TWO STEPS UPGRADING OF BEECH WOOD FAST PYROLYSIS BIO-OIL WITH NICKEL-BASED CATALYSTS

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Upgrading of fast pyrolysis bio-oil through catalyst hydrotreatment has been suggested as a complementary step to produce oil with improved properties. The upgrading reduces the oxygen and water concentration at the same time that allows the carbon recovery in the bio-oil. Reactive compounds are stabilized and organic acids are mostly concentrated in the aqueous phase formed after the reaction. Due to the high activity and low cost, nickel-based catalysts are promising for production of upgraded oils. Although almost half of the oxygen is removed with a single step upgrading, deeper hydrodeoxygenation is required in order to obtain organic liquids miscible with petroleum-derived products. It can be achieved by sequential hydrotreatment with specific catalysts in each of the steps. Hence, in the present work a beech wood fast pyrolysis bio-oil was upgraded in two steps applying two nickel-based catalysts. A catalyst with higher hydrodeoxygenation activity (Ni/SiO_2, 7.9 wt.%) was used in the first step, whereas a catalyst with higher hydrogenation activity (Ni-Cr/SiO_2, 30 wt.% metallic nickel, 26 wt.% NiO, 15 wt.% of Cr_2O_3 and 1.5 wt.% of graphite in diatomaceous earth support 27 wt.%) was employed in the second step. The reactions were conducted in a batch autoclave at 325 ºC and 80 bar of H_2. The bio-oil initially hydrotreated with a Ni/SiO_2 catalyst prepared by wet impregnation showed a reduction of 44.85 % of the oxygen content and 77.8 % less water in comparison to the initial bio-oil. Carbon, on the other hand increased from 59.9 wt.%, dry basis to 72.9 wt.%, dry basis, respectively. After the second upgrading reaction with Ni-Cr/SiO_2, the oxygen concentration was further reduced to 11.6 wt.%, reducing 64.8 % of the original oxygen concentration, and reducing around 90 % of the water content. Additionally, most of the organic compounds were concentrated in the upgraded oil, as the aqueous phase after the second upgrading step was composed by 97 % of water. Such improvement was reflected in the high carbon concentration in the upgraded oil ([C] = 78.6 wt.%), in the HHV (36.9 MJ/Kg), 90.1 % higher in comparison to the original beech wood fast-pyrolysis bio-oil and in the hydrocarbons identified in the two-steps upgraded oil. Hence, the two steps hydrotreatment with adequate catalyst seems to be a promising upgrading process in order to obtain fast pyrolysis oil with improved properties.

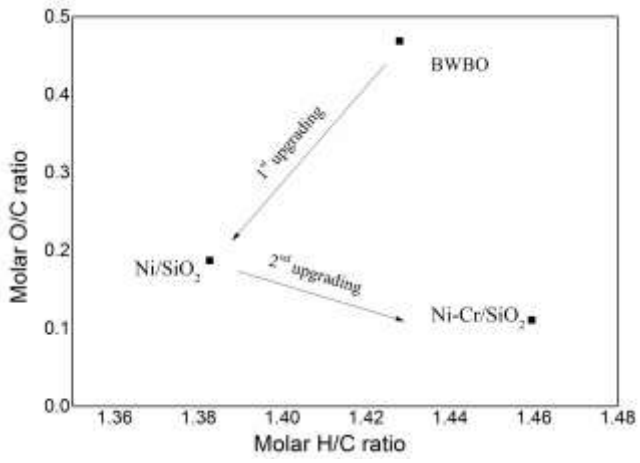

Figure 1 – Van Krevelen Plot in dry basis of beech wood fast pyrolysis bio-oil and upgraded oils after the first and second hydrotreatment reaction