




Free-Methane - from the Ionosphere of Mars Towards a Prototype Methanation Reactor: A Project Producing Fuels via Plasma Assisted Carbon Dioxide Hydrogenation

Stefano Falcinelli¹ (✉) , Marzio Rosi^{1,2}, Marco Parriani¹, and Antonio Laganà^{2,3}

¹ Department of Civil and Environmental Engineering, University of Perugia,
Via G. Duranti 93, 06125 Perugia, Italy

{stefano.falcinelli,marzio.rosi}@unipg.it

² SCITEC, CNR,

Via Elce di Sotto 8, 06123 Perugia, Italy

³ Department of Chemistry, Biology and Biotechnologies, University of Perugia,
Via Elce di Sotto 8, 06100 Perugia, Italy

Abstract. A major challenge in the scientific research for strategies that use low-cost renewable energy is to design and develop heterogeneous /homogeneous catalysis processes that use waste CO₂ to produce fuels in a circular economy regime. In this paper a theoretical and experimental study aiming at reusing CO₂ and implementing a validated laboratory technology based on a prototype methanation reactor producing carbon neutral methane through the chemical conversion of CO₂ waste flue gases using renewable energies, is presented. The first operational line of the work is the theoretical, computational and experimental treatment of elementary reactive and non-reactive molecular processes occurring inside the reactor in order to optimize its operating conditions and to identify possible technological improvements that are more compatible with the environment. Experimental determinations of methane yield by the reactor have been carried out using CO₂ either taken from commercial bottles or produced from fermentation of wine and vegetable exhausted materials. To this end we have also undertaken a computational and experimental 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 or by vacuum ultraviolet (VUV) photons on CO₂ + H₂ gas mixtures. The measurements performed using a microwave discharge beam source developed in our laboratory gave useful indications on how to proceed to develop alternative solutions to the present Ni catalysed apparatus by resorting to a gas-phase-only process for the reduction of CO₂ to CH₄. These results demonstrate that the chemical reactivity of plasmas containing CO₂ should be strongly increased thanks to the presence of CO⁺ and O⁺ ions having a very high kinetic energy. These ionic species are produced via Coulomb explosion of CO₂²⁺ molecular dications by the same process responsible for the erosion of the atmosphere of Mars.

Keywords: Carbon dioxide · Fuels · Methanation · Renewable energy · Circular economy · Molecular dications · Coulomb explosion · Planetary ionospheres · Ion escape · Atmospheric erosion

1 Introduction

The global warming environmental problem is mainly due to strategy globally used in the production of energy employing fossil fuels [1, 2] with the subsequent emission in atmosphere of carbon dioxide which is the greenhouse gas responsible for the estimated increase in the average temperature of the Earth of about 1 °C. Because of this we brought together a team of scientists and technologists having the expertise necessary to design and build an apparatus converting waste carbon dioxide into (re-usable) methane. This effort gathered around the research laboratories of the University of Perugia - Italy (UPG), some Spanish scientists from the University of the Basque Country in Vitoria (EHU), the University of Barcelona (UB), the University of Toulouse – France (UT) as well as some technologists from Italian research institutions and companies: ENEA, EOS Energetics s.r.l.s. - Roma (EOSE), Master-up s.r.l. - Perugia (MUP), PLC System s.r.l. – Acerra (PLCS), FASAR Elettronica s.r.l. - Senigallia (FE) and RDPower s.r.l. - Terni (RDP). The collaboration between these partners provides both the skills on the theoretical-computational treatment of elementary molecular processes [3–5] and the measuring of molecule-(atom)molecule and light-(atom)molecule collision cross section and rate coefficient [6–8] and the capacity of designing and assembling computer controlled apparatuses. As a result, the project “Free-methane (Fuel from Renewable Energies – methane) was worked put and submitted to the Horizon 2020 Call H2020-LCE-2016-2017 (COMPETITIVE LOW-CARBON ENERGY) as a Research and Innovation Action (Proposal number: 763936-1). The project, aimed at building a solid background for the assembling of a novel apparatus using renewable energies to produce carbon neutral fuels through a chemical catalytic conversion of carbon dioxide waste flue gases was leveraging:

- 1) a first operational line based on the design of the molecular processes involved in the various stages of the apparatus: (A) the electrolytic production of H₂, (B) the Paul-Sabatier (PS) catalytic reduction of CO₂ to CH₄, (C) the formation of CH₄ clathrate hydrates from a water solution supported by the relevant theoretical, computational and experimental treatment of elementary reactive and non-reactive molecular processes (see the sketch of Fig. 1);
- 2) a second operational line on the design and implementation of the technological components of the low-cost hydrogen generation (Department of Enterprise Engineering - University of Rome “Tor Vergata”, EOSE) and methane production steps (with the related automation and numerical control (FE)). Despite the failure of the proposal, we built the prototype apparatus PROGEO (thanks to the additional financial and technical support of the company PLCS).

2 The PROGEO Prototype Reactor

The PROGEO apparatus built at the PLCS site is a 30 kW (scalable to 1 MW) innovative prototype reactor [3, 9]. It is based on a validated laboratory technology for the production of carbon neutral methane using electricity from the public net and hydrogen generated by a commercial electrolyser (optimized to maximize the H₂ production rather than its purity) to feed the catalytic conversion of a CO₂ flux originating from any kind of sources (including off-line filled bottles). As already mentioned, such indirect use of H₂ as an energy vector (the direct and systematic use of H₂ is more difficult because of its low viscosity and high diffusivity) reduces the carbon dioxide on a Nickel based commercial catalyser leveraging so far the scientific and technological skills of the consortium members. In particular, the hinge of the scientific components of the project were the know-how of ENEA, EOSE and UPG (Dipartimento di Ingegneria Civile ed Ambientale (DICA) and Dipartimento di Chimica, Biologia e Biotecnologie (DCBB)) on the theoretical-computational treatment of elementary molecular processes and the expertise on molecule-(atom)molecule and light-(atom)molecule collision cross section and rate coefficient measurements [4–8]. In addition, the project levered also the electronic structure calculation competences of LCPQ [10], the fitting and modelling of potential energy surfaces together with their use for dynamical calculations by EHU [11] and the integration of coupled kinetic equations related to the mechanism of catalysed reactions of UB [12]. Technological competences of ENEA, EOSE, FE, MUP, RDP and PLCS [13, 14] were also extensively exploited.

More in detail the component “Theoretical and computational investigations of the molecular processes” has consisted in: a) high level accurate and approximate *ab initio* and model calculations of the electronic structure of the involved molecular systems; b) fitting *ab initio* values to a suitable functional form or, for heavier or more complex systems, formulate the interaction in terms of force fields; c) performing accurate quantum, quantum-classical, quasi-classical dynamical calculations of the detailed dynamical properties of the system on the assembled potential energy surface; d) statistically averaging the detailed outcomes of dynamical calculations over the unobserved parameters (e.g. thermal distributions over initial internal energy) in order to provide realistic estimates of physical observables; e) modelling the temperature dependence of thermal rate coefficients for their composition in complex kinetic schemes; f) compare the outcomes of the simulation with measurements of the apparatus yields to validate the model; g) learn from the analysis of the results of the calculations on the rate determining steps of the simulation for possible improvements of the process.

At the same time, the component “Designing and assembling the laboratory apparatuses” has consisted in: a) designing the composition of the different hardware components of the overall PROGEO apparatus; b) selecting and integrating the commercial electrolyser for the production of H₂; c) setting the characteristics of the Paul Sabatier reactor so as to maximize the recovery of the heat produced by the process (the process is exoergic with $\Delta G_{298K} = -130.8$ kJ/mol and this makes the reaction self-sustainable with no need of external energy supply other than the activation one at the beginning of the reaction process); d) adopting the solid state catalyser (KATALCOJM 11-4MR, a Ni based metal alloy commercialized by Johnson Matthey [15]); e) measuring typical yields of the PROGEO apparatus.

The measured yields of PROGEO are given in a previous publication [3] for different values of the CO_2/H_2 ratios and were recorded at the operating conditions of 2 bar and 300 °C. Optimizations can be obtained by: a) introducing automated control procedures for temperature by pre-warming the reactants reusing the heat released by the process and b) regulating the hydrogen/carbon dioxide molar ratio in excess to the stoichiometric one.

3 Computational Results

The first important goal of the PROGEO project was to compare accurate theoretical simulations to the experimental outcomes of a low-level agile demonstrator of the technology and provide a flexible test bed for enabling both a scale up and an improvement of the process. To this end the Kinetic Monte Carlo Method (KMC) [16] was used to simulate the kinetics of the (surface) catalyzed process by solving the set of differential equations arising from the proposed mechanism. In the KMC approach the catalyst is represented as a symbolic grid of sites on which the different elementary processes happen at a rate in general proportional (through a rate coefficient) to the concentration of the intervening species powered to the reaction partial order and consequently forming and

Step	E_a forward (kJ/mol)	E_a reverse (kJ/mol)
$\text{CO}_2 + * \leftrightarrow \text{CO}_2^*$	0.0	8.3
$\text{H}_2 + 2* \leftrightarrow 2\text{H}^*$	4.0	77.1
$\text{CO} + * \leftrightarrow \text{CO}^*$	0.0	127.7
$\text{H}_2\text{O} + * \leftrightarrow \text{H}_2\text{O}^*$	0.0	49.0
$\text{CO}_2^* + \text{H}^* \leftrightarrow \text{COOH}^* + *$	113.1	155.6
$\text{CO}_2^* + 2\text{H}^* \leftrightarrow \text{C}(\text{OH})_2^* + 2*$	292.3	217.8
$\text{CO}_2^* + * \leftrightarrow \text{CO}^* + \text{O}^*$	93.7	169.3
$\text{COOH}^* + * \leftrightarrow \text{CO}^* + \text{OH}^*$	306.8	308.7
$\text{C}(\text{OH})_2^* + \text{H}^* \leftrightarrow \text{CH}_2\text{O}^* + \text{OH}^*$	98.7	125.7
$\text{CH}_2\text{O}^* + \text{H}^* \leftrightarrow \text{CH}_2^* + \text{OH}^*$	163.7	154.1
$\text{CO}^* + * \leftrightarrow \text{C}^* + \text{O}^*$	237.4	111.8
$\text{CO}^* + 2\text{H}^* \leftrightarrow \text{CH}^* + \text{OH}^* + *$	221.4	146.1
$2\text{CO}^* \leftrightarrow \text{CO}_2^* + \text{C}^*$	339.6	109.0
$\text{C}^* + \text{H}^* \leftrightarrow \text{CH}^* + *$	69.2	154.1
$\text{CH}^* + \text{H}^* \leftrightarrow \text{CH}_2^* + *$	68.2	61.9
$\text{CH}_2^* + \text{H}^* \leftrightarrow \text{CH}_3^* + *$	71.4	105.6
$\text{CH}_3^* + \text{H}^* \rightarrow \text{CH}_4 + 2*$	137.4	178.7
$\text{O}^* + \text{H}^* \leftrightarrow \text{OH}^* + *$	137.9	116.0
$\text{OH}^* + \text{H}^* \leftrightarrow \text{H}_2\text{O}^* + *$	137.9	99.9
$\text{H}^* + * \leftrightarrow * + \text{H}^*$	13.0	13.0
$\text{CO}^* + * \leftrightarrow * + \text{CO}^*$	10.0	10.0
$\text{O}^* + * \leftrightarrow * + \text{O}^*$	48.0	48.0
$\text{OH}^* + * \leftrightarrow * + \text{OH}^*$	21.0	21.0

Fig. 1. Elementary processes intervening in the $\text{H}_2 + \text{CO}_2$ and related activation energies (with the source reference in the rhs) for the forward and reverse process. Species with an asterisk (*) aside refer to adsorbed ones, meanwhile asterisk by their own refer to free adsorption sites.

consuming the involved species weighted by the adsorbed fraction. The Fig. 1 shows the considered elementary processes with related forward and backward activation energy.

Despite the complexity of the system of elementary processes involved in the PS reaction, a very important contribution of our computational investigations to the rationalization of its mechanism, was the singling out that the rate-determining step is the intermediate adsorption of CO on the surface of the catalyser which accounts for the almost totality of the produced methane.

Further investigations will be carried out to understand whether the adsorbed CO goes through a dissociation into C and O first before adding H₂ to form CH₄ or the adsorbed CO undergoes a disproportion or gets hydrogenated directly. After all such result indicates that the stretching of the CO bond is a preliminary condition for the production of CH₄ and is a clear indication that any research effort spent in enhancing processes weakening the CO bond directly in the gas phase (as we have already anticipated in Ref. [3]) shall provide valid alternatives to the heterogenous catalysis.

4 The Plasma Assisted Catalysis

In this section very recent progress made in the DICA laboratory on the generation and characterization of different microwave discharge plasmas containing CO₂/H₂ mixtures are discussed. By such an experimental strategy we have been able to convert carbon dioxide into various hydrocarbons such as: methane, formic acid and/or dimethyl ether as well as small amounts of HCO⁺, H₂CO⁺, H₃CO⁺, HCO₂⁺ ions. In addition, CO⁺ and O⁺ ions, are also generated in the plasmas with a high content of translational energy ranging between 2 and 6 eV. These ionic species are the fragmentation products of the Coulomb explosion of CO₂²⁺ molecular dications: i.e. the same process responsible for the erosion of the atmosphere of Mars as demonstrated by our research group in a recent study (see for instance Ref. [3] and references therein). The high kinetic energy of the CO⁺ and O⁺ ions formed increases the chemical reactivity of the generated microwave discharge plasmas using gaseous CO₂/H₂ mixtures and allows us to consider the plasma-assisted technique as a pivotal strategy for the CO₂ conversion into CH₄ fuel in the field of chemical engineering master plans for new emerging catalysts development.

The relevant experimental investigation is based on two main steps: i) an experimental characterization of the main operative working conditions of the prototype methanation reactor PROGEO (see Fig. 2); ii) the production and relative chemical characterization of generated microwave plasmas containing CO₂/H₂ mixtures having different chemical compositions (1:3 and 1:5, respectively).

As mentioned above, for the generation of CO₂/H₂ containing plasmas a microwave discharge beam source specially built in our laboratory and jointly working with a molecular beam apparatus operating at high vacuum conditions ($\sim 10^{-7}$ – 10^{-8} mbar) has been employed. Such an experimental apparatus, able to perform chemical characterization of generated plasmas by mass spectrometry [17, 18] and fully described elsewhere [19–21], is showed in the upper (a) panel of Fig. 3, while in the lower panel (b) of the same Figure a scheme of the microwave discharge can be seen. The latter is essentially made by a cylindrical quartz pipe (5 cm in length and 2 cm of diameter) inside a brass and water-cooled resonant cavity (2450 MHz and 70–200 kW typical operating power range) by a klystron and a devoted electronic control unit specially developed by FE.



Fig. 2. The PROGEO apparatus: a methanation prototype reactor working in the Laboratory of Chemical Technologies of the DICA – University of Perugia (Italy).

The analysis of the best working conditions for the PROGEO reactor, allowed us to record the yields of carbon dioxide methanation when using a Ni-based solid catalyst as a function of the CO_2/H_2 molar ratio [3].

To verify the possibility that the methanation reaction can take place via a plasma catalytic conversion by a plasma assisted version of the PROGEO apparatus, we explored the generation of various CO_2/H_2 plasma mixtures using our microwave discharge device shown in Fig. 3. With a 1:1, 1:3, and 1:5 $\text{CO}_2:\text{H}_2$ composition, we determined the percentage of CO_2 dissociation according to the following reactions:



Figure 4a reports such data (see the upper panel) as a function of the applied power to the microwave discharge.

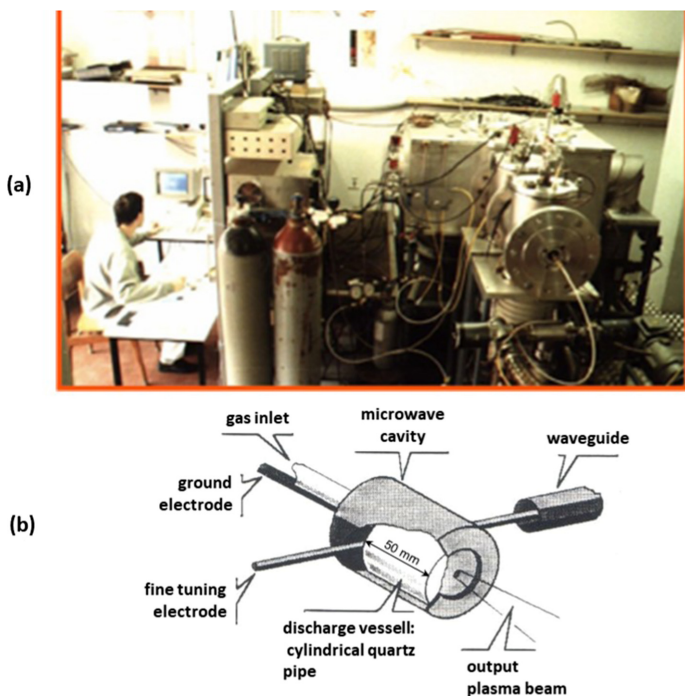


Fig. 3. (a) The molecular beam apparatus used for CO_2/H_2 plasmas generation; (b) A scheme of the microwave discharge plasma source designed and built in the Laboratory of the University of Perugia (see text).

The data shown in Fig. 4 were obtained by determining the CO_2 dissociation percentage ($\%\text{CO}_2\text{diss}$) from the recording the CO_2^+ ion intensity in the two experimental conditions of microwave discharge off (I_{off}) and on (I_{on}) via the following relation:

$$\%\text{CO}_2\text{diss} = 100(I_{\text{off}} - I_{\text{on}})/I_{\text{off}} \quad (3)$$

The obtained data of Fig. 4a are in very good agreement with previous measurements performed in our and other laboratories [22, 23]. They clearly point out that the dissociation of CO_2 is growing when the concentration of H_2 increases: it is of about 50% higher in the case of the $\text{CO}_2:\text{H}_2$ 1:5 mixture than the 1:1 one, reaching its maximum value of about 62% for a 200 W applied power. Such data agree with previous determinations by de la Fuente *et al.* [24]. Indeed, these authors found higher CO_2 decomposition values when the $\text{CO}_2:\text{H}_2$ concentration ratio decrease and reaches up to about 80% for a $\text{CO}_2:\text{H}_2$ ratio of 1:3, since H_2 is able to act as a “catalyst” for such a process.

Using the crossed beam apparatus showed in Fig. 4 and the procedure described above, we were able to analyze and characterize from a chemical point of view our generated plasmas [25]. In Fig. 4b (see the lower panel) is showed the recorded mass spectrum of the plasma having a 1:5 $\text{CO}_2:\text{H}_2$ composition. Such a spectrum clearly reveals the generation of: i) various hydrocarbons: methane, formic acid and/or dimethyl ether; ii) small amounts of HCO^+ , H_2CO^+ , H_3CO^+ , HCO_2^+ ions; iii) considerable amounts of

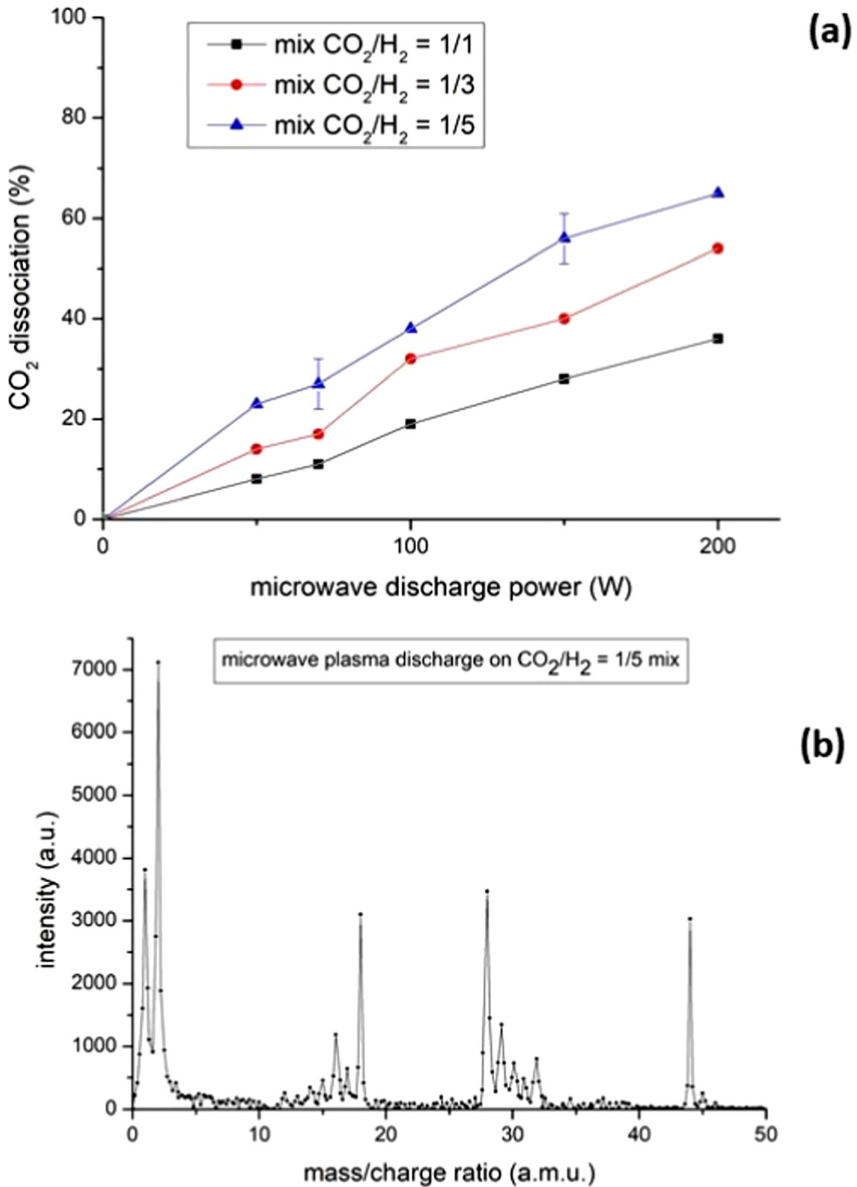


Fig. 4. (a) The CO₂ dissociation experimentally determined at different values of the applied microwave discharge power. The inlet gas pressure is kept at a constant value of ~1800 Pa and for three different plasmas using 1:1, 1:3 and 1:5 CO₂:H₂ gas mixtures (see text). (b) The mass spectrum collected by the microwave discharge plasma with a 1:5 CO₂:H₂ gas mixture composition (applied microwave discharge power ~180 W; inlet gas pressure ~1800 Pa).

the following ionic species: H⁺, H₂⁺, H₂O⁺, CO⁺ and CO₂⁺. Our results are in fairly good agreement with previous data from Hayashi *et al.* [26] who were able to produce

methane, dimethyl ether and formic acid as well as several intermediate species as O, OH, and CO in their surface discharge experiments. Furthermore, our data confirm also the observations by de la Fuente *et al.* [24] who detected H^+ , H_2^+ , H_2O^+ , CO^+ and CO_2^+ ions and small amounts of methanol and ethylene in their microwave plasma reactor.

5 From Distributed to Cloud Computing Activities

The above reported evolution of our theoretical, computational and experimental research on chemical reactions and its applications has since the beginning levered the advantages of distributed and collaborative computing. For this purpose, we have implemented in the past the Simulator of Molecular Beam Experiments (SIMBEX) [27] and Grid Empowered Molecular Simulator (GEMS) [28] assembled out of computer programs distributed over the Grid aimed at modelling the efficiency of chemical processes under the different conditions of accuracy sensitive applications (e.g. astro-chemistry, combustion, environment, etc.). To this end we levered in the past the work carried out using infrastructures and services established by the members of the Molecular Science (MS) community within the COMPChem VO [29], CMMST VRC [30], D23 [31] and D37 [32] COST Actions, ECTN [33], EGEE III [34] and EGI Inspire [35] initiatives. More recently these activities have evolved into the Open Molecular Science Cloud (OMSC) ones [36] as part of the European Open Science Cloud (EOSC) initiative [37] and its application oriented EOSC-Pillar [38] infrastructural activities whose operational schema is given in Fig. 5.

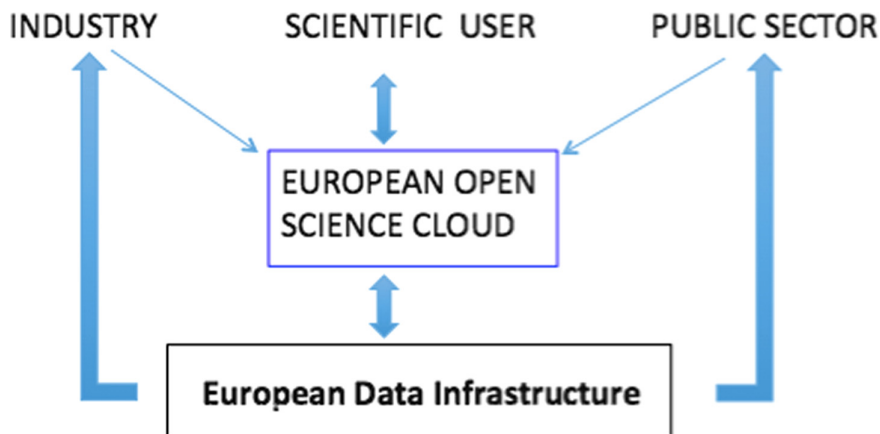


Fig. 5. The basic scheme of EOSC.

As shown in Fig. 5, EOSC provides the support of the European governments' network infrastructure to the private companies, public sector and scientific community the support necessary to share on the cloud the scientific knowledge made available by the members. In particular, within EOSC-Pillar, we have made available to the OMSC community the cloud services of the MOSEX (Molecular Open Science Enabled Cloud

Services) project [39, 40] related to the efficiency of elementary gas phase processes. Related blocks of the MOSEX operational diagram inspired to the GEMS simulator are:

- i) the construction of the potential energy surface governing the process out of the implemented electronic structure calculations,
- ii) the evaluation of the rate coefficient of the reactive process out of the cloud implemented integration of the dynamical equations of the involved atomic nuclei,
- iii) the Data Handling cloud services for making available to the users the validated efficiency parameters.

In particular MOSEX is meant to provide the cloud support [41] for:

- a) producing/discovering and downloading data for the open collaborative and fully re-usable databases and repositories (like those of the already implemented EChemTest® service of the European Chemistry Thematic Network (ECTN) for assessing chemical competences at school, University and Life-Long-Learning levels [42]);
- b) running/checking/correcting (where possible) or discarding and validating data through iterative cycles collaboratively undertaken by the members of the community (like the Learning Objects of ECTN);
- c) annotating/curating/preserving data of service for a more efficient re-use (see e.g. [43–49]);
- d) evaluating the quality of services provided by the members of the MS community;
- e) offsetting debits with credits of the adopted Prosumer (Producer + Consumer) model (at present experimented only for the electronic assessment EChemtest® product) in which the community members are at the same time users (making debits for used services) and producers (gaining credits against produced services) [42].

6 The Prosumer Model and Circular Economy

The MOSEX theoretical, computational and experimental activities for the post PRO-GEO development of renewable energies storage pursues not only the research illustrated in Sect. 4 but also the implementation of its circular economy and Prosumer articulation. An illustration of the circularity plan discussed with some colleagues of the Agricultural Faculty [50] and Technological Park [51], is given in Fig. 6.

In Fig. 6 the scheme of an experimental plant agreed among the partners for enriching biogas produced by agricultural feedstock by converting the fraction (about 50%) of the biogas generated by fermentation. To this end the previous composition of the informal consortium has been reformulated for establishing, under the coordination of DICA, a formal consortium with DCBB and some companies. It will operate within the MOSEX project in particular for implementing on the cloud circular economy initiatives based on the Prosumer model leveraging on Green Chemistry. As already mentioned in item (e) of the MOSEX mission illustrated above, the Master-UP member of the PROGEO consortium has already adopted the Prosumer scheme for implementing the cloud service of EChemTest® running the Self Evaluation Sessions for the assessment of Chemistry

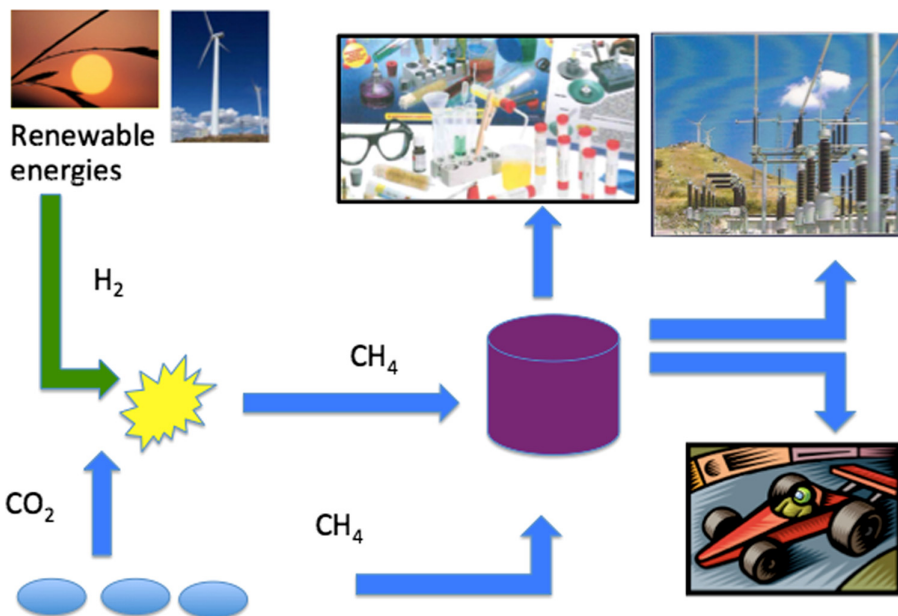


Fig. 6. The scheme of the circular economy Prosumer for PROGEO. In the lower-left corner of the figure the production of biogas is schematized: CO_2 and CH_4 main components, after a proper purification by specific membrane filtration technologies, are sent to the methanation reactor (vertical arrow), and to the gaseous fuel storage tank (horizontal arrow), respectively.

competences using the ECTN libraries of Questions and Answers and for acting as an ECTN Agency [48].

The implementation of a green chemistry circular economy initiative for PROGEO-like activities has been already proposed in Ref. [43] for the simpler case of a large winery wishing to convert to methane the carbon dioxide accumulated from the fermentation of wines during the related season (the higher simplicity of the considered case lies in the fact that the accumulated CO_2 is virtually pure and does not require costly filtering technologies). In that case it was found that the company gets positive returns out of the innovation and will be also encouraged to increase the quantity of CO_2 to convert because this increases the production efficiency. The process will continue, in fact, to produce at standard methods (still satisfying the market demand) while investing at the same time on R&D to increase the productivity of the production factors and shift the isoquant to higher efficiency when moving to next steps (the Research and development variable cost can be kept unaltered thanks to its positive effect on a perspective of profit increase even further in subsequent steps). This means that the circular economy reuse of energy guarantees, through the registering of patents and the consequent temporary monopolistic situations, the fulfilment of the conditions of Positive Ecological Externality for the involved societies and clusters of companies.

7 Conclusions

A prototype reactor (PROGEO) devoted to carbon dioxide methanation was developed to produce carbon neutral methane via chemical conversion of CO₂ waste flue gases using renewable energy, in a circular economy strategy. It was characterized in its best operative conditions determining yields of methanation by the Sabatier reaction of about 84%, where a Ni-based solid catalyst has been employed.

Furthermore, an experimental effort aimed to investigate a new reaction pathway without the use of the solid catalyst, has been undertaken. Interesting and promising data collected exploring mechanisms via plasma generation using microwave discharges over CO₂ + H₂ gas mixtures are presented and discussed. They demonstrate the generation in the exploited plasmas of simple hydrocarbons as methane, formic acid and/or dimethyl ether, small amount of HCO⁺, H₂CO⁺, H₃CO⁺, HCO₂⁺ ions, and considerable quantities of CO⁺ and O⁺ ions, with high kinetic energy content, ranging between 2 and 6 eV. These ionic species are produced via Coulomb explosion of CO₂²⁺ molecular dications by the same process responsible for the erosion of the atmosphere of Mars as demonstrated by our previous investigations [52–54]. Indeed, CO⁺ and O⁺ ions formed by Coulomb explosion of CO₂²⁺ molecular dications, could be the responsible of the enhanced chemical reactivity of the generated plasmas. Further theoretical and experimental efforts will be done by our group in two directions: i) to make the use of the PROGEO prototype suitable to be employed in the industrial chain in order to treat waste gases and convert them into valuable fuels in a circular economy logic: to do this it will be necessary to develop a new type of low-cost hydrogen gas generator through a project that EO is working on; ii) to develop a hybrid plasma-catalytic solid system or a homogeneous gas-phase reaction where CO₂/H₂ reagent mixtures activated by a plasma generation could realize the methanation reaction by new microscopic mechanisms more favorable from both a kinetic and energetic point of view.

In conclusion, we expect that new theoretical method able to fully describe state-to-state prototype oxidation processes [55, 56], as well as experimental efforts on the characterization of microscopic dynamics of elementary reactions [57–60], will provide reliable data useful for a better understanding and perspectives for innovative carbon neutral technologies as reported in various interesting papers [61–63]. Industry and regional authorities could include them into future energy strategy and systems for innovation and environmental-sustainable development, as well as for new catalysts able to maximize the products yield in plasma assisted reactions.

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