Analysis of Simultaneal Hydrotreatment Process
During Coprocessing of Pyrolysis Oil and VGO.

The sixth assessment report recently published by the United Nations Intergovernmental Panel on Climate Change has warned about the threat we are facing as humankind if urgent measures are not taken to decrease CO2 emissions [[i]1]. Several sectors and companies are proposing net zero CO2 emissions by 2050 to cope with this challenge. With this target the energy sector will need significant changes including a higher demand of renewable energies like eolian, wind, solar, photovoltaic, hydro and geothermal. In the transportation sector, the use of low emissions biofuels, synthetic fuels, electric and hybrid vehicles will increase significantly. One option to decrease CO2 emissions in petroleum refineries is the coprocessing of biomass derivatives like vegetable, recycled and pyrolysis oils in already existing process units. In this work a study is presented about coprocessing vacuum gasoil and pyrolysis oil obtained from soft wood. The experiments were carried out in a fixed bed hydrotreatment pilot plant at a temperature of 390°C, a pressure of 96 bar, a H2/liquid relation of 650 NL/L and using an arrangement of commercial Co-Mo/Al2O3 and NiMo/Al2O3 catalysts. The reaction severity was modified changing space velocity in the range of 1.8 to 1.0 h^{-1}. Emulsions of pyrolysis oil and vacuum gasoil up to 3 % v/v were prepared using ultra - turrax blenders and these emulsions were used as feedstocks to the pilot plant. The reaction products were analyzed by conventional ASTM analytical methods and by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR/MS). Preliminary results showed that coke formation tendency in the reactor is reduced when the Bio-Oil droplet size is smaller. Hydrodenitrogenation reactions velocity, measured by the apparent rate constant k_{app}, are inhibited when the Bio-Oil is present as droplets of large size. FT-ICR/MS showed that this inhibitory effect, at molecular level, is due to a lesser saturation of nitrogen containing aromatic rings; the first step in HDN mechanism. These inhibitory effects does not occur when the size of the droplet of the pyrolysis oil is in the 1-3 micrometers range. This results suggest that mass transfer of hydrogen from gas to liquid phase plays a vital role to control activity and selectivity when coprocessing dissimilar feedstocks like pyrolysis and vacuum oils.

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1. Intergovernmental Panel on Climate Change (2021), Climate Change 2021 The Physical Science Basis.