NOVEL PROCESS FOR *CYAN* HYDROGEN PRODUCTION AND SIMULTANEOUS CO_2 VALORISATION

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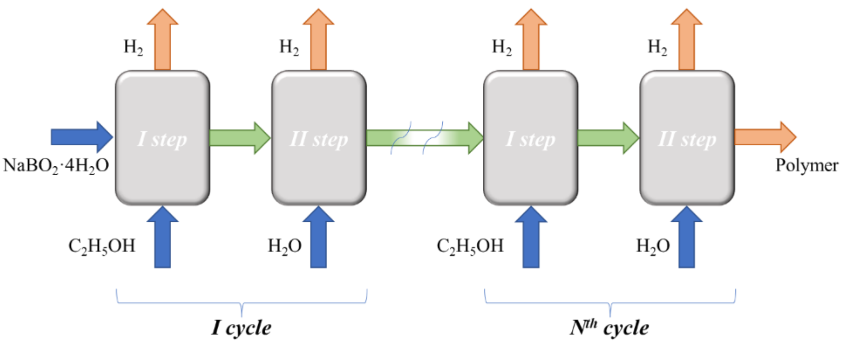
Climate neutral economy is globally recognized as one of the main challenges for a sustainable future. Scholars in both industry and academia agree in foreseeing a radical shift in sustainability and climate policy in the next future. The increasing importance is testified by the amount of resources currently allocated for a sustainable paradigm shift. The chemical industry has a key role in the development of a circular sustainable economy, integrating the needs of the society and environment. Nevertheless, on a global scale, the use of renewable materials and energy is still problematic, with oil, natural gas, and coal still covering most of the world energy consumption. According to the European Union directives and the Paris Agreement, hydrogen and gas infrastructure will play a fundamental role in the transition to a climate neutral economy by 2050. Hydrogen is one of the main building blocks of the bulk and fine chemical industry and a promising energy carrier. The main advantages of hydrogen as an energy carrier are related to its high calorific value and the absence of carbonaceous gases deriving from its combustion. However, most hydrogen is currently produced from fossil fuels, via hydrocarbon reforming or pyrolysis processes. Processes from renewable sources include biological and thermochemical treatment of biomass and water splitting. Both hydrogen production from fossil fuels and thermochemical processes of biomass requires high temperature.

This PhD thesis aims to investigate and optimize a new process for hydrogen production under mild conditions, based on multi-step cycles starting from sodium metaborate ($NaBO_2$) and bio-derived chemicals. Sodium metaborate $NaBO_2$ is a readily available and relatively cheap oxide with a wide range of industrial applications. It is also a by-product of the hydrolysis reaction of sodium borohydride:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2$$

In aqueous solution, $NaBH_4$ can undergo a catalysed hydrolysis reaction, releasing 90% of the stoichiometric hydrogen and producing sodium metaborate $NaBO_2$. The bottleneck for the wide adoption of $NaBH_4$ for hydrogen storage is represented by the difficult regeneration of $NaBH_4$ from $NaBO_2$, consisting of multi-step process, which is inefficient, costly and with high environmental impact.

The investigated process (patent pending) consists in consecutive redox cycles with the transformation of the starting material, $NaBO_2$ and bio-based organics, such as bio-ethanol, in intermediates able to produce hydrogen. The carbon of the feedstock is mostly fixed in polymeric structures with high added-value. As a result, conversion to (bio)polymers and highly pure hydrogen can be simultaneously achieved, under conditions that are milder than the ones usually adopted for hydrogen generation from natural gas.



During the first year of PhD, experimental tests were conducted to optimise the operating conditions of the process and to standardise the experimental procedure and characterisation techniques. For the next years, the objectives are the identification of reaction intermediates, study the kinetics and develop a continuous process.

Alessandra Di Nardo, PhD student XXXVII cycle, July 2022