Property-Reactivity Correlation for HDS of Middle Distillates

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Introduction
The ever-tightening sulfur specifications in transportation fuels (e.g., gasoline and diesel) have made it mandatory to develop new or much improved hydrodesulfurization (HDS) catalysts and/or processes. A most challenging task is to achieve deep HDS at low hydrogen pressures because removing sulfur heteroatom from refractory sulfur species, being a high hydrogen intensity process, is very slow with current commercial catalysts. There is a substantial incentive to do so since the capital expenditures required for high-pressure HDS reactors can be very high. As a first step, catalyst and process developers would like to have quantitative property-reactivity correlations for HDS feedstocks. Correlations of this type can guide feedstock selection/blending/purchase, experimental design, kinetic data interpretation, and economics/planning studies. They can also be embedded in hydrouprocessing process models. To be practically useful, the correlation should be based on readily available feed characterization data.

Shih et al. [1] developed a property-reactivity correlation over 520°F to 780°F. The reactivity, defined as the temperature required to achieve 500 wppm product sulfur, is a function of two feed properties: the sulfur content of the 600°F-plus fraction of the feed and the feed nitrogen content. The former is more important than the latter in ranking HDS feedstocks. In contrast, van Looij et al. [2] found for prehydrotreated feeds that the most important property affecting the HDS level appears to be basic organonitrogen even at trace levels (< 30 ppm). The organonitrogen inhibitory effect can be quantified by a -0.15 power in the concentration of organonitrogen. As significant as these prior studies are, their applications may be limited because the properties of the feedstocks used do not cover a sufficiently wide range. This study aims to gain a quantitative understanding of feedstock effects on HDS of middle distillates by developing an overall property-reactivity correlation.

Results and Discussion
We take a two-step approach. A chemometric analysis is performed to sift through a large number of feed properties to identify the dominant ones that govern the underlying property-reactivity relationship. Following this is the construction of a correlation based on the insights gained from the chemometric analysis. The data space consists of HDS reactivities of 13 high-sulfur (0.95-3.17 wt%) feeds, each characterized by 24 physicochemical properties. Results from
the chemometric analysis reveal that the dominant features of the system can be projected onto a three-dimensional subspace spanned by the following properties in order of importance: degree of feed saturation >> sulfur steric hindrance > organonitrogen poisoning. This leads to a correlation for distillate HDS reactivity in terms of the API gravity, and DBTs (dibenzothiophene + sterically hindered dibenzothiophenes), and organonitrogen content (N). These three properties represent the minimum information required for data correlation. And they are not correlated with each other.

Specifically, the correlation gives a scaling "law" of the form

\[ \text{HDS reactivity} \propto (\text{API})^{2.18}(\text{DBTs})^{-0.31}(\text{N})^{-0.2} \]

As the following parity plot shows, the correlation correctly predicts the reactivities of a wide variety of feeds.

![Observed vs. Predicted HDS Reactivity](image)

One sees that in developing property-reactivity correlation, microscopic information (molecular structure of sulfur species) is as important as macroscopic properties (API gravity, feed nitrogen).

References