

CHEMICAL ENGINEERING

Catalytic production of renewable H₂ from wastes

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Supervisor	PIRONE RAFFAELE - raffaele.pirone@polito.it
Contact	
Context of the research activity	<p>Wastewater is of general concern for environmental sustainability. Lignocellulosic biomass processing (such as hydrolysis, pyrolysis, and hydrothermal liquefaction) results in secondary aqueous streams in which a high fraction of the initial carbon content of the biomass is virtually lost; also food industry produces streams with a variety of organic load. Among other valorisation alternatives for such wastes, aqueous phase reforming (APR) has been proposed as a process driven at relatively mild conditions, able to convert oxygenated molecules into hydrogen. Despite its potential, APR has commonly been investigated with model compounds, and a systematic study on the possible fields of application of this technology is lacking</p>
Objectives	<p>Aqueous phase reforming (APR) has been proposed to convert oxygenated hydrocarbons dissolved in water into hydrogen at milder conditions compared to steam reforming (230-270 °C and autogenous pressure). The reaction is catalytically activated often by a noble metal supported catalyst (commonly Pt). This process may be exploited by coupling it with industries which need a way to reduce the organic content of their liquid by-products (for environmental obligations) and at the same time obtain a higher value product (overcoming economical constraints). Despite the potential of this process, APR has been mostly investigated with simple model compounds, such as glycerol, methanol, sorbitol. On the other hand, more challenging solutions, such as multi-component synthetic mixtures or even actual wastewaters, were less investigated. The aim of this proposed PhD research is to extend the knowledge of the process to more realistic feeds.</p> <p>The APR reaction tests are performed in a series of 100-500mL mini benchtop reactors (Parr) equipped with a model reactor controller. The reactor is charged with a certain volume of the desired solution (feed of the test); a precise amount of catalyst (typically 5% Pt/C) is also suspended in the reacting water. Once fastened, the reactor was purged with nitrogen and pressurized at a certain precise pressure of N₂ (typically 0.2-0.3MPa). The absence of external mass transfer limitation is assured increasing gradually the stirring. This is the standard lab reactor configuration, but aim of the PhD student is also to design a novel reactor assembly to succeed in shortening</p>

the warm-up time.

Reaction time and temperature are key parameters to be investigated. At the end of the reaction, the reactor is cooled down thanks to an internal cooling loop and external water bath, and the gas phase is collected in a syringe and analyzed by μ GC. The liquid phase is instead filtered by gravity to recover the catalyst and then analyzed through TOC and HPLC analysis. The spent catalyst was dried in an oven overnight (100-120°C) and weighted afterward. Sometimes, it can be interesting to the catalyst, performing reaction tests with an aged catalyst used as such, without any further treatment.

The characterization of APR products focused on both gas and liquid phases, by means of a Micro-GC, and HPLC analysis. Total organic carbon (TOC) analysis is also performed using a TOC-VCSH analyzer to obtain carbon balance closure within limited errors.

The involved catalyst must be characterised with several techniques (TPR/TPD/TPO, H₂ pulse chemisorption, XPS, XRD, RAMAN, FTIR, TEM, SEM and others).

The general aim of the research is to use all these procedures (and others) to unravel the mechanisms of reaction activated by the catalysts in more realistic wastewater conditions compared to the studies on single model molecules

Skills and competencies for the development of the activity

the candidate should be an expert of chemical processes, possibly she/he must be skilled in catalytic processes, in both reaction conduction and characterization analysis (of both liquid and solid compounds).

Presumably, optimal candidates are chemical, materials and energy engineers, but also industrial chemists or general chemists.