Kinetics of the thermal decomposition of sulfur compounds

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Abstract

In this contribution the kinetics of the thermal decomposition of sulfur compounds will be discussed both experimentally and theoretically under typical steam cracking and pyrolysis conditions. The experimental investigation has been conducted in a new 85 cm long annular quartz flow reactor, having an outer and inner tube diameters of 2.1 and 1.5 cm respectively. Both pure sulfur compounds pyrolysis in nitrogen (0.04 mol% S in N_2) as well as in the presence of hydrocarbons (0.04 mol% S and 13.7 mol% of HC in N_2) were studied covering a wide temperature range of 600 to 850 °C, at a fixed pressure of 1.5 bara and residence time of ~0.5 s. The reaction effluent is sampled on-line at 300 °C. The unique on-line sampling system consists of valve-based sampling manifold and uniformly heated transfer lines connected to a comprehensive two-dimensional gas chromatograph (GC × GC) equipped with a flame ionization detector (FID) and a sulfur chemiluminescence detector (SCD). This dedicated set-up allows to detect and quantify both pure (with the FID) and sulfur-containing hydrocarbons (with the SCD) using heptane and 3-chlorothiophene as internal standards, respectively. The GC × GC-FID/-SCD settings are optimized for trace analysis of sulfur compounds in olefin-rich (ethylene- and propylene-) hydrocarbon matrices produced during steam cracking.
To understand the underlying decomposition mechanism of sulfur compounds in the presence of a complex hydrocarbon matrix formed by its decomposition, a group additive kinetic model was constructed via an in-house automated reaction mechanism generation software called Genesys [1]. It relies on ab-initio CBS-QB3 based kinetic coefficients for the reference/ parent reactions for each elementary reaction family, and for the others, contribution of groups to the single event Arrhenius parameters. No adjustment of the Arrhenius parameters to the experimental data is performed. The kinetic model is validated by comparison with the set of experimental data gathered in the annular quartz flow reactor by providing a satisfactory representation of the latter.

[1] Nick M. Vandewiele, Kevin M. Van Geem, Marie-Françoise Reyniers, Guy B. Marin, Genesys: Kinetic model construction using chemo-informatics, Chemical Engineering Journal, Volumes 207-208, 2012, Pages 526-538.