plAsma liquid coupled with Catalysis for Hydrogen productIon and selective aLcohoL conversion (ACHILLES)

Objectives: **The idea of ACHILLES is to convert alcohols into hydrogen and aldehydes using an innovative plasma process** operating at room temperature. Hydrogen is considered to be one of the most important clean energy vectors for the future. Hydrocarbon reforming processes are currently used in industry to produce hydrogen. However, a lot of CO_2 is also produced. **Clean hydrogen production is a priority for the EU's post-COVID-19 economic recovery** [1]. Clean hydrogen can be produced by electrolysis, photoelectrochemical or thermochemical processing of water or **alcohols**, but also **by means of plasma discharges produced directly in these liquids**. However, today clean hydrogen is 2 to 3 times more expensive to produce than "grey" hydrogen [1]. One way to make alternative processes competitive compared to conventional petrochemistry is **to valorize all the reaction products. This is particularly the case when hydrogen is produced from alcohol, where the reactions can be controlled to obtain selectively desired carbonaceous molecules such as aldehydes** [8]. Producing aldehydes **maintains the carbon in a liquid state** and also yields molecules serving as reaction intermediates in chemistry. Obtaining **aldehydes from alcohols** by plasma at normal pressures would be a significant advantage, especially when aldehyde production is **combined with that of hydrogen.**

Context: **ACHILLES aims to valorize alcohols by means of plasma discharges in contact with liquid and catalysis**. The study of non-equilibrium plasmas generated in contact with or inside liquids, referred to as **Plasma-Liquids (PLs)** [12], is a topic that has gained much importance during the last 20-25 years. PLs are sources of radicals as well as UV light emission [3] and can also produce shock waves when discharges are intense [4]. Due to their properties, PLs are currently mainly used for water disinfection, the production of Plasma-Activated Water (PAW) for agriculture and medicine, or the synthesis of nanomaterials [5]. PLs are also studied in ethanol to produce hydrogen, and depending on the conditions, the carbon is either converted into CO and hydrocarbons in a non-selective way or more recently in the form of carbon nanodots [6]. ACHILLES is based on preliminary results obtained during the PhD of A. Moussalem [7], which showed the feasibility of this novel process, even if several problems remain to be solved and many questions are still open. **The originality of ACHILLES is the selective conversion of alcohols into aldehydes while producing H_2 by means of atmospheric pressure plasma discharges, and to unravel the reaction mechanisms.**

Methodology and scientific approach: A preliminary batch plasma reactor has been developed and will be improved upon in this project. A DBD type electrode configuration was selected with one of the electrodes above the liquid phase, creating a large contact surface between the two phases. DBD discharges have a very pronounced non-equilibrium character, offering high chemical reactivity while allowing the liquid medium to be maintained at room temperature. The reactor is connected to a flow measurement system and to a gas chromatograph, enabling on-line quantification of the effluents. The liquid phase can also be injected into the chromatograph to analyze low-volatility or non-volatile products. **Selectivities up to 80% in aldehyde conversion were obtained for ethanol and butanol (to produce ethanal and butanal, respectively) in a batch reactor, and the energy consumption is estimated around 1.5-2 kWh/m^3 of H_2 produced, which is a promising preliminary result.** We propose in this project i) to improve the selectivity by adding catalysts without using noble metals. These catalysts will be deposited on the electrode immersed in the liquid., ii) to follow the process in real time and to understand the mechanisms by performing in-situ diagnosis of the plasma/liquid interface by Raman spectroscopy.

1) Optimization of the plasma process (LISE + LRS): One of the first objectives will consist of **optimizing the geometry of the plasma reactor**. Our preliminary results have shown that the nature of the electrodes (metal and dielectric used), as well as their shape and relative position plays a very important role both for the energetic character of the discharges (mild plasma treatment conditions are desirable to avoid cracking of the alcohols). The influence of the discharge parameters on the reaction products will also be studied. Secondly, the reactor which currently operates in batch mode

will be modified **to run in continuous (or flow) operation,** like all industrial H_2 production processes. Alcohols will be continuously fed into the reactor and transformed, **which also allows control of the residence time in the reactor. The effect of catalyst addition** [9-11] will also be studied to show **whether the yield and selectivity can be improved compared to the action of the plasma alone.** The modifications of the surface of the catalysts before and after plasma exposure will be characterized by classical methods in heterogeneous catalysis (EPR, chemisorption, TEM, XPS…).

2) In-situ diagnostics of plasma/liquid interface (LPP): The liquid-phase diagnostics of the plasma-liquid interfacial region can provide new insight into how the plasma transforms alcohol. Existing techniques suffer variously from a lack of selectivity, spatial resolution, and/or degradation of dyes, chemical probes, or spin traps/probes. Most diagnostics must be performed *ex situ*, removed from the plasma reactor and after treatment. ***In situ*** **Raman spectroscopy**, however, can be completely non-intrusive and highly selective over a wide range of species, being a bond-specific vibrational spectroscopy. D. Pai has reported the liquid-phase structure of the interfacial region of plasma-water interaction during PAW generation [13]. The introduction of a light-sheet microscopy technique enabled the in-situ measurement of NO_3^- and H_2O_2 concentrations with µm-scale depth resolution, revealing that the interfacial layer was 28 µm deep. In similar fashion, in ACHILLES we **seek to track the formation of aldehydes** as well as intermediate reaction products near the plasma-liquid interface with **micron-scale depth resolution** during plasma treatment as a function of time and space [14]. Also, the Raman spectrum of the solvent may provide information on the **physical/chemical environment** of the reaction zone. For example, the **Stokes/anti-Stokes intensity ratio may be employed to determine the temperature** of the alcohol, and distortions of the Raman spectral profile may be correlated with parameters related to the decomposition of alcohol. **Finally, we will develop an initial numerical model of the PL system. We aim to develop a basic model in steady state, which accounts for key physical and chemical interactions at the plasma-liquid interface, major transport phenomena, and a simplified reaction mechanism** that captures the essential features of our experimental results.

Adequacy of the project to the IPI call: ACHILLES aims to control the chemical reactivity of non-equilibrium plasmas in contact with a liquid to obtain selective reactions. The fundamental and ambitious aspect of this project is therefore linked to **the detailed real-time characterization of plasma/liquid interfaces in a non-aqueous medium**, with the aim of understanding the reaction mechanisms involved, by identifying the intermediate species for the formation of aldehydes. This project also proposes to couple plasmas to catalysts in a liquid phase medium, which constitutes an innovation and an additional challenge because plasma/catalysis processes are generally studied in the gas phase. **The ACHILLES project is thus at the crossroads of plasma physics, chemistry, catalysis and chemical engineering**, which justifies the complementarity of the 3 project partners.

Role of each supervisor

J. Pulpytel (LISE): plasma process design and optimization

D. Pai (LPP): plasma diagnostics

G. Laugel (LRS): catalysis and surface characterization

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