Available online at www.sciencedirect.com
SCIENCE @ DIRECT®

Catalysis Today 109 (2005) 16–23

CATALYSIS TODAY

www.elsevier.com/locate/cattod

# Effect of nitrogen removal from light cycle oil on the hydrodesulphurization of dibenzothiophene, 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene

Hong Yang [*], Jinwen Chen, Yevgenia Briker, Renata Szynkarczuk, Zbigniew Ring

*The National Centre for Upgrading Technology, Devon, Alt., Canada T9G 1A8*

---

**Abstract**

Five light cycle oil feeds (LCO) with nitrogen contents ranging from 744.9 to 16.5 mg/L were prepared by removing organic nitrogen compounds gradually through adsorption on a silica column. These feeds were hydrotreated over a commercial Ni-Mo/$Al_2O_3$ catalyst to study the effect of nitrogen compounds on the hydrodesulphurization (HDS) of dibenzothiophene, 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene. It was found that nitrogen compounds had the most negative impact on the HDS of 4- and/or 6-substituted dibenzothiophenes. The temperatures to achieve 50% HDS conversion were 5, 20 and 25 °C lower for dibenzothiophene, 4-methyldibenzothiphene and 4,6-dimethyldibenzothiophene, respectively, when the nitrogen content in the feed was reduced from 744.9 to 16.5 mg/L. Our results also revealed that, at lower temperatures, about 20% of the nitrogen compounds from the original light cycle oil were adsorbed on the catalyst's surface. The HDS of 4,6-dimethyldibenzothiophene was retarded until the HDN rate became greater than the adsorption rate, which might have freed some hydrogenation sites for adsorption. This phenomenon was not observed for the HDS of DBT. Our results suggest that nitrogen compounds and 4,6-dimethyldibenothiophene competed for the same type of active sites, and dibenzothiophene also could have been converted over a different site. In addition, the hydrodenitrogenation activity was also enhanced by the removal of nitrogen compounds. The experimental data was fitted to a Langmuir–Hinshelwood type of kinetic equation by assuming that the inhibition only affected the hydrogenation pathway.

*Keywords:* Dibenzothiophene; Hydrodesulphurization; Nitrogen compounds inhibition

---

## 1. Introduction

The inhibition effect of organic nitrogen compounds on the deep hydrodesulphurization process has become a hot research topic recently as the research community searches for more efficient ways of sulphur removal to meet ever more stringent regulations on sulphur content in diesel fuels. These studies can be divided into two categories: the first covers the use of model nitrogen and sulphur compounds in pure solvents [1–5], and the second deals with the effect of nitrogen on HDS of total sulphur or a group of sulphur species in real feed [6–8]. Only recently, papers were published on the effect of nitrogen on HDS of individual sulphur compounds, especially substituted dibenzothiophenes in studies involving real feeds [9,10]. Most of the quantitative analysis of the inhibition effects in the model compound studies [2,4] was attempted by fitting the Langmuir–Hinshelwood type of kinetics equation. Although the use of a model system simplifies the quantification of the overall inhibition effect for individual sulphur compounds and for the detailed effects on the different reaction pathways, the hydrocarbon matrix of the model feed, which also plays an important role in HDS, was very different from the real feeds encountered under industrial hydrotreating conditions. Therefore, the model compound studies could not fully capture the interactions between different types of hydrocarbons present in a real feed. In order to bridge the gap between the study of inhibition on an individual sulphur compound using a model compound system, and the study of the inhibition effect on total or group sulphur compounds using real feeds, a different approach has been taken at the Canadian National Centre for

---

[*] Corresponding author. Fax: +1 780 987 5349.
*E-mail address:* hyang@nrcan.gc.ca (H. Yang).

0920-5861/$ – see front matter. Crown Copyright © 2005 Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.08.028

Upgrading Technology (NCUT). Nitrogen inhibition effects on individual sulphur compounds were examined using a real feedstock with the nitrogen content adjusted at several levels. This study, complementary to our previously published paper using three LCO feedstocks [9], presents the results obtained with 5 LCO-derived feedstocks with nitrogen contents ranging from 16.5 to 744.9 mg/L.

Twenty-eight mono, di and tri alkyl-substituted dibenzothiophenes were positively identified by GC-AED and using NCUT's database of retention times. They are classified into three groups according to the position of the alkyl substituents. The first group includes dibenzothiophenes without 4 or 6 substituents, the second group includes dibenzothiophenes with either 4 or 6 substituents, and the third group includes dibenzothiophenes with 4 and 6 substituents. Our previous results indicated that each of these groups had distinguishable value of the pseudo-first-order HDS rate constants [11]. In this paper, the nitrogen inhibition effect is examined in detail for dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT), selected as representatives of the three groups of dibenzothiophenes.

U.S. and Canadian refineries will produce ultra-low sulphur diesel starting from June 2006 and January 2007, respectively. Hydrotreating is the main process to reduce the sulphur content in diesel fuel. When the sulphur content is reduced from the current 500 to 15 ppm, refractory sulphur compounds such as DBT, 4-MDBT and 4,6-DMDBT will become the major target in the HDS process. The results obtained in the present work will certainly provide useful information for achieving ultra-low sulphur diesel fuel.

## 2. Experimental

Five feedstocks with varied nitrogen contents and similar hydrocarbon and sulphur compositions were used in this work. LCO from a fluid catalytic cracking unit was used in the preparation of feedstocks. In addition to the original LCO, the other four feedstocks were prepared by passing the LCO through a silica gel column (100 cm × 4.5 cm, 70–230 mesh, Aldrich) by gravity at room temperature. Three fractions – F1, F2 and F3 – with increasing nitrogen contents, were collected at the outlet of the column. Another feedstock, F1 + F2, was prepared by blending a calculated amount of F1 and F2 to obtain a feed with desired nitrogen content.

The hydrotreating experiments were conducted using an automated fixed-bed microreactor (0.635 cm × 30.5 cm) operated in the continuous up-flow mode and heated by a three-zone electric furnace. More information on the reactor system can be found in the work of Yang et al. [12]. A commercial sulphided Ni-Mo/$Al_2O_3$ hydrotreating catalyst was crushed and particles in the size range of 250–500 μm (6 mL) were loaded into the reactor without dilution. The catalyst was sulphided with 3% $H_2S$ in $H_2$ prior to the hydrotreating experiments. The experiments were conducted at a total pressure of 70 atm, temperatures in the range of 240–380 °C, and liquid hourly space velocities (LHSV) between 1.0 and 3.0 $h^{-1}$. The liquid product was collected after the system was brought to a steady state as determined by monitoring the density of the liquid product for each reaction condition. This experimental program took 145 days to complete and the results presented in this paper were collected between the 53th and 145th days. No catalyst deactivation was observed during this time period as indicated by repeated runs at a check-back condition throughout this program.

The concentrations of DBT, 4-MDBT and 4,6-DMDBT were determined from GC-AED sulphur chromatograms. The total nitrogen content was analyzed by GC-NSD. The amount of basic nitrogen was determined as total base number (mg KOH/g sample) using ASTM D2896. Total sulphur was also determined by energy-dispersive X-ray fluorescence spectroscopy (ASTM 4294). Saturate and aromatic contents of the feeds were determined by GC–MS method [12]. ASTM 4052 was used for density (g/mL, 15.6 °C). A detailed description of analytical methods can be found elsewhere [9].

## 3. Results and discussion

### 3.1. Feed preparation

The possibility of nitrogen removal by adsorption through silica column was first tested in a small column (20 cm × 1 cm) loaded with 10 mL silica gel. Several fractions, each about 3.5 mL, were collected and the nitrogen contents were analyzed. Fig. 1 presents the nitrogen concentration in each collected fraction against the total amount of liquid accumulated. The results indicate that a nitrogen content below 10 mg/kg can be obtained for the first liquid fraction. This means that about 4 mL of ultra-low nitrogen feed can be produced with 10 mL silica gel. The nitrogen content increases rapidly as the volume of collected liquid sample increases. After the trial with the small silica column, a larger silica column (100 cm × 4.5 cm) was used to prepare a sufficient amount of feed for the hydrotreating experiment. Three fractions – F1, F2 and F3 – were collected from the "production" column. F1 + F2, as the name suggests, was made of the mixture of F1 and F2. Major physical properties and chemical compositions of the five LCO

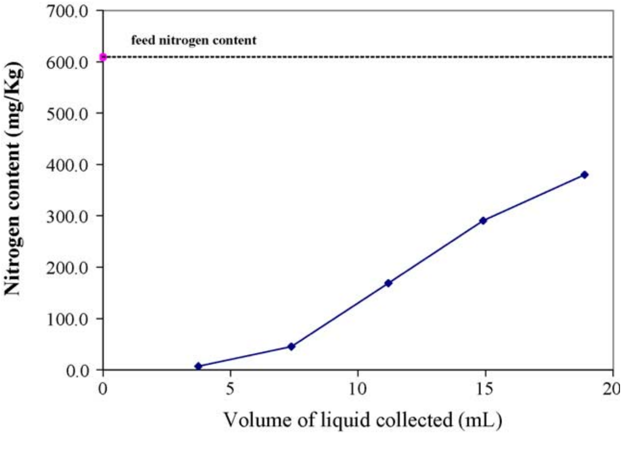

Fig. 1. Nitrogen content in liquid fractions as function of accumulated liquid sample volume (10 mL silica gel).

Table 1
Physical and chemical properties of the LCO feeds

| Feed | Nitrogen (mg/L) | TBN (mg KOH/g) | Sulfur (wt%) | Saturates (wt%) | Aromatics |
|---|---|---|---|---|---|
| LCO | 744.9 | 0.39 | 1.18 | 28.7 | 71.3 |
| F3 | 498.4 | 0 | 1.17 | 29.9 | 70.1 |
| F2 | 339.0 | 0 | 1.18 | 27.6 | 72.4 |
| F1 + F2 | 158.6 | 0 | 1.12 | 29.3 | 70.2 |
| F1 | 16.5 | 0 | 1.11 | 29.8 | 70.7 |

feedstocks used in the hydrotreating experiment are compared in Table 1. The results show that only nitrogen compounds were removed by silica column, while sulphur, saturate and aromatic contents were not altered by the treatment. The fact that only the original LCO contained basic nitrogen compounds indicates that those most polar nitrogen species were completely adsorbed by the silica column. The nitrogen content in the last fraction (F3) is 498.4 mg/L, corresponding to a reduction of 33% from the original LCO. This number is very close to the ratio (0.3) of basic nitrogen to the total nitrogen in a similar untreated LCO used in our previous study [11], which indicates that probably just the basic nitrogen compounds were removed from F3. The feed preparation results in this section indicate that the five LCO feeds had essentially the same chemical compositions with the exception of nitrogen compounds. Therefore, they were suitable for studying the influence of nitrogen compounds on the HDS reaction in a real feedstock. Furthermore, it seems that most of the nitrogen compounds removed in F3 were basic nitrogen, which would provide additional information on how basic and non-basic nitrogen affect the HDS reaction.

### 3.2. *Nitrogen effect on HDS reactivity of dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT)*

Figs. 2–4 compare the conversion of DBT, 4-MDBT and 4,6-DMDBT as a function of reaction temperature, at 70 atm and 1.6 $h^{-1}$ LHSV, in the hydrotreating of the original LCO and ultra-low nitrogen F1. The conversion of nitrogen compounds for the original LCO was also plotted in Fig. 4 (triangles). Comparing LCO and F1, little difference was observed for the conversion of DBT, while a noticeable increase in the conversions of 4-MDBT and 4,6-DMDBT was found. The temperatures required to achieve 50% HDS conversion were estimated by interpolating the conversion-temperature curve. It was found that temperatures of 5, 20 and 25 °C lower were required for DBT, 4-MDBT and 4,6-DMDBT when the nitrogen content in the feed was reduced from 744.9 to 16.5 mg/L.

In HDS, the sulphur atoms in heterocyclic sulphur compounds are removed by two pathways: direct removal by hydrogenolysis, and hydrogenation of one or both aromatic rings followed by C–S bond cleavage. Perpendicular one-point adsorption ($\eta_1$S) and flat multi-point adsorption are believed to be the major configurations separately responsible for hydrogenolysis and hydrogenation pathways. Over a Ni-Mo/$Al_2O_3$ catalyst, DBT reacts mainly through the hydrogenolysis pathway. Due to the steric hindrance of methyl groups in the 4 and/or 6 positions, the direct perpendicular bonding ($\eta_1$S)

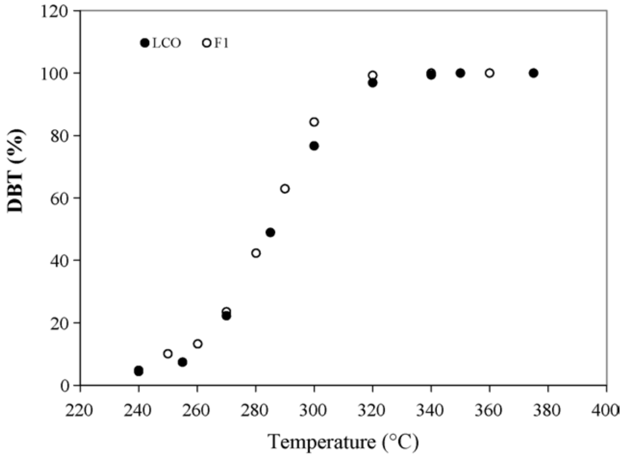

Fig. 2. Comparison of the conversion of DBT as function of reaction temperature in LCO and F1 (70 atm, 1.6 $h^{-1}$).

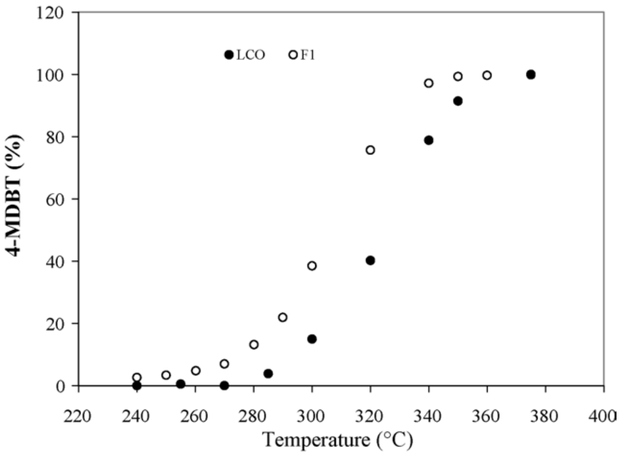

Fig. 3. Comparison of the conversion of 4-MDBT as function of reaction temperature in LCO and F1 (70 atm, 1.6 $h^{-1}$).

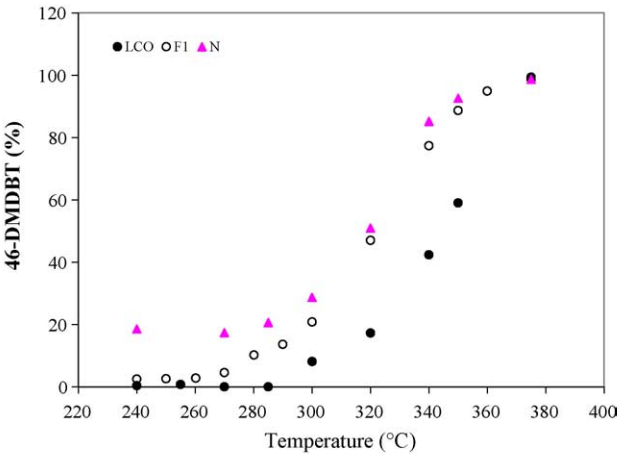

Fig. 4. Comparison of the conversion of 4,6-DMDBT as function of reaction temperature in LCO and F1 (70 atm, 1.6 $h^{-1}$).

through the sulphur atom to the coordinatively unsaturated sites of the catalyst surface becomes difficult. This forces the HDS reaction of 4-MDBT and especially 4,6-DMDBT to rely more heavily on the hydrogenation pathway (involving the flat adsorption configuration) [15–19].

In the present study, when nitrogen content in the feed decreased from 744.9 to 16.5 mg/L, higher drops in temperature are achieved for 4-MDBT and 4,6-DMDBT than for DBT, to obtain the same 50% HDS conversion. The fact that removal of nitrogen compounds promotes the HDS of 4- or/and 6-substituted DBTs indicates that nitrogen compounds preferentially inhibit the hydrogenation pathway. A similar trend was observed by several other research groups [14,19,20]. Nagai et al. studied the effect of acridine on the HDS of dibenzothiophene over a sulfided Ni-Mo/$Al_2O_3$ catalyst. The presence of acridine lowered the amount of cyclohexylbenzene, a product from the hydrogenation path, and enhanced the amount of biphenyl, a product from the hydrogenolysis path [14]. Egorova and Prins approved this finding in studies of the mutual influence of DBT or 4,6-DMDBT with methylpridine [19,20].

Fig. 4 shows that a 20% conversion of nitrogen (triangles) was achieved at temperatures as low as 240 °C for the original LCO feed. However, there was not any HDS conversion until temperatures reached higher than 280 °C. Furthermore, Figs. 3 and 4 also demonstrate that 4-MDBT and 4,6-DMDBT are not reacting at temperatures below 280 and 300 °C, respectively. Their conversions only start after nitrogen compounds begin to react. The observed retardation of the HDS reaction for 4-MDBT and 4,6-DMDBT may be caused by their low reactivity at low temperatures or inhibition by nitrogen compounds. The first possibility can be ruled out based on Fig. 2. With the ultra-low nitrogen feed F1, no such delay of HDS reaction was observed for either 4-MDBT or 4,6-DMDBT. Since 4-MDBT and 4,6-DMDBT are converted predominately by the hydrogenation path, this result suggests that almost all the hydrogenation sites were occupied by the nitrogen compounds at lower temperatures. In the temperature range of 240–280 °C, the concentration of nitrogen in liquid product remained constant.

One reason can be given for the constant nitrogen concentration: at steady-state plug flow, a constant concentration in liquid product could indicate that the active sites necessary for nitrogen removal are saturated and any excess nitrogen remains unreacted. At temperatures above 280 °C, the HDN rate becomes greater than the adsorption rate. 4-MDBT and 4,6-DMDBT molecules can take advantage of the freed active sites, and the HDS reactions start. This interpretation is supported by the conclusion given by Egorova and Prins, who also suggested that hydrogenation sites for nitrogen- and sulphur-containing compounds may be the same, while the C–N and C–S bond breaking may take place at different sites [19]. Another explanation for the unvaried nitrogen concentration may be that, initially, there are enough basic nitrogen compounds (very strongly adsorbed) in LCO to occupy all the available sites, preventing HDS. When the temperature increases and the HDN rate for basic nitrogen compounds increases, the basic nitrogen is depleted and some hydrogenation sites are freed to the competition between DBTs and non-basic nitrogen compounds. However, this possibility can be ruled out by the plots of nitrogen concentration as a function of temperature for feeds F3, F2 and F1 + F2, where basic nitrogen compounds were removed by silica column. In all cases, a constant nitrogen concentration below 280 °C was observed (data not shown).

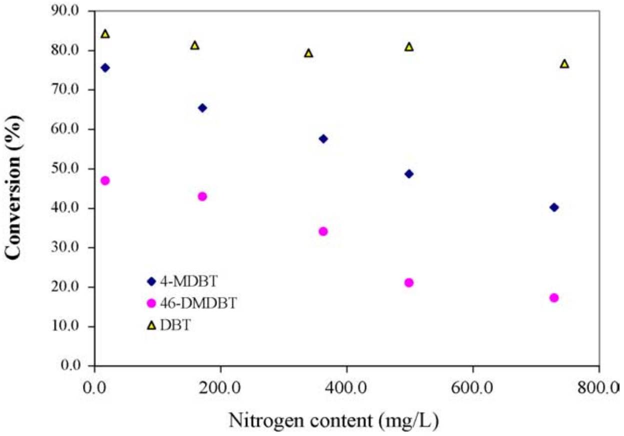

Fig. 5. Conversion of DBT, 4-MDBT and 4,6-DMDBT as function of LHSV (70 atm, 320 °C).

The inhibition of nitrogen compounds on the hydrogenation pathway can also be understood from the reaction mechanism of HDN, where the HDN of the heterocyclic nitrogen compounds generally is thought to proceed through the hydrogenation of the nitrogen atom-containing ring [13]. It is, therefore, reasonable to assume that nitrogen compounds adsorb competitively with sulphur compounds on the hydrogenation sites, and affect only the hydrogenation pathway.

Fig. 5 presents the conversions of DBT, 4-MDBT and 4,6-DMDBT as functions of the total nitrogen content in the feed. The results reveal the same trend as that presented by Figs. 2–4, which indicate that the inhibition effect of nitrogen compounds is more profound for 4-MDBT and 4,6-DMDBT than for DBT. It is worth noting that when feed is changed from the original LCO to F3 (removal of basic nitrogen compounds), no sharp increase in conversion is observed, as we could expect if basic nitrogen had a stronger inhibition effect than non-basic nitrogen. On the contrary, a somewhat smaller increase in conversion is seen when feed is shifted from the original LCO to F3 than when feed is changed from F3 to F2. This result confirms our previous finding and several published papers that the inhibition effect of basic nitrogen is not stronger than that of non-basic nitrogen [9,21,22].

### 3.3. Sulphur composition analysis

Thiophenic, benzothiophenic and dibenzothiophenic sulphur compounds with different types of substituents are the major sulphur species in the LCO used in the current study. They were divided into ‘‘easy’’ sulphur and ‘‘hard’’ sulphur according to their HDS reactivity. Sulphur species, such as thiophenes, benzothiophenes and a small amount of alkyl

Table 2
Distribution of sulphur compounds at different reaction conditions (70 atm, 1.6 $h^{-1}$)

| Sulphur composition (ppm) | Feed | LCO 350 °C | LCO 375 °C | F1 375 °C |
|---|---|---|---|---|
| Total sulphur | 8842.1 | 497.7 | 102.7 | 17.6 |
| Easy sulphur | 4227.6 | 11.1 | 10.4 | 4.6 |
| Hard sulphur | 4614.5 | 481.4 | 91.4 | 12.9 |
| DBTs without 4 and 6 substituents | 810.9 | 2.7 | 0.0 | 0.0 |
| DBTs with 4 or 6 substituents | 867.0 | 68.9 | 11.8 | 0.4 |
| DBTs with 4 and 6 substituents | 314.0 | 100.6 | 9.9 | 2.9 |
| Other hard sulphur | 2622.7 | 309.2 | 69.7 | 9.7 |

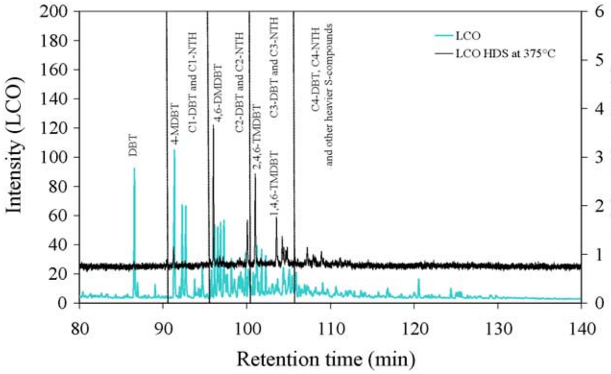

Fig. 6. Comparison of GC-AED sulfur chromatogram of LCO and product of LCO hydrotreated at 375 °C (DBT: dibenzothiophene, NTH: naphothothiophene).

sulphide and mercaptan eluting before dibenzothiophene, are called easy sulphurs. The hard sulphurs include dibenzothiophene, alkyl-substituted dibenzothiophenes, naphthothiophenes, and other heavier unidentified sulfur compounds. Table 2 summarizes the sulphur compositions obtained under three reaction conditions. In addition to total sulphur, easy sulphur and hard sulphur, 28 mono, di and tri C1 to C3 alkyl-substituted DBTs (up to 3 substituents with maximum 3 carbon in total) identified by GC-AED were summarized into three groups according to the position of the alkyl substituents (also listed in Table 2). The original LCO was used for the first two conditions (columns) and F1 was used for the third condition. The total pressure was 70 atm and LHSV was 1.6 $h^{-1}$. The sulphur contents were reduced from 8842.1 to 497.7, 102.7 and 17.6 ppm, respectively. Among those three sulphur contents, the 497.7 ppm is close to the current diesel sulphur specification and the 17.6 ppm sulphur content is close to the future 15 ppm specification. The results indicate that hard sulphur species are the predominant sulphur compounds that remained, regardless of the feed and HDS conditions.

DBTs without 4 and 6 substituents are relatively easy to remove. Using the high nitrogen original LCO feed, at 350 °C, they were reduced to 2.7 ppm (from 810.9 ppm), which corresponds to a conversion of 99.7%. The conversions for DBTs with either 4 or 6 substituents, and DBTs with both 4- and 6 substituents, are 92.1 and 68%, respectively. When the temperature increased to 375 °C, there was a complete conversion of DBTs without 4 and 6 substituents. However, the total sulphur content was only reduced to 102.7 ppm, far from the future 15 ppm specification. Only when the original LCO was replaced by the ultra-low nitrogen LCO (F1), could a total sulphur content close to 15 ppm be achieved. Under this condition, the content of DBTs with 4- or/and 6 substituents was 3.3 ppm. It is interesting to note that even when the content of 4- or/and 6-substituted DBTs is reduced to as low as 20.7 ppm, there is still a substantial amount of other hard sulphur species (49 ppm). Fig. 6 compared the GC-AED chromatograms of the original LCO feed and LCO hydrotreated at 375 °C. It can be observed that in addition to 4- or/and 6-substituted DBTS, there were substantial amounts of other sulphur-containing species that remained after hydrotreatment. Due to an absence of standards, those sulphur species can only be identified according to their masses as C3 substituted naphthothiophenes, C4$^{+}$ alkyl-substituted DBTs, and four-ring sulphur compounds such as benzonaphthothiophenes and phenanthrothiophenes.

HDS of alkyl-substituted DBTs has been studied by several groups. The activities of these DBTs depend mainly on the position of the substituents, which can be divided into three groups: DBTs without 4 and 6 substituents have the highest activity, followed by DBTs with 4 or 6-substitutents, and DBTs with both 4 and 6 positions substituted are the least active sulphur species [9,17,18]. Therefore, we could speculate alkyl-substituted DBTs with more than four carbon atoms in the substituents should have higher HDS activity than 4,6-DMDBT if either of the 4 and 6-positions were not occupied, but they should have similar activity as 4,6-DMDBT (and be converted to the same extent) if both of the 4 and 6 positions were occupied.

Benzonaphthothiophenes and phenanthrothiophenes were hardly studied. Lower HDS reactivity than that of 4,6-DMDBT could be expected for these sulphur compounds, not only because of their bulky molecular structures but also because of the way that thiophene attaches to napththalene or phenanthrene. The latter factor determines the steric effect around the sulphur atoms. Recently, 4,6-DMDBT has been commonly considered as the most refractory sulphur compound in many HDS studies [5,20]. Our results indicate, however, attention should also be paid to benzonaphthothiophenes and phenanthrothiophenes in the deep HDS process.

### 3.4. Hydrodenitrogenation

We used pseudo-first-order kinetics to compare the hydrodenitrogenation (HDN) rates of the five feedstocks. At 320 °C and 70 atm, good linear relationships were obtained between $\ln(C_0/C)$ and 1/LHSV (Fig. 7), where $C_0$ and $C$ are the concentrations of total nitrogen compound in the feed and product, respectively. The results show that the removal of some of the nitrogen compounds enhances the HDN rate of the remaining nitrogen compounds. The greater the initial concentration of total nitrogen compounds, the lower the HDN rate. The experimental HDN rates were found to follow the order: F1 > F1 + F2 > F2 > F3 > LCO.

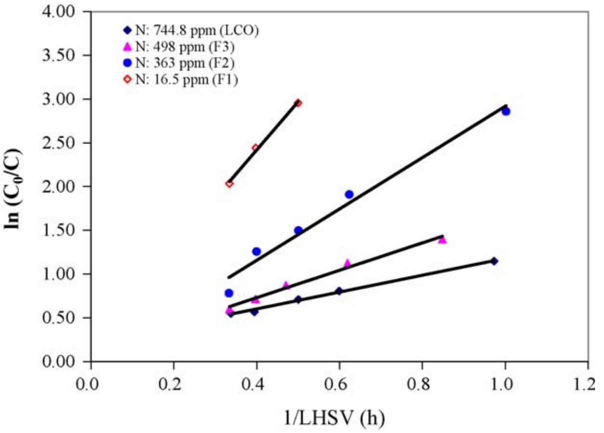

Fig. 7. Comparison of the plots of $\ln(C_0/C)$ as function of 1/LHSV for HDN (70 atm, 320 °C).

Since the HDN rate of basic nitrogen compounds is in general higher than that of non-basic nitrogen compounds [6], we would expect a decrease in the HDN rate of the total nitrogen compounds when the basic nitrogen compounds were removed from the feed, as happened for feed F3. Two factors may be responsible for such an increase in HDN rate: (1) self-inhibition; (2) some of the refractory non-basic nitrogen compounds were also adsorbed by the silica column. Self-inhibition of nitrogen compounds on the HDN rate has already been observed by several groups [6,23,24]. McIlvried found that the HDN of piperidine followed a pseudo-first-order kinetics, and that the HDN rate decreased with the increase in piperidine concentration, implying a self-inhibition of HDN by piperidine. He modeled the piperdine HDN by the following equation:

$$r_{\mathrm{HDN}} = \frac{k * P\mathrm{piperidine}}{1 + K * P\mathrm{piperidine0}} \tag{1}$$

where the subscript 0 denotes initial piperidine partial pressure [23]. To better understand the HDN of individual nitrogen compounds as well as their particular effect on the HDS reaction, NCUT is working on nitrogen speciation and nitrogen distribution by boiling point, and detailed HDN results will be available in the future. In this section, pseudo-first-order kinetics was used to quantitatively compare the HDN rate under various nitrogen levels; a more sophistic kinetic expression is suggested in the next section on kinetic modeling.

### 3.5. Kinetic modeling

As mentioned in Section 3.2, the HDS of heterocyclic sulphur compounds proceeds through two reaction pathways: direct removal by hydrogenolysis and hydrogenation of one or both aromatic rings followed by C–S bond cleavage. The total HDS rate for an individual sulphur compound can be expressed by the following equation:

$$r_{\mathrm{HDS}} = r_{\mathrm{D}} + r_{\mathrm{H}} \tag{2}$$

where $r_{\mathrm{D}}$ represents the hydrogenolysis rate and $r_{\mathrm{H}}$ represents the hydrogenation rate. If we assume that the rate-limiting step is a surface reaction between molecularly adsorbed hydrogen on one site, and a sulphur compound on the other sites, the inhibition effect of sulphur compounds and $H_2S$ is negligible compared to nitrogen compounds. From published results and our present work [9], it seems that nitrogen compounds compete with sulphur compounds only on the hydrogenation sites and inhibit the hydrogenation path way. Therefore, under excess of hydrogen, a Langmuir–Hinshelwood equation as below can be used to analyze the kinetic data for sulphur and nitrogen compounds:

$$\frac{\mathrm{d}C_i}{\mathrm{d}Z} = -\frac{1}{\mathrm{LHSV}}\left(k_{\mathrm{D}}C_i + \frac{k_{\mathrm{H}}C_i}{1 + K_{\mathrm{N}}C_{\mathrm{N}}^n}\right) \tag{3}$$

$$\frac{\mathrm{d}C_{\mathrm{N}}}{\mathrm{d}Z} = -\frac{1}{\mathrm{LHSV}}\left(\frac{k_{\mathrm{N}}C_{\mathrm{N}}}{1 + K_{\mathrm{N}}C_{\mathrm{N}}^n}\right) \tag{4}$$

where $C_i$ is the concentration of an individual sulphur compound, $Z$ a dimensionless reactor bed length and LHSV is the hourly liquid space velocity. In the inhibition term, we used the total nitrogen concentration, $C_{\mathrm{N}}$, and the corresponding adsorption constant, $K_{\mathrm{N}}$, for the total nitrogen. $n$ is a fractional constant to correct the overlooking of nitrogen compound inhibition at lower concentrations [2,25,26].

A Langmuir–Hinshelwood type equation has been widely applied in the kinetics study of HDS reactions, especially in model compound systems. Inhibiting effects of nitrogen compounds using a Langmuir–Hinshelwood type equation have also been reported [2,4,25,26]. Laredo et al. examined the effect of quinoline, indole and carbazole on the HDS of DBT over a Co-Mo/$Al_2O_3$ catalyst in hexadecane [2]. At different nitrogen levels, the HDS of DBT was fitted to a pseudo-first-order rate equation. The HDS rate was expressed as:

$$r_{\mathrm{HDS}} = k'_{\mathrm{DBT}} = \frac{k_{\mathrm{DBT}}C_{\mathrm{DBT}}}{1 + K_{\mathrm{N}}C_{\mathrm{N}}^n} \tag{5}$$

where $k'_{\mathrm{DBT}}$ is the pseudo-first-order rate constant inhibited by the nitrogen compound, $k_{\mathrm{DBT}}$ the intrinsic rate constant, $C_{\mathrm{N}}$ the initial concentration of nitrogen compounds and $n$ is used to correct the underestimation of the adsorption of nitrogen compounds at lower partial pressure. Values of 0.25, 0.5 and 0.5 for $n$ were obtained for quinoline, indole and carbazole. This model did not take into account the variation of nitrogen concentration along the reactor bed nor did it consider the two reaction pathways in the HDS reaction. Ho developed a similar expression as Eqs. (3) and (4) in his study of the inhibiting effect of carbazoles on the HDS of 4,6-ethyldibenzothiophene [4]. He later neglected the variation of $1 + KC_{\mathrm{N}}$ along the reactor length for the nitrogen removal, and simplified Eq. (3) to pseudo-first-order reaction to account for the disappearance of nitrogen compounds along the reactor bed. However, the total HDS rate, without distinguishing between hydrogenolysis and hydrogenation pathways, was considered

Table 3
Kinetics parameters by solving Eqs. (3) and (4) (70 atm, 320 °C)

| | Kinetic parameters | | |
|---|---|---|---|
| | $k_D$ ($h^{-1}$) | $k_H$ ($h^{-1}$) | $k_H/k_D$ |
| DBT | 4.97 | 2.91 | 0.58 |
| 4-MDBT | 0.53 | 1.73 | 3.25 |
| 4,6-DMDBT | 0.23 | 0.76 | 3.26 |
| | $k_N$ ($h^{-1}$) | $K_N$ $(L/mg)^n$ | |
| Total nitrogen | 6.70 | 0.042 | |
| *n* | | 0.73 | |

in their kinetic expression. Our kinetics model has an advantage over the above-mentioned ones in that it not only takes into account of the nitrogen concentration variation along the reactor but also considers the two pathways in the HDS reaction.

Eqs. (3) and (4) were fitted simultaneously at 320 °C and the kinetics parameters obtained are presented in Table 3. The results indicate that for both sulphur removal pathways (hydrogenolysis and hydrogenation), HDS rate decreased in the order of DBT > 4-MDBT > 4,6-DMDBT. For DBT, the hydrogenation path was slower than the hydrogenolysis path. The reverse was observed for 4-MDBT and 4,6-DMDBT. Our results are in good agreement with the published results [15–17]. It is well known that HDS reactivity depends critically on the molecular size and structure of the sulphur molecules. Alkyl substituents at the aromatic carbon adjacent to the sulphur atom are thought to sterically hinder the adsorption of these compounds on the catalyst surface. A low reaction rate in direct sulphur removal by hydrogenolysis has been attributed to the reduction in the total HDS rate of 4- and 4,6-substituted benzothiophenes [16].

Figs. 8 and 9 compare the calculated and experimental concentrations of total nitrogen, DBT, 4-MDBT and 4,6-DMDBT for the original LCO and the ultra-low nitrogen feed F1. The calculated results fit well with the experimental results.

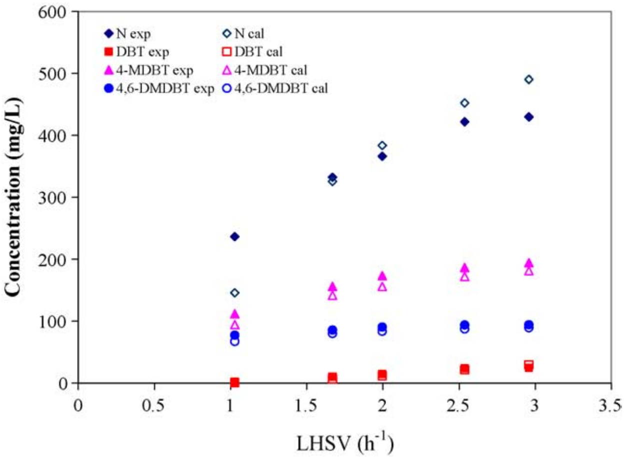

Fig. 8. Comparison of the calculated and the experimental concentrations of total nitrogen, DBT, 4-MDBT and 4,6-DMDBT for the original LCO (70 atm, 320 °C).

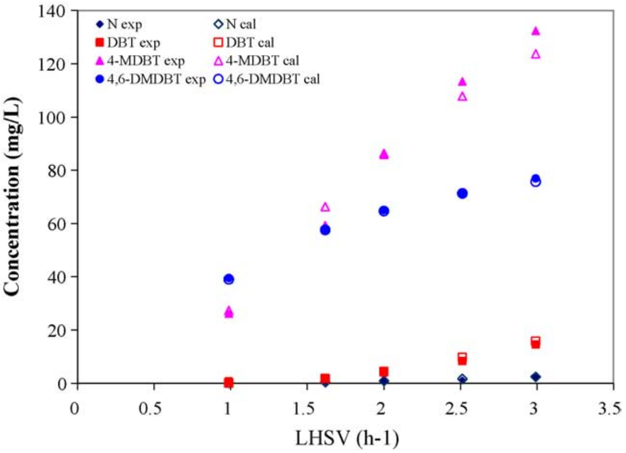

Fig. 9. Comparison of the calculated and the experimental concentrations of total nitrogen, DBT, 4-MDBT and 4,6-DMDBT for the F1 feed (70 atm, 320 °C).

Satisfactory fitting was also obtained for feed F3, F2 and F1 + F2.

## 4. Conclusions

The Inhibition effect of nitrogen compounds on the hydrodesulphurization of DBT, 4-MDBT and 4,6-DMDBT was investigated using five LCO feeds with varied nitrogen contents. The results demonstrated that reducing nitrogen content from 744.9 to 16.5 mg/L improved dramatically the HDS reactivity of 4-MDBT, 4,6-DMDBT and, to a smaller extent, that of DBT. In the hydrotreating of the original LCO, stable conversion of nitrogen compounds was observed at lower temperatures. The conversion started to increase at above 280 °C where the HDS of 4-MDBT and 4,6-DMDBT started. Since 4-MDBT and 4,6-DMDBT are converted mainly through the hydrogenation pathway, the results indicate that nitrogen compounds preferentially adsorbed on the hydrogenation sites and inhibited the removal of sulphur compounds by the hydrogenation pathway. Over the Ni-Mo/$Al_2O_3$ catalyst used in this work, at 70 atm and 375 °C, 15 ppm of sulphur specification could only be achieved by hydrotreating of the ultra-low nitrogen LCO feed. Analysis of the sulphur compounds distribution in the reaction products indicated that even when the content of substituted 4- and 6-DBTs was reduced to as low as 2.9 ppm, there was still a substantial amount of other hard sulphur species, probably benzonaphthothiophenes and phenanthrothiophenes, which should be given at least the same attention as 4- and 6-substituted DBTs in the deep HDS process. The present work also revealed that the hydrodenitrogenation rate decreased as the nitrogen content in the feed increased, which may imply self-inhibition of the nitrogen compounds. A modified Langmuir–Hinshelwood type equation, assuming the inhibition only affected the hydrogenation pathway, was used to analyze the HDS results. Good agreement between experimental data and predicted data was obtained.

## Acknowledgments

Partial funding for this work has been provided by the Canadian Program for Energy Research and Development (PERD), the Alberta Research Council and The Alberta Energy Research Institute. The authors gratefully acknowledge NCUT pilot plant staff for operating the hydrotreating unit, and NCUT analytical laboratory staff for determining the feed and product properties. The editorial assistance of Norman Sacuta is greatly appreciated.

## References

[1] C. Kwak, J.J. Lee, J.S. Bae, S.H. Moon, Appl. Catal. B 35 (2001) 59.
[2] G.C. Laredo S., J.A. De Los Reyes H., J.L. Cano D., J.J. Castillo M., Appl. Catal. A 207 (2001) 103.
[3] T. Koltai, M. Macaud, A. Guevara, E. Schulz, M. Lemaire, R. Bacaud, M. Vrinat, Appl. Catal. A 231 (2002) 253.
[4] T.C. Ho, J. Catal. 219 (2003) 442.
[5] V. Rabarihoela-Rakotovao, S. Brunet, G. Berhault, G. Perot, F. Diehl, Appl. Catal. A 267 (2004) 17.
[6] P. Zeuthen, K.G. Knudsen, D.D. Whitehurst, Catal. Today 65 (2001) 307.
[7] Y. Sano, K.H. Choi, Y. Korai, I. Mochida, Appl. Catal. B 50 (2004) 169.
[8] K.H. Choi, Y. Korai, I. Mochida, J.W. Ryu, W. Min, Appl. Catal. B 50 (2004) 9.
[9] H. Yang, J.W. Chen, C. Fairbridge, Y. Briker, Y.J. Zhu, Z. Ring, Fuel Process. Technol. 85 (2004) 1415–1429.
[10] S.S. Murti, H.J. Yang, K.H. Choi, Y. Korai, I. Mochida, Appl. Catal A 252 (2003) 331–346.
[11] H. Yang, C. Fairbridge, J.W. Chen, Z. Ring, Catal. Lett. 97 (2004) 17.
[12] H. Yang, M. Wilson, C. Fairbridge, Z. Ring, Energy Fuels 16 (2002) 855.
[13] H. Topsøe, B.S. Clausen, F.E. Massoth, in: J.R. Anderson, M. Boudart (Eds.), Catalysis Science and Technology, vol. 11, Springer-Verlag, New York, 1996.
[14] M. Nagai, T. Sato, A. Aiba, J. Catal. 97 (1986) 52.
[15] D.D. Whitehurst, T. Isoda, I. Mochida, Adv. Catal. 42 (1998) 345.
[16] M. Houalla, D.H. Broderick, A.V. Spare, N.K. Nag, V.H.J. de Beer, B.C. Gates, H. Kwart, J. Catal. 61 (1980) 523.
[17] B.C. Gates, H. Topsøe, Polyhedron 16 (1997) 3213.
[18] H. Yang, C. Fairbridge, Z. Ring, Energy Fuels 17 (2003) 387.
[19] M. Egorova, R. Prins, J. Catal. 221 (2004) 11.
[20] M. Egorova, R. Prins, J. Catal. 224 (2004) 278.
[21] F. Van Looij, P. van der Laan, W.H.J. Stork, D.J. DiCamillo, J. Swain, J. Appl. Catal. A 170 (1998) 1.
[22] M.J. Girgis, B.C. Gates, Ind. Eng. Chem. Res. 30 (1991) 2021.
[23] H.G. McIlvried, Ind. Eng. Chem. Process. Des. Dev. 10 (1971) 125.
[24] G.C. Laredo, E. Altamirano, J.A. De los Reyes, Appl. Catal. A 242 (2003) 311.
[25] V. LaVopa, C.N. Satterfield, J. Catal. 110 (1998) 375.
[26] L.C. Gutberlet, R.J. Bertolacini, Ind. Chem. Prod. Res. Dev. 22 (1983) 246.