Chemical investigation of plastic pyrolysis oils

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In 2019 more than 450 million tons of plastic were produced in the world [1]. Chemical recycling, particularly pyrolysis of plastic wastes, could be a valuable solution to provide an alternative pathway to produce "recycled" chemical products for the petrochemical industry. Nevertheless, the pyrolysis oils need a detailed characterization before re-using them to generate new recycled products. Indeed, even though the chemical compositions of pyrolysis plastic waste oils show similarities with fossil-based oils, e.g. PIONA related compounds, the relative proportions of the chemical classes are significatively different, resulting in important changes in the global properties of these fluids.

Comprehensive two-dimensional gas chromatography (GC×GC) coupled to photoionization (PI) high-resolution time-of-flight mass spectrometry (HRTOFMS) has proven to be well suited for the compositional elucidation of petroleum products [2,3]. We therefore applied GC×GC-(PI)HRTOFMS for group-type analysis of various plastic pyrolysis oils using normal and reverse column sets. Compared to what can be achieved with more classical electron ionization (EI) that does not allow to preserve significant signals for the molecular ions of many species, the use of PI allowed to take advantage of the 2D-structured chromatograms more extensively.

As a matter of fact, the characteristic 2D-GC plot location provided a sort of chemical fingerprint composed of different chemical classes from which structural information were extrapolated. The presence of parent ions as well as specific fragments permitted to determine precise structures of relevant chemical species such as alkanes, olefins, di-olefins, polyolefins saturated hydrocarbons (POSH), polyolefins mono-unsaturated hydrocarbons (POMH) and polyolefins di-unsaturated hydrocarbons (PODH) [4].

The known capability of GC×GC-(PI)HRTOFMS for the identification of olefin isomers [5] was especially useful to differentiate olefins from naphthenes by in-depth consideration of MS spectra, despite the fact that such compounds were very close eluters in the 2D chromatographic space. It was used to monitor the efficiency of different upgrading (hydrogenation) processes that were applied to the oils to remove the olefin contaminants. Such upgrading processes serve to eliminate specific contaminants to improve the quality of the product and avoid problems in the steam cracker unit. The characterization was further supported by GC coupled to vacuum ultraviolet detection (VUV) that has the potential to differentiate olefins VUV spectra from spectra of other PIONA compounds.

This multiple-technique approach has the potential to support the production of plastic pyrolysis oils that could efficiently be reintroduced in the steamcracker unit, leading to the production of monomers and later polymers, ensuring economic circularity needs.

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