ECOLEFINS context

Chemical industry is a major global warming contributor, responsible for the 5.8 % of global CO_2 emissions (not accounting the 3 % of the cement and the 7.2 % of the steel industry), whereas the petrochemicals amount up to a 3.6 %. To stop or better **reverse this impact** and remove CO_2 from the atmosphere, the chemical industry should transition to **renewable electricity for hydrogen** production and neutral or **negative carbon sources**; the latest referring to atmospheric or industrial CO_2 emissions and offering the option of transforming the chemical industry into a vast carbon sink.

Light olefins ($C_{2-4}^{=}$s) are top chemicals (ca. 150 and 100 Mtns, annual ethylene and propylene global production), and the key building blocks for a vast range of products (plastics, gels, fibers, elastomers, resins etc.). Today, $C_{2-4}^{=}$s are produced by the energy intensive processes of naphtha steam-cracking or ethane thermal-cracking, which charge each ton of olefins with on average 3 – 5 $tnCO_2/tnC_{2-4}^{=}$, depending upon the production route and the carbon and energy sources. In this context, ECOLEFINS aims to establish a new, all-electric paradigm for the conversion of H_2O and CO_2 emissions into $C_{2-4}^{=}$s, and **reverse their carbon-heavy, petroleum-based production to a carbon negative one**. That is to reverse the 3 – 5 $tnCO_2/tnC_{2-4}^{=}$ emissions to -3 $tnCO_2/tnC_{2-4}^{=}$ capture and valorization, summing up to a total of up to 8 $tnCO_2/tnC_{2-4}^{=}$ carbon gain; and moreover to achieve this gain **by a route of substantially increased energy-efficiency and light olefins yield**.

ECOLEFINS concept and objectives

To this aim, ECOLEFINS introduces the core breakthrough of **co-ionic electrolytes**, for the simultaneous protons (H^+) supply and oxide anions (O^{2-}) withdrawal to/from CO_2. The operating principal of the co-ionic Electro-chemical Membrane Reactor, is shown in Fig. 1. According to this concept, steam electrolysis, at the anode, generates protons that are electro-chemically transferred to the cathode to hydrogenate CO_2. Simultaneously, CO_2 is electro-lyzed at the cathode, and its oxygen is electro-chemically removed, in order to suppress the formation of the major H_2O and CO by-products and **shift the CO_2-to-olefins equilibrium**. Thus, the core ECOLEFINS' objective is to prove the concept's effectiveness, and:

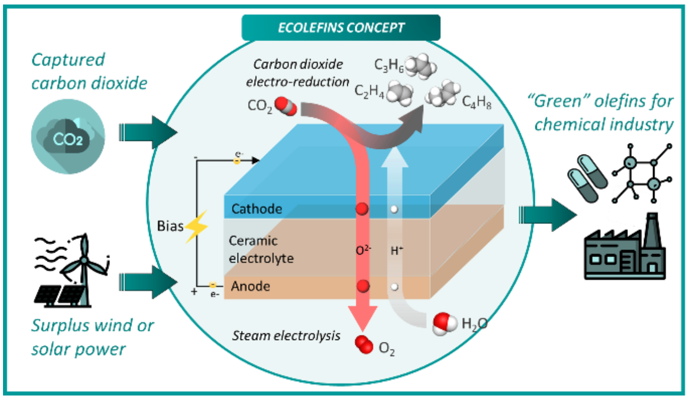

Fig. 1. ECOLEFINS concept for the simultaneous H^+/O^{2-} supply/removal to/from CO_2, for light-olefins yield

(1) **over-double the 15 % $C_{2-4}^{=}$ yield** of the conventional, thermo-catalytic CO_2-to-$C_{2-4}^{=}$ hydrogenation at high pressures (~30 bars), by**: (i) employing protons** as the active hydrogen species for electrolyzed CO_2 hydrogenation, **(ii)** controlling hydrogen flooding and **determining the hydrogen/carbon ratio** at the (electro)catalyst, by the electrochemical supply of hydrogen, and (iii) **forcing forward the hydrogenation equilibrium**, by suppressing the oxygen-containing by-products,

(2) **bypass the high-pressure requirement of the catalytic CO_2-to-$C_{2-4}^{=}$ hydrogenation**, by the substitution of the high-pressure flow-work with the direct expenditure of electrical work, which, in the case of N_2 hydrogenation to NH_3 has be proven drastically more effective, and

(3) electrolyze steam within the same electrochemical reactor, thus taking advantage of the **enhanced electrolysis efficiency at moderate temperatures** (<500 ^oC) and **bypassing the ohmic losses of a separate electrolysis cell**; overall to **increase the CO_2-to-$C_{2-4}^{=}$ energy efficiency by up to 25 %**, compared to high-pressure, thermo-catalytic CO_2-to-$C_{2-4}^{=}$ hydrogenation combined with a separate electrolysis cell.

Within these overall objectives, ECOLEFINS will also aim to:

(4) develop **reliable, atomic-scale models** to design moderate temperature co-ionic electrolytes,

(5) apply **dense, durable and thin co-ionic membranes**, of single (H^+ conductors of increased O^{2-} conductivity), or dual phase (by the solid-state mixing of a H^+ and an O^{2-} conductor), for co-ionic current densities > 0.1 A/cm^2 and Area Specific Resistances <10 Ωcm^2 at moderate temperatures (< 400 ^oC),

(6) fabricate and operate durable (maintain initial performance for at least 100 hours) and efficient **planar and tubular test-cells** and **prototype short stacks and tubular modules**,

(7) identify the spatial/time distributions of the (electro)chemical and transport phenomena of ci-EMR unit-cells, short-stacks and tubular modules, and **verify CFD models against experimental operation**,

(8) **design and simulate ECOLEFINS total-plants** of industrial scale (from CO_2 capture to light olefins production and purification), and develop a digital modelling tool to optimize its performance, upon a range of key inputs (capacity, conversion/selectivity, ci-EMR areas and area specific resistances etc.),

(9) conjunct an **economic performance calculator** to the digital modelling tool, for a range of economic criteria (i.e. internal rate of return, pay out time, etc.), upon variable economic inputs (technology and electricity cost, products pricing etc.),

(10) perform a **Life Cycle Sustainability Analysis** (LCSA) of real scale ECOLEFINS solutions, including LCA, LCC, and S-LCA, comparatively against the economic and sustainability profile of oil-to-$C_{2-4}^{=}$ routes,

(11) elaborate preliminary **business plans**, entailing business canvas, scenario, PEST and SWOT analysis, as well as competitive matrices, for: **(i)** the electrochemical $C_{2-4}^{=}$ production by current producers or end users, in conjunction with exploitable CO_2 sources, and **(ii)** the marketization of ci-EMR materials, planar/tubular cells and stack/module prototypes and systems.

(12) record and promote **social acceptance**, among an extensive range of stakeholders, by questionnaire-based surveys and the creation of training guides.

ECOLEFINS **ambition** entails a multi-disciplinary task of highly tuned synergies among cutting edge research in: **(i)** advanced materials science & engineering, for co-ionic electrolytes and nano-engineered electrodes, the latest including a range of nano-formulations, as well as composite oxides with exsolved nano-phases and organometalics derived catalysts, **(ii)** electrochemical processes engineering, **(iii)** catalysis science and engineering, **(iv)** computer aided materials design and atomic scale modelling, to guide the development of co-ionic conductors, **(v)** CFD modelling of the novel co-ionic reactors for the complex CO_2-to-$C_{2-4}^{=}$ reaction-system, **(vi)** the solid-oxide stacks technology, **(vii)** the industrial-scale, integrated processes modelling and economic evaluation, **(viii)** the comprehensive sustainability assessment, **(ix)** the applied social research for impact framing, as well as **(x)** the marketization planning of the developed new materials (co-ionic conductors and nano-formulated catalyst), electrochemical reactors/cells and for light olefins electrification.

Work performed in the first year and main achievements

During the midterm of the project, atomic scale modelling explored composite oxides of predominately protonic conductivity, and suggested targeted doping to induce oxide ion conductivity. Applying these suggestions, certain composites were manufactured and found to obtain >20 % oxide ion conductivity, aiming for the stoichiometrically ideal 50 %. In parallel, dual-phase composites, incorporating separate proton and oxygen conducting phases have been developed and are currently studied for their intra-facial stability and ion-conducting properties. ECOLEFINS has also developed 3D planar and tubular configurations and mapped the co-ionic counter-fluxes, by literature-validated CFD simulations of predominantly H^+ conductors, which are ready to incorporate the incoming measurements for co-ionic conductors and CO_2-to-olefins electro-kinetics.

Regarding CO_2-to-olefins electro-catalysts (cathodes), a range of mono- and bi-metallic materials in various nano-geometries with exposed iron and cobalt phases has been developed and tested, exhibiting top olefins yields (>16 %), for high pressure, catalytic CO_2-hydrogenation. Screened catalysts have already been examined as cathodes in predominantly H^+ conducting reactors, and grounded the operability of the concept. Moreover, metal-organic frameworks with targeted metal contents, have also been developed and examined as catalysts' precursors. Regarding anodes for steam electrolysis, praseodymium perovskites with alkali dopants, applied by the cutting-edge acid-etching technique to predominantly proton conducting cells, have obtained current densities of 150 mA cm^{-2}, at 450 ^oC, confronting with the project's objective of > 100 mA cm^{-2} at 400 ^oC. Moreover, extensive discussions have paved the way for the coming efforts to upscale the co-ionic reactors to short stacks of "windows" configuration.

Finally, for the simulation and the economic evaluation of real-scale ECOLEFINS plants, an equivalent system design for the co-ionic electrochemical reactor, consisting of combined reactors for the cathode and the anode, has been developed; along with an innovative configuration of sequential gas-separation and low temperature distillation for ethylene, propylene and butylenes purification. Both these configurations are to be integrated with an already developed simulation of a mono-ethanolamine CO_2 separation unit, into a thermally integrated, total ECOLEFINS plant.

Results beyond the state of the art

ECOLEFINS core aim is to prove the effectiveness of novel electrochemical reactors of dual ionic conductivity, which lie beyond the current state of art. This ground-braking idea was inspired by the very nature of the benchmark CO_2-to-olefins reaction system, an equilibrium limited hydrogenation where most of the supplied hydrogen is consumed by the CO_2's oxygen content towards steam or the mild CO_2 reduction to CO. Thus, the central innovation to induce O^{2-} conductivity, in order to withdraw CO_2's oxygen from the CO_2-to-olefins equilibrium, results in the additional beyond the state of the art aim, to conduct a benchmark reaction of major economic interest, under conditions of oxygen removal. Conditions that may very well alter the complex mechanisms of the CO_2-to-olefins reaction system, to shift its equilibrium to hydrogenated products, and critically suppress hydrogen losses to either steam or oxygen containing products of CO_2 activation.

Oxygen removal from CO_2-to-olefins hydrogenation, in conjunction with the supply of hydrogen in the form of protons, form a totally altered CO_2-to-olefins reaction system, studied by ECOLEFINS in order to drastically increase olefins yields. Increased yields along with the elimination of the high pressure requirements and the high temperature steam electrolysis, within the same reactor, pave the way for increased energy efficiencies. Energy efficiency is a crucial aspect, since electrification induces the electricity cost to light olefins pricing. Increased yields and the energy savings for pressurization and electrolysis can cut half down this cost, as well as the overall electricity demand for ethylene and propylene electrification, which is estimated at 35 % of the total EU electricity consumption, for their total inland production.

Besides the core idea of electrified olefins production in co-ionic reactors, the ECOLEFINS pathway entails numerous beyond the current state of art innovations, regarding:

- the atomic scale modelling of complex oxides of co-ionic conductivity,
- the CFD modelling of co-ionic electrochemical reactors, for the CO2-hydrogenation complex reaction,
- the development of proton-conducting single phases of advanced oxide-ions conductivity, as well as of dual-phase, co-ionic conductors, by merging proton and oxygen conducting phases,
- the development of nano-formulated catalysts of remarkable light olefins yields, as well as metalorganic frameworks of targeted (bi-)metallic contents,
- the development of modified state-of-art electrodes for steam electrolysis, and

which have already proceeded during the project, as well as:

- the up-scaling of the innovative co-ionic, membrane reactors towards short-stacks,
- the development of a digital tool for the process modelling and economic assessment,
- the life-cycle sustainability assessment of light olefins electrification, the ECOLEFINS concept and the innovative, nano-engineered, co-ionic reactors, and
- the social acceptance and the marketing planning of ECOLEFINS solutions for light olefins electrification, or the materials and the know-how developed within the process of proving the ECOLEFINS concept,

which are foreseen, within the ongoing period. In the remaining of the project, the **ECOLEFINS** innovations will be prioritized, according to their maturity level, which is expected to end up at TRL 3-4 during the course of the project. In addition, the long term (ECOLEFINS $C_{2-4}^{=}$ electrification), medium term (ci-EMR stacks/modules and processes) and intimate (ci-EMR cells and materials) market opportunities, will be researched, followed by dedicated business models in accordance to their nature and the owner's profile.

Aligned with the IPR strategy, the generation of joint or individual exploitation roadmaps, including patent applications, will be conceptualized and private or public funding schemes will be explored. Spin-offs creation will also be considered, for the identified growing markets for materials and EMRs. In this context, ECOLEFINS team members participated the **EIC Tech to Market Entrepreneurship Programme**, and plan to frequently take advantage of the European Innovation Council Booster and Business Acceleration services. Regarding impact maximization, the project already executes a broad portfolio of outreach activities to exploit ECOLEFINS materials, cells, prototypes and modelling tools; whereas for dissemination, 3 journal publications and 10 conference papers have been produced, along with the ECOLEFINS participation in the workshop of the relevant EU funded project FRESH on CO_2 valorization to chemicals.

At full scale deployment, the ECOLEFINS long term impacts are: **(1)** to decouple major petrochemicals from petroleum and expand light olefins production to end users, **(2)** to save/capture up to 20% of EU's industrial CO_2 emissions, and **(3)** to cut half down the electrified olefins production energy consumption and costs, compared to the high pressure thermo-catalytic alternative with low temperature electrocatalytic hydrogen. These major impacts, are fully aligned with EU's Green Deal, which assess energy-intensive chemical industries as indispensable solution providers to multiple value chains, for Europe's transition to carbon-neutrality. These solutions, as the ECOLEFINS one, could fundamentally transform EU's petrochemical industry into a global innovation hub and investments' hotspot for climate-neutral technologies, and strengthen its worldwide competitiveness.