CO_2 - Loop for Energy storage and conversion to Organic chemistry Processes through advanced catalytic Systems

PROJECT FINAL REPORT

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Title:

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4.1 Final publishable summary report

A) Executive summary

CEOPS project focused on a sustainable approach for the production of methanol from CO_2, which is a precursor for fine chemical. The concept relied on two chemical pathways, CO_2 to CH_4 (pathway A) and CH_4 to CH_3OH (pathway B) with the intermediate carbon vector: methane. Methane benefits from the extended and existing natural gas network infrastructure.

The technological work was based on the development of advanced catalysts and electro-catalytic processes. CEOPS investigated advanced catalysts for application in three promising electro-catalytic processes (Dielectric barrier discharge plasma catalysis, Photo-activated catalysis and Electro-catalytic reduction) to increase their efficiency for both pathways.

For CO_2 conversion to CH_4, two DBD catalysts 20%Ni-30%Ce/Cs-USY and $Ce_{0.9}Zr_{0.1}O_2$-15% Ni present a synergy with a DBD plasma below 200°C on the CO_2 hydrogenation with a conversion rate of about 80%. For the partial oxidation to methanol the DBD plasma presented demonstrated the ability to produce methanol but with limited conversion and selectivity.

The PEC process allowed the synthesis of methane but with a limited selectivity (CH_4 vs CO). The photocatalytic process allowed the synthesis of methanol from methane with a selectivity of nearly 50% and a conversion rate limited at 2%. Two photocatalysts based on mesoporous WO_3-1%La, and on a zeolite-based and 1%Ni-15%W/HBEA catalysts presented the highest efficiency.

Methane formation by CO_2 electro-reduction with CO_2 dissolved in ionic-liquid was demonstrated. The best result, obtained with Ni-Cu bimetallic cathodes presented CH_4 selectivity about 100%, with productivity of about 400 mol.CH_4 h^{-1} kg catalyst^{-1}. Up to date no reports of methane production by electrochemical reduction in ionic-liquids have been published and so these results are clearly beyond the SoA. However, a lack of reproducibility of methane formation was observed.

The performances of the studied catalyst and process schemes were benchmarked and the most efficient for each pathway were: the pathway A with a gas fluidised bed reactor with a DBD plasma assistance; the pathway B with a photocatalyst slurry reactor with methane with assistance of UV light.

Prototype reactors were developed, built and tested to assess their performances for the two catalytic pathways, which were respectively the synthesis of methane from a mixture of CO_2 and H_2 and the synthesis of methanol from methane.

The pathway A gave noticeable results at low temperature (<200°C) with the zeolite based catalyst. A 60% conversion with 99 % selectivity in methane was obtained, with a plasma power consumption of 32 kJ/mol. The pathway B gave a very low production of methanol with both optimised catalysts which confirms the challenge of this reaction.

In the present market conditions and current regulations methane will be produced at a cost of 135 €/MWh_{HCV}, including investment costs, considering electricity average price of 42€/MWh. In the case of methanol, the final price will be close to 184 €/MWh_{HCV}. The electricity price per MWh to make methane competitive is close to 3€/MWh. For methanol it will be around 16€/MWh.

At the current stage, the environmental impacts of Pathway A and Pathway B are larger than the impacts of currently available technologies. This is mainly due to the large energy demand and the current electricity mix in the EU. An energy mix of 100% of renewable energy can become an environmentally favourable alternative to methane and methanol from current sources.

During the project, 16 papers were published and 70 dissemination activities were done. Six workshops and two summer schools were organised to promote the project, the carbon dioxide utilisation approach and disseminate the results.

B) Description of project context and objectives

i) Context & concept

The overall carbon footprint of the expected demand will exceed 40 Gt/year of CO_2 emissions by 2030[2]. From CO_2 valorisation standpoint, scientific, industrial and societal authorities are urged to propose new schemes for producing, consuming and recycling carbon from fossil fuels for energy market and chemical industry. In this context, valorisation of CO_2 (CCU approach) emissions constitute a complementary strategy and not a competition to CO_2 geological sequestration (CCS approach). CO_2 transformation into added value products will contribute to the transition from carbon fossil sources products to low carbon footprint ones. To this end, the intensive industries (e.g. cement industry), as large emitters of CO_2, represent a non-exploited source of carbon. The worldwide production of cement represents 1.5-2 Gt, which is about 5% of anthropogenic global CO_2 emissions. To significantly reduce CO_2 emissions, United Nations Industrial development Organization predicts for the cement industry that 1.1 Gt of CO_2 should be reduced (Capture nearly 50%) from the expected 2.5-3Gt of CO_2 by 2050[3]. This will entail an additional cost of 40 – 80 €[4] per ton of CO_2 captured, which would have a severe impact on cost of cement.[5]

From a fine chemicals standpoint, methanol is a major intermediate molecule for chemical industry and fine chemical products with an average cost of 300 \$/ton metric. Industrially, methanol is synthesised from fossil fuel by steam reforming of methane followed by hydrogenation of CO. Its production has increased for many years and should exceed 100 million metric tons in the next few years. Methanol is an important and versatile building block, which can play the role of chemical storage molecule for energy and used for the synthesis of products such as acetic acid, formaldehyde, olefins. Valorisation of CO_2 emissions represents a major stake of competitiveness for large CO_2 emitters and especially for the cement industry.

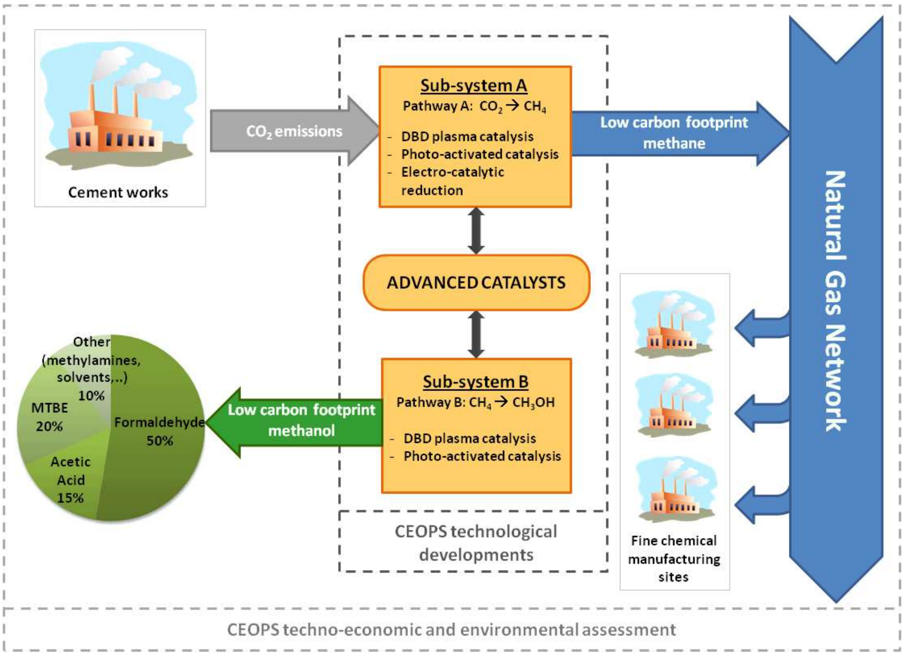

Figure B1: CEOPS project concept

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[2] World energy, technology and, climate policy outlook 2030, WETO report
CO2 Emissions from fuel combustion, I E A - Statistics - 2010 Edition

[3] Global Technology Roadmap for CCS in industry, Sectoral Assessment: Cement, Mott MacDonald 2010

[4] "Cement Technology Roadmap 2009" edited by World Business Council for Sustainable Development

[5] European Cement Research Academy, Technical Report TR-ECRA-106/2009

The concept of the project (Figure B1) relies on the development of two chemical pathways based on: Sub-system A: Upstream, CO_2 to methane conversion will be realised with advanced catalysts to promote the efficiency of $CO_2 \rightarrow CH_4$ electro-catalytic process (pathway A) at the point of CO_2 emission (cement works). Methane will act as an easy storable and transportable carbon vector.

Sub-system B: Downstream, the direct conversion of methane to methanol will be done at the point of fine chemicals production with advanced catalysts to promote the partial oxidation of methane into methanol called "the direct pathway" (pathway B) instead of using the current pathway consisting of a steam reforming of CH_4 which represents 60-70% of cost production of current methanol, followed by the CO hydrogenation reaction.

While large CO_2 emitters and fine chemicals producers are currently and geographically dispersed throughout Europe, CEOPS concept proposes the use of the existing wide natural gas network via the injection and transportation of an intermediate product: methane. Indeed, CH_4 is easily transported. Furthermore, methane already benefits from the extended and existing European natural gas network infrastructure, so its distribution will prevent additional CO_2 emissions for transportation. This sustainable approach will thus enable the decentralisation of methanol production, which will favour the emergence of distributed, small and flexible production units of fine chemicals. This vision will pave the way for several novel and sustainable production schemes. Moreover, the flexibility of CEOPS production scheme, in low consumption period (< a threshold price of energy / MWh) or surplus of renewable energy production should ensure the competitiveness of the concept.

CEOPS was focused on the development of advanced catalysts and electro-catalytic processes for sub-systems A and B. The most promising process for each pathway was selected to provide a proof of concept via the construction of prototype system. This prototype integrated both reactors: CO_2 reduction to methane (pathway A) and methane oxidation to methanol (pathway B) in order to demonstrate the pertinence of the concept.

ii) Scientific and technical objectives

Both pathways (CO_2 to CH_4 and CH_4 to CH_3OH) have been developed by thermal catalysis for several years with remaining drawbacks such as low catalysts efficiency (conversion rate * selectivity) and deactivation. CEOPS have developed and evaluated efficient advanced catalytic materials for application in three promising electro-catalytic processes (see figure B1) in order to increase their conversion rates and selectivity:

- DBD (Dielectric Barrier Discharge) plasma catalysis,
- Photo-activated catalysis,
- Electro-catalytic reduction.

The performances of the studied catalyst and process schemes were benchmarked. The most efficient and durable scheme for both pathways was selected on the basis of conversion rate, selectivity and energy (electricity) consumption.

A prototype of sub systems A and B was implemented with integrated prototype reactors. This prototype integrated the selected schemes to demonstrate the proof of concept and to generate the required data for the techno-economic assessment. The scalability of both schemes was studied with the support of the industrial partners.

The project was structured with 4 scientific and technical objectives s described as follows:

Objective 1: Advanced catalytic materials development (IST, IREC and OMNIDEA)
Catalysts were developed in order to increase the conversion rate and selectivity of the studied pathways for sub-systems A&B:

- Nanostructured zeolite in combination with metal oxides and mesoporous metal oxides for DBD plasma catalysis for both pathways,
- Nanostructured TiO_2 (nanotubes) for pathway A and mesoporous tungsten oxides and beta zeolites for photo-activated catalysis for pathway B,
- Multifunctional cathode materials with bimetallic nanoparticles for electro-catalytic reduction of CO_2 [Pathway A].

Objective 2: Enabling electro-catalytic processes (UPMC, CEA, IREC, NOVA)
Electro-catalytic processes were developed to promote the sustainable production of fine chemicals from emitted CO_2 via pathway A and pathway B.
Pathway A: The chemical pathway starts by electrolysis of water followed by the CO_2 hydrogenation.

$$H_2O \rightarrow H_2 + \tfrac{1}{2} O_2 \qquad \Delta H > O$$

$$CO_2 + 4\,H_2 \rightarrow CH_4 + 2H_2O \quad \Delta H < O$$

and the overall reaction is the sum of those two : $CO_2 + 2\,H_2O \rightarrow CH_4 + 2\,O_2$
Pathway B: The partial oxidation of methane to methanol.

$$CH_4 + \tfrac{1}{2} O_2 \rightarrow CH_3OH \;\; ; \quad \Delta H < O$$

The performance objectives for the competitiveness of both pathways set by the project was expressed of **conversion rate, selectivity** and **electricity consumption** as shown in the table below:

	Pathway A	Pathway B
DBD plasma catalysis	**CO_2 hydrogenation** ● Conversion rate > 65 % ● Selectivity > 90% ● Electricity consumption (<12kJ/mole$_{CH4}$)**(*)**	● Conversion rate > 30% ● Selectivity > 50% ● Electricity consumption (<5kJ/mole $_{CH4}$)
Photo-activated catalysis	**CO_2 reduction to CH_4** ● Conversion rate > 65 % ● Selectivity > 90% ● Electricity consumption (<1,64 MJ/mole $_{CH4}$)**(*)**	
Electro-catalytic reduction		**NA**

(*)The energy required to produce 1 mol H_2 by water electrolysis is 407 $KJ.mol_{H2}^{-1}$ for a yield of 70% [NREL data][6]. 1,628 MJ are consumed to produce 4 moles of H_2 necessary for the CO_2 hydrogenation. With the objective of 12kJ/mole$_{CH4}$ for the CO_2 hydrogenation pathway the overall consumption for the pathway A is the same as the two other processes (1,64 MJ/mole$_{CH4}$).

These electro-catalytic processes were developed in lab-scale reactors, incorporating advanced catalysts (objective 1) as follows:

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[6] http://www.nrel.gov/hydrogen/pdfs/36734.pdf

- **DBD plasma catalysis** was implemented on **fixed bed reactor** (UPMC) for mechanisms studies and in parallel on a **fluidized bed reactor** (CEA) for performance assessment. This was done for both pathways. The plasma creates active species by pulse plasma nearby the catalyst surface and improves kinetic by both surface reaction and, desorption of by-products liable to deactivate catalysts active sites during operation.

- **Photo-activated catalysis** (IREC):
  The photon activation of catalysts promotes low electricity consumption and an enhancement of the conversion rate and selectivity.
  - **Photo-electro-catalytic** technology was implemented on a **photo-electrochemical cell (PEC)** with an innovative photo-anode (pathway A).
  - **Photocatalytic technology** was implemented on a **fixed bed reactor (pathway B).**

- **CO_2 electro-catalytic reduction** (NOVA) was developed with ionic liquid which could be also used for CO_2 capture instead of current amine based solvents. The electro-reduction reactor integrates **multifunctional cathode materials**.

Objective 3: Set-up of a prototype for sub-systems A&B (CEA + UPMC, IREC, IST)
The most efficient and durable catalytic scheme was selected for each pathway at M20. Catalysts and processes were scaled up to a prototype scale and tested at CEA in a test bench. The same performance indicators and targets (Objective 2) were addressed at the prototype level.
This prototype allowed the evaluation of thermal balance, electricity consumption, and catalytic efficiency of both sub-systems.

Objective 4: Techno-economic and environmental assessments (Industrial partners and CEA)
Based on the above evaluation, the economic and environmental competitiveness of the CEOPS process routes from industrial CO_2 emitters to fine chemical customers was finally determined in terms of:

- Techno-economic performances assessment;
- Environmental impact assessment for industrial CO_2 valorisation and “renewable” methanol market evaluation of the need for low carbon footprint methanol;
- Comparison of the competitiveness and the overall efficiency of the low carbon footprint methanol with the one produced today from fossil source by current technology (thermal catalysis).

C) A description of the main S&T results/foregrounds

The core developments of the project was developed in the WP2 dedicated to advanced catalyst and in the WP3 dedicated to electro-catalytic processes. The developed catalysts were characterised and then supplied to WP3 for their catalytic performance evaluation. In WP3 lab-scale reactors processes were set-up with integrated catalytic materials and their efficiency was measured with respect to conversion rates, selectivity and energy consumption for both sub-systems A&B. At M20, a decisional milestone selected the most performing process for each pathway A&B based on the objectives 2.

i) Catalyst developments performed in the WP2:

● Development of advanced catalysts for DBD plasma catalysis (IST & IREC)

Pathway A:

Zeolite based catalyst:

Zeolite-based catalysts were investigated through the use of bi/multi-functional systems, composed of zeolites and metal species stabilised on zeolite framework (USY/FAU). **IST** prepared and characterized samples of initial and optimised Ni-zeolite catalysts. All catalysts were based on ultra-stable FAU structure (USHY form), taking into account the good resistance of this particular structure to water vapour presence, at high temperature. Ni was introduced by incipient wetness impregnation and Ni content varied between 2 and 30 wt.%.

Different parameters were studied, including: Ni content, addition of Ce (activity and selectivity promoter) and introduction of alkaline (Cs, Na) and alkaline-earth (Mg) cations. Different zeolite properties were also evaluated: acidity/basicity (sodium content), the influence of the presence of extra-framework aluminium species, global Si/Al ratio type of structure compensating cation (Na, K, Mg, Cs). Catalysts were characterised by N_2 adsorption, DRS-UV-Vis spectroscopy, hydrogen temperature programmed reduction (H2-TPR), transmission electron microscopy (TEM), XRD (X-Ray diffraction) and thermal catalysis (considered a characterisation technique for all Pathway A, DBD plasma prepared catalysts).

The performances of the prepared catalysts were evaluated under *thermal catalysis*, by calculating the obtained CO_2 conversion and CH_4 selectivity. It is important to refer that the only secondary product found in the reactor effluent was CO, the carbon molar balances closing at about 97-102%. Catalytic tests were carried out in a flow tubular reactor in Pyrex, under atmospheric pressure. Before the reaction, catalysts were pre-reduced in-situ at 470°C during 1h, under 80%H_2/N_2 stream, with a total gas flow of 250 cm^3 min^{-1}. For the reaction, a mixture of hydrogen, carbon dioxide and nitrogen was fed into the reactor at gas hourly space velocities (GHSV) of 43000 h^{-1}.

The first optimized catalysts contained 14 wt.% Ni in a USHY zeolite with a global Si/AL ratio of 40, ion-exchanged with Na. 15 and 30 wt.% of Ce was added to the catalysts. Results of *thermal catalysis* are presented on Figure C-1.

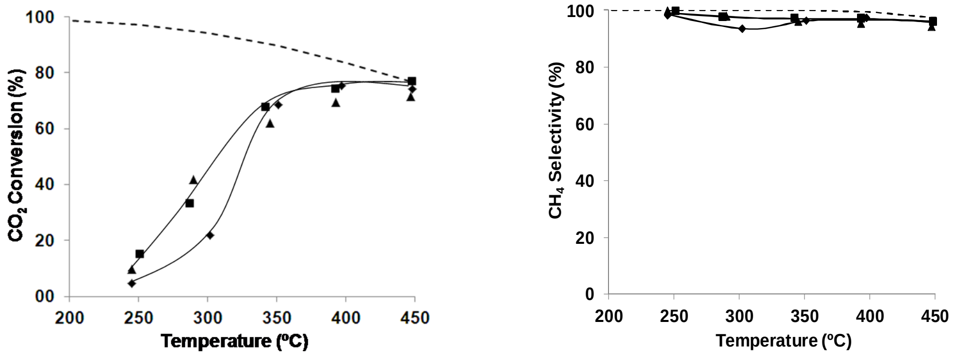


Figure C-1: (a) Evolution of the CO_2 conversion and (b) methane selectivity with temperature for the 14%NiNaUSHY (♦), 15%Ce14%NiNaUSHY (■) and 30%Ce14%NiNaUSHY (▲) catalysts, tested under thermal catalysis. Thermodynamic values: dashed line.

A second set of optimised catalysts was prepared, using Cs instead of Na as alkaline promoter. Mixtures of Na-Cs ion-exchanged catalysts were also tested. Results of thermal catalysis are depicted on Figure C-2.

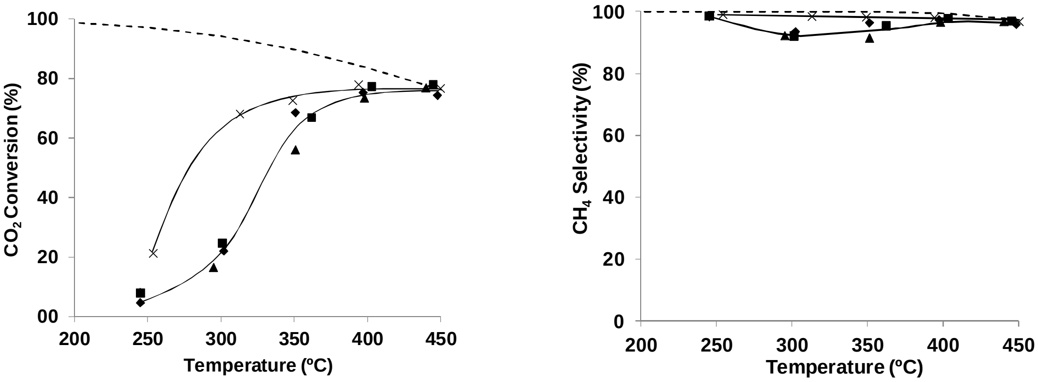


Figure C-2: (a) Evolution of the CO_2 conversion and (b) methane selectivity with temperature for the 14%NiNaUSHY (♦), 14%NiNaCsUSHY (■), 14%NiCs (▲) and 30%Ce14%NiCsUSHY (x) catalysts, tested under thermal catalysis. Thermodynamic values: dashed line.

For all DBD plasma catalysts (Pathway A) the testing under conventional thermal heating was considered, from the very beginning of the project, a reliable evaluation method of the catalytic activity, as, in fact, it was possible to roughly correlate the catalytic behaviour under thermal and plasma induced catalysis. This was performed for **IST** and **IREC** catalysts, at IST catalytic test unit. This procedure allowed the catalytic evaluation of a large number of parameters, also reflected in the final results at UPMC (WP3).

Mesoporous catalysts:

Mesoporous nickel-ceria-zirconia catalysts were obtained by replication method of mesoporous silica. Mesoporous silica was synthesised under acidic conditions using a non-ionic triblock copolymer surfactant (EO20PO70EO20, Pluronic P123 from BASF) as a structure-directing agent.

A SBA-15 (two-dimensional hexagonal with p6mm symmetry mesoporous silica) was obtained and used. SBA-15 was impregnated with solutions of nitrate salts of the metal precursors. After calcination at 800ºC, samples were hot-etched using NaOH in order to remove the silica template, to attain the mesoporous nickel-ceria-zirconia catalysts. The metal ratio $[Zr^{4+}]/([Zr^{4+}]+[Ce^{3+}])$ was varied between 0 to 0.2, and the nickel content

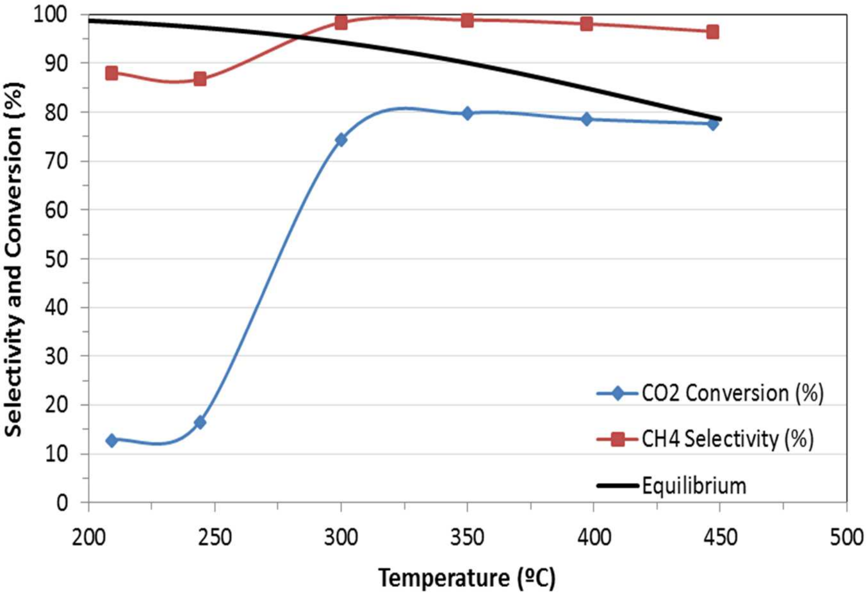


Figure C-3: CO_2 hydrogenation to methane, obtained under conventional heating, for mesoporous 15 wt.% Ni – $Ce_{0.9}Zr_{0.1}O_2$ catalyst.

between 5 and 15%. Samples were prepared, characterised and sent to IST (to thermal catalysis characterisation) and to UPMC for DBD catalysis evaluation. The catalyst had high surface area, with BET values ranging between 120 and 150 m^2/g. XRD measurements showed that all the samples crystallise on the fluorite structure (cubic) and no evidences of NiO formation was found. Raman also corroborates the nickel (Ni^{2+}) insertion on the ceria lattice, which can be partially ejected as metallic nickel (identified by XRD) after the pre-reduction treatment, in agreement with H2-TPR results.
Thermal catalysis carried out at IST demonstrates the high conversion rate at low temperatures (300ºC) and the high selectivity (higher than 98%). Also, stability tests carried out during 10h, at 300ºC or 400ºC showed virtually no degradation of the catalyst. As depicted from figure C-3, the highest conversion was obtained with 15 wt.% Ni – $Ce_{0.9}Zr_{0.1}O_2$ catalyst and this composition was chosen for up scaling. A batch of 100 g was prepared and sent for testing at CEA.

Stability tests (Figure C-4) showed virtually no degradation of the catalyst, which corroborates that the stabilization at high temperature inside the template can lead to nanocrystals with stable performance under the operation conditions without sintering.

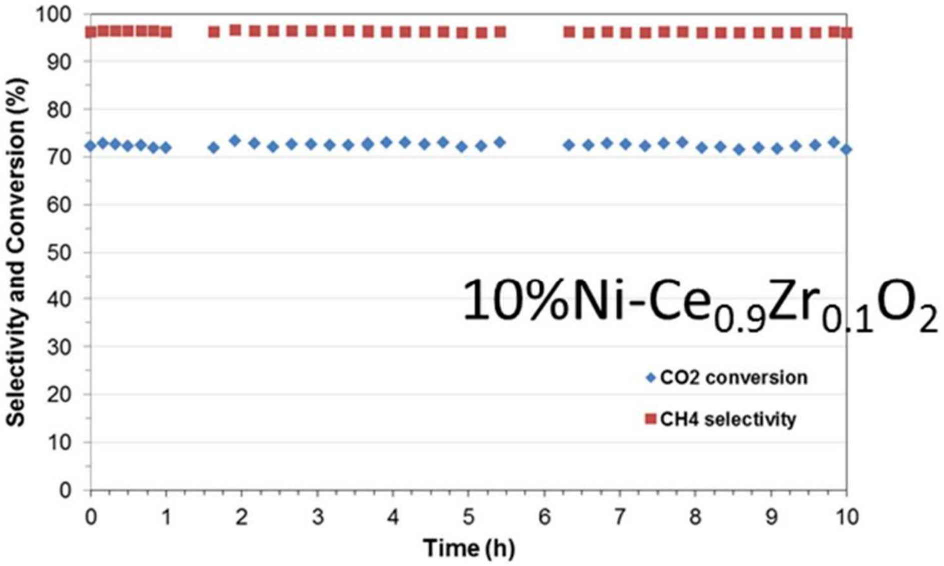


Figure C-4 : Stability test at 400°C (conventional heating) of 10%Ni-$Ce_{0.9}Zr_{0.1}O_2$

Pathway B:

Zeolite based catalyst:

Two different zeolite structures were used: MFI (ZSM-5), and FAU (Y zeolite) also used as methanation catalysts support, in the present study, both with 5wt.% Fe.
For all Fe/zeolite prepared samples, some common conclusions can be obtained from characterisation:

- XRD results suggest good dispersion of iron species on the zeolite structure; no FexOy species were detected in the catalysts, prepared using $(NO_3)_3.9H_2O$ precursor; no modification of cristallinity was detected;
- Nitrogen adsorption/desorption measurements do not indicate pore blockage due to introduction of the metal;
- The assessment of the distribution of iron species inside the zeolite structure shows:
    - a heterogeneous distribution of iron species in samples prepared via impregnation techniques, while in ion-exchanged samples only one reduction process was observed;
    - this evaluation should be complemented with the results of CH_4 to MeOH activity, under DBD plasma conditions (UPMC, WP3).

Until the end of WP2, it was not possible, to get insight of the role of the different iron species detected on Fe-zeolite catalysts, mainly due to their poor catalytic activity (WP3).

Mesoporous catalysts:

Mesoporous Cu-Fe-ceria-zirconia, with SBA-15 as hard template, was prepared for Pathway B, using the same synthetic route previously described for the preparation of catalyst for the pathway A, but using copper and iron nitrate salts as precursors. It was prepared 15% Cu, 15% Fe, 15% Cu-Fe samples ($Ce_{0.9}Zr_{0.1}O_2$/SBA-15), using the same composition as the optimized for CO_2 hydrogenation. Prepared samples were directly sent to UPMC, to be tested in plasma-induced catalysis reaction (WP3).

● Development of advanced photo-catalysts for the photo anode (Pathway A CO_2 to CH_4) IREC

IREC was focused in the synthesis of photo-anodes units based on nanostructured titanium oxide (TiO_2) and tungsten oxide (WO_3), prepared over transparent conductive substrates (glass coated with fluorine tin oxide (FTO)). The optical absorption of TiO_2 in the visible solar spectrum has been implemented through a surface modification of TiO_2 nanostructures by thermal treatment in a reductive medium (ammonia or hydrogen).

The synthesis procedure of titanium dioxide nanorods uses titanium butoxide as titania precursor. It was introduced in a teflon-lined stainless steel autoclave, together with a piece of FTO glass, with the FTO side against the wall, at 200ºC for 4 hours. In order to get electrical access to the FTO, substrates were partially covered with Kapton tape. The as-prepared samples were cleaned by sonication in water, dried under nitrogen stream and finally treated at 450ºC in air in order to remove any residual from the synthesis procedure.

Titania rutile nanorods were also surface modified by heat treatment under ammonia atmosphere at different temperatures, aiming at improving PEC performances by nitrogen doping. Figure C-5a shows that ammonia treatments increased the photocurrent density up to 2-fold with respect to bare TiO_2 (NH_3−300 °C). However, IPCE measurements (Figure C-5b) revealed that the increasing photocurrent density was mainly due to a more efficient photocurrent response of the UV part of the spectrum and to a lesser extent in the bandgap region also.

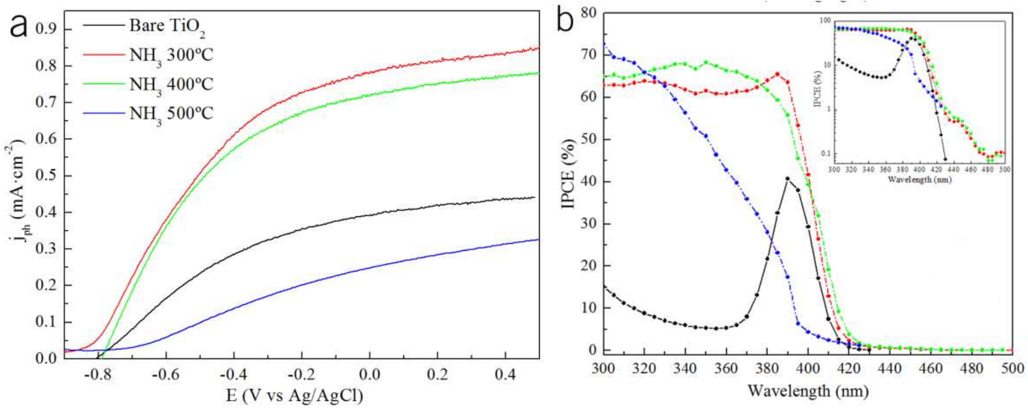


Figure C-5 : Voltammogram under AM 1.5 illumination (a) and incident photon-to-electron conversion efficiency (IPCE) taken at 0 V vs Ag/AgCl (b) of the ammonia-treated samples at 300, 400, and 500 °C together with the non-treated sample.

Finally, due to the limited absorption of TiO_2, WO_3 photo-anodes were synthetized using pulsed laser deposition. For the synthesis a pure WO_3 sputtering target from Goodfellow® was vaporised using a

KrF laser and the material was deposited over the glass/FTO substrate heated at 400ºC. Then, the layer is recrystallized during synthesis, providing an excellent performance as photo-anode, providing almost 2 mA cm^{-2} under 1 sun illumination.

● Development of photo-catalysts for the Pathway B CH_4 to CH_3OH (IST & IREC)

Zeolite based catalyst:

IST work consisted in the preparation of modified Beta (BEA structure) zeolites, presenting several levels of aluminium removal from the framework, obtained by (i) controlled dealumination followed by hydrothermal treatments, (ii) acid treatments and (iii) desilication, in order to obtain different concentration and types of silanol (SiOH) groups. Furthermore, different photoactive metal species (V, W, Mo) containing samples were also prepared.

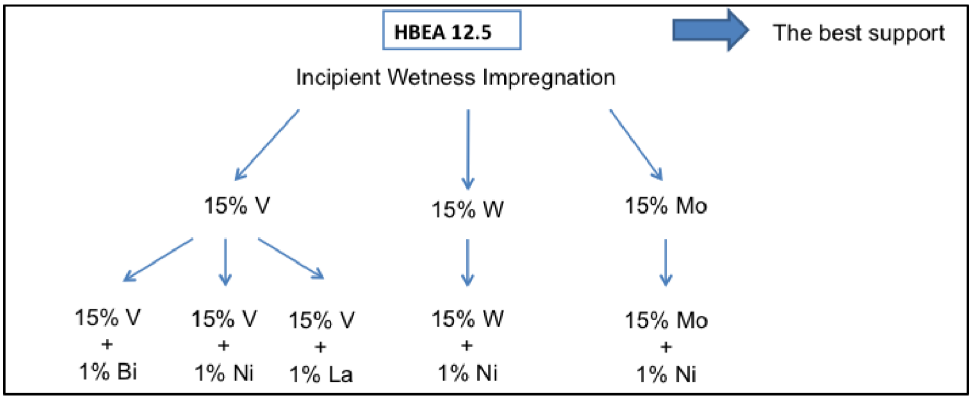


Figure C-6 : Metal containing BEA zeolite photocatalysts for Pathway B

Parent Beta zeolite catalysts, in acidic form, were ion-exchanged into the Na form. Different samples, with different Si/Al were used: Si/Al = 255; 32.5; 12.5)

HBEA (Si/Al = 32.5) was impregnated with 15%wt of Zn, under acidic and sodium forms. After first tests (at **IREC**), it was verified that the best support was HBEA (Si/Al= 12.5). Over this sample, different metals (V, Bi, Ni, La, W, Mo) were introduced (Figure C-6). Final versions of BEA-based catalysts, containing Ni and V, W or Mo were sent to **IREC** to be tested under photo-catalysis for the partial oxidation of CH_4 to MeOH (WP3).

Mesoporous catalysts:

Mesoporous tungsten oxide (WO_3), was prepared at **IREC** by replication technique of KIT-6 silica template. Additionally, this mesoporous WO_3 were doped with metals to enhance electron-hole separation and avoid charge recombination. La-doped WO_3 /was obtained by adding lanthanum nitrate to the precursor of WO_3 following the same procedure of pure WO_3 synthesis. M-doped WO_3 (M=Fe, Cu and Ni) was prepared by impregnation. The optimized nickel and lanthanum loading was found to be 1%.

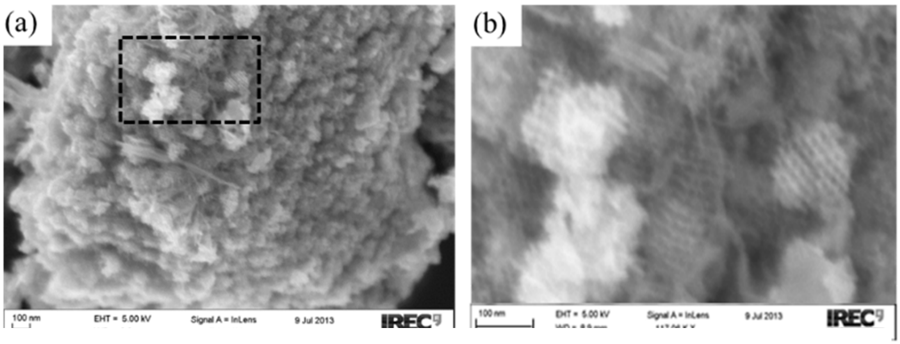


Figure C-7: SEM image of (a) mesoporous WO_3 and (b) image extracted from the area marked by the dotted line square.

KIT-6 mesoporous silica template, with three-dimensional cubic Ia3d structure, synthesized in acidic conditions using a mixture of Pluronic P-123 and 1-butanol, consists of two set of mesopores connected by micro-bridge channels. Ordered mesoporous WO_3 was prepared by incorporating as-prepared KIT-6 silica under stirring. After calcination, WO_3 inside the hosting silica material was obtained. The obtained material was then suspended under stirring in a 10 % wt HF solution to remove the KIT-6 silica template. The mesoporous WO_3 catalyst was separated by centrifugation, washed sequentially with water and ethanol and dried at room temperature.

Bismuth-based nano-catalysts:

Other types of materials forecasted in the DoW were prepared, such as Bi_2WO_6 and $BiVO_4$. Indeed, the latter is a very promising oxide for selective oxidation reactions as, according to its band edge positions, its valence band exhibits a more negative potential than TiO_2, WO_3 and Bi_2WO_6, which makes this material less oxidizing In principle, higher selectivity into CH_4 can be expected, with less CO_2 formation in oxidation processes.

Nanoparticles of Bi_2WO_6 or $BiVO_4$ were prepared by mixing the corresponding amounts of $Bi(NO_3)_3 \cdot 5H_2O$ and $Na_2WO_4 \cdot 2H_2O$ or $NaVO_3$ dissolved in glacial acetic acid. The resulting suspension was transferred into a Teflon recipient inside of stainless steel autoclave, where a hydrothermal treatment was performed at 140ºC for 20 hours. After filtration and thermal treatments, prepared catalysts were characterized by UV-Vis, BET, XRD and SEM. Results show that the most promising material is $BiVO_4$. Then, $BiVO_4$ doped with Mo and W was synthetized, resulting in higher photoactive materials but losing selectivity.

According to the obtained results in the photocatalytic partial oxidation of methane to methanol, two extreme situations are presented. By on hand, Bi_2WO_6, which is a more photoactive material with relatively high oxidizing potential, leads to better conversion values at expenses of lower selectivity. $BiVO_4$, on the other hand, is more selective but less oxidizing, so probably it is a more proper candidate for this kind of reaction.

● **Development of advanced catalysts for electro-catalytic reduction (OMNIDEA)**

The novelty of the strategy followed in CEOPS to achieve electrochemical reduction of CO_2 into methane was to develop bimetallic Zn-Cu catalysts and bimetallic Ni-Cu catalysts and to couple these catalysts with ionic liquids-based electrolytes with high solubility for CO_2. Zn was chosen to evaluate the capability of this metal in promoting the first mechanistic steps of CO_2 reduction, due to its known selectivity for CO production. Nickel was chosen for its known low hydrogen overvoltage to improve the efficiency of water electrolysis. It was decided to focus the work on the preparation of cathodes based upon copper foil substrates.

Zinc-copper bimetallic cathodes:

Work was carried out to investigate the preparation conditions that yield reproducible compositions and morphologies. The compositions of Zn–Cu alloy coatings were determined by EDS measurement. It was observed that all coatings are mainly composed of Zn and Cu elements except a small amount of O atoms due to the partial surface oxidation.

Several cathodes were prepared with compositions ranging from pure copper (0% atomic Zn) up to pure zinc (100% atomic Zn) and were characterized by cyclic voltammetry under high pressure (30 bar), at 45ºC. Cyclic voltammetry was useful to compare the different cathodes among themselves. The current densities give an indication of the magnitude of all the reactions that occur at the cathode and the potential of onset currents are a measure of the reversibility of the system. As the potential of onset current becomes less negative, the lower will be the energy that is necessary to supply to the system for an electrochemical reaction to occur. This information allowed the preliminary selection of the best cathodes, prior to the tests carried out under the scope of WP3.

It was observed that all these cathode materials were active towards CO_2 reduction, showing the catalyst Zn:Cu (80:20) at.% significantly higher currents than the pure metals.

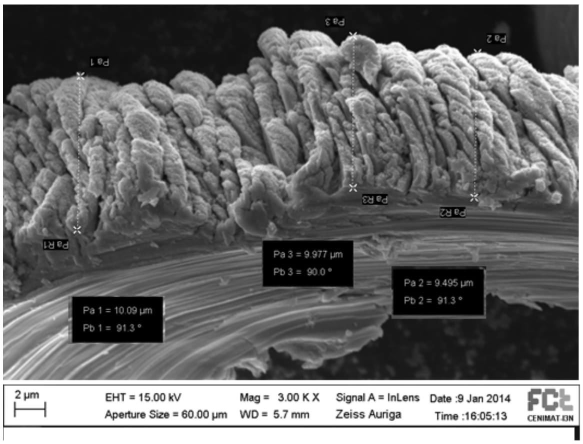


Figure C-8: Zn:Cu 5:95% atomic, catalyst SEM analysis of the cross-section of the electrodeposit

Nickel-copper bimetallic cathodes:

Work was also carried out to investigate the preparation conditions that yield reproducible compositions and morphologies. The compositions of Ni–Cu alloy coatings are determined by EDS measurement. All the electrodeposits were mainly composed of Ni and Cu elements.

Bimetallic Ni:Cu catalysts were prepared both by controlled potential electro-deposition and current controlled electro-deposition, current controlled deposition yielded more reproductive results.

Crystalline structures of the bimetallic Ni-Cu electrodeposits were determined by X-ray diffraction. The diffraction spectra only showed peaks of copper and nickel. No Ni_xCu_y compounds were detected. Several cathodes were prepared with compositions ranging from pure copper (0% atomic Ni) up to pure nickel (100% atomic Ni) and were characterized by cyclic voltammetry, as described for the Zn-Cu catalysts.

Cathodic curves obtained with cathodes prepared by current controlled electro-deposition showed no significant differences in currents and onset potentials between bimetallic cathodes and pure copper with exception of the Ni:Cu (50:50) at.%, in which the current seems to be suppressed in comparison with pure copper at more negative potentials. However, different purities of ionic liquid was used in the different batches, that seemed to play an important role in the electrochemical reaction, prevent to obtain definitive conclusions about the observed different catalytic behaviour of the Ni:Cu (50:50) at.% atomic catalyst.

Similarly to Zn-Cu cathodes high faradaic efficiencies (> 60%) for methane were obtained specially for the composition Ni:Cu (70:30)% atomic. However, lack of reproducibility of CH_4 production was also observed.

ii) Processes development performed in the WP3:

● **Plasma catalysis process (UPMC & CEA)**

Lab scale reactors implemented at UPMC & CEA

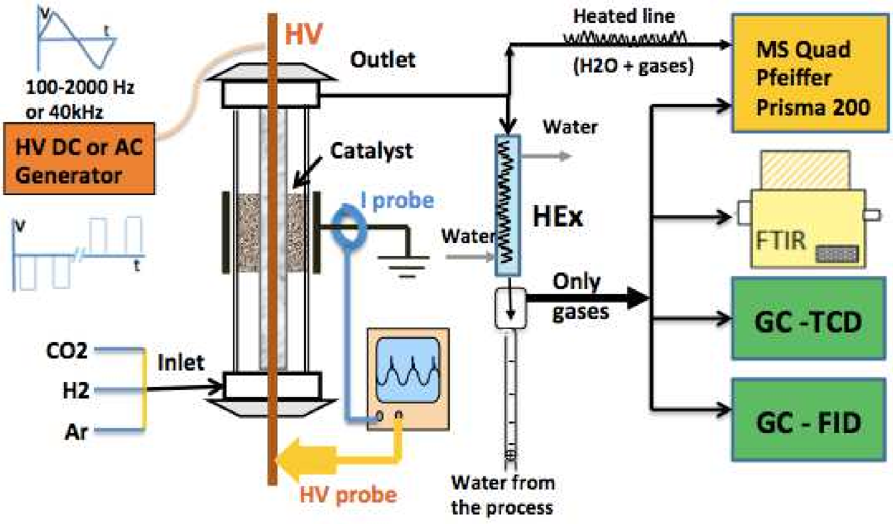


Figure C-9: Scheme of the experimental setup for methane production (UPMC)

UPMC designed and implemented a laboratory scale DBD plasma catalysis reactor in fixed bed configuration, for both pathways, methane and methanol synthesis. The reactor consists of two coaxial tubes with integrated electrodes for the plasma discharge and it can be heated up to 550ºC by an external heat-gun. Figure C-9 shows a scheme of the experimental setup for methane production. The same setup is used for methanol production using FTIR and GC with FID detector for the quantification.

CEA has designed and implemented a lab scale DBD plasma catalysis fluidized-bed reactor. The main characteristics of the reactor are mentioned in Figure C-10. This reactor (in stainless steel) was used up to 500°C.

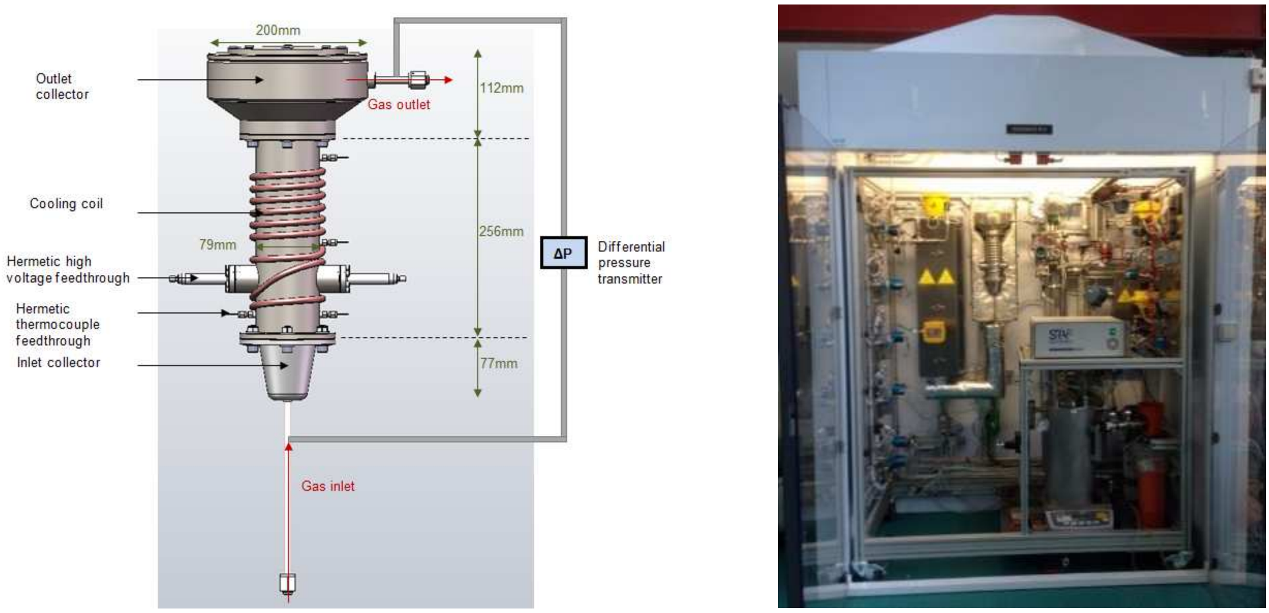


Figure C-10: Overview of the fluidized-bed reactor and of the test bench

It integrates a cooling coil in order to evacuate the heat released by the reactions (cooling by the wall). The surface plasma technology is also integrated into this reactor. The size of the reactor allows a CO_2+H_2 flow of 12.5slm. This reactor was used for both pathways and was integrated to a test bench. The test bench for CEOPS project at the CEA (Figure C-10) is composed of valves and mass flow controllers for each gas (H_2, CO_2, Ar, CH_4, Ar/O_2), a preheater, the reactor, a bursting disc and safety valves (7bar_{eff}), a plate condenser, pressure regulation valves and the gas analyser (µGC).

<u>CO_2 hydrogenation to CH_4:</u>

Fixed bed:

Catalysts in powder form were supplied by IST and IREC. Also, one commercial catalyst was supplied by CEA (IBERCAT, 10%Ni-NiO on Al_2O_3). Before each experiment the catalysts (300mg) corresponding to a GHSV of 20 000 h^{-1} were activated in H_2 flow for 3 hours at the temperature 400°C. The experiments were performed at 20°C, 320°C, 370°C and 420°C, with and without plasma. Typical voltage values used were between 10 to 16 kV at a frequency of 40 kHz. This gives energy in the range of 20 - 80 µJ/cycle, corresponding to a power between 0.8 and 3.2 W.

For the catalyst 15%Ni-$Ce_{0.9}Zr_{0.1}O_2$ SBA-15 (IREC), the experiences under adiabatic (120°C-170°C, without external heating) and isothermal (220°C-420°C with external heating) conditions were performed. The results, (Figure C-11) show a very low (under 1%) production of CO for all temperatures except at 420°C and large amounts of CH_4 and water. This catalyst is active under adiabatic (120°C-170°C, without external heating), with plasma, producing only CH_4 (not CO or other C_xH_y) with conversions of 75 to 90%. Without plasma, with external heating up to 170°C this catalyst is totally inactive.

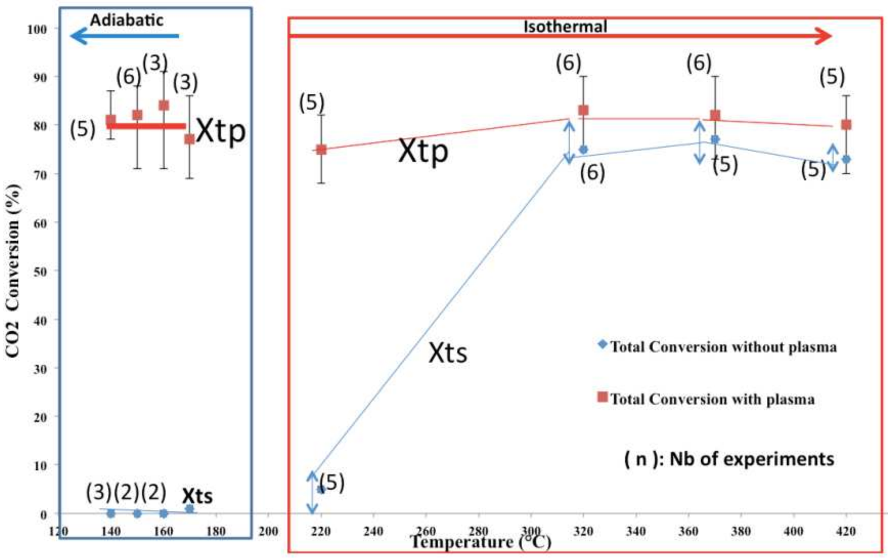


Figure C-11: CO_2 Conversion with(Xtp) and without(Xts) plasma for the catalyst 15%Ni-$Ce_{0.9}Zr_{0.1}O_2$ SBA-15 (IREC)

It was expected an increase of total conversion with the plasma at 250°C- 300°C but not at 140°C and without external heating. For this reason experiments were repeated several times (numbers in bracket) and the effect of the DBD plasma on CO_2 conversion at low temperature was confirmed.

As conclusion, the action of the plasma was pointed out. With all catalysts, an increase of CO_2 total conversion was observed when plasma operates. With some catalysts this action occurs at low temperature 150°C and without external heating, a total conversion as high as 80% was obtained with selectivity to CH_4 formation 100%. In particular all these catalysts contain Ce. Action of Ce should be investigated in cooperation with IST and IREC partners. The key step of the reaction, at this range of temperatures should be the water desorption from the catalytic sites enhanced by the plasma.

Fluidised bed:

The needed quantity of catalyst for the experiments in the fluidized-bed reactor at CEA was around 300g of 200µm catalytic particles. Partners working on WP2 (IST, IREC) could not provide such quantities and were not able to make this size of catalyst. For the experiments, 300g of a commercial Ni-NiO/γ-Al_2O_3 catalyst supplied by IBERCAT were used (10 wt% Ni-NiO/Al_2O_3, BET=169$m^2.g^{-1}$, d=850$kg.m^{-3}$). Before the experiments, the catalyst was reduced inside the fluidized-bed reactor during 6 hours. The temperature was kept at 300°C and the pressure at 3bar. The volume flow was 4slm of a mixture of 50%Ar-50%H_2 which corresponds to a GHSV of 500h^{-1}. The inlet gas mixture consisted of H_2 and CO_2 with a stoichiometric ratio H_2/CO_2=4. Different parameters were studied such as the pressure (from 1.1 to 2.5bar), the temperature (from 280 to 350°C) and the GHSV (from 1250 to 2500h^{-1}).

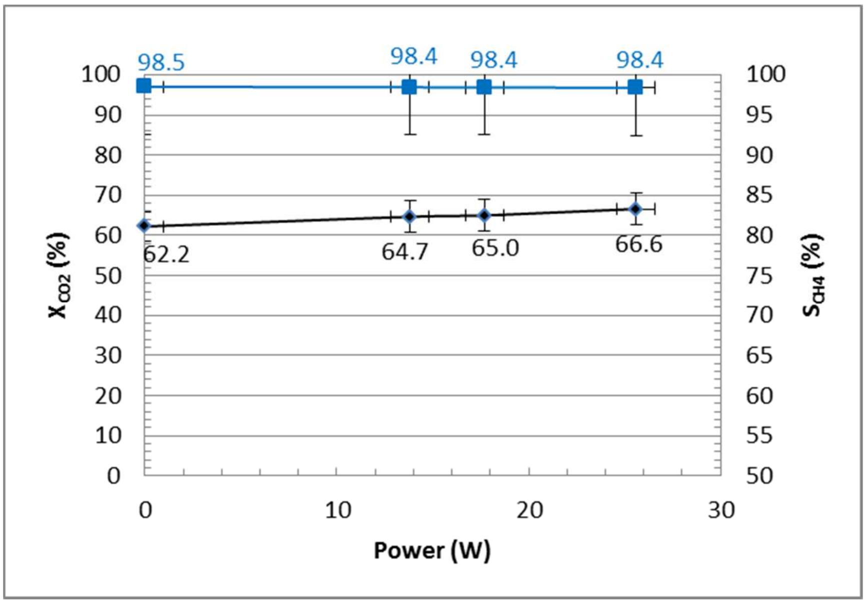


Figure C-12 : Evolution of CO_2 conversion and CH_4 selectivity as function of injected power in the plasma at 330°C for a total inlet gas flowrate of 3.75slm at 4.8bar_{abs}

The evolution of CO_2 conversion and CH_4 selectivity as function of injected power in the plasma is given on Figure C-12. At set residence time, thermal boundary conditions of the bed and pressure, an increase of the injected power in the plasma leads to an enhancement of the CO_2 conversion into CH_4. Even though advanced catalysts were not tested. These results confirm the plasma effect on the CO_2 conversion. Furthermore CEA demonstrated the integration of the DBD surface plasma into a fluidized bed reactor and a good stability of the plasma at 5 $bar_{abs.}$

Partial oxidation of CH_4 into CH_3OH:

Partial oxidation of methane to methanol at atmospheric pressure was investigated in the same experimental set-up as for the methanation (Figure C-13). Catalysts were introduced to study the effect of the catalyst in the plasma zone. The feed gas was a mixture of methane and oxygen. Some tests were performed with Argon on the line (60% total flow). The partial oxidation of methane was separately performed with a CH_4/O_2 molar ratio of 3:1. 100-200 mg of catalyst were placed in the annular space of the discharge zone. The tests were conducted at three temperatures: 20, 150 and 200°C and a total flow rate of 160sccm (with argon 260). The product analysis was done with the use of two gas chromatographs (GC/TCD) and (GC/FID) and a FTIR. Outlet gases of the reaction were cooled down to 1-3°C in order to collect liquid products.

Under plasma conditions, when the discharge was switched on, temperature increased slowly till 150°C. However the amount of the liquid collected was very low. In order to recover a sufficient amount to make a balance, it is necessary to operate for at least 1 hour. In 1 hour experiment nearly 0.3ml of liquid were collected. Direct conversion of methane to methanol by partial oxidation in a DBD reactor has a poor yield of about 2% which is less than the expected economical yield of about 10%. DBD plasma reactor was proposed as a promising approach, due to strength of the electrical energy which can break C-H bonds of methane.

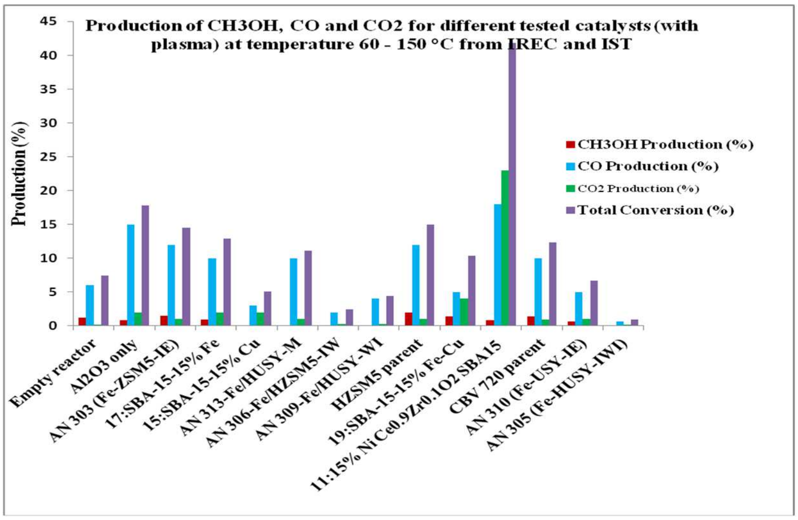


Figure C-13: Comparison between different catalysts tested with plasma of the total conversion and CH_4, CO and CO_2 production

● Photo-activated catalysis process (IREC)

PEC reactor for pathway A (CO_2 to CH_4)

IREC designed and implemented a PEC reactor for the conversion of carbon dioxide to methane, with a size of electrodes of 10 cm^2. The test bench also allows the adjustment of the photon flux of the solar simulator and to introduce and external polarization by a potentiostat (Figure C-14).

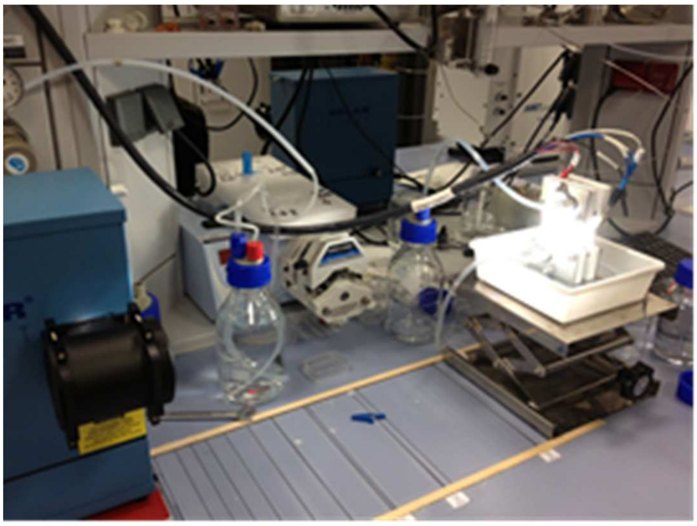


Figure C-14: IREC test bench for photoelectrochemical reactor

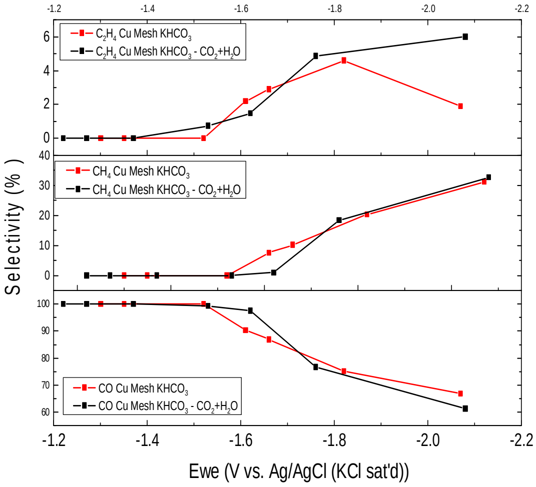


Figure C-15 Selectivity to C_2H_4, CH_4 and CO for different cathode polarizations, with CO_2 dry or humid as inlet gas.

As photoactive material, it has been tested photoanodes developed in the WP2 based on nanostructured TiO_2 and WO_3 prepared over transparent conductive substrates (glass coated with fluorine tin oxide (FTO). In this cell, it is also required a cathode, which should be copper based for optimizing methane formation. The cathode was composed of electrodeposited copper or a pure copper mesh, using $KHCO_3$ or $NaHCO_3$ as catholytes. Results show a higher carbon dioxide conversion when using $KHCO_3$ as well as a higher selectivity to methane when using a pure copper mesh. Using copper mesh and $KHCO_3$ as catholyte, it was optimized carbon dioxide conversion by prehumidification of the inlet flow of CO_2 into the cell, without a loss of methane selectivity (Figure C-15), which is in the range of 20-30% for polarizations of -1.8 to -2.0 V vs Ag/AgCl(reference electrode). This allows to quantify the energetic requirements for the PEC conversion, that will range between 1.2 – 1.5 V under illumination when using TiO_2, and higher than 2V for WO_3.

Photocatalytic reactor for pathway B (CH_4 to CH_3OH)

IREC implemented a photocatalytic reactor setup for the partial oxidation of methane to methanol, to evaluate the catalysts within WP2 (from IREC and IST).

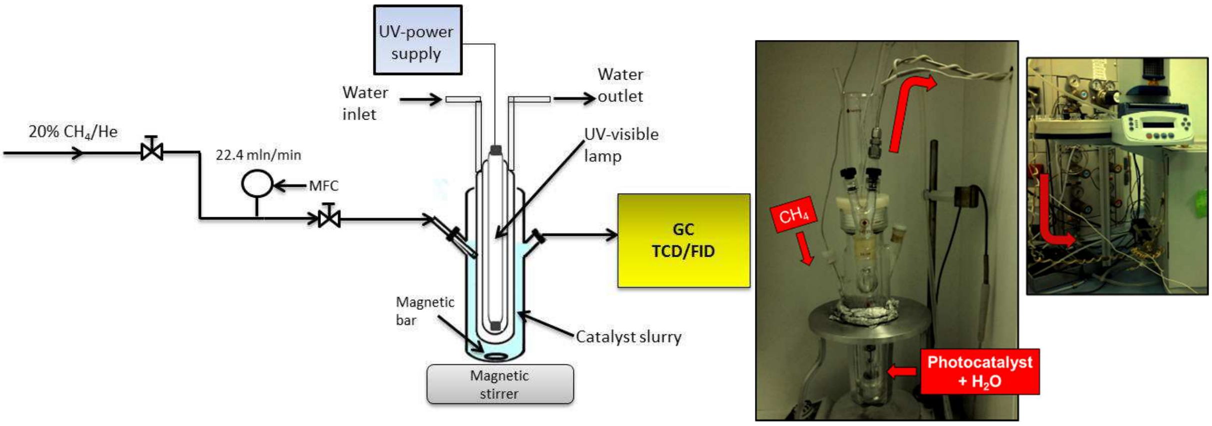


Figure C-16: Scheme of the photocatalytic reactor (left) and bench test at IREC (right)

UV irradiation of water at 185nm leads to the generation of hydroxyl radicals by photolysis. Free hydroxyl radicals can activate methane, so methyl radicals are formed. A series of subsequent reactions involve the production of methanol, ethane, CO_2 and other by-products.

Table C-1: Results on productivity rates, methane conversion and selectivity to methanol, for some selected samples

	Rate (μmol g^{-1} h^{-1})				
	CH_3OH	CO_2	C_2H_6	% Conversion	% Selectivity
WO_3	16.8	49.0	5.7	1.9	23.5
WO_3-1%La	31.0	32.7	3.0	1.7	46.5
WO_3-1%Ni	11.0	19.3	1.3	1.4	46.0
$BiVO_4$	21.0	17.7	2.3	1.1	51.2

Figure C-16 right shows some of the most significant results obtained in the photocatalytic reactor. First, mesoporous WO_3 (IREC) was selected as reference photocatalyst since it has a moderate oxidizing power. However, after 2h of reaction, it was observed (for WO_3) a self-reduction process due to the energetic position of the conduction band, which is not able to transfer the photogenerated electrons for hydrogen production. To solve this, the use of electron scavengers (like Fe^{3+}), doping (La/WO_3) or p/n junctions (like WO_3/NiO) are required. When using electron scavengers, the production rates are highly favored but the selectivity to methanol is decreased due to a parallel photo-phenton process which favors an overoxidation of the methanol formed.

Alternatively to WO_3, $BiVO_4$ has an adequate position of the valence and conduction bands. Additionally, despite a moderate conversion rate, the selectivity is relatively high, which can be further improved by the addition of nitrite in the reactant solution. For $BiVO_4$ based photocatalysts, several attempts have been done to dope either with W or Mo, resulting in higher photoactivity (%conversion) but losing selectivity.

● CO_2 electroreduction process (OMNIDEA-NOVA)

Design and construction of the CO_2 electro-catalytic reduction reactor

During the project, three types of high-pressure electrochemical cells were designed and built:
(1) a one-compartment test-bed for fast comparison of the performance of catalytic cathodes and ionic liquids for carbon dioxide reduction to methane, including a sacrificial zinc anode.
The simple design allowed a rapid construction, and it was used for intensive testing and optimisation of carbon dioxide reduction. It allowed proof of methane electrochemical production from CO2, using an ionic liquid as an electrolyte, a result that had not been reported before.
(2) a complete electrolyser with recirculation of the saturated ionic liquid electrolyte, with two compartments separated by a membrane. The design used a tubular configuration, with an inner anode chamber separated from an outer cathode compartment by a tubular proton exchange membrane.
(3) As the membrane suffered significant deformation during operation, a radical rethinking of the design led to a new cell with a membrane planar configuration. It accommodates 6 x 6 cm electrodes, a planar ionic exchange membrane between electrodes and it has a pressure rating of up to 100 bar. View ports were also incorporated allow the observation of the behavior of the electrodes during operation.

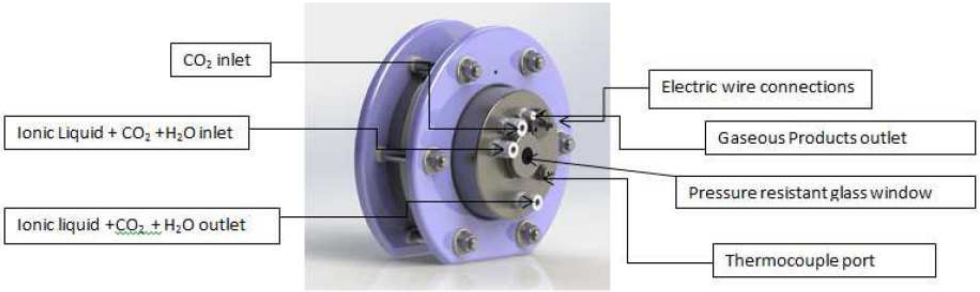


Figure C-17 : General view and cross section of planar high-pressure electrolyser

CO_2 electro-catalytic reduction tests

For the evaluation of the copper based electrodes developed in WP2, experiments carried out in test-bed (1). Methane was produced production with selectivity near 100% and with faradaic efficiencies better than 60%. Ionic liquids 1-Buthyl-3-methylimidazolium tetrafluoroborate (BMIMBF4) and 1-Ethyl-3-methyl-imidazolium triflate were used as electrolytes, and water was added in significant amounts. Methane production was found dependent of the impurity profile of different ionic liquid batches. Thus, methane seems to be produced by a combined mechanism of heterogeneous and homogeneous catalysis due to impurities present in commercial batches of ionic liquids.

● Selection of the most efficient process for each pathway

An evaluation grid was constructed in order to compare the electro-catalytic processes in term of efficiency (conversion rate and selectivity), electricity consumption, and scalability. The following process was selected for each pathway:

<u>Pathway A:</u>

The DBD plasma was selected which involved UPMC and CEA

For the catalyst, one from IREC (mesoporous Ce-ZrO_2-Ni) and one from IST (zeolite based with Ce + alkaline metal) was up-scaled for the evaluation of the process in fluidized bed.

<u>Pathway B:</u>

The photocatalysis process was selected which involved IREC.

For the catalyst, one from IREC (WO_3-La) and one from IST (HBEA Ni-W) will be up-scaled for the evaluation of the photocatalytic reactor.

iii) Implementation of prototype reactors and their performance assessment in a test bench:

● Fluidized bed DBD plasma catalysis reactor for pathway A

The prototype reactor for pathway A is a DBD plasma fluidized bed reactor, in which the methane production is performed:

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \qquad \Delta H°_{298K} = -165kJ/mol$$

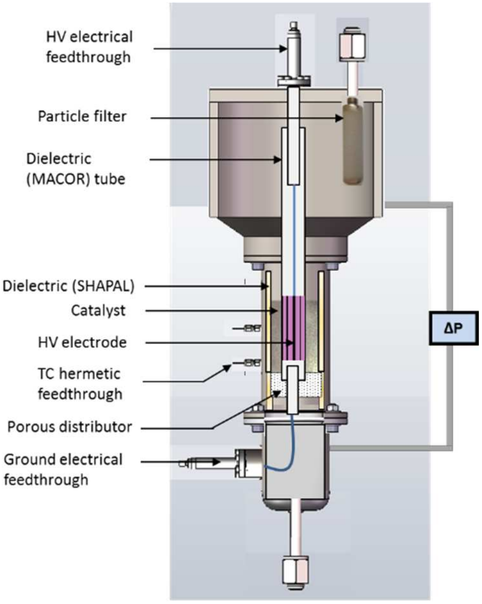


Figure C-18: Sectional view of the prototype DBD plasma reactor.

The main parameters for the tests are the reactor cooling temperature [200- 350°C], the gas outlet pressure [0-4 bar_{abs}], and the inlet gas flowrates of hydrogen and carbon dioxide [respectively: 0-10 and 0-3slm]. CEA was responsible for DBD plasma fluidized-bed reactor design, taking into account the different issues of fluidization and surface DBD plasma technologies. The reactor, made of stainless steel, was designed to work at a temperature up to 400°C and a pressure up to $4bar_{abs}$ (Figure C-18)

The reactive part is composed of assembled components related to DBD plasma catalytic fluidization. Contrary to the previous plasma fluidized reactor developed for WP3, the prototype fluidized bed reactor has an annular geometry in order to increase the ratio plasma surface over catalyst volume. The annular space, which width can be adjusted from 5 to 15mm is filled with catalyst (40-120g). Inside the reactor tube, at the center, is inserted a MACOR tube (in purple on the figure C-18) including the two electrodes (high voltage and ground electrodes) needed to generate a DBD plasma. The high voltage (HV) comes from the top and passes through the reactor *via* a hermetic electrical feedthrough whereas the counter electrode is connected to the ground at the bottom of the reactor. The branches of the HV electrode are located on the external surface of the central MACOR tube. The electrodes height is equivalent to the bed height. The dielectric material between the high voltage and the ground electrodes is MACOR. An alumina tube is inserted between the catalytic bed and the metallic wall of the reactor to avoid electric arc due to the

DBD plasma ignition in the reactor. The wall of the reactor is cooled by an oil circulation, generally at a temperature of 300°C.

IST catalyst: 30%Ce 20%Ni Cs CBV780

Different synthesis methods were investigated in order to meet the fluidization requirements. Catalyst reshaping at the required particle size have been obtained by making extrudates of catalyst in alumina gel, followed by gridding and sieving of the particles to the required particle size. The ratio catalyst/alumina in the final mixture was about 30%/70%. Compared to the initial nanometric catalyst, the scaled-up catalysts are less efficient, which was expected because the ratio of catalyst on alumina is only 30%. The catalyst synthesized showed quite satisfying catalytic performances in terms of CO_2 conversion (at 1atm, 70% at 350°C compared to 80% with the initial catalyst) and CH_4 selectivity (close to 1).

Some tests performed at UPMC showed an effect of plasma less noticeable with the reshaped catalyst compared to the results obtained with the one optimized in the WP2 at the nanometric size. 350 g of catalyst was sent to the CEA for the tests in the fluidized bed reactor prototype.

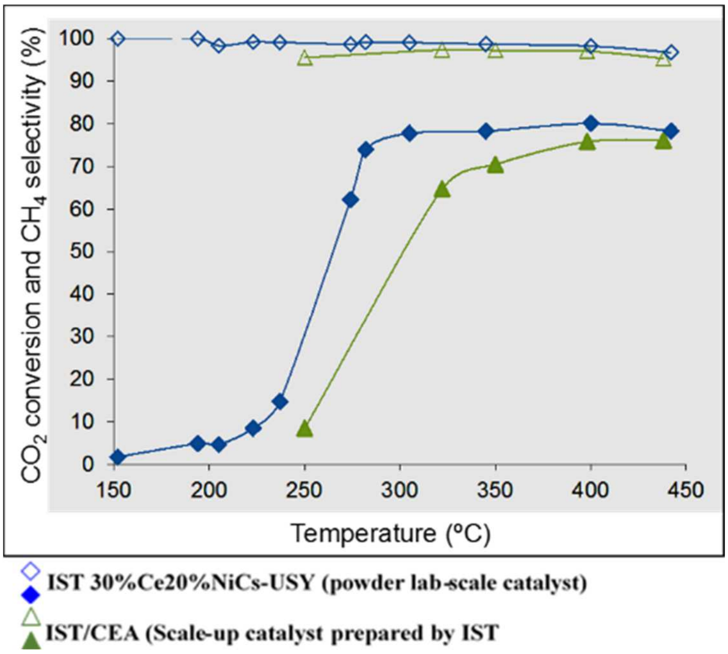


Figure C-19: Thermal catalytic test – performance of the catalyst developed in WP2 and the Reshaped catalyst using alumina gel

IREC catalyst: 15%Ni $Ce_{0.9}Zr_{0.1}O_2$

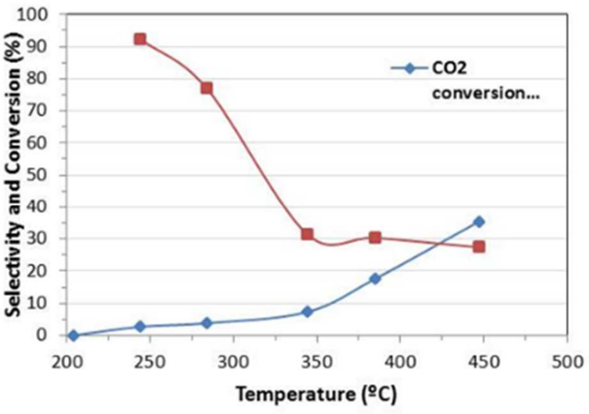


Figure C-20: Thermal catalytic test - Reshaped catalyst using colloidal silica

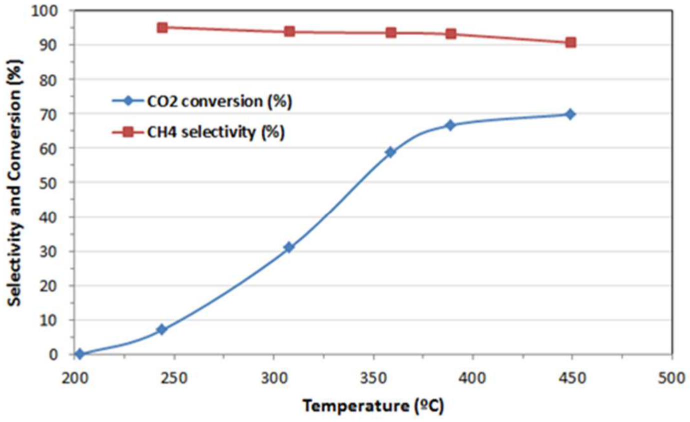


Figure C-21: Thermal catalytic test - Reshaped catalyst using alumina (IST method)

IREC has the same issue than IST on the catalyst manufacturing. Several trials were made at IREC in order to reshape the catalyst. The reshaping process to the required particle size was finally obtained using colloidal silica, but the catalytic performances (both CO_2 conversion and CH_4 selectivity) were lower than previously. Eventually the reshaping **method developed by IST was used.** This new reshaped catalyst was tested at IST and UPMC and shows quite noticeable results. Five batches of 50g were sent to CEA with a ratio catalyst/alumina of 30/70 (one was pre-reduced at 470°C during 2h in Ar/5%H_2), and one of the batches had a higher ratio catalyst/alumina (45/55).

● Photocatalytic reactor for pathway B

The prototype reactor for pathway B is a photocatalytic reactor, in which the methanol production was tested:

$$CH_4 \xrightarrow{h\nu,\, H_2O} CH_3OH$$

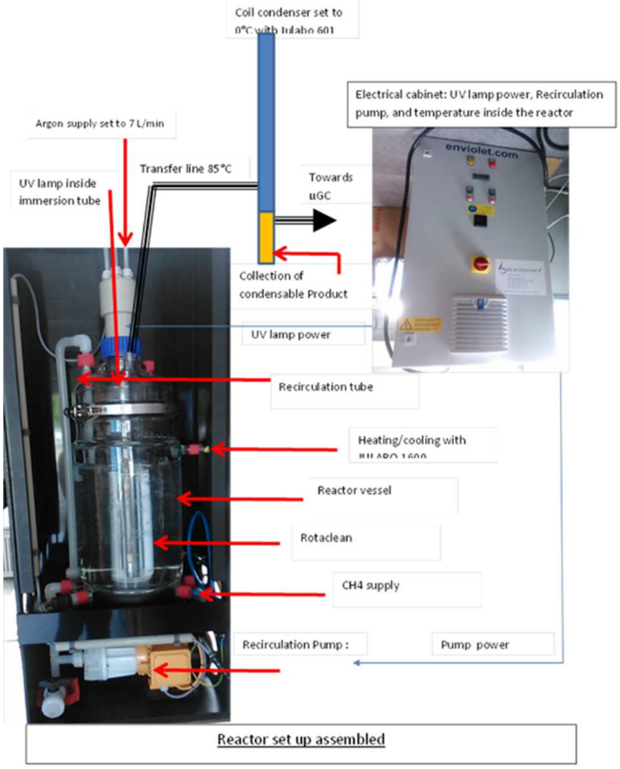


Figure C-22: Photocatalytic prototype reactor

This reaction is a gaseous/liquid catalytic (slurry) reaction. IREC was in charge of the manufacturing of this reactor. The maximum inlet gas temperature is about 80°C and the maximum pressure is 1bar_{abs}. The maximum CH_4 flow rate permitted by the test bench is 5Nl/min. The photo-reactor consists of a cylindrical vessel with a double cooling jacket (see figure 16). The wall of the vessel is in Pyrex. The volume for the slurry is about 11 liters. The gas is injected at the bottom of the vessel. The UV light source is a mercury vapor lamp with a spectra band from 200 to 600 µm. It is immersed in the slurry, on the center axis. It is cooled by an internal argon flow.

The slurry is contained in the annular space between the lamp and the inner vessel wall. It is stirred by a recirculation flow from top to bottom realized by an external recirculating pump. To improve the mixing of the gas and the slurry a "rotaclean" body is moving inside the annular gap by the motion of the recirculating flow.

The temperature of the slurry is controlled by a thermo-regulated ethylene glycol (30%) water mixture circulation in the double cooling jacket of the vessel. This glycol- water mixture is coming from an external Julabo thermo-regulator device. The range of the working temperature is 70-90°C. The gas emerging on the top of the slurry is sent via a temperature controlled pipe (85 °C) to a condenser which wall temperature is fixed below 0°C. The out gas phase is directed to a µ-gas chromatograph in which it is analyze in line. The condensed liquid is collect to be analyzed at the end of the test with a gas chromatograph coupled with a mass spectrometer.

Catalysts preparation for pathway B

The catalyst manufacturing was the same as during the WP2. The catalyst as a size of about 1µm. The composition of catalysts supplied by IREC and IST were the following:

- Catalyst from IREC: the composition is **WO_3/1%La.**
- Catalyst from IST: the composition is **1%Ni15%V/HBEA 12.5.**

Nearly 80 g for each formulation was received at CEA

● Testing and validation of both prototype reactors in a test bench

The flowmeters are working in a special range: 0.5-10Nl/min for argon and hydrogen, 0.15 to 3Nl/min for CO_2, 0.2 to 5Nl/min for CH_4 and 1 to 20Nl/min for argon/oxygen. The H_2 and CH_4 lines are provided with a flow restrictor respectively at 27 and 10Nl/min.

The pressure is regulated by a system of two pressure control valves. The gases are heated to the set point temperature by a preheater and trace heating tapes.

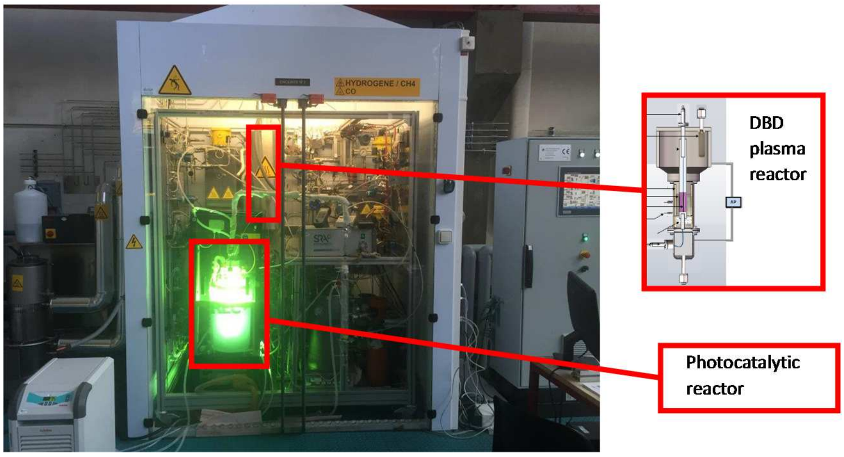


Figure C-23: CEA test bench including both sub-reactors

CO_2 methanation pathway A :

Methanation tests were performed under stoichiometric conditions and with two annular spaces 5mm and 15mm, in which respectively 40g and 120g of catalyst have been inserted. Before test, the catalysts were activated to transform NiO of the catalyst in Ni at 325°C, 3bar_{abs} during 4h with a flowrate of 3slm (respectively 6slm) of Ar/H_2 (80% of H_2). Tests without and with plasma assistance were performed for different flowrate values (3-12slm), pressures (1 to 3.5bar_{abs}) and temperatures (150 to 325°C). The applied voltage during the tests with plasma assistance ranges between 4 and 10kV and the frequency from 100 to 4000Hz, which corresponds to an injected power in the catalytic bed up to about 50W.

With an annular space of 15mm, the mass of catalyst inserted in the reactor is 120g (Volume =150mL). The total inlet gas flowrate is 10slm (GHSV=4000h^{-1}, 1.4 to 2.6Q_{mf}) and the pressure is 3bar_{abs}. The evolution of CO_2 conversion and CH_4 selectivity as function of wall temperature is given in Figure C-24 for IREC catalyst and IST catalyst.

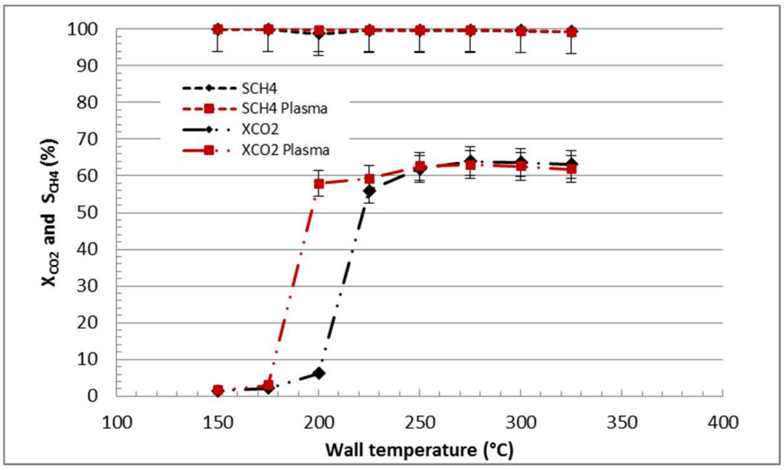


Figure C-24: Evolution of CO_2 conversion and CH_4 selectivity with IST catalyst as function of wall temperature for a total inlet gas flowrate of 10slm at $3bar_{abs}$.

A noticeable effect of the annular bed width is observed **with the IST** catalyst **as soon as 170°C and with a jump of the conversion from 0 to 60% at this temperature!** We can notice that the conversion rate is limited to 62% but it is mainly the height of the catalyst bed. A higher height of bed would have allowed a higher conversion rate.

<u>Partial oxidation of methane to methanol. Pathway B:</u>

The total amount of catalyst was first mixed with one liter of distilled water. This slurry was introduced in the reactor and ten liters of distilled water were added to obtain the final catalyst concentration in the slurry. The conditions of the tests made are summarised in the following table.

	Trial N°1	Trial N°2	Trial N°3	Trial N°4	Trial N5	Trial N°6
Catalyst	IREC	IREC	IST	IST	IST	without
Concentration g/L	0.25	0.5	0.25	0.5	0.5	0
CH4 flow (slm)	0.2	0.2	0.2	0.2	0.4	0.2
Duration (hours)	1h30	1h30	1h30	1h30	1h30	1h30
Temperature of the liquid pool	85 °C	85 °C	85 °C	85 °C	85 °C	85 °C

Table C-2: Results on photocatalytic tests

For each experiment, near 10 ml of condensed phase were obtained. The analysis of each one with a GC/MS revealed that methanol was below the detection limit. At IREC the preliminary test allowed the detection of methanol but at low concentration.

The µGC signal shows only CH4 on the outlet gas phase of the condenser.

Nota Bene: The rate of methanol in the catalyst suspension (liquid phase) was not tested because of the presence of particles in.

- **Conclusion**

Tests were conducted to give some performances data for the two catalytic pathways A and B, which are devoted to synthetize respectively methane from a mixture of CO_2 and H_2 and methanol from methane. The pathway A was done with a gas fluidized bed with a plasma assistance. The pathway B was done with a catalyst slurry percolated with methane with assistance of UV light.
The pathway A has given some noticeable results at low temperature (<200°C) with the IST catalyst. A 60% conversion with >99 % selectivity in methane was obtained, with a plasma power consumption of 32 kJ/mol. The pathway B has not given any production of methanol with both the two catalysts provided by IST and IREC which confirms the challenge of this reaction.

iv) Techno-economic and environmental assessments of the CEOPS concept

- **Techno-Economic Assessment of the CEOPS process**

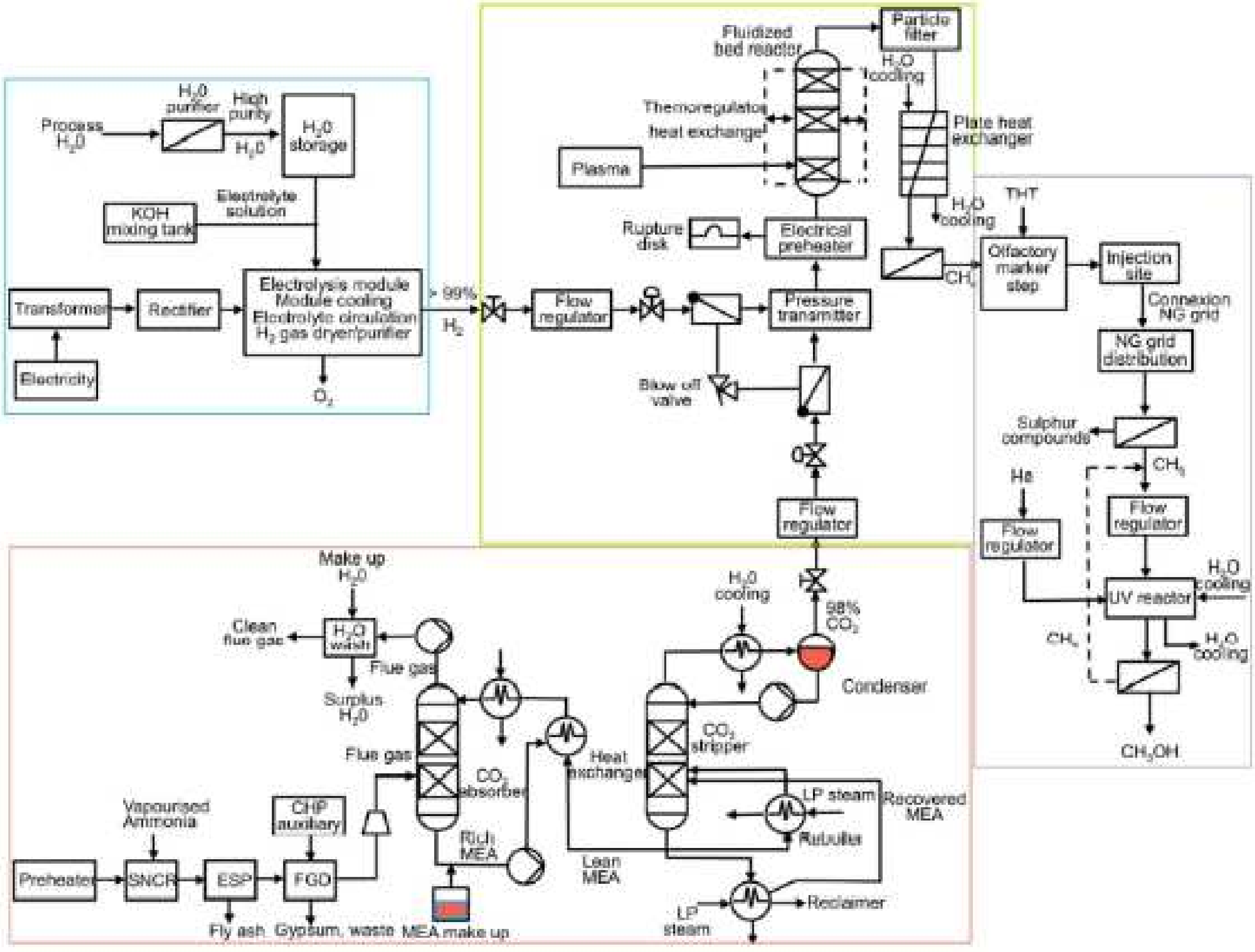


Figure C-25 : Overall CEOPS process flow.

The CEOPS project introduces a novel approach to carbon dioxide trapping and valorization. Such an approach is best suited to the European case in view of the upcoming chronical overproduction of energy as consequence of the development of renewable resources. The CEOPS project innovates with new reaction paths and methods to valorize the energy overproduction by conversion into chemical energy carriers. The objective of the project is to make available competitive methanol and methane products, when compared to the same products derived from fossil fuel resources.

The process flow for CEOPS can be represented on the Figure C-25. It assembles the four technological bricks described in part I: alkaline electrolysis, CO_2 capture with amines, DBD plasma catalysis for CO_2 conversion into CH_4, methane injection into the natural gas network and its partial oxidation into methanol.

The total investment for this capture and transformation facility, including the electrolysis process, is around 969M€. This installation will allow the treatment of 160 tons/h of CO_2. The installation will need a 1500 MW (0.646M€/MW) alkaline electrolyser for stoichiometric feed of the methanation step, implying a constant feed of 225 tons/h of water for a 25 tons/h of hydrogen stream. The operational cost for this installation will be close to 70 k€/h including the hydrogen production (93.9%), CO_2 capture (2.4%), methanation step (1.9%) and partial oxidation to methanol, representing 49% of the CAPEX every year. The production energies per ton of trapped CO_2 are slightly higher (+5-10%) than the classic methanol production method (syngas and Lurgi process) but lower than the green methanol production from CRI at the Olah plant in Iceland (-9%). On the capture department, the MEA step lowers by 90% CO_2 emissions, the methanation step 85% of the initial flow and Pathway B only 81%.

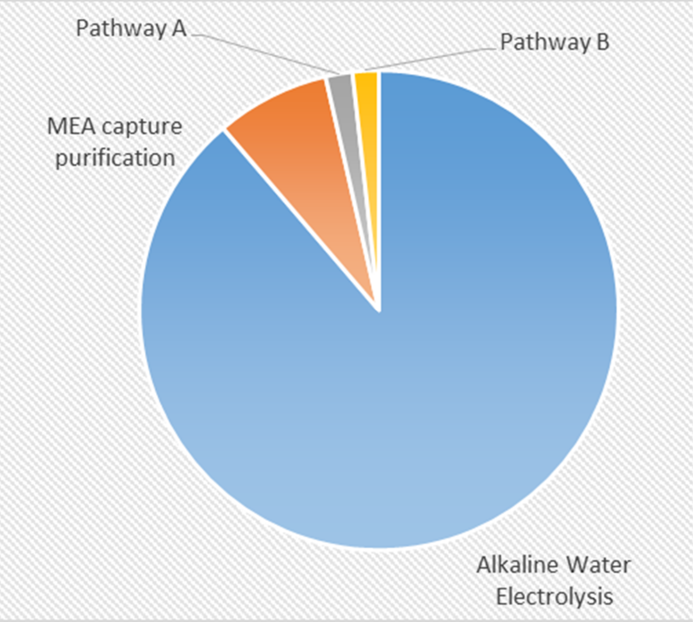


Figure C-26: CEOPS project energy distribution by unitary process

In terms of performance, the hydrogen produced will be approximately 110 €/MWh_{HCV}. Methane under standard conditions will be produced at a cost of 96.8 €/MWh_{HCV} and with a final price of 135 €/MWh_{HCV}, including investment costs. This figure could be lowered by selling the oxygen produced at an optimum price of 42€/bottle, giving a void cost.
In the case of methanol, the final price will be close to 133 €/MWh_{HCV}; the investment will increase this price by 1.38 times to 184 €/MWh_{HCV}.

As to the electricity cost, the MWh price to make methane competitive is close to 3€/MWh. For methanol it will be around 16€/MWh. These prices are calculated based on the methane and methanol prices as at January 2016.

● Life Cycle Impact Assessment

The impact assessment focussed on the impact categories Global Warming Potential (GWP in kg CO2e) and primary energy consumption from non-renewable sources (PENRT in MJ) and the results were compared to methane and methanol from fossil or renewable sources (biogas, syngas). The current European energy mix was considered in this assessment.

Methane production:

The results show, that 1 kg of CEOPS methane is associated with a GWP of 3.7 kg CO2e and a PE of 62 MJ. As the following figure shows, the main contributions to the environmental impacts come from the electrolysis and carbon capture processes.

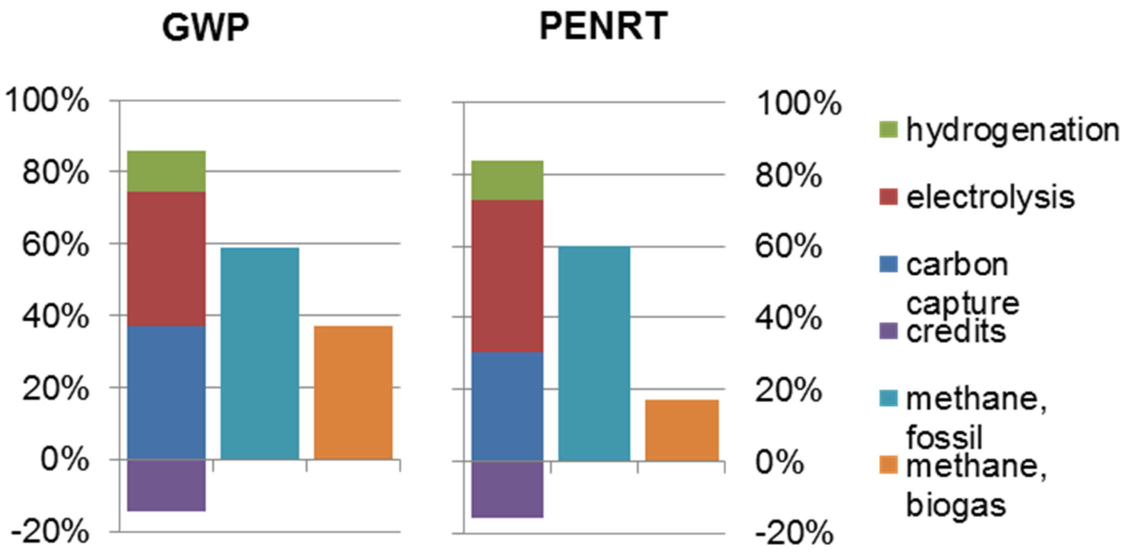


Figure C-27: Environmental impacts of CEOPS methane compared to methane from fossil and biogenic sources. Avoided emissions from the CEOPS process are taken into account.

Hence, at the current stage, the environmental impacts are 20 – 80 % larger than for methane from other sources. However, different scenarios show a big potential for reducing the environmental impacts, mainly from:

- a decreasing energy demand of the alkaline electrolysis and the carbon capture process;
- covering the thermal energy demand by utilising excess heat from the cement plant;
- improvements in the methane yield;
- an increasing share of electricity from renewable sources in the future (cf figure C-28).

With the shift in electricity production to renewable sources in 2020 and 2030, the impacts of the CEOPS process decrease. While the difference in GWP is only 0 – 5 % (due to the large share of coal), PENRT decreases by 30 – 60 %. At the same time, PERT increases significantly due to the change in electricity composition.

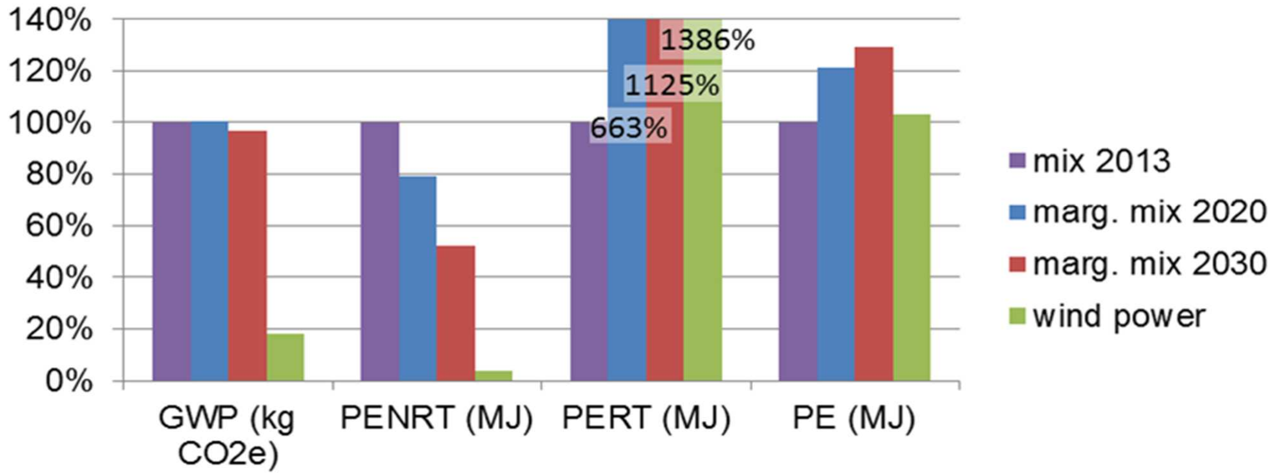


Figure C-28: Environmental impacts of 1 kg CEOPS methane in scenario S7 (different electricity mixes), compared to the baseline year 2013. The results for PERT are cut.

In the case of using only surplus wind power, the GWP decreases by 80 % and PENRT decreases by more than 95 %. This shows that the source of electricity used has a significant influence on the environmental impacts. The larger the share of renewable energy becomes, the lower are the GWP and fossil energy demand.

Methanol production:

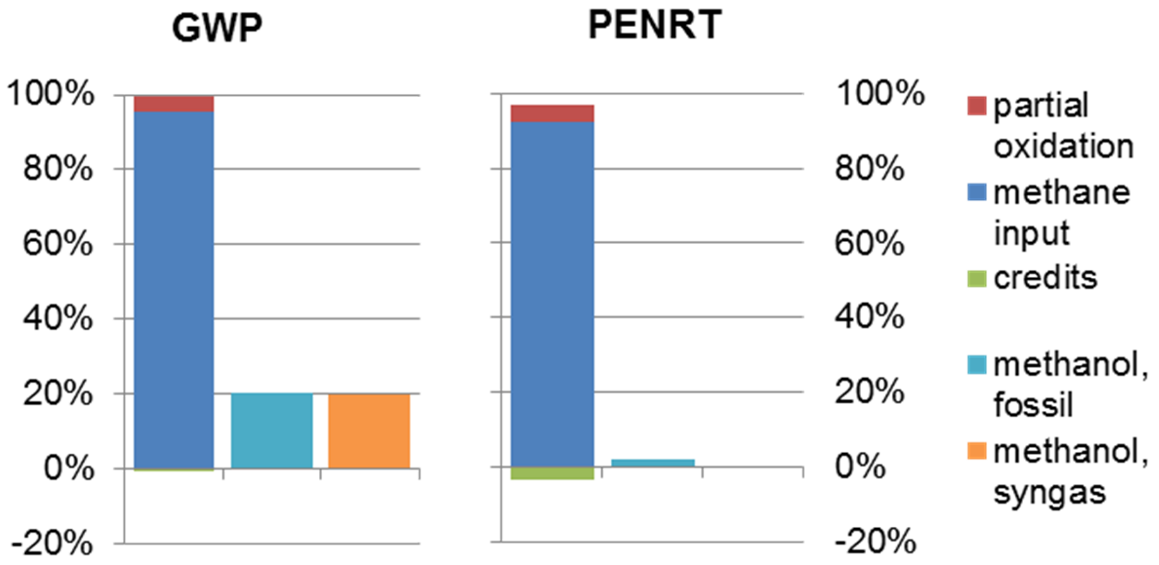


Figure C-29: Environmental impacts of CEOPS methane compared to methanol from fossil and biogenic sources. Avoided emissions from the CEOPS process are taken into account.

The results for 1 kg of methanol from Pathway B are less favourable. A GWP of about 100 kg CO_{2e} and a PE of around 1.6 GJ is obtained, which is mainly due to the very small yield for methanol of less than 2 % and the high CO_2 production rate of 70 %. Therefore, the large amount of methane input necessary to produce 1 kg of methanol is the responsible for most of the environmental impacts, as the following figure shows.

Hence, the impacts of Pathway B are at least 5 times higher than for methanol from fossil or renewable sources. Here, only significantly increased yields will improve the results. In a scenario with a higher methanol yield of 10 % and a substantially reduced CO_2 production rate of 25 %, the environmental impacts can be reduced by a factor of 5, thus closing the gap to conventional methanol.

● Conclusion

The global impact of the production of methane and methanol is greatly dependent on the performance of the reactant preparations. The investment for the treatment process is overwhelming for any company given the high price of the electrolysis process. The size of such units should be adapted according the local context and according to the synergy with energy storage. Indeed units for energy storage should have an average power from few MW to few tens of MW. The production of synthetic natural gas and methanol following the CEOPS project concept allows for the production of high purity and quality products. Given that intermediates, too, are of high grade, it is illusory to simplify production viability to the final price to compete with lower grade products. A choice has therefore to be made as to whether we still want to depend on cheaper fossil resources or make an energy transition to higher quality and greener fuels.

At the current stage, the environmental impacts of Pathway A and Pathway B are larger than the impacts of currently available technologies. This is mainly due to the large energy demand and the current electricity mix in the EU, as well as poor yields in the case of Pathway B. Given that improvements in the areas mentioned above, mainly with the energy mix, can be achieved, methane from Pathway A can become an environmentally favourable alternative to methane from other sources. In the case of methanol from Pathway B, the situation is less clear. To make the process viable, significant improvements in the process yields are necessary.

D) The potential impact (including the socio-economic impact and the wider societal implications of the project so far) and the main dissemination activities and exploitation of results.

Publications, patents and roadmaps:

The CEOPS project has allowed the creation of new knowledge on the two chemical pathways and electrocatalytic processes with publications and patents. A bottom-up approach was proposed whereby the rational design of various relevant advanced catalysts (chemical contents, morphology, size, density, structure, conductivity) resulted in CO_2 conversion and CH_4 conversion processes with low energy consumption at the system scale.

i) DBD plasma catalysis:

Publications:

Title	Main author	Title of the periodical or the series
CO2 Hydrogenation Over Ni-Based Zeolites: Effect of Catalysts Preparation and Pre-reduction Conditions on Methanation Performance	C. Henriques, J.M. Lopes	Topics in Catalysis
Insight into CO2 methanation mechanism over NiUSY zeolites: An operando IR study	C. Henriques, J.M. Lopes	Applied Catalysis B - Environmental
CO2 hydrogenation into CH_4 on NiHNaUSY zeolites	C. Henriques, J.M. Lopes	Applied Catalysis B - Environmental

Patents :

Application reference(s) (e.g. EP123456)	Subject or title of application	Applicant (s) (as on the application)
FR 13 58965, 18/09/2013	Electrode (surface plasma) and cooling system integration into a fluidized bed reactor	Commissariat à l'énergie atomique et aux énergies alternatives
P201530109. Spain. 28/01/2015	Process for the carbon dioxide reduction to methane by BDB plasma activated catalyst	Fund. Institut Recerca Energia Catalunya (30%), Universitat de Barcelona (10%), Université Pierre Marie et Curie (40%), Instituto Técnico Superior Lisboa (20%)

For catalysts investigations, new formulations have been developed and higher efficiency at low temperature was demonstrated. To go further, an industrial catalyst manufacturer should be identified in order to accelerate the industrialisation of one of these formulations (30%Ce 20%Ni / CsUSY(40)) from IST and (15%Ni $Ce_{0.9}$ $Zr_{0.1}$ O from IREC) .

Concerning the DBD plasma process, UMPC and CEA has demonstrated and validated the benefit of plasma on the catalytic activity at low temperature. UMPC has planned to continue fundamental studies to investigate mechanism which improves the activity at lower temperature.

CEA will continue the technological developments of the DBD surface plasma integrated in fluidized bed. The CEA will investigate this technology for other chemicals reactions and also for endothermic reactions. CEA has discussed with some industrials concerning this technology. The interest is confirmed but seems to be too risky for industrials so far. More investigations must be conducted in order to demonstrate the up-scalability of this promising technology.

ii) Photo-activated catalysis:

Publications:

Title	Main author	Title of the periodical or the series
Partial oxidation of methane to methanol using bismuth-based photocatalysts	Murcia-López, S., Villa, K., Andreu, T., Morante, J.R.	ACS Catalysis
Mesoporous WO3 photocatalyst for the partial oxidation of methane to methanol using electron scavengers	Villa, K., Murcia-López, S., Andreu, T., Morante, J.R.	Applied Catalysis B: Environmental
Tuning the fermi level and the kinetics of surface states of TiO2 nanorods by means of ammonia treatments	Fàbrega, C., Monllor-Satoca, D., Ampudia, S., Parra, A., Andreu, T., Morante, J.R.	Journal of Physical Chemistry C
On the role of WO3 surface hydroxyl groups for the photocatalytic partial oxidation of methane to methanol	Villa, K., Murcia-López, S., Andreu, T., Morante, J.R.	Catalysis Communications
Improved selectivity for partial oxidation of methane to methanol in the presence of nitrite ions and BiVO4 photocatalyst	Murcia-López, S., Villa, K., Andreu, T., Morante, J.R.	Chemical Communications
An insight on the role of La in mesoporous WO3 for the photocatalytic conversion of methane into methanol	Villa, K., Murcia-López, S., Morante, J.R., Andreu, T.	Applied Catalysis B: Environmental
Photocatalytic behavior of TiO2 films synthesized by microwave irradiation	Daniela Gomes	Catalysis Today
Efficient WO_3 photoanodes fabricated by pulsed laser deposition for photoelectrochemical water splitting with high faradaic efficiency	Fàbrega, C., Murcia-López, S., Monllor-Satoca, D., Prades, J.D., Hernandez-Alonso, M.D., Penelas, G., Morante, J.R., Andreu, T.	Applied Catalysis B: Environmental

The potential of PEC technology for CO_2 conversion into methane has been proved and results are promising, saving energy and offering room enough for increasing performances. So, the overall productivities must still be improved in comparison to the coupling of photovoltaic and electrolysis technologies. Further scientific and technological investigations are still required for envisioning their development at upper scale.

For methane to methanol conversion by photocatalysis (PC) was investigated. PC technology is already an industrial technology mostly implemented for water depollution. During the project IREC has demonstrated the suitability of this process for obtaining the partial oxidation using catalysts developed by IST and IREC. The achievement of methanol production is a success. But the upscaling has not confirmed the promising result obtained with the lab-scale reactor. Higher efficiencies with more efficient photocatalysts (WO_3 mesoporous, $BiVO_4$, Bi_2WO_6) must be reached to be commercially viable. However, once achieved time to market can be short due to the large market of photocatalysis for air and water depollution.

iii) Electro-catalytic reduction:

Publications:

Title	Main author	Title of the periodical or the series
Copper-zinc catalysts for electrochemical CO2 reduction in ionic liquid-based electrolytes	Ana Machado	Green Chemistry
Charging effects and surface potential variations of Cu-based nanowires	Daniela Gomes	Thin Solid Films
Room Temperature Synthesis of Cu2O Nanospheres: Optical Properties and Thermal Behavior	Daniela Gomes	Microscopy and Microanalysis
Cu 2 O polyhedral nanowires produced by microwave irradiation	Daniela Gomes	Journal of Materials Chemistry C

Patents :

Application reference(s) (e.g. EP123456)	Subject or title of application	Applicant (s) (as on the application)
PT2015/108442	Catalytic System for Syngas Production and Process thereof	Omnidea, Lda

This technology is promising but for a time to market of at least 5 years. This process could also produce syngas with a high selectivity, an association with methanol synthesis, DME synthesis or FT synthesis should pave the way to advanced process of energy storage based on the power to liquid concept.

Roadmaps of results:

The CEOPS project has allowed significant progress beyond the State of the Art. As the project was focused on future emerging technologies, the TRL level was below TR5 at the end of the project, further works are required to bring one or several technologies to the market level.
The consortium assessed the roadmap of results and it is presented on the figure D-1.

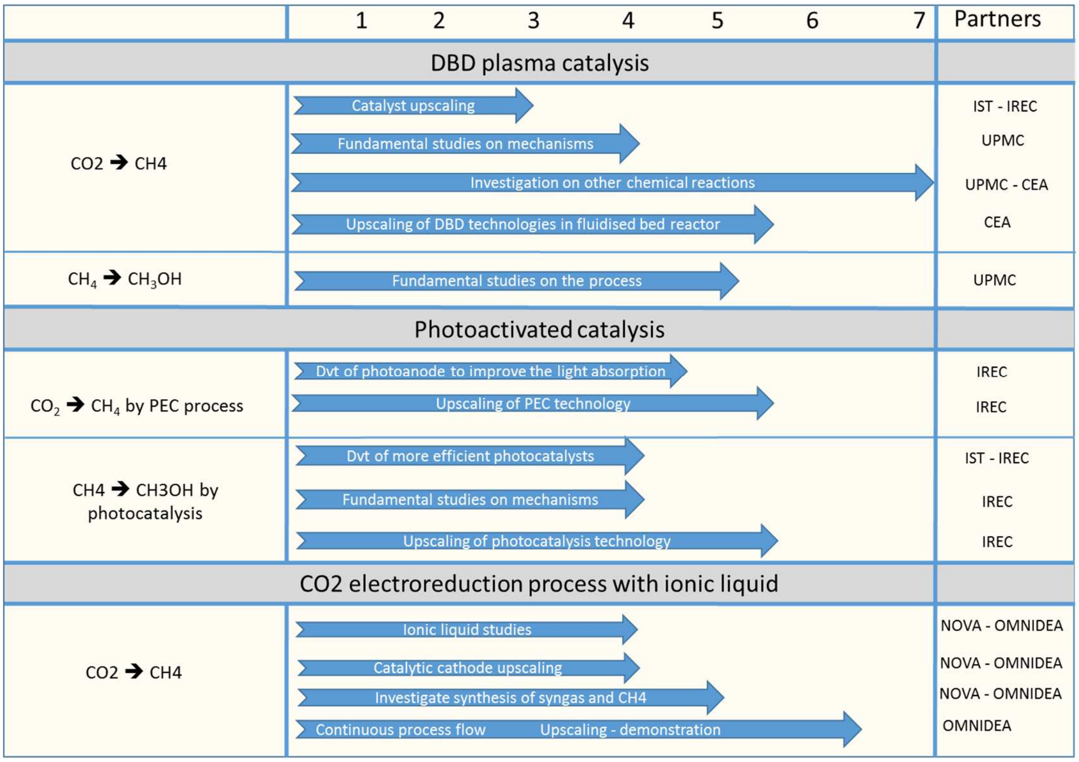


Figure D-1: Roadmap of results proposed by partners

Workshops and summer schools:

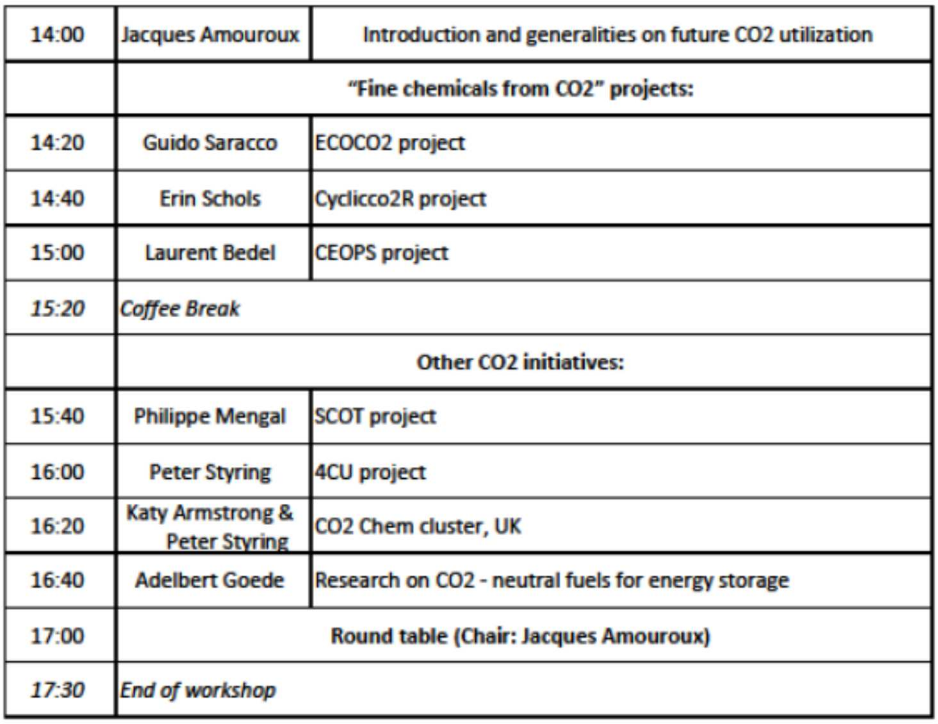
i) *Workshops*

CEOPS contributed to the promotion of the carbon capture and utilization approach which is complementary to the sequestration one. During the project three workshops were organised in the frame of the E-MRS conference in 2014 and 2015 and CCB organised three workshops during the general assembly of CCB cluster with all the members where the results of the CEOPS projects were presented.

First CEOPS workshop:

It was organised in the frame of the EMRS spring conference in May 26, 2014. It was the opportunity to interact with other coordinators of project focused of CO_2 utilisation.

Agenda:

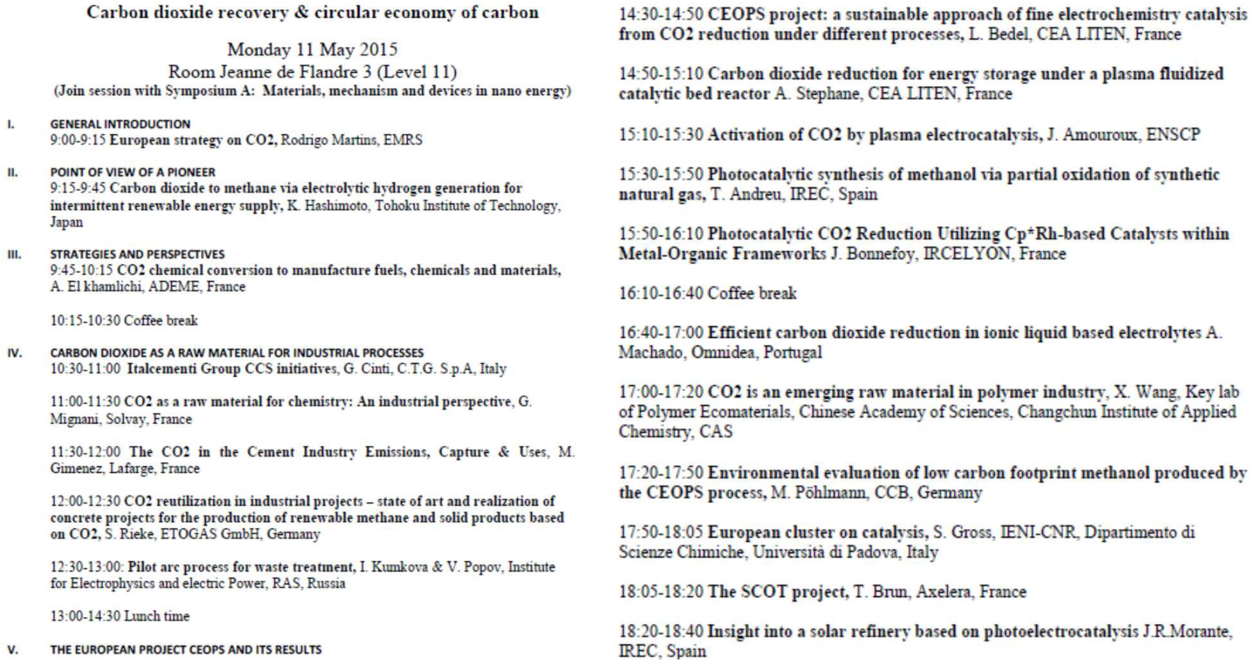


14:00	Jacques Amouroux	Introduction and generalities on future CO2 utilization
	"Fine chemicals from CO2" projects:	
14:20	Guido Saracco	ECOCO2 project
14:40	Erin Schols	Cyclicco2R project
15:00	Laurent Bedel	CEOPS project
15:20	*Coffee Break*	
	Other CO2 initiatives:	
15:40	Philippe Mengal	SCOT project
16:00	Peter Styring	4CU project
16:20	Katy Armstrong & Peter Styring	CO2 Chem cluster, UK
16:40	Adelbert Goede	Research on CO2 - neutral fuels for energy storage
17:00	Round table (Chair: Jacques Amouroux)	
17:30	*End of workshop*	

Second CEOPS workshop:

The topic of the 2nd workshop was on the CO2 recovery and circular economy of carbon. It was organised on May 11, 2015 during the EMRS spring conference.

Agenda:



Carbon dioxide recovery & circular economy of carbon

Monday 11 May 2015
Room Jeanne de Flandre 3 (Level 11)
(Join session with Symposium A: Materials, mechanism and devices in nano energy)

I. **GENERAL INTRODUCTION**
9:00-9:15 **European strategy on CO2,** Rodrigo Martins, EMRS

II. **POINT OF VIEW OF A PIONEER**
9:15-9:45 **Carbon dioxide to methane via electrolytic hydrogen generation for intermittent renewable energy supply,** K. Hashimoto, Tohoku Institute of Technology, Japan

III. **STRATEGIES AND PERSPECTIVES**
9:45-10:15 **CO2 chemical conversion to manufacture fuels, chemicals and materials,** A. El khamlichi, ADEME, France

10:15-10:30 Coffee break

IV. **CARBON DIOXIDE AS A RAW MATERIAL FOR INDUSTRIAL PROCESSES**
10:30-11:00 **Italcementi Group CCS initiatives,** G. Cinti, C.T.G. S.p.A, Italy

11:00-11:30 **CO2 as a raw material for chemistry: An industrial perspective,** G. Mignani, Solvay, France

11:30-12:00 **The CO2 in the Cement Industry Emissions, Capture & Uses,** M. Gimenez, Lafarge, France

12:00-12:30 **CO2 reutilization in industrial projects – state of art and realization of concrete projects for the production of renewable methane and solid products based on CO2,** S. Rieke, ETOGAS GmbH, Germany

12:30-13:00: **Pilot arc process for waste treatment,** I. Kumkova & V. Popov, Institute for Electrophysics and electric Power, RAS, Russia

13:00-14:30 Lunch time

V. **THE EUROPEAN PROJECT CEOPS AND ITS RESULTS**

14:30-14:50 **CEOPS project: a sustainable approach of fine electrochemistry catalysis from CO2 reduction under different processes,** L. Bedel, CEA LITEN, France

14:50-15:10 **Carbon dioxide reduction for energy storage under a plasma fluidized catalytic bed reactor** A. Stephane, CEA LITEN, France

15:10-15:30 **Activation of CO2 by plasma electrocatalysis,** J. Amouroux, ENSCP

15:30-15:50 **Photocatalytic synthesis of methanol via partial oxidation of synthetic natural gas,** T. Andreu, IREC, Spain

15:50-16:10 **Photocatalytic CO2 Reduction Utilizing Cp*Rh-based Catalysts within Metal-Organic Frameworks** J. Bonnefoy, IRCELYON, France

16:10-16:40 Coffee break

16:40-17:00 **Efficient carbon dioxide reduction in ionic liquid based electrolytes** A. Machado, Omnidea, Portugal

17:00-17:20 **CO2 is an emerging raw material in polymer industry,** X. Wang, Key lab of Polymer Ecomaterials, Chinese Academy of Sciences, Changchun Institute of Applied Chemistry, CAS

17:20-17:50 **Environmental evaluation of low carbon footprint methanol produced by the CEOPS process,** M. Pöhlmann, CCB, Germany

17:50-18:05 **European cluster on catalysis,** S. Gross, IENI-CNR, Dipartimento di Scienze Chimiche, Università di Padova, Italy

18:05-18:20 **The SCOT project,** T. Brun, Axelera, France

18:20-18:40 **Insight into a solar refinery based on photoelectrocatalysis** J.R.Morante, IREC, Spain

Third CEOPS workshop:

The last workshop was devoted to CO2 valorisation topic. It was organised on Sept 17-18, 2015 in Warsaw during the EMRS fall conference. The title of this workshop was “Materials for CO_2 capture and storage”.

Agenda:

Programme Sept 17:

8.30-9.00: General introduction, Rodrigo Martins, FCT / UNINOVA, Portugal

9.00-9.30: Methane formation from carbon dioxide via electrolytic hydrogen generation - Koji Hashimoto, Tohoku Institute, Japan

9.30-10.00: Advanced CO2 capture pilot plant at Toron’S coal –fired power plant - Wieclaw-Solny, Institute of chemical processing of Coal, Poland

10.00-10.20: Environmental Assessment of solid sorbents towards ‘safe by design’ - Andy Booth, Sintef Material and chemistry, Norway

10.20-10.40: CO2 capture on solid sorbents, Urszula Narkiewicz, West Pomeranian Univ. of technology, Poland

11.00-11.20: Calcium oxide based CO2 sorbents: fundamental aspects of carbonation - Christoph Müller, ETH Zurich, Switzerland

11.20-11.40: MOF’s for adsorptive CO2 capture – critical aspects, Richard Blom, Sintef, Norway

11.40-12.00: Preparation of activated carbons from coal as the CO2 adsorbents - Karolina Glonek, West Pomeranian Univ. of Technology, Poland

12.00-12.20: Commercial activated carbons enhancement toward better CO2 capacity – Rafal Wrogel, West Pomeranian Univ. of Technology, Poland

14.00-14.25: Challenges for CO2 Utilizations- Opportunities for materials? Richard H. Heyn, Sintef Materials and chemistry, Norway

14.25-14.50: Conversion of CO2 into high value added chemical by a catalytic approach - Zhenshan Hou, Research institute of industrial catalysis, China

14.50-15.10: Comparison of activated carbons and zeolites in CO2 capture Michal Zgrzebnicki, West Pomeranian Univ. of Technology, Poland

15.10-15.30: Steam assisted carbon dioxide permeation through a dual phase molten salt membrane – Brian Ray, Newcastle University, UK

15.50-16.10: Dynamics and energetics of carbon dioxide adsorption on carbon compounds Jacek A. Majewski, University of Warsaw, Poland

16.10-16.30: CO2 capture by mesoporous alumino silicate spheres prepared by drip casting method - Sanosh Kunjalukka , University de Salento, Italy

16.30-16.50: CO2 separation via dual phase high temperature membrane
Wen Xing, Sintef, Norway

16.50-17.10: Activated carbons obtained from sugar industry waste, as CO2 sorbents - Jacek Młodzik, West Pomeranian Univ. of Technology, Poland

17.10-18.00: Forum Discussion On Co2 Capture

Programme Day 2:

14.00-14.25: Perspective in catalytic CO2 conversion into valuable products, Wojciech GAC, Maria-Curie–Sklodowska University, Poland

14.25-14.50: Copper based materials for CO2 reduction, Mohammed Bettahar, Lorraine university, France

14.50-15.10: CEOPS project & last international results, Laurent Bedel, CEA, France

15.10-15.30: Photocatalysis process for CO2 reduction, Juan Ramon Morante, IREC, Spain

15.30-15.50: The development of Ni-zeolite catalysts for the methanation of carbon dioxide with hydrogen: a case study - Carlos Henriques, IST, Portugal

16.10-16.30: Low temperature plasma catalytic methanation of carbon dioxide over ceria zirconia catalyst - Magdalena Nizio, University Pierre et Marie Curie, France

16.30-16.50: Pilot arc process for waste treatment, Victor Popov, Institute for Electrophysics and Electric Power RAS, Russia

16.50-17.10: Production of CaMnOxFeyTiO3z granules optimization of their Redox kinetic rate - Vincent Thoreton, NTNU, Nosecond worway
17.10-17.30: Pb-Ag bimetallic catalysts for selective formic acid decomposition toward hydrogen and sequestration ready CO2 - Olga Sneka, Lodz University, Poland
17.30-17.50: H-Bonded organic semiconductor thin films for electrochemical capture and release of carbon dioxide - Dogukan Hazar Apaydin, Johannes Kepler University, Austria
17.50-18.10: The role of ionic liquids from CO2 capture to CO2 valorization, Ana Machado, Omnidea Lda , Portugal

CCB workshops: The three workshops were organised at the same time of the annual general assembly of the CCB cluster gathering all members.

On November 2013, the CEOPS project was presented during the CCB general assembly and a discussion occurred with the members.

During the second workshop on Nov. 2014, the main achievements of the project during the first 18 months were presented. Laurent Bedel contributed to the round table on the topic of CO_2 utilization and also during the poster session.

The last CCB workshop was organized in November 2015 was devoted to CO_2 valorization with external speakers, and a debate was organized of CO_2 utilization for fuels.

	Parallel dazu im Säulensaal: CEOPS Workshop on CO_2-Valorization
15:30 Uhr	**Results of the FP7 Project CEOPS** (CO_2-loop for Energy storage and conversion to Organic chemistry Processes through advanced catalytic Systems)
	GRTgaz and its P2G Demonstration Plant Laurent Bedel, CEA Liten
15:55 Uhr	**CO_2-Circular Economy** Prof. Dr. Jaques Amouroux, European Materials Research Society
16:10 Uhr	**CO_2-Valorization** Dr. Hans Jürgen Wernicke, CCB Steering Committee
16:30 Uhr	**The AUDI e-gas project** Elias Hammer, AUDI AG
16:50 Uhr	**Open Discussion**

ii) ***Summer schools***

Summer schools were organised during EMRS conferences. They were composed of PhDs, post-doc and academy people.

The main topic of the first Summer School was: “Carbon dioxide recovery”.

Agenda:

Time	Presentation Title	Speaker
9.00 - 9.30	Registration	
9.30 - 10.00	Carbon recovery and circular economy	J. Amouroux, ENSCP/UPMC/EMRS (France)
10.00 - 10.30	An industrial point of view	G. Mignani, Solvay (France)
10.30 - 11.00	Coffee break & posters	
11.00 - 11.30	Catalysis for industrial challenges	Z. Ismagilov, Boreskov Institute of Catalysis, RAS (Russia)
11.30 - 12.00	Photo catalysis and hydrogen	J.R. Morante, IREC (Spain)
12.00 - 12.30	Questions & challenges, posters	
12.30 - 14.00	Lunch & posters	
14.00 - 14.30	An overview of our future	K. Hashimoto, Tohoku Institute of Technology Tohoku University (Japan)
14.30 - 15.00	Electro catalysis – Presentation of the European project CEOPS	L. Bedel, CEA Liten (France)
15.00 - 15.30	Waste treatment and carbon dioxide	I. Kumkova, Institute for Electrophysics and electric Power, RAS (Russia)
15.30 - 16.00	Coffee break & posters	
16.00 - 16.30	European Cluster on catalysis	S. Gross, IENI-CNR, Dipartimento di Scienze Chimiche, Università di Padova (Italy)
16.30 - 17.00	An overview of the world CO2 industrial program	J. Amouroux, ENSCP/UPMC/EMRS (France)
17.00 - 18.00	Questions & discussion, posters	

Second CEOPS Summer School

The second Summer School took place in the frame of the E-MRS Fall meeting on 19 September 2015 in Warsaw. The main topic of this intergenerational forum for students and scientists was: "Carbon dioxide Management: the raw material of the industrial revolution of the 21st century".

Agenda:

First part: the circular economy of carbon: the challenge of the next 50 years
9.00-9.30: General introduction, Rodrigo Ferrao de Paiva Martins, CEMOP / UNINOVA, Portugal Member of the advisory Board of Horizon 2020 in DG Research and Innovation
9.30-10.00: Carbon recovery and circular economy: from research to industrial scale up, Jacques Amouroux, UPMC/ENSCP DHC, E-MRS, France
10.00-10.30: Carbon dioxide and energy storage of renewable energy sources, Koji Hashimoto, Tohoku Institute of Technology/Tohoku University, Japan
10.30-11.00: Coffee break and posters
11.00-11.30: Photocatalysis and new materials for hydrogen production, Juan-Ramon Morante, IREC, Spain
11.30-12.00: Discussion with the audience

Second part: innovations and new materials
14.00-14.30: Advanced CO2 capture pilot plant at Toron's coal-fired power plant, Lucyna Wieclaw-Solny, Institute of chemical processing of Coal, Poland

14.30-15.00: Carbon capture on solid sorbents, Urszula Narkiewicz, West Pomeranian University of Technology, Poland
15.00-15.30: Waste treatment and carbon dioxide, Victor Popov, Institute of Electrophysics and Electric power, RSA, Russia
15.30-16.00: Electrocatalysis for Carbon dioxide recovery, Laurent Bedel, CEA, France
16.00-16.30: Coffee break and posters
16.30-17.00: Catalysis innovation a key step for Carbon dioxide reduction, Carlos Henriques, IST University, Portugal
17.00-17.15: Bio-fixation of CO2 emitted from cements plants through micro algal culture: the Italcementi experience
Piero Negro, Italcementi, Italy
17.15-17.30: Perspective in catalytic CO2 conversion into valuable products, Wojciech Gac, Marie-Curie-Sklodowska University, Poland
17.30-18.00: Forum of discussion and industrial development followed by poster presentations.

iii) ***Website and newsletters***

The CEOPS website (http://www.ceops-project.eu/) was implemented during the first 6 months of the project. It presents the project, and it was used to disseminate the main results of the project through the 6 newsletters published every 6 months. To ensure the large dissemination, these newsletters circulated through the EMRS and CCB networks.

iv) CEOPS vision: high environmental value chemicals from CO2 and use of carbon as a flexible energy vector

The project proposed the development and the assessment of an innovative route for converting CO_2 into added value chemicals. This is completed with the contribution to the storage of renewable energies. The interest of energy storage by Power to Gas and Power to Chemicals is nowadays investigated at EU level with several demonstration projects. CEOPS did not investigate mature technologies but future emerging technologies which should overcome the limitations of current technologies in terms of CAPEX and efficiency. The concept proposed by CEOPS fits perfectly with the requirement of storage and conversion of surplus of intermittent of renewable energies.

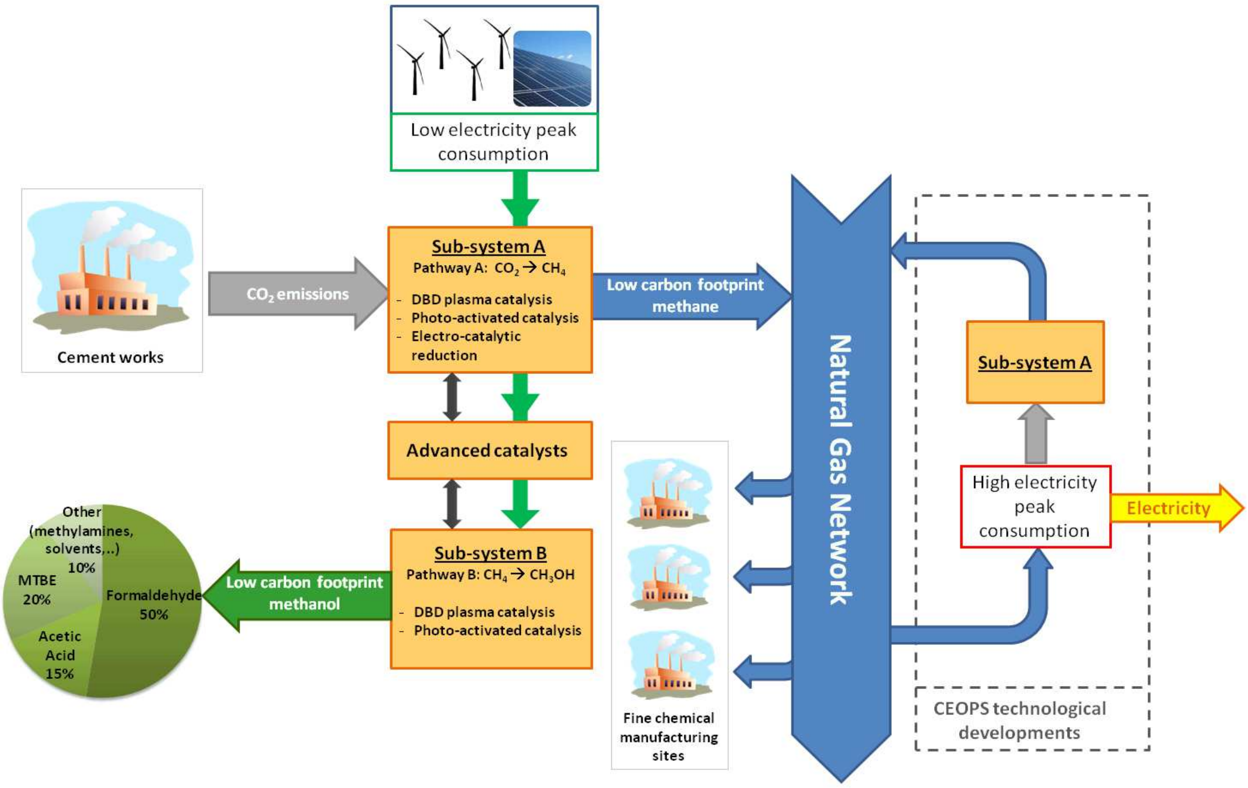


Figure D-2: CEOPS concept extended to renewable energy storage

4.2 Use and dissemination of foreground

Section A (public)

TEMPLATE A1: LIST OF SCIENTIFIC (PEER REVIEWED) PUBLICATIONS, STARTING WITH THE MOST IMPORTANT ONES

NO.	Title	Main author	Title of the periodical or the series	Number, date or frequency	Publisher	Place of publication	Year of publication	Relevant pages	Permanent identifiers[7] (if available)	Is/Will open access[8] provided to this publication?
1	Partial oxidation of methane to methanol using bismuth-based photocatalysts	Murcia-López, S., Villa, K., Andreu, T., Morante, J.R.	ACS Catalysis	4 (9)	ACS publications	Washington, US	2014	3013-3019	http://dx.doi.org/ 10.1021/cs500821r	No
2	Mesoporous WO3 photocatalyst for the partial oxidation of methane to methanol using electron scavengers	Villa, K., Murcia-López, S., Andreu, T., Morante, J.R.	Applied Catalysis B: Environmental	163	Elsevier		2015	150-155	http://dx.doi.org/10.1016/ j.apcatb.2014.07.055	No
3	Tuning the fermi level and the kinetics of surface states of TiO2 nanorods by means of ammonia treatments	Fàbrega, C., Monllor-Satoca, D., Ampudia, S., Parra, A., Andreu, T., Morante, J.R.	Journal of Physical Chemistry C	117 (40)	ACS publications		2013	20517-20524	http://dx.doi.org/10.1021/jp407167z	No
4	On the role of WO3 surface hydroxyl groups for the photocatalytic partial oxidation of methane to methanol	Villa, K., Murcia-López, S., Andreu, T., Morante, J.R.	Catalysis Communications	58	Elsevier		2015	200-203	http://dx.doi.org/10.1016/ j.catcom.2014.09.025>.	No
5	Improved selectivity for partial oxidation of methane to methanol in the presence of nitrite ions and BiVO4 photocatalyst	Murcia-López, S., Villa, K., Andreu, T., Morante, J.R.	Chemical Communications	51 (33)	RSC Pub.	London, UK	2015	7249-7252	http://dx.doi.org/ 10.1039/C5CC00978B	Yes
6	An insight on the role of La in mesoporous WO3 for the photocatalytic conversion of methane into methanol	Villa, K., Murcia-López, S., Morante, J.R., Andreu, T.	Applied Catalysis B: Environmental	187	Elsevier		2016	30-36	http://dx.doi.org/10.1016/ j.apcatb.2016.01.032	No
7	Efficient WO_3 photoanodes fabricated by pulsed laser deposition for photoelectrochemical water	Fàbrega, C., Murcia-López, S., Monllor-Satoca, D., Prades, J.D., Hernandez-	Applied Catalysis B: Environmental	189	Elsevier		2016	133-140	http://dx.doi.org/ 10.1016/j.apcatb.2016.02.047	no

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[7] A permanent identifier should be a persistent link to the published version full text if open access or abstract if article is pay per view) or to the final manuscript accepted for publication (link to article in repository).

[8] Open Access is defined as free of charge access for anyone via Internet. Please answer "yes" if the open access to the publication is already established and also if the embargo period for open access is not yet over but you intend to establish open access afterwards.

	splitting with high faradaic efficiency	Alonso, M.D., Penelas, G., Morante, J.R., Andreu, T.								
8	Copper-zinc catalysts for electrochemical CO2 reduction in ionic liquid-based electrolytes	Ana Machado	Green Chemistry	submitted	Royal Society of Chemistry	London				no
9	CO2 Hydrogenation Over Ni-Based Zeolites: Effect of Catalysts Preparation and Pre-reduction Conditions on Methanation Performance	C. Henriques	Topics in Catalysis	Volume 59 (2) February 2016	Springer International Publishing AG	Cham (ZG), Switzerland	2016	Pp 314-325	http://link.springer.com/article/10.1007/s11244-015-0435-4/fulltext.html	no
10	Insight into CO2 methanation mechanism over NiUSY zeolites: An operando IR study	C. Henriques	Applied Catalysis B - Environmental	Volume: 174 Published: SEP 2015	Elsevier Science BV	Amsterdam, Netherlands	2015	Pp 120-125	http://apps.webofknowledge.com/full_record.do?product=UA&search_mode=GeneralSearch&qid=4&SID=T1DSehg3CEpKOy39yYT&page=1&doc=1	no
11	Charging effects and surface potential variations of Cu-based nanowires	Daniela Gomes	Thin Solid Films	published	Elsevier		2016	25-53		no
12	Photocatalytic behavior of TiO2 films synthesized by microwave irradiation	Daniela Gomes	Catalysis Today	published	Elsevier		2016			no
13	Room Temperature Synthesis of Cu2O Nanospheres: Optical Properties and Thermal Behavior	Daniela Gomes	Microscopy and Microanalysis	published	MRS	USA	2015			no
14	Cu 2 O polyhedral nanowires produced by microwave irradiation	Daniela Gomes	Journal of Materials Chemistry C	published	Royal Society of Chemistry		2014	6097-6103		no
15	CO2 hydrogenation into CH_4 on NiHNaUSY zeolites	C. Henriques	Applied Catalysis B - Environmental	Volume: 147 Published: APR 5 2014	Elsevier Science BV	Amsterdam, Netherlands	2014	Pp 101-110	http://apps.webofknowledge.com/full_record.do?product=UA&search_mode=GeneralSearch&qid=4&SID=T1DSehg3CEpKOy39yYT&page=1&doc=2	no
16	Carbon dioxide: A new material for energy storage	Jacques Amouroux	Progress in Natural Science: Materials International	Volume 24, Issue 4	Elsevier production and Elsevier hosting ISSN 1002-0071	Chinese MRS, International Union of Materials Research Society	August 2014	p. 295–304		No

TEMPLATE A2: LIST OF DISSEMINATION ACTIVITIES

NO.	Type of activities[9]	Main leader	Title	Date/Period	Place	Type of audience[10]	Size of audience	Countries addressed
1	Presentation	CEA - L. Bedel	Europe in motion: Storage and valorization of renewable energy by hydrogenation of captured CO2 for energy and chemical markets	21/05/2013	E-MRS Spring Meeting 2013, Strasbourg, France	Scientific Community	40	Europe
2	Presentation	CEA - L. Bedel	CO2 - loop for Energy storage and conversion to Organic chemistry Processes through advanced catalytic Systems	25/06/2013	International Conference on Carbon Dioxide Utilization, Washington DC, USA	Scientific Community	100	International
3	Presentation	CEA - L. Bedel	CO2 - loop for Energy storage and conversion to Organic chemistry Processes through advanced catalytic Systems	26/05/2014	1st CEOPS Workshop (Lille) EMRS spring meeting	Scientific Community	30	International
4	Presentation	CEA - L. Bedel	CEOPS project: a sustainable approach of fine electrochemistry catalysis from CO2 reduction under different processes	10/05/2015	2nd CEOPS Workshop (Lille) EMRS spring meeting	Scientific Community	30	International
5	Presentation	CEA - L. Bedel	CEOPS project & last international results	18/09/2015	3sd CEOPS Workshop (Warsaw) EMRS fall meeting	Scientific Community	30	International
6	Presentation	CEA - L. Bedel	Electro catalysis and European program CEOPS	09/05/2015	1st Summer School (Lille)	Scientific Community	20	International
7	Presentation	CEA - L. Bedel	CEOPS project & last international results	19/09/2015	2nd Summer School (Warsaw)	Scientific Community	20	International
8	Presentation	CEA - L. Bedel	CO2 Reduction for chemical energy storage A reasonnable technology	03/11/2014	2nd CCB Workshop (Munich)	CCB Members	130	Germany
	Presentation	CEA - L. Bedel	Results of the FP7 Project CEOPS GRTgaz and its P2G Demonstration Plant	09/11/2015	3rd CCB Workshop (Munich)	CCB Members	130	Germany

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[9] A drop down list allows choosing the dissemination activity: publications, conferences, workshops, web, press releases, flyers, articles published in the popular press, videos, media briefings, presentations, exhibitions, thesis, interviews, films, TV clips, posters, Other.

[10] A drop down list allows choosing the type of public: Scientific Community (higher education, Research), Industry, Civil Society, Policy makers, Medias, Other ('multiple choices' is possible).

9	Presentation	EMRS – UPMC J. Amouroux	Carbon dioxide a raw material for energy storage	12-13/09/2013	RIH2013, Le Havre, France	Scientific Community, policy makers	80	Europe
10	Presentation	EMRS – UPMC J. Amouroux	Carbon Recovery for a Sustainable Development	23/09/2013	IUMRS-ICAM meeting, Qingdao, China	Scientific Community	2500	Asia
11	Workshop	EMRS – UPMC J. Amouroux	Forum for Next Generation Researchers: Materials: A Key Enabling Technology for Secure Energy & Sustainable Development	12-13/10/2013	"IV World Materials Summit", Council of Europe, Strasbourg, France	Scientific Community, policy makers	50	Europe
12	Presentation	IREC - J.R. Morante	Nanostructured Electrodes in Photoelectrochemical Cells for Solar Fuel Production	10-14/03/2014	Nano and Giga 2014, Phoenix, USA	Scientific Community, policy makers	80	USA
13	Workshop	EMRS – UPMC J. Amouroux	Carbon dioxide a material for sustainable development and energy storage	20/03/2014	Paul Scherrer Institut, Villingen, Switzerland	Scientific Community	30	Europe
14	Presentation	IREC - T. Andreu	CO2 - loop for Energy storage and conversion to Organic Chemistry Processes through advanced catalytic Systems	28/03/2014	NIS Colloquium Photo and Electrochemical Cells for Solar Fuels, Torino, Italy	Scientific Community, policy makers	50	Europe
15	Workshop	EMRS – UPMC J. Amouroux	R&D on CO2 utilization in Europe	26/05/2014	E-MRS spring meeting 2014, Lille, France	Scientific Community	50	Europe + Asia
16	Presentation	EMRS – UPMC J. Amouroux	Valorisation du CO2	07/07/2014	Ademe, Paris, France	Scientific Community	30	France
17	Presentation	EMRS – UPMC J. Amouroux	Carbon Recovery	23/02/2015	Meeting on Carbon Dioxide and Carbon Recovery by Clara de la Torre - European deputy, Brussels, Belgium	Scientific Community, policy makers	30	Europe
18	Presentation	EMRS – UPMC J. Amouroux	Les ateliers de la valorisation du dioxide de carbone	04/05/2015	Chaire de l'Ecole des Mines, Le Havre, France	Scientific Community	70	France
19	Summer School	EMRS – UPMC J. Amouroux	1st CEOPS Summer School on Carbon dioxide recovery	10/05/2015	Lille, France	Scientific Community	20	Europe + Asia
20	Workshop	EMRS – UPMC J. Amouroux	Carbon dioxide recovery and circular economy of carbon	11/05/2015	E-MRS spring meeting 2015, Lille, France	Scientific Community	130	Europe + Asia
21	Workshop	EMRS – UPMC J. Amouroux	Materials and devices for energy and environment applications: Materials for CO2 capture and storage	17-18/09/2015	E-MRS fall meeting 2015, Warsaw, Poland	Scientific Community	50	Europe + Asia
22	Summer School	EMRS – UPMC J. Amouroux	2nd CEOPS Summer School: Carbon dioxide Management: the raw material of the industrial revolution of the 21st century	19/09/2015	Warsaw, Poland	Scientific Community	20	Europe + Asia

23	Presentation	EMRS – UPMC J. Amouroux	Circular Economy of Carbon	09/11/2015	Chemie-Cluster Bayern, Munich, Germany	Scientific Community	180	Germany
24	Presentation	EMRS – UPMC J. Amouroux	Biomimetisme et chimie durable	10/11/2015	Maison de la Chimie, Paris, France	Scientific Community	120	France
25	Presentation	UPMC - S. Cavadias	Liquid fuels from carbon dioxide and hydrogen: a way to safely transport and distribute, hydrogen. What non - thermal plasma can do?	2-5 mars 2014	Ile de Tatihou	Scientific Community	40	France
26	Poster	UPMC - M. Nizio	CO_2 methanation by plasma assisted catalysis	10 May 2015	Summer school, EMRS, Lille	Scientific Community	100	International
27	Presentation	IREC - JR. Morante	High throughput production of synthetic methane using dielectric barrier discharge reactor and mesoporous Ni/Ce based catalyts from RT to 400 ºC	5-9 July 2015	The International Conference on Carbon Dioxide Utilization (ICCDU). Singapore	Scientific Community	250	Singapore
28	*Poster*	*Omnidea – A. Machado*	Electrochemical Reduction of Carbon Dioxide Dissolved in Ionic Liquids	*10 May 2015*	*EMRS Spring Meeting* *Lille, France*	*Scientific Community and Industry*	*1000*	International conference
29	*Oral communication*	*Omnidea – A. Machado*	Efficient Carbon Dioxide Electrochemical Reduction in Ionic Liquid- Based Electrolytes	*11 May 2015*	*EMRS Spring Meeting* *Lille, France*	*Scientific Community and Industry*	*70*	International conference
30	*Oral communication*	*Omnidea – A. Machado*	The role of ionic liquids from CO2 Capture to CO2 Valorization	*18 September 2015*	*EMRS Fall Meeting* Warshaw Poland	*Scientific Community and Industry*	70	International conference
31	*Poster*	NOVA	Electrochemical reduction of Carbon Dioxide Dissolved in Ionic Liquids	*19 September 2015*	*EMRS Fall Meeting* Warshaw Poland	*Scientific Community and Industry*	70	International conference
32	Web page	Omnidea	Synthetic Fuels from CO_2		www.omnidea.net			International dissemination
33	*Thesis*	*IREC*	*Andrés Parra Puerto. Towards artificial phtosynthesis: Photoelectrochemical* CO_2 *reduction to solar fuels*	*2012-2015 (26/11/2015)*	*University of Barcelona (Spain)*	Scientific Community (higher education)	1	*Thesis*
34	Workshop	IREC - J.R. Morante	Energy storage using sun fuels	12-13/10/2013	Forum next generation researchers (school) Strasbourg (France)	Scientific Community (higher education)	2	Workshop
35	Conference	IREC - J.R. Morante	Optimization of surface charge transfer processes on rutile TiO2 nanorods photoanodes for water splitting. Oral.	1-5/04/2013	International battery association, 2013. San Francisco, US	Scientific Community (higher education, Research), Industry	3	Conference

36	Conference	IREC - J.R. Morante	Modified Metal Oxide Based Nanostructures for Renewable Fuels from Photo Electro Chemical CO2 Reuse.	3/04/2013	2013 MRS Spring Meeting - Symp Z: Nanotechnology and Sustainability San Francisco, US	Scientific Community (higher education, Research), Industry		Conference
37	Conference	IREC - J.R. Morante	Materials for green energy.	14-15/10/2013	IV World Material Summit. Strasbourg (France)	Scientific Community (higher education, Research), Industry		Conference
38	Conference	IREC - J.R. Morante	On the Synergistic Effect of Ammonia Treatments over TiO2 Rutile Nanorods: Tuning the Fermi Level and the Kinetics of Surface States.	27-31/05/2013	E-MRS 2013 Spring meeting Strasbourg, France	Scientific Community (higher education, Research), Industry		Conference
39	Workshops (3) and Summer schools (2)	EMRS	CEOPS	01/02/2013-31/01/2016	Organised in parallel of EMRS conferences	Scientific Community (higher education, Research), Industry		Conferences
40	Workshop – summer school	IREC - J.R. Morante	Energy storage using sun fuels	12-13/10/2013	Forum next generation researchers (school). Strasbourg (France)	Scientific Community (higher education, Research),		Workshop – summer school
41	Conference - workshop	IREC – T. Andreu	CEOPS project	18/03/2014	Photo and Electrochemical Cells for Solar Fuels (NIS Colloquium). Torino (Italy)	Scientific Community (higher education, Research)		Conference - workshop
42	Conference	IREC - J.R. Morante	Nanostructured Electrodes in Photoelectrochemical Cells for Solar Fuel Production	10/04/2014 - 14/04/2014	Nano and Giga Challenges in Electronics, Photonics and Renewable Energy From Materials to Devices to System Architecture Symposium and Spring School. Phoenix, Arizona	Scientific Community (higher education, Research)		Conference
43	Conference	IREC – S. Murcia	New 3D Structured Photo Anodes based on Pulsed Laser Deposition of Tungsten Oxide	27/07/2014 - 01/08/2014	20th International Conference on Conversion and Storage of Solar Energy. Berlin (Germany)	Scientific Community (higher education, Research)		Conference
44	Conference	IREC - JR Morante	Tungsten Oxide PhotoAnodes Deposited by Pulsed Laser deposition for Water Splitting Devices. Oral	17/02/2014 - 20/02/2014	2014 MRS Spring Meeting. San Francisco, US	Scientific Community (higher education, Research), Industry		Conference

45	Conference	IREC - JR Morante	Insight into the Surface Characterization of the Photoelectrochemical Cell Electrode Materials for Sustainable Solar Fuel Production	17/02/2014 - 20/02/2014	2014 MRS Spring Meeting. San Francisco, US	Scientific Community (higher education, Research), Industry		Conference
46	Conference	IREC - JR Morante	Improved metal oxide based photoanodes for photoelectrochemical cells	15/10/2014 - 17/10/2014	5th international symposium on Transparent Conductive Materials Platanias-Chania, Greece	Scientific Community (higher education, Research), Industry		Conference
47	Conference	IREC – S. Murcia	Photocatalytic oxidation of methane to methanol using BiVO4 in presence of scavengers. Poster	11-15/05/2015	2015 E-MRS Spring Meeting. Lille (France)	Scientific Community (higher education, Research), Industry		Conference
48	Conference	IREC – A. Parra	Cu and CuxO Electrodes for Selective conversion into Hydrocarbons in Different Electrolytes. Poster	11-15/05/2015	2015 E-MRS Spring Meeting. Lille (France)	Scientific Community (higher education, Research), Industry		Conference
49	Conference	IREC - K. Villa	Photocatalytic conversion of methane into methanol over ordered mesoporous La/WO3 . Oral	11-15/05/2015	2015 E-MRS Spring Meeting. Lille (France)	Scientific Community (higher education, Research), Industry		Conference
50	Conference. Workshop	IREC - T.Andreu	Photocatalytic synthesis of methanol via partial oxidation of synthetic natural gas	11-15/05/2015	2015 E-MRS Spring Meeting. CEOPS workshop. Lille (France)	Scientific Community (higher education, Research), Industry		Conference. Workshop
51	Conference Workshop	IREC – JR Morante	Photo Catalysis and hydrogen	11-15/05/2015	2015 E-MRS Spring Meeting. CEOPS summer school. Lille (France)	Scientific Community (higher education, Research),		Conference Workshop
52	Conference	IREC - J.R. Morante	Photo electrocatalysis process for CO2 reduction	15-18/09/2015	2015 E-MRS fall Meeting. Warsaw, Poland	Scientific Community (higher education, Research), Industry		Conference
53	Conference Workshop	IREC - J.R. Morante	Photo electrocatalysis and new materials for hydrogen production	15-18/09/2015	2015 E-MRS fall Meeting. CEOPS Summer school. Warsaw, Poland	Scientific Community (higher		Conference Workshop

						education, Research), Industry		
54	Conference	IREC - T. Andreu	Room temperature synthesis of synthetic natural gas using a catalytic-dielectric barrier discharge (BDB) plasma reactor. Poster	7-8/05/2015	2nd International Conference on Renewable Energy Gas Technology. Barcelona, Spain	Scientific Community (higher education, Research), Industry		Conference
55	Workshop	IREC - T. Andreu	CO2 valorization to fuels based on a photoelectrochemical process. Oral invited	17/12/2015	CO2 Capture & utilization (XARMAE network). Barcelona, Spain	Scientific Community (higher education, Research), Industry		Workshop
56	Conference	IREC - S. Murcia	Partial oxidation of methane to methanol with bismuth-based photocatalysts	30/08/2015 - 04/09/2015	Europacat XII. Kazan, Russia	Scientific Community (higher education, Research), Industry		Conference
57	Conference	IREC - K. Villa	Conversion of methane into methanol over doped mesoporous WO3. Poster	30/08/2015 - 04/09/2015	Europacat XII. Kazan, Russia	Scientific Community (higher education, Research), Industry		Conference
58	Conference	IREC - K. Villa	Ordered mesoporous WO3 photocatalyst for the selective oxidation of methane to Methanol. Oral	11-16/08/2015	4th International Symposium on Energy Challenges and Mechanics (ECM4) Aberdeen, United Kingdom	Scientific Community (higher education, Research), Industry		Conference
59	Workshop	IREC - J.R. Morante	CO2 reutilization. Oral	18/06/2015	X conference: Barcelona Global Energy Challenges: Workshop II - CO2 valorization and synthetic fuels	Scientific Community (higher education, Research), Industry		Workshop
60	Conference	IREC - J.R. Morante	InsighT.into added value chemicals from reused CO2 based on photoelectrochemistry processes. Oral	5-9/7/2015	The International Conference on Carbon Dioxide Utilization (ICCDU). Singapore	Scientific Community (higher education, Research), Industry		Conference
61	Conference	IREC - J.R. Morante	Earth Abundant Materials for a Photo Electrochemical Based Solar Refinery. Oral invited	28/06/2015 - 03/07/2015	ICMAT.2015 & IUMRS-ICA2015. Singapore	Scientific Community (higher education, Research), Industry		Conference

62	*workshop*	*CCB*	*1st Workshop with CCB members*	*11.3.2013*	*Roche Diagnostics Site in Penzberg, Germany*	*Industry Scientific Community*	*16*	Germany
63	*workshop*	*CCB*	*2nd Workshop with CCB members*	*03.11. 2014*	*Künstlerhaus, Munich,, Germany*	*Industry Scientific Community*	*180*	Germany
64	*workshop*	*CCB*	*3rd Workshop with CCB members*	*09.11. 2015*	*Event Forum Fürstenfeld, Germany*	*Industry Scientific Community*	*155*	France, Germany, Netherlands, Spain, Portugal
65	*6th International Annual Meeting of GDRI*	*IST - C. Henriques*	*From a greenhouse waste to a valuable raw-material: CO_2 for methane production*	*9-13 September 2013*	*Wierzba, Poland*	*Scientific Community*	*~100*	-
66	*XXIV Congresso Ibero–Americano de Catálise*	*IST - F. Ribeiro*	*Conversion of CO2 into methane, using nickel catalysts supported on zeolite USY*	*14-19 September 2014*	*Medellin, Colombia*	*Scientific Community*	*~500*	
67	*EMRS Spring Meeting*	*IST - C. Henriques*	*The development of Ni-zeolite catalysts for the methanation of carbon dioxide with hydrogen: a case study*	*11-15 May 2015*	*Lille, France*	*Scientific Community*	*~100*	-
70	*EMRS Fall Meeting 2015*	*IST - C. Henriques*	*Ni based USY zeolites for CO2 conversion into methane: evaluation of magnesium incorporation on the catalytic performances*	*15-18 September 2015*	*Warsaw, Poland*	*Scientific Community*	*30*	-
69	*EMRS Fall Meeting 2015*	*IST - C. Henriques*	*Hydrogenation of CO_2 over Ni-Zeolite catalysts: a case study*	*15-18 September 2015*	*Warsaw, Poland*	*Scientific Community*	*-50*	-
70	*CEOPS Website*	*EMRS*	*CEOPS Website*	*01/05/2013*	www.ceops-project.eu	*All*		*International*

Section B (Confidential[11] or public: confidential information to be marked clearly)
Part B1

TEMPLATE B1: LIST OF APPLICATIONS FOR PATENTS, TRADEMARKS, REGISTERED DESIGNS, ETC.					
Type of IP Rights[12]:	Confidential Click on YES/NO	Foreseen embargo date dd/mm/yyyy	Application reference(s) (e.g. EP123456)	Subject or title of application	Applicant (s) (as on the application)
Patent	No		FR 13 58965, 18/09/2013	Electrode (surface plasma) and cooling system integration into a fluidized bed reactor	Commissariat à l’énergie atomique et aux énergies alternatives
Patent	No		P201530109. Spain. 28/01/2015	Process for the carbon dioxide reduction to methane by BDB plasma activated catalyst	Fund. Institut Recerca Energia Catalunya (30%), Universitat de Barcelona (10%), Université Pierre Marie et Curie (40%), Instituto Técnico Superior Lisboa (20%)
Patent	No		PT2015/108442	Catalytic System for Syngas Production and Process thereof	Omnidea, Lda

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[11] Note to be confused with the "EU CONFIDENTIAL" classification for some security research projects.

[12] A drop down list allows choosing the type of IP rights: Patents, Trademarks, Registered designs, Utility models, Others.

Part B2

Type of Exploitable Foreground[13]	Description of exploitable foreground	Confidential Click on YES/NO	Foreseen embargo date dd/mm/yyyy	Exploitable product(s) or measure(s)	Sector(s) of application[14]	Timetable, commercial or any other use	Patents or other IPR exploitation (licences)	Owner & Other Beneficiary(s) involved
1 - PATENT	1) NEW HIGH-PRESSURE CO$_2$ ELECTROLYSER 2) NEW PROCESS FOR PRODUCING SYNGAS	YES	FROM 06/05/2015	1. CO2 ELECTROLYSER 2. SYNGAS	1. C27 - Manufacture of electrical equipment 2. C20.1.1 - Manufacture of industrial gases 3. C20 - Manufacture of chemicals and chemical products	2021	*PAT APPL. PT2015/108442*	OMNIDEA (OWNER) UNIVERSIDADE NOVA DE LISBOA, ROYALTIES
2 - PATENT	INTEGRATION DBD SURFACE PLAMSA TECHNOLOGY INTO A FLUIDISED BED REACTOR	YES	FROM 18/09/2013	1. FLUIDISED BED REACTOR 2. SYNTHESIS OF CHEMICAL PRODUCTS	1. C20 - Manufacture of chemicals and chemical products 2. C27.9.0 - Manufacture of other electrical equipment 3. C20.1.1 - Manufacture of industrial gases	2020	Patent application FR 13 58965,	ROYALTIES
3 - PATENT	PROCESS FOR THE CARBON DIOXIDE REDUCTION TO METHANE BY BDB PLASMA	YES	FROM 28/01/2015	1. PROCESS OF CO2 REDUCTION INTO METHANE	1. C20.1.1 - Manufacture of industrial gases C27.9.0 - Manufacture of other electrical equipment 2. C20 - Manufacture of chemicals and chemical products	2020	Patent application P201530109	ROYALTIES
4- EXPLOITATION OF R&D RESULTS	CATALYST FORMULATION	YES	FROM JANUARY 2016	CATALYST FORMULATION FOR METHANE AND METHANOL SYNTHESIS	C24.4.5 - Other non-ferrous metal production	2020	Patents are planned to protect formulations	ROYALTIES
5- EXPLOITATION OF R&D RESULTS	PHOTOCATALYTIC PROCESS	YES	FROM JANUARY 2016	PHOTOCATALYTIC PROCESS FOR PARTIAL OXIDATION OF METHANE	C20 - Manufacture of chemicals and chemical products	2020	Patents is planned to protect a reactor configuration	ROYALTIES

In addition to the table, please provide a text to explain the exploitable foreground, in particular:

- Its purpose
- How the foreground might be exploited, when and by whom

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[19] A drop down list allows choosing the type of foreground: General advancement of knowledge, Commercial exploitation of R&D results, Exploitation of R&D results via standards, exploitation of results through EU policies, exploitation of results through (social) innovation.

[14] A drop down list allows choosing the type sector (NACE nomenclature) : http://ec.europa.eu/competition/mergers/cases/index/nace_all.html

- IPR exploitable measures taken or intended
- Further research necessary, if any
- Potential/expected impact (quantify where possible)

1- CO_2 ELECTROREDUCTION PROCESS USING IONIC LIQUID:

A new high-pressure CO_2 electrolyser that is capable to work at pressures up to 100 bar at near room temperature was developed by Omnidea and Universidade Nova de Lisboa. This high-pressure electrolyser includes an innovative catalytic system, developed also by Omnidea and Universidade Nova de Lisboa which is able to produce fuels, such as methane and syngas. As the results for syngas production were more promising and in a more advanced stage of development, Omnidea, Lda will focus its exploitation activities on syngas. It will commercialize the technology directly or by licensing the technology to syngas producers that will use CO_2 as feedstock instead of methane derived from fossil fuels, coal, or biomass.

Energy intensive industries can also convert CO_2 into syngas and use it as a substitution fuel. The technology still needs further development before entering a demonstration stage. Time to market will be at least five years.

The technology under development is expected to open-up new technological possibilities for the design and development of industrial processes with significantly reduced GHG emissions as syngas is a very valuable and versatile product. It provides opportunities for its use as either a heating gas (due to the heating value of CO and H_2), or by using H_2 and CO as the basic building blocks for chemical and fuel production applications. The market of syngas for gasification represents more than 100 GW thermal and could exceed 117GW by 2018 with an expected annual growth rate of more than 8%[15].

In 2005 the total world annual use of fossil-derived syngas has been calculated[16] to be approximately 6000 PetaJ/year which represents 2% of the total primary energy consumption. Considering that all syngas is produced by steam reforming of natural gas and the heating value of demethanized syngas is 1152 kcal/m^3 [17] at H_2/CO ratio of 5:1, this process produces large quantities of CO_2, ranging from 0.35 to 0.42 m^3 of CO_2 per m^3 of H_2 produced [18], due to both reaction and the heat requirements. If all methane steam reforming would be replaced by a technology where energy is supplied from renewable or non-fossil sources, as is the case of CEOPS technology, this technology could reduce 654 MTon-785 MTon of CO2 emissions annually in the worst case scenario. It is the worst case scenario, because although syngas production from methane steam reforming is the technology which operates with less CO_2 generation from the current industrial employed technologies the actual trends are that more polluting technologies are being more and more deployed. In particular, reforming of naphtha and coal is often preferred when they are available at lower

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[15] http://www.technavio.com/blog/global-syngas-market-heating-up ; Global Syngas Market Heating Up

[16] H.Boerrigter, A. van der Drift Bio key intermediate in production of renewable transportation fuel, Chemicals and Electricity, Optimum and Economic Properties of Fisher-Tropsch Plants, ETA, 2005

[17] Emmanuel O. Oluyede. "Fundamental Impact of Firing Syngas in Gas Turbines". Clemson/EPRI

[18] B. Fidalgo and J. A. Menéndez In: Syngas: Production, Applications and Environmental Impact ISBN: 978-1-62100-870-5
Editors: A. Indarto, J. Palguandi. 2013 Nova Science Publishers, Inc. pp: 121-149

cost with comparison to natural gas[19] and the coal gasification is growing at a fast pace. These latter raw materials are responsible for generating larger amounts of GHG emissions.

2- INTEGRATION DBD SURFACE PLAMSA TECHNOLOGY INTO A FLUIDISED BED REACTOR

The integration of DBD surface plasma into a fluidized bed reactor is a technological success. Furthermore, this technology of plasma allows the achievement of a stability up to at least 5 bar. The results on CO_2 conversion into methane confirms the results obtained in fixed bed reactor with a volumetric DBD plasma. CEA has planned to investigate this technology for other chemicals reactions and also for endothermic reactions. CEA has discussed with some industrials concerning this technology. The interest is confirmed but seems to be too risky for industrials. More investigations must be conducted in order to demonstrate the up-scalability of this technology which is promising.

3- PROCESS FOR THE CARBON DIOXIDE REDUCTION TO METHANE BY DDB PLASMA

CEOPS was a project of three years and excellent results were obtained but fundamental studies are still to be conducted to:

- investigate mechanism which improves the activity at lower temperature. The hypothesis of water desorption from active sites was proposed but not demonstrated.
- the influence of plasma parameters
- identify the role active species generated by the plasma
- Identify the role of photons created by the plasma

4- CATALYST FORMULATION

Zeolite based catalyst:

The application of zeolite-based catalysts to CO2 methanation and/or to methane to MeOH conversion is a recent subject and is related to some of the cited developments that also constitute global new challenges in catalysis, also reflected in CEOPS catalysts development.

CEOPS zeolite-based catalysts preparation and optimization was centred in three types: (i) Ni containing USHY catalysts for DBD plasma CO2 to methane (Pathway A), (ii) Fe containing FAU and MFI structures, for DBD plasma partial oxidation of CH4 to MeOH conversion (Pathway B) and (iii) modified BEA zeolites and Zn, V, W, Mo, Bi-V, Ni-V, La-V, Ni-W and Ni-Mo promoted BEA catalysts, also for Pathway B, by photocatalysis.

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[19] Office of Air and Radiation, U.S. Environmental Protection Agency Technical support document for hydrogen production: proposed rule for mandatory reporting of greenhouse gases (2008)

For the CO_2 methanation catalysts developed, they present a higher activity in thermal catalysis than industrial ones. However the upscaling done has shown a reduction of activity at 300°C. IST has planned to discuss with catalyst manufacturers to assess the opportunity to industrialize the formulation developed in the frame of the CEOPS project. IST is being assessed the patentability of a formulation. A time to market is dependent on the interest of catalyst manufacturer.
For the use of catalyst with DBD plasma technology a parallel development must be done with partners involved in the DBD technologies.

Mesoporous based catalyst:
Mesoporous nickel-ceria zirconia catalyst has achieved a high catalytic activity together with unique properties for DBD plasma catalysis for CO2 conversion to methane. A patent was done with UPMC and IST on these developments. The second main challenge was their implementation on fluidized bed reactor which was also achieved.
The expected roadmap in their development to commercialization IREC has planned a way to the industrialization of their catalyst in two steps:

- Investigate deactivation mechanisms, and establish regeneration protocols (if required)
- Identify possible industrial manufacturers

In both cases, CEA is interested by these active formulations since it develops milli-structured Heat Exchanger Reactors. An industrial catalyst manufacturer should be identify in order to accelerate the industrialisation of one of these formulations (30%Ce 20%Ni / CsUSY(40)) from IST and (15%Ni Ce0.9 Zr0.1 O from IREC) .

5- PHOTOCATALYTIC PROCESS

For methane to methanol conversion, a photocatalytic (PC) technology was investigated. PC technology is an already industrial technology mostly implemented for water depollution. During the project IREC has demonstrated the suitability of this process for obtaining the partial oxidation using catalysts developed by IST and IREC. The achievement of methanol production is a success by itself. This process was selected for the prototype system. But the upscaling has not confirmed the promising result obtained with the lab-scale reactor. According to the catalytic material and reaction conditions, methane to methanol conversion can be realized with a selectivity close to 50%, but with low conversion rate. Higher efficiencies with more efficient photocatalysts (WO_3 mesoporous, $BiVO_4$, Bi_2WO_6) must be reached to be commercially viable. However, once achieved time to market can be short due to the large market of photocatalysis for air and water depollution

4.3 Report on societal implications

Replies to the following questions will assist the Commission to obtain statistics and indicators on societal and socio-economic issues addressed by projects. The questions are arranged in a number of key themes. As well as producing certain statistics, the replies will also help identify those projects that have shown a real engagement with wider societal issues, and thereby identify interesting approaches to these issues and best practices. The replies for individual projects will not be made public.

A General Information *(completed automatically when **Grant Agreement number** is entered.*

Grant Agreement Number:	309 984
Title of Project:	CO2 - Loop for Energy storage and conversion to Organic chemistry Processes through advanced catalytic Systems
Name and Title of Coordinator:	Ing. Bedel Laurent

B Ethics

1. Did your project undergo an Ethics Review (and/or Screening)? E) If Yes: have you described the progress of compliance with the relevant Ethics Review/Screening Requirements in the frame of the periodic/final project reports? Special Reminder: the progress of compliance with the Ethics Review/Screening Requirements should be described in the Period/Final Project Reports under the Section 3.2.2 *'Work Progress and Achievements'*	No
2. Please indicate whether your project involved any of the following issues (tick box) :	
RESEARCH ON HUMANS	
F) Did the project involve children?	No
G) Did the project involve patients?	No
H) Did the project involve persons not able to give consent?	No
I) Did the project involve adult healthy volunteers?	No
J) Did the project involve Human genetic material?	No
• Did the project involve Human biological samples?	No
• Did the project involve Human data collection?	No
RESEARCH ON HUMAN EMBRYO/FOETUS	
K) Did the project involve Human Embryos?	No
L) Did the project involve Human Foetal Tissue / Cells?	No
M) Did the project involve Human Embryonic Stem Cells (hESCs)?	No
N) Did the project on human Embryonic Stem Cells involve cells in culture?	No
O) Did the project on human Embryonic Stem Cells involve the derivation of cells from Embryos?	No
PRIVACY	
P) Did the project involve processing of genetic information or personal data (eg. health, sexual lifestyle, ethnicity, political opinion, religious or philosophical conviction)?	No
Q) Did the project involve tracking the location or observation of people?	No
RESEARCH ON ANIMALS	
R) Did the project involve research on animals?	No
S) Were those animals transgenic small laboratory animals?	No

T) Were those animals transgenic farm animals?	No
U) Were those animals cloned farm animals?	No
V) Were those animals non-human primates?	No
RESEARCH INVOLVING DEVELOPING COUNTRIES	
W) Did the project involve the use of local resources (genetic, animal, plant etc)?	No
X) Was the project of benefit to local community (capacity building, access to healthcare, education etc)?	No
DUAL USE	
• Research having direct military use	No
Y) Research having the potential for terrorist abuse	No

C Workforce Statistics

3. Workforce statistics for the project: Please indicate in the table below the number of people who worked on the project (on a headcount basis).

Type of Position	Number of Women	Number of Men
Scientific Coordinator		4
Work package leaders	1	6
Experienced researchers (i.e. PhD holders)	12	20
PhD Students	6	
Other	10	8

4. How many additional researchers (in companies and universities) were recruited specifically for this project?	7
Of which, indicate the number of men:	3

D Gender Aspects

5. Did you carry out specific Gender Equality Actions under the project? For 4/10 partners the main scientific contact was a female.	○ ●	Yes No

6. Which of the following actions did you carry out and how effective were they?

		Not at all effective				Very effective
☐	Design and implement an equal opportunity policy	●	○	○	○	○
☐	Set targets to achieve a gender balance in the workforce	●	○	○	○	○
☐	Organise conferences and workshops on gender	●	○	○	○	○
☐	Actions to improve work-life balance	●	○	○	○	○

● Other: For 4/10 partners the main scientific contact was a female.

7. Was there a gender dimension associated with the research content – i.e. wherever people were the focus of the research as, for example, consumers, users, patients or in trials, was the issue of gender considered and addressed?

○ Yes- please specify

● No

E Synergies with Science Education

8. Did your project involve working with students and/or school pupils (e.g. open days, participation in science festivals and events, prizes/competitions or joint projects)?

● Yes- please specify: 2 summer schools were organised during the project

○ No

9. Did the project generate any science education material (e.g. kits, websites, explanatory booklets, DVDs)?

● Yes- please specify: IST included results of the project in lesson for students

○ No

F Interdisciplinarity

10. Which disciplines (see list below) are involved in your project?

○ Main discipline[20]: 2.3

○ Associated discipline[20]: 1.2 ○ Associated discipline[20]: 1.3

G Engaging with Civil society and policy makers

11a Did your project engage with societal actors beyond the research community? *(if 'No', go to Question 14)*	○ ●	Yes No

11b If yes, did you engage with citizens (citizens' panels / juries) or organised civil society (NGOs, patients' groups etc.)?

○ No

○ Yes- in determining what research should be performed

○ Yes - in implementing the research

○ Yes, in communicating /disseminating / using the results of the project

11c In doing so, did your project involve actors whose role is mainly to organise the dialogue with citizens and organised civil society (e.g. professional mediator; communication company, science museums)?	○ ○	Yes No

12. Did you engage with government / public bodies or policy makers (including international organisations)

● No

○ Yes- in framing the research agenda

○ Yes - in implementing the research agenda

○ Yes, in communicating /disseminating / using the results of the project

13a Will the project generate outputs (expertise or scientific advice) which could be used by policy makers?

○ Yes – as a **primary** objective (please indicate areas below- multiple answers possible)

○ Yes – as a **secondary** objective (please indicate areas below - multiple answer possible)

● No

13b If Yes, in which fields?

Agriculture Audiovisual and Media Budget Competition Consumers Culture Customs Development Economic and Monetary Affairs Education, Training, Youth Employment and Social Affairs		Energy Enlargement Enterprise Environment External Relations External Trade Fisheries and Maritime Affairs Food Safety Foreign and Security Policy Fraud Humanitarian aid		Human rights Information Society Institutional affairs Internal Market Justice, freedom and security Public Health Regional Policy Research and Innovation Space Taxation Transport	

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[20] Insert number from list below (Frascati Manual).

13c If Yes, at which level?

- ○ Local / regional levels
- ○ National level
- ○ European level
- ○ International level

H Use and dissemination

14. How many Articles were published/accepted for publication in peer-reviewed journals?	**16**
To how many of these is open access[21] provided?	**0**
How many of these are published in open access journals?	**0**
How many of these are published in open repositories?	**0**
To how many of these is open access not provided?	**16**
Please check all applicable reasons for not providing open access:	
☐ publisher's licensing agreement would not permit publishing in a repository ☐ no suitable repository available ■ no suitable open access journal available ☐ no funds available to publish in an open access journal ☐ lack of time and resources ☐ lack of information on open access ☐ other[22]: ……………	

15. How many new patent applications ('priority filings') have been made? *("Technologically unique": multiple applications for the same invention in different jurisdictions should be counted as just one application of grant).*	**3 during the during the project + 1 in progress**

16. Indicate how many of the following Intellectual Property Rights were applied for (give number in each box).	Trademark	**0**
	Registered design	**0**
	Other	**3**

17. How many spin-off companies were created / are planned as a direct result of the project?	**0**
Indicate the approximate number of additional jobs in these companies:	

18. Please indicate whether your project has a potential impact on employment, in comparison with the situation before your project:

■	Increase in employment, or	■	In small & medium-sized enterprises
☐	Safeguard employment, or	☐	In large companies
☐	Decrease in employment,	☐	None of the above / not relevant to the project
☐	Difficult to estimate / not possible to quantify		

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[21] Open Access is defined as free of charge access for anyone via Internet.

[22] For instance: classification for security project.

19. For your project partnership please estimate the employment effect resulting directly from your participation in Full Time Equivalent (*FTE = one person working fulltime for a year*) jobs:	*Indicate figure:*
Difficult to estimate / not possible to quantify	■

I Media and Communication to the general public

20. As part of the project, were any of the beneficiaries professionals in communication or media relations?

● Yes (EMRS & CCB) ○ No

21. As part of the project, have any beneficiaries received professional media / communication training / advice to improve communication with the general public?

○ Yes ● No

22 Which of the following have been used to communicate information about your project to the general public, or have resulted from your project?

☐ Press Release
☐ Media briefing
☐ TV coverage / report
☐ Radio coverage / report
■ Brochures /posters / flyers
☐ DVD /Film /Multimedia

☐ Coverage in specialist press
☐ Coverage in general (non-specialist) press
☐ Coverage in national press
☐ Coverage in international press
■ Website for the general public / internet
■ Event targeting general public (festival, conference, exhibition, science café)

23 In which languages are the information products for the general public produced?

☐ Language of the coordinator
☐ Other language(s)

■ English

2. FINAL REPORT ON THE DISTRIBUTION OF THE EUROPEAN UNION FINANCIAL CONTRIBUTION

This report shall be submitted to the Commission within 30 days after receipt of the final payment of the European Union financial contribution.

Report on the distribution of the European Union financial contribution between beneficiaries

Name of beneficiary	Final amount of EU contribution per beneficiary in Euros
Commissariat à l'énergie atomique et aux énergies alternatives	775 348,00
C.T.G. SPA	87 193,89
Instituto Superior Técnico	374 770,55
OMNIDEA	165 512,00
Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa	225 176,00
GDF-Suez Energy Romania	16 535,50
Fundacio Institut De Recerca De L'energia De Catalunya	484 065,70
European Materials Research Society	83 893,68
Chemie-Cluster Bayern	146 350,53
Université Pierre et Marie Curie	211 283,00
Total	2 643 210,41