Hydrothermal pretreatment and fractionation of agricultural lignocellulosic waste biomass towards furanics and lignin based chemicals

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The depletion of fossil fuel and the effort to replace the petroleum derived products, fostered research towards alternative sources of fuels and chemicals. Lignocellulosic biomass derived from agricultural and forestry residues (e.g. prunings, straw) as well as food industry wastes (e.g. kernels, shells) can be valorized into fuels and a wide variety of value-added chemicals. Within an integrated "biorefinery" context, the three main components of the lignocellulosic biomass, cellulose, hemicellulose and lignin can be converted into platform chemicals with many industrial applications. The most important step in the valorization process, is the selective fractionation of raw materials into main components. One of the most effective fractionation methods, is the hydrothermal pretreatment in pure water (Nitsos, 2013, Nitsos, 2016). Via 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 and can be further separated via extraction of lignin with ethanol or acetone or via enzymatic hydrolysis of cellulose (Nitsos, 2019). Furthermore, (bio)catalytic processes can be applied for the valorization of each stream. Cellulose can be converted to glucose towards the production of bioethanol via fermentation or sugar derived platform chemicals. Hemicellulose stream can be utilized as furanic rich feedstocks in resins production or can be converted to other furanic compounds via catalytic processes which can be used also in resins synthesis or as fuel additive. Finally, lignin can be used in epoxy/phenol resins as additive for the partial substitution of phenol or can be converted to aromatic and/or phenolic monomers via (catalytic) fast pyrolysis and hydrogenolysis reactions. In the present work, we investigate the selective fractionation of lignocellulosic biomass feedstocks derived from different agricultural and food industry wastes, towards liquid (hemicellulose/furanics) and solid (lignin/bio-oil) streams that could be utilized in the production of phenol formaldehyde (PF) resins.

Within this context, the waste biomass feedstocks studied were grapevine and olive tree prunings and peach kernels. All three wastes exhibited similar composition in terms of carbohydrates, i.e. 32-39 wt.% cellulose and 13-16 wt.% hemicellulose, but different lignin content (19-22 wt.% for olive tree and grapevine prunings and 42 wt% for peach kernels), and amount of extractives (18-24 wt.% for olive tree and grapevine prunings and 4 wt% for peach kernels). The hydrothermal pretreatment of biomass feedstocks was carried out under varying severity conditions, at the temperature range of 170-220 ^{o}C, for 15-180 min. All types of biomass exhibited high solubilization (19-47 wt.%) and removal of hemicellulose as xylan oligomers or monomers, as well as organic acids (e.g. acetic, succinic, lactic, formic and levulinic acid) and furans (HMF and furfural) at increasing severity conditions. The origin of biomass feedstocks had a significant influence on the composition of the liquid products. For example, in the case of peach kernels, xylose can be more easily extracted in the liquid fraction either as monomeric xylose at intermediate severity conditions or as furfural at more intense conditions, as can be observed in Figure 1. The remaining solids of the hydrothermal pretreatment of biomass are enriched in cellulose and lignin and can be more easily hydrolyzed by enzymes towards glucose, compared to the parent biomass [1-3]. The remaining after hydrolysis lignin-rich biomass samples can be subjected to fast (catalytic) pyrolysis, producing a bio-oil enriched in alkoxy/alkyl-phenols which could be utilized in the production of PF resins, substituting partially or fully the petroleum based phenol.

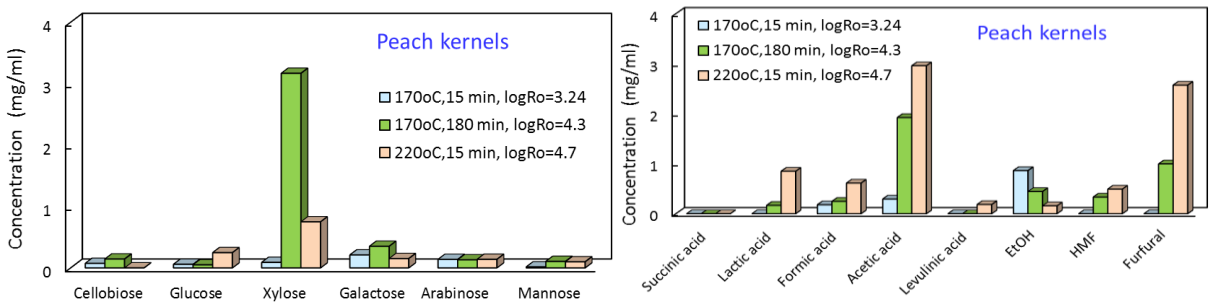

Figure 1. Composition of liquid fraction obtained from the hydrothermal pretreatment of peach kernels.

Considering all the above, within an integrated biorefinery concept, the selective fractionation of lignocellulosic biomass feedstocks into cellulose, hemicellulose and lignin can facilitate the potential valorization of each stream into value added chemicals with many industrial applications, including the production of bio-based PF resins. Furthermore, the composition of the derived fractions can be controlled via the careful selection of hydrothermal pretreatment conditions.

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