RESEARCH NOTES

Deep Desulfurization of Distillates

In response to the need for production of very low-sulfur distillates (<0.05 wt % sulfur) in medium pressure hydrodesulfurization (HDS) units, we studied desulfurization of individual feed components. A total of eight feedstock components were evaluated, including straight-run gas oil (GO), coker gas oil (CGO), and FCC light cycle oil (LCO). The results show that, under typical HDS unit conditions (2.5 liquid hourly space velocity (LHSV), 625 psig, and 1500 ft^3(STP)/barrel H$_2$) over a commercial CoMo/Al$_2$O$_3$ catalyst, the temperature requirement for desulfurization to 0.05 wt % sulfur can be correlated with the concentration of 600+ °F sulfur and total nitrogen in the feed, *independent* of the feedstock source. A simple empirical correlation was developed to describe the temperature required for desulfurization of distillates to 0.05 wt % sulfur. This correlation can be used by refineries to rank feed components and to develop a strategy for manufacturing 0.05 wt % sulfur diesel fuel.

Introduction

Recently, the Environmental Protection Agency has proposed new rules limiting sulfur to 0.05 wt % in highway diesel fuels (*Federal Register*, 1990). Most distillate fuels, including diesel fuels, are desulfurized in catalytic hydrodesulfurization (HDS) units which operate at relatively low pressure, ranging from 200 to 1000 psig. Depending on refinery complexity, the HDS unit feed components may comprise a variety of distillate sources including straight-run gas oil (GO), coker gas oil (CGO), and FCC light cycle oil (LCO). LCO and CGO are highly aromatic and more refractory for desulfurization to current sulfur specification (0.2–0.5 wt % sulfur) than GO (Nash, 1989; Yoes and Asim, 1987; Gates et al., 1979). In this study, the desulfurization of potential HDS unit feed components is examined. The focus is on the reactivity of individual feeds for deep desulfurization to 0.05 wt % under typical HDS unit conditions.

Experimental Section

The properties of the eight HDS feedstocks evaluated in this study are summarized in Table I. A sample of No. 2 fuel oil (desulfurized distillate product; 0.3 wt % sulfur) was also included in the study. GO was further distilled into 600– °F LGO and 600+ °F HGO fractions.

The sulfur distribution of all feedstocks and their products was determined to be a function of boiling point by a simulated distillation GC (D2887 method) equipped with a sulfur-specific detector (Brody and Chaney, 1966). All experiments were conducted over a CoMo/Al$_2$O$_3$ catalyst. The catalyst was sized to 14/22 mesh and loaded into a 10-cm^3 reactor with 3 cm^3 of 60/120 mesh sands to improve the flow distribution in a small reactor. Then, the catalyst was pre-sulfided using the straight-run gas oil. A standard activity check was then conducted with the same straight-run gas oil. This activity check is used to ensure that catalyst desulfurization activity agrees with previous evaluations. The activity check also equilibrated the catalyst for further experiments. All the experiments reported here were conducted at 2.5 liquid hourly space velocity (LHSV), 625 psig total pressure, and a 1500 ft^3-(STP)/barrel once-through pure hydrogen circulation rate in co-current, down-flow mode. These conditions are compatible with high-severity HDS units that will be required to produce 0.05 wt % sulfur products. Data reported here should be considered as fresh catalyst activity.

Results and Discussion

Resistant Sulfur Compounds. Figure 1 shows a high-resolution gas chromatographic analysis of a mixed HDS feed and its desulfurized products at various sulfur levels by raising the reactor temperature. The GC system and operating procedures used to obtain Figure 1 are similar to those described by Brody and Chaney (1966). The results confirm earlier work (Frye and Mosby, 1967; Houalla et al., 1977; Gates et al., 1979; Houalla et al., 1980) that alkyl-substituted dibenzothiophenes are the most refractory sulfur types in the HDS unit feeds. After being desulfurized to less than 0.24 wt % sulfur (1.9 wt % sulfur in the feed), only dibenzothiophene (DBT) and its alkyl derivatives remain in the products. The GC traces in Figure 1 show the relative resistance of various alkyldibenzothiophene isomers to desulfurization. This high-resolution GC system was designed to provide qualitative information only. The resolutions were not sharp enough to obtain quantitative data for detailed kinetic analyses based individual sulfur-containing compounds. However, an improved GC system with better resolutions suitable for analyzing light petroleum streams is available elsewhere (Chawla and Di Sanzo, 1991).

Feedstock Characterization. All the feedstocks were analyzed with a regular simulated distillation GC (ASTM D2887 method) equipped with a sulfur-specific detector. The sulfur spectrum of the mixed HDS feed is shown in Figure 2 as an illustration. Since dibenzothiophene has a normal boiling point of 630 °F, each figure also shows sulfur attributable to 600– °F and 600+ °F fractions. The selection of the 600 °F cut point ensures all dibenzothiophenes are included in the 600+ °F fraction. Table II lists the feedstocks in the order of increasing concentration of 600+ °F sulfur in the feed.

Effect of Feedstocks on Catalyst Activity. Figure 3 shows the relationship between product sulfur and the reactor temperature required for the eight HDS feedstock components studied. As expected, heavy kerosene required a very low temperature (593 °F) but LCO required a very high temperature (775 °F) for achieving desulfurization to 0.05 wt % sulfur. The mixed HDS unit feed, which

Table I. Feedstock Properties

	mixed HDS feed	heavy kerosene	CGO	LCO	No. 2 fuel oil	GO full range	GO 600– °F	GO 600+ °F
general properties								
gravity, °API	28.0	35.8	33.6	10.3	32.1	34.6	38.9	30.4
hydrogen, wt %	11.85	13.38	12.59	9.12	12.61	13.43	13.61	12.97
total sulfur, wt %	1.9	1.1	2.2	3.2	0.3	1.38	0.8	1.8
600+ °F sulfur, wt %	0.61	0.1	0.42	1.6	0.2	0.84	0.09	1.47
nitrogen, ppmw	370	30	750	870	200	120	11	220
basic nitrogen, ppmw	97	22	39	63	52	34	6	54
distillation (ASTM D2887 method),[a] °F								
IBP	248	215	245	256	284	290	243	557
10%	389	413	392	455	382	451	399	599
50%	495	527	494	578	483	583	508	651
90%	615	588	615	722	600	694	568	710
EP	728	631	700	820	822	770	611	765

[a] IBP = initial boiling point; EP = end point.

Table II. Feed Properties and Catalyst Activities

	600+ °F sulfur,[a] wt %	total	total nitrogen, ppmw	at 0.05 wt % sulfur temp, °F	at 0.05 wt % sulfur HDS,[b] %	HDN, %
600– °F GO	0.09	0.8	11	532	94	15
heavy kerosene	0.1	1.1	30	593	96	70
No. 2 fuel oil	0.2	0.3	200	625	83	35
CGO	0.42	2.2	750	656	98	69
HDS mixed feed	0.61	1.9	370	672	97	59
full-range GO	0.84	1.38	120	645	96	50
600+ °F GO	1.47	1.8	220	731	97	25
LCO	1.6	3.2	870	775	98	28

[a] Concentration of 600+ °F sulfur in the feed. [b] Conditions: 2.5 LHSV, 625 psig, and 1500 ft³(STP)/barrel H_2 circulation rate.
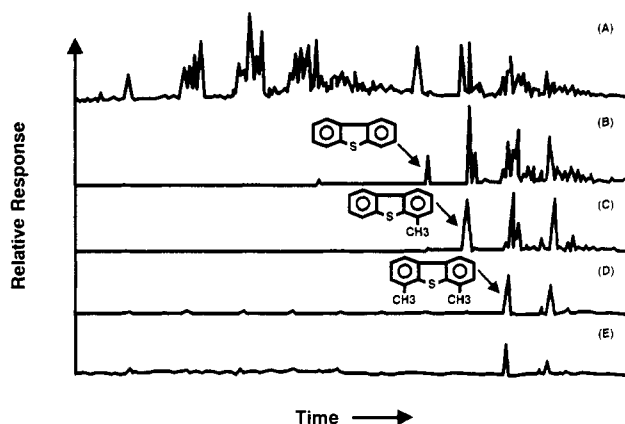

Figure 1. High-resolution GC spectra of HDS feedstock and products using a sulfur-specific detector: (A) feedstock, 1.9 wt % S; (B) 0.24 wt % S; (C) 0.11 wt % S; (D) 0.018 wt % S; (E) 0.008 wt % S.

Figure 2. Low-resolution GC spectrum of HDS feedstock using a sulfur-specific detector: 1.9 wt % total sulfur; 0.6 wt % 600+ °F sulfur.

Figure 3. Residual sulfur as a function of reactor temperature: (▽) LCO; (◇) 600+ °F gas oil; (●) mixed HDS feed; (□) full-range gas oil; (△) coker gas oil; (○) No. 2 fuel oil; (♦) heavy kerosene; (■) 600– °F gas oil.

contains 30% LCO, could be desulfurized to 0.05% sulfur at 675 °F under the current experimental conditions. These results are consistent with previous reports which show that the catalyst performance is strongly dependent on the LCO concentration of HDS feed blends (McCulloch et al., 1987).

Most importantly, we have found that the temperature requirement for desulfurization to 0.05 wt % sulfur can be correlated with the concentration of 600+ °F sulfur in the feed, *independent* of the feedstock source, as shown in Figure 4. In general, the temperature requirement could be correlated well with the total sulfur concentration in the feed except for the further desulfurization of No. 2 fuel oil (Figure 5). Since most sulfur in this No. 2 fuel oil is the 600+ °F sulfur, it did not desulfurize as readily as other feedstocks having the same total but more 600– °F sulfur. Therefore, for deep desulfurization *0.05 wt % sulfur*, the concentration of 600+ °F sulfur in the feed is a better parameter to determine the catalyst activity independent of feedstock source.
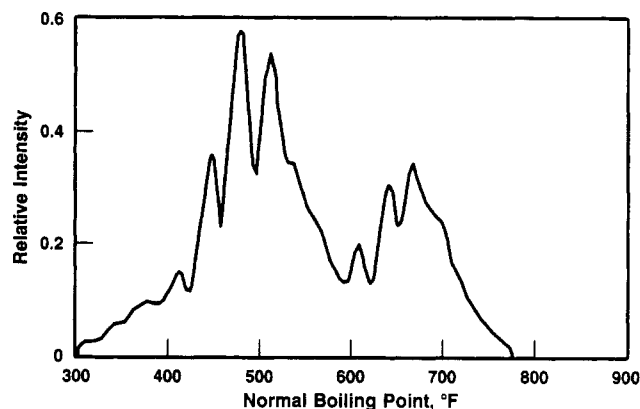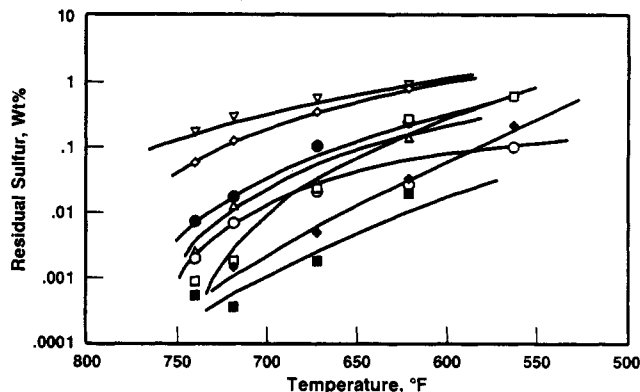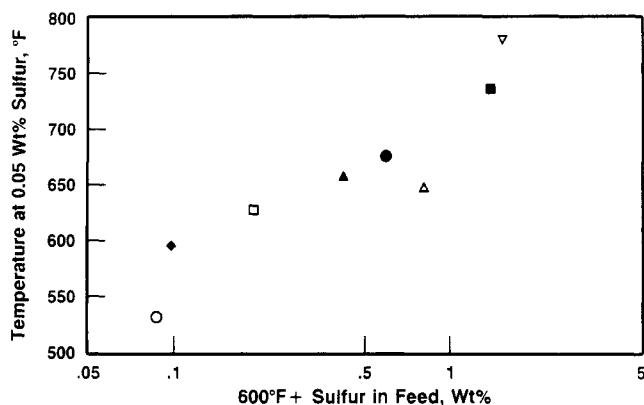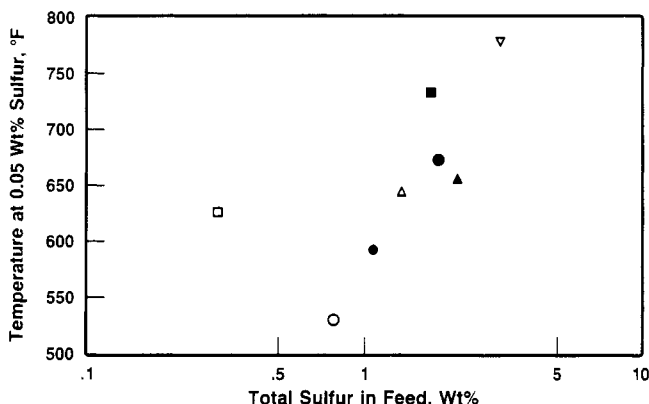
In addition, the catalyst performance can be affected by hydrogen sulfide and nitrogen-containing compounds in

Figure 4. Temperature requirement at 0.05 wt % sulfur as a function of 600+ °F sulfur content in feed: (▽) LCO; (■) 600+ °F gas oil; (●) mixed HDS feed; (△) full-range gas oil; (▲) coker gas oil; (□) No. 2 fuel oil; (♦) heavy kerosene; (○) 600– °F gas oil.
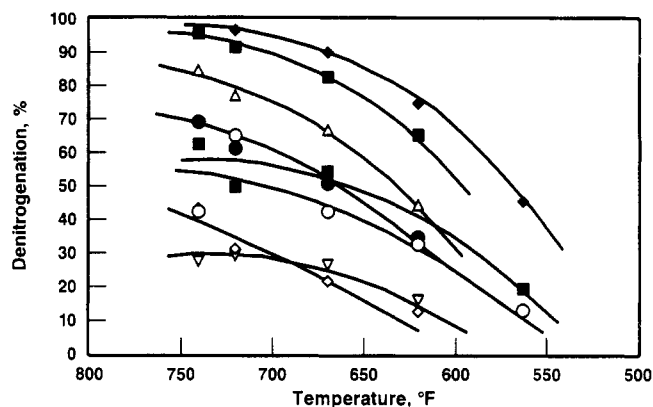

Figure 5. Temperature requirement at 0.05 wt % sulfur as a function of total sulfur content in feed: (▽) LCO; (■) 600+ °F gas oil; (●) mixed HDS feed; (△) full-range gas oil; (▲) coker gas oil; (□) No. 2 fuel oil; (♦) heavy kerosene; (○) 600– °F gas oil.

Figure 6. Degree of denitrogenation as function of reactor temperature: (▽) LCO; (◇) 600+ °F gas oil; (●) mixed HDS feed; (□) full-range gas oil; (△) coker gas oil; (○) No. 2 fuel oil; (♦) heavy kerosene; (■) 600– °F gas oil.

Figure 7. Hydrogen content of hydrotreated products as function of reactor temperature: CoMo/Al$_2$O$_3$, 2.5 LHSV, and 625 psig.
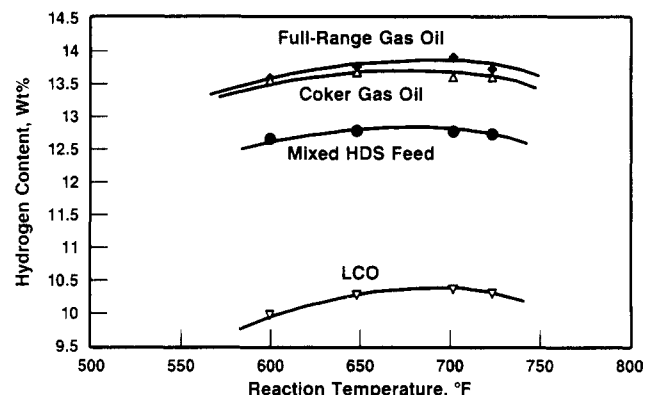
the feed. Catalyst activity inhibition by hydrogen sulfide, which is proportional to the total sulfur concentration, is well-known. It is also known that some nitrogen-containing compounds inhibit desulfurization activity (LaVopa and Satterfield, 1988). Consequently, stocks with a higher nitrogen content require more severe operating conditions than stocks with a similar concentration of 600+ °F sulfur but lower nitrogen content. For example, straight-run gas oil has a higher concentration of 600+ °F sulfur than the mixed HDS unit feed (0.84 vs 0.61 wt %), but it can be desulfurized to 0.05 wt % sulfur at lower temperature (645 vs 672 °F) since straight-run gas oil has a lower total nitrogen content (120 vs 370 ppmw, Table II).

Denitrogenation. Besides desulfurization, denitrogenation and aromatic saturation reactions also took place simultaneously. Nitrogen-containing compounds were more refractory for removal than sulfur-containing compounds. For example, at 600 °F, the degree of desulfurization for LCO—the most refractory feedstock—was 73%, compared to 12% denitrogenation at the same temperature (Figure 6). Similar to desulfurization of alkyl substituted aromatic sulfur compounds, denitrogenation rates are affected by alkyl substituents and their locations (Ho, 1988). The production of 0.05 wt % S distillates required a high degree of desulfurization, 83–98% depending on feedstock sulfur contents. At these conditions, the degree of denitrogenation varied from 15 to 70% only as shown in Table II.
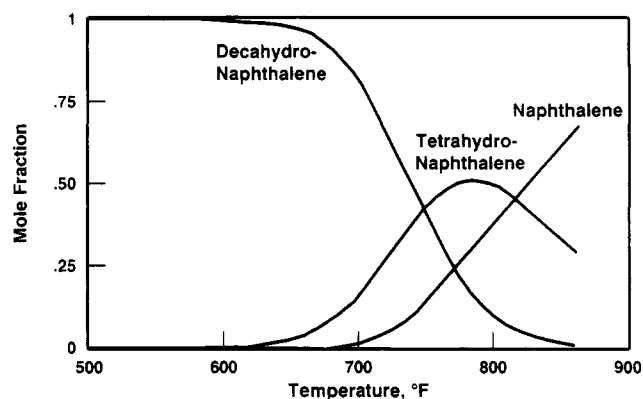
Aromatics Saturation. In addition to sulfur content, the aromatics content of diesel fuel may also be limited in the future. While we focused primarily on desulfuri-

Figure 8. Calculated thermodynamic equilibria for hydrogenation of naphthalene at 615 psia and 10/1 hydrogen to hydrocarbons molar ratio.

zation, we can make some observations concerning aromatics saturation. The extent of hydrogenation is a function of both feedstock and reactor temperature. All feedstocks show a maximum hydrogen content at a 660–680 °F reactor temperature (Figure 7), indicating a thermodynamic limit. Higher reactor temperatures result in a decrease of hydrogen content of the desulfurized oils. Similar results have been previously reported (Unzelman, 1987; Nash, 1989; Yoes and Asim, 1987). As an example, we analyzed the thermodynamics of naphthalene hydrogenation, an aromatic typically found in this boiling range. The calculations showed that the naphthalene concentration starts to increase at 660 °F under conditions (10/1 hydrogen to hydrocarbons molar ratio at 615 psia) similar
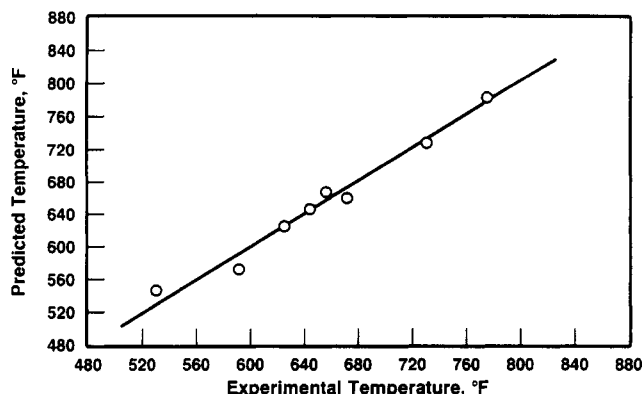
Figure 9. Experimental versus predicted temperature requirements for desulfurization to 0.05 wt % sulfur distillates.

to those in this study for a system consisting of naphthalene, tetrahydronaphthalene, decahydronaphthalene, and hydrogen (Figure 8). This maximum hydrogenation temperature at which the maximum hydrogenation is observed might be the ceiling temperature for a stable operation under these conditions. The thermodynamics of naphthalene hydrogenation provides an indication of a potential operating window under specific conditions. More detailed kinetics and thermodynamics for hydrogenation of aromatic model compounds are available in literature (Sapre and Gates, 1981; Fisher and Wilson, 1987). Kinetics of aromatic hydrogenation for synthetic distillates derived from coal and tar sands has also been reported (Shih and Angevine, 1985; Yui and Sanford 1985).

Reactivity Correlation. On the basis of the above observations, we have developed a simple empirical correlation to describe the temperature required for desulfurization of distillates to 0.05 wt % sulfur. This correlation is intended to be used to rank feed components and to determine their appropriateness for the manufacture of 0.05 wt % sulfur diesel fuel. More rigorous kinetic modeling can be done by determining intrinsic kinetics of individual sulfur compounds if quantitative data on each compound are available. The models should also include denitrogenation kinetics and catalyst inhibition by hydrogen sulfide and nitrogen-containing compounds. The correlation is based on the concentration of 600+ °F sulfur and the total nitrogen content in the feed:

$$T = T_0 + A \exp(S_{600+ \, °F}) + B \ln C_N \qquad (1)$$

where T = temperature for desulfurization to 0.05 wt % sulfur (°F), T_0 = a constant (°F), $S_{600+ \, °F}$ = concentration of 600+ °F sulfur in the feed (wt %), C_N = total nitrogen content (ppmw), and A and B = constants (°F). For the data shown in Table II, the parameters of eq 1 are

T_0	A	B	std dev
454 °F	31.39 °F	25.05 °F	10.1 °F

The temperatures calculated from eq 1 agree well with those observed experimentally (Figure 9). This same approach can be used by refiners using feedstocks and process conditions specific to their application.

This correlation is valid for fresh catalyst performance only. Long-term catalyst aging and effects of pressure/space velocity were not studied.

Conclusions

We have evaluated a total of eight HDS unit feedstocks. The results show that the temperature requirement for desulfurization to 0.05 wt % sulfur can be correlated with the concentration of 600+ °F sulfur and total nitrogen content in the feed, independent of the feedstock source. A simple correlation ranks potential diesel fuel components based on ease of desulfurization to 0.05 wt % sulfur. Refiners may find this approach useful in developing a strategy for the manufacture of low-sulfur diesel fuels.

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