PYROLYSIS'S AQUEOUS-PHASE LIQUID (APL) UPGRADE TROUGH HYDROTHERMAL-CARBONIZATION PRE-TREATMENT

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In the last decade the need to reduce our dependence from oil derivatives pushed the research towards the identification of green pathways, able to supply low or negative/neutral carbon chemicals and materials. Thermochemical processes, and in particular pyrolysis, have been proposed as a green alternative able to provide a large variety of chemical from renewable resources such as biomass or waste. One of the main hurdles of pyrolysis is the complexity of pyrolysis products, especially pyrolysis-oil (or biooil) which is formed by hundreds of molecules[1] prone to aging and polymerization and hampers the upgrading pathways [2]. Hybrid thermochemical-biological processes could, in principle, circumvent some of the limitations of chemical upgrading, funnelling the complex products into few valuable chemicals such as ethanol or Volatile Fatty Acids [3]. Within pyrolysis-fermentation pathways, the increase the yield of easily fermentable compounds, such as anhydrosugars, plays a fundamental role for system performance. In this study, with the aim to increase sugar content and easily fermentable fraction in overall process, fir sawdust was selected as a representative lignocellulosic biomass and Hydrothermal-Carbonization (HTC) was used as pre-treatment before pyrolysis. Fir sawdust and Hydrochar produced with HTC at different temperature (150°C and 200°C) were subjected to pyrolysis (550°C for 15 min) in a bench-scale pyrolyze. Aqueous-Phase Liquid (APL) of the obtained biooils as well as HTC liquid (HTC-L) were characterized by GC-MS and HPLC-SEC. Composition and yield of HTC and pyrolysis products were obtained providing, through molecular and COD approach[3], an overall evaluation of the partitioning of chemical energy (then the maximum output of fermentation product obtainable) with different HTC-pyrolysis combinations. HTC of fir sawdust yielded an easily filtrable suspension that, upon filtration provided a cake with 40% dry weight and clear yellowish HTC liquid. Analysis of HTC liquid shows that HTC mainly involve hemicellulose fraction with generation of solubilized sugars (mannose, xylose, glucose, etc.), dissolved hemicellulose and organic acids. Overall results revealed that combination of HTC-pyrolysis increases COD yield of sugars-like compounds (sugars, and anhydrosugars) and decrease the concentration of high molecular weight compounds within thereof (*Figure 1*). In particular, the 200°C HTC increased the anhydrosugars yield by a factor of three. Such effect, which is common when biomass is washed with diluted mineral acids[4], was attributed to the removal of biomass K^+ and Na^+ by means of the organic acids generated by HTC. Results obtained suggests that the combination of HTC and pyrolysis can be a reliable tool to increase the yield of pyrolysis liquid, mainly through an improvement the s

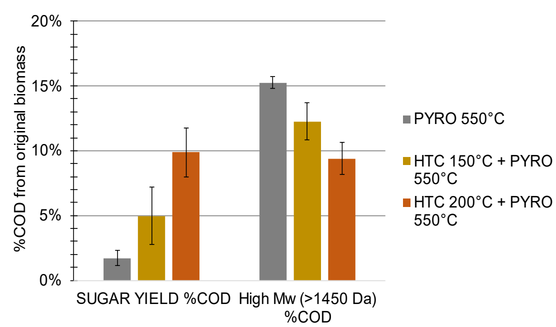

Figure 1. Sugar and High molecular weight compound yield (Liquid fraction, %COD respect initial biomass) obtained from different thermochemical processes

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