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Exploring molecular composition of upgraded pyrolysis bio-oil by using GC×GC-(EI/PI)-TOF MS

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Bio-oils produced from the pyrolysis of lignocellulosic biomass have proven to be a promising renewable energy source. These bio-oils are very complex organic mixtures consisting of thousands of compounds covering a wide range of mass and polarity. However the liquid obtained after pyrolysis is rich in oxygen which causes instability and corrosion problems. It therefore requires dedicated post-pyrolysis treatments such as hydrotreatment to increase the H/C ratio of the products to be used as fuels or chemicals. Here the bi-dimensional gas chromatography-mass spectrometry (GC×GC MS) was used to characterize a bio-oil and its hydrotreated effluents allowing a molecular characterization of volatile compounds. The GC×GC MS was interfaced with an electron ionization (EI) source coupled to a quadrupole time-of-flight (QTOF) MS. With this system two column sets were investigated: a normal phase (nonpolar × mid-polar) and a reverse phase (mid-polar × non-polar). The results revealed a great potential to trace bio-oil molecular composition as a function of hydrotreatment time on stream and to understand the chemistry of recalcitrant difficult-to-process species. A clear change in composition was observed. Regarding hydrocarbon species polyaromatics increased significantly while cycloalkanes and monoaromatics decreased. Concerning the oxygen compounds their quantity and diversity also increased significantly over time. Results highlighted the occurrence of catalyst deactivation. From an industrial point of view these observations will help to adapt bio-oil hydrotreatment processes.