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Gas oil deep hydrodesulfurization: refractory compounds and retarded kinetics

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Abstract

While progressing lower sulfur levels in diesel fuel force increasing demands for gas oil deep HDS in the refineries, problems of refractory sulfur compounds and inhibiting/competitive retarding effects in hydrodesulfurization reactions gain growing importance. High performance sulfur and carbon-specific capillary gas chromatographic analysis combined with computer-aided chromatogram evaluation has been applied as a powerful tool for determination of the feedstock processability and the investigation of gas oil composition and the course of reactions. Gas oil matrices have been found as of high influence on the reaction rates of sulfur compounds. Reaction rates have been measured and correlated predominantly with the total initial sulfur content of the gas oil. The inhibiting species are visualized as strongly adsorbed remarkably stable intermediates, which are formed through partial hydrogenation of multi-ring sulfur compounds. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Deep HDS; Gas oil; Refractory sulfur compounds; Matrix effect; Selective inhibition

1. Introduction

Deep hydrodesulfurization of gas oils has achieved much attention since the tolerated sulfur concentration in diesel fuel is being lowered more and more, e.g. to 500 ppm by weight within the European Union recently and it shall be reduced further [1], because sulfuric acid from the fuel sulfur is adsorbed on the emitted soot particles, making these more toxic, and disturbing exhaust gas cleaning systems [2,3].

For the analysis of the minute amounts of sulfur compounds in original and hydrotreated gas oils, high resolution capillary gas chromatography and sulfur-specific detectors are the adequate tools. The question then is, “Is there anything special in deep HDS, is there anything of different quality pertinents for this low-level-sulfur-conversion?”

In principle it has to be admitted that sulfur in petroleum is distributed over a large number of sulfur compounds and then it should be assumed that the more reactive compounds are converted first and the last remaining ones are the most refractory. It has been observed, that alkyl substituents in the neighbourhood to the sulfur atom in dibenzothiophenes hinder hydrogenative sulfur removal [4–7] and thus, surviving compounds of this type are preferentially found in hydrotreated gas oil [5–7,9,10].

Catalytic hydrodesulfurization is known to be affected by further components in the reaction mixture such as organic heterocompounds and polyaromatic hydrocarbons [4,7]. Organic nitrogen compounds in petroleum are generally less reactive than the sulfur

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compounds. They are converted mainly under more severe conditions than the sulfur compounds and the reaction mechanisms are principally different because of the stronger C/N bond as compared with analogous C/S bonds [8] (in heterocyclic ring system). Recently HDS was reported to be influenced by the type of solvent which had been used to dilute the petroleum fraction [12–16]. Rate constants when using saturated or mono-aromatic hydrocarbon solvents differed up to one order of magnitude and the difference in temperature to obtain the same degree of conversion amounted to about 10°C. The addition of polyaromatic compounds (e.g. naphthalene) had a strong effect [12–16] also.

In general, the following order of inhibition has been noticed. Saturated and mono-aromatic hydrocarbons < condensed aromatics $\approx$ oxygen compounds $\approx H_2S$ < organic sulfur compounds < basic nitrogen compounds.

Ammonia and basic nitrogen compounds have been addressed as the strongest inhibitors in HDS [4]. But even within this group, adsorption constants differ over nearly two orders of magnitude (e.g. from ammonia to 5,6,7,8-tetrahydroquinoline) [17].

The use of technical oils as a solvent in model compound HDS was found to cause strong inhibition. With a 'light cycle oil' instead of decaline as the solvent an approximately 50°C higher temperature was needed for the same conversion [12,13,18]. With light catalytic cycle oil as compared with a straight run gas oil the rate constant for 4,6-dimethyl-dibenzothiophene HDS declined by the factor 10 [16].

For the desulfurization of 'real feeds' (normally straight run gas oils) obviously a multiplicity of influencing parameters of the reactions mixture composition has to be taken into account which commonly in its complexity may be termed as the oil matrix.

2. Experimental

Gas oil samples from five original crude oils have been kindly supplied by OMW refinery at Karlsruhe. Boiling ranges, sulfur contents, nitrogen contents, aromaticities, and densities are recorded in Table 1 which gives the data of a commercially hydrotreated gas oil also (kindly supplied by Shell). Gas chromatographic separation was performed with a Varian STAR 3400 cx GC system using a 105 m (0.25 mm i.d.) fused silica capillary column with dimethyl–siloxane as the stationary phase (Restek Corp.). The gas flow from the column was split for a stream to the PFPD (Pulsed Flame Photometric Detector) for sulfur recording and a stream to the FID (Flame Ionization Detector) for recording of organic carbon. Particularly the newly commercialized PFPD turned out to be a powerful tool. The detector signal was linearized for proportional chromatogram recording.

Comparative hydrodesulfurization of the gas oils was performed, after their vaporization into a hydrogen stream, on a fixed bed of a sulfided CoMo alumina catalyst (conventional-type, provided by the Catalysis Institute of the Université Catholique de Louvain: 2.1 wt.% Co, 8.6 wt.% Mo). 1 g of catalyst

Table 1
Gas oil data and feed stocks for HDS

	Crude oil					Commercially hydrotreated gas oil
	Nigeria Forcados	Brent	Syrian Light	Oural	Arabian Heavy	
Classification of crude	Naphthenic	Paraffinic	Paraffin	Intermediate	Aromatic	
Properties						
Boiling range, °C, (5–95%)	296–380	301–405	296–382	298–400	293–399	220–380
S-content (wt.%)	0.25	0.43	0.61	1.18	2.10	0.076
N-content (ppm by wt.)	359	343	271	509	421	60
Aromatic C[a] (%)	17	11	11	12	16	–
Density (g/ml)	0.882	0.857	0.849	0.877	0.879	0.840

Straight run gas oils from OMW refinery Karlsruhe; Hydrotreated gas oil from Shell Pernis refinery.

[a] Determined by ^1H NMR, as percentage of total carbon, corresponding to [19].

($d_p < 100$ μm) was diluted with 9 g of quartz particles (d_p ca. 0.2 mm), catalyst bed volume 10 ml; reaction pressure 50 bar ($p_{oil} = 0.07$ bar, assumed oil average molecular weight 282 g/mol same as that of a paraffin C_{20}, $p_{H_2} = 49.4$ bar, $p_{H_2S} = 0.5$ bar); $WHSV_{cat} = 0.1$ 1/h. The temperature of reaction was varied in the range 250–320°C. Catalyst pretreatment: drying in a nitrogen flow at 110°C; reduction/sulfidation in a $H_2SH_2 = 1 : 9$ gas flow 100 ml/min at 1 bar, heating rate 4°C/min, then 4 h at 450°C (final temperature). Special devices had been developed for providing the minute flow of the oil and its steady non-discriminating vaporization.

3. Results and discussion

3.1. *Sulfur compounds and sulfur compound distributions of original and hydrotreated gas oils*

The determination of sulfur compounds in petroleum has efficiently become feasible through capillary gas chromatography in combination with a sulfur-specific detector, in particular the pulsed flame photometric detector. When now comparing the chromatogram of the sulfur compounds (Fig. 1, middle) with that of the hydrocarbons (more accurately 'the organic carbon' as detected with the flame ionization detector, Fig. 1, top) of the heavy gas oil fraction of the Brent crude oil, a totally different structure of the chromatograms is noticed: The hydrocarbon distribution reflects the fossile nature of the oil, as being regularly shaped by high peaks of the normal paraffins at each carbon number and two peaks of the terpenoid hydrocarbons Pristane and Phytane on top of a broad hill of the many unresolved small peaks.

The sulfur chromatogram exhibits tall peaks of dibenzothiophene (DBT), (for molecule structures see Fig. 2), the group of C_1-dibenzothiophenes (from 1- to 4-MDBT), and the group of C_2-dibenzothiophenes. Among these the 4,6-dimethyl-dibenzothiophene is famous for its high stability against hydrodesulfurization [4–7,9–11] as explained by spatial/geometric/steric effects around the sulfur atom. It follows the fingerprints-like group of the already many, not so tall and not so much resolved peaks of the C_3-alkylated dibenzothiophenes (C_3-DBTs). Peak identification was based on GC/MS studies, reference compound chromatography and literature [5,6,9–11]. A broad hill, representing many unresolved peaks of sulfur compounds, occurs. However, its shape is different from that of the hydrocarbons : non symmetrical, more complex and irregularly structured.

The chromatograms of organic carbon and sulfur reflect also the distillation cuts, which principally represent hill-like distributions over boiling point, respectively, this carbon number (see Fig. 1). In order to eliminate this influence of destillative fractionation, the carbon distribution (carbon GC) has been smoothed computer aided and then the sulfur distribution (sulfur GC) divided by the smoothed carbon GC to obtain now a highly resolved sulfur concentration profile, free from the overlaid cut distribution (Fig. 1, bottom). Now the regularities of the distribution of sulfur compounds in the oils are well visible, with the occurrence of the individual families and groups of isomers and the increase of sulfur concentration with increasing boiling point.

By computer-aided smoothing of the sulfur concentration profile the smoothed S-profile, shown also in Fig. 1 (bottom), is obtained. By comparison with the non-smoothed profile in the same figure it is understood that the steps in the curve represent new benzologues families of compounds. The areas of the three sulfur compound families (2-ring-, 3-ring- and 4-ring-compounds) are also shown in the Fig. 1 (bottom). This estimation of the amounts of the three families of sulfur compounds in original and hydrotreated gas oil samples is used later for kinetic purposes.

As relevant to this investigation, we want to stress that the kinetic principles of hydrodesulfurization can be investigated efficiently on this basis, in spite of the fact that only a small number of substances is determined individually, and the rest of sulfur compounds is discriminated only as for groups, families and boiling point.

Sulfur-specific chromatograms of the five gas oils are shown in the Fig. 3. As the total sulfur content in these gas oils differs by a factor of about 8 (0.25–2.1 wt.% of sulfur) the representation of the chromatograms has been normalized (normalization to the same area for the sulfur in the boiling range 327–377°C). A detailed comparison of the chromatograms shows important differences, however, the initial

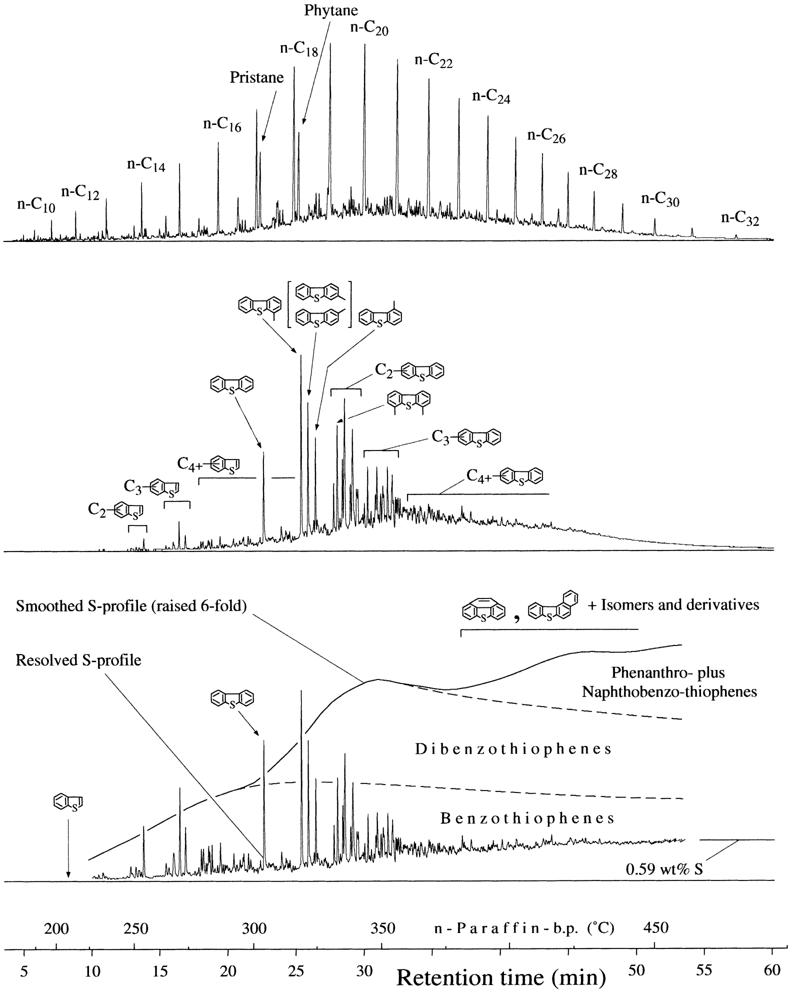

Fig. 1. Carbon- and sulfur-specific chromatograms and a computer-calculated sulfur concentration profile of the Brent heavy gas oil (see Table 1). Top: carbon-specific chromatograms (flame ionisation detector). Mid: sulfur-specific chromatogram (pulsed flame photometric detector, linearized). Bottom: sulfur concentration profile. Resolved S-profile and 'smoothed S-profile' with estimated contributions of 2-ring, 3-ring and 4-ring S compounds (– – –).

impression about all the chromatograms is that for 'petroleum sulfur compounds in the gas oil range.'

The differences in these sulfur distributions become more obvious in the respective sulfur concentration profiles (Fig. 4). In the profile of the most immature, high sulfur, aromatic oil from the Arabian Heavy crude one sees particularly the peak ratio of benzothiophenes to dibenzothiophenes to be high, whereas in the more mature, low sulfur, paraffinic oils (Brent and Syrian Light) this ratio is low. The peak ratio of dibenzothiophene to the alkylated dibenzothiophenes varies as well, being very low with the immature oil and high with the mature ones. This reflects geochemical rules of sulfur compound conversion during oil maturation [20–22].

By smoothing of the sulfur concentration profiles in Fig. 4 the curves of Fig. 5 left have been obtained. Each of the curves shows the characteristic steps, which are caused by new benzologues families of sulfur compounds, being possible with increasing boiling point: benzothiophenes, dibenzothiophenes, naphthobenzothiophenes plus phenanthrothiophenes.

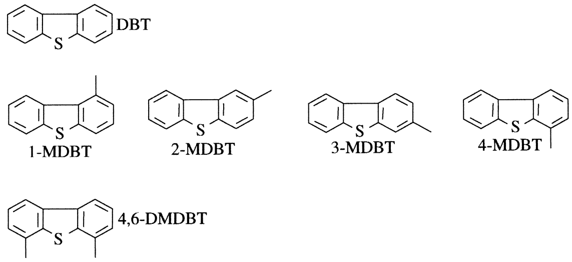

Fig. 2. Dibenzothiophene structures. The conversion of these compounds in the heavy gas oils has been measured individually. DBT = dibenzothiophene, MDBT = methyldibenzothiophene, DMDBT = dimethyldibenzothiophene.

The distances between the steps (in retention time, respectively boiling point) actually are that for enlarging the ring system by one more aromatic ring.

From the comparison of the normalized smoothed curves in Fig. 5 right it is understood, that the concentration ratios of these 2-ring, 3-ring and 4-ring sulfur compounds differ remarkably for the five oils. Specifically in the immature aromatic Arabian Heavy crude oil the fraction of the 2-ring compounds is relatively high and in the mature paraffinic oils it is low. A similar shift is observed when regrading the ratio of the concentrations of 4-ring to 3-ring compounds for the immature Arabian Heavy and e.g. the mature Brent paraffinic oil.

When now comparing the sulfur concentration profiles of the original Brent heavy gas oil with two of its HDS reactions products, being reduced in sulfur content from 0.43 wt.% of the original oil to 0.138 wt.% and further 0.037 wt.% respectively strong selectivities of conversion can be noticed (Fig. 6). Through the first ca. 65% HDS conversion almost all of the sulfur from the 2-ring compounds has been removed (Fig. 6, middle). After about 91% HDS conversion (Fig. 6, bottom) the sulfur concentration profile of the 3-ring S-compounds has been changed. Among the monomethyl-dibenzothiophenes the 4-methyl substituted isomer has solely survived in part. Among the dimethyl-dibenzothiophenes, the 4,6-substituted is preferentially left and it can thus be concluded, that the principle of selectivity of HDS conversion is now the accessibility of the sulfur in the molecule, which is affected (declined) through neighbouring alkyl groups. It may be assumed that this principle generally applies for the structure changes of the S-profile. The structure has become simpler, the background having developed a more pronounced profile and it is concluded that the remaining sulfur compounds belong preferentially to the group of geometrically hindered ones, among the 3-fold and 4-fold alkyl-substituted dibenzothiophenes and to the 4-ring hindered sulfur compounds also. Which are the major refractory 4-ring S-compounds is not to be deduced from these results. As there are no pronounced individual peaks in the respective profile area, it is concluded that not the base structures but their substituted homologues with their many isomers are the relevant compounds. Then deep HDS has particularly to deal with this multiplicity of refractory sulfur compounds, as specified by this work.

The same sort of sulfur distribution and sulfur concentration profile was observed with the commercially hydrotreated gas oil (see Table 1) as shown in Fig. 7, which proves the same rules of HDS selectivity to apply for fixed bed/gas-phase as well as for trickle bed conversion.

3.2. *Hydroconversion of the sulfur compounds in the gas oils*

Through fixed bed/gas-phase hydrotreating, the sulfur compounds of the gas oils have been reacted at several temperatures. The results were evaluated in the form of conversion as a function of reaction temperature. The 4-methyl-dibenzothiophene is represented by a nice individual tall peak in the chromatograms and is suited for quantitative evaluation. Then Fig. 8 left top shows the results for 4-methyl dibenzothiophene conversion as a function of reaction temperature for the five gas oils. As to be expected, the curves are ‘S’-shaped. Remarkably, depending on the sort of oil, same degree of conversion is attained at quite different temperatures. For example, 50% conversion for the Nigeria Forcados gas oil needs only 268°C, but for the Arabian Heavy gas oil it needs 300°C.

It is concluded, that the ‘oil matrix’ causes these big differences in reaction rate; but then, the question specifies to, “which aspect of oil composition causes the effect?” Are there some strongly adsorbed nitrogen compound with their basic properties, the aromatics, or other sulfur compounds present in the oil?

The curves in the Fig. 8 left, top have been calculated using the kinetic approach which is outlined in

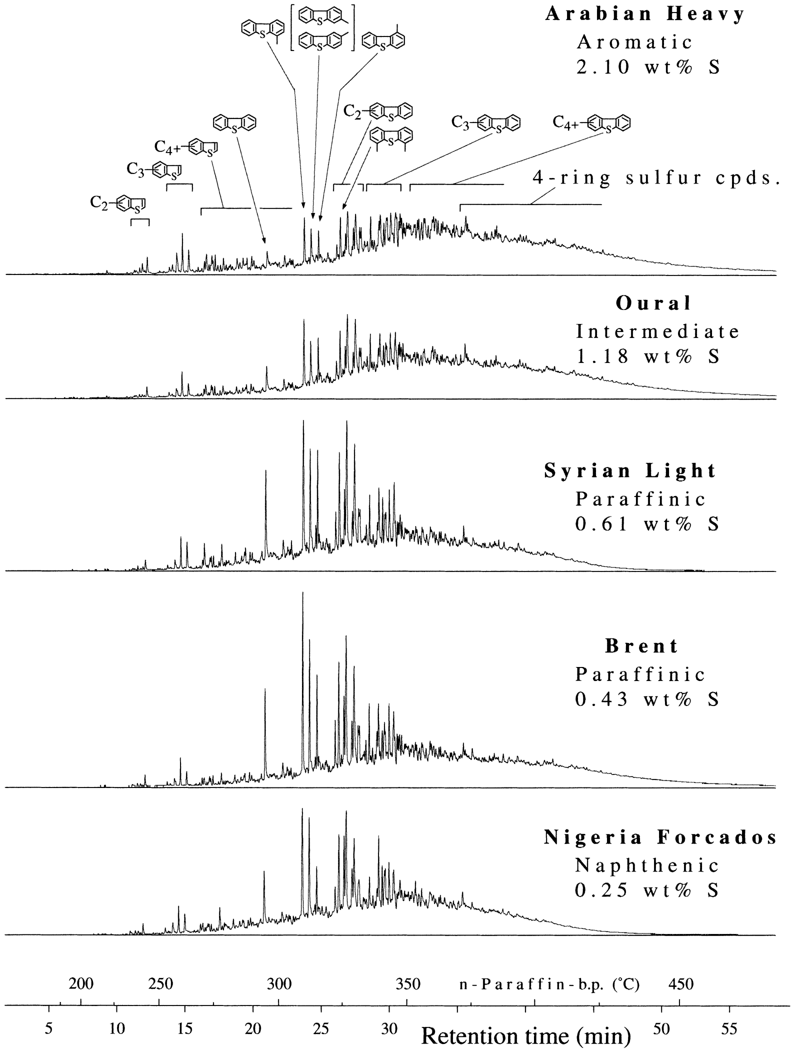

Fig. 3. Sulfur-specific chromatograms of the heavy gas oils from five selected crude oils (see Table 1). Representation of the chromatograms is normalized to the sulfur amount in the 327–377°C boiling range.

Fig. 9 and shown by Eqs. (1–6) therein. The general rate equation for conversion of an individual sulfur compound 'i' of the oil is written as Eq. (1). In the present case of high surplus of hydrogen, '$f(p_{H2})$' is assumed to be constant and the same is assumed for the 'inhibition by the oil matrix' $(1+\sum K_j \times p_j)^n$ when regarding one individual oil. Then the rate equation simplifies to Eq. (2). Having in mind this simple first-order rate equation in its linear form as Eq. (3), the results have been plotted in Fig. 8 left, bottom as $\ln(\ln(1/(1-X)))$ against $1/T$. The straight parallel lines have been calculated, as for the best correlation in Fig. 8 right, bottom, assuming that the strong inhibition is caused by the total sulfur. Then the rate law can be written as Eq. (4). The obtained straight line from plotting $\ln(\ln(1/(1-X))) + \ln(C_{S,O})$ against $1/T$ is justified by a correlation coefficient of as high as $-r = 0.978$ (see Fig. 8 right, bottom). Thus, the matrix effect documents itself as an additive value '$\ln(C_{S,O})$' to $\ln(\ln(1/(1-X)))$. This effect is so strong that the initial rate equation can be written as Eq. (6) (rearranged via Eq. (5)).

It has been found, that an even better correlation than with the total sulfur content is obtained

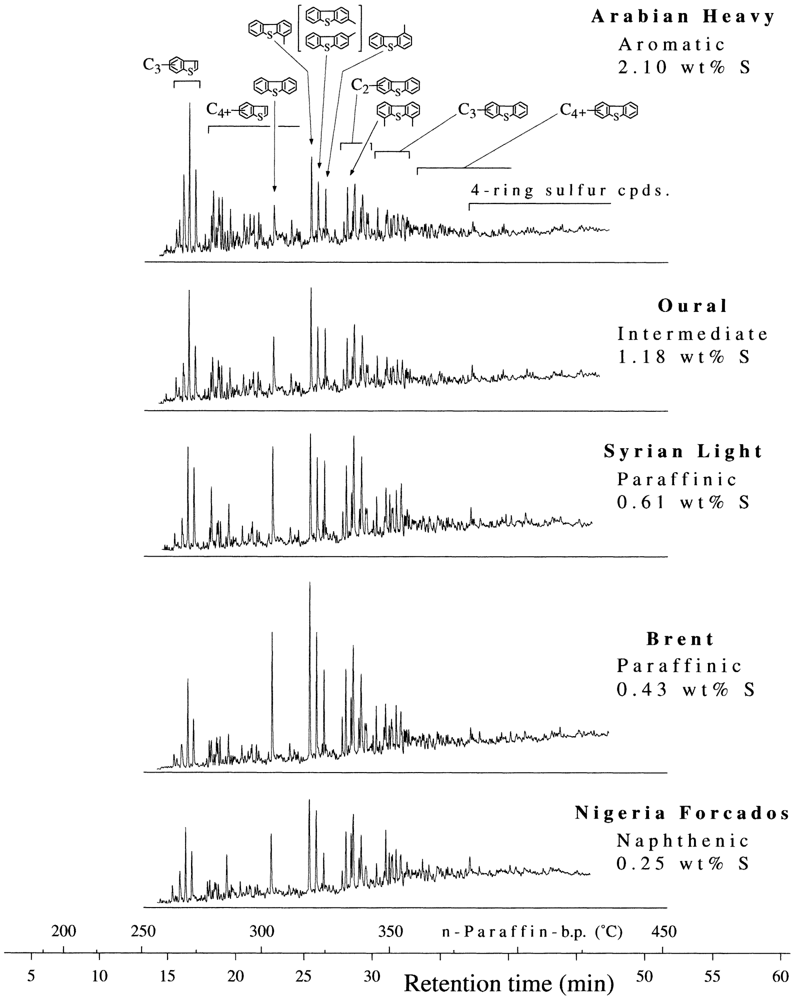

Fig. 4. Sulfur concentration profiles of the heavy gas oils from the five crude oils. Profiles are normalized to the amount of sulfur in the 327–377°C boiling range.

with the dibenzothiophene plus naphthobenzothiophene sulfur content of the gas oils and with the naphthobenzothiophenes sulfur in particular ($-r = 0.990$).

From this evaluation it is concluded, that the strong inhibiting effect of the gas oil matrix is preferentially and specifically due to higher benzologues sulfur compounds.

It has been also investigated, which correlations might exist with the nitrogen content and the content of the aromatics of the gas oils and it was found, that these properties have by far no sufficiently strong effect on the reaction rate, to explain the matrix influence. And the correlation index was poor for both the nitrogen content and the aromaticity.

Fifty percent conversion temperatures T_{50} for several sulfur compounds and compound families of the five gas oils, together with differences of 50% conversion temperature ΔT_{50} are presented in Table 2.

Reactivities of dibenzothiophene, individual methyldibenzothiophenes and the families of dibenzothiophenes and benzothiophenes in the form of relative first-order rate constants are given in Table 3. In particular it is to be noticed that the dibenzothiophenes are about 10 times less reactive than the benzothiophenes.

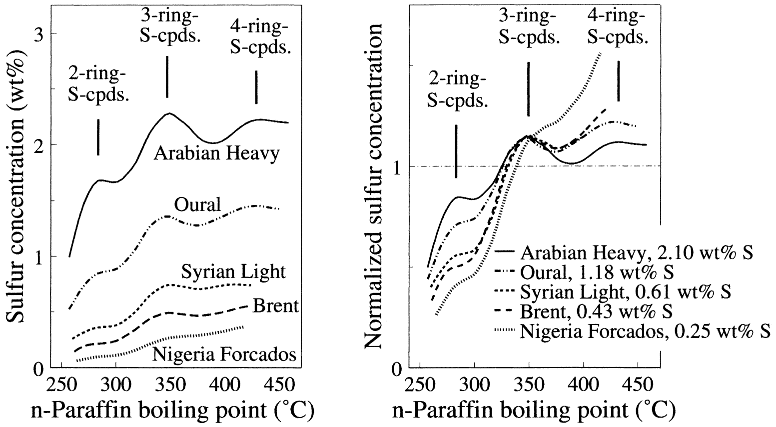

Fig. 5. Smoothed sulfur concentration profiles of the heavy gas oils from the five crude oils. Left: original profiles. Right: normalized profiles (normalized to the amount of sulfur in the 327–377°C boiling range).

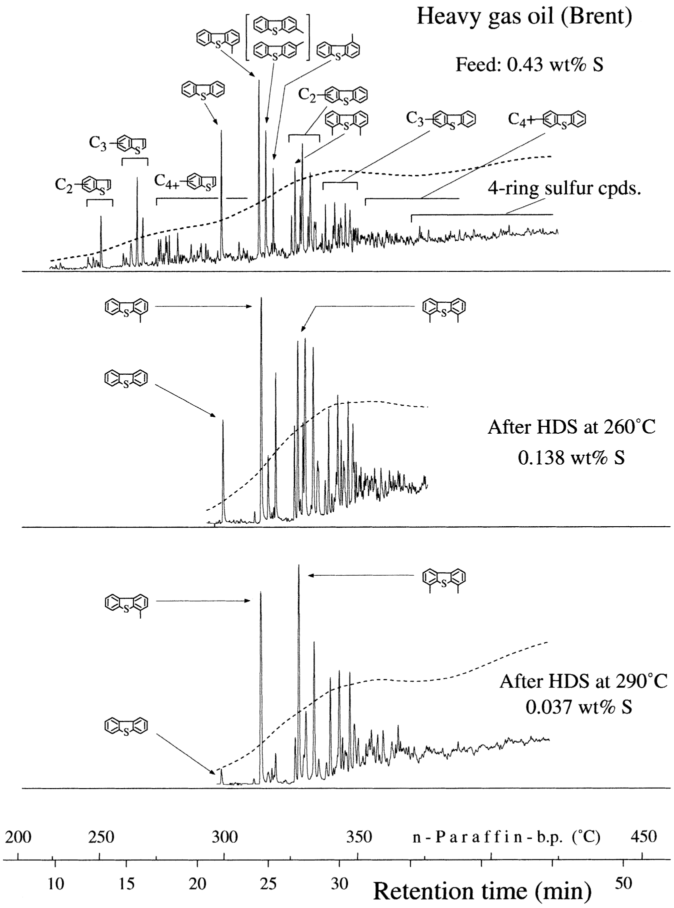

Fig. 6. Sulfur concentration profiles of the Brent heavy gas oil (see Table 1) and its products from high pressure gas-phase hydrotreating (sulfided $CoMo/Al_2O_3$, $p_{H_2} = 49.4$ bar, $p_{H_2S} = 0.5$ bar, $p_{oil} \approx 0.07$ bar, WHSV $= 0.1$ $g_{oil}/(g_{cat}$ h), H_2/oil $= 60 \times 10^3$ ml (STP)/g). Profiles are normalized as corresponding to the equal to amount of total sulfur.

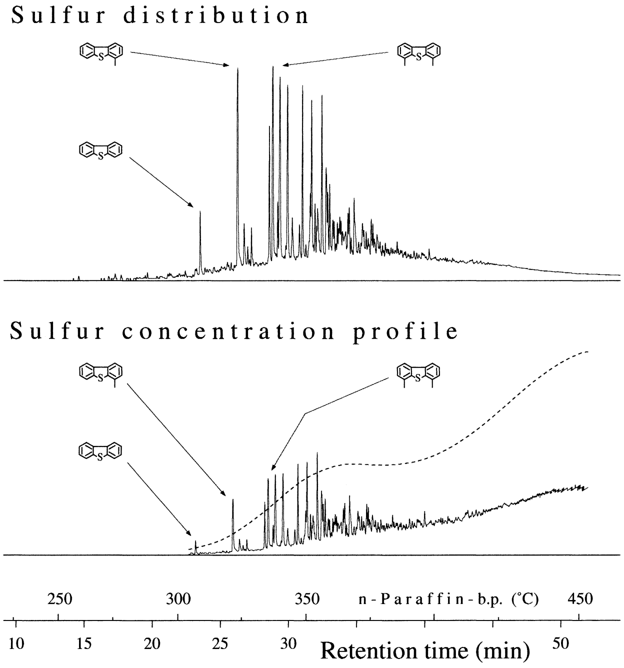

Fig. 7. A sulfur-specific chromatogram (above) and the computer-calculated sulfur concentration profile (bottom) of technically hydrotreated gas oil (the dotted curve represents the smoothed sulfur concentration profile, 3-fold magnified ordinate). Curves are normalized corresponding to Figs. 3 and 6.

Table 2
Fifty percent conversion temperatures T_{50} (°C) and differences thereof (ΔT_{50}) as a measure of HDS reactivity of individual sulfur compounds and families of sulfur compounds in five gas oils of different origins (see Table 1)

Sulfur compounds and sulfur compound families	T_{50} and (ΔT_{50})[a] values for crude oils				
	Nigeria Forcados	Brent	Syrian Light	Oural	Arabian Heavy
Dibenzothiophene	250	258 (8)	263 (13)	273 (23)	281 (31)
2- + 3-Methyl-dibenzothiophene	241	249 (8)	255 (14)	266 (25)	275 (34)
1-Methyl-dibenzothiophene	257	266 (9)	272 (15)	283 (26)	293 (36)
4-Methyl-dibenzothiophene	268	276 (8)	281 (13)	291 (23)	300 (32)
All Dibenzothiophenes	261	271 (10)	278 (17)	291 (30)	304 (43)
All Benzothiophenes	211	221 (10)	228 (17)	240 (29)	252 (41)
Total sulfur compounds	235	242 (7)	244 (9)	252 (17)	260 (25)

[a] The ΔT_{50} values (in brackets) characterize the matrix effect in relation to the Nigeria Forcados heavy gas oil.
Values of T_{50} are taken from plots such as Fig. 8 top left. For reaction conditions see Section 2.

4. Conclusions about the matrix effect

From the above results the following is concluded:

- A very strong inhibiting matrix effect of the gas oils themselves on the HDS-reaction rate of sulfur compounds is existing.
- This effect is predominantly due to other sulfur compounds in the oil.
- These sulfur compounds are of the type of the highly stable ones, in the range of the multi-ring compounds.

It cannot be thought, that these compounds produce the inhibiting effect just by simple adsorption. Then

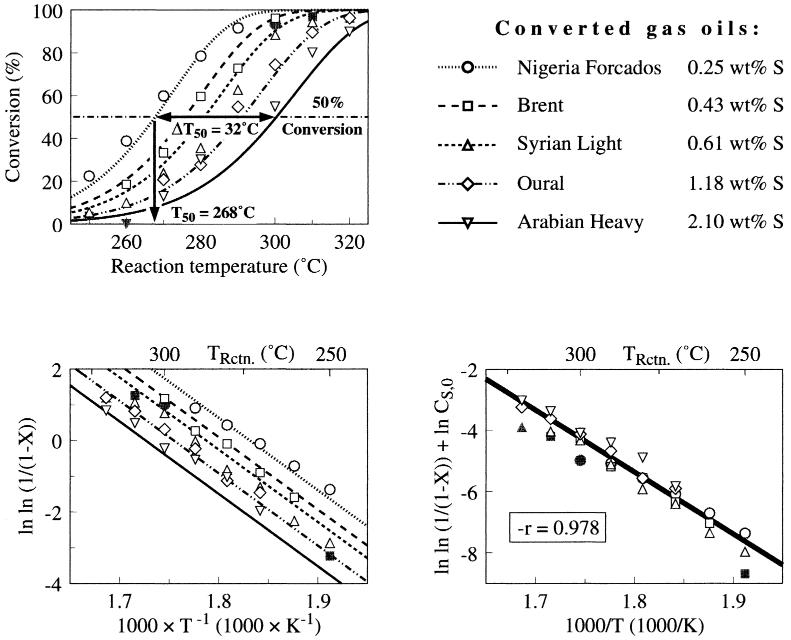

Fig. 8. Conversion of 4-methyldibenzothiophene during gas phase hydrotreating of the five heavy gas oils as a function of reaction temperature. (Full grey symbols mark values, which have not been used for modelling, because of their minor reliability in the 95% conversion range.) Top left: plot of conversion X against T. Curves have been calculated (see text). Arrows indicate the 50% conversion temperature (T_{50}) and the difference of those (ΔT_{50}) as an example. Bottom left: plot of $\ln(\ln(1/(1-X)))$ against $1/T$. Lines have been calculated (see text). Bottom right: plot of $\ln(\ln(1/(1-X))) + \ln(C_{S,O})$ against $1/T$. With best-fitting straight line the correlation index is $-r = 0.978$.

Table 3
Relative reactivities of benzothiophenes and dibenzothiophenes in heavy gas oil conversion

Sulfur compounds	Relative reactivity at 277°C
Dibenzothiophene	1.00
1-Methyl-dibenzothiophene	0.52
2- + 3-Methyl-dibenzothiophene	1.47
4-Methyl-dibenzothiophene	0.30
All dibenzothiophenes[a]	0.37
All benzothiophenes[b]	4.00

[a] Including a small amount of higher benzologues sulfur compounds.

[b] Including a small amount of lower sulfur compounds.

Data are relative first-order rate constants and are taken from straight lines of $\ln(\ln(1/(1-X))) + \ln(C_{S,O}) = f(1/T)$ plots (as Fig. 8 bottom right).

See Table 1, reaction conditions see Section 2.

our suggestion is that these compounds, by addition of one H atom, react to strongly chemisorbed rather stable intermediates, and these are the real inhibiting species. Such intermediates are tentatively pictured in Fig. 10. The corresponding naphthobenzothiophenes and phenanthro-[4,5-b,c,d]-thiophene have been reported to occur in various oils [29–32].

There is substantial support for this hypothesis:

- The postulated species, obtained by addition of one H atom, are highly stabilized because many mesomeres contribute to their electron delocalization.
- In literature [23–28] special kinetic effects have been reported which should have the same theoretical bases. The kinetics of hydrogenation of toluene are explained by inhibition through an in principle similar species (one H added).
- Saturation of the respective double bond (addition of a second H) would lead to a highly tensioned structure.
- In HDN reactions we have recently found [33] that similar chemisorbed species of considerable life time do best explain the observed selectivity.
- There also exist analogies in the Fischer–Tropsch synthesis where during secondary olefin hydro-

$$r_i = \frac{k_i \cdot p_i}{(1+\sum K_j \cdot p_j)^n} \cdot f(p_{H2}) \qquad \text{(eqn. 1)}$$

$$-\frac{dp_i}{d\tau} = k_i' \cdot p_i \qquad \text{(eqn. 2)}$$

$$\ln\ln\left(\frac{1}{1-X}\right) = \ln(k_i' \cdot \tau) - \left(\frac{E_A}{R} \cdot \frac{1}{T}\right) \qquad \text{(eqn. 3)}$$

$$\ln\ln\left(\frac{1}{1-X}\right) + \ln C_{S,0} = \ln(k_i'' \cdot \tau) - \left(\frac{E_A}{R} \cdot \frac{1}{T}\right) \qquad \text{(eqn. 4)}$$

$$-\frac{dp_i}{d\tau} = k_i'' \cdot p_i \cdot \frac{1}{C_{S,0}} \qquad \text{(eqn. 5)}$$

$$r_i = \frac{k_i'' \cdot p_i}{C_{S,0}} \qquad \text{(eqn. 6)}$$

Fig. 9. Kinetic modeling. Derivation of the rate law for sulfur-matrix influence on the rate of individual sulfur compound conversion (r_i = rate of conversion of reactant i, k_i = the reaction rate constant, p_i = partial pressure, K_j and p_j = adsorption constants and partial pressures of compounds adsorbed competitively, n = exponent, τ = space time, X = conversion, E_A = apparent activation energy, R = gas constant, T = absolute temperature, $C_{S,O}$ = gas oil initial total sulfur content).

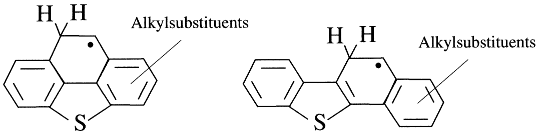

Fig. 10. Possible structure types of postulated strongly adsorbed stable intermediates.

genation the first step of hydrogen addition is reversible, as consistent with a relatively high stability of the species obtained by addition of one H atom (and the addition of the second H is slow and irreversible) [34].

The results and conclusions of this work could have importance for the practice of gas oil deep hydrodesulfurization.

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