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BOOK OF ABSTRACTS

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OC25. BIPHASIC OXIDATIVE DENITROGENATION WITH H_2O_2 OF A SIMULATED FUEL USING SUSTAINABLE CARBON NANOTUBE CATALYSTS

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The presence of nitrogenated compounds in liquid fuels (*e.g.* quinoline (QN), azapyrene, pyrrole, indole or carbazole) is associated with a series of environmental and health issues [1], as upon their combustion, noxious NO_x gases are formed. Typically, those heteroatoms are removed by hydrodenitrogenation (HDN), a process based on the application of H_2 under high temperature and pressure [2]. However, due to the type of nitrogenated compounds found in crude oils, which consist mostly of cyclic structures containing two double bonds between N and C atoms, HDN fails to efficiently remove nitrogen without affecting the properties of the fuel [1]. Thus, alternatives to HDN have been sought, the removal of those nitrogenated compounds via oxidative processes being found as promising [1]. In oxidative denitrogenation (ODN), nitrogen-based compounds are oxidized towards more polar compounds, which can be further removed from the fuel with an extractant [3]. Furthermore, another contemporary issue is the production and accumulation of residues, especially plastic solid waste (PSW). PSW can be used as precursors for the synthesis of sustainable carbon nanotubes (CNTs), which could be further applied as catalysts in ODN. In this work, a nitrogen-rich fuel was simulated by dissolving QN ($C_{QN\text{-}i\text{-octane},0} = 1$ g L^{-1}) in 2,2,4-trimethylpentane (*i*-octane), and ODN was carried out using H_2O_2 as oxidant and CNTs (derived from a mixture of polymers simulating PSW) as catalysts, under a biphasic system (oxidation and extraction co-occurrence).

The CNTs were synthesized via chemical vapour deposition (CVD) over an iron-based material supported in alumina (Fe/Al_2O_3) and a mixture of polyolefins as carbon sources (low-density polyethylene, high-density polyethylene and polypropylene, in a proportion of 35:25:40 (mass basis)). CVD was conducted at 800 °C under nitrogen atmosphere (40 mNL min^{-1}) for 1 h, considering 5 g of the polymer mixture and 1 g of Fe/Al_2O_3, leading to the sample named CNT-MIX. CNT-MIX was subjected to acid washing under reflux (50% vol. H_2SO_4, 140 °C, 3 h) to remove the residual Fe/Al_2O_3. ODN was carried out at 80 °C in a biphasic system (*i*-octane:aqueous phase), considering a volume ratio of O/W = 80:20, for 1 h. The initial pH of the aqueous phase was set to 3 by means of a 1 M H_2SO_4 solution, and the concentration of H_2O_2 was chosen as 10 times the stoichiometric amount for complete QN degradation (247 g L^{-1}). CNT-MIX and a CNT commercial sample (Sigma-Aldrich) were tested as catalysts ($C_{cat} = 2.5$ g L^{-1}, considering the total volume of the reaction). A non-catalytic run (N.C.) was also considered for comparison. QN was measured by UV-Vis in both oily and aqueous phase at a wavelength of 313 nm. Studies considering only adsorption and only extraction were also carried out under the same conditions for comparison. Oxidation of *i*-octane was assessed without the presence of QN and it was found it was negligible under the operating conditions used.

The results obtained are summarized in Fig. 1. As it can be observed, extraction-only hardly removes QN from the oily phase. Similarly, adsorption can only account for a removal in the range of 4-10% of QN, depending on the catalyst used. H_2O_2 addition without catalyst (N.C.) has not impact on the removal of QN. On the other hand, ODN experiments were able to almost fully remove QN from *i*-octane (98% after 1 h of reaction) using CNT-MIX catalyst, which greatly surpassed the results obtained in the presence of the commercial CNT sample (only 43% removal after 1 h). The activity of CNT-MIX allowed reaching 99.8% of QN removal in 2 h of reaction. Thus, these results suggest that upcycling PSW into CNTs is a viable option for effective removal of hazardous compounds from oily phases by oxidation with hydrogen peroxide.

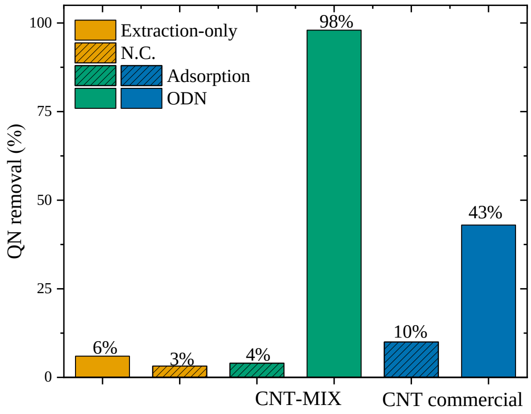

Figure 1. QN removal by extraction, adsorption and ODN considering CNTs as catalysts. (Operating conditions: O/W = 80:20, $C_{QN\text{-}i\text{-octane},0} = 1$ g L^{-1}, $pH_{aqueous\ phase,0} = 3.0$, $C_{H_2O_2,0} = 247$ g L^{-1} (for **ODN** runs), $C_{material} = 2.5$ g L^{-1} (0 g L^{-1} for extraction run), 80 °C, 1 h)

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