Desulfurization of Fossil Materials for Clean Fuels-the Contribution of Analytical Chemists

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Sulfur is the third most abundant element in petroleum, often being found in concentrations above 1 %, but it is highly problematic. On combustion it forms sulfur oxides that return to earth as sulfuric acid, “acid rain”. Many sulfur compounds act as poisons, especially for transition elements that are frequently used as catalysts. Therefore they cause problems in many refinery operations. In the last years strong legislation in many countries has mandated a lowering of the sulfur level in all products derived from petroleum, especially in transportation fuels.

As the price of petroleum continues to climb and crudes that are low in sulfur are progressively depleted, materials of higher sulfur content and fractions of higher boiling ranges find increased interest. The hydrodesulfurization (HDS) is a standard technology today for lowering the sulfur level in transportation fuel to below the legal limit of 50 ppm in the European Union or 10 ppm in Germany. It operates under high hydrogen pressure and at elevated temperatures (e.g. 300°C).

However, some sulfur compounds are refractory and remain in the product after HDS. This is especially true of the heavier fractions of petroleum. The reason for this behavior is unknown but one may speculate that the chemical structure of the polycyclic aromatic sulfur heterocycles (PASH), which are known to be among the most difficult to desulfurize compound classes, plays a role. Therefore it is of major interest to learn about the structure of the PASHs in the desulfurized fractions and to find out if there is a common structural motif among the aromatics that are refractory to HDS. Different analytical methods are used depending on the volatility of the compounds.

Traditionally the speciation of PASHs is performed using gas chromatography with various detectors. It is now quite well-known what the pattern of the refractory sulfur compounds in gasoline and diesel looks like. Analyses have shown that among the most persistent compounds are dibenzothiophenes (DBT) with alkyl groups near the sulfur atom, in the 4- and 6-positions. Examples will be shown also for higher alkylated DBTs and how their structures can be identified.

For the non-volatile fractions, GC is not suitable and a combination of liquid chromatographic methods followed by ultra-high resolution mass spectrometry becomes necessary. Here the sample complexity is extreme and individual compounds may never be identified, so that statistical data will be collected. A range of LC separation steps will be presented to show how the combination of them, in conjunction with Fourier transform ion cyclotron resonance mass spectrometry, can help in elucidating the refractory compounds in such fractions.