HYDROTREATING OF WASTE PLASTIC PYROLYSIS OIL WITH INCREASED CHLORINE AND NITROGEN CONTENT

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Polyolefin plastics can be quite easily depolymerized *via* pyrolysis to monomers, or to pyrolysis oil which can be used for steam cracking. However, when real post-consumer waste plastics are pyrolyzed, a significant amount of problematic heteroatoms can be present in the oil, which will limit its use in the steam cracker. The common limits for steam crackers are 2000, 500, 100, and 3 ppm for nitrogen, sulfur, oxygen and chlorine [1], respectively. These limits can be reached only after upgrading using the hydrotreating process. When hydrotreating would be deeper, alternative transportation fuels could be produced from plastic pyrolysis oil.
In this research, we studied the hydrotreating of pyrolysis oil made from mixed post-consumer waste foils and cups created preferably by polyethene and polypropylene, respectively. The oil was produced by industrial-scale pyrolysis and contained a significant amount of heteroatoms: 5500 ppm of nitrogen, 250 ppm of sulfur and especially 685 ppm of chlorine. Hydrotreatment was carried out in a laboratory fixed-bed catalytic unit with a tube reactor and a co-current flow of the feedstock and hydrogen. The sulfided Ni-Mo/γ-Al_2O_3 catalyst was used for upgrading. In the first step, we tested the chlorine effect on hydrotreating using model feedstock consisting of light cycle oil with added 1-tetradecene and limonene which should simulate olefins present in plastic pyrolysis oils. This feedstock was spiked with model chlorine compounds that simulated the main chlorine species created by the pyrolysis of PVC. The total chlorine concentration in the chlorine model feedstock was 500 ppm. The hydrotreating of this feedstock with and without chlorine was tested at temperatures 180-360 °C and pressures 6 and 10 MPa. After completing the testing of model feedstock, the real pyrolysis oil described above was hydrotreated at the same range of conditions. In total, the catalyst was operated for 700 h of TOS with these feedstocks.

The model feedstock test showed that the presence of chlorine affected quite significantly hydrodesulfurization activity, but only during the hydrotreating at temperatures 200-300 °C. Although most of the chlorine was removed at 180 °C, temperatures around 300 °C are necessary for the complete removal of chlorine (Figure 1).

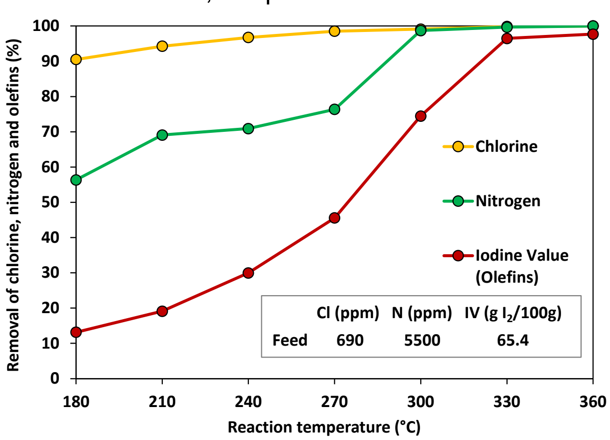

Figure 1 – Improvement of chosen parameters after hydrotreatment at 10 MPa

In the case of real pyrolysis oil, at temperatures 330 and 360°C, sufficient improvement of all problematic parameters was observed, i.e., complete removal of chlorine, elimination of sulfur and nitrogen under 10 ppm and significant saturation of olefins. The pressure significantly improved especially the effectivity of olefins saturation. Around 60% of the liquid product was created by middle distillates (kerosene and atmospheric gas oil), which proved very good properties and could be used as alternative fuels. During the conference, the results of the detailed analysis of liquid products as well as their redistilled fractions will be presented, and possible ways of products utilization will be proposed.

[1] M. Kusenberg, A. Eschenbacher, M.R. Djokic, A. Zayoud, K. Ragaert, S. De Meester, K.M. Van Geem, Opportunities and challenges for the application of post-consumer plastic waste pyrolysis oils as steam cracker feedstocks: To decontaminate or not to decontaminate?, Waste Management, 138 (2022) 83-115.