Shale oil as steam cracking feedstock: GC × GC characterization and COILSIM1D modeling

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Abstract

Even though, shale oil is commonly considered as a potential alternative energy resource, the complex chemical composition of the feedstock imposes a challenge for refining and in particular for petrochemical processes. To assess the potential of shale oil utilization as a steam cracking feed and co-feed, a detailed compositional analysis of a pyrolysis shale oil sample is performed and steam cracking product yields are estimated using the COILSIM1D software [1]. The complex chemical composition was unraveled by GC × GC analysis separation coupled to various detectors, i.e. time-of-flight mass spectrometer, flame ionization detector, sulfur and nitrogen chemiluminescence detector, allowing to quantify also hetero-atomic molecular families. High amounts of unsaturated hydrocarbons are characteristic for shale oil produced via kerogen pyrolysis. In this case the olefin concentration was shown to be as high as 18 wt.%. Cycloalkanes and monoaromatics are present in significant concentrations, i.e. 17 wt.% and 11 wt.%, respectively. On the other hand, paraffin content of 8 wt.%, makes shale oil far less advantageous for steam cracking compared to conventional feedstocks. Furthermore, considerable concentration of oxygenates was detected, mainly belonging to chemical families of benzendiols (13 wt.%), hydroxybenzofurans (10 wt.%), phenols (4 wt.%) and ketones (9 wt.%). Nevertheless, shale oil quality is considered satisfactory, as sulfur (0.7 wt.%) and nitrogen (300 ppmw) content is low and the carbon number range is favorable, i.e. C_3 to C_{26}. The obtained chemical composition, in which the compounds were grouped according to carbon number and molecular family, was used to define the feedstock in COILSIM1D. In order to apply the latter the reaction network was extended to oxygen containing species before yields of steam cracking products were simulated by applying the single event microkinetic modelling methodology [2]. Product yields for steam cracking of pure shale oil, shale oil blended with naphtha (20:80 wt.%) and kerosene (20:80 wt.%) at typically industrially relevant coil outlet temperatures (800, 820 and 840°C) and steam dilution ratios (0.5, 0.75 and 1 kg/kg) were obtained.

References

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