FREE-METHANE: A PROJECT FOR PRODUCING FUEL FROM WASTE CO_2 USING RENEWABLE ENERGIES

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Abstract
In this paper we illustrate the Free-methane (Fuel from RenewablE Energies – methane) proposal submitted to the Horizon 2020 Call H2020-LCE-2016-2017 (COMPETITIVE LOW-CARBON ENERGY) as a Research and Innovation Action (Proposal number: 763936-1) for the first step of a two-stage process. The project is 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. The first operational line of the proposal is the theoretical, computational and experimental treatment of elementary reactive and non-reactive molecular processes on which the project is grounded. The second operational line of the proposal is the designing and fabricating the technological components of the proposed apparatus. The project will lead to the production of three basic innovative components of the apparatus: a new electrolyser and two highly efficient reactors producing methane and its clathrate hydrates.

1. THE COMPETENCES

The FUEL from RENEWABLE ENERGIES – Methane (**FREE-METHANE**) proposal has been submitted to Horizon 2020 for the call "SECURE, CLEAN AND EFFICIENT ENERGY" (COMPETITIVE LOW-CARBON ENERGY) within the LCE-2016-2017 "FUELS FROM RENEWABLE ENERGIES" topic that aims at reducing the carbon dioxide generated as a by-product by several industrial and agricultural processes to methane. The objective of the proposal is the development of the competences necessary to build a novel 50 kW (scalable to 1 MW) validated laboratory technology for producing carbon neutral methane from renewable energies and a catalytic conversion of CO_2.

The laboratories of the University of Perugia (UPG), of the University of the Basque Country in Vitoria (EHU), of the University of Barcelona (UB), and of the University of Toulouse (UT) provide the research lines supporting the project. ENEA (the Agenzia Nazionale per le Nuove Technologie, L'Energia e lo Sviluppo Economico Sostenibile of Frascati), Master-up s.r.l. (MUP), RDPower s.r.l. (RDP) and RPC s.r.l. (RPC) provide the technological skills supporting the project. In particular, the hinge of the scientific components of the project are the know how of UPG (in particular of the Department of Chemistry, Biology and Biotechnology and of the Department of Civil and Environmental Engineering) on the theoretical-computational treatment of elementary molecular processes [1] and the expertise on molecule-(atom)molecule and light-(atom)molecule collision cross section and rate coefficient measurements [2-4]. Furthermore, the project relies on the electronic structure calculation competences of LCPQ [5], on related fitting and modelling of potential energy surfaces together with the ability of performing dynamical calculations on them of EHU [6] and the integration of coupled kinetic equations related to the mechanism of catalysed reactions of UB [7]. Technological development and patenting is in charge to ENEA and to the participating SMEs MUP, RDP and RPC [8,9].

In more detail *"Theoretical and computational investigations of the molecular processes"* (**UPG, UB, LCPQ, EHU**) consist of: a) high level accurate and approximate ab initio as well as 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 (eg. thermal distributions over initial internal energy) in order to provide realistic estimates of physical observables; e) modelling the

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temperature dependence of thermal rate coefficients for their composition in complex kinetic schemes for all the three already mentioned components of the laboratory prototype. The focus of the computational investigation will be the integration of the system of kinetic equations describing the reaction of CO_2 with H_2 to form methane under the assistance of a solid state catalyst and the check of the computed yields against the experimental ones. To this end the simulation results will be compared with measurements performed on the experimental apparatus located at UPG whereas for simulations run entirely in gas phase checks will be performed against experiments carried out at the ***synchrotron*** and ***Free Electron Laser*** of Trieste using spectroscopy, beams, plasmas, time of flight mass spectrometry and electron ion-ion coincidence technologies.

In more detail "*Designing and assembling the laboratory components*" (**ENEA, RPC, UPG, MUP**) consists of the building of three components of an industrial apparatus producing CH_4 out of H_2 and CO_2 and storing it for deferred use. The central component of the apparatus is a reactor based on the Sabatier scheme that leverages on the catalytic action of a commercial Ni based metal alloy. Initial tests will be performed on an already assembled (manually operated) prototype experimental apparatus to measure actual under reference operating conditions (2 bar; 300°C). The process is exoergic and once activated does not need to be sustained by supplying extra energy. Already planned tasks to optimize the yields are: a) the automated control of the temperature by a pre-warming of the reactants reusing the heat released by the process and b) the increase of the hydrogen/carbon dioxide molar ratio in excess to the stoichiometric one. This will be pursued by means of an improved design of the reactor and a careful selection of the catalyser. An even more ambitious task is the goal of switching from heterogeneous to homogenous catalytic processes based on RF and microwave discharges, lasers, and tunable synchrotron radiation producing plasmas, Penning ionization, etc [3,10,11]. An important component of the apparatus that will significantly increase the performance/cost ratio will be the design of a more efficient electrolytic cell using novel nanostructured materials. The third component of the apparatus will impact the way methane is stored and transported. The choice of methane as target fuel relies on the fact that its technology is mature and of immediate utilization because it can not only rely on a capillary network of distribution pipelines but also the innovative technology of methane capture as clathrate hydrate. The latter offers a cheap and safe way of deferring its use. To this end the presently used manually operated component of the prototype experimental reactor devoted both to the management of the processes leading to the formation of clathrate hydrates and to the exploitation of the action of the additives in the related mechanisms will be improved. Important hints on the innovation needed will be provided by molecular dynamics simulations.

2. THE KEY OBJECTIVES OF THE PROJECT

The main objective of the project is the *actual design and building of an efficient laboratory validated technology transforming CO_2 generated by waste flue gases into (synthetic) methane through chemical catalytic conversion using renewable energies by combining high level theoretical and computational molecular science investigations with advanced experimental and engineering technologies.* This will be grounded on the already mentioned high level of expertise of the partners of the project in designing/implementing both advanced theoretical/computational tools and technological innovation. In particular, the teams of university researchers (**UPG, UT, UB, EHU**) excel in investigating theoretically chemical processes using advanced computational methods. Three teams excel in designing and building highly technological apparatuses (one from a public institution (**ENEA**) and two from SMEs (**PRC srl and RDPower srl**)) while another SME (**MUP**) excels in handling networked knowledge (distributed databases and repositories) for managing scientific, educational and technological data and information. The synergistic nature of the exploitation of these competences within the project is well represented by the fact that the coordinating Institution **UPG** (in particular the Department of Civil and Environmental Engineering and the Department of Chemistry, biology and Biotechnology involved in the project) at the same time manages both locally (crossed beams) and externally (Elettra Synchrotron beam line) experiments, theory and computations and is involved as well in the ITN-EJD-642294 Theoretical Chemistry and Computational Modelling (TCCM) project in which is responsible for the research line ESR04 "Networked computing for ab initio modelling the chemical storage of alternative energy".

A second key objective is the building of the prototype apparatus with the *creation of the basic knowledge elements for a possible future implementation of an Open science platform in research and education* aimed at both enhancing the awareness of generic people for environment in general and training younger generations of chemists to develop a proactive environmental care, in particular. To this end, synergies will be activated between the activities carried out by **MUP** (by handling the data and knowledge bases of the project) and the networked activities in developing and managing e-learning products, tools, infrastructures

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of **ECTN** (European Chemistry Thematic Network) through its network of test sites (for the assessment) and distributed repositories (for teaching) using related Learning objects in connection also with life long learning initiatives.

A third key objective of the project *"accumulation" of electric energy (either "in excess" or "not produced") under the form of chemical energy of the methane molecules produced from CO_2 by enhancing the reuse of CO_2 by means of renewable energies.* This will mitigate the impact of industrial and agricultural waste flue gases and, at the same time, will offer an efficient way of utilizing unused energy. This feature of the technology proposed for reusing waste flows of CO_2 and generating synthetic methane (in a circular economy approach) will not give rise to environmental, resource efficiency and safety concerns because of its carbon neutral nature and excite well established social and market acceptance (as a valid alternative to the past heavily carbon dominated energy technologies). In addition, the proposed technology offers a natural way of exploiting discontinuous energy sources (as it is often the case of the renewable ones). The proposed apparatus is in fact able to accumulate any provided amount of energy (this will eliminate the problem of blocking electricity generation when its production does not match consumption). This will turn to be useful also when the amount of generated electricity cannot be varied to the extent in which demand fluctuates (as is the case of nuclear and large scale thermoelectric plants). Finally, the economic impact and the social benefits obtained from the proposed technology are evident when considering the flexibility of modulating the use of accumulated methane to generate electricity, feed pipelines, bottle it and even to form clathrate hydrates for safe and cheap distribution to deferred and delocalized consumption. The proposed apparatus can, in fact, be used both as an energy "**accumulator**" and as a "**subsidiary carbon neutral fuel production plant**".

3. THE INNOVATIVE COMPONENTS OF THE PROJECT

As already mentioned the key components of the project are:
A) *the modelling, design and building of an efficient innovative electrolyser producing H_2 with a significant increase of the yield/cost ratio over the available electrolysers,*
B) *the modelling, design and building of a new heterogeneous/homogeneous catalytic reactor using CO_2 as raw material to produce synthetic fuels in a circular economy scheme,*
C) *the modelling, design and building of a reactor for producing a clathrate hydrate for storing the produced carbon neutral fuel using a technology cheaper than the traditional cooling and compressing for bottling and deferred utilization with minimal safety risks during transportation.*
The assemblage of the three components both into a distributed collaborative simulator of the whole process and into an articulated experimental apparatus is the innovative technological target of the project aimed at storing electricity produced from renewable sources into a fuel to be reused to produce carbon neutral energy.

The first component of the apparatus is more specifically an innovative yield/cost optimized electrolyser. As is well known, in fact, there is an appreciable fraction of the produced electricity offered on the market (about 40% in Italy) that goes unsold. This fraction becomes much larger when the cost of not produced renewable energy is included. Yet, the use of present commercial electrolytic generators of hydrogen aiming almost exclusively at high yields irrespective of the purpose of its practical use make the produced hydrogen too costly. This has a large impact on the price of the commercial electrolyser (about 1 Meur per 500 kW that amounts to about half of the whole cost of the methanation reactor planned in our project) and drastically curtail the market penetration of the apparatus due to its excessively long pay back time. As a matter of fact less than 5% of the presently produced hydrogen is generated from water electrolysis that requires 45 kWh (with the DOE recommendation for the year 2020 being less than 43 kWh; this amount can be reduced to 18.5 kWh by properly using carbon nanotube technologies and ethanol, also commonly called ethyl alcohol). The focus of the new experiment is the use of "electro-catalytic" anodes with nanoparticles of palladium on a support of nanotubes of titanium [12].
Still at present the largest part (48%) of hydrogen is produced from natural gas reforming, 30% from oil distillation and reforming and 18% from carbon with a price to pay in terms of CO_2 production of 9 kg per kilogram of produced hydrogen. The line pursued by the project is to obtain a drastic reduction of costs (of about 90%) by simplifying the electrolyser to an acceptable level of purity of the hydrogen produced and ready for the following methanation process.

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The second component of the apparatus is a catalytic P. Sabatier reactor. Our laboratory equipments allow already a (manually controlled) production of methane from CO_2. The presently running apparatus is assembled out of a reactor in which the flowing gases react thanks to the adsorption on the surface of a Ni based commercial catalyser Johnson Matthey Katalco$_{JM}$ 11-4MR. The catalyst is cylindrically shaped; the substratum is in alumina Al_2O_3; the morphological analysis shows micro holes and different shaped grains (Al silicate and Ni-Mg oxide).

The third component of the apparatus is a clathrate hydrate formation reactor. Experiments producing methane clathrate hydrates catalysed by sodium dodecyl sulphate have been already carried out. Methane clathrate hydrates have shown to be a cheap and safe way of storing and transporting methane at mild temperature (about 0°C) and pressure (1 bar) values. Transport of methane, in fact, under hydrate form may be 24% cheaper once compared with Liquified Natural Gas (LNG) technology [13]. As a matter of fact, the Mitsui Engineering & Shipbuilding Co., Ltd. (MES) has developed a few years ago the process and the infrastructure to transport methane under hydrate form [14].

The final product will consist of the assembled overall apparatus made of the three A + B + C components that by inputting renewable energy, water and carbon dioxide produce methane clathrate.

Together with the experimental apparatus, the components of distributed computer simulator based on the integration of a Kinetic Monte Carlo (KMC) software package for simulating molecular phenomena on catalytic surfaces and on the integration of molecular dynamics equations for simulating the formation of clathrate hydrates will be assembled. This will be used to the end of analysing the overall efficiency of the system by comparing simulation outcomes with those of the experimental apparatus aimed both at evaluating the optimum conditions for producing and storing the methane clathrate hydrate and to rationalizing the mechanisms involved.

The assembling of these data and of the resulting knowledge (which impact environmental, resource efficiency and safety concerns) is of strategic relevance for the enhancing of social acceptance of green technologies and for the adoption of carbon neutral fuels. To this end specific learning objects and self-assessment libraries as part of the educational European standards in chemistry degrees will be elaborated.

4. A LOOK FORWARD

The results of this research are expected to provide better scientific understanding and guidance of carbon neutral technologies enabling industry and regional authorities to insert them in the future energy system. The utilization of integrated production of carbon neutral methane from *waste* CO_2 using renewable energies and *cheap electrolytic production of* H_2 *combined with* its safe storage and transportation as clathrate hydrates is already under preliminary discussion for a first specific action being concerted between the partners of the proposal and the local authorities of the Umbria region to specialize a version of the apparatus for a conventional electric power station. The second specific action will be the structuring of the knowledge produced into learning objects and self-evaluation sessions for an Europe wide diffusion within the molecular science education system and some application databases of ECTN. The third specific action is concerned with the preparation of a technical study on the implementation of related technologies for a medium-low level application concerning the production of carbon neutral methane from CO_2 obtained from grapes fermentation for a wine producer in Sicily.

The results of this research are expected to lead to new advanced innovative ideas that will provide new impetus to technology pathways, and to new contributions to the energy challenge worldwide. Among the innovative technological solutions adopted for the proposed project there are two still quite embryonic ones, which promise to provide new impetus to carbon neutral energy challenge worldwide: the electrolyser and the methanation. The yield/cost optimization process, in which the quality of hydrogen produced is calibrated on the purity needed by the process, is expected to lead to even more advanced solutions than the one adopted (this expectation is reasonable though rather uncertain).

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