Fuel production from waste CO_2 using renewable energies

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ABSTRACT

An experimental study aiming at reusing CO_2 and implementing a validated laboratory technology based on a prototype methanation reactor (ProGeo) producing carbon neutral methane through the chemical conversion of CO_2 waste flue gases using renewable energy in a circular economy scheme, is presented. ProGeo is able to produce a CH_4 flux of 1 Nm^3/h, using the Sabatier reaction at high pressure (1.5–3 bar) and temperature (200–400 °C) with a solid phase catalyst. Furthermore, the investigation of a new methanation pathway by exploring mechanisms involving a plasma generation by electrical discharges on $CO_2 + H_2$ gas mixtures has been undertaken. Obtained results indicate the formation of hydrocarbons as methane, formic acid and/or dimethyl ether as well as small amounts of HCO^+, H_2CO^+, H_3CO^+, HCO_2^+ ions. These ionic species together with CO^+ and O^+ ions, having a very high kinetic energy content, should increase the chemical reactivity of generated plasmas playing a pivotal role in the plasma-assisted CO_2 conversion on CH_4 fuel. Further experimental work is in progress to optimize the experimental conditions of the CO_2 methanation process via alternative microscopic mechanisms, using plasma assisted catalyzed reactions that are of great importance in new emerging catalysts development in chemical engineering.

1. Introduction

Nowadays one of the critical environmental problems in a global scale is the production of energy using technological methodologies reducing greenhouse gas emission and employing renewable resources. It is well known that the widespread and continued use of fossil fuels has made carbon dioxide the main greenhouse gas: it accounts for ∼60% of the total green gas emission with its estimated annual emission of about 35 $GtCO_2$ [1]. In particular, in the last investigated 2008–2017 decade, the fossil CO_2 emissions resulted of 9.4 ± 0.5 GtC yr^{-1} with a growth of about 1.6% in 2017 (9.9 ± 0.5 GtC yr^{-1}) and an averaged global atmospheric CO_2 concentration of 405.0 ± 0.1 ppm [1], being a value of about 45% higher than the concentration at the beginning of the industrial revolution, started in the second half of the nineteenth century with the invention of the steam engine. Currently, China, USA, UE and India are the Countries that contribute most to the global annual emission of CO_2 with about 27%, 15%, 10% and 7%, respectively. Regrettably, preliminary data for 2018, attest a further growth of about 2.7% in such emissions in atmosphere [1] and this projection is a source of great concern for the future of our Planet. In has to be noted that on October 2018 the Intergovernmental Panel on Climate Change (IPCC), the world's leading scientific authority on climate change, presented a special report, stating that nowadays the consequent global warming of the planet is attested on 1 °C [2].

Following the current rate of accumulation of greenhouse gases in the atmosphere, the Earth would reach 1.5 °C of heating between 2030 and 2052, dangerously approaching the value of 2 °C for which IPCC foresees catastrophic effects such as devastating floods, melting of polar ice caps, rising seas level. After the Paris climate conference (COP21) on December 2015, 195 countries adopted the first universal and legally binding global climate agreement according to which it is necessary to maintain the average global temperature increase below 2 °C compared to pre-industrial levels, aiming to limit such increase to 1.5 °C, as this would significantly reduce the risks and impacts of climate change. This statement of work requires to develop reliable strategies for a rapid reductions of greenhouse gases emissions (mainly CO_2) in accordance with the most advanced scientific and technological available solutions. In this context, the conversion of CO_2 into other useful chemical compounds has become an important research field in the last decades that is constantly increasing as demonstrated by the huge number of papers published every year on such a topic: the reader interested in having a broad overview in this field of research can refer to some recent review articles (see for example Refs. [3–5] and references therein). Furthermore, it has to be noted that carbon deposition responsible of the catalyst deactivation is still one of the main problems to be overcome for industrial applications of the CO_2/CH_4 reaction (see for example Refs. [6,7] and references therein).

In general, to date, the main strategies employed are based on

electro- and photo-chemical methods, biological and catalytic processes where, in the latter case, plasma assisted CO_2 conversion is a technology increasingly widely investigated. In this way it is possible to convert CO_2 in valuable and useful chemical compounds such as alcohols, carboxylic acids, urea, polymeric materials, etc. (see Ref. [8] and references therein). For such a purpose, Cu-based catalyst are commonly used for CO_2 to methanol convertion at high pressure and temperature ($\sim$ 40-50 bar and $\sim$ 240–260 °C, respectively) [9–12]. Recent studies shown that by adding small amounts of Ga and Pd an improvement of the Cu/Zn-based catalysts can be obtained [13,14], but the CH_3OH experimental yield is still below 30%, indicating that the method is not yet convenient from an economic point of view.

Recently, our research group was involved in a research project named "Free-Methane" aimed to develop and characterize the optimal operating working conditions of a methanation reactor ProGeo having a 20 kW output power. This project combines the skills of various researchers belonging to six different public and private Italian institutions: the "Department of Civil and Environmental Engineering" and "Department of Chemistry, Biology and Biotechnologies" of the University of Perugia (Perugia, Italy); the ENEA C.R. (Frascati, Italy); the "PLC System S.r.l." (Acerra, Italy); the "FASAR ELETTRONICA S.r.l." (Senigallia, Italy); the "VIS MEDICATRIX NATURAE S.r.l." (Marradi, Italy). ProGeo 20 kW is a prototype reactor for the CO_2 conversion to CH_4 using the well known Sabatier reaction and a solid phase Ni-based catalyst (see Section 3.1). The hydrogenation of carbon dioxide producing methane towards the Sabatier reaction has been recently performed by a hybrid plasma-catalytic device [15] and the CO_2 dissociation using water [16,17], as well as its reduction by H_2, started to be widely studied [18–20].

The main goal of "Free-Methane" project is to use either low cost or renewable energy to reuse waste CO_2, generated by various industrial activities, as for example the ones produced in the ratio of 1.9 kg per liter from grapes fermentation of Marsala wine from Sicily (Italy), and those from fermentation of vegetable exhausted material supplied by the pharmaceutical drugs and herbal industry "VIS MEDICATRIX NATURAE S.r.l." (Marradi, Italy), to create methane in a circular economy scheme. To this end we have also undertaken the investigation of a new methanation pathway aimed at avoiding or reducing the use of the solid catalyst, by exploring mechanisms involving a plasma generation by electrical discharges or by vacuum ultraviolet (VUV) photons on $CO_2 + H_2$ gas mixtures [21–23]. The experimental determinations performed using a microwave discharge beam source developed in our laboratory [21,24,25], gave useful indications on how to proceed to develop alternative solutions to the present Ni catalysed Progeo apparatus by resorting to a gas-phase-only process for the reduction of CO_2 to CH_4. These results were very interesting indicating that the chemical reactivity of plasmas containing CO_2 should be strongly increased because the presence of CO^+ and O^+ ions having a very high kinetic energy [21].

In the present paper we report on very recent progresses made in our laboratory along this direction. In particular, we generated and characterized different microwave discharge plasmas containing CO_2/H_2 mixtures with a 1:3 and 1:5 relative composition. The obtained data indicate the formation of hydrocarbons as methane, formic acid and/or dimethyl ether as well as small amounts of HCO^+, H_2CO^+, H_3CO^+, HCO_2^+ ions. These ionic species together with CO^+ and O^+ ions, also generated in our plasmas with a very high kinetic energy content, should increase the chemical reactivity of plasmas generated by a microwave discharge in a gaseous $CO_2 + H_2$ mixtures playing a pivotal role in the plasma-assisted CO_2 conversion on CH_4 fuel that is of great interest in chemical engineering in the field of new emerging catalysts development. Finally, it should be noted that the present work does not concern the characterization of the catalyst used in the methanation reaction, since it is a commercial catalyst (see Section 2.1) already extensively tested and characterized by the manufacturer [26]. The purpose of the work is to optimize the operating conditions of the

presented reactor prototype (ProGeo 20 kW) and to identify possible alternative routes to the use of heterogeneous solid phase catalysis. For this reason, experimental data obtained using the technique of generation of microwave plasmas on CO_2/H_2 mixtures of various concentrations are presented and discussed. The obtained results are very encouraging in future applications for methanation reactions using the plasma-assisted catalysis technique. This is a motivation for future collaborations with research groups able to develop innovative methanation catalysts in order to be able to use them in the ProGeo prototype, characterizing their performance both through their direct use and through plasma-assisted catalysis.

2. Material and methods

The data here presented and discussed concern: i) the deeper experimental characterization of the operative working conditions of the prototype methanation reactor ProGeo 20 kW respect to the preliminary previous attempt [21]; ii) the production and chemical characterization of different microwave plasmas containing CO_2/H_2 mixtures at various relative compositions (1:3 and 1:5, respectively). In the latter case we used a dedicated molecular beam experimental apparatus allowing the relatively easy production of gaseous plasmas by a microwave discharge beam source. In the following two next subsections are summarized the main characteristics of either used experimental setups.

2.1. The ProGeo 20 kW methanation reactor

The prototype methanation reactor (ProGeo 20 kW) produces carbon neutral methane through the chemical conversion of CO_2 waste flue gases using renewable energies. It was designed to produce a CH_4 flux of 1 Nm³/h, using the well known Sabatier reaction (1) at moderately high pressure (1.5–3 bar) and high temperature (200–400 °C) with the use of a solid phase catalyst (nickel or ruthenium):

$$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O \quad \Delta H_{298}^0 = -165 \text{kJmol}^{-1} \qquad (1)$$
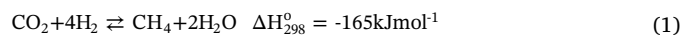
In the case of the present work, the obtained results (see next section) show a complete compatibility with the used catalyser being a commercial KATALCOJM 11-4MR produced by Johnson Matthey (UK) whose features are fully provided by the manufacturer [26]. A scheme of the reactor is shown in Fig. 1 (upper panel) where also a picture of the apparatus is reported (see Fig. 1 – lower panel).

A full detailed description of ProGeo 20 kW is already published in a recent paper [21] to which the interested reader can refer. The experimental determinations of methane yields by ProGeo, reported and discussed in the next section, have been carried out using CO_2 either by commercial bottles purchased from Air Liquide (grade of purity 99.95%) as well as carbon dioxide produced (in the ratio of 1.9 kg per liter) from grapes fermentation of Marsala wine (from Sicily, Italy), and from fermented exhausted plant material coming from extractions performed in traditional herbalist processing on officinal plants by the industry "VIS MEDICATRIX NATURAE S.r.l." of Marradi (Florence, Italy).

2.2. The microwave discharge plasma source

The plasmas containing CO_2/H_2 mixtures have been produced by a microwave discharge beam source mounted in a molecular beam apparatus differentially pumped and operating in high vacuum conditions ($\sim 10^{-7}$-10^{-8} mbar). This experimental device (see the scheme reported in Fig.2 - left panel (a)) is a prototype specially built to perform research on Penning ionization reactions [27,28] in which the production of the excited metastable species (being the autoionizing agents) can be obtained using both electron bombardment or microwave discharge plasma sources. For the purposes of the present study we used the
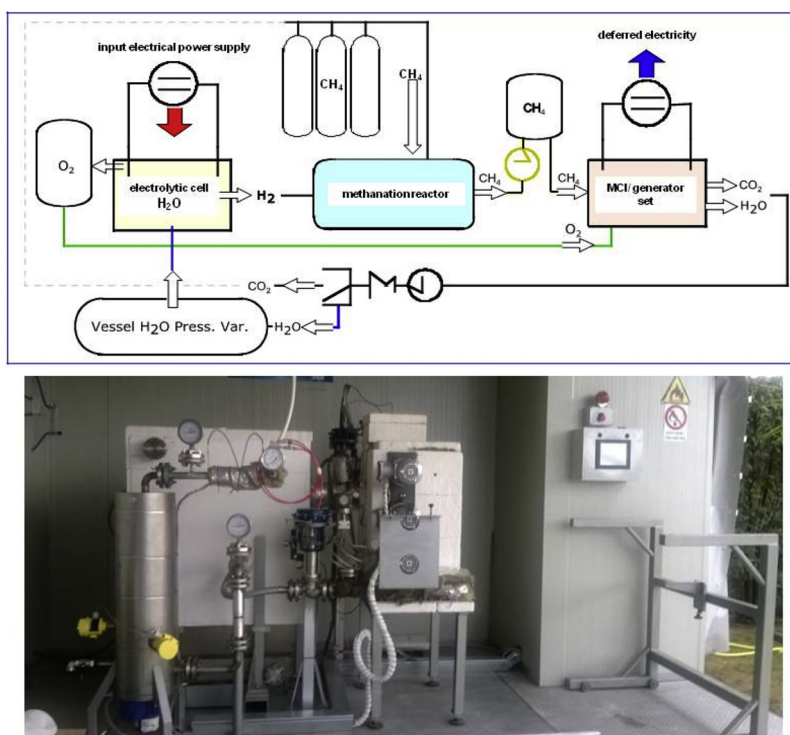
Fig. 1. The prototype methanation reactor (ProGeo 20 kW) for the hydrogenation reaction of CO_2 using the Sabatier reaction (1) (see text). Upper panel: a scheme of the set-up. Lower panel: a picture of such apparatus.

microwave discharge source operating on two different mixtures with a CO_2:H_2 ratio of 1:3 and 1:5, respectively. A scheme of our microwave discharge plasma source is reported in the right panel (b) of Fig. 2. It was widely used to produce various type of plasmas containing excited atomic and molecular species and is described in detail elsewhere [24,28]. Here, only its main features are summarized. A cylindrical quartz pipe (being transparent to the working operating frequency), of about 5 cm in length and 2 cm of diameter, is inserted in the resonant cavity (realized in brass and water cooled) operating at 2450 MHz with a working power in the range of 70–200 kW (the reflected power is

maintained lower than 5%), using a klystron and a developed electronic control unit provided by "FASAR ELETTRONICA S.r.l." (Senigallia, Italy). This plasma source generates an effusive molecular beam since the nozzle has a diameter of 1 mm.

By regulating the gas flow, the operating power of microwave discharge and the feed gas composition, we are able to vary the relative production of chemical species inside the generated plasma. In such a way our microwave discharge beam source has been widely employed during last three decades for the production of atomic and molecular excited species (in particular, metastable hydrogen [29,30] and rare gas
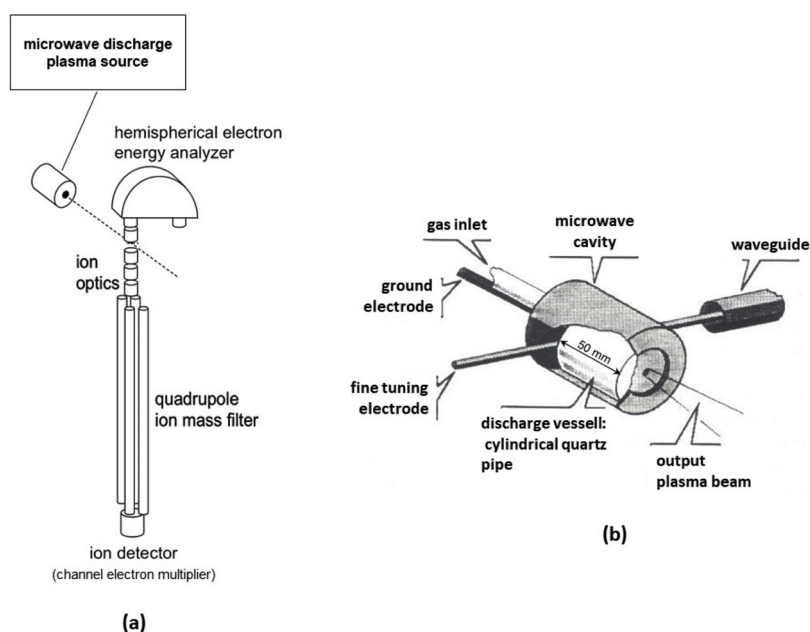
Fig. 2. Left panel (a): The molecular beam apparatus used for the generation and characterization of the investigated CO_2/H_2 plasma mixtures (see text). Right panel (b): A scheme of the used microwave discharge plasma source.

atoms [31,32]), neutral atoms (mainly H and O atoms), atomic and molecular ionic species (as for example O^+, CO^+, CO_2^{2+}) in the thermal and sub-thermal regime [33,34], by electron impact excitation, dissociation, recombination reactions and ionization processes. The typical used gas flow rates can be regulated in the range of about 10–500 ml/min, producing a plasma working pressure ranging between 1000 and 3000 Pa, with typical operating values for the presented experiments of about 1600–2200 Pa.

As mentioned above, for the chemical characterization of produced plasmas, the molecular beam apparatus generally employed in the study of Penning ionization reactions (see Fig. 2 – left panel (a)) has been used applying the same procedure as already done in previous plasmas generation experiments [21,35]. By mass spectrometry we were able to reveal the main chemical species flowing out from the plasma microwave discharge beam source working in a typical effusive regime (see Fig. 2 – right panel (b)). For such a purpose, an ion extractor device coupled with a focusing electrostatic lens system allows the injection of ionic species (produced in the plasma source) into a quadrupole mass filter which is located orthogonal to the molecular beam direction (see Fig. 2 – left panel (a)).

3. Results and discussion

In this section we present and discuss the experimental data obtained in the characterization of the optimal working conditions of: i) the methanation reactor ProGeo 20 kW; ii) the plasma source used in the attempt to convert different CO_2/H_2 mixtures into methane without the use of the solid catalyst.

3.1. The methanation reactor optimal yields by Ni-based catalyst

In order to determine the best operating conditions of the ProGeo 20 kW reactor, we measured the yields of CO_2 conversion in methane produced by reaction (1), with the use of a Ni-based solid catalyst (see Section 2.1), as a function of the molar ratio of CO_2/H_2 reagents, and of the operating temperature and total pressure inside the reactor. In the upper panel of Fig. 3 are reported the average percentage of the produced CH_4 for three different used reagent compositions (CO_2:H_2 with 1:3, 1:4 and 1:5 molar ratios, respectively) as a function of the reactor temperature.

It is clear that the best methane yield formation of 84 ± 2% is obtained at a constant total pressure of about 2 bar when the temperature is in the range of 350–450 °C, and for a 1:5 CO_2:H_2 reagent mixture molar ratio. Furthermore, a threshold temperature for the methanation process can be extracted from the experimental data obtaining a value of ~250 °C. These data are in good agreement with previous preliminary data already published where a lower temperature of optimal CH_4 yield (~83%) was estimated in the range of 300–350 °C with a 240 °C threshold temperature [21]. In addition, we performed also experimental determinations of the methanation reaction yield as a function of the total pressure for the 1:5 CO_2:H_2 reagent mixture, being the most effective obtained in Fig. 3 – upper panel. These determinations are shown in the lower panel of Fig. 3 where it is evident that the best operative conditions of the ProGeo 20 kW methanation reactor are the following: CO_2:H_2 reagent mixture 1:5; range of temperature 350–450 °C; total pressure ~2 bar; maximum yield of CH_4 production 84 ± 2%. In such conditions the carbon dioxide conversion and methane selectivity were calculated according to the following Eqs. (2) and (3), respectively:

$$CO_2 \, conversion = \frac{CO_2 \, reacted}{CO_2 \, in} \, 100 \tag{2}$$

$$CH_4 \, selectivity = \frac{CH_4 \, produced}{CO_2 \, reacted} \, 100 \tag{3}$$

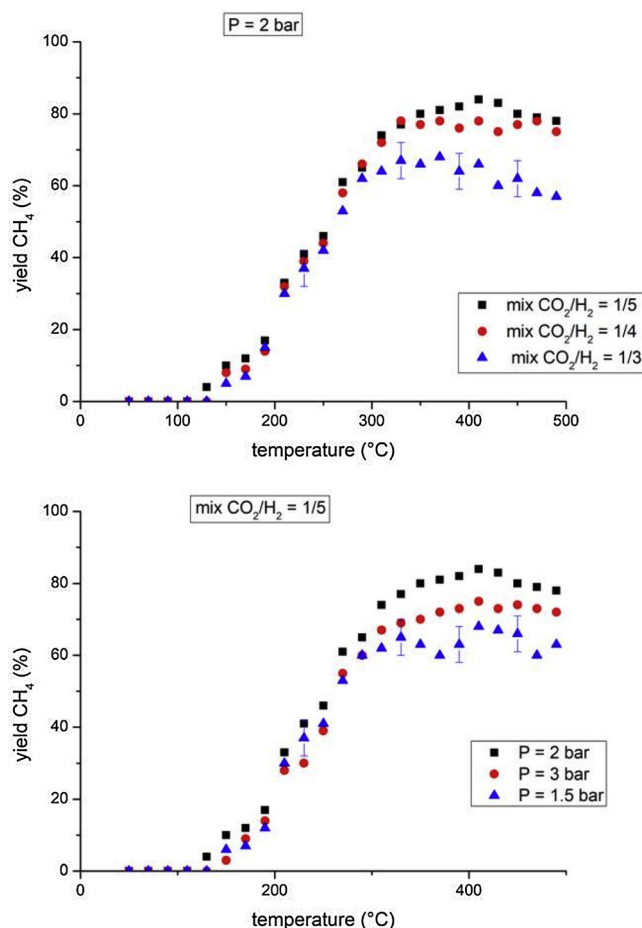determining the following values: $CO_2 \, conversion = 86.1 \pm 1.7\%$ and

Fig. 3. The yield of produced methane using the ProGeo 20 kW reactor of Fig. 1, as a function of the temperature for three different reagent CO_2/H_2 mixtures (upper panel), and as a function of the working total pressure inside the reactor for the best 1:5 CO_2:H_2 reagent mixture molar ratio (lower panel).

$CH_4 \, selectivity = 98.2 \pm 1.3\%$.

3.2. The methanation by plasma generation without solid catalyst

To explore the possibility of realizing the reaction (1) in a plasma catalytic conversion using a modified version of the ProGeo 20 kW reactor, we started our investigation attempting to perform reaction (1) without the use of the solid catalyst. For such a purpose, we explored the production of different plasmas by a microwave discharge working over CO_2:H_2 mixtures having 1:1, 1:3, and 1:5 ratio percentage composition, respectively. First of all, we measured the percentage of CO_2 dissociation, according to reactions (4) and (5) below, in microwave discharge plasma source produced with the three mentioned CO_2:H_2 different compositions.

$$CO_2 + e^- \rightarrow CO + O + e^- \tag{4}$$

$$O + O \rightarrow O_2 \tag{5}$$

These data are reported in Fig. 4 as a function of the applied microwave discharge power, and are determined using the same procedure already published in a recent paper [21] to which the reader can refer. The CO_2 dissociation percentage (%CO_2diss) was obtained by recording the CO_2^+ intensities measured with the microwave discharge off (I_{off}) and on (I_{on}) using the simple Eq. (6) below, and the method already applied [21].
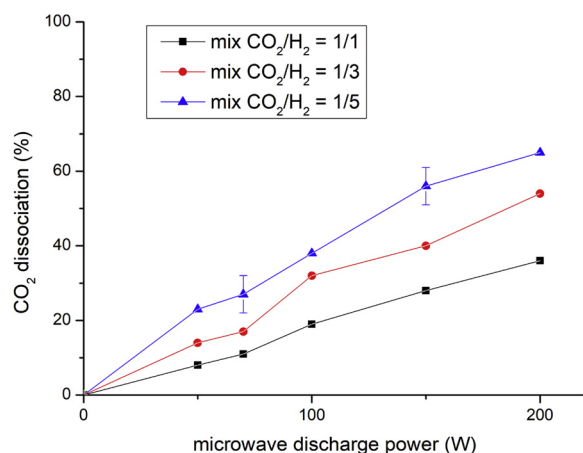
**Fig. 4.** The CO_2 dissociation percentage obtained by recording the CO_2^+ intensities measured with the microwave discharge off and on using the procedure already used [21] (see text) as a function of the applied microwave discharge power. The data are determined by keeping the inlet gas pressure at a constant value of ~1800 Pa and for three different generated plasmas using 1:1, 1:3 and 1:5 CO_2:H_2 gas mixtures.

$$\%CO_2\, diss = \frac{I_{off} - I_{on}}{I_{off}} 100 \tag{6}$$

The data are determined by keeping the inlet gas pressure at a constant value of ~1800 Pa.

The data of Fig. 4 related to the percentage of CO_2 dissociation in the case of the 1:1 CO_2:H_2 plasma mixture are in good agreement with our previous determinations, and with those obtained in other laboratories [36,37]. In the present work we extended our determinations to two more different plasmas obtained by a microwave discharge operating with a 1:3 and 1:5 CO_2:H_2 mixtures, respectively. The data of Fig. 4 clearly indicate that the percentage of CO_2 dissociation increases as the H_2 concentration increases, being about 50% higher in the case of the 1:5 CO_2:H_2 mixture respect to the 1:1 CO_2:H_2 ones, for all applied microwave discharge power values, reaching its maximum value of about 62% at a power of 200 W. These results confirm the previous experimental observation by de la Fuente et al. [38] who found that with low CO_2:H_2 ratios their plasma reactor is characterized by a high CO_2 decomposition (reaching a value over 80% when the CO_2:H_2 ratio is 1:3), since H_2 is able to act as a "catalyst" for such a process. The possible explanation of this behavior should be due to the production of high quantities of both H and O atoms in the plasmas, being the dominant intermediates species found in CO_2:H_2 low ratio mixtures [38]. In such cases, the electron density and the temperature of the generated plasma increase because of the increased concentration of H atoms, being characterized by a lower ionization energy respect to CO_2. This generates an increase of the ionization processes inside the plasma, producing higher electron densities. Since H atoms cannot absorb energy in vibrational or rotational excitations, the produced electrons are able to gain high kinetic energy content increasing all ionization reaction rates inside the plasma. Finally, when the CO_2:H_2 ratio is decreased, one can expect that two effects contribute to promote larger CO_2 conversions in the plasma: i) the decrease of the CO_2 concentration; ii) the increase of both electron density and plasma temperature [38].

The chemical characterization of the produced plasmas has been done using mass spectrometry with the apparatus and procedure described in Section 2.2. In Fig. 5 are reported the mass spectra related to the generated microwave discharge plasmas, working with an input power of ~180 W, a pressure of ~1800 Pa, and with two different CO_2:H_2 compositions: 1:5 (upper panel) and 1:3 (lower panel), respectively. The mass spectra of Fig. 5 show the production of hydrocarbons as methane, formic acid and/or dimethyl ether as well as small
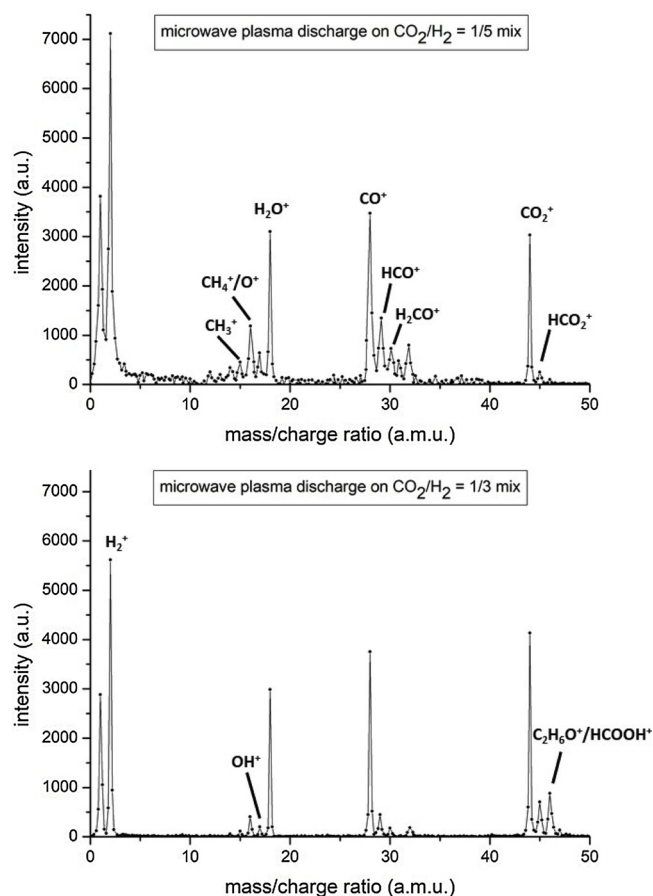
Fig. 5. The mass spectra recorded for the generated microwave discharge plasmas (total inlet gas pressure ~1800 Pa; applied microwave discharge power ~180 W): Upper panel - plasma produced with a 1:5 CO_2:H_2 gas mixture composition; Lower panel - plasma produced with a 1:3 CO_2:H_2 gas mixture composition.

amounts of HCO^+, H_2CO^+, H_3CO^+, HCO_2^+ ions. The main recorded species in our mass spectra were H^+, H_2^+, H_2O^+, CO^+ and CO_2^+. These results are in agreement with previous investigations by other laboratories: first of all, Hayashi et al. [39] produced methane, dimethyl ether and formic acid as well as several intermediate species as O, OH, and CO in their surface discharge experiments in a $CO_2(50\%)$/$H_2(50\%)$ gaseous mixture; after, de la Fuente et al. [38] were able to detect also small amounts of methanol and ethylene in their microwave plasma reactor operating with different gas feed composition (H_2:CO_2 ratios of 1 and 3) where the main produced ions were H^+, H_2^+, H_2O^+, CO^+ and CO_2^+.

It has to be noted that the possible formation of H_2CO and H_2CO^+ in our plasmas is not surprising since formaldehyde is a well-known widespread abundant interstellar organic molecule, very important in space where about 99.9% of the matter of Universe is made up of plasma [40]. One of the proposed mechanisms for its astrochemical formation involves, first the radiative association of HCO^+ ions (see Eq. (7) below):

$$HCO^+ + H_2 \rightarrow H_3CO^+ + h\nu \tag{7}$$

Followed by dissociative recombination (reaction (8) below) [40]:

$$H_3CO^+ + e^- \rightarrow H_2CO + H \tag{8}$$

Note that HCO^+ ions were detected in our mass spectrometry determinations reported in Fig. 5 with a higher abundance respect to both H_2CO^+ and H_3CO^+ that can be formed in our plasmas by either reaction (7) and (8).

Furthermore, HCO^+ is also a very important species in space probably generated in our plasmas by $CO_2^+ + H$ ion atom reaction (7) [41,42],

$$CO_2^+ + H \rightarrow HCO^+ + O \tag{7}$$

occurring when we use plasma CO_2/H_2 mixtures with high H_2 concentrations which favorize the production of hot plasmas containing high quantities of H atoms as discussed above [38]. On the other hand, the observed formation of HCO_2^+ (being more intense in our plasma having the 1:3 CO_2:H_2 gas mixture composition – see lower panel of Fig. 5) can be ascribed to the analogous $CO_2^+ + H_2$ ion molecule reaction (8) below [41,42],

$$CO_2^+ + H_2 \rightarrow HCO_2^+ + H \tag{8}$$

which is favored by lower collision energies respect to reaction (7) and by higher H_2 concentrations [41,42]. As already mentioned above, following the suggestions by de la Fuente et al. [38], such two conditions occur with higher probability in our plasma CO_2/H_2 mixtures having a less hydrogen concentration and, consequently, characterized by a lower averaged temperature. It has to be noted that the recorded signal intensities of peaks at a mass over charge ratio m/z = 29, 30, 31, 45, and 46 (assigned to HCO^+, H_2CO^+, H_3CO^+, $C_2H_6O^+$ and/or $HCOOH^+$, respectively) are too high respect to the possible ^{13}C and ^{18}O isotope natural contributions (being only of 1.108% and 0.204%, respectively).

Despite previous experiments performed at the GasPhase Beamline of the Elettra Synchrotron Radiation Facility, Trieste (Italy) where carbon dioxide CO_2^{2+} molecular dications were produced and characterized by ionizing gaseous mixtures of $CO_2 + H_2$ with different compositions [21,43], no evidences for the formation of CO_2^{2+} dications have been found in the present experiments. This is not surprising because CO_2^{2+} is a metastable species with a life time of about 3.1 μs which dissociates by Coulomb explosion producing CO^+ and O^+ fragment ions having a high total kinetic energy content ranging between 2 and 6 eV [44–46]. This is confirmed by the recorded mass spectra of Fig. 5 where the peak related to CO^+ ion is clearly evident. The fact that the signal at m/z = 16, that in our spectra can be due to either CH_4^+ or O^+ ions, is much less intense that the one of CO^+, is probably due to the fact that the possible formation of O^+ ions is not detected in our mass spectra because of their very high reactivity inside the produced plasmas. In fact, the fraction of O^+ ions coming out from the Coulomb explosion of CO_2^{2+} dications are characterized by a very high translational energy (about 3.8 eV) which allow them to be very reactive, for example with H and H_2 producing OH and H_2O both in neutral or ionic form inside the investigated plasmas [21,45]. For such a reason, the recorded peak at m/z = 16 in mass spectra of Fig. 5 should be related to CH_4 formation. This hypothesis appears to be confirmed by the detection of small signals at m/z = 15, 14, and 13 related to the CH_4 fragmentation patterns forming CH_3^+, CH_2^+, and CH^+, respectively.

4. Conclusions

A prototype methanation reactor (ProGeo 20 kW) developed by our group and devoted to produce carbon neutral methane through the chemical conversion of CO_2 waste flue gases using renewable energy, is characterized in its best operative working conditions. First of all, the yields of CO_2 conversion in methane produced by the used Sabatier reaction (1), with a Ni-based solid catalyst, as a function of the molar ratio of CO_2/H_2 reagents, and of the operating temperature and total pressure inside the reactor are determined. The best recorded operative conditions were the following: CO_2:H_2 reagent mixture 1:5; range of temperature 350–450 °C; total pressure ~2 bar; maximum yield of CH_4 production ~84%.

After that, an investigation of a new methanation pathway aimed at avoiding the use of the solid catalyst, by exploring mechanisms involving a plasma generation by electrical discharges on $CO_2 + H_2$ gas mixtures has been also undertaken. Using a microwave discharge beam source developed in our laboratory, mass spectrometry determinations demonstrated that microwave plasmas containing CO_2/H_2 mixtures indicates the formation of hydrocarbons as methane, formic acid and/or dimethyl ether as well as small amount of HCO^+, H_2CO^+, H_3CO^+, HCO_2^+ ions. These ionic species together with CO^+ and O^+ ions, having a very high kinetic energy content, since generated by Coulomb explosion of CO_2^{2+} molecular dications, should increase the chemical reactivity of plasmas generated by a microwave discharge in a gaseous $CO_2 + H_2$ mixtures playing a pivotal role in the plasma-assisted CO_2 conversion on CH_4 fuel. Further experimental efforts are in progress in our laboratory in order to find the best experimental operative conditions of CO_2/H_2 plasma microwave and RF discharges in the attempt to perform the CO_2 methanation reaction via alternative methods and microscopic mechanisms respect to the commonly used heterogenous Sabatier reaction with a solid catalyst. They are: i) a hybrid plasma-catalytic solid system or ii) a homogeneous gas-phase reaction in which the CO_2/H_2 reagent mixture is activated by a plasma generation, being either of great importance in new emerging catalysts development in chemical engineering. Even if the present work does not concern the characterization of the catalyst used in the methanation reaction (it is a commercial KATALCOJM 11-4MR produced by Johnson Matthey (UK) [26]), one of the aims of this work is to stimulate future collaborations with research groups capable of developing innovative catalysts for the methanation reaction so that they can be used in the ProGeo reactor, characterizing their performance both for their direct use and through plasma-assisted catalysis.

The results of this research are expected to provide better scientific understanding and guidance of carbon neutral technologies enabling industry and regional authorities to incorporate them: i) into future energy systems for energy innovation and sustainable development, ii) for the development and production of new catalysts able to maximize yields conversion in plasma assisted heterogenous reactions.

Acknowledgements

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