainless steel electrode inside the reactor (1,0mm) and a copper electrode wrapped around the quartz tube (50 mm long, 25 mm wide and 25 μm thick. Advance tapes- AT526). A thin liquid film of water was flowing along the co-axial tube (0.02 to 0.1 ml.min^{-1}) via a peristaltic pump (Metrohm, model 765). Liquid phase products were recovered by condensation in a cold trap located at the reactor outlet for further analysis, whereas gas phase was analyzed on-line by gas chromatography. The total reaction time was adjusted to one hour, and the liquid was collected over that time.
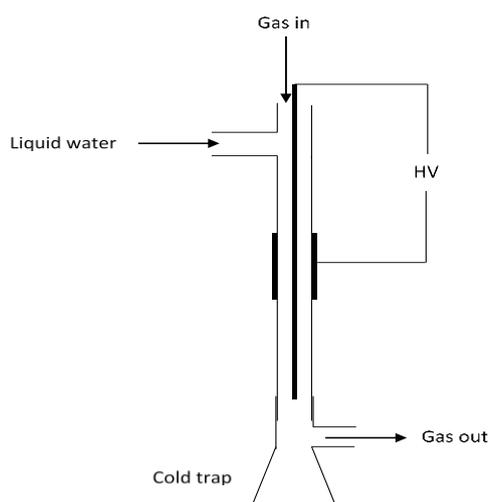

Figure 1: Schematic of the DBD plasma reactor

A sinusoidal signal was used for the reaction (TG1010A Aim-TTi, Thurlby Thandar Instruments Brand). The discharge power, calculated through the figure of Lissajous, was fixed at 6 watts, keeping the frequency constant at 5 kHz (voltage was between 16 and 18 kV). The electrical signals were monitored with high voltage probes (PMK, model PHV4-2757) connected to an oscilloscope (waveRunner 62 Xi, Lecroy).
The total gas flow was adjusted to 40 mL/min with a constant flow of helium of 30 ml/min as diluting gas and 10 ml/min of reactants (Using MFC Bronkhorst Brand). The gas phase was analyzed with gas chromatography (Varian 4900, using two capillary columns: poraplot Q and Molsieve 5A for the monitoring of reactants and products (CH_4, CO_2, CO, O_2, C_2H_2, C_2H_4, C_2H_6, H_2,). Products in the liquid phase were analyzed by liquid and gas chromatography (GC Varian 3900- capillary columns Agilent CP-wax 58FFAP CB; LC Synergi 4μm Hydro-RP 80Â, phenomenex, using 0.5 g.L^{-1} H_2SO_4 as solution of elution). A Total Organic Carbon

Analyzer (TOC-V CSH, Shimadzu brand) was used to determine the amount of organic compounds in the condensated phase as soon as liquid water was introduced. The conversion and selectivity are defined as follows:
Conversion (%) of CH_4 (or CO_2) = 100 * mole of CH_4 (or CO_2) converted/mole of CH_4 (or CO_2) in the feed

Selectivity to CnHyOz (%) = 100*n*mole of CnHyOz/ (mole of CH_4 converted + mole of CO_2 converted)

III. RESULTS AND DISCUSSION

The study was performed using helium as diluent gas since it is admitted in the literature, and as we have observed in previous experiments [33], that the presence of a noble gas such as He or Ar, in the plasma discharge favors CH4 and CO2 activation through an energy transfer or a charge transfer from excited He species (He*) to molecules in ground state, so called Penning ionization effect [32-36]. From this effect, in the presence of helium in excess (75% vol.), the probability of collision between He atoms and electrons (according to (4) - (7)) is much higher than that of electrons with CH_4 or CO_2 via reactions (1) and (2) [35, 37]:

$$CO_2 + e- \rightarrow CO + O + e- \qquad (1)$$
$$CH_4 + e- \rightarrow CH_3 + H + e-´ \qquad (2)$$
$$He + e- \rightarrow He* + e- \qquad (3)$$
$$He* + CH_4 \rightarrow CH_3 + H + He \qquad (4)$$
$$He* + CO_2 \rightarrow CO + O + He \qquad (5)$$
$$He* + CH_4 \rightarrow CH_4* + He \qquad (6)$$
$$He* + CO_2 \rightarrow CO_2* + He \qquad (7)$$
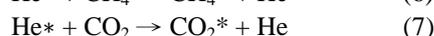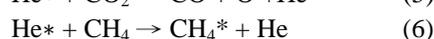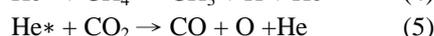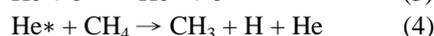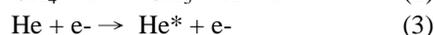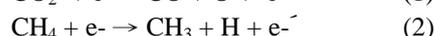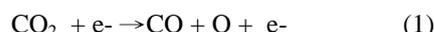
A. Effect of CH_4/CO_2 ratio

The effect of CH_4/CO_2 ratio on conversions is reported in Figure 2.

In the absence of liquid water, CH_4 conversion decreased from 25.4 to 16.8% when the CH_4/CO_2 ratio increased from 0.4 to 2.3 while the CO_2 conversion remains almost constant. Similar results were observed by different authors using the same plasma reactor configuration [12, 13, 38, 39]. The higher reactivity of methane compared to CO_2 particularly when an excess of CO_2 is used can be explained by the activation of CH_4 by an active oxygen species issued from CO_2, according to reactions (5) and (8).
$$O + CH_4 \rightarrow CH_3 + OH \qquad (8)$$
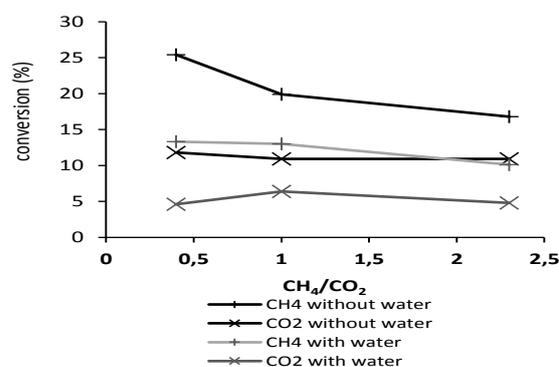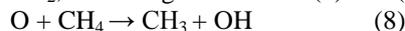
Figure 2: Effect of CH_4/CO_2 ratio and liquid water (0.06 ml/min) on reactant conversion, gas flow: 40mL/min (75% of He), P=6W

When water was added to the reactor, a drastic decrease in conversion for both methane and carbon dioxide was observed. The introduction of water leads to the involvement of other chemical reactions and various changes in the plasma discharge behavior. The water modifies the plasma electric field and reduces mobility of charge carriers [40]. The energy is also partly used to activate water molecules and not CH_4 or CO_2. Water molecules dissociates then by impact with electrons or oxygen radicals leading to the formation of hydroxyl radicals [41], which are highly oxidative. But this effect is cancelled out by the reduction of plasma microdischarges due to the presence of water.

The selectivity to gaseous products is reported in Figure 3.
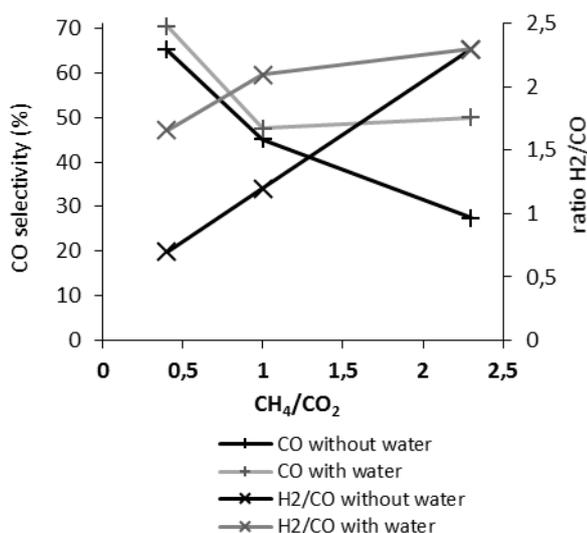
Figure 3: Effect of CH_4/CO_2 ratio and liquid water (0.06 ml/min) on selectivity to CO and H_2/CO ratio, gas flow: 40mL/min (75% of He), P=6W

The main product formed is carbon monoxide. Interestingly, the amount of C2 hydrocarbons was always very low (<1%) while no C3 hydrocarbons were detected. This result can be explained by the geometry of the plasma reactor and principally by the low gap (1.5 mm) chosen. In fact, similar results were observed by Larkin *et al.* [42]. The authors showed that decreasing the gap from 12 to 4 mm led to an increase of the electric field from 18 to 30 V/cm/Torr, which resulted in a shift in the product selectivity from ethane and acetylene to organic oxygenate liquids [16-17]. However, under the experimental conditions used in the present study oxygenated compounds were obtained only in presence of water in the feed gases. Additionally, from studies carried out by Goujard *et al.* [33] and by Indarto *et al.* [34], the low concentration of hydrocarbons could be associated with the high presence of helium in the feed.

It can be observed that without water, an increase of CH_4/CO_2 ratio leads to a significant decrease of the selectivity towards CO due to carbon deposition as observed by black residue at the surface of the inner electrode after reaction. In the presence of liquid water, the carbon deposition is limited and the selectivity towards CO is maintained at 50%. The H_2/CO ratio is higher when a liquid water is introduced especially at low CH_4/CO_2 ratio. This result suggested that water

participated to the hydrogen production, most probably according to reactions (9) to (12). The calculation of the selectivity towards hydrogen taking methane as the only source of hydrogen production, exhibited values higher than 100%, corroborating the hypothesis raised.

$$H_2O + e- \rightarrow OH^\bullet + H^\bullet \qquad (9)$$
$$H_2O + e- \rightarrow O + 2H^\bullet + e- \qquad (10)$$
$$H_2O + e- \rightarrow O^- + H_2 \qquad (11)$$
$$2H^\bullet \rightarrow H_2 \qquad (12)$$
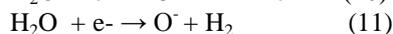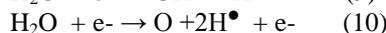
Without water addition, the amount of liquid phase collected at the exit of the reactor was very low, which did not allow the quantification of oxygenated products. The analysis of the liquid phase was only possible using a liquid film of water into the plasma reactor.

The influence of the ratio CH_4/CO_2 on the selectivity into liquid oxygenated product is shown in Table 1. The flow of water was kept constant at 0.06 mL/min.

Ratio CH_4/CO_2	Selectivity (%)						Σ sel.
	M.	E.	Pr.	Ac.	F.A.	A.A.	
0.4	2.7	0.3	0	0.1	0.1	0	3.2
1	2.9	0.5	0.1	0.2	0.2	0	3.9
2.3	4.4	1.1	0.4	0.5	1.1	0.5	8.0

M: methanol; E: ethanol; Pr.: propanol; Ac.: acetaldehyde; F.A: Formic Acid; A.A: Acetic Acid

Experimental conditions: flow of water: 0.06 mL/min, gas flow: 40mL/min (75% of He), P=6W.

Table 1 Selectivity to products for different CH_4/CO_2 ratio in presence of water

The results reported in Table 1 show that the formation of organic compounds is favored in the presence of water. The flow of a thin layer of water allowed the dissolution and protection of newly formed oxygenated compounds in the plasma discharge volume that would have been, in dry conditions, further oxidized by the plasma active species. The main organic compounds formed are methanol, ethanol and also propanol, acetaldehyde, formic acid and acetic acid in lower content. An excess of methane favors the formation of methanol due to the increase of methyl radicals and their rapid reaction with hydroxyl radicals.

*B. Effect of the flow of water*

According to the results presented above showing that the selectivity to oxygenated products is favored with an excess of methane, it was decided to use a ratio CH_4/CO_2 of 2.3 for the following experiments. The influence of the flow of water was investigated within a range: 0-0.1 mL/min. The use of a higher flow rate of distilled water was not possible due to the instability of the plasma discharge.

Figure 4 shows that CH_4 and CO_2 conversions decrease as the flow rate of liquid water is increased, while the selectivity to CO is favored for the highest flow of water (Figure 5).
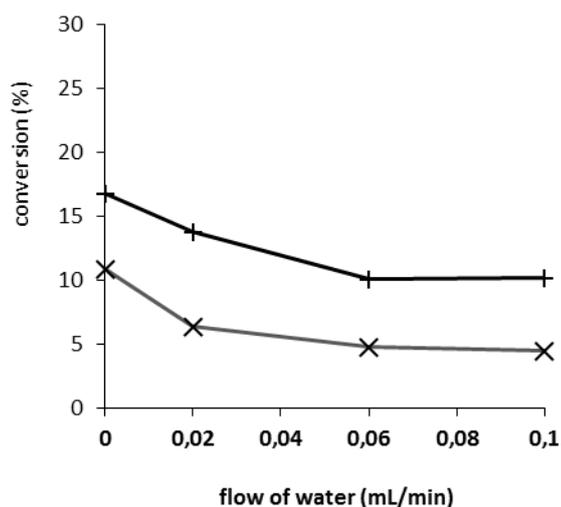
Figure 4: Effect of the flow of liquid water, on reactant conversion. Gas flow: 40mL/min (75% of He), $CH_4/CO_2=2.3$, P=6W

As discussed above, the introduction of water as a liquid film into the plasma reactor leads to a low carbon deposition and the formation of CO is increased. A possible route that could explain the enhanced formation of CO in presence of water, is the increase of reactive oxygen species concentration associated with reactions (10) and (11). This possibility arises from the directly proportional relation between the water flow and the selectivity towards CO as shown in Figure 5. Moreover, the decrease of CO_2 and CH_4 conversions can be explained by the modification of the discharge electronic density in presence of humidity, reducing the concentration of energetic electrons required for the reactants activation [40, 43]. It is interesting to note that the ratio H_2/CO is particularly high, always higher than 2. It is also an appropriate composition to be used in conventional methanol synthesis process [44], which could give an additional added value to a reaction system valorizing a dielectric barrier discharge plasma.
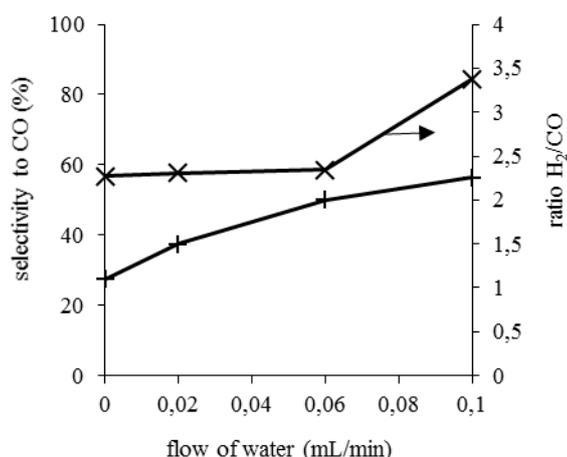
Figure 5 Effect of the flow of liquid water, on selectivity to CO and ratio H_2/CO, gas flow: 40mL/min (75% of He), $CH_4/CO_2=2.3$, P=6W

From Table 2 it can be seen that the presence of water in the feed also greatly changes the selectivity towards oxygenated compounds. The selectivity to methanol increases

significantly with an increase of the flow rate of water, reaching 10.3% with a flow rate of 0.1 mL/min. The selectivity to other oxygenated compounds is also improved especially the synthesis of formic acid. The presence of humidity increases the concentration of OH radicals that can play an important role in the formation of such oxygenated compounds. Additionally, the increase of the liquid flow rate facilitates and increases the solubility of the products, shifting the reaction equilibriums to the formation of products.

Flow of water mL/min	Selectivity (%)						Σ sel.
	M.	E.	Pr.	Ac.	F.A.	A.A.	
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.02	2.5	0.6	0.3	0.1	1.9	2.1	7.5
0.06	4.4	1.1	0.4	0.5	1.1	0.5	8.0
0.1	10.3	2.5	0.5	0.8	4.0	3.1	21.2

M: methanol; E: ethanol; Pr.: propanol; Ac.: acetaldehyde; F.A: Formic Acid; A.A: Acetic Acid
Experimental conditions: $CH_4/CO_2=2.3$, gas flow: 40mL/min (75% of He), P=6W.

Table 2 Selectivity to products for different flow rate of water

From published data and our experimental work, it may be suggested that the main reactions involved [45] can be summarized as follow:

$$CH_4 + He^* \rightarrow CH_3^. + H + He \qquad (13)$$
$$H_2O + e- \rightarrow OH^. + H^. \qquad (14)$$
$$CH_3^. + OH^. \rightarrow CH_3OH \qquad (15)$$
$$CH_3^. + CH_3^. \rightarrow C_2H_6 \qquad (16)$$
$$C_2H_6 + H^. \rightarrow C_2H_5^. + H_2 \qquad (17)$$
$$C_2H_5^. + OH^. \rightarrow C_2H_5OH \qquad (18)$$
$$C_2H_5^. + CH_3^. \rightarrow C_3H_8 \qquad (19)$$
$$C_3H_8 + H^. \rightarrow C_3H_7^. + H_2 \qquad (20)$$
$$C_3H_7^. + OH^. \rightarrow C_3H_7OH \qquad (21)$$
$$CH_4 + CO \rightarrow CH_3CHO \qquad (22)$$
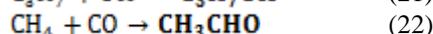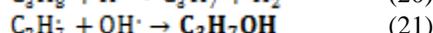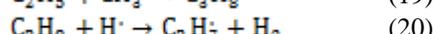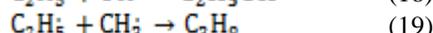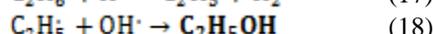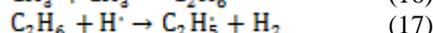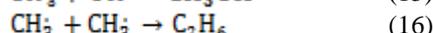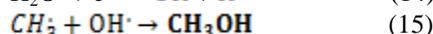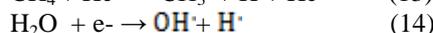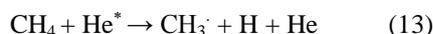
Both acids may arise from methanol and ethanol degradations [46, 47] in the plasma discharge, showing the importance of collecting continuously the oxygenated products to avoid their degradation. The following reactions may occur:

$$CH_3OH \rightarrow CH_2OH^. + H^. \qquad (23)$$
$$CH_2OH^. \rightarrow HCHO + H^. \qquad (24)$$
$$HCHO + OH^. \rightarrow HCOOH + H^. \qquad (25)$$
$$C_2H_5OH \rightarrow C_2H_4OH^. + H^. \qquad (26)$$
$$C_2H_4OH^. + O^. \rightarrow CH_3CHO + OH^. \qquad (27)$$
$$CH_3CHO + O^. \rightarrow CH_3CO^. + OH^. \qquad (28)$$
$$CH_3CO^. + O_2 \rightarrow CH_3CO_3^. \qquad (29)$$
$$CH_3CO_3^. + OH^. \rightarrow CH_3COOH + O_2 \qquad (30)$$
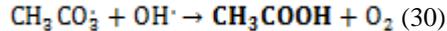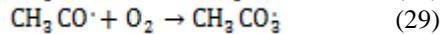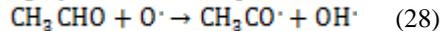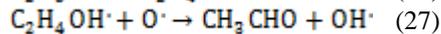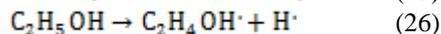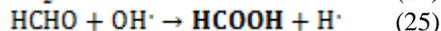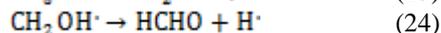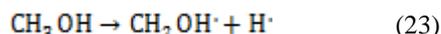
The formation of these acids from CO_2 has also been proposed by Wang et al [35] using Density Functional Theory, although these reactions are less likely to occur due to the lower conversion of CO_2 according to the information shown in the Figure 4. The reactions given are the following:

$$CO_2 + e- \rightarrow CO_2^- \qquad (31)$$
$$CO_2^- + H \rightarrow COOH^- \qquad (32)$$
$$COOH^- + CH_3 \rightarrow CH_3COOH + e- \quad (33)$$
$$COOH^- + H \rightarrow HCOOH + e- \qquad (34)$$

Monitoring of the discharge power in the reactor as well as the temperature of the outer wall (using an infrared pyrometer), were carried out in order to obtain complementary information about the reaction. The results obtained are presented in Figures 6 and 7.
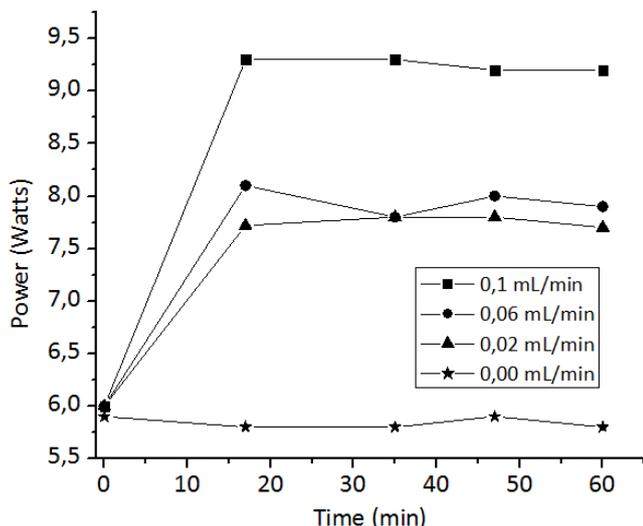
Figure 6: Monitoring the discharge power during the reaction time. Experimental conditions: $CH_4/CO_2=2.3$, gas flow: 40mL/min (75% of He), Frequency=5 kHz

Changes occur in the discharge power when the reaction is carried out with or without water. When the water flow increases, the discharge power also increases, without significant variations in the course of time for any of the reaction performed. The increase of the power in the presence of water flow, may be associated with the increase of ions and radicals formed as a result of the decomposition of water. Theses species allow the increase of the discharge current and therefore the power, following the Lissajous calculations.
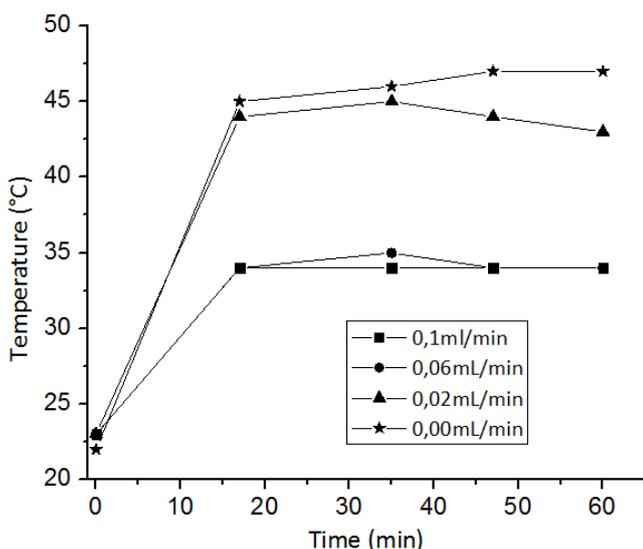
Figure 7 Monitoring of the temperature of the reactor wall (outside) during the reaction time. Experimental conditions:

$CH_4/CO_2=2.3$, gas flow: 40mL/min (75% of He), P=6W

Regarding the temperature evolution of the system, it is observed, after a few minutes, that the temperature rises and stabilizes after 17 mins. An interesting feature concerns the presence of water circulating through the reactor that allows the reduction of the temperature of the coaxial reactor walls. This aspect could also have some influence on the selectivity results of oxygenated compounds as proposed by Bugaev *et al.* [48], who showed that by reducing the temperature of the reactor, the condensation of oxygenated products on the walls of the reactor was favored. This effect, in addition to the water flow in the reactor, would favor the formation and rapid dissolution of the oxygenated compounds from the plasma region in the liquid phase. It would also prevent their decomposition, which would explain part of the selectivity results obtained in this work.

IV. CONCLUSIONS

The results of the present study suggest a great potential in using the dielectric barrier discharge plasma technique to obtain oxygenated compounds when multiphase feed composed of methane, carbon dioxide and liquid water was used. Additionally, It was evidenced that:
- In the absence of water and using a gas rich in carbon dioxide, the highest conversion of the reactants is reached, but the production of oxygenated products remains very low. The selectivity to oxygenated compounds does not exceed 1%.
- The presence of water thin film in the feed increased significantly the production of oxygenated compounds. The continuous removal of the oxygenated molecules, formed by condensation on the reactor wall by the flow of water, and the presence of OH· species, resulting from the hydrolysis of water, could be responsible of the changes in the selectivity towards oxygenated compounds. This last fact is based on the direct and proportional relationship between the production of oxygenates and the water flow rate present in the feed.
- A multiphase feed rich in methane allows to reach the best levels of selectivity towards oxygenated compounds. By feeding a water flow rate of 0.1 ml.min^{-1}, with 7 ml.min^{-1} of CH_4 and 3 ml.min^{-1} of CO_2, a selectivity level of 21% was reached (by GC / LC analysis). The main oxygenated products were methanol and formic acid.

REFERENCES

[1] R.G. Herman, Q. Sun, C. Shi, K. Klier, C.B.Wang, H. Hu, M. Bhasin, (1997) "Development of active oxide catalysts for the direct oxidation of methane to formaldehyde". *Catal. Today*, 37(1), pp. 1-14.
[2] A.E. Said, M.M.A. El-Wahab, M.N. Goda. (2016) Selective synthesis of acetone from isopropyl alcohol over active and stable CuO–NiO nanocomposites at relatively low-temperature. *Egyptian Journal of Basic and Applied Sciences. 3 (4).* pp 357-365.

Synthesis of oxygenated compounds from methane, carbon dioxide and liquid water using non-thermal plasma

[3] X. Liu, X., Y. Liu, Y. Cao. (2015) Formic acid: A versatile renewable reagent for green and sustainable chemical synthesis. *Chin. J. Catal. 36*(9), pp1461-1475.

[4] K.A.Ali, A.Z.Abdullah, A.R. Mohamed. (2015) Recent development in catalytic technologies for methanol synthesis from renewable sources: A critical review. *Renewable Sustainable Energy Rev. 44*, pp508-518.

[5] A.Riaz, G. Zahedi, J.J. Klemeš. (2013)A review of cleaner production methods for the manufacture of methanol. *J. Cleaner Prod. 57*, pp19-37.

[6] H.Karaca,, O.Safonova, R. Chambrey, P. Fongarland, A. Khodakov. (2007) Structure and catalytic performance of Pt-promoted alumina-supported cobalt catalysts under realistic conditions of Fischer–Tropsch synthesis. *J. Catal. 277*, pp14-26

[7] T. Nozaki, A. Ağıral, S.Yuzawa, J.H. Gardeniers, K. Okazaki. (2011) A single step methane conversion into synthetic fuels using microplasma reactor. *Chem. Eng. J. 166*(1). pp288-293.

[8] N. R.Foster. (1985) Direct catalytic oxidation of methane to methanol—a review. *Appl. Catal. 19*(1), pp1-11.

[9] J.H.Lunsford. (2000) Catalytic conversion of methane to more useful chemicals and fuels: a challenge for the 21st century. *Catal. Today. 63*(2), pp165-174.

[10] B.Eliasson, U. Kogelschatz. (1991) Nonequilibrium volume plasma chemical processing. *IEEE Trans. Plasma Sci. 19*(6), pp1063-1077.

[11] B.Eliasson, W. Egli, U. Kogelschatz. (1994) Modelling of dielectric barrier discharge chemistry. *Pure Appl. Chem. 66(6),* 1275-1286.

[12] X. Tu, X., B.Verheyde, S. Corthals, S. Paulussen, B.F. Sels. (2011) Effect of packing material on methane activation in a dielectric barrier discharge reactor. *Phys. Plasmas.* 18, pp80702-80710

[13] U. Kogelschatz. (2003) Dielectric-barrier discharges: their history, discharge physics, and industrial applications. *Plasma Chem. Plasma Process. 23(1)*, pp1-46.

[14] Y.P. Zhang, Y. Li, Y. Wang, C.J. Liu, B. Eliasson. (2003) Plasma methane conversion in the presence of carbon dioxide using dielectric-barrier discharges. *Fuel Process. Technol. 83(1),* pp101-109.

[15] A.M. Ghorbanzadeh, S.Norouzi, T. Mohammadi. (2005) High energy efficiency in syngas and hydrocarbon production from dissociation of CH_4–CO_2 mixture in a non-equilibrium pulsed plasma. *J. Phys. D: Appl. Phys. 38(20),* p3804.

[16] X.Tao, M. Bai, X. Li, H.Long, S. Shang, Y. Yin, Y., X. Dai. (2011). CH_4–CO_2 reforming by plasma–challenges and opportunities. *Prog. Energy Combust. Sci. 37*(2), 113-124.

[17] Supat, K., S. Chavadej, L.L. Lobban, R.G. Mallinson. (2003). Combined steam reforming and partial oxidation of methane to synthesis gas under electrical discharge. *Ind. Eng. Chem. Res. 42(8),* pp1654-1661.

[18] M. Khoshtinat, N.A.S. Amin, I. Noshadi. (2010) A review of methanol production from methane oxidation via non-thermal plasma reactor. World Academy of Science, *Engineering and Technology. 62.* pp354-358.

[19] A. Indarto. (2008) A review of direct methane conversion to methanol by dielectric barrier discharge. *IEEE Trans. Dielectr. Electr. Insul.* 15(4), pp1038-1043.

[20] Y.F. Wang, C.H. Tsai, M. Shih, L.T. Hsieh, W.C. Chang. (2005) Direct conversion of methane into methanol and formaldehyde in an RF plasma environment I: a preliminary study. *Aerosol Air Qual. Res. 5,* pp204-210.

[21] F.M.Aghamir, N.S. Matin, A.H. Jalili, M.H. Esfarayeni, M.A. Khodagholi, R. Ahmadi. (2004) Conversion of methane to methanol in an ac dielectric barrier discharge. *Plasma Sources Sci. Technol. 13(4),* 707.

[22] A.A.Khassin, B. L. Pietruszka, M. Heintze, V.N. Parmon. (2004) Methane oxidation in a dielectric barrier discharge. The impact of discharge power and discharge gap filling. *React. Kinet. Catal. Lett. 82(1)*, pp111-119.

[23] H. Matsumoto, S. Tanabe, K. Okitsu, Y. Hayashi, S. L. Suib. (2001) Selective Oxidation of Methane to Methanol and Formaldehyde with Nitrous Oxide in a Dielectric-Barrier Discharge− *Plasma Reactor. J. Phys. Chem. A. 105*(21), pp5304-5308.

[24] A. Ağıral, T.Nozaki, M. Nakase, S. Yuzawa, K. Okazaki, J.H. Gardeniers. (2011) Gas-to-liquids process using multi-phase flow, non-thermal plasma microreactor. *Chem. Eng. J. 167(2),* pp560-566.

[25] T.Tsuchiya, S. Iizuka. (2013) Conversion of methane to methanol by a low-pressure steam plasma. *J. Environ. Eng. Technol. 2.* pp35-39.

[26] W. Maqbool, E.S. Lee. (2014) Syngas Production Process Development and Economic Evaluation for Gas-to-Liquid Applications. *Chem. Eng. Technol. 37(6),* pp995-1001.

[27] L.C. Martins das Neves, A. Converti, T.C. Vessoni Penna. (2009) Biogas production: new trends for alternative energy sources in rural and urban zones. *Chem. Eng. Technol. 32(8),* pp1147-1153.

[28] P.M. Cox, R.A. Betts, C.D.Jones, S.A. Spall, I. J. Totterdell. (2000) Acceleration of global warming due to carbon-cycle feedbacks in a coupled climate model. *Nature. 408(6809),* pp184-187.

[29] T. Nozaki, A. Hattori, K. Okazaki, K. (2004) Partial oxidation of methane using a microscale non-equilibrium plasma reactor. *Catal. Today. 98.* pp607-616

[30] T. Nozaki, S. Kado, A.Hattori, K. Okazaki, N. Muto. (2004) Micro-plasma technology direct methane to methanol in extremely confined environment. *Stud. Surf. Sci. Catal. 147.* pp 505-510

[31] T. Nozaki, V. Goujard, S. Yuzawa, S. Moriyama, A. Agiral, K. Okazaki. (2011) Selective conversion of methane to synthetic fuels using dielectric barrier discharge contacting liquid film*, J. Phys. D: Appl. Phys. 44* pp 274010-274016

[32] V. Havran, M.P. Dudukovic, C.S. Lo. (2011) Conversion of methane and carbon dioxide to higher value products. *Ind. Eng. Chem. Res. 50(12).* pp7089-7100.

[33] V. Goujard, J.M. Tatibouët, C. Batiot-Dupeyrat. (2011) Carbon dioxide reforming of methane using a dielectric barrier discharge reactor: effect of helium dilution and kinetic model. *Plasma Chem. Plasma Process. 31(2).* pp 315-325.

[34] A. Indarto, J.W. Choi, H. Lee, H.K. Song. (2006) Effect of additive gases on methane conversion using gliding arc discharge. *Energy. 31(14).* pp2986-2995.

[35] J.G. Wang, C.J. Liu, B. Eliassion. (2004) Density functional theory study of synthesis of oxygenates and higher hydrocarbons from methane and carbon dioxide using cold plasmas. *Energy Fuels. 18(1).* pp148-153

[36] N. Seyed-Matin, A.H. Jalili, M.H. Jenab, S.M. Zekordi, A. Afzali, C. Rasouli, A. Zamaniyan. (2010*).* DC-Pulsed Plasma for Dry Reforming of Methane to Synthesis Gas *Plasma Chem. Plasma Process. 30.* pp. 333-347

[37] S. L. Brock, M. Marquez, S. Suib, Y. Hayashi, H. Matsumoto. (1998). Plasma decomposition of CO_2 in the presence of metal catalysts. *J. Catal.* 180, pp225-233

[38] K. Zhang, U. Kogelschatz, B. Eliasson. (2001) Conversion of greenhouse gases to synthesis gas and higher hydrocarbons. *Energy and Fuels. 14*, pp398-402,

[39] Q. Wang, B.H. Yan, Y. Jin, Y. Cheng. (2009) Investigation of dry reforming of methane in a dielectric barrier discharge reactor. *Plasma Chem. Plasma process.* 29(3), pp217-2228

[40] L. Fouad, S. Elhazek. (1995) Effect of humidity on positive corona discharge in a three electrode system, *J. Electrost.* pp21-30

[41] R. Ono, T. Oda. (2002) Measurement of hydroxyl radicals in pulsed corona discharge. *J. Electrost. 55*, pp333-342.

[42] D.W. Larkin, L. L. Lobban, R.G. Mallinson. (2001) The direct partial oxidation of methane to organic oxygenates using a dielectric barrier discharge reactor as a catalytic reactor analog. *Catal. Today. 71* pp199-210

[43] Z. Falkenstein, J.J. Coogan. (1997) Microdischarge behaviour in the silent discharge of nitrogen-oxygen and water-air mixtures, *J. Phys. Appl. Phys.* 30. p817.

[44] G.A.Olah, A. Goeppert, M; Czaun, M., G.S. Prakash. (2012) Bi-reforming of methane from any source with steam and carbon dioxide exclusively to metgas (CO–$2H_2$) for methanol and hydrocarbon synthesis. *J. Am. Chem. Soc. 135*, pp648-650.

[45] C.J.. Liu, G.H.. Xu, T. Wang, (1999) Non-thermal plasma approaches in CO_2 utilization*, Fuel Processing Technology, 58*, pp119–134

[46] M. Sugasawa, T. Terasawa, S. Futamura. (2010) Additive Effect of Water on the Decomposition of VOCs in Nonthermal Plasma, *IEEE trans. Ind.* Appl. 46, pp1692-1698

[47] S. Lovascio, N. Blin-Simiand, L. Magne, F. Jorand, S. Pasquiers. (2015) Experimental Study and Kinetic Modeling for Ethanol Treatment by Air Dielectric Barrier Discharges, *Plasma Chemistry and Plasma Processing.* 35, pp279–301

[48] S.P. Bugaev, A.V. Kozyrev, V.A. Kuvshinov, N.S. Sochugov, P.A. Khryapov. (1998) Plasma-Chemical Conversion of Lower Alkanes with Stimulated Condensation of Incomplete Oxidation Products. *Plasma Chem. and Plasma Process. 35.* pp 279–301

John Freddy Gelves Diaz. He received the Ph.D. degree in engineering from the National University of Colombia (Medellín) in 2017. He is currently Professor at the Libre University of Colombia. His current research interests include the selective catalytic reduction of NOx, the synthesis of oxygenated products from methane using non-thermal plasmas, applied mineralogy and ceramic materials. He has authored or coauthored 11 published works.

Ludovic Dorkis (G. Sierra) Professor at the **National** University of Colombia. He received the Ph.D. degree in catalysis using perovskites from the University of Poitiers, Poitiers, France, in 2007. He has authored or coauthored 28 published works (h-index: 11). He current research in areas as the catalytic carbon dioxide reforming of methane, Carbon Nanotubes production, characterization and applications, geo-catalysis, and nano-material and composed materials.

Elodie Fourré is a CNRS researcher at the university of Poitiers. She has received her PhD degree in Surface Science and Catalysis Studies of the Structure and Reactivity of Model Catalysts at the university of Cardiff, Wales, UK in 2006. She has authored or coauthored 15 publications (h-index 10). Her scientific project focuses on the understanding of the complex interactions between the species generated by a non thermal plasma discharge and the surface of a material, applied to VOC elimination and biopolymer functionalization and depolymerization.

Catherine Batiot-Dupeyrat, Professor at the University of Poitiers. She received the Ph.D. degree in synthesis of substitute for CFCs from the University of Poitiers, Poitiers, France, in 1994. She has authored or coauthored 57 published works (h-index: 21). Her current research interests include the catalytic carbon dioxide reforming of methane, the reforming of methane using non-thermal plasmas, and the VOC removal by photocatalysis coupled with non-thermal plasmas.