Synthesis of oxygenated compounds from methane, carbon dioxide and water in liquid phase using a plasma-catalytic system

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Abstract. Direct synthesis of methanol and other oxygenated compounds (ethanol, propanol, acetaldehyde, formic acid, acetic acid and propanoic acid) was carried out through the partial oxidation of methane process using carbon dioxide (greenhouse gas) and water in liquid phase (water has only been used in the form of steam). The activation process was carried out with dielectric barrier discharge plasma (sinusoidal power) and in the presence of a catalyst. A Colombian natural zeolite, glass wool and a material composed of magnesium oxide and alumina were used in this scientific investigation as catalysts. Tests in the presence/absence of catalyst, presence/absence of liquid water and combinations of the previous tests were carried out in order to establish which conditions allow to obtain the highest conversion of reagents and selectivity to oxygenated compounds. It was evidenced that the glass wool allows to obtain the highest levels of reagent conversion, followed by the magnesium catalyst and finally the natural zeolite. Regarding selectivity, the natural zeolite showed to be efficient for the obtaining of oxygenated compounds. It was also established that the presence of liquid water in the reactor decreases the conversion of the reactants, but favors the formation of carbon monoxide, hydrogen and especially oxygenated compounds.

1. Introduction
The direct synthesis of methanol and other oxygenates (methanol is one of the main chemical intermediaries worldwide and its production has doubled in the last 20 years) has attracted the attention of researchers for a long time [1,2]. Despite the efforts, the traditional two-stage process (obtaining the synthesis gas and its subsequent reaction in a new catalytic system it involves long manufacturing times and large money investments) is still the most viable route to produce methanol [1,2].

Activation by non-thermal plasma has emerged as a new alternative that could compete with the traditional process [3,4]. The results evidenced in the literature show that this route allows a range of oxygenated compounds to be obtained directly, from the partial oxidation of methane (CH₄) with...
reagents such as oxygen, nitrogen oxides, water and carbon dioxide (CO₂) [3-6]. In the latter case, the reaction is of greater importance since it would be giving applicability to two of the gases that contribute significantly to the greenhouse effect [1].

A new alternative that has been imposed in the academic community that works with non-thermal plasma, is to introduce a catalyst to the reaction system, analogous to what happens with thermal or traditional activation processes. Even so, the reported results show that there is no clear correlation for the activity of the catalyst between the two activation systems [2,7-9].

On the other hand, despite the fact that the use of plasma-catalyst systems for the activation of CH₄ and CO₂ has become popular in the literature, most of them have focused on the generation of synthesis gas (syngas) or value-added hydrocarbons like ethylene [7,8]. Only a few works have been directed to the use of catalysts to obtain oxygenated compounds [9].

The aim of the present work was to explore new ways to increase the selectivity towards oxygenated compounds from the activation by plasma of CH₄ and CO₂. In this case, the use of a plasma-catalyst reaction system (using three types of materials) was proposed. The system was fed with gaseous reactants and water in liquid phase, evidencing the effects on the discharge power of the system, the conversion of reactants and especially the selectivity of the reaction towards oxygenated compounds.

2. Materials and methods

2.1. Materials

The gas feed to the reactor was adjusted to 40 ml/min (using MFC Bronkhorst Brand). Helium was used as a diluent (30 ml/min) since it has been evidenced in the literature that its presence favors the activation of reagents in the plasma due to the Penning ionization effect [10]. The flow gas of methane and carbon dioxide were adjusted at 7 ml/min and 3 ml/min respectively, since this relationship favors the formation of oxygenates, according to a previous published study [10]. Ultra pure water was used in the reaction, using a flow of 0.02 ml/min through a peristaltic pump (Metrohm, model 765). The reactor used was made in quartz (internal diameter: 4 mm; External diameter: 6 mm), inside it was placed a stainless-steel electrode (1.0 mm) connected to the high voltage generation system. A copper tape (50 mm long, 25 mm wide and 25 μm thick, advance tapes - AT526) was used to cover a region of the quartz tube, to act as a ground electrode. The essential characteristics of the catalysts used are: the natural zeolite (NZ) used is originally from Colombia, was characterized in a previous study [11], highlighting that this material contains 70% of zeolite type heulandite, 25% of plagioclase (feldspars) and 5% mica type celadonite. The zeolite stands out for its lamellar morphology, with a high predominance of the plane (0 2 0). Chemically, zeolite is rich in calcium and potassium as exchange cations, the silicon / aluminum ratio is around 4.0 and has an iron content of 4.5% expressed as Fe₂O₃, which is characterized by being in an oxidation state (Fe³⁺) according to results of Mössbauer spectroscopy performed. It was used in the reaction, 612 mg to fill the reaction volume using a grain size between 250 μm and 1000 μm; a traditional catalyst of magnesium (7% MgO/Al₂O₃) sasol germany GmbH) named (MgO) was also used in this study (378 mg), the material presented the same granulometry conditions as the natural zeolite, however the latter was previously calcined at 500 °C for 2 hours; The third and last material was glass wool (across organics), the same one used to support catalysts in laboratory tests, 357 mg were used to fill the reaction volume.

The reaction was carried out at room temperature and at atmospheric pressure. The total reaction time was adjusted to one hour. A cold trap was used to condensate the liquid products formed during the reaction and later analyzed by liquid chromatography (LC) (synergi 4 μm Hydro-RP 80 Å, phenomenex, using 0.5 g.L⁻¹ H₂SO₄ as solution of elution for analysis of HCOOH, CH₃COOH and CH₃(CH₂)COOH) and by gas chromatography (GC) (Varian 3900- capillary columns Agilent CP-wax 58FFAP CB for analysis of CH₃OH, C₂H₅OH, CH₃CH₂CH₂OH, CH₃CH₂CH₂CH₂OH and CH₃CHO). This last technique was also used for the continuous monitoring of the reaction (conversion of reagents) and to analyze the gas phase products formed (Varian 4900, using two capillary columns:
poraplot Q and Molsieve 5 Å for the monitoring of CH$_4$, CO$_2$, CO, O$_2$, C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$, and H$_2$). A Total organic carbon analyzer (TOC-V CSH, Shimadzu brand) was used to determine the amount of organic compounds in the condensate container once the reaction was finished.

The conversion and selectivity are defined by the following Equation (1) and Equation (2):

\[
C = \frac{(100 \cdot mc)}{mf} \quad (1)
\]

\[
S = \frac{100 \cdot n+m(C_{n}H_{y}O_{z})}{mc(CH_{4})+mc(CO_{2})} \quad (2)
\]

Where, $C =$ conversión percentage of CH$_4$ or CO$_2$ (%), $S =$ selectivity to oxygenated products C$_{n}$H$_{y}$O$_{z}$ (%), $mc =$ moles converted of CH$_4$ or CO$_2$, $mf =$ moles in the feed of CH$_4$ or CO$_2$, $n =$ moles of carbon present in each oxygenated phase obtained C$_{n}$H$_{y}$O$_{z}$.

A sinusoidal signal was used to carry out the reaction in the plasma reactor (TG1010A Aim-TTi, Thurlby Thandar instruments brand). The power discharge was initially fixed at 6 watts, keeping the frequency constant at 5 kHz (voltage was between 16 kV and 18 kV). The discharge power, calculated through the figure of Lissajous, (using high voltage probes PMK, model PHV4-2757, connected to an oscilloscope, waveRunner 62 Xi, Lecroy). This type of discharge was used because it allows to carry out the chemical reaction at atmospheric pressure, it is easy to elaborate and it is well documented in the literature [5], especially for sinusoidal type signals. The essential characteristics of the coaxial dielectric barrier discharge reactor are shown in Figure 1.

![Figure 1. Schematic of DBD plasma reactor.](image)

3. Results and discussion

Preliminary results (not shown here), allowed to establish that the conversion of the reagents remained constant during the reaction time independent of the presence of liquid water feeding the system. Likewise, it was evidenced that the addition of liquid water to the reactor allows to lower the external temperature of the reactor, going from 50 °C to about 46 °C for all reactions (using an infrared pyrometer). Regarding the discharge power (experimental conditions: CH$_4$/CO$_2$ = 2.3, gas flow: 40 ml/min (75% of He), frequency 5 kHz), when adding liquid water to the system, the power was increased according to the following order: natural zeolite (6.8 watts), MgO catalyst (7.0 watts), only plasma (7.5 watts) and glass wool (7.8 watts). Although there are many aspects that could explain this behavior, the formation of ions and radicals produced by the decomposition of water, would be responsible for increasing the discharge current and therefore the power, according to the data obtained from the Lissajous methodology [10]. From the power data obtained, it is interesting to highlight the values of the natural zeolite, since they are those that offer the lowest increases in the
discharge power. This behavior could be associated to the fact that this class of materials naturally contains structural water, which modifies to some extent the power of discharge established at the beginning of the test.

The conversion results of the gaseous reactants are presented in Table 1. It is evident that the presence of solid phases (catalyst) inside the reaction volume maintains or improves the conversion of CH$_4$ and CO$_2$ when the reaction is carried out in absence of liquid water. This behavior could be explained from several points of view. The first is that the presence of solid phase increases the difficulty for the diffusion of the reagents, which translates into a longer exposure time of the reagent molecules with the plasma (contact with electrons and with excited helium species in accordance with Penning effect), however it is appreciated that for the case of natural zeolite, this proposition is not met (although there is a greater mass of catalyst), which leads to think that there are other factors that may influence the result. The dielectric constant (k) has also been included within the variables that could explain the increases in the conversion of CH$_4$ and CO$_2$ [8], in this case it has that the alumina can have a value of k between 9 and 10 [12], glass wool between 6 and 8 [13] and for zeolites (Si/Al ratio <10, powder, as in the case of the heulandite phase) is between 2 and 4 [14]. These data allow a better explanation of the results obtained.

| Table 1. Conversion results. |
|-----------------------------|
| Test$^a$ | % conversion |
|        | CH$_4$ | CO$_2$ |
| P-0.00H$_2$O | 16.85 | 10.95 |
| P-0.02 H$_2$O | 13.80 | 6.40  |
| NZ-P-0.00 H$_2$O | 15.98 | 10.62 |
| NZ-P -0.02 H$_2$O | 11.92 | 5.15  |
| GW-P-0.00 H$_2$O | 22.83 | 15.81 |
| GW-P-0.02 H$_2$O | 15.44 | 6.74  |
| MgO-P-0.00 H$_2$O | 19.12 | 12.15 |
| MgO-P-0.02 H$_2$O | 17.38 | 6.54  |

$^a$ Experimental conditions: CH$_4$/CO$_2$ = 2.3, gas flow: 40.0 ml/min (75% of He), P = 6W (without water).

On the other hand, it has the conversion results in the presence of water, in this regard it is observed that the presence of it, reduces the conversion of the reactants, but with a more significant effect for CO$_2$. The explanation to this behavior could be associated to that a part of the energy of the system, is used for the hydrolysis of the water [10] according to the Equation (3) to Equation (5) and because the CO$_2$ can be better solubilized in the water [15], reducing the direct contact of this molecule with the plasma (P).

$$\text{H}_2\text{O} + e^- \rightarrow \text{OH}^- + \text{H}^+ \quad (3)$$
$$\text{H}_2\text{O} + e^- \rightarrow 2\text{H}^- + e^- \quad (4)$$
$$\text{H}_2\text{O} + e^- \rightarrow \text{O}^- + \text{H}_2 \quad (5)$$

The results of gas phase selectivity are presented in Table 2, it is evident as major products to hydrogen (H$_2$) and carbon monoxide (CO), which can be formed by the three reagents according to the Equation (5) to Equation (15) [16].

$$\text{CH}_4 + e^- \rightarrow \text{CH}_3 + \text{H}^- + e^- \quad (6)$$
$$2\text{H}^- \rightarrow \text{H}_2 \quad (7)$$
$$\text{CH}_4 + e^- \rightarrow \text{CH}_3 + \text{H}_2 + e^- \quad (8)$$
$$\text{CO}_2 + e^- \rightarrow \text{CO} + \text{O}^- \quad (9)$$
$$\text{CO}_2 + e^- \rightarrow \text{CO} + \text{O} + e^- \quad (10)$$
$$\text{CH}_3 + e^- \rightarrow \text{CH}_2 + \text{H}^- + e^- \quad (11)$$
These authors like that of Kim and his team [17] who have discussed the role of zeolites as a catalyst in a plasma compounds is noteworthy. Although there is not much literature on the subject, there are some works Regarding the role played by the catalysts, the role of natural zeolite for obtaining oxygenated compounds is noteworthy. These identified solids were only visible on the reactor wall and on the high voltage electrode when the reaction was carried out in the absence of water. The magnesium catalyst showed the least increase in selectivity towards CO, a fact that has been associated with the formation of solid phase that was not converted even in the presence of water according to the analysis of Table 4.

The minority phases identified were some low molecular weight hydrocarbons that could be formed by CH₃ and CH₂ species as in the case of the Equation (15) [16]. The presence of hydrogen was not quantified for the reactions in the presence of water, since it was evidenced that part of the hydrogen obtained comes from the decomposition of the same according to the Equation (3) to Equation (5). In the same way it is observed in Table 3 that due to the presence of water in the reactor the selectivity towards carbon monoxide increases. The explanation for this behavior could be associated with the oxidation of the solid phases formed as a result of Equation (9) to Equation (14).

These identified solids were only visible on the reactor wall and on the high voltage electrode when the reaction was carried out in the absence of water. The magnesium catalyst showed the least increase in selectivity to CO, a fact that has been associated with the formation of solid phase that was not converted even in the presence of water according to the analysis of Table 4.

| Test         | H₂      | CO    | C₂H₅ | C₃H₄ | C₃H₂ | C₂H₆ |
|--------------|---------|-------|------|------|------|------|
| P-0.00 H₂O  | 40.45   | 27.47 | 0.57 | 0.00 | 0.11 | 0.00 |
| P-0.02 H₂O  | ---     | 37.51 | 0.74 | 0.00 | 0.00 | 0.00 |
| NZ-P-0.00 H₂O | 31.93  | 28.67 | 0.55 | 0.00 | 0.16 | 0.00 |
| NZ-P-0.02 H₂O | ---    | 51.49 | 0.37 | 0.00 | 0.10 | 0.00 |
| GW-P-0.00 H₂O | 36.52  | 36.13 | 0.56 | 0.07 | 0.42 | 0.00 |
| GW-P-0.02 H₂O | ---    | 67.49 | 0.38 | 0.00 | 0.09 | 0.00 |
| MgO-P-0.00 H₂O | 28.80  | 30.17 | 0.39 | 0.02 | 0.31 | 0.00 |
| MgO-P-0.02 H₂O | ---    | 36.73 | 0.33 | 0.00 | 0.09 | 0.00 |

Experimental conditions: CH₂/CO₂ = 2.3, gas flow: 40.0 ml/min (75% of He), P = 6 W (without water).

The results of selectivity in the liquid phase are presented in the Table 3 and Table 4, showing the formation of oxygenated compounds such as methanol, ethanol and formic acid, according to the Equation (16) to Equation (21) [16]:

\[
\begin{align*}
\text{CH}_3 + \text{OH} & \rightarrow \text{CH}_3\text{OH} \\
\text{H}^+ + \text{C}_2\text{H}_5 & \rightarrow \text{C}_2\text{H}_4 + \text{H}_2 \\
\text{C}_2\text{H}_5 + \text{OH} & \rightarrow \text{C}_2\text{H}_4\text{OH} \\
\text{CO}_2 + \text{e}^- & \rightarrow \text{CO}_2^- \\
\text{CO}_2 + \text{H} & \rightarrow \text{COOH}^- \\
\text{COOH}^- + \text{H} & \rightarrow \text{HCOOH} + \text{e}^- 
\end{align*}
\]

Table 3 shows the role played by the presence of liquid water in the increase in selectivity towards oxygenated compounds for all the reactions carried out. Processes of hydrolysis to form OH + H species that favor the synthesis of alcohols and acids and a possible protective effect of liquid water to avoid the exposure of oxygenate molecules to plasma have been proposed as an explanation for this result [10]. In all cases it is appreciated that methanol is the phase of highest production among oxygenated compounds, a fact that is of great importance due to the role played by this compound as a chemical intermediate, its commercial value and the growing demand evidenced in the last decade [2].

Regarding the role played by the catalysts, the role of natural zeolite for obtaining oxygenated compounds is noteworthy. Although there is not much literature on the subject, there are some works like that of Kim and his team [17] who have discussed the role of zeolites as a catalyst in a plasma reactor. These authors were able to identify that when using different types of exchange cations (Fe,
Ag), the lower Si/Al ratios allowed higher deposits of oxygen species at the surface level (Equation (4), Equation (5), Equation (9) and Equation (10)) favoring the oxidation of organic species. In the case of natural zeolite something similar happens, since this material has a low Si/Al ratio (~4) and also has a significant concentration of iron, allowing the formation of deposits of oxygen species, which would favor the synthesis of oxygenated compounds. In the case of the magnesium catalyst, it was considered that this material could have generated another type of phases in the liquid state (oxygenated compounds and/or hydrocarbons) that were not quantified by gas chromatography, therefore a test was carried out in a total organic compounds analyzer (TOC) in order to establish the actual amount of dissolved carbon in the collected liquid fractions. With the results obtained by GC, LC and TOC, the carbon balance presented in Table 4 was established.

| Test       | M  | E  | P  | B  | Ac | FA | AA  | PA  | Total |
|------------|----|----|----|----|----|----|-----|-----|-------|
| P-0.00H₂O  | 0.01 | 0.01 | 0.01 | 0.02 | 0.02 | NA | NA  | NA  | 0.07  |
| P-0.02H₂O  | 2.49 | 0.63 | 0.28 | 0.07 | 0.06 | 0.03 | 0.00 | 0.00 | 3.56  |
| NZ-P-0.00H₂O | 0.03 | 0.05 | 0.02 | 0.01 | 0.00 | NA | NA | NA | 0.11  |
| NZ-P-0.02H₂O | 5.91 | 1.04 | 0.27 | 0.04 | 0.32 | 0.53 | 0.77 | 0.93 | 9.81  |
| GW-P-0.00H₂O | 0.58 | 0.22 | 0.12 | 0.04 | 0.00 | NA | NA | NA | 0.96  |
| GW-P-0.02H₂O | 5.00 | 0.92 | 0.29 | 0.05 | 0.33 | 0.00 | 0.89 | 1.69 | 9.17  |
| MgO-P-0.00H₂O | 0.02 | 0.01 | 0.00 | 0.00 | 0.00 | NA | NA | NA | 0.04  |
| MgO-P-0.02H₂O | 3.20 | 0.55 | 0.23 | 0.05 | 0.11 | 0.00 | 0.00 | 0.00 | 4.13  |

NA: Not available; M: Methanol; E: Ethanol; P: Propanol; B: Butanol; Ac: acetaldehyde; FA: Formic acid; AA: Acetic acid; PA: Propanoic acid. Experimental conditions: CH₄/CO₂ = 2.3, gas flow: 40.0 ml/min (75% of He), P = 6 W (without water).

| Test       | Fraction in gas phase (%w/w) | Fraction in liquid phase by GC/LC (%w/w) | Fracción in liquid phase by TOC (%w/w) | CB (1+2) (%w/w) | CB (1+3) (%w/w) |
|------------|-------------------------------|------------------------------------------|----------------------------------------|-----------------|-----------------|
| P-0.02 H₂O | 38.75                         | 4.55                                     | 12.65                                  | 43.29           | 51.40           |
| NZ-P-0.02 H₂O | 52.31                      | 8.90                                     | 23.05                                  | 61.21           | 75.35           |
| GW-P-0.02 H₂O | 67.04                      | 9.18                                     | 29.46                                  | 76.22           | 96.50           |
| MgO-P-0.02 H₂O | 37.56                      | 4.14                                     | 11.96                                  | 41.70           | 49.52           |

As can be seen in Table 4, the concentration of carbon dissolved in the liquid medium obtained by TOC is much higher than that analyzed by GC/LC, that is, that there are effectively other phases that were not identified. Even so, in the case of the magnesium catalyst, it is evident that this material does not favor the formation of compounds in liquid phase, even the concentration obtained from carbon by TOC is lower than that of the reaction with only plasma. On the other hand, when observing the carbon balance calculated with the TOC data it can be observed that the reaction with glass wool is what allows to obtain the best explanation about the reacted carbon, followed by the zeolite and in the last place the catalyst of magnesium, which leads to suppose that the remaining carbon could be in solid phase on the surface of the catalyst.

4. Conclusion

It was shown that it is possible to maintain the activity of the plasma in the reaction volume, despite the existence of catalyst and liquid water flow. The catalysts of glass wool and natural zeolite proved to be the most efficient for obtaining oxygenated compounds. The addition of liquid water in the plasma-catalyst reaction system allowed to increase the synthesis of oxygenated compounds in comparison with the data obtained by reaction with only plasma. Alcohols and carboxylic acids of low molecular weight were evidenced within the oxygenated products analyzed. Methanol, ethanol, formic acid and acetic acid were the main oxygenates evidenced.
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