



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

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## 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<sub>2</sub>O<sub>3</sub> 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-methyldibenzothiophene 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-dimethyldibenzothiophene 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. Crown Copyright © 2005 Published by Elsevier B.V. All rights reserved.

**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 diben-

zothiophenes 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

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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<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>S in H<sub>2</sub> 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<sup>-1</sup>. 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

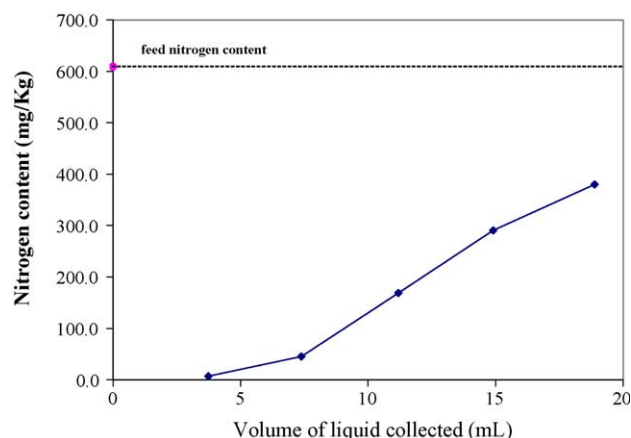


Fig. 1. Nitrogen content in liquid fractions as function of accumulated liquid sample volume (10 mL silica gel).

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