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Deep hydrotreating of middle distillates from crude and shale oils

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Abstract

The potential scientific and technological solutions to the problems that appear as a result of shifting the hydrotreating of crude oil middle distillates and shale oils from the 'normal' to the 'deep' mode are considered on the basis of the reactivities and transformation routes of the least-reactive sulfur-, nitrogen-, and oxygen-containing compounds. The efficiency of selecting the optimal feedstock, increasing the process severity, improving the catalysts activity, and using alternative catalytic routes are compared, taking into account the specific issues related to deep hydrodesulfurization/hydrodenitrogenation/hydrodeoxygenation, i.e., chemical aspects, kinetics and catalysts.

Keywords: Hydrodesulfurization; Hydronitrogenation; Hydrodeoxygenation; Crude oil; Shale oil; Middle distillate

1. Introduction

Hydrotreating as a means of reducing the sulfur, nitrogen and oxygen contents in fuels continues to be one of the main catalytic processes in petroleum refining. It is currently the technology of choice in the production of fuels from alternate hydrocarbon feedstocks, which are important reserves of synthetic oil, such as shale oils, liquefied coals, and bituminous sands, since these materials have high contents of heteroatoms.

The development of catalytic processes – including the catalytic system, the reactor design and the technological solutions (from selection of the proper feedstock to the separation mode of the final products) – must be based on a knowledge of the required chemical transformations of the starting molecules. For hydrotreating processes this is not possible, since in real feedstocks sulfur, nitrogen and oxygen are present in hundreds of different compounds that cannot be quantitatively separated and analyzed, and the situation is even more complicated for the products of hydroconversion. Therefore, classical hydrotreating processes were designed on the basis of an 'average' chemical transformation approach. Empirical information about the effects of process variables and catalyst properties on the removal rates of sulfur, nitrogen or oxygen thus constituted the basis for process design.

By the beginning of the 1980s, application of this empirical approach – in combination with a tremendous volume of experimental work – enabled oil refineries all over the world to reach a ceiling of about 90% of sulfur removal from crude-oil middle distillates (MD), corresponding to a residual sulfur content of about 0.1 wt% at hydrogen pressure ranging 25–50 atm, start-of-the-run (SOR) temperature ranging

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330–350°C and liquid-hour-space-velocity (LHSV) ranging 3–6 h^{-1} [1–3]. This technical level may be designated 'normal' desulfurization. For shale oils, pilot-scale application of the 'average' approach to hydrotreating with the commercial catalysts used for middle and heavy distillates of crude oils gave a 'normal' technical level of hydrotreating, i.e., removal of >95% sulfur, >90% oxygen, and >70% nitrogen (corresponding to residual sulfur, oxygen, and nitrogen contents of <0.05, <0.1, and <0.5 wt%, respectively) at hydrogen pressure ranging 100–150 atm, SOR temperature ranging 400–440°C and LHSV of 1 h^{-1} [4,5].

During the past decade, success in the separation and quantitative analysis of individual heterocompounds from hydrocarbon feedstocks has substantially clarified the picture of their chemical transformations in hydrotreating processes. This is particularly true for the least-reactive heterocompounds remaining in the products after 'normal' hydrotreating, since they belong to the groups of polyaromatic compounds.

The proliferation of emission regulations and the corresponding tightening of fuel-quality requirements in the past decade [6–9] have provided the thrust for intensification of the development of hydrotreating processes to further reduce the contents of heterocompounds, i.e., a shift from the 'normal' to the 'deep' hydrotreating mode. Deep hydrotreating presupposes removal of >95% of sulfur from crude oil MD in the production of diesel fuels. Legislation in the USA and Western Europe calls for a residual sulfur content of <0.05 wt% by the end of 1996, with a further reduction to <0.01 wt% in the future. Production of fuels from shale oils requires – in addition to deep hydrodesulfurization (HDS) – deep hydrodenitrogenation (HDN), corresponding to a residual nitrogen concentration of <0.05 wt%.

The shift from normal to deep hydrotreating is a very complicated technical problem that requires a significant breakthrough in the development of catalysts and process technology in the short period of time available before the new legislation goes into effect: the potential of the current 'averaged' approach to catalyst and process development is clearly limited. We believe that the information already available on the chemical transformations of individual heterocompounds in the hydrotreating of crude and shale oil MD is sufficient to facilitate a shift from normal to deep hydrotreating conditions on the basis of an 'individual' approach. An 'individual' approach comprises the following steps:

- classification of the heterocompounds present in raw feedstocks according to their HDS, HDN, and hydrodeoxygenation (HDO) reactivities under real hydrotreating conditions;
- definition of the least-reactive groups of heterocompounds that cannot be efficiently removed in 'normal' processes;
- study of the reaction networks of the latter compounds with 'normal' commercial hydrotreating catalysts, together with a review of the information available on their catalytic and noncatalytic conversion; and
- identification of the specific requirements of the hydrotreating technology and catalysts that will facilitate solutions to the deep hydrotreating problem.

The first attempt in this direction was made a few years ago in the excellent review of Girgis and Gates [10], who considered the thermodynamics, reactivities, reaction networks and reaction kinetics of individual sulfur, nitrogen and oxygen compounds found in industrial feedstocks and their mixtures. However, data pertaining to the reactivities of industrial feedstocks were not included because of the lack of relevant quantitative information. Thus, the task of this paper is to review the data on the reactivities of individual heterocompounds in industrial feedstocks, especially the information published in recent years, and to use the 'individual' approach defined above for the formulation of potential scientific and technological solutions to the deep hydrotreating problem.

2. Deep desulfurization of crude-oil MD

2.1. Nature and distribution of sulfur compounds

The MD of crude oil that could potentially be used for diesel-fuel production include straight-run middle distillates (SR-MD), light cyclic oil (LCO) from catalytic cracking and gas oils from thermal processes like visbreaking, delayed coking and fluid coking [14]. The sulfur compounds present in MD have different natures and boiling points. These compounds are distributed nonuniformly in their boiling range, the character of the nonuniformity depending on the origin of the crude oil, as illustrated in Fig. 1 and Table 1 [11–14]. Total sulfur distribution has been determined by analysis of the sulfur content in both narrow and wide fractions of the MD (the fractions being obtained by changing the distillation range). The available data show that in all cases of SR-MD, the sulfur content rises by increasing the boiling points, from the initial boiling point to about 340°C, while at higher boiling points, up to 400°C, there is no particular correlation between the sulfur content and the boiling point. For LCO-MD, the sulfur distribution shows two maxima, one at 240–290°C and the other at 330–370°C [11,12].

Table 1
Effect of increasing boiling points on sulfur content in SR-MD

Distillation range (°C)	Sulfur content (wt%)
[14]	
160–351	1.20
228–392	1.53
260– >400	1.85
[29]	
153–320	0.65
153–380	1.33
153–403	1.37

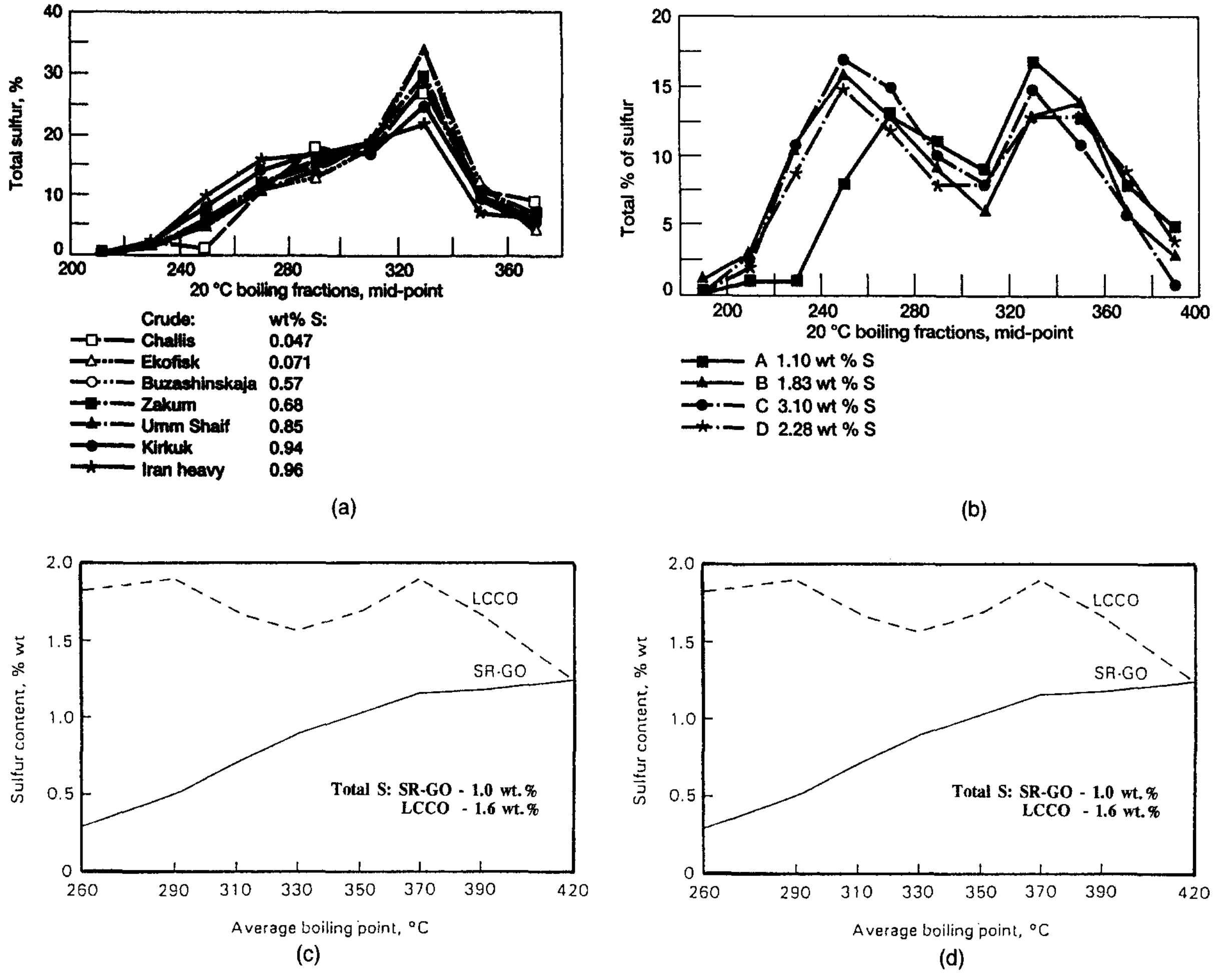
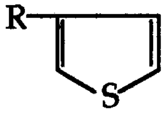


Fig. 1. Distribution of sulfur in SR-MD and LCO-MD: (a) and (b) are reproduced with permission from Ref. [11] (Copyright 1992 by Gulf Publishing Co., all rights reserved); (c) is adapted from Ref. [12]; and (d) is adapted from Ref. [13].

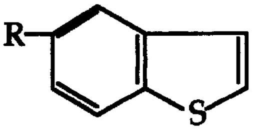
The sulfur compounds present in crude oil MD may be divided into five classes [1,15–17]:

Thiols	RSH
Sulfides	RSR

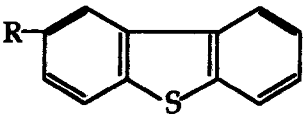
Thiophenes



Benzothiophenes



Dibenzothiophenes



Generally, these five classes of compounds may be assigned to one of the two groups displaying different HDS reactivities: (1) aliphatic and nonheterocyclic aromatic sulfur compounds (AASC), which include thiols, sulfides and thiophenes, where *R* is an alkyl or phenyl substituent, and (2) polyaromatic sulfur compounds (PASC), which include benzothiophenes (BTs) and dibenzothiophenes (DBTs). The amount of single-ring thiophenes is negligible, and the distribution of the other four classes of sulfur compounds is determined by their boiling points, which are related to the numbers of carbon atoms in the molecules (Fig. 2) [16]. For SR-MD, the ratio of the amount of sulfur in AASC to that in PASC depends strongly on the origin of the crude oil and the distillation range of the MD. The ratio varies from about 20:80 for heavy Middle-East Crude in the boiling range 200–450°C [16] through 30:70 for Middle-East Crude at 232–365°C [18] to 60:40 for Arabian Light Crude at 245–374°C [19], while in LCO-MD, the sulfur is present almost exclusively in the PASC [11]. The ratio between the amounts of sulfur in BTs and DBTs is close to 1 for heavy SR-MD boiling out in the range 200– $\geq$400°C [11,16,18,19] and is much higher for LCO-MD [11,20].

Since the reactivity of the AASC under normal HDS conditions is higher by more than one order of magnitude than that of the PASC [1,21,22], the AASC are usually not present in desulfurized MD, even under comparatively mild conditions. A number of workers [11,17,19,22,23], who determined the sulfur distribution in MD of different origins that had been desulfurized to different extents, found only PASC. Since the deep HDS problem has become increasingly important in the past few years, much attention has been paid to the identification of individual PASC in MD and to classify them according to their reactivities in HDS.

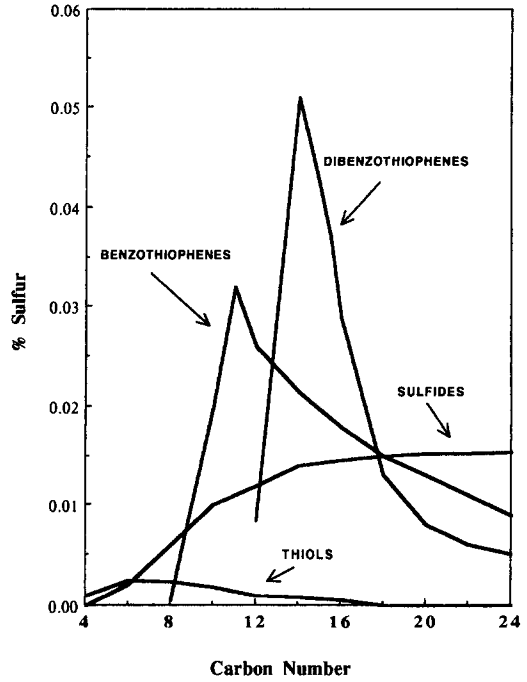


Fig. 2. Types of sulfur compounds by carbon number in Middle-East crude (adapted from [16]).

Qualitative and quantitative identification of individual PASC in MD is very complicated because of their low concentrations ($\leq$200 ppm), chemical similarity to one another and close boiling points. Analysis of individual PASC may be performed by a combination of special separation methods (liquid chromatography, ligand-exchange chromatography and simulated GC-distillation), with high-resolution gas chromatography using selective detectors (flame photometric (FPD), microwave-induced plasma atomic emission spectroscopic (MIP-AED), various sulfur chemiluminescence (SCD), etc.) and GC-MS [11,16,24–26].

The development of analytical schemes at the beginning of the 1990s has facilitated the collection

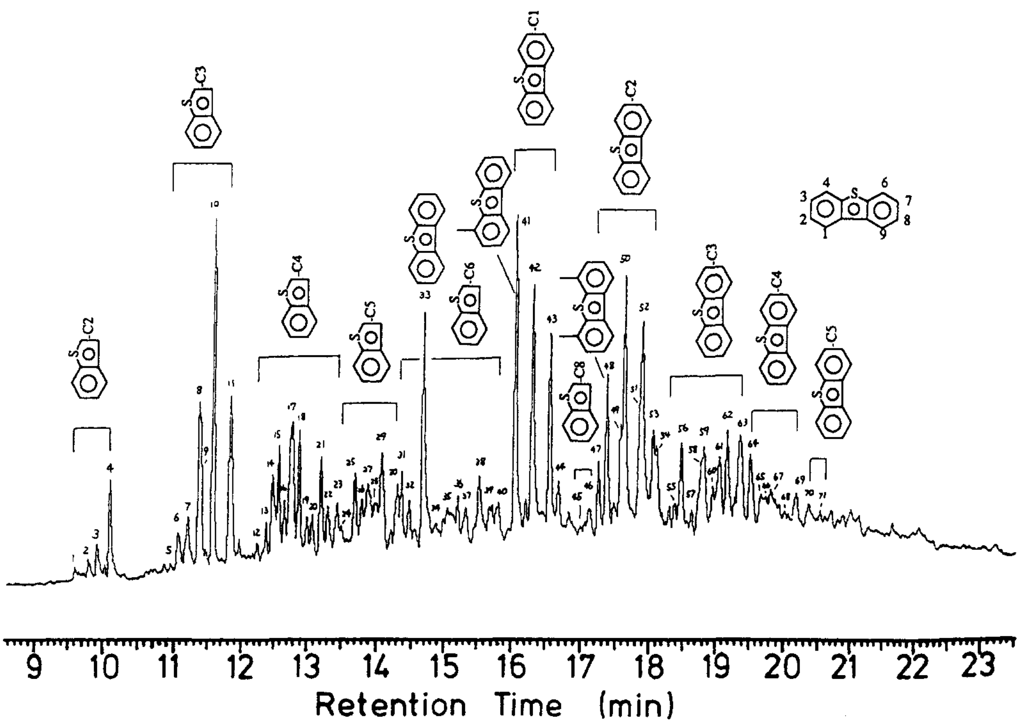
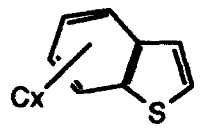
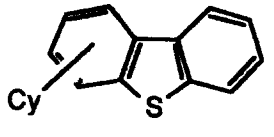


Fig. 3. GC-AED chart of PASC in SR-MD of Arabian light crude (reproduced with permission from Ref. [19]. Copyright 1992 by American Chemical Society, all rights reserved).

of detailed information about the nature of PASC present in both SR-MD and LCO-MD. The bulk of the analytical work was performed by Kabe et al. [19] and Ma et al. [18]. The former group identified 71 individual PASC in a 245–374°C SR-MD of Arabian light crude oil containing 1.46 wt% S (Fig. 3), and the latter group reported 61 individual PASC in a 232–365°C fraction of SR-MD of Middle-East Crude containing 0.706 wt% S. The PASC comprised two main groups of sulfur compounds that are homologs of BTs and DBTs alkylated at different positions. The first group included BTs with alkyl substituents containing 1–7 carbon atoms, and the second group comprised DBTs with alkyl substituents containing 1–5 carbon atoms; the amounts and positions of substituents for molecules with alkyl chains containing ≥ 2 carbon atoms could not, however, be fixed. For example, in the 232–365°C fraction of SR-MD of Middle-East crude, the following BTs and DBTs were identified: one Me-BT; four C_2-BTs; five C_3-BTs; eleven C_4-BTs; four C_5-BTs; six C_6-BTs; two C_7-BTs; DBT; 4-Me-DBT; three other Me-DBTs; 4,6-diMe-DBT; six C_2-DBTs; seven C_3-DBTs; five C_4-DBTs; and two C_5-BTs [19]. The structures of only three PASC were completely identified: DBT, 4-Me-DBT and 4,6-diMe-DBT, which represented about 10% of the total sulfur in the PASC.

These results were confirmed by other workers who obtained similar results using sulfur-sensitive gas chromatography of separated PASC fractions and dividing the PASC into a number of groups according to their retention times [11–13,20,23]. It is now clear that the PASC in SR-MD consist of two groups of sulfur compounds:





where x=1–7 and y=0–5 and the corresponding sulfur content of each individual compound varies in the range 0.5–5% of the total sulfur content in the PASC. In LCO-MD, boiling out in the range 184–328°C, the BTs identified among the PASC had values of x and y

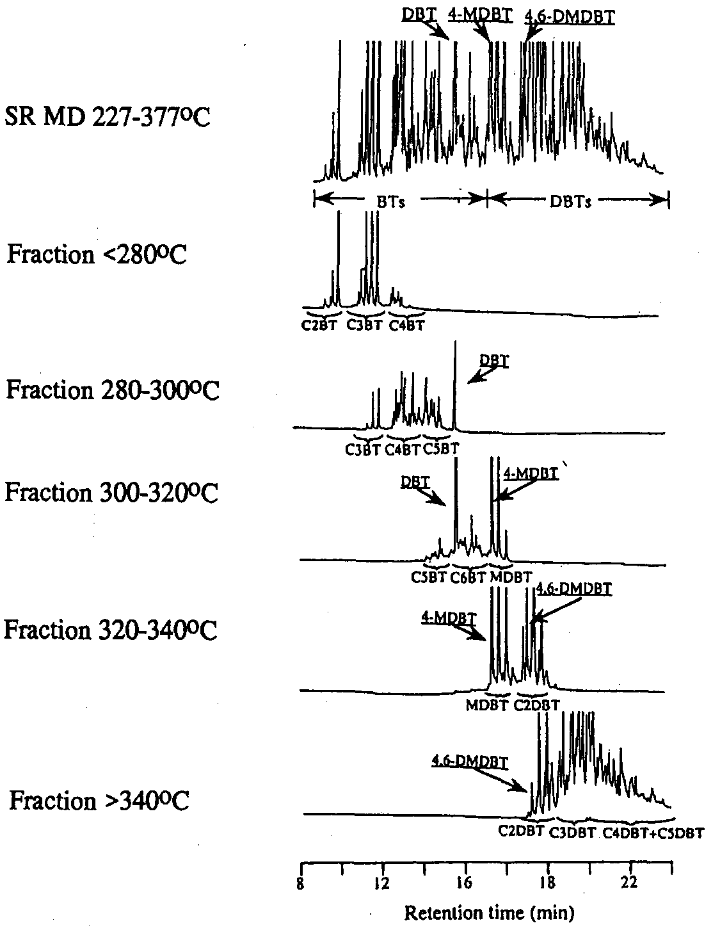


Fig. 4. GC-FPD charts of PASC in SR-MD of Arabian light crude and its narrow fractions (adapted from Ref. [13]).

that varied in the ranges 0–4 and 0–2, respectively [20]. For heavier LCO-MD, x=0–5, y=0–4, and the relative amounts of BTs and DBTs with x,y=0–2 were much higher than those for SR-MD [11]. In narrow MD fractions, the PASC are distributed in accordance with their boiling points (Fig. 4) [11,13]: C_x-BTs are concentrated mainly in fractions boiling out at $\leq$300°C and C_y-DBTs at 300–400°C, while fractions boiling out at 300–320°C contain DBTs together with C_5- and C_6-BTs.

2.2. *Relative HDS reactivities of sulfur compounds and reaction networks*

As was mentioned above, the AASC do not cause problems in industrial desulfurization of MD, as a result of their high reactivities. Therefore, in the past decade, great attention has been paid to a comparison of the reactivity and desulfurization mechanisms of sulfur compounds belonging to the PASC group. The HDS rates of individual PASC measured with a particular catalyst (usually Co–Mo–Al or Ni–Mo–Al) depend on the operating conditions: temperature, pressure, hydrogen sulfide and hydrogen concentrations, nature of the solvent, and presence of other sulfur or nitrogen compounds [2,10]. The following approaches have been attempted to uncover the relative reactivities of the PASC present in the MD:

- kinetic measurements of HDS of individual PASC in clean solvents;
- kinetic measurements of HDS of individual PASC mixed with other sulfur- and nitrogen-containing

compounds in clean solvents used to model HDS of real MD;

- kinetic measurements of HDS of individual PASC in real MD; and
- identification of the PASC remaining in real MD after desulfurization at different degrees of HDS.

Collection of data on the relative reactivities of individual PASC in clean solvents is limited by difficulties in the synthesis and separation of alkylated BTs and DBTs and it accounts for the lack of complete identification of this group of compounds in real MD. So far, only compounds with methyl substituents have been synthesized. The available data are summarized in Table 2. Because a variety of catalysts, solvents, and conditions have been used by different workers, direct comparison of the numbers is not possible. Data have, therefore, been compared by normalizing the reaction rates, the rate constants, or the fractional conversions measured in each investigation by assigning the number 100 for the most-reactive PASC and calculating the relative reactivities as follows: $R_{\mathrm{rel}} = (R_i/R_{\max}) \times 100$. There is a contradiction between the relative HDS reactivities of BTs and DBTs reported in Refs. [21,27,53] and those given in Refs. [28,54,55]: the former three publications reported equal reactivity for these compounds, while the latter three found the reactivity of DBT to be 3–10 times lower. This contradiction could be the result of different testing conditions, especially the hydrogen pressure, as proposed by Vrinat [35].

Introduction of methyl substituents to both BT and DBT reduced their HDS reactivity (excepting 2,8-diMe-DBT [27]), and this reactivity-depression effect depended strongly on the amounts and positions of the substituents. At atmospheric pressure, monosubstituted BTs showed equal reactivities (about 70% of that of nonsubstituted BT), while introduction of a second methyl group (3,7-diMe-BT) yielded a further decrease in the HDS reactivity to 24% of that of BT [27]. At 50 atm, there was a substantial difference in the reactivities of 2- and 3-Me-BT, but 2,3-diMe-BT was less reactive [52], in agreement with the results reported in Ref. [59]. Introduction of methyl groups to DBT in the 4-position, especially in the 4,6-positions, reduced its HDS reactivity to 7–32% of that of the DBT, the 4,6-compound being 30–80% less reactive than 4-Me-DBT. Introduction of two methyl groups in other positions in the DBT molecule (2,8- or 3,7-) had less impact on the reactivity (Table 2). Thus, it may be concluded that the position of the alkyl substituent has a greater impact on HDS reactivity than the number of substituents.

The effect of competitive HDS for different PASC dissolved in clean solvents has been studied by addition of BT or DBT as a second sulfur compound to a methylated BT or DBT at the same concentration [27,31]. Addition of the second sulfur compound did not change the relative reactivities of the PASC, but the absolute HDS rates of both sulfur compounds in mixed feedstocks were substantially reduced compared to individual PASC (by 1.2–2.9 times depending on their nature).

The relative desulfurization rates of individual PASC in real MD were reported by Ma et al. [18] and Frye and Mosby [20]. The relative HDS rates of two trimethyl-BTs boiling out at different temperatures and of DBT in light LCO-MD with Co–Mo–Al as the catalyst at 288°C and 15 atm pressure ranged from 100 (for triMe-BT-1) through 87 (for triMe-BT-2) to 33 (for DBT) [20]. In this case, triMe-BT-1, which boiled out at a lower temperature than did triMe-BT-2, showed a lower reactivity. Measurements of the pseudo-first-order rate constants of 55 PASC for the HDS of SR-MD at 360°C and 29 atm pressure with Co–Mo–Al as the catalyst enabled Ma et al. [18] to divide the PASC into four classes according to their HDS reactivities (Table 3). Taking into account the reactivities measured for the well-characterized individual PASC, 4-Me-DBT and 4,6-diMe-DBT, in clean solvents and the fact that they fall into different reactivity classes, they proposed that (i) class II includes homologs of DBTs not having substituents in the 4- and 6- positions, (ii) class III comprises alkyl-DBTs with one of the alkyl groups at either the 4- or the 6-position, and (iii) class IV contains alkyl-DBTs with two of the alkyl groups at the 4- and 6-positions close to the sulfur atom. Analogously, they supposed that in the Me-BT molecules falling into the second reactivity class, the methyl groups are located in the 2- or 7-position close to the sulfur atom. The available data do not give indications of the effect of the alkyl chain length on the HDS reactivity of the PASC. It may be supposed that the chain length is not a significant factor, since BT and DBT homologs contain-

Table 2
Comparison of HDS reactivities of individual PASC in clean solvents

Reference	[27]	[59]	[52]	[30]	[31]	[32]	[33]	[33]	[34]	[34]
Catalyst	Co–Mo–Al	Co–Mo–Al	Co–Mo–Al	Co–Mo–Al	Co–Mo–Al	Co–Mo–Al	Co–Mo–Al	Ni–Mo–Al	Co–Mo–Al	Ni–Mo–Al
Solvent	n-C_7+n-C_{12}	—	n-C_{12}	n-C_{16}	n-C_{16}	decalin	n-C_{12}		n-C_{10}+n-C_{18}+tetralin	
Testing conditions:										
Temperature, °C	450	—	250	300	300	280	290	290	360	360
Pressure, atm	1	—	50	104	102	—	50	50	54	54
PASC type:										
BT	58	100	100	—	—	—	—	—	—	—
2-methyl-benzothiophene	42	66	37	—	—	—	—	—	—	—
3-methyl-dibenzothiophene	39	33	18	—	—	—	—	—	—	—
7-methyl-benzothiophene	42	60	—	—	—	—	—	—	—	—
2,3-dimethyl-benzothiophene	—	16	11	—	—	—	—	—	—	—
3,7-dimethyl-benzothiophene	14	25	—	—	—	—	—	—	—	—
2,7-dimethyl-benzothiophene	—	45	—	—	—	-	—	-	—	—
2,3,7-trimethyl-benzothiophene	—	17	—	—	—	-	—	—	—	—
DBT	50	—	—	100	100	100	100	100	100	100
4-methyl-dibenzothiophene	19	—	—	21	9	32	21	20	—	—
4,6-dimethyl-dibenzothiophene	9	—	—	—	7	8	—	—	23	26
2,8-dimethyl-dibenzothiophene	100	—	—	—	94	—	—	—	—	—
3,7-dimethyl-dibenzothiophene	14	—	—	—	49	—	—	—	—	—

Table 3
Distribution of PASC in SR-MD according to relative HDS reactivity [18]

PASC reactivity class	PASC chemical type	Relative HDS reactivity (a.u.)
I	29 C_1-C_6-BT	>100
II	C_3-BT, C_4-BT and C_7-BT with nonidentified distribution of alkyl C atoms, DBT and 2 C_1-DBT with nonidentified position of CH_3	34–100
III	4-Me-DBT, 4 C_2-DMDBT, 3 C_3-DBT and 2 C_4-DBT with nonidentified distribution of alkyl C atoms	13–34
IV	4,6-diMe-DBT, 3 C_3-DBT and 1 C_5-BT with nonidentified distribution of alkyl C atoms	5–13

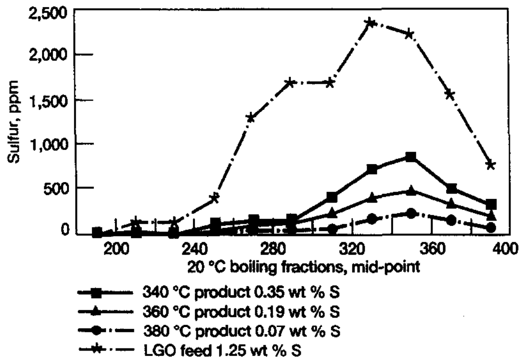


Fig. 5. Sulfur distribution in SR-MD feed and hydrotreated products (reproduced with permission from Ref. [11]. Copyright 1992 by Gulf Publishing Co., all rights reserved).

ing alkyl groups with 1 to 7 carbon atoms fall into the same reactivity classes (Table 3).

Results for the identification the PASC that remained unconverted after different degrees of HDS of real MD [11–13,19,22,23] are in good agreement with their relative HDS reactivities. When the degree of HDS of MD reached ≥70%, the sulfur distribution in the desulfurized feed changed drastically (Fig. 5) so that the residual sulfur was distributed mainly in the boiling range 300–370°C, which corresponds to the boiling points of alkylated DBTs. Desulfurization of narrow fractions of SR-MD with an Ni–Mo–Al catalyst at 360°C and 29 atm showed that C_2- to C_5-BTs present in fractions boiling out at 227–300°C were completely removed (corresponding to about 100% HDS of those fractions), while DBT and its alkylated homologs in fractions boiling out at 300–377°C were only partially converted [13]. Identification of the residual PASC in SR-MD containing 1.46 wt% S after HDS with Co–Mo–Al at 350–390°C, 30 atm, and an LHSV of 4.0 h^{-1} showed that all the BTs and DBTs were completely removed at 350°C, which corresponds to 83.5% HDS [19,22]. A further increase in temperature yielded a gradual decrease in the concentrations of alkylated DBTs, and the product with ≤0.05 wt% S contained mainly 4-Me- and 4,6-diMe-DBTs. Similar results were obtained by other workers [11,12,23].

It is apparent that normal desulfurization processes are highly effective in removing from MD the AASC and PASC belonging to the first two classes of HDS reactivity, which include alkylated DBTs without substituents in the 4- or 6- position [18]. In the transition from normal to deep HDS of MD, the required technical efficiency may be maintained by the introduction of new catalysts and new reactor designs aimed at increasing the process efficiency by removing the DBTs alkylated in the 4-(6-) or 4,6-positions. Such solutions may be developed on the basis of information about the reaction mechanisms and networks of PASC, especially 4,6-disubstituted DBTs.

The reaction networks for HDS of BT and DBT with classical Co(Ni)–Mo–Al catalysts are shown in Fig. 6 [21,36,51]. Introduction of substituents does not change these networks substantially [23,31,33,36]. For DBTs containing only one substituent in the 4-

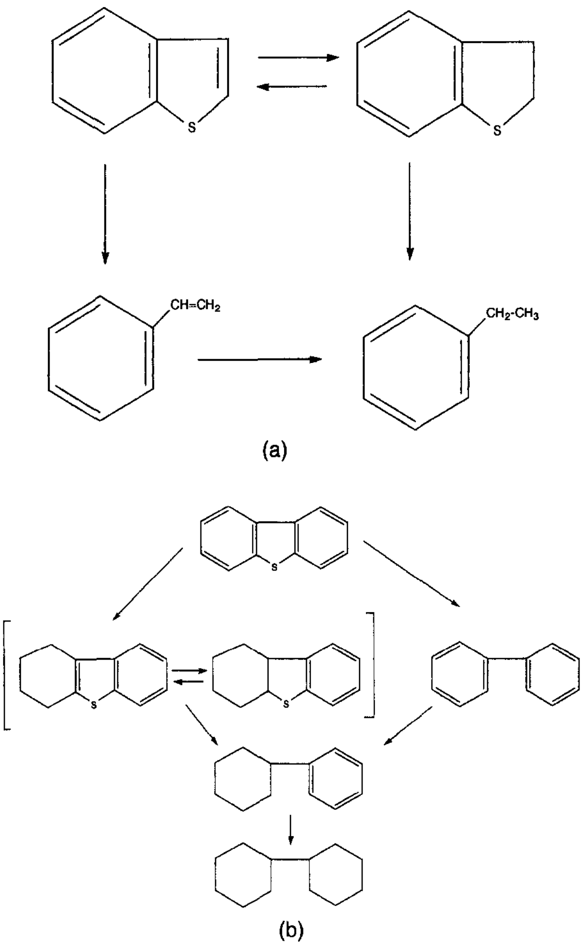


Fig. 6. Reaction networks for HDS of (a) BT and (b) DBT, with the Co–Mo–Al catalyst.

or 6-position, the reaction network is slightly modified, i.e., partially hydrogenated intermediates are formed via saturation of the aromatic ring, which may or may not contain an alkyl substituent (Fig. 7) [37]. In general, DBTs are converted via two main routes: direct elimination of sulfur to form the corresponding biphenyl (BPH), and elimination of the sulfur atom after saturation of one of the aromatic rings to form the corresponding cyclohexylbenzene (CHB). Other conversion routes for DBTs – including demethylation, isomerization (changing the position of the alkyl substituents), transalkylation and cracking of the thiophenic ring – are possible with special catalysts containing acidic zeolites [34,38].

The substituents affect the HDS of DBTs in two ways: they reduce their HDS reactivity, and they change the ratios between the rates of the reactions comprising the reaction network, resulting in quantitative redistribution of the products. The available data on the effects of alkyl substituents on the HDS reactivity of DBTs are summarized above. The main change in the distribution of the products is a substantial increase in the ratio between CHBs and BPHs as a result of the higher contribution of the 'hydrogenation' route (through saturation of one of the aromatic rings) relative to direct desulfurization of the DBT molecule.

The ratio of CHB to BPH (selectivity parameter α) increases with increasing overall conversion of DBT [39]. Therefore, the effects of substituents on the conversion selectivity of DBTs have to be compared at equal conversions of the corresponding DBTs. The available data are summarized in Table 4. Introduction of methyl substituents in the 4- or 4,6-positions of the DBT molecule substantially increases the relative amount of partially hydrogenated products, which, in turn, decreases the overall DBT desulfurization. This means that the 'hydrogenation' pathway becomes dominant for substituted DBTs, while desulfurization of nonsubstituted DBT at normal HDS conditions proceeds mostly directly. Decreasing the HDS reactivity of DBTs by introducing alkyl groups in the 4,6-positions leads to depression of the direct desulfurization route, while the 'hydrogenation' route remains almost unaffected. The methyl groups increase the activation energy of the direct desulfurization of DBTs by a factor of 1.3–1.7, but the activation energy of desulfurization of DBTs by the 'hydrogenation' route

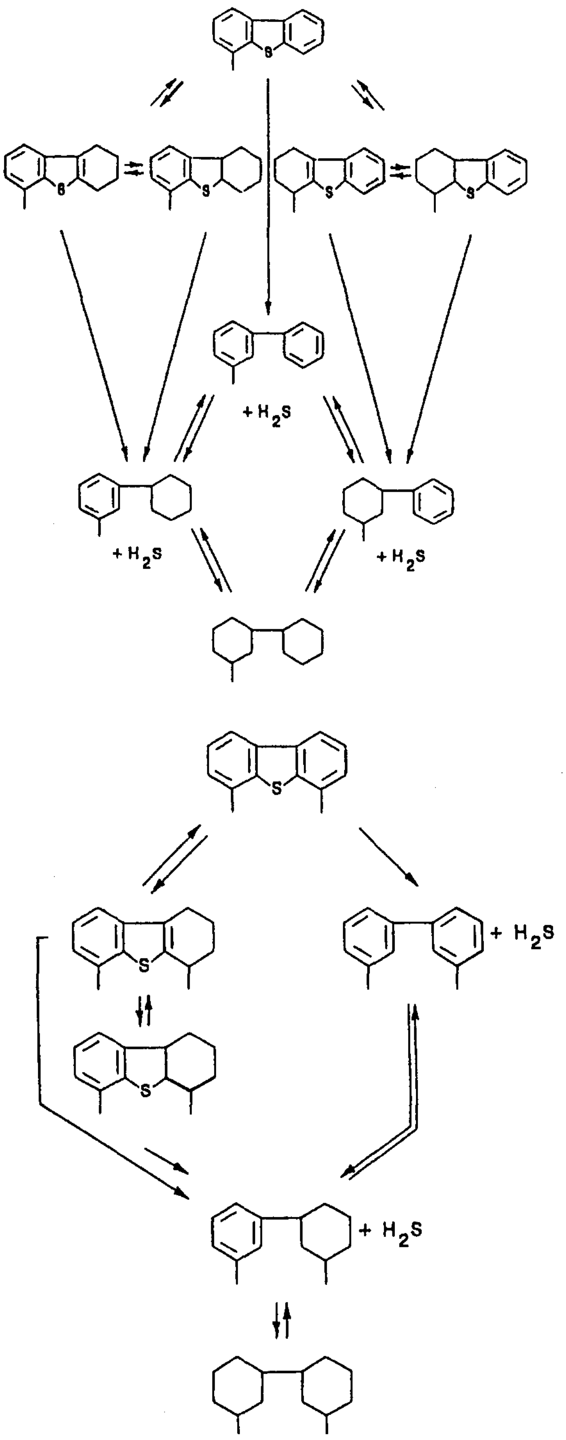


Fig. 7. Reaction networks for HDS of alkyl-substituted DBTs (adapted from Ref. [37]).

Table 4
Effect of alkyl substituents on the HDS selectivity of DBTs (α=CHB/BPH) at equal conversions of the corresponding DBTs

Reference	[32]	[33]	[34]	[34]	[23]	[23]	[40]
Catalyst	Co–Mo–Al	Ni–Mo–Al	Co–Mo–Al	Ni–Mo–Al	Co–Mo–Al	Ni–Mo–Al	Ni–Mo–Al
PASC conversion(%)	20	20	57	78	60	60	—
PASC:							
DBT	0.10	0.12	0.10	0.40	—	—	0.06
4-Me-DBT	0.40	0.70	—	—	—	—	1.70
4,6-diMe-DBT 0.54	0.54	—	0.75	1.75	2.2	8.4	7.33

remains almost unchanged [32]. The second factor increasing the contribution of the ‘hydrogenation’ route in the HDS of DBTs with alkyl substituents is the increase in the DBT reactivity as a result of hydrogenation of the aromatic rings [34,36]. The contribution of the ‘hydrogenation’ route in the conversion of DBTs is also a function of the catalyst’s hydrogenation activity. Ni–Mo–Al catalysts display higher activity in the saturation of aromatics than Co–Mo–Al [41] and, thus, show higher values of the selectivity parameter α (Table 4).

The effect of the nature of the substituents on the conversion of DBTs – (i) hindering the overall desulfurization rate, (ii) increasing the hydrogenation rate of aromatic rings, and (iii) changing the preference in the reaction network from direct desulfurization to the ‘hydrogenation’ route – may be explained as follows. It is widely accepted that there are two distinct types of catalytic site at the surface of sulfided Co(Ni)–Mo–Al catalysts: σ-sites for hydrogenolysis of the heteroatom and τ-sites for hydrogenation of the aromatic rings [42,75]. These two types of site can be interchanged under hydrotreating conditions. The hydrogenolysis reactions involve noncoplanar adsorption through the sulfur atom at the σ-sites, while hydrogenation of the aromatic ring proceeds via flat η^5 or η^6 bonded adsorption through the π-electrons of the aromatic rings at the τ-sites [32,36,43,44]. For model sulfur-, nitrogen- and oxygen-containing aromatic molecules, it was shown that hydrogenation is favored by strongly electron-donating substituents, and hydrogenolysis by weakly electron-donating or electron-withdrawing substituents [45–47]. Being strong electron donors, the methyl substituents should promote flat adsorption of the DBT molecule at the τ-sites, thus increasing the hydrogenation reactivity and reducing the HDS reactivity. According to Kabe et al. [32], under HDS conditions, the heat of adsorption at the surface of the sulfided Co–Mo–Al catalyst increased from 12 kcal mol^{-1} for DBT to 20 kcal mol^{-1} for 4-Me-DBT and 21 kcal mol^{-1} for 4,6-diMe-DBT. Improved adsorption of DBT at the surface of the sulfided Co–Mo–Al catalyst after introduction of methyl substituents also follows from the results of competitive experiments performed by Houalla et al. [31]: addition of DBT only slightly affected the desulfurization of methyl-substituted DBTs, while desulfurization of DBT in presence of methyl-substituted DBTs was substantially depressed. Shifting the adsorption mode of DBT from vertical or tilted at the σ-sites to flat at the τ-sites as a result of the electronic effect of the alkyl substituents could be one of the causes of depression of direct desulfurization and promotion of the ‘hydrogenation’ route.

Another reason for inhibition of the direct desulfurization of DBTs with alkyl substituents in the 4- or/and 6-positions could be the steric hindrance of its adsorption at the σ-sites in the sulfur-bonded mode [23,32–34,36,40]. Simulations of the geometry of such molecules [23,34] showed that the sulfur atom in the DBT molecule is screened by bulky methyl groups in the 4- and 6-positions adjacent to it. If the aromatic ring is hydrogenated and the methyl group is located at an axial position in the cyclohexyl ring (Fig. 8), the steric hindrance of the methyl group to C–S scission becomes small [32]. This assumption also explains the higher efficiency of the ‘hydrogenation’ route for 4- and/or 6-substituted DBTs. As was shown by Houalla et al. [36], hydrogenation of one of the aromatic rings in nonsubstituted DBT increases its desulfurization rate by about four times (the mode of action being an electronic effect). Removal of the source of steric hindrance in substituted DBTs, as a result of their partial hydrogenation, makes the more

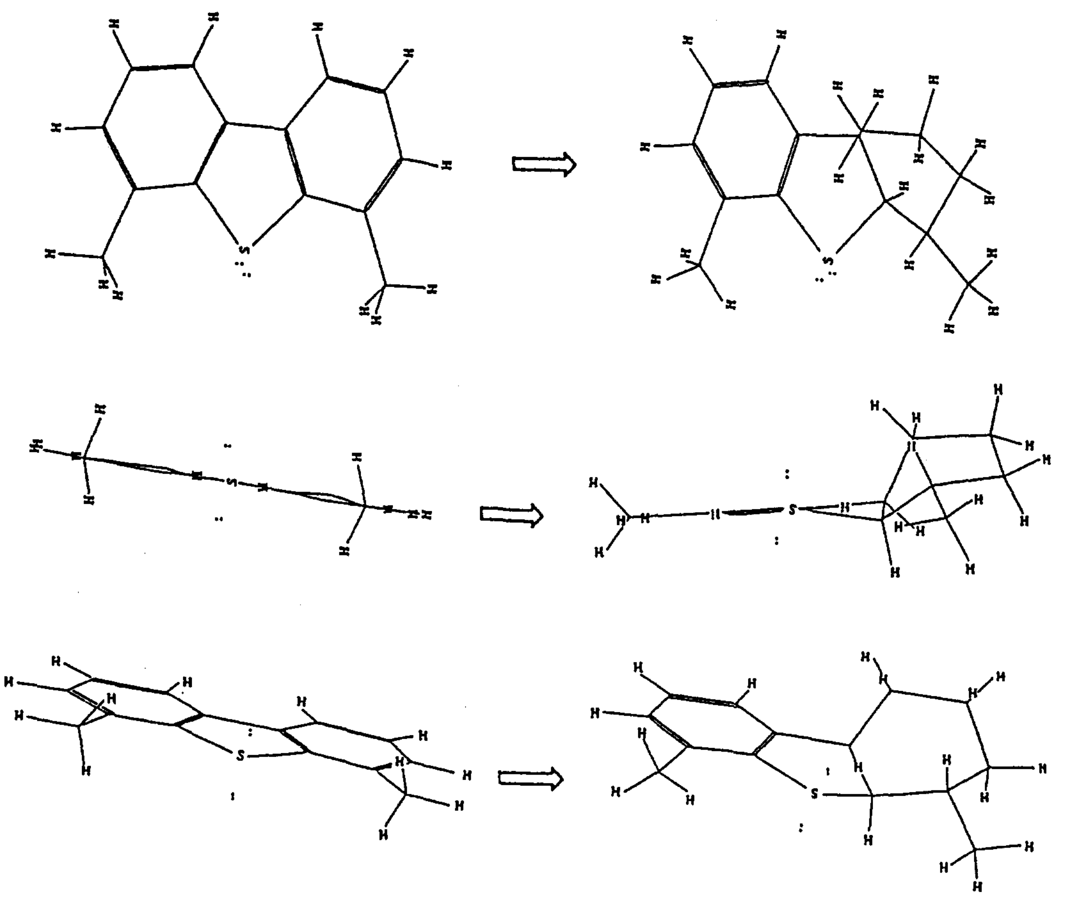


Fig. 8. Computer simulations of 4,6-diMe-DBT molecule structure before and after partial hydrogenation (reproduced with permission from Ref. [34]. Copyright 1996 by Academic Press Inc., all rights reserved).

efficient desulfurization route the predominant reaction pathway.

The relative influence of electronic and steric factors on reactivities of substituted DBTs has not yet been resolved. Based on the model attributing the sulfur withdrawal reactivity to the electron availability in the C–C bond adjacent to the sulfur atom and the literature of steric effects in organic chemistry, Kwart et al. concluded that the reactivity of 4,6-DBT is affected mainly by electronic contribution of substituents together with slight degree of steric hindrance [48]. Quantum chemical calculations of the reactivities of different sulfur compounds, reported recently by Ma et al. [49], showed that hydrogenolysis reactivities are governed mainly by the electron density on the S atom, while the hydrogenation – by the order of bonds which have been hydrogenated. According to Ma et al. [50], introduction of methyl substituents in 4- and 6-positions of DBT molecule only slightly increase the electron density on the S atom (5.758–5.760), while hydrogenation of the benzene ring adjacent to the S atom increases its electron density by about 0.2. These results suppose the main role of steric hindrance in lowering the DBT HDS reactivity by introduction of methyl substituents in 4,6-positions and explain the higher HDS reactivity of partially hydrogenated DBTs.

2.3. *Specific issues related to deep desulfurization of MD*

The information available on the distribution of sulfur compounds in MD, their relative reactivities, and their reaction networks enables us to outline some issues specific to deep desulfurization that have not been considered in the development of catalysts and desulfurizers for normal desulfurization.

2.3.1. *Chemical aspects*

Deep desulfurization is used for removal of the least-reactive sulfur compounds, i.e., alkylated DBTs substituted mainly in the 4- and/or 6-positions. Electronic and steric effects of the substituents on the adsorption equilibrium constants and the rate coefficients have to be taken into account in developing a fundamental understanding of the process. The following assumptions [37] made for the structural contributions of the least-reactive sulfur compounds have to be confirmed and quantified in further investigations:

- in adsorption, electronic and steric effects should be considered separately;
- alkyl groups at a distance from the sulfur atom beyond the α-position exert only electronic effects on the adsorption;
- only the alkyl groups on the aromatic rings exert an electronic influence;
- alkyl groups in the 4- and/or 6-positions sterically hinder the adsorption;
- once a molecule is adsorbed, only the electronic effects of the alkyl groups are of importance; and
- the number of alkyl substituents – and not their position relative to the sulfur atom – has to be taken in account for adsorption at the τ-sites and reaction between adsorbed species.

This list of assumptions should be supplemented by an additional question of particular importance: are partially hydrogenated DBTs subsequently desulfurized at the same sites (apparently after interconversion of τ- to σ-sites) or must the partially hydrogenated DBTs be readsorbed on the σ-sites? Because the 'hydrogenation' route dominates for substituted DBTs, the efficiency of the catalysts should be improved by increasing the surface concentration of the τ-sites. The question remains whether it is sufficient to increase the overall HDS or whether a concomitant increase in the sites responsible for S–C bond scission is required. Another means of improving the catalyst comes from a consideration of the formation of BPH and CHBs from a common intermediate precursor at only one type of catalytic site [24,57].

For a long time, industrial desulfurization catalysts were improved in terms of their ability to split the C–S bonds in sulfur-containing organic compounds. In substituted DBTs, this function is sterically hindered. It is thus important to shift the direction of catalyst development by seeking alternative catalytic routes, including fast intermediate transformation of the molecules to remove the screening effect. In addition to the hydrogenation of the aromatic rings, there could be important positional isomerization of alkyl groups, and dealkylation and transalkylation reactions that require substantial revision of the catalyst composition. Such catalyst modifications have to be undertaken with care in order to maintain the current technical level of the existing catalysts relative to AASC and more reactive PASC.

2.3.2. *Kinetics*

The kinetic data on deep desulfurization are important since they facilitate the following:

- investigation of reaction pathways;
- development of a kinetic model for the process; and
- selection of the best parameters for the purpose of comparison of the activity of different catalysts.

The form of a kinetic equation and the estimated values of its parameters are derived from a model, such as Langmuir–Hinshelwood, which assumes various forms of competitive and noncompetitive adsorption. Kinetic measurements under a wide range of experimental conditions are not currently available for alkyl-substituted DBTs. On the basis of the kinetics for HDS of DBT [35] – measured with Co–Mo–Al catalysts at pressures in the range of 1–80 atm, at which the contribution of the 'hydrogenation' route is negligible – it could be concluded that the Langmuir–Hinshelwood rate expression is consistent with the experimental data:

$$R_{\mathrm{HDSD}} = k\frac{\mathrm{K_{DBT}P_{DBT}}}{(1+\mathrm{K_{DBT}P_{DBT}}+\mathrm{K_{H_2S}P_{H_2S}})^{n}}\cdot\frac{\mathrm{K_{H_2}P_{H_2}}}{1+\mathrm{K_{H_2}P_{H_2}}} \qquad (1)$$

where n=1 or 2.

Kinetic measurements at a high hydrogen pressure of 180 atm, at which the contribution of the 'hydrogenation' conversion route is comparable to that of direct desulfurization, showed that the overall reaction rate should be expressed by using two equations [56]: the first for direct HDS, as given above (R_{HDSD}), and the second for desulfurization through the 'hydrogenation' route:

$$R_{HDSH} = k\frac{P_{DBT}P_{H_2}}{1 + K_{DBT}P_{DBT}} \quad (2)$$

so that the overall desulfurization rate may be expressed as a sum, as follows:

$$R_{HDSO} = \eta_1 R_{HDSD} + \eta_2 R_{HDSH} \quad (3)$$

where the coefficients η_i are the relative weightings given to the two routes ($\eta_1+\eta_2=1$). Since the desulfurization kinetics of individual PASC in different solvents and in real MD may be described by a pseudo-first-order kinetic equation, it has been proposed [37] that the ratios of the pseudo-first-order rate constants measured at standard conditions by variation of the spacing time may be used for calculation of the values of η_i.

For substituted DBTs, the 'hydrogenation' route plays a more significant role than direct desulfurization, even at low pressures, and other conversion routes that remove the steric hindrance of the alkyl substituents, such as dealkylation or isomerization, could thus become important with modified catalysts. Therefore, mechanistic kinetic studies must take into account all the possible conversion routes, expressing the overall HDS rate as a sum (or some other function) of the conversion rates:

$$R_{HDSO} = F(\eta_i, R_{HDSi}) \quad (4)$$

It must also look separately for the form of the kinetic expressions describing R_{HDSi} by every catalytic route. Otherwise, the calculated adsorption coefficients, heats of adsorption, and reaction orders, being sensitive to the form of kinetic equation, will not reflect the real reaction mechanism(s). The failure to undertake a comprehensive kinetic study could explain, for example, the contradiction between the calculations of Kabe et al. [32] and those of Lamure-Meille et al. [33] for the relative adsorption strength of DBT and the findings for its methyl-substituted homolog at the surface of a Co–Mo–Al catalyst. According to Kabe et al. [32], introduction of a methyl group into the 4-position of DBT molecule increases its adsorption strength at 563 K by about 20 times, but the adsorption equilibrium constants calculated by Lamure-Meille et al. [33] for the same two molecules at the same conditions were equal. Kabe et al. [32] used the classic Langmuir–Hinshelwood rate equation such as Eq. (1), without taking into account the 'hydrogenation' component (Eq. (2)) in Eq. (3), while the calculations of Lamure-Meille et al. [33] were based on a consideration of both reaction routes proceeding through a common intermediate precursor.

The development of a mechanistic kinetic model for HDS of MD must take into account the desulfurization kinetics of all the sulfur compounds present in the feedstock. The existing models used for the design of normal desulfurizers (up to 0.1 wt% of residual sulfur) do not take into consideration the kinetics of alkyl-substituted DBTs. Shifting to deep HDS requires the introduction of this kinetic information which is, unfortunately, not yet available. Estimations made by Froment et al. [37] for the PASC showed that mono-, di- and tri-methyl-DBTs alone account for 84 compounds that are transformed in accordance with the reaction networks shown in Fig. 7; the number of kinetic parameters that have to be determined and integrated into the model reaches 1133, a number that is clearly unrealistic.

Therefore, for deep desulfurization the common practice of using empirical power-rate laws with adjustable parameters [3,35] will be continued. As mentioned already, the HDS kinetics of all the individual PASC in pure solvents and real MD are well described by the pseudo-first-order equation [18,31,58]:

$$\ln(C_0/C_t) = kt \quad (5)$$

where C_0 and C_t are the sulfur concentrations of the PASC at initial time and reaction time t, respectively, and k is the rate constant.

The empirical description of the desulfurization kinetic of real MD considers the feedstock as a mixture of sulfur compounds reacting at different rates that are proportional to their concentrations; in this case, the overall HDS rate could be expressed as a sum of HDS rates of the fractions of sulfur compounds with equal reactivity [1]:

$$W_{HDSO} = \Sigma\alpha_i k_i C_{si} \quad (6)$$

where α is the share of sulfur compounds with reactivity i in the overall sulfur concentration and k_i is the rate constant; the partial pressures of H_2 and H_2S are constant. This superposition of pseudo-first-order equations yields a kinetic curve shape equivalent to the formal kinetics of a noninteger order n:

$$dC_s/d\tau = -kC_s^n \tag{7}$$

where C_s is sulfur concentration or in integral form:

$$Y^{1-n} = 1 - (1-n)k_0\tau \tag{8}$$

where $Y = C_t/C_0$, $k_0 = kC_0^{n-1}$ and n is a function of α_i and k_i in Eq. (6).

For normal desulfurization of MD up to 0.1 wt% of residual sulfur, the value of n lies in the range 1.5–2.0, depending on the origin of the MD [35,60]. It has also been shown that normal desulfurization kinetics of SR-MD could be described as a sum of HDS rates of three groups of sulfur compounds with different reactivities expressed according to Eq. (7) with n=1, 1.5 or 2.0, taking into account their share of the total sulfur concentration [17].

For deep HDS of MD, the sulfur compounds with reactivity lower by about two orders of magnitude than in normal HDS are involved. The approximation described above could become invalid at the highest fractional removals of sulfur so that the actual Y values will be less than those predicted by extrapolation of the curve given by a second-order kinetic equation (Eq. (8)). Fig. 9 illustrates the sensitivity of the formal reaction order n to the differences in reactivity of sulfur compounds (k_i=0.1–10), their shares in the total sulfur concentration (α=0.05–0.34), and the number of groups of sulfur compounds with different reactivities (Eq. (3) or Eq. (5)) involved in a computer simulation of HDS kinetics of MD according to Eqs. (6)–(8). Involving the less-reactive sulfur compounds (k=0.5 and 0.1), in addition to the highly reactive ones (k=1–10) in the calculations, increased the pseudo-reaction order from 1.77 to 2.25 or 3.0, depending on the shares of the different reactivity groups.

Calculation of the pseudo-reaction order according to Eq. (8) using the experimental data for SR-MD HDS with Co–Mo–Al as the catalyst [29] at 98–99.8% HDS (S_0 = 1.33 wt%) showed (Fig. 10) that the kinetics are described by a power law with a non-integer order 1.7. The second-stage desulfurization data for the same feedstock at the same conditions (S_0 = 0.113 wt%) [29] could be approximated by the pseudo-first-order equation (Fig. 10). In this case,

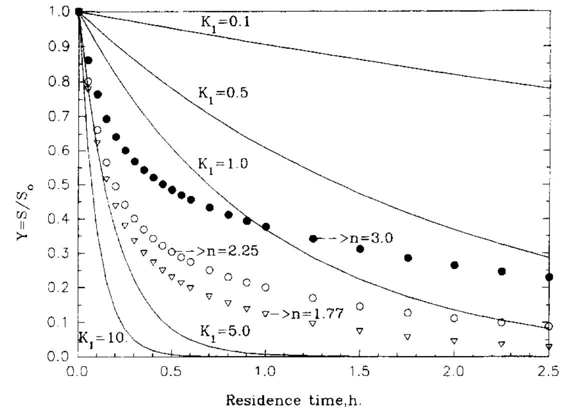


Fig. 9. Computer simulations of desulfurization kinetics for hypothetical MD: • – total HDS kinetics for a mixture of equal shares of all the S-compounds (K_1=0.1, 0.5, 1.0, 5.0 and 10.0); ○ – total HDS kinetics for a mixture of all the S-compounds with shares: 0.05 (K_1=0.1), 0.1 (K_1=0.5), 0.25 (K_1=1.0), 0.3 (K_1=5.0) and 0.3 (K_1=10.0); ▽ – HDS kinetics for a mixture of the most reactive S-compounds with shares: 0.33 (K_1=1.0), 0.33 (K_1=5.0) and 0.34 (K_1=10.0); and — – pseudo-first-order kinetics for HDS of S-compounds with different reactivities.

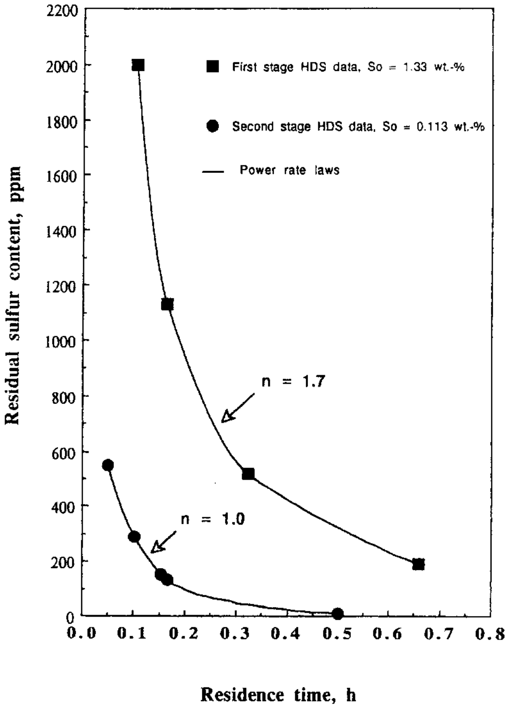


Fig. 10. Power-rate laws describing the deep HDS kinetics of SR-MD according to the fractional sulfur conversion measured with Co–Mo–Al catalyst at 360°C and 54 atm [29].

only the least-reactive PASC with nearly equal reactivities remained after the first HDS stage and the empirical HDS kinetics were close to those observed with individual sulfur compounds.

2.3.3. Catalysts

For many years, the best MD-HDS catalysts were Co–Mo–Al compositions with different modifications [1–3,62]. In deep HDS of MD, the involvement of the least-reactive PASC may change preferences in the selection of the catalysts. Ni–Mo–Al catalysts were found to be more effective in the second-stage HDS of SR-MD, where the residual sulfur is found mostly in substituted DBTs [18,23,63], in desulfurization of narrow fractions of SR-MD boiling out at 300–377°C and containing the same PASC [3], and in HDS of individual DBTs methylated in 4- and 6-positions [33,40]. Introduction of zeolite HY into the Co–Mo–Al composition increased the HDS rate of 4,6-diMe-DBT by about three times [34]. These changes could be explained in terms of the specificity of the HDS reaction networks for the least-reactive PASC: the higher hydrogenation activity of the Ni–Mo–Al catalysts facilitates conversion of the least-reactive PASC via a 'hydrogenation' route that is not sterically hindered, while demethylation on the acidic zeolite removes the methyl substituents hindering the direct sulfur withdrawal from the DBT molecules. The other technical requirements for deep desulfurization catalysts, like pore-size distribution, pellet size and shape, should remain the same as those for the normal process.

2.4. Potential scientific and technological solutions to the deep HDS problem

The transition from normal to deep desulfurization of MD in diesel production may be achieved in one of the following two ways: (1) by changing the process technology (selection of the proper feedstocks, increasing the severity of the process, decreasing the concentration of hydrogen sulfide in reactor, staging, continuous catalyst regeneration, etc.) so as to accelerate sulfur removal with existing commercial catalysts, or (2) by introduction of new, more effective catalysts that enable to reach low sulfur levels without changing the hydrotreating mode. In the second case, it is important to consider the potential ways of increasing the HDS activity of traditional Co–Mo–Al catalysts and of using catalysts active in the alternative catalytic routes to remove the least-reactive PASC.

2.4.1. Selection of feedstock

A simple solution to the production of diesel fuels with <0.05 wt% sulfur without any change in normal desulfurizers is selection of a feedstock with a low content of PASC having low reactivities. Since these compounds are concentrated in the 300°C+ fractions of MD [11,13] and the residual sulfur retained after normal desulfurization is to be found in fractions boiling out at 320–370°C [11–13,23,64], exclusion of those fractions from the feedstocks at the distillation stage solves the deep HDS problem. Decreasing the final boiling point of SR-MD from >400°C to 351°C facilitates an increase in the LHSV required for reaching the target sulfur content of 0.05 wt% in a standard desulfurizer by about five times or a decrease in the required temperature at the same LHSV by about 70°C [14]. The data obtained from the pilot plant of Ben-Gurion University (BGU) showed that the reducing the final boiling point of the same SR-MD in the range 403–380°C by distillation had a minimal impact on the residual sulfur content, while further decreasing the final boiling point to 320°C by distillation facilitated a reduction of the residual sulfur content from 0.04 to 0.004 wt%, under the same conditions (Table 5).

Increasing the %HDS of the feedstock by lowering the initial sulfur concentration may be achieved by facilitating removal of S from sulfur-containing compounds remaining in the low-boiling fractions.

Use of light gas oils for diesel production facilitated the production of the environmental classes of diesel

Table 5
Effect of the final boiling point of SR-MD on residual sulfur content [29]

Final BP of MD (°C)	Feedstock S content (wt%)	Residual S content (wt%)	%HDS
403	1.37	0.05	96.3
380	1.33	0.04	96.9
320	0.65	0.004	99.3

Hydrotreating conditions: commercial Co–Mo–Al catalyst, P=54 atm, T=360°C, LHSV=2.5 h^{-1}, V_{H_2} =500 Nl l^{-1}.

Table 6
Effect of LCO addition on HAGO HDS with commercial Co–Mo–Al catalysts [29]

Volume%	Sulfur content		Cetane index		Density at 15°C (g cm^{-3})	
LCO	Starting mixture (wt%)	After HDS (ppm)	Starting mixture	After HDS	Starting mixture	After HDS
0	0.520	10	52.0	56.5	0.8492	0.8365
10	0.632	110	47.5	51.5	0.8602	0.8472
15	0.684	110	46.5	50.5	0.8642	0.8502
20	0.741	80	45.5	49.0	0.8700	0.8548
25	0.792	140	44.5	47.5	0.8755	0.8583
30	0.843	180	43.5	46.0	0.8803	0.8620

Conditions: P=800 psi, LHSV=2.5 h^{-1}, T=360°C,V_{H_2}=500 Nl l^{-1}.

fuels commercialized in Sweden in 1992: class I, S≤10 ppm, 95% with BP ≤285°C; and class II, S≤50 ppm, 95% with BP ≤295°C [14,65]. This solution limits the overall diesel-production capacity of the oil refineries and forces them to select the heavier MD like North Sea gas oils with sulfur contents of ≤0.5 wt%.

The problem may be partially solved by mixing low-sulfur SR-MD with LCOs. The PASC present in LCOs are substantially dealkylated compared to those in SR feedstocks [11,20], which increase the HDS reactivity. On the other hand, LCOs do not contain highly reactive AASC, making their overall HDS reactivity lower than that of SR-MD [14]. The data obtained in the BGU pilot plant (Table 6) showed that addition of up to 30 vol% LCO to SR-MD only slightly decreased the percentage HDS from 99.8 to 97.8, while the initial sulfur content became 1.6 times higher. The addition of LCO is limited to 30 vol% because of the resultant reduction in the cetane index to 46 – the minimal value according to diesel specifications [14,65] – and the increase in the product's density.

2.4.2. *Process severity and mode*

Numerous papers [14,61,64–69] published recently on the conventional approach to upgrading the MD using the single-stage technology showed that low sulfur specifications could be met by using conventional hydrotreating catalysts at more extreme conditions than those of normal desulfurization. The three main operational parameters of commercial desulfurizers have an impact on the residual sulfur content: temperature, LHSV and hydrogen pressure.

Changing the target residual sulfur in SR-MD from 0.1–0.3 to <0.05 wt% requires an increase in the SOR reaction temperature by 30–50°C (Table 7). Using this parameter for adjusting the required low sulfur level causes two problems: it shortens the catalyst's lifetime and it causes color degradation of the products [14,64]. Consequently, a severe temperature limitation has to be imposed, especially for heavier MD at catalyst end-of-the-run conditions.

Increasing the space time by increasing the reactor volume (corresponding to lower LHSV) eliminates these problems: this is the best solution to provide good flexibility for feedstock and product qualities, but requires additional capital investment. Reducing

Table 7
Temperature increase required for shifting from normal to deep desulfurization with commercial catalysts

Catalyst	Feed type	Operating conditions		Sulfur content (wt%)		ΔT (°C)	Reference
		LHSV (h^{-1})	P_{H2} (atm)	After normal HDS	After deep HDS		
—	SR-MD	—	—	0.3	0.05	40	[14]
Co–Mo–Al	SR-MD	2.6	54	0.126	0.03	38	[61]
Co–Mo–Al	SR-MD	4.0	30	0.17	0.04	30	[19]
—	—	3–6	40	0.1–0.3	<0.05	40	[64]
Ni–Mo–Al	LCO	2.0	69	0.12	0.06	50	[68]

the residual sulfur in SR-MD at the same temperature and pressure from 0.1–0.3 wt% to <0.05 wt% requires a decrease in the LHSV by about 3–4 times for feedstocks with an initial sulfur content of $\geq$1.2 wt% [14,61,65,69], in keeping with the power-law kinetic equations (Eqs. (7) and (8)) with n>1.5.

Generally, for low-sulfur and light feedstocks treated in an existing HDS unit designed to provide a sulfur content of 0.1 wt% in the end products, reduction of the outlet sulfur concentration to <0.05 wt% can be achieved by a moderate temperature increase. Switching to heavier feedstocks requires a combination of an increase in the temperature and a decrease in the LHSV [14,61,65]. For example, reducing the outlet sulfur concentration from 0.1 to 0.03 wt% in HDS of SR-MD with an initial sulfur content of 1.2 wt% using a commercial Co–Mo–Al catalyst could be achieved by increasing the temperature by 25°C and decreasing the LHSV by a factor of 2 [61].

Hydrogen pressure has a much smaller impact on the efficiency of the HDS process. Increasing the pressure by up to 80–100 atm yielded a moderate decrease of 0.02–0.06 wt% in the outlet sulfur concentration [61,65,68], which leveled-off on increasing the pressure to 170 atm. Thus, the impact of hydrogen pressure on HDS efficiency is not sufficient to shift the desulfurization mode from normal to deep, even at high pressures close to 150 atm.

Increasing the hydrogen pressure facilitates hydrogenation of the aromatic rings of the DBT molecule. Kinetic measurements obtained with the Co–Mo–Al catalyst at 26–31 atm indicated that partially hydrogenated tetra- and hexahydro-BTs were not formed [39,57]. At 50–102 atm, these partially hydrogenated compounds were detected in small amounts, <10% of the overall DBT conversion, especially at high hydrogen sulfide concentrations in the feed, which inhibited the direct desulfurization route [33,36]. Increasing the pressure to 180 atm in the presence of the Co–Mo–Al catalyst yielded a substantial increase in the concentrations of partially hydrogenated DBTs, corresponding to >30% of the overall DBT conversion [56]. Because the HDS reactivity of individual partially hydrogenated DBTs with Co–Mo–Al catalysts is much higher than that of DBT [36,83], the desulfurization stage in the 'hydrogenation' route becomes limited at high pressures by the catalyst's HDS activity. The explanation of this effect comes from kinetic data available for DBT. According to Eq. (1), the direct desulfurization route loses its sensitivity to hydrogen pressure at relatively high P_{H_2} values, and the input of the second 'hydrogenation' route, which is sensitive to the hydrogen pressure in terms of Eq. (2), is low with the Co–Mo–Al catalyst. For hindered alkyl-substituted DBTs, the 'hydrogenation' route, which is sensitive to hydrogen pressure (Eq. (2)), predominates [32], and the impact of P_{H2} on the HDS rate should be much higher than that measured in the experiments. One of the possible explanations for this contradiction could be over-reduction of the active 'Co–Mo–S' phase at the catalyst's surface at high hydrogen pressures, leading to a change in the sulfidation state and reducing the concentration of the σ-active sites responsible for direct desulfurization [75,76]. This, in turn, could explain the low impact of hydrogen pressure on desulfurization efficiency in deep HDS of MD.

The changes in the HDS process mode, that could facilitate the transition from normal to deep desulfurization of MD, include technical solutions facilitating a reduction in the hydrogen sulfide concentration in the reactor [18,61,63,70–73] and sulfur adsorption by the catalyst, in addition to catalytic HDS [74].

It is well known that hydrogen sulfide has a reversible inhibitory effect on HDS reactions, so that the HDS rate decreases by 5–15% for each mole (or volume) percentage of hydrogen sulfide in the reaction mixture, depending on the type of feedstock and the operating conditions [1,3]. Increasing sulfur removal in deep HDS of MD increases the hydrogen sulfide concentration, especially in the lower catalyst layers that come in contact with the least-reactive PASC. HDS with the Co–Mo–Al catalyst of DBTs alkylated in the 4- and 6-positions is very sensitive to hydrogen sulfide. Increasing the hydrogen sulfide concentration at the beginning of the run from 0 to 1.45 atm reduced the conversion of 4,6-diMe-DBT in decalin at 360°C from 64 to 45% [18]. Introducing fresh hydrogen in a batch reactor after a 30 min-run increased the reduction of 4-Me-DBT and 4,6-diMe-DBT from the SR-MD in the subsequent 20 min by about 2.5 and 4.5 times, respectively, compared to the same period in a straight run [18]. For SR-MD, dividing HDS with the Co–Mo–Al catalyst at 320°C and 50 atm in a batch reactor into two stages, with intermediate hydrogen renewal, facilitated a reduction of the residual sulfur

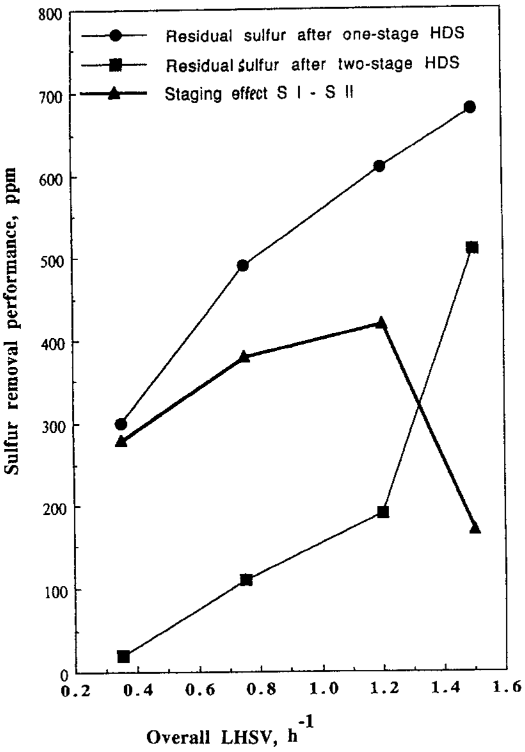


Fig. 11. Effect of staging on sulfur removal from SR-MD (1.2 wt% S) with the commercial Co–Mo–Al catalyst at 360°C and 54 atm [29].

content from 0.16 to 0.08 wt% in the same overall reaction time [63].

Technical solutions for reducing the hydrogen sulfide concentration include staging using fresh hydrogen at the second stage [61,63,70,71] and supplying the reactor system with a hot, high-pressure separation pathway through the catalyst system [72,73]. The effect of staging can be illustrated by the data obtained from the BGU pilot plant (Fig. 11). The experiment [29] compared the residual sulfur content in SR-MD after one-stage hydrotreating and two-stage hydrotreating (fresh hydrogen at the second stage), with the LHSV in both the first and the second stage being twice as high as that in the one-stage experiments, so that the overall space-time remained the same. The staging effect (ΔS) depends on the overall LHSV influencing the hydrogen sulfide concentration at the second stage as a result of different sulfur conversions at the first stage. It is clear that dividing the catalyst into two reactors with intermediate separation of hydrogen sulfide from the effluent gas allows to solve the deep HDS problem with minor adjustments in the temperature and overall LHSV. In this case, using a combination of the Co–Mo and the Ni–Mo catalysts in the first and second stages facilitates further improvements in the process [63,70,71], because the Ni–Mo–Al catalyst is superior to Co–Mo–Al in the removal of methyl-substituted DBTs as a result of its higher hydrogenation activity [18,23,33]. Use of the Ni–Mo–Al catalyst in the second stage also improves the color stability of diesel fuel [63,70,71].

Modeling the effects of variables in deep desulfurization of SR-MD by artificial neural network techniques [61] allowed to calculate the causal indexes for every variable that gave a clear picture of their relative significance. The positive value of causal index means that an increasing value of this variable increases the outlet sulfur concentration and vice versa. The relative significance of process variables diminishes in the following sequence:

LHSV (14.6) > Temperature (7.44) > Recycling (−6.39) > Inlet sulfur concentration (5.83) $\gg$ Hydrogen pressure (−0.78)

Loading the second-stage reactor with a partially sulfided or oxyregenerated Co–Mo–Al catalyst reduces the outlet sulfur content in the SR-MD by 200–300 ppm during the 20–60 h period required for full sulfidation of the catalyst [74]. Recycling the catalyst using a continuous catalyst regeneration (CCR) reactor system could be a practical solution.

2.4.3. HDS activity of the catalyst

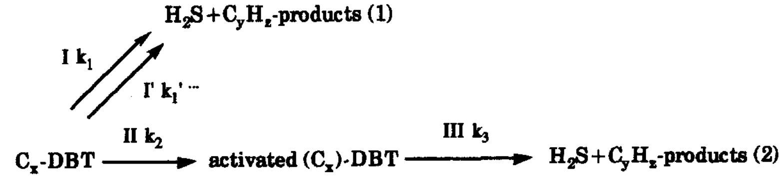
Because all the technical solutions to the deep HDS problem that involve increasing the process severity or changing the mode require new capital investments, development of improved catalysts with HDS activity that facilitates deep desulfurization under normal conditions appears to be the most attractive approach. This could be achieved in one of the two ways: either traditionally, by increasing the concentration per volume or the turnover numbers of the appropriate active sites in the classical Co–Mo–Al catalyst, or by revision of the basic catalyst compositions, enabling them to perform in alternative catalytic routes by removing the hindrance to HDS of alkyl substituents on the DBTs. Improvement in Co–Mo–Al catalysts in the traditional way is a very complicated problem that includes modifications of supports, optimizaion of the methods for introduction of the precursors of the active metals, thermotreatment, sulfidation, and selection of special promoters [62,77]. Therefore, over a period of about 5 years, new generations of commercial hydrotreating catalysts have been produced, and the differences in HDS activity from generation to generation are about 20%. For example, it was recently announced that a new generation of hydrotreating catalysts in the Co–Mo series [14,78] have a desulfurization activity that is higher by 15–40% than that of the former generation, depending on the application and the operating conditions. However, the question still remains as to whether these developments are sufficient to solve the deep HDS problem without further capital investment.

The normal desulfurization processes completely remove from MD AASC, nonalkylated DBTs and other PASC of the second reactivity group (Table 3) [11,13,19,22]. According to Ma et al. [18] in SR-MD with a sulfur content of 0.706 wt%, the concentration of sulfur in the PASC belonging to the III-IV reactivity groups (i.e., DBTs alkylated in the 4- and/or 6-positions), is 0.1024 wt%, whereas that in DBT is 0.0149 wt%. In SR-MD containing 1.46 wt% sulfur, the concentration of 4-Me-DBT and 4,6-diMe-DBT alone corresponds to a sulfur content of 0.04 wt% [19]. Therefore, reduction in the sulfur content of MD to <0.1 wt% under normal desulfurization conditions requires a catalyst displaying at least the same HDS reaction rate for 4- and/or 6-alkylated DBTs as the existing commercial catalysts do for the nonalkylated DBTs. The HDS rates of 4- and/or 6-alkyl-DBTs in clean solvents and in real MD with commercial Co–Mo–Al catalysts are lower by 3–10 times than those for DBTs (Tables 2 and 3). This brings us to the conclusion that complete removal of sulfur from MD with a final boiling point of ≥370°C requires a catalyst in the Co–Mo series that is at least 3 times more active than the available commercial catalysts.

Increasing the residual sulfur content to 0.01–0.05 wt% reduces the requirements for catalyst activity. These requirements may be estimated from the available empirical kinetic data that obey the power law. On the basis of Eq. (8), with the most commonly used order of $n = 1.7$, it may be easily calculated that reducing the outlet sulfur content in MD with $S_0 = 1.5$ wt%, from 0.1 wt% to 0.05 or 0.01 wt%, at an LHSV of 3 h^{-1}, requires an increase by 1.6 and 5.0 times, respectively, in the HDS rate constant. For higher reaction orders, the difference could reach 10 times. These estimations are in good agreement with the conclusion made above, which was based on differences in PASC reactivities. Taking into account that the stable outlet sulfur content in the deep HDS process used for producing diesel fuel with <0.05 wt% sulfur has to be adjusted to a level of about 0.03 wt% to exclude problems originating from deviations of the feed quality and operating conditions, the catalyst's activity has to be increased by a factor of at least two and preferably by a factor of ≥3 to meet further diesel specifications for <0.01–0.001 wt% S.

2.4.4. Alternative catalytic routes

The use of alternative catalytic routes supposes that the desulfurization reaction takes place via two routes, one being the transformation of a group of sulfur-containing compounds, via two consecutive reactions II and III (consecutive alternative routes), and the other being the direct desulfurization I that could proceed in parallel via different intermediates depending on the nature of the active sites involved (parallel alternative routes):



The stringent requirements governing catalyst activity for deep desulfurization are the outcome of the hindrance by the alkyl substituents in the 4- and/or 6-positions of the DBT molecule to direct sulfur withdrawal [32]. Alternative catalytic routes that involve some intermediate transformations of the molecule, such as hydrogenation of the benzene rings, demethylation, scission of the single C–C bond in the thiophene ring, transalkylation or positional isomerization

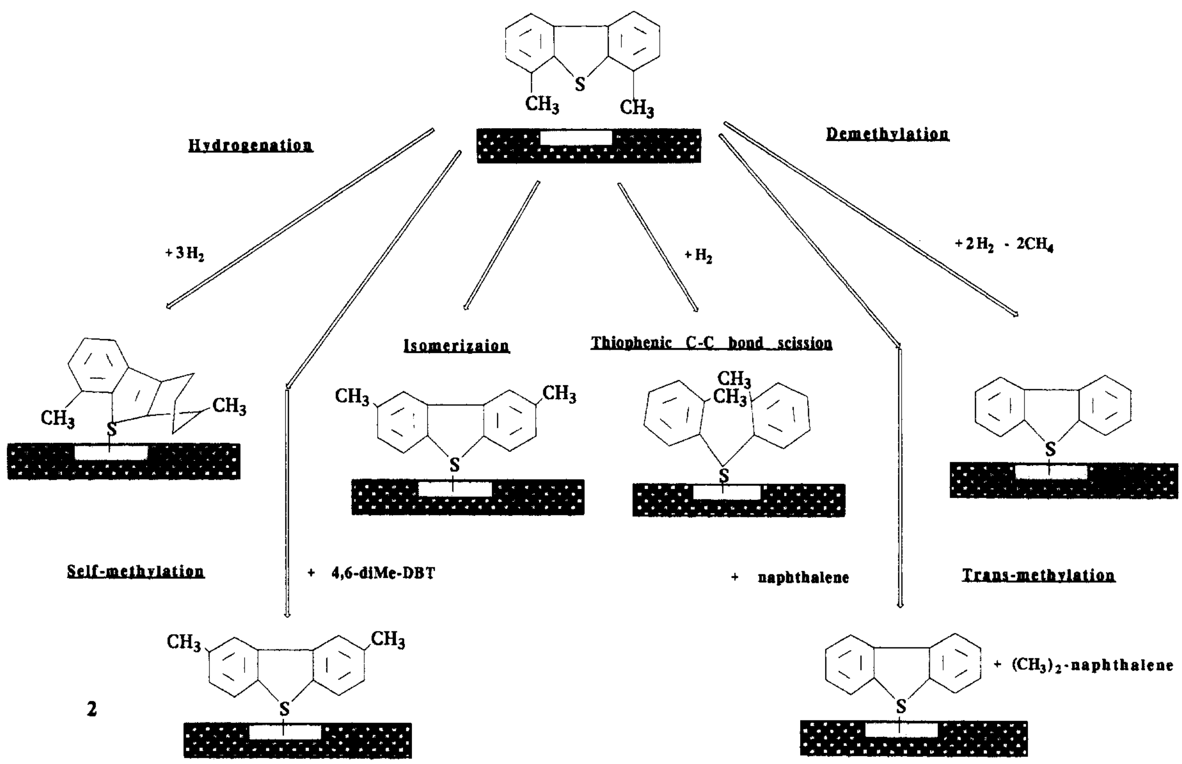


Fig. 12. Consecutive alternative catalytic routes for 4,6-diMe-DBT HDS.

of alkyl substituents, could be more efficient than direct sulfur withdrawal (Fig. 12) [23,32,34,38,40]. Alkyl substituents in the 4- and/or 6-positions do not hinder the formation of the corresponding CHBs [32], which are the desulfurization products of hexahydro-DBTs that display higher HDS reactivity than those of corresponding DBTs [36]. Scission of the single C–C bond in the thiophene ring transforms the molecule into the corresponding dialkyldiphenyl sulfide, which belongs to the AASC group of compounds with high HDS reactivity [34]. Demethylation, transalkylation, or positional isomerization of alkyl substituents removes them from the 4- and 6-positions, shifting the molecule from PASC reactivity class III/IV to class II (Table 3).

Introducing acidic zeolites in Co(Ni)–Mo–Al catalyst could, for example, yield a parallel alternative route that includes adsorption of S-compounds on Bronsted-acid sites followed by removal of H_2S via β-elimination [140] in addition to direct desulfurization on sulfide active sites.

In addition to the kinetic factors already discussed, the efficiency of alternative HDS routes could be affected by the thermodynamic equilibrium. It is well known that such reactions as hydrogenation of aromatic rings or isomerization at high temperatures used for desulfurization of MD are thermodynamically limited, while HDS of organosulfur compounds is exothermic and essentially irreversible under the reaction conditions used in commercial desulfurizers [10,141]. There are no thermodynamic data available for multi-ring heterocyclic sulfur compounds like 4- and/or 6- alkyl-substituted DBTs, but it has been proposed [10] that alternative pathways involving prior hydrogenation or isomerization can be affected by thermodynamics because intermediate reactions are equilibrium-limited. The following considerations show that it could not be the case.

If hydroaromatics or the corresponding isomers of aromatic compounds – the products of hydrogenation or isomerization of aromatic hydrocarbons – remain in the system, hydrogenated 4- and/or 6-alkyl-substituted

DBTs or 2-,3-,7-,8-alkyl-substituted DBTs, being the products of isomerization of 4- and/or 6-alkyl-DBTs, are further consumed in the second HDS stage of the consecutive route that is thermodynamically unlimited. The case in which the rate of the second stage in the consecutive route (k_3) is high enough, the 'effective' aromatic saturation in 4- and/or 6-alkyl-DBTs or the extent of their isomerization at high temperatures could be increased beyond the thermodynamic limits as a result of continuous removal of the products from the system.

This concept is illustrated in Fig. 13 which shows the conversion of aromatics vs. temperature plot for a known thermodynamic equilibrium for BPH hydrogenation. Line *T* represents the equilibrium conversion of BPH to CHB as a function of temperature. The lines *A* and *B* indicate the variations with temperature, at fixed hydrogen partial pressure, of the conversion of BPH to CHB using fixed quantities of two catalysts, *A* and *B*, for which the hydrogenation activity of catalyst *B* is higher than that of catalyst *A*.

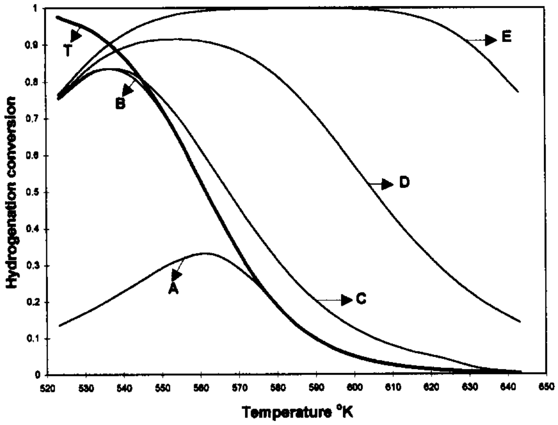
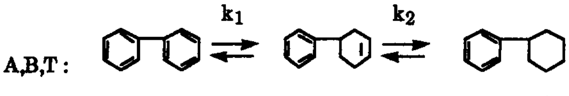
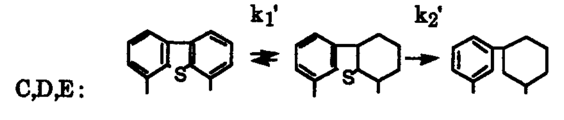


Fig. 13. Effect of temperature on 'hydrogenation' conversion of BPH and 4,6-diMe-DBT: computer simulations.



A - k_1(513 K)=0.1; *B* - k_1(513 K)=1.0; *T* - equilibrium conversion



k_1'(513 K)=1.0; *C* - k_2'(513 K)=0.1; *D* - k_2'(513 K)=1.0; *E* - k_2'(513 K)=10.

At comparatively low temperatures, where the driving force required by the catalyst is comparatively high, the difference in saturation of the aromatics obtained with the two catalysts will be significant (higher with catalyst *B*). However, with rising temperature, the extent of aromatics saturation will pass through a maximum (at a lower temperature for catalyst *B*) and a further rise in temperature will not affect the aromatics saturation, so it becomes almost equal, corresponding to thermodynamic equilibrium, for the two catalysts as a result of negligible driving force. Lines *C*, *D* and *E* represent the 'effective' saturation of aromatic rings in 4,6-diMe-DBT with catalysts displaying the same hydrogenation activity (k_1') as for catalyst *B* and different activities in desulfurization of hydrogenated 4,6-diMe-DBT (k_2'). The simulations were done assuming the same equilibrium conversions in hydrogenation of 4,6-diMe-DBT as for hydrogenation of BPH and pseudo-first-order kinetics in hydrogenation and desulfurization stages. Desulfurization activity of the catalyst has to be one order of magnitude higher than hydrogenation to facilitate significant hydrogenation conversion at temperatures $\geq$640 K, commonly used in commercial desulfurizers. The same conclusion could be reached concerning the extent of isomerization of alkyl-substituted DBTs compared to conventional alkyl aromatics.

This means that, for high efficiency of consecutive alternative HDS routes, the rates of both the steps are kinetically and thermodynamically important. Eq. (3), which includes the relative weights of the direct and consecutive routes (η_i), may be transformed into two equations by considering kinetics of each step to be pseudo-first-order and expressing the rate of direct desulfurization (R_I) as a sum of the rates of the possible parallel reactions:

$$R_{HDSO} = \eta_1 \Sigma R_{Ii} + \eta_2 R_{II};\ k_3/k_2 \geq 1 \tag{9}$$

$$R_{HDSO} = \eta_1 \Sigma R_{Ii} + \eta_2 R_{III};\ k_3/k_2 < 1 \tag{10}$$

depending on the ratio between the rate constants k_2 and k_3. For successful deep desulfurization via the alternative consecutive route, the ratio k_3/k_2 must be $\geq$10 and the value of k_2 at normal conditions has to be at least the same as that of k_1, for modern commercial Co–Mo–Al catalysts that provide complete removal of AASC and PASC of the I-II reactivity classes from the MD.

In the light of the available data on the efficiency of the alternative 'hydrogenation' route, it may be concluded that the disadvantage of the Co–Mo–Al catalysts is the low value of k_2. The ratio k_2/k_1 for DBT with the Co–Mo–Al catalyst at 300°C and 102 atm was found to be 6.6×10^{-2}, while the ratio k_3/k_2 was 2.6×10^3 [36]. As a result, the ratio between the yields of C_yH_z-products – (2)/(1), i.e., CHB to BPH, in HDS of DBT with Co–Mo–Al catalysts at normal pressures – does not exceed 0.2, even at conversions exceeding 90% [34,39,57]. Introduction of methyl groups in the 4- and 6-positions of the DBT molecule increases the ratio of the C_yH_z-products, (2)/(1), by a factor ranging 5–10 [31,33,34], with a decrease in the overall desulfurization rate by the same factor and an increase in the selectivity for partially hydrogenated DBTs [33]. This could be a result of decreasing k_1 and increasing k_2 in such a way that k_2/k_3 becomes <1 and the desulfurization of the partially hydrogenated DBTs becomes the limiting step. The same effect – increasing the selectivity for partially hydrogenated products – was observed for HDS of DBT with the Co–Mo–Al catalyst after increasing the hydrogen pressure from 102 [36] to 180 atm [56] to facilitate the hydrogenation step II.

Appearance of partially hydrogenated products after introduction of the alkyl group in DBT is difficult to explain: HDS of hydrogenated alkyl-DBTs is not hindered sterically [32,34] and the HDS reactivity of hydrogenated alkyl-DBTs should be much higher than that of the starting alkyl-DBTs, as was shown for the nonalkylated DBTs [36,83]. Possibly, the increase in the selectivity for partially hydrogenated DBTs is also a result of the higher space-time required for conversion of the partially hydrogenated DBTs to C_yH_z-products (Eq. (2)) through two additional basic steps: desorption from the τ-sites and readsorption at the σ-sites. If this is the case, the rate of conversion of hydrogenated alkyl-DBTs to CHBs (R_{III}) could be increased by increasing the hydrogenation activity of the catalysts. This would increase the value of k_1 and accelerate the subsequent transformation of partially hydrogenated DBTs as a result of their higher surface concentration. Further work has to be performed in order to understand the nature of this effect.

One of the best known ways of increasing a catalyst's hydrogenation activity is to change the composition from Co–Mo to Ni–Mo or Ni–W. The data available on the results of this change are contradictory. Replacing Co–Mo–Al with Ni–Mo–Al yielded an increase in the conversion of 4,6-diMe-DBT at 320°C and 34 atm from 60 to 82% by increasing the ratio of (diMe-CHB + diMe-diCH) to diMe-BPH from 3 to 6.8 [23]. The Ni–Mo–Al catalyst was slightly inferior to the Co–Mo–Al catalyst for HDS of C_3-BT and C_3-DBT in SR-MD, and slightly superior to Co–Mo–Al in HDS of 4-Me and 4,6-diMe-DBT [18]. At 290°C and 50 atm, the formation of desulfurized products from 4-Me-DBT with the Ni–Mo–Al catalyst was 2.6 times faster than that with the Co–Mo–Al catalyst, giving lower Me-CHB/Me-BPH ratios, 0.17 and 0.41, respectively, and there was a higher selectivity for the partially hydrogenated Me-DBT [33]. In the HDS of DBT and 4,6-diMe-DBT at 360°C and 54 atm, the Ni–Mo–Al catalyst gave a ratio of CHB to BPH that was two or more times greater than that produced with Co–Mo–Al, while the desulfurization rate with the Co–Mo–Al catalyst in both reactions was 2.1–2.3-times higher [34].

These contradictions could be the result of different methods used in the preparation of the catalysts and testing them at different hydrogen sulfide concentrations in the reaction mixture. Hydrogenation (τ) and desulfurization (σ) sites at the surface of the catalysts are related to different structural elements of the sulfide phase – the corners and edges of the MoS_2 crystals [47], and the rim and edge parts of MoS_2 crystal-edge planes [79]. Therefore, the ratio between hydrogenation and desulfurization activities of Ni–Mo catalysts strongly depends on the nature of the oxide precursors [80–82] in spite of possible interconversion of the active sites. The highest hydrogenation activity was displayed by the sulfidation products of the $NiMoO_4$ phase [80,81]. Testing such catalysts in the HDS of DBT and 4,6-diMe-DBT at 360°C and 55 atm showed that they are superior to Co–Mo–Al in the desulfurization of 4,6-diMe-DBT, but are inferior to the Co–Mo–Al catalyst in the desulfurization of DBT [33].

A clear correlation was found between the ratio of 4-Me- or 4,6-diMe-DBT to DBT reactivity and HDS selectivity of DBT for CHB, which represents the hydrogenation activity of the catalysts (Fig. 14). The figures presented in Fig. 14 for 4-Me-DBT were calculated from the reaction rates and selectivities measured by Lamure-Meille et al. [33] for Ni–Mo–Al

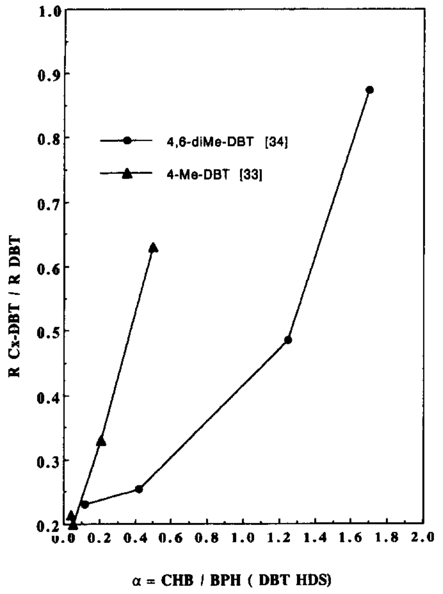


Fig. 14. Correlation between the ratios of C_x-DBT/DBT HDS rates to CHB selectivity.

and Co–Mo–Al catalysts. This correlation is the result of increasing the efficiency of the 'hydrogenation' route for methyl-substituted DBTs with increased catalyst hydrogenation activity (k_2) by decreasing the efficiency of the direct desulfurization route (k_1). Since direct desulfurization is the main catalytic route for removing the AASC and PASC of I and II reactivity groups, catalysts that are highly effective in removing the least-reactive PASC – as a result of their high hydrogenation activity – would be less effective in desulfurization of real MD containing a variety of sulfur compounds. Further investigations are needed to verify this point.

Information on the efficiency of other alternative routes in HDS of alkyl-substituted DBTs is limited. It was shown that introduction of the acid zeolite HY into the Co–Mo–Al composition increased the overall desulfurization rate of 4,6-diMe-DBT by three times at 360°C and 54 atm [34]. In this case, the products (toluene, benzene, CHB and BPH) obtained via scission of a thiophenic C–C bond, by demethylation, or by a combination of these two reactions were detected together with diMe-BPH. The ratios between the 4,6-diMe-DBT conversion rates through thiophenic C–C scission, (thiophenic C–C scission + demethylation), demethylation, through hydrogenation, or through direct HDS, estimated according to the product distribution, were 30/12.2/3.9/10.3/3.6, respectively [34]. This means that classic acid components such as zeolite HY could accelerate the desulfurization of the least-reactive PASC, mainly via the thiophenic C–C bond-scission route, and in this case, the value of k_2 is about ten times higher than that of k_1.

It was found that the methyl groups in methylcyclohexyltoluene and dimethyl-bicyclohexyl, which are products of the desulfurization of 4,6-diMe-DBT via the 'hydrogenation' route with Co–Mo–Al and Ni–Mo–Al catalysts, migrate from their original positions, while those in diMe-BPH stayed in their original positions [23] (kinetic data on the efficiency of this migration are not available). This was explained as a result of self-transmethylation of the 4,6-diMe-DBT molecules, accelerating their transformation via the 'hydrogenation' route. It was shown that large-pore zeolites are efficient in the removal of methyl groups from substituted polymethyl-polynuclear thiophenes by transmethylation with polynuclear aromatics [38], but no information was given about the efficiency of this route in their desulfurization.

3. Deep desulfurization/denitrogenation/deoxygenation of shale oils

A variety of materials that could be recovered from oil shales by retorting or thermal solution have been identified as sources of crude-oil substitutes [84]. They constitute a very large reserve of synthetic oil [85]. Shale oils, being the products of thermocatalytic decomposition of kerogens, contain up to 60% of MD, 0.6–9% of sulfur, 0.8–3% of nitrogen, and 1–5% of oxygen, and thus contain <40% of hydrocarbons without heteroatoms [86,87]. Upgrading of shale oils by hydrotreating after removal of the heavy metals (particularly arsenic) requires simultaneous desulfurization, denitrogenation and deoxygenation. The order of difficulty of removing the heteroatom from shale oils by hydrotreating is $S \leq O \ll N$ [88,89,114]. As a result, the deep hydrotreating of shale oils is a significantly different operation from that of crude oil MD.

While the deep hydrotreating of crude-oil MD is limited only by the residual sulfur content (which is a fuel-quality parameter), deep hydrotreating of shale oils is limited primarily by nitrogen removal. Low residual nitrogen (<0.001 wt%) is an important fuel-quality parameter, since it results in a reduction of NO_x emissions on combustion and an increase (together with low oxygen) in the stability of fuels on storage [90]. In addition, reduction of the residual nitrogen to <0.05 wt% is required for further upgradation of the heavy fractions of shale oil in fluid catalytic cracking or hydrocracking processes, since the nitrogen compounds cause deactivation of the catalysts [91].

Since HDN takes place slower than HDS and HDO, 'three-way' hydrotreating of shale oils with classical Ni(Co)–Mo–Al catalysts has to be carried out at conditions more severe than those for HDS of crude-oil MD, i.e., at $LHSV \leq 1$ h^{-1}, $T \geq 400°C$, $P >$ 100 atm, conditions at which the sulfur and oxygen levels corresponding to deep hydrotreating requirements are usually assured, but those for nitrogen remain problematic (Table 8).

Another important feature of the hydrotreating of shale oils is the interdependence between the extent of heteroatom removal and the yield of white products, mainly distillates but also some naphtha [97]. This interdependence is a result of the high (>60%) content of heteroatomic molecules, especially in the high-boiling fractions of shale oils, which yield lighter hydrocarbon fragments after removal of the heteroatoms. This results in decrease in the 50% of the boiling point of the shale oil by 70–100°C after hydrotreating with classical Co(Ni)–Mo–Al catalysts [86,97]. This effect is insignificant for crude-oil MD, in which the content of sulfur compounds does not exceed 10%. But in shale oils, it constitutes another important reason to look at deep HDS/HDN/HDO.

As already mentioned, technology for the production of MD fuels from crude oils is significantly different from those for shale oils: crude-oil MD are hydrotreated after separation from the raw petroleum material by distillation, while shale oils are hydrotreated directly, producing upgraded MD. Therefore, the specific issues considered here for crude-oil MD have to be considered in terms of the whole raw material for shale oils. We should also remember that because hydrotreating of shale oils is still not commercialized on an industrial scale, the term 'normal hydrotreating' (compared with deep upgrading of the feedstocks) cannot be used for shale oils.

Information about the chemistry, technology, and kinetics of hydrotreating shale oils and the effects of

Table 8
Hydrotreating of shale oils: comparison of existing results

Shale-oil origin	Catalyst	Hydrotreating conditions			Content in hydro-treated shale oil (wt%)		References
		LHSV (h^{-1})	P (atm)	T (°C)	N	S	
Colorado	Ni–Mo–Al	0.6	150	408	0.05–0.1	—	[92]
Colorado	Ni–Mo–Al	0.4	112	405	0.05	0.0002	[93]
	(Shell-324)						
Colorado	Ni–Mo–Al	1.0	102	430	0.9	0.006	[94]
	(Harshaw-4303E)						
Colorado	Co–Mo–Al	1.0	68	440	0.44	0.03	[86]
Colorado	Co–Mo–Al	1.0	204	418	0.25	0.01	[95]
Paraho	Ni–Mo–Al	0.9	141	416	0.19	0.024	[87]
	(Am. Cyanamide HDS-3A)						
Occidental	—"—	0.9	141	416	0.25	0.01	[87]
Tosco	—"—	0.9	141	416	0.60	0.023	[87]
Geokinetics	—"—	0.9	141	416	0.33	0.01	[87]
Irati	Ni–Mo–Al [a]	1.0	122	400	0.409	<0.06	[96]

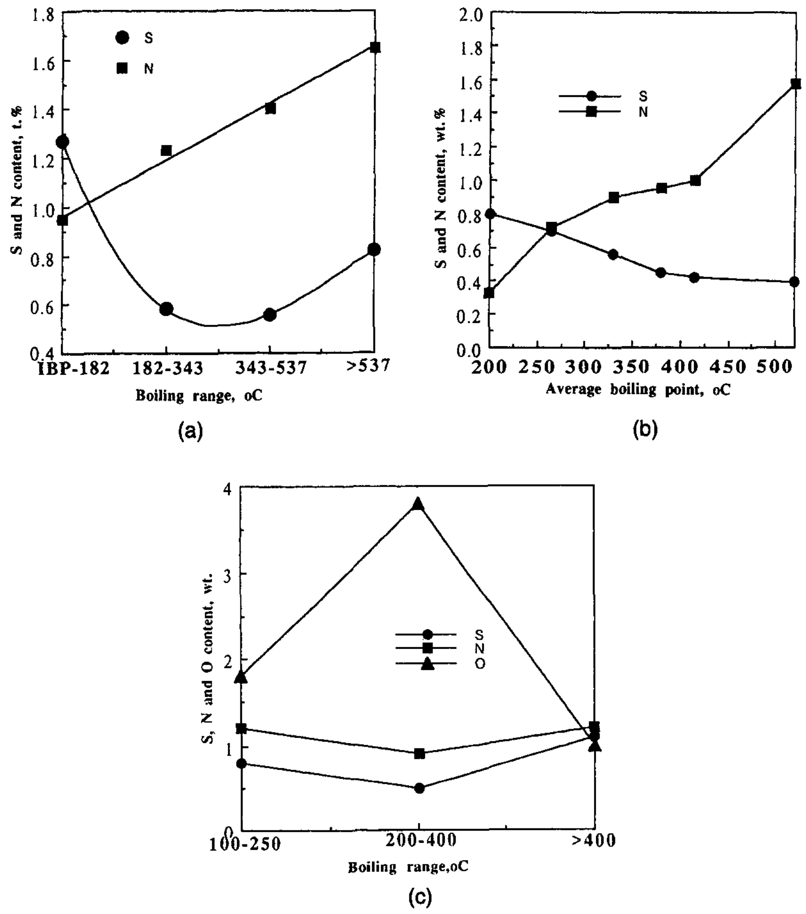
[a] Three-phase fluidized-bed reactor.

the properties of the catalysts is limited compared to the data available on the hydrotreating of crude oil materials. This makes consideration of all the questions discussed in Section 2 difficult, and therefore, the available information about the nature, distribution and relative reactivities of sulfur-, nitrogen-, and oxygen-containing compounds in shale oils are discussed in brief, together with potential solutions for their deep HDS/HDN/HDO.

3.1. Nature and distribution of sulfur-, nitrogen- and oxygen-containing compounds

Sulfur and nitrogen are distributed nonuniformly in the boiling range of shale oils, depending on their origin. In contrast to crude-oil MD, sulfur in Colorado and Israeli shale oils is concentrated mainly in the light fractions boiling out at <320°C, while the nitrogen concentration gradually increases with increased boiling temperature (Fig. 15). In Rundle shale oil, for example, the sulfur and nitrogen concentrations showed minima in the middle-boiling fraction, while oxygen was concentrated mostly in middle-boiling fraction (Fig. 15).

Most of the information available about sulfur compounds relates to shale oils containing 0.6–0.9 wt% sulfur, which is present mostly in the form of substituted thiophenes and BTs, with minor amounts of thiols and sulfides in the light fractions [86,100] or in the polyaromatic fraction of whole shale oil [101].



(a)

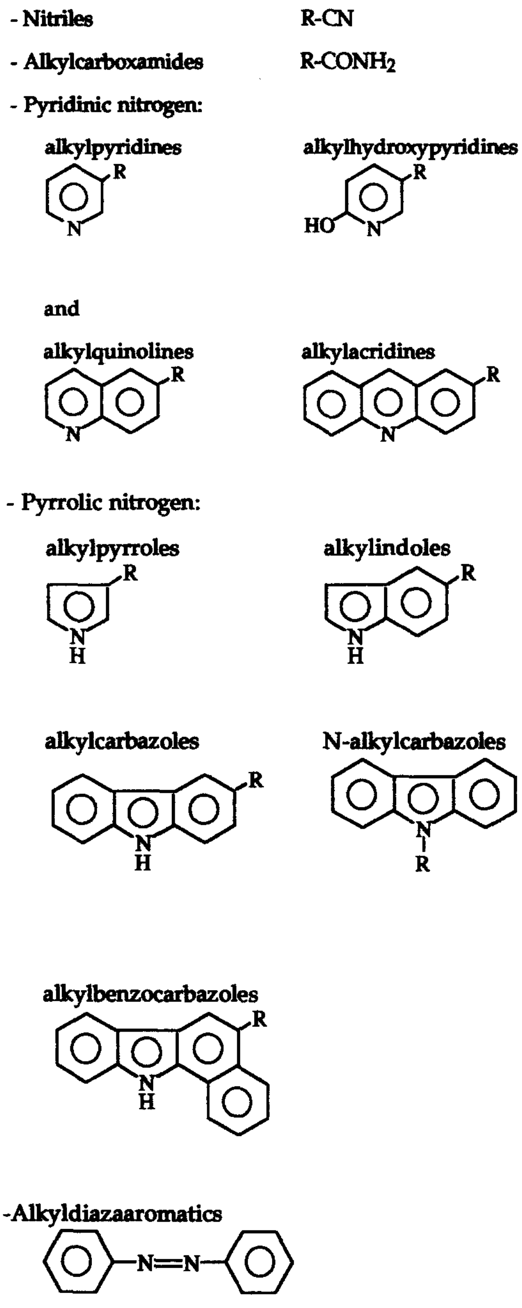
(b)

(c)

Fig. 15. Distribution of sulfur, nitrogen and oxygen in shale oils: (a) Colorado (adapted from Ref. [98]); (b) Israeli (adapted from Ref. [97]); and (c) Rundle (adapted from Ref. [99]).

In Irati shale oil containing 0.82 wt% sulfur, it was found that there were 2.1 wt% alkylthiophenes and only 0.3 wt% BTs and DBTs, the latter two being completely removed after hydrotreating with the Ni–Mo–Al catalyst [96]. In Israeli shale oil containing about 9 wt% sulfur, aliphatic sulfides, BTs and DBTs were also detected [102]. Even in this case, the concentration of the least-reactive PASC – substituted DBTs as individual molecules or fragments of heavy asphaltenes and asphaltols – does not exceed 0.02%. This could be a second reason, in addition to high process severity, for the facile removal of sulfur (vs. nitrogen and oxygen) from shale oils by hydrotreating. Oils and asphaltene and asphaltol fractions of Israeli shale oil and their subfractions (straight and branched-chain aliphatic, aromatic and polar substances) contained, on an average, 4 sulfur atoms for every 100 carbon atoms [102].

Direct information about the structure and distribution of individual nitrogen compounds in shale oils is limited because of difficulties in their separation, in contrast to thiophenes and PASC, which can be isolated, for instance, by ligand-exchange chromatography followed by GC analysis. IR, GC, GC-MS or GC-MS ion monitoring of shale-oil fractions obtained by extraction with pentane or benzene and adsorption chromatography with basic and neutral alumina and silica indicated that the nitrogen in shale oils could be assigned to five classes of compound [88,89,99,101–107] (Scheme 1).



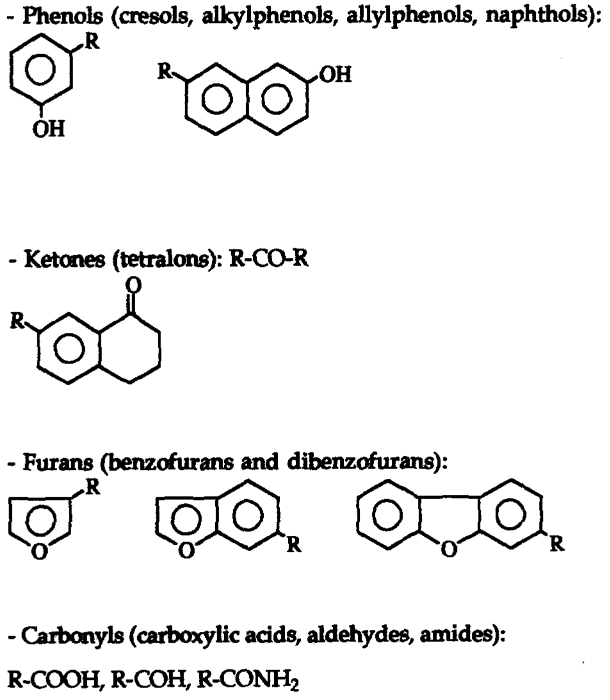
Scheme 1.

Amides, perhaps originally present in the kerogen, are partially converted to nitriles by dehydration during thermodecomposition of the kerogen [104]. Oils and asphaltene and asphaltol fractions of Israeli shale oil contained, on average, 2, 3 and 8 nitrogen atoms for every 100 carbon atoms, respectively [102], reflecting the increasing nitrogen content in the higher boiling fractions. In Paraho shale oil, the ratio, 4.2:1.9:2.5:1.0, was found for basic nitrogen compounds (pyridine type):weak nitrogen bases (alkylhydroxypyridine type):non-basic compounds (alkylcarboxamides and diaza-aromatics):pyrrolic compounds [89]. The concentrations of nitrogen in amide, nitrile, basic and asphaltene fractions derived from Rundle shale oil were 2.3–2.4, 1.3–1.5, 6.3–7.0 and 3.9–5.0 wt%, respectively, and the nitrile fraction contained about 20% of the total nitrogen [104]. In the aromatic subfraction of oil separated from Israeli shale oil, nitrogen exists mainly in the form of pyridines, while in asphaltenes it is found in the form of quinolines and indoles [102]. Generally, substituted C_1–C_6-pyridines are the most abundant pyridinic nitrogen compounds in light shale-oil fractions, while alkyl-substituted

C_1–C_3-quinolines are the major components of the bases in the middle and heavy fractions [99,104,106]. The boiling points of these individual nitrogen compounds indicate that they could indeed exist in shale-oil naphthas and MD. In the oil part of the heavy fractions boiling out at 400°C+, pyridinic and pyrrolic rings are likely to be associated with long aliphatic chains or naphthenic rings (oils), while in heavy asphaltenes and asphaltols they could be fragments of high-molecular weight polyaromatic structures described in Ref. [3]. The nitrogen compounds of the jet fuel cuts of Occidental shale oil had an aromaticity of 50–60%, while those of the diesel and heavy gas-oil cuts were about 28 and 34%, respectively, the latter containing more quinolines [104]. This reflects the relative enrichment of heavy shale-oil fractions by nonaromatic nitrogen compounds – nitriles and amides.

Oxygen in shale oils exists in oxygen-containing organic compounds that can be divided into four classes [99,102,104–115] (Scheme 2).

Phenols are the most abundant oxygen compounds in shale oils, with a predominance of monocyclic polyalkylphenols containing 2–3 carbon atoms in the side chains [99,104,109]. The carboxylic acids detected in Irati shale oil were essentially linear, from n-C_6–n-C_{26}, with maxima at C_{16} and C_{18} [109]. The carbon chain-length distribution of alkylketones measured in Rundle shale oil was in the C_8-C_{25} range, with two maxima at C_{16} and C_{23} [104]. Furanic oxygen was found mainly in heavy asphaltene and asphaltol fractions of Israeli shale oil, while in the oil fraction it was represented mostly by phenols, so that oils asphaltenes and asphaltols contained, on average, 0.4, 10.0, and 37.0 oxygen atoms for every 100 carbon atoms, respectively [102].



Scheme 2.

3.2. *Relative reactivities of sulfur-, nitrogen- and oxygen-containing compounds*

Although the information about the nature and distribution of sulfur compounds in shale oils is limited, it seems that most of them belong to the AASC and highly reactive PASC, which do not cause problems for deep HDS with modern commercial catalysts.

Attention has thus been paid to identification of the least-reactive groups of nitrogen compounds that cause the major problems. Comparison of the distribution of nitrogen compounds in starting and hydrotreated shale-oil materials using commercial Co(Ni)–Mo–Al and Ni–W–Al catalysts showed that the nitrogen present in the form of nitriles, amides, diazaaromatics, and hydroxypyridines was completely removed, while the residual nitrogen, corresponding to 50–98% HDN, was present mostly in the form of pyridines (quinolines) and pyrroles (indoles, carbazoles), with small amounts of amides [89,96,110]. The least-reactive nitrogen compounds are N-alkylpyrroles, which remain unconverted, and N-alkylpyridines that mainly undergo hydrogenation to the corresponding piperidines [89]. Increasing the concentration of the pyridines by about 1.7 times and pyrroles by 2.5 times, in shale oil, after hydrotreating [89] is an evidence for the lower reactivity of pyrroles. This conclusion was confirmed by the increase in the ratio of pyrroles to pyridines in the hydrotreated Paraho shale oil from about 2.1 to 5–6 by increasing the %HDN from 80 to 95–98% [110]. The ratio of the HDN rate constants for quinoline to indole with Co–Mo–Al catalysts at 50 atm and 344°C was 1.2–1.5, depending on the catalyst [21]. It was shown that the pyridines present in the Paraho shale oil could be further subdivided into three reactivity groups: nonhindered, less hindered and hindered. The reactivity of the pyrrolic compounds falls between the reactivities of the less hindered and hindered pyridines [89].

The 'hindrance' effect is not connected to the basicity of alkyl- and naphthene-pyridines, but rather to a weaker adsorption ability: hindered pyridines with high molecular weights elute earlier during separation by adsorption chromatography. According to spectroscopic data, the difference between the nitrogen compounds in raw and hydrotreated shale-oil distillates is primarily related to the degree of substitution and the chain length [103]. The susceptibility of different types of nitrogen compounds to HDN cannot be determined definitively on the basis of the analysis of starting and hydrotreated shale oils, because a substantial part of these compounds undergoes conversion to other types of nitrogen compounds, such as alkylamines, alkylpiperidines, or alkylanilines [89,111,112]. The available data allow us to arrange the nitrogen compounds present in shale oils into six general classes according to their HDN reactivity (Table 9) [88,89,110,113,114]. The figures given in Table 9 are based mostly on the relative %HDN measured by Holmes and Thompson [89] for different groups of nitrogen-containing compounds. The relative reactivities shown in Table 9 are tentative and can change depending on the composition of the catalyst and the severity of the process [113,114]. Only the nitrogen compounds of the first reactivity class could be completely removed from shale oils with commercial Ni(Co)–Mo(W)–Al catalysts.

Some information about the nature of the hindrance effects in HDN may be obtained from the HDN results of individual nitrogen-containing compounds in clean solvents. The effects of alkyl substituents on HDN reactivity of pyridine and quinoline molecules have been reviewed by a number of workers [10,111,112]. It was shown that introduction of alkyl substituents into the pyridine molecule decreased its HDN reactivity by about one order of magnitude, while for quinoline, their effect – like the effect of conjugated benzene rings – appears to be relatively small. Alkylpyridines with substituents far away from the nitrogen atom are much less reactive than those with sterically crowded nitrogen, which is an evidence for the predominantly electronic, rather than steric, nature of the hindrance effect. It has been proposed [112] that in pyrroles, the effect of alkyl substituents is less important as a result of the higher electron density of the five-membered rings and the wider bond angle between the N atom and the neighboring substituent. This could explain why pyridinic N compounds differ widely in their HDN reactivity, while all the pyrrolic compounds belong to the same reactivity class. The lowest HDN reactivity of N-alkylated pyridines and pyrroles seems to be the result of complete screening of the N-heteroatom.

Direct information about the relative HDO reactivities of oxygen-containing compounds was obtained by comparison of their distribution in raw and hydrotreated products of Rundle and Irati shale oils [88,96,109,114]. For Irati shale oil, the distribution of acidic oxygen compounds comprising phenols and carboxylic acids remained unchanged after hydrotreating, as was expected from their close HDO reactivity [109]. According to Souza et al. [96], the %HDO values for phenols, carboxylic acids and ketones (mainly alkylnaphtholes and tetralones) in Irati shale oil with the Ni–Mo–Al catalyst at 125 atm and 400°C were 87.5, 83.3 and 60.0%, respectively. At conditions

Table 9
Susceptibility of nitrogen compounds in shale oils to nitrogen removal by catalytic hydroprocessing

N-compound reactivity class	N-compound chemical type	Relative HDN reactivity, a.u.
I	Nitriles, diazaaromatics, alkylhydroxypyridines	$\gg$100
II	Amides and nonhindered alkylpyridines, alkylquinolines and alkylacridines	100
III	Less hindered alkylpyidines, alkylquinolines and alkylacridines	75
IV	Pyrroles, indoles, carbazoles and benzocarbazoles	50
V	Hindered alkylpyidines, alkylquinolines and alkylacridines	35
VI	N-alkylpyrdines (quinolines, pyrroles, carbazoles)	$\ll$35

close to those given above, the aliphatic ketones were completely removed from Rundle shale oil, while alkylphenols (to C_7), indanoles (to C_2) and naphtholes (to C_2) were significantly removed with a %HDO close to the %HDN of nonhindered and less-hindered pyridines (to C_6) and quinolines (to C_3) and much higher than %HDN of pyrroles [88,114]. Some more-precise information on the relative reactivities of alkylphenols based on HDO data for individual compounds is available [10,21,116–121]. The HDO reactivity of *ortho*-substituted alkyl- and arylphenols is 5–10 times lower than that of *meta*- and *para*-substituted molecules. Information about the relative reactivity of furanic compounds in shale oils is not available, but comparison of the HDO rate constants for individual compounds provides evidence of their lower reactivity compared to alkylphenols (especially dibenzofuran) [21,121].

The oxygen-containing compounds in shale oils may be arranged only qualitatively, according to their HDO reactivities:

> aliphatic ketones $\gg$ nonhindered alkylphenols (indanols, naphthols) $\geq$ carboxylic acids $\sim$ carboxamides > alkylnaphthones (tetralones) > hindered alkylphenols $\sim$ furans.

This arrangement differs significantly from that given by Furimsky [119], which was based on the thermostability of different oxygen compounds at 400–450°C. He claims that carboxylic acids can lose oxygen as CO_2 or H_2O at the temperatures normally used in hydrotreating of shale oils without catalysts, hydrogen or hydrogen donors; ketones and amides require only a reducing agent, while phenols and furans may be completely deoxygenated in the presence of a catalyst. Further studies are needed to establish a more accurate trend for the stability of the oxygen-containing compounds, taking into account their possible interactions with the other components of the shale oil. On the basis of the considerations described above, the least-reactive oxygen compounds in shale oils are likely to be the hindered phenols and dibenzofurans.

Transition to deep hydrotreating of shale oils requires the removal of nitrogen- and, sometimes, the oxygen-containing compounds, i.e., dealing with the following least-reactive nitrogen and oxygen compounds:

- hindered alkylpyridines (quinolines, acridines)
- pyrroles (indoles, carbazoles)
- hindered *ortho*-alkyl-substituted phenols
- dibenzofurans

Although the full picture of the HDN/HDO reaction pathways of these least-reactive compounds is not yet available, some patterns that have been established with commercial hydrotreating catalysts may be used as a basis in the search for potential solutions to the deep hydrotreating problem [10,111,112,118,119]:

- Removal of nitrogen and oxygen from heterocyclic compounds is preceded by hydrogenation of heterocycles and intermediates like anilines or alcohols (Fig. 16).
- At temperatures >350°C and pressures >100 atm, the limiting step of HDN/HDO for heterocyclic compounds (especially pyrroles and furans) is hydrogenation of heterocycles and conjugated aromatic rings, whereas HDN of hindered alkylpyridines is limited by hydrogenolysis.
- HDO of hindered *ortho*-substituted phenols proceeds in two parallel routes: a direct route and a route preceded by aromatic ring hydrogenation (Fig. 17), where substituents sterically hinder the direct HDO, being the fastest route for nonhindered phenols.

The lower reactivity of nitrogen- and oxygen-containing five-membered heterocyclic compounds (pyr-

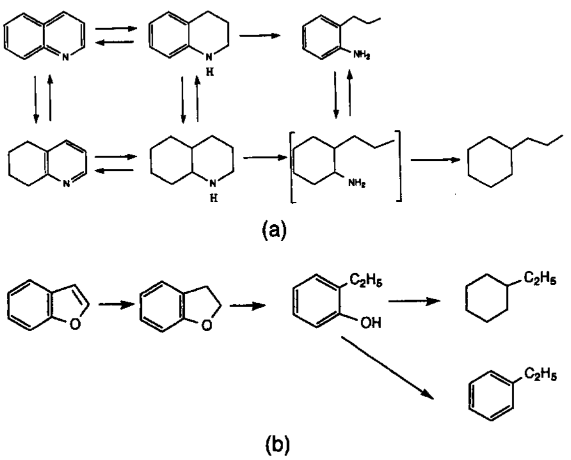


Fig. 16. Reaction networks in HDN of (a) quinoline and (b) benzofurane, representing heterocyclic N- and O-compounds.

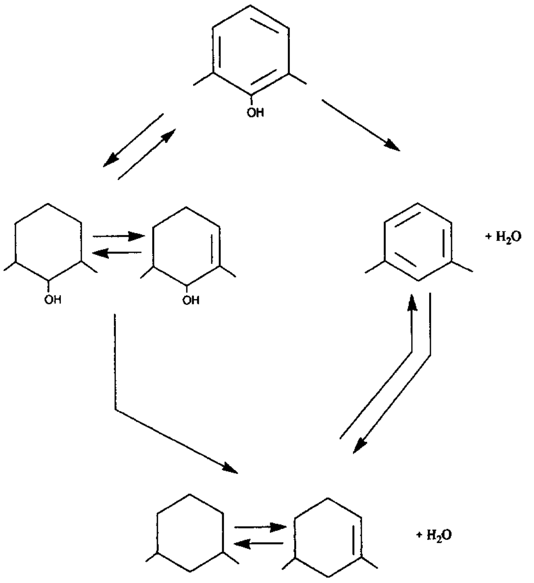


Fig. 17. Reaction networks in HDO of alkyl-substituted phenols.

roles and furans) compared to the corresponding BTs and DBTs is commonly explained in terms of the higher C=N bond strength (147 kcal mol^{-1} vs. 128 kcal mol^{-1} for C=S [122]) and lower atomic radius of N and O atoms (0, 75 and 0.65 Å vs. 1.09 Å for S) so that they are screened by the carbon atoms of the neighboring benzene rings, even if they do not have alkyl substituents. Hydrogenation of the polyaromatic system decreases the C-heteroatom bond strength (73 kcal mol^{-1} for C–N [122]) and removes the steric effect of the neighboring benzene rings, as for methyl-substituted DBT (Fig. 8). The nature of the hindrance effect of alkyl substituents in the 3-, 4-, and/or 5-positions of pyridine molecule [123] is not clear, while conjugated aromatic rings could screen the N-atoms, as was supposed for five-membered nitrogen heterocycles (acridine and benzoacridines are 1.5–2.3 times less reactive than quinoline [111]). Therefore, preliminary hydrogenation becomes more important as the number of aromatic rings increases [113], but for alkyl-hindered pyridines, for which hydrogenation is fast, the overall HDN is limited by hydrogenolysis [124,125]. As for HDS of alkyl-substituted DBTs, phenols undergo HDO via two parallel routes: (1) direct oxygen withdrawal and (2) deoxygenation after saturation of the aromatic ring (Fig. 17). The input of direct deoxygenation with Co–Mo–Al catalysts for phenol and its *meta*- and *para*-alkyl-substituted analogs is about 90% [117–120]. The *ortho*-alkyl substituents hinder only direct oxygen withdrawal from the phenol molecule, which requires vertical O-bonded adsorption on the catalytic sites, thus increasing the ratio of alkyl-cyclohexenes (cyclohexanes) to alkylbenzenes in HDO products by one order of magnitude [46,118]. This is an evidence for the strong steric hindrance to direct HDO of phenol by alkyl substituents in the 2- and 6-positions.

3.3. Potential solutions for deep hydrotreating of shale oils

Because hydrotreating of shale oils has not yet been commercialized, we can define the 'normal' hydrotreating level for shale oils as the %HDS/HDN/HDO achieved with commercial catalysts according to available publications. From Table 8, it may be seen that the conditions for 'normal' hydrotreating of shale oils are: temperature, 405–440°C; hydrogen pressure, 100–150 atm; and LHSV, 1 h^{-1}. Assuming the average sulfur and nitrogen contents in shale oils to be 0.8 and 1.5 wt%, respectively, and taking into account the results summarized in Table 8 and [96], we observe that under these conditions, the sulfur removal is 96–99.9%, a value that meets the deep hydrotreating requirements, while the nitrogen removal is 60–90%, a value much below these requirements and close to the 'normal' desulfurization level of crude oil MD. The %HDO of shale oils reported with commercial Co(Ni)–Mo(W)–Al catalysts at similar conditions was $\geq$87% [88,109,114] that is close to deep hydrotreating requirements, which causes some problems in comparison with HDS of shale oils. Thus, the 'normal' hydrotreating level for shale oils at the conditions mentioned earlier could be tentatively defined as %HDS/HDO/HDN=95+/90+/70+ corresponding to residual S, O and N contents in the hydrotreated products of <0.05/<0.1/<0.5 wt%. In keeping with this line of thought, the deep hydrotreating level could be defined as <0.05 wt% each of residual S, N and O.

3.3.1. Processing of feedstock

The difficulty of performing HDN typically increases with increasing boiling point of the feedstock [111]. This could be a result of reduced accessibility of the nitrogen-containing fragments of the molecules by increasing the size of their nonnitrogen-containing parts [126], especially for nitrogen-containing fragments of asphaltenes and asphaltols. Furthermore, the heavy shale-oil fractions boiling out at ≥400°C often contain 40–50% of the total nitrogen [97,98]. Excluding these heavy parts from the shale oils could solve the deep hydrotreating problem with commercial catalysts. Hydrotreating the 100–400°C fraction of Rundle shale oil with commercial Co–Mo–Al and Ni–Mo–Al catalysts at 400°C, 1 h^{-1} LHSV and 138 atm hydrogen pressure gave products with 0.02 and 0.005 wt% residual nitrogen, respectively [114]. Similar results were obtained in the hydrotreating of the 111–361°C fraction of Israeli shale oil, comprising about 60% of the whole raw material, with a proprietary Ni–Mo–Al catalyst at 150 atm, 400°C and 1 h^{-1} LHSV [29]. However, with some other shale oils, deep HDN was not achieved after reducing the final boiling point of the starting material below 343°C [87].

Even in cases when reducing the final boiling point of the shale-oil feedstock is beneficial for deep hydrotreating, the reduction results in substantial losses of the naphtha and MD products yielded from the heavier fractions as a result of removal of the heteroatoms from the high-molecular weight substances. Hydrotreating of whole shale oils with commercial Ni–Mo–Al catalysts yields about 40% conversion of heavy fractions into white products [29,96,97], while hydrotreating of shale oil with a reduced final boiling point ranging 350–400°C is accompanied by negligible or modest changes in distillation patterns, being mostly a result of hydrocarbon hydrocracking [88].

There are no indications for the existence of any special shale oils with nitrogen contents far below 0.8–1 wt%. Together with the considerations discussed above, this means that the opportunities to reach deep hydrotreating of shale oils by selection of proper feedstock are limited.

3.3.2. *Process severity and mode*

Shifting the hydrotreating of shale oil to the deep mode by increasing the process severity is problematic. The available data corresponding to conditions defined as 'normal' were obtained at temperatures >400°C, i.e., close to the 'end of the run' for normal hydroprocessing of crude oil heavy distillates. Information about the stability of the catalysts during the hydrotreating of shale oils at such temperatures is limited. The Ni–Mo–Al catalysts showed stable performance at 400°C in hydrotreating of Rundle and Irati shale oils during 30–72 h [96,114], but it has been reported that after 220 h of hydrotreating of Irati shale oil with the Ni–Mo–Al catalyst at 125 atm, 1 h^{-1} LHSV and 410°C, the density and viscosity of the product were increased due to partial catalyst deactivation [132]. In the long run, serious deactivation problems may thus be envisaged as a result of coking, so that there is a requirement of decrease rather than increase in the temperature of 'normal' hydrotreating.

Decreasing the LHSV to 0.4–0.6 h^{-1} facilitates a reduction of the residual nitrogen content towards to 0.05–0.1 wt% [29,92,93], apparently solving the deep HDO problem. But a further increase in the space-time does not seem to be realistic, making the upgrading of shale oils noncompetitive with the corresponding hydroprocessing of crude oils, even if the costs for retorting or thermodissolving of kerogen are not taken into account.

High hydrogen pressures of up to 150 atm are required for hydrotreating shale oils [87,92–96], even for the 'normal' hydrotreating that is necessary – for kinetic and thermodynamic reasons – for intermediate hydrogenation of nitrogen- and oxygen-containing compounds [111,112,119]. Improvement in the HDN efficiency of shale oils by increasing the pressure beyond 150 atm looks doubtful. For crude oil, vacuum gas oils and residua, complete nitrogen removal was not achieved at about 400 atm, and there was a gradual decrease in nitrogen concentration in the products up to 1600 atm [127]. At 210 atm hydrogen pressure, the hydrogenation of pyrrolic compounds still remained the limiting step in HDN with a Co–Mo–Al catalyst at 350–400°C [128]. Taking into account the high costs of running the process at ultra-high pressures, the transition of shale-oil hydrotreating to the deep mode by further increasing the hydrogen pressure is also unrealistic.

In contrast to HDS, which is inhibited by hydrogen sulfide, HDN of nitrogen-containing compounds with the Co(Ni)–Mo–Al catalysts is accelerated in the presence of H_2S at temperatures >325°C [112–130]. Therefore, staging should not be necessary to enhance the HDN efficiency of shale oils, since they are deeply desulfurized in a one-stage process. Addition of a second stage with the same Ni–Mo–Al catalyst facilitated an increase in the overall HDN of Israeli or Irati shale oils only by about 10%, despite the increase in the overall space-time and the increase in temperature in the second stage [29,96]. A multistep process involving continuous hydrotreating of shale-oil distillate fractions, with inclusion of the products from delayed coking of the heavy part, facilitated removal of 98% of the nitrogen [131].

Staging could be favorable for deep hydrotreating of shale oil when different catalysts are used at the first and second stages [97,133]. It was shown that hydrotreating of Israeli shale oil with a wide-pore Ni–Mo–Al catalyst converted the high-molecular weight N compounds, apparently the N-heterocyclic parts of large asphaltene and asphaltol molecules, into low-molecular weight N-compounds with increased mobility, as a result of HDS/HDO [97]. These low-molecular weight nitrogen-containing compounds were effectively denitrogenated in the second stage with a narrow-pore Co–Mo–Al zeolite catalyst, leaving <0.002 wt% nitrogen in the product at 380°C. Loading the same two catalysts into a single reactor in series facilitated >98% HDN of Israeli shale oil at 380–390°C [133].

3.3.3. *HDN activity of the catalysts*

As was the case for sulfur removal from MD, the HDN kinetics of hydrocarbon feedstocks at fixed hydrogen pressures could be empirically described by the power law according to Eqs. (7) and (8). In this case, HDS of real feedstocks may be described by a pseudo-first-order equation (Eq. (5)), while HDN of individual nitrogen compounds conforms to reaction orders of less than unity [112]. Because the overall hydrotreating efficiency of the shale oils is limited by HDN, the requirements for improving the catalyst's activity – in order to reach deep hydrotreatment – could be estimated on the basis of residual nitrogen concentrations (0.5 wt% for 'normal' and 0.05 wt% for deep hydrotreatment) and a pseudo-first-order kinetic equation (Eq. (5)). Reducing the outlet nitrogen concentration in shale oil with $N_o = 1.5$ wt% from 0.5 to 0.05 wt% at 1 h^{-1} LHSV requires an increase in the HDN rate constant (representing the catalyst's activity) by a factor of 3.1, i.e., about two times higher than the requirement for increasing the catalyst's activity in order to perform deep HDS of crude-oil MD, which is a very complicated problem using the traditional approach for development of the hydrotreating catalysts of the Co(Ni)–Mo(W)–Al type. This corresponds to the relative HDN reactivities of nitrogen compound groups in shale oils, given in Table 9: the average reactivity of the least-reactive groups – pyrroles, hindered pyridines, and N-alkylated pyridines and pyrroles – is about three times lower than that of the highly reactive groups.

3.3.4. *Alternative catalytic routes*

Based on the available information about the limiting steps of HDN and HDO of the least-reactive nitrogen- and oxygen-containing compounds discussed above, it could be supposed that:

- increasing the efficiency of removal of hindered pyridines requires a substantial increase in the hydrogenolysis rate of their hydrogenated products;
- increasing the efficiency of removal of pyrroles and benzo (and dibenzo) furans requires a parallel increase in the hydrogenation and hydrogenolysis rates of their hydrogenated products, while keeping the balance between these two functions; and
- increasing the efficiency of removal of hindered phenols requires acceleration of their conversion via a consecutive route 'hydrogenation' (similar to that of 4- and/or 6-diMe-DBT HDS); other transformations of *ortho*-substituted phenols, like dealkylation, positional isomerization of alkyl groups and transalkylation, should be favorable as intermediate steps in consecutive alternative catalytic routes.

No data are available on the effectiveness of alternative catalytic routes in HDN and HDO, with one exception: It has been proved that increasing the acidity of the Ni(Co)–Mo(W)–Al catalysts by the introduction of halogens [134–136] or acidic zeolites [97,98,133,137–139] increases their HDN efficiency. This is apparently the result of opening an additional parallel route for denitrogenation of hydrogenated pyridines via β-elimination or nucleophilic displacement involving adsorption on acid sites with the formation of the carbonium ion, in addition to hydrogenolysis on the sulfide sites [111,112,139].

Introduction of zeolite HY into the Ni–Mo–Al catalyst increased the selectivity of tetrahydroquinoline conversion to the final HDN product, propylcyclohexane, by 1.3–3.2 times, depending on the space-time, while with the reference Ni–Mo–Al catalyst, the main product was *ortho*-propylaniline [139]. A Ni–W catalyst supported on amorphous Al–Si almost completely removed the alkylpyridines and quinolines from Rundle shale oil, but the Ni–Mo and Co–Mo catalysts supported on less acidic alumina left about 50% of alkylpyridines and anilines in the polar material of hydrotreated shale oil [114]. Introduction of zeolite USY [98,137,138] or HY [97,133] into the Co–Mo–Al catalyst facilitated the deep denitrogenation of Occidental and Israeli shale oils in one-stage (415–430°C) and two-stage (380–390°C) processes, respectively.

4. Conclusions

4.1. *Crude-oil MD*

Transition from 'normal' to deep desulfurization of crude-oil MD requires technical solutions facilitating desulfurization of the DBTs alkylated in the 4- and/or 6-positions that remain unconverted in 'normal' commercial desulfurizers.

The relevant technical solutions comprise combinations of the following changes in the process mode and catalyst properties:

1. Selecting a feedstock with a final boiling point of <320°C.
2. Increasing the process severity, mainly by reducing the LHSV by more than two-fold.
3. Dividing the process into two stages, with intermediate removal of H_2S, or supplying the reactor with a hot, high-pressure H_2S separation pathway through the catalyst layer.
4. Use of a the partially sulfided or oxyregenerated catalyst with continuous addition of fresh catalyst in the second stage.
5. Increasing the activity of the classical Co–Mo–Al catalyst by a factor of 2 to give <0.05 wt% residual sulfur or a factor of 5 to give <0.01 wt% residual sulfur.
6. Use of a catalyst displaying both high activity in the hydrogenolysis of sulfur-containing compounds and significant activity in the hydrogenation of the aromatic rings in 4- and/or 6-alkyl-DBT, in dealkylation, in cracking of the thiophenic C–C bond, in positional isomerization of alkyl groups or in transalkylation, facilitating the removal of the steric hindrance of alkyl groups in consecutive alternative catalytic routes.

4.2. *Shale oils*

Deep hydrotreating of shale oils is limited by HDN of substituted pyrrols and hindered alkylpyridines. To some extent, it is also limited by HDO of *ortho*-substituted alkylphenols and dibenzofurans, although desulfurization to <0.05 wt% residual sulfur is not a problem. The possibility of reaching deep hydrotreating of shale oils by selecting a proper feedstock, increasing the process severity or changing the process mode are limited. Deep denitrogenation to <0.05 wt% residual nitrogen requires increasing the activity of conventional Ni(Co)–Mo–Al catalysts by a factor of 3. Use of catalysts displaying higher acidity and significant activity in hydrogenation of aromatic rings, dealkylation, positional isomerization or transalkylation could enable deep hydrotreating of shale oils at 'normal' conditions, as a result of opening of new, parallel and consecutive alternative catalytic routes for conversion of the least-reactive nitrogen- and oxygen-containing compounds.

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