Winery wastes valorization based on the "integrated biorefinery" concept

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Lignocellulosic biomass derived from agricultural and forestry residues (e.g. prunings) as well as food industry wastes (e.g. kernels, shells) can be converted not only into fuels but also into a wide variety of value-added chemicals. Within an integrated "biorefinery" context, the three main components of the lignocellulosic biomass (cellulose, hemicellulose, lignin) can be converted into platform chemicals with many industrial applications. The first step of the proposed concept (Figure 1) is the selective fractionation of the biomass into its main components and can be achieved via the hydrothermal pretreatment in pure water (Nitsos, 2016). In this process, hemicellulose oligomers, monomers (xylose/xylan) and degradation products (e.g. acetic and formic acid, furfural, etc.) are isolated in the liquid fraction while cellulose and lignin remain at the solid fraction. Another effective process is the organosolv pretreatment, in presence of ethanol-water mixture as solvent, resulting in the recovery of the three biomass component in one step. Furthermore, (bio)catalytic processes can be applied for the valorization of each stream. Cellulose can be converted to glucose which can be used for the production of bioethanol via fermentation or sugar derived platform chemicals. Lignin can be utilized in epoxy/phenol resins or can be converted to aromatic and/or phenolic monomers via catalytic fast pyrolysis and hydrogenolysis reaction (Margellou, 2019).

Based on the circular bio-economy idea, wineries could provide large quantities of lignocellulosic wastes each year, produced in different steps of the vinification process: prunings provided direct from the crops, stems produced during the destemming of grapes and before their crushing and grape pomace obtained after the crushing and pressing procedures. In this work, winery wastes were obtained by a local winery and valorized via thermochemical and (bio)catalytic processes. After the analytical characterization of the biomass feedstocks, the main components were separated via hydrothermal pretreatment. Afterwards, cellulose rich pulp was converted to glucose via enzymatic hydrolysis and lignin to a bio-oil rich in alkoxy-phenols via catalytic hydrogenolysis reaction.

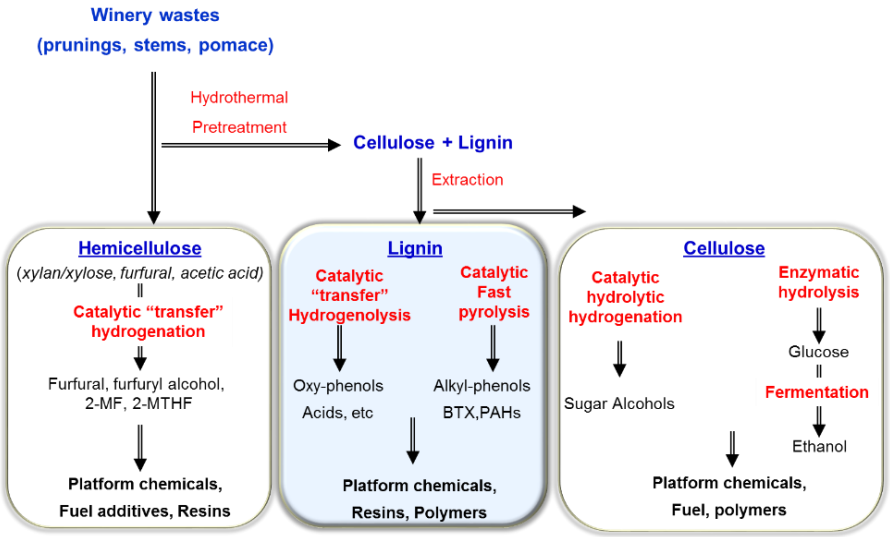

Figure 1. Biorefinery concept proposed for the efficient valorization of winery wastes.

Considering the hydrothermal pretreatment, in pure water, all the winery wastes showed high solubilization and removal of hemicellulose into the liquid fraction, while cellulose and lignin remain in the solid fraction. In a second step, surface lignin was extracted from the pretreated biomass with "green" solvents (Nitsos, 2019). Alternatively, in the organosolv process, cellulose is obtained in solid fraction while hemicellulose and lignin were isolated in the liquid fraction and after precipitation, lignin is obtained as solid. Cellulose rich pulps obtained after the hydrothermal pretreatment were hydrolyzed to glucose in presence of enzyme cocktail of cellulases and hemicellulases. High amounts of glucose were achieved and correlated with the properties of the initial feedstock.

The highest enzymatic conversions were observed in the solid obtained from the organosolv procedure and in the solid remained after the extraction of surface lignin. Furthermore, the hemicellulose traces in the cellulose pulp were also converted into xylose, increasing the total sugars concentration. Increase in the severity of the hydrothermal pretreatment led to decrease of the glucose production due to the higher xylose isolation in the liquid fraction (Figure 2).

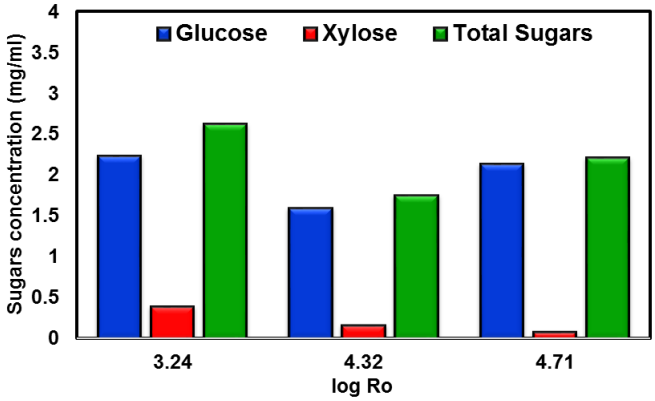

Figure 2. Sugars production via the enzymatic conversion of vine prunings.

The lignin isolated either via the hydrothermal-extraction or the organosolv process were converted to bio-oil rich in alkoxy-phenols via the hydrogenolysis reaction, under mild conditions, in presence of metallic catalysts supported on micro/mesoporous carbons and hydrogen donor solvent (ethanol). An optimization of the process determining parameters (temperature, time, catalyst type and mass, etc.) were carried out using Kraft lignin derived from the pulp/paper industry. All the hydrogenolysis derived bio-oils mainly contain alkoxy-phenols (>85%). The monomer yield was proved to be influenced from the reaction parameters, the feedstock properties and the procedure followed for the isolation of lignin.

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