Screening of pyrolysis oils from plastic by GC×GC-PI-TOFMS and GC-VUV

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Pyrolysis of plastics is of high industrial concern as it allows both converting large amount of wastes and reaching circular economy needs while opening possibilities in terms of usage as complementary energy fuel contribution. Even though the chemical composition of pyrolysis plastic waste oils shares similarities with fossil-based hydrocarbons fluids, e.g. PIONA related compounds, the relative proportions and overall compositions are different. For instance, pyrolysis plastic oil contains large amounts of olefins (linear, branched and di-olefins) which makes the detailed group-type analysis a real analytical challenge.

In order to avoid problems in the steam cracker unit during the plastic oil upgrading, as well as the choice the best feedstock, the composition of pyrolysis oils from plastics must be evaluated in detail. In order to do it, an analytical method based on comprehensive two-dimensional gas chromatography (GC×GC), specially coupled with photoionization (PI) – time-of-flight mass spectrometry (TOFMS) was developed to obtain a detailed plastic pyrolysis oil composition. A reverse-phase column combination (mid-polar in the 1st dimension and non-polar in the 2nd dimension) allowed to obtain a good bidimensional resolution for the detection by FID (quantitative aspects) and TOFMS (qualitative aspect). PIONA analysis was achieved thanks to detection of molecular ion by PI-TOFMS. Moreover, olefins were successful distinguished from naphthenes by in-depth consideration of soft ionization MS spectra, even though such compounds elute together in the 2D chromatographic separation space. Certain olefins identification achieved by PI was further confirmed by chromatography coupled to vacuum ultraviolet detection (GC-VUV) once olefins VUV spectra differs from other PIONA compounds. The overall combination of the entire set of data was fundamental to explain the pyrolysed plastic composition as well as checking the efficiency of different upgrading processes that have been applied to eliminated specific contaminates and obtain new recycled products that could be reintroduce in the market to attain the economic circularity.