



Kinetics of HDS and of the inhibitory effect of quinoline on HDS of 4,6-DMDBT over a Ni–Mo–P/Al₂O₃ catalyst: Part I

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H I G H L I G H T S

- ▶ The effect of Q and its reaction byproducts on the HDS of 4,6-DMDBT was studied.
- ▶ HDS and HDN reactions were studied under industrial operating conditions.
- ▶ This study demonstrates the advantages of combining kinetic modelling with experimental data.
- ▶ Q and 1,4-THQ inhibited HDS reactions at lower Q conversions.
- ▶ DHQ inhibited HDS reactions at higher Q conversions.

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The kinetic effect of quinoline (Q) and its reaction by-products, i.e. 1,2,3,4-tetrahydroquinoline (1,4-THQ), decahydroquinoline (DHQ) and orthopropylaniline (OPA), on the hydrodesulfurization (HDS) of 4,6-dimethyldibenzothiophene (4,6-DMDBT) was studied in the presence of a commercial NiMoP/Al₂O₃ catalyst under operating conditions relevant to industrial applications. Kinetic observations and modelling based on a Langmuir–Hinshelwood–Hougen–Watson (LHHW) mechanism, accounting for most of the observed Q and 4,6-DMDBT by-products, indicated that Q, 1,4-THQ and DHQ are the main HDS reaction inhibitors, even at nitrogen concentrations as low as 25 ppm. To some extent Q and 1,4-THQ were adsorbed favorably on the HDS catalytic active sites, being more reactive than most of the sulfur and nitrogen-containing molecules. Besides, DHQ was less reactive than Q and 1,4-THQ, despite a significant adsorption affinity on the HDS catalytic active sites. As a consequence, Q and 1,4-THQ inhibited HDS reactions at lower Q conversions, whereas DHQ inhibited them at higher Q conversions.

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1. Introduction

Worldwide regulations to reduce the amount of sulfur in diesel to 10 ppm are constantly increasing pressure on the oil industry [1]. Hydrodesulfurization (HDS) of these oil fractions is one of the major catalytic processes used to contend with these environmental regulations. A better understanding of the kinetics related to the HDS of both major sulfur-containing, and sulfur-refractory, molecules in oil fractions has been achieved in the last few decades. Most studies have focused on the HDS of alkyl-substituted dibenzothiophenes (a-DBTs), and particularly on the HDS of 4,6-dimethyldibenzothiophene (4,6-DMDBT), since this molecule is recognized to be among the least reactive of those desulfurized in deep HDS [2,3]. Nevertheless, the kinetic role of heteroatoms

contained in aromatic molecules has also gained worldwide attention, since nitrogenated compounds are among the main compounds inhibiting HDS reactions [4–6,8]. In particular, basic and non-basic nitrogenated compounds, i.e. quinoline (Q), indol (I) and carbazole (C), have been identified as the primary molecules that inhibit HDS. However, the catalytic HDS of a gas oil containing a-DBTs and nitrogenated compounds demands highly-specialised active catalysts and extremely operating conditions (reaction pressures and temperatures exceeding 50 bar and 350 °C, respectively), which result in elevated operating costs. In an effort to overcome this, several groups [4–8] have attempted to optimize catalytic hydrodenitrogenation (HDN) and adsorption processes, in order to remove nitrogen-containing molecules from diesel before HDS takes place, although so far without significant success. Consequently, a better understanding of the kinetics related to the HDS of both major sulfur-containing, and sulfur-refractory, molecules in the presence of nitrogen-containing molecules is mandatory.

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