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HDS kinetics study of dibenzothiophenic compounds in LCO

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Abstract

HDS kinetics experiments were conducted in a pilot plant trickle-bed hydrotreater packed with a commercial $NiMo/Al_2O_3$ hydrotreating catalyst and a commercial sample of fluid catalytic cracking light cycle oil (LCO). Speciation of dibenzothiophenic compounds in the feed and hydrotreated effluents was conducted using a GC-AED method developed in-house. It was found that at high temperature (above 385 °C) the hydrogenation/dehydrogenation equilibrium effect became significant and the HDS kinetics of each individual sulphur compound was no longer of pseudo-first order. Therefore, a two-route HDS kinetics model was used to model the hydrogenation/dehydrogenation equilibrium effect by assuming first-order reactions with respect to sulphur, and zero-order with respect to hydrogen for the four reactions involved. The kinetics parameters for each reaction were determined for 14 dibenzothiophenic compounds based on experimental data. As expected, the activation energy for dehydrogenation was always higher than that for hydrogenation. The averaged difference between these two activation energies was about 43.5 kJ/mol. This difference explained the lower sensitivity of the HDS rate to temperature at higher temperatures. The kinetics parameters showed that the hydrogenolysis route contributed less than the hydrogenation route to the overall HDS, which is consistent with observations reported in other similar studies.

Keywords: Light cycle oil (LCO); Dibenzothiophenic compounds; Hydrogenation/dehydrogenation; Hydrodesulphurization (HDS)

1. Introduction

In the last several years, due to tougher environmental legislation, ultra-low-sulphur diesel (ULSD) fuel production has been a focal point for the petroleum refining industry and research community. Ultra-low-sulphur diesel containing 15 ppm or less sulphur will become mandatory in most developed countries in the next several years [1–3]. Although some new technologies have been proposed and are being commercialized [3,4], it is expected that hydrodesulphurization (HDS) will continue to play the most dominant role in ULSD production [1]. To achieve deep desulphurization, goals also push hydrotreater operation towards higher severity and into a territory that is not as well-known. Process simulation and optimization plays an important role in this transition in helping to maximize catalyst performance and minimize energy and hydrogen consumption. However, process simulation requires detailed HDS kinetics models [5,6] and this paper is an attempt to address this need.

There is an ongoing effort at the National Centre for Upgrading Technology (NCUT) to develop a predictive hydrotreating process model [7]. This model differs from some commercial process simulation programs in its treatment of HDS kinetics. The ''peak-by-peak'' chromatographic analysis of individual sulphur compounds coupled with a large in-house sulphur speciation database, allows us to follow HDS kinetics of individual sulphur species rather than treat sulphur as a single or multiple lump(s). For now, this approach is limited to cracked or pretreated feedstocks in which the number of sulphur species is manageable but a separate effort in identification of all sulphur peeks in any middle distillate is being made.

In a middle distillate feedstock, heavy thiophenic sulphur compounds (dibenzothiophene, naphthothiophene and their alkylated derivatives) are much more difficult to remove by HDS than light thiophenic and aliphatic sulphur compounds. It is these refractory sulphur species that create technological challenges in ULSD production. This study focuses on the HDS kinetics analysis of the most

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refractory sulphur species, especially those with methyl substitutes at 4 and/or 6 positions, such as 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT).

2. Experimental

A detailed description of the experimental set-up, procedure, feed properties, and sulphur speciation analysis has been reported elsewhere [8–10]. Only a brief summary is given below.

A bench-scale tubular reactor with co-current down-flow (trickle flow) of gas and liquid was used to conduct the hydrotreating experiments. The reactor, 100 cm in length and 2.54 cm in diameter (ID), was packed with 150 ml of a commercial $NiMo/Al_2O_3$ hydrotreating catalyst (extrudes of 1.6 mm in diameter and approximately 5 mm in length) and diluted with 0.2 mm glass beads in a 1:1 volumetric ratio. Isothermal operations were maintained for all the experimental runs. The feed used was a commercial sample of fluid catalytic cracking light cycle oil (LCO) with a boiling range of 139.5–446.5 °C. The feed and hydrotreated products were analyzed using standard ASTM methods for C, H, S and N, simulated distillation (SimDis), and density. Sulphur speciation was conducted with GC-AED chromatograms using an in-house-developed method [8–10]. In order to generate kinetics data relevant for commercial operation, the experimental operating conditions covered the commercial range of temperatures, pressures, liquid hourly space velocities (LHSV), gas-to-oil ratios, H_2S and NH_3 concentrations in treat gas, and hydrogen partial pressures. The numerical ranges for all these conditions have been given elsewhere [8]. Since this experimental program took about 100 days to complete, catalyst deactivation was monitored by conducting check-back experiments periodically under the same operating conditions. This procedure allowed decoupling of catalyst deactivation from the performance data.

There is no universal definition as to what group of thiophenic sulphur compounds should be classified as refractory sulphur. Even dibenzothiophene, naphthothiophene and some of their alkyl substitutes can be completely removed under relatively mild hydrotreating conditions [8]. In the present paper we focus our discussion on 14 dibenzothiophene/naphthothiophene derivatives, ranging in reactivity from 4-MDBT to 4,6-DMDBT. These sulphur compounds could not be completely removed in our system (at 375 °C, a LHSV of 1.56 h^{-1}, a gas-to-oil ratio of 1000 NL/kg, and a pressure of 69 atm). These refractory sulphur compounds are listed in Table 1. At this stage, 9 of the 14 dibenzothiophenic/naphthothiophenic compounds are positively identified while the other 5 are referred to by their corresponding GC retention times. For example, RT-107.8 represents the sulphur compound with a GC retention time of 107.8 min.

Table 1
Refractory sulphur compounds investigated in this study

Sulphur compound	Retention time (min)
4-MDBT	91.2
4,6-DMDBT	96.0
4-E-6-M-DBT	100.1
2,4,6-TMDBT	101.0
3,4,6-TMDBT	103.5
1,4,6-TMDBT	104.2
1,4,7-TMDBT	104.4
RT-104.6	104.6
3,4,7-TMDBT	104.9
RT-105.7	105.7
PN(4,5)T	107.1
RT-107.8	107.8
RT-108.1	108.1
RT-108.9	108.9

3. Kinetics modeling

HDS kinetics modeling has been an important research subject in the past three decades. Numerous kinetics models have been reported in the literature. These published studies can be divided into three different categories:

1. Reaction mechanism studies using model sulphur compounds (such as DBT, 4,6-DMDBT) dissolved in pure solvents and with either commercial hydrotreating catalysts or laboratory-made hydrotreating catalysts. A Langmuir–Hinshelwood type of kinetics model was generally applied with a number of kinetics parameters evaluated for each model compound [11–14].
2. Apparent reaction kinetics studies using real petroleum feedstocks and commercial hydrotreating catalysts. In these studies relatively simple kinetics models were assumed, such as pseudo-first order or *n*-th power law, and the sulphur compounds in the feeds were either lumped together or treated individually [8,15–20].
3. Sophisticated kinetics studies at the molecular level with real petroleum feedstocks. The HDS kinetics of various aromatic sulphur compounds were modeled by a so-called structural contribution approach [6,21]. These were relatively rare because of the need for estimation of a large number of kinetics parameters, even after model simplification.

In this paper we use simplified models to establish the HDS kinetics of the 14 refractory sulphur compounds.

3.1. Experimental observations

Fig. 1(a) and 1(b) show the plots of $\ln(-Sv\ln(C/C_0))$ versus $1/T$ for 4-ethyl-6-methyl-dibenzothiophene (4E-6M-DBT) and phenanthro(4,5)thiophene [PN(4,5)T], respectively, where C and C_0 are the total sulphur concentrations at reactor inlet and outlet, respectively, T is the absolute reactor temperature, and Sv is the liquid hourly space

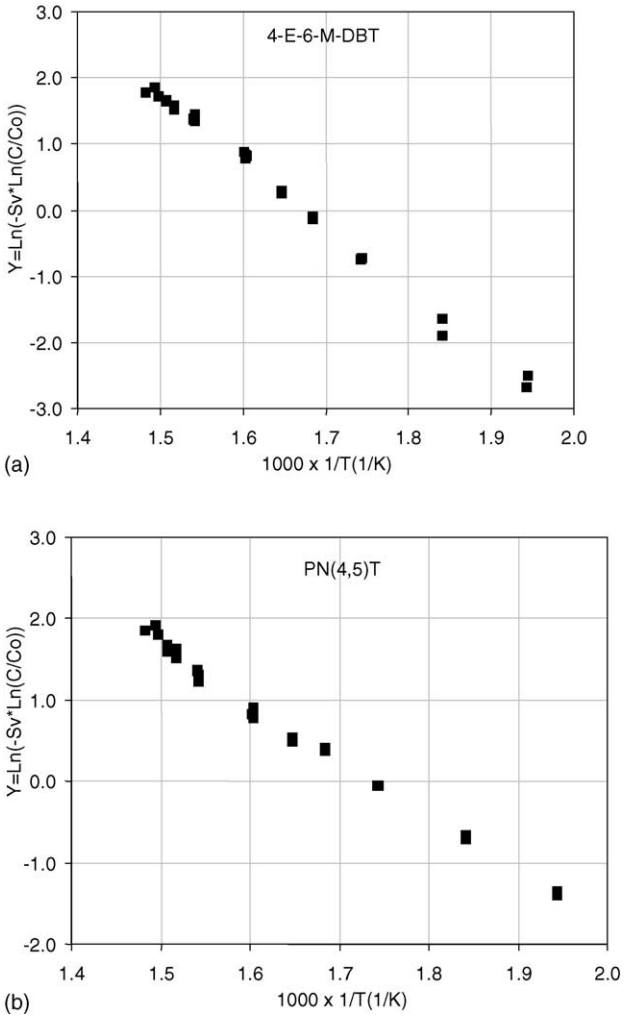

Fig. 1. HDS reactivity with temperature: (a) (4-E-6-M-DBT); and (b) (PN(4,5)T).

velocity. These two plots are typical for the group of 14 dibenzothiophenic compounds identified above. The operating conditions were: pressure of 69 atm, LHSV of 1.56 h^{-1}, gas/oil ratio of 1000 NL/kg, and H_2S concentration in treat gas of 0.5 vol.%. For a first-order reaction conducted in a plug-flow reactor, $(-Sv \ln(C/C_0)$ represents the reaction rate constant (k). Therefore, according to Arrhenius equation the plots of $\ln(-Sv \ln(C/C_0))$, or $\ln(k)$, versus $1/T$ should yield a straight line with the slope and intercept representing the activation energy (E_a) and pre-exponential factor (k_0), respectively. In Fig. 1(a), $\ln(-Sv \ln(C/C_0))$ versus $1/T$ can be approximated as a straight line when the temperature is below 385 °C. However when the temperature is higher than 385 °C $\ln(-Sv \ln(C/C_0))$, the activation energy decreases with increasing severity, indicating the decreasing sensitivity of the overall reaction rate to temperature. This well-known behaviour has been reported earlier [8,9] and by other researchers [15], and it has been attributed to the hydrogenation/dehydrogenation equilibrium effect. In addition, the vapour–liquid phase equilibrium effect might also play a role in reduced temperature sensitivity at high temperature, because under these conditions, over 50% of the sulphur compounds (DBTs) might be present in the vapour phase, which could not directly contact with the catalyst surface for HDS reactions. The vapour–liquid phase equilibrium study of the system is underway at NCUT and the results will be published in the near future. In this paper, the phase equilibrium effect is not taken into account. Nevertheless the commonly used pseudo-first order reaction kinetics model is no longer applicable in this temperature range [8]. Careful visual examination reveals two differences between Fig. 1(a) and (b). First, above 385 °C the trend of $\ln(-Sv \ln(C/C_0))$ versus $1/T$ in Fig. 1(a) is flatter than that in Fig. 1(b), indicating that the hydrogenation/dehydrogenation equilibrium affect more 4E-6M-DBT than PN(4,5)T. Second, the trend in Fig. 1(b) shows an ''inflexion point'' in the middle of the temperature range (about 350 °C), indicating decreased activation energy, while in Fig. 1(a) no ''inflexion point'' is observed. This ''inflexion point'' cannot be explained by the pseudo-first order reaction assumption either, and it is discussed further below.

It is well accepted that HDS of dibenzothiophenic and naphthothiophenic compounds hydrotreated over NiMo and CoMo-based catalysts progresses through two reaction routes: direct HDS by hydrogenolysis of the reactants and indirect HDS by hydrogenation of one of the two aromatic rings followed by C–S bond cleavage of the hydrogenated intermediate products [5,6,11,12,15,18,22]. With NiMo-based catalysts, such as the one used in this study, the indirect route plays a more important role [5,15]. Since the hydrogenation reaction is reversible, at higher temperatures equilibrium limitation becomes significant and, therefore, raising reactor temperature does not effectively increase the HDS conversion.

As mentioned earlier, the catalyst deactivation was monitored throughout this experimental program. From the start to the end of the program the catalyst activity decreased on average by about 40%. The deactivation rate varied during the program and was the highest during the catalyst age from 1200 to 1500 h. Fig. 2(a) and (b) show the catalyst deactivation, represented by the change in the pseudo-first order reaction rate constant with time for 4E-6M-DBT and PN(4,5)T, respectively. Clearly, there is no significant difference in the shape of the two curves, which suggests on the one hand that the catalyst deactivates similarly for both molecules and, on the other, that these data are quite consistent. All the experimental results presented in this paper have been corrected for catalyst deactivation.

3.2. Kinetics modeling with the two-route model

Fig. 3 illustrates the two-route HDS kinetics model. Assuming first-order reactions with respect to sulphur, and zero-order with respect to hydrogen (large excess hydrogen was used in our experiments) for all four reactions, the HDS reaction rates can be written as:

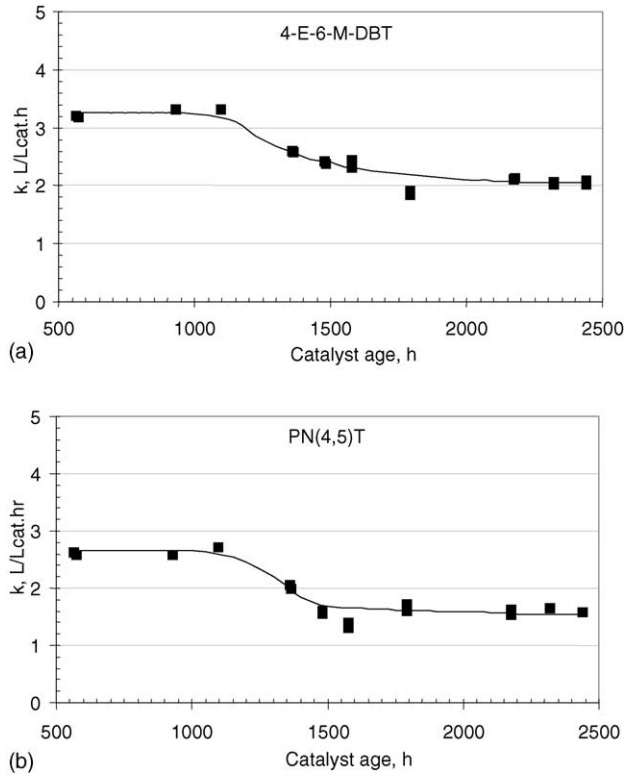

Fig. 2. Catalyst deactivation with time: (a) (4-E-6-M-DBT); and (b) (PN(4,5)T).

- Direct route:

$$r_{\mathrm{HDS1}} = k_1 C_{RR'\mathrm{DBT}} \tag{1}$$

k_1 is the direct hydrogenolysis reaction rate constant; RR'DBT is RR'dibenzothiophene, and R or R' can be any possible alkyls at any possible positions.

- Indirect route:

$$r_{\mathrm{HDS2}} = k_2 C_{RR'\mathrm{DBT}} - k_3 C_{RR'\mathrm{THDBT}} \tag{2}$$

$$r_{RR'\mathrm{THDBT}} = k_2 C_{RR'\mathrm{DBT}} - k_3 C_{RR'\mathrm{THDBT}} - k_4 C_{RR'\mathrm{THDBT}} \tag{3}$$

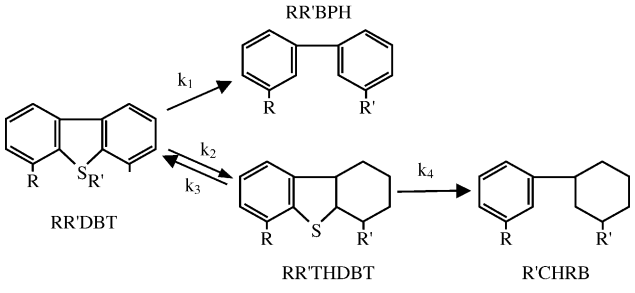

Fig. 3. General two-route reaction kinetics model (RR'DBT: RR'dibendibenzothiophene; RR'BPH: RR'biphenyl; RR'THDBT: RR'tetrahydroditetrahydrodibenzothiophene; R'CHRB, R'cyclohexylRbezene. R, R' can be any possible alkyls at any possible positions).

k_2 and k_3 are the hydrogenation and dehydrogenation rate constants; RR'THDBT: stands for RR'tetrahydrodibentetrahydrodibenzothiophene; and k_4 is the C–S bond cleavage reaction rate constant.

In Fig. 3, it is assumed that the hydrogenation of RR'DBT to RR'THDBT is a reversible reaction. In the mean time, RR'THDBT is further converted into R'CHRB through C–S bond cleavage. Generally, the reversible hydrogenation of RR'DBT to RR'THDBT cannot be assumed at thermodynamic equilibrium unless the following C–S bond cleavage reaction rate (k_4) is small enough. However, experimental measurements have showed that the concentration of hydrogenated intermediates (RR'THDBT) in the HDS reaction product was very small [21]. Therefore, as the first approximation, we assume that the net rate of RR'THDBT formation is close to zero ($r_{RR'\mathrm{THDBT}} = 0$) [5], combining Eqs. (1)–(3) yields the total HDS reaction rate:

$$r_{\mathrm{HDS}} = \left(k_1 + \frac{k_2 k_4}{k_3 + k_4}\right) C_{RR'\mathrm{DBT}} = k_{\mathrm{HDS}} C_{RR'\mathrm{DBT}} \tag{4}$$

The reaction rate constants can be expressed by Arrhenius equation:

$$k_i = k_{i,0} \exp\left(-E_{\mathrm{a}_i}/RT\right), \quad i = 1, 4 \tag{5}$$

where $k_{i,0}$ is the pre-exponential factor, E_{a_i} the activation energy, T the temperature, and R the gas rate constant.

4. Results and discussion

The pre-exponential factors and activation energies in Eq. (5) for all the 14 refractory sulphur compounds were obtained by fitting the kinetics model (Eq. (4)) to our experimental data. The values of these parameters are shown in Table 2 and the model fits for 4-4E-6M-DBT and PN(4,5)T are shown in Fig. 4(a) and (b).

In Table 2, the activation energies for the direct hydrogenolysis (k_1) route range from 99.3 to 144 kJ/mol. The activation energies for hydrogenation reactions (k_2) are in the range of 82.7–120 kJ/mol, while those for dehydrogenation reactions (k_3) are in the range of 121–147 kJ/mol. The activation energies for the C–S bond cleavage reactions of the hydrogenated intermediate products (k_4) are in the range of 80.9–92.6 kJ/mol. As expected, the activation energy for dehydrogenation is always higher than that for hydrogenation. The averaged difference between these two activation energies is about 43.5 kJ/mol.

In Fig. 4(a), the model for 4E-6M-DBT follows the loss of temperature sensitivity with increasing temperatures (hydrogen/dehydrogenation equilibrium effect). The "inflexion point" for PN(4,5)T is fairly well captured by the model, as shown in Fig. 4(b). Clearly, the combination of different first-order reactions (shown in Fig. 3) with different activation energies can result in a complicated apparent kinetic behaviour. In most of the temperature range used, the

Table 2
Kinetics parameters obtained by fitting experimental data with kinetics model

S compound	Hydrogenolysis		Hydrogenation		Dehydrogenation		C–S bond cleavage	
	k_{01}	Ea_1	k_{02}	Ea_2	k_{03}	Ea_3	k_{04}	Ea_4
4-MDBT	2.67E+09	1.16E+05	4.17E+10	1.20E+05	1.32E+14	1.47E+05	7.21E+09	8.61E+04
4,6-DMDBT	1.52E+09	1.29E+05	2.68E+08	9.55E+04	1.64E+14	1.45E+05	8.02E+09	9.02E+04
4-E-6-M-DBT	6.34E+08	1.25E+05	3.19E+08	9.55E+04	1.53E+14	1.45E+05	3.75E+09	8.61E+04
2,4,6-TMDBT	2.77E+08	1.06E+05	2.03E+08	8.94E+04	6.29E+14	1.45E+05	3.17E+09	8.57E+04
3,4,6-TMDBT	2.47E+07	9.93E+04	9.79E+07	8.27E+04	1.27E+12	1.21E+05	1.68E+08	8.09E+04
1,4,6-TMDBT	4.26E+08	1.07E+05	7.93E+07	8.88E+04	3.09E+12	1.33E+05	1.05E+09	8.37E+04
1,4,7-TMDBT	4.67E+08	1.08E+05	1.04E+08	8.91E+04	1.43E+12	1.26E+05	6.20E+08	8.16E+04
RT-104.6	1.02E+09	1.15E+05	9.10E+08	8.82E+04	1.06E+13	1.29E+05	1.04E+08	8.30E+04
3,4,7-TMDBT	4.83E+09	1.19E+05	1.21E+09	9.69E+04	1.20E+14	1.39E+05	2.42E+09	8.78E+04
RT-105.7	3.18E+10	1.27E+05	1.78E+09	9.63E+04	3.83E+14	1.47E+05	1.30E+09	9.11E+04
PN(4,5)T	4.38E+11	1.44E+05	5.67E+09	9.79E+04	3.27E+14	1.42E+05	2.75E+08	8.47E+04
RT-107.8	9.03E+09	1.29E+05	4.35E+09	9.59E+04	4.51E+14	1.43E+05	1.87E+09	9.26E+04
RT-108.1	1.29E+11	1.37E+05	6.12E+09	9.63E+04	3.32E+14	1.42E+05	1.45E+09	9.18E+04
RT-108.9	2.24E+10	1.28E+05	6.84E+09	1.04E+05	3.49E+14	1.45E+05	1.54E+09	9.05E+04

fit between the model's calculated and experimental values is reasonably good. This is also true for the other 12 sulphur compounds. However, a better fit would be expected if the vapour–liquid phase equilibrium effect were taken into account. Such an effort will be made and published in the future.

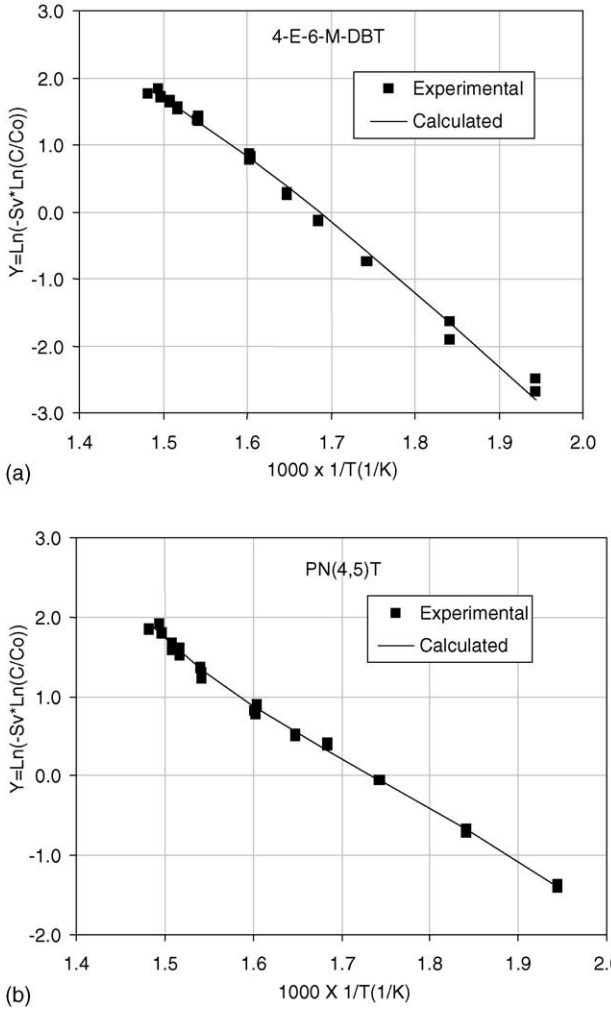

Fig. 4. Experimental data and kinetics model prediction: (a) (4-E-6-M-DBT); and (b) (PN(4,5)T).

By using the kinetics parameters listed in Table 2, the values of k_1 and k_{HDS} in Eq. (4) were calculated at two temperatures, 360 and 400 °C, as shown in Table 3. The values of k_1/k_{HDS} are also listed in the table. Assuming that this kinetics model is correct and neglecting the vapour–liquid phase equilibrium effect, k_1/k_{HDS} represents the contribution of HDS through hydrogenolysis to overall HDS. It is noted in Table 2 that at both temperatures k_1/k_{HDS} is less than 0.5 for all the sulphur compounds discussed in this study except for RT-105.7, which has the k_1/k_{HDS} value slightly higher than 0.5 (0.53) at 400 °C. This observation indicates that for those DBTs with substituting methyl/ethyl groups at 4 and/or 6 positions the hydrogenolysis route contributes less than the hydrogenation route to the overall HDS rate. Similar observations have been reported in the literature [18,23,24]. Our preliminary quantum chemistry simulation results also showed that the methyl groups at 4

Table 3
Reaction rate constants

S compound	k_1 (h^{-1})		k_{HDS} (h^{-1})		k_1/k_{HDS}	
	360 (°C)	400 (°C)	360 (°C)	400 (°C)	360 (°C)	400 (°C)
4-MDBT	0.68	2.53	4.90	16.78	0.14	0.15
4,6-DMDBT	0.035	0.15	2.30	5.21	0.015	0.028
4-E-6-M-DBT	0.031	0.13	2.80	6.26	0.011	0.020
2,4,6-TMDBT	0.50	1.67	2.75	5.31	0.18	0.31
3,4,6-TMDBT	0.16	0.48	3.47	6.29	0.045	0.077
1,4,6-TMDBT	0.62	2.09	3.61	9.14	0.17	0.23
1,4,7-TMDBT	0.57	1.92	3.64	8.81	0.16	0.22
RT-104.6	0.33	1.20	2.92	5.48	0.11	0.22
3,4,7-TMDBT	0.71	2.72	3.94	8.83	0.18	0.31
RT-105.7	1.01	4.24	3.29	8.06	0.31	0.53
PN(4,5)T	0.61	3.09	2.82	6.65	0.22	0.46
RT-107.8	0.21	0.88	3.33	6.23	0.062	0.14
RT-108.1	0.64	3.01	4.34	9.40	0.15	0.32
RT-108.9	0.62	2.61	2.85	6.77	0.22	0.39

and/or 6 positions of substituted DBTs prevent the bonding of the sulphur atom with the molybdenum atom on catalyst surface in the perpendicular mode adsorption, which leads to the hydrogenolysis of the sulphur compounds [25]. However, these methyl groups do not inhibit the bonding of the sulphur atom with the catalyst surface in the flat adsorption mode, which favorites the hydrogenation of the aromatic rings of the sulphur compounds [25]. As seen in Table 3, those DBTs with the strongest sterical hindrance effect by the methyl/ethyl groups at 4 and 6 positions, such as 4,6-DMDBT, 4-E-6-M-DBT, and 3,4,6-TMDBT, have k_1/k_{HDS} values even less than 0.1, indicating that the hydrogenation route is dominant. On the other hand, 1,4,6-TMDBT and 2,4,6-TMDBT, which also have two methyl groups at 4 and 6 positions, have higher k_1/k_{HDS} values than 4,6-DMDBT, 4-E-6-M-DBT, and 3,4,6-TMDBT. A possible explanation for this observation is that the third methyl group at the remote position from the sulphur atom slightly enhances the perpendicular adsorption (note that even 3,4,6-TMDBT has slightly higher k_1/k_{HDS} value than 4,6-DMDBT and 4-E-6-M-DBT) and therefore enhances the hydrogenolysis of these sulphur compounds. Although no other direct observations or quantum chemistry computations have been found in the literature to support such an explanation, it has been reported that the methyl group at remote positions from the sulphur atom in DBTs has positive effect on the overall HDS (enhances the overall HDS reaction rate) [10,26–28]. In Table 3, it is also noted that k_1/k_{HDS} increases with the increase in temperature (almost doubled from 360 to 400 °C except for 4-MDBT), indicating an increasing contribution from hydrogenolysis to the overall HDS. This observation can be explained with the increased hydrogenation/dehydrogenation equilibrium effect at high temperatures. As discussed earlier, for all the sulphur compounds discussed in this paper the activation energy of the dehydrogenation reaction is higher than that of the hydrogenation reaction. Therefore, increasing temperature is more favourable to the dehydrogenation reaction than to the hydrogenation reaction and the increase in the apparent reaction rate constant through the hydrogenation route ($k_2k_4/(k_3 + k_4)$) with temperature is significantly retarded. However, the apparent reaction rate constant through the hydrogenolysis route (k_1) is not affected and therefore, k_1/k_{HDS} is increased with increased temperature.

5. Summary

The HDS kinetics of 14 refractory dibenzothiophenic sulphur compounds in a LCO was studied. The experiments were conducted over a commercial $NiMo/Al_2O_3$ hydrotreating catalyst in a bench-scale hydroprocessing unit over a wide range of operating conditions to obtain meaningful and reliable kinetics data. The sulphur speciation and quantification were conducted using GC-AED. It was found that the commonly used pseudo-first order reaction kinetics model could not satisfactorily describe the HDS behaviour of the 14 sulphur compounds over the whole temperature range investigated in this study. However, the two-route HDS kinetics model proved to be capable of describing the observed hydrogen/dehydrogenation equilibrium effect at high temperature. The ''inflexion point'' observed in the $\ln(-Sv\ \ln(C/C_0))$ versus $1/T$ curve also could be attributed to a combination of the different first-order reactions with different activation energies based on the two-route HDS kinetics model. The kinetics parameters in the two-route HDS model were determined by fitting the model to experimental data. The activation energy for the dehydrogenation reaction was about 43.5 kJ/mol higher than the corresponding hydrogenation reaction, which explains the observed increased hydrogenation/dehydrogenation equilibrium effect at high temperature. Neglecting phase equilibrium effects, the kinetics data obtained here also suggested that the hydrogenation route contributed more than the hydrogenlysis route in the HDS of these 14 refractory sulphur compounds, which is consistent with experimental observations reported in other similar studies. For those DBTs with methyl/ethyl groups at 4 and 6 positions, which have the strongest sterical hindrance effect, the hydrogenation route was dominant. However, with the increase in temperature the hydrogenation/dehydrogenation equilibrium effect increased and therefore, the contribution of hydrogenation route to overall HDS decreased.

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