Design of non-conventional chemical processes for biomass valorization

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Despite chemical industry still runs mainly with fossil feedstock, the demand for renewable sources has steadily increased over the last two decades. In this frame, biomass and bio-wastes have been recognized as renewable source of fixed carbon for the production of valuable platform chemicals for industrial applications. In the meantime, new enabling technologies for processes intensification have been developed and successfully applied in this field. Microwaves (MW), ultrasound (US), hydrodynamic cavitation (HC) may generate high-energy microenvironments. The aim of this PhD thesis was the design of new processes based on non-conventional technologies for biomass extraction and selective conversion. The investigation started on batch reactors provided suitable data for systems scale up, towards industrial applications. Furthermore, the target is a zero-wastes protocol to treat different biomasses following a circular economy approach. The combination of new green solvents, sustainable heterogeneous catalysts and non-conventional chemical reactors opened new paths for biomass conversion. Well-balanced cascade process enabled a full valorization of biomass constituents and by-products into high-value-added chemicals. According to this strategy, four pivotal steps have been deeply investigated: (I) Metabolites Extraction, (II) Pre-treatment, (III) Structural Conversion and (IV) Platform Modification.

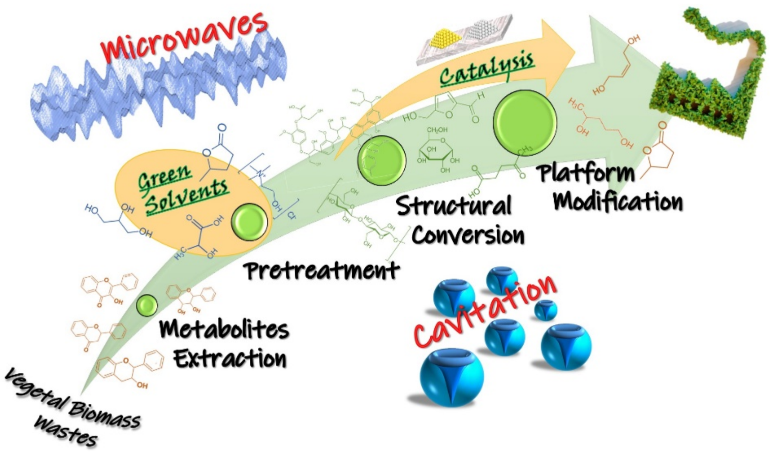

Fig. 1: Biorefinery cascade approach for vegetal residues.

Extractions (I) can provide several valuable secondary metabolites, such as polyphenolic compounds. Different protocols have been optimized, by kinetic studies, among vegetal residual matrixes: cocoa shells, curcuma, tea, grape stalks and pomace. Structural biopolymers, as alginates from algae, pectins from citrus wastes, and lignin from lignocellulosic materials could be isolated within the same protocols. Green solvents play a key role for new and sustainable pre-treatment (II), showing surprising synergies with non-conventional techniques to achieve fractions enriched in lignin-derived polyphenols and solid residues suitable for the conversion into fermentable sugars, after enzymatic hydrolysis. Pre-treatment can also be implemented before the extraction phase, in order to cripple recalcitrant biomasses, enhancing the final metabolites recovery. Enabling technologies exhibit synergistic effects also with heterogeneous catalysts, mainly due to hot-spots generation on the active sites. This feature can be applied for structural biopolymers conversion (III) into valuable building blocks: hydrolysis and isomerization have been exploited to produce monosaccharides, hydroxymethylfurfural (HMF) or levulinic acid from cellulose and hemicellulose. For these purposes, solid acid catalysts as sulfated zirconia and zeolites have been studied. A further modification of biobased derivatives could be carried out *via* reduction reactions under heterogeneous catalysis with Au, Pd or Ru nanoparticles supported on TiO_2, ZrO_2, Al_2O_3 or AC. The main products obtained were γ-valerolactone (GVL) and 1,4-pentanediol. The best performing protocols of the cascade process have been chosen for the scaling up, increasing batch volumes towards pilot scales (75L), or moving to flow systems, with pre-industrial flow-rates (from 1L/h to 20L/min). Final tests were carried out in a plant working with 50 kg/die of lignocellulosic residues to obtain fermentables, boosting the delignification percentage of the matrix. On the other hand, the biomass delignification was also achieved through an integrated process: biowastes were treated in GVL to recover pure lignin and to convert cellulose into levulinic acid, which was then hydrogenated to GVL. Following a circular approach, the solvent was regenerated and recycled for next delignification steps.