



Research article

Effect of organic nitrogen compounds on deep hydrodesulfurization of middle distillate



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ABSTRACT

An effect of organic nitrogen compounds on deep hydrodesulfurization catalyst (CoMo/Al₂O₃) has been carried out using micro-flow reactor at 5 MPa hydrogen pressure, 1.5 h⁻¹ liquid hours space velocity, and 330 to 380 °C temperature. The experiments were conducted in two steps; at first, prepare nitrogen free Kuwaiti straight run gas oil (SRGO) while in the second step is to test hydrotreating (HDT) catalytic activities using synthetic diesel feed to achieve ultra-low sulfur diesel (ULSD). Hence the role of nitrogen compounds and their effect on HDS activity was studied with nitrogen-free SRGO and spiked (added indole and quinoline), which indicated an apparent tendency of strong inhibition effect by basic nitrogen on deep HDS process.

Indeed, inhibition and deep HDS conversion are also dependent on the H₂ partial pressure and its dissociative species (i.e., H^{δ+} and H^{δ-}). It is expected that basic nitrogen compounds can easily consume H^{δ+} ions during hydrotreating which is assumed to be the rationale behind the stronger inhibition of the hydrogenation function. It was found that quinoline has a more noticeable adverse effect than indole, particularly at a lower temperature. HDS activity results indicated that the adsorbed nitrogen species showed more acceptable behavior at a lower temperature while at high-temperature inhibition effect is not very significant, which could be because of the adsorption nature of nitrogen species.

1. Introduction

Worldwide urbanization, motorization, and demand for clean fuel are the primary drivers for this study, particularly the demand for diesel as a fuel paying enormous attention to lower sulfur, nitrogen, and aromatics. On the other hand, good quality sweet crude oil production is dwindling while sourer and heavy crude is increasing, which processing is more demanding particularly more sulfur compounds are refractory in nature. However due to the environmental legislation it is necessary to remove total sulfur including least-reactive or sterically hindered (refractory) sulfur compounds that are present in the diesel feeds. Moreover, the world market has become more distillate focused; refiners have limited options to maximize clean diesel fuel production [1,2]. In addition, considering deep HDS one must presume high conversion (> 90%), which catalytic chemistry has a complex nature with the other hetero-atoms, mainly nitrogen and sulfur compounds. It was also well known that nitrogen and HDT reaction by-products (H₂S and NH₃) competitively adsorbed on the catalytic sites that significantly reduce the number of catalytic sites and as a result lower HDS [1]. Hence the inhibition effect is one of the most critical factors that lead to restrained catalytic activity and generates an adverse effect on the

reaction products. The nitrogen compound's co-existence in diesel exerts competitive adsorption on the catalytic sites, and thus, contributes to the difficulty in meeting clean fuel demand [3,4]. In literature, many approaches have been suggested to produce ultra-clean transportation fuel [1,5]. One of the essential approaches has been recommended to remove organic nitrogen before it goes to hydrotreating (HDT) reactor, i.e., pretreatment of diesel [6–12]. The separation of nitrogen compounds not only improves the HDT efficiency but can also minimize storage instability problems [13]. Hence the removal of nitrogen averts some difficulties to achieve clean fuel. Several methods have been established to separate basic nitrogen compounds using solvent extraction, ion exchange, liquid-liquid, and liquid-solid extractions are the most common [12–18].

Nitrogen compounds are known for the detrimental role in HDS, catalyst deactivation and product stability are a subject of interest to petroleum refiners [13,19–23]. Usually, basic nitrogen compounds (i.e., quinoline, acridine) are stronger inhibitors for the HDS reactions than the nonbasic moieties, i.e., carbazole and indole [3,24–26]. However, the detrimental effect due to nonbasic nitrogen species cannot be overlooked entirely, which convert their molecular nature after the hydrogenation (HYD) of the ring [1]. HYD is the principal reaction

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route for refractory sulfur compound's conversion; if the nitrogen compounds inhibit this route, it will be impossible to achieve ULSD [1,27,28]. Though, there are a number of process variables which attempt to enhance deep HDS such as i) selection of multi-bed/multi-reactor catalyst (CoMo/NiMo) loading, ii) high hydrogen partial pressure, iii) high temperature in order to enhance conversion, iv) inter-stage NH_3 scrubber in order to keep active acid sites, and v) complex catalyst composition (support, metal or noble metals) or various type of catalytic sites such as type I or type II and their existence, etc.

Moreover, it is well known that N–C cleavage in nitrogen compounds is more complex and cannot proceed without hydrogenation of aromatic ring. Therefore, HDN is kinetically difficult and high consumption of hydrogen than HDS, which is a crucial factor to obtain deep HDS. An account of hydrogen consumption has been reported Eijsbouts, et al. 1991 [29] where 4H atoms per S atom for HDS of DBT while 8–14H atoms are needed for the removal of N from quinoline. Current existing refineries that produce ULSD fuel, most of them opted one of the above-said points to either enhance HYD or the prevent nitrogen inhibition in the reactor. In addition, the adsorptive denitrogenation (ADN) process can be used at atmospheric pressure without H_2 , which will significantly reduce refinery costs (CAPEX or OPEX) without major revamp in the existing refinery set-up.

The crux of the present work is to understand organic nitrogen compounds inhibition behaviors during the hydrodesulfurization of diesel fuel. Elimination of basic and nonbasic nitrogen compounds from diesel fraction were carried out by using simple and cost-effective methods. The diesel was spiked with added model nitrogen type (indole or quinoline) and concentration (0 to 200 ppm), which were tested for hydrodesulfurization at various temperatures (350 °C, 365 °C 380 °C). Synthesis of nitrogen free diesel and their removal indeed provide useful information to achieve ULSD fuel. The removal of sulfur in presence of quinoline and indole were studied as a non-basic and basic nitrogen, respectively. The degree of inhibition effect on the deep HDS was calculated as a function of spiking agent and temperature.

2. Experimental

2.1. Diesel feedstock and its composition

Straight run gas oil (diesel) feedstocks consist of boiling range 220–350 °C with \pm some front or back ends (overlapping), which was obtained from the atmospheric distillation of Kuwait Export Crude (KEC). Liquid and solid phase extraction methodologies were used to separate the nitrogen compounds. The amount of basic nitrogen was determined by calculating the difference between total and the non-basic nitrogen compounds. The difference between physicochemical properties and composition with or without nitrogen are shown in Table 1.

2.2. Preparation of nitrogen free diesel feedstock

The nitrogen-containing compounds were separated into basic and non-basic types using two different procedures. The nitrogen removal experiments were conducted in two steps. The first step is to treat virgin diesel with acid to separate the basic nitrogen compounds while the second step is to carry out selective adsorption of non-basic nitrogen compounds. Hence, the current method is much simplified and easy, which involved two steps as described in Fig. 1. In the first step, a defined acid-molar concentration (1–3 M) of acid was mixed in a glass separating funnel with the diesel and was shaken gently to vigorously for an hour. After the mixing, the solution was left for 30 min and subsequently both the phases separated, and the organic phase was washed with distilled water. The traces of acid were removed by water washing and the “basic nitrogen” neutralize at high pH (8–9) with Na_2CO_3 . The filtered polar hydrocarbon, including “non-basic nitrogen”, was passing over solid material ($\text{SiO}_2/\text{Al}_2\text{O}_3/\text{carbon}$) column

Table 1

Properties of Kuwait SRGO before and after nitrogen removal.

Properties	Feedstock	
	SRGO	N Free SRGO
Density @ 15 °C, g/cm ³	0.8376	0.8296
Sulfur, ppm	12,406.06	1050
Nitrogen, ppm	149.84	1.0
Distillation (ASTM 2887)		
IBP	135.0	145.5
5%	204.0	202.0
10%	230.5	227.0
20%	256.5	254.0
30%	273.0	271.5
40%	288.0	286.0
50%	303.0	299.0
60%	317.5	313.5
70%	334.0	330.0
80%	354.5	348.0
90%	381.0	374.0
FBP	452.5	435.5

IBP: Initial boiling point; FBP: Final boiling point.

for adsorption. The fuel was separated by gravity, and solid will retain only non-basic nitrogen compounds. The column washed with pentane. Subsequently, polar non-basic nitrogen compounds were washed with methylene chloride. The typical limitation of this process is hydrocarbon volume loss (10–15%) during the batch adsorption, which could be considerably improved by using flow mode adsorption.

2.3. Characterization of fresh and spent adsorption material

The nitrogen sorption measurements were performed on a Quantachrome at -196 °C. The deposited hydrocarbons (i.e., coke deposits) were analyzed by Quantachrome Instrument (TPRwin v2.0) using temperature-programmed oxidation (TPO) aligned with an online MS. The TPO of the spent catalyst (5–6 mg) was carried out in the presence of O_2/He (5–95 vol%) flow (25 ml/min) using a 15 °C/min heating ramp from 30 to 800 °C.

2.4. Catalytic activity

Hydrotreatment of the virgin and spiked feeds was performed in a down-flow fixed bed micro-reactor using a commercial NiMo catalyst, which was loaded into three sections using 1:1 ratio of catalyst and the diluent (carborundum). The catalyst was sulfide in-situ with a sulfiding feed containing a 2 wt% CS_2 in gas oil under 5 MPa pressure; 350 °C temperature, 200 ml/ml hydrogen-to-oil ratio; and a 1.5 h⁻¹ liquid hourly space velocity (LHSV). The sulfiding was continued for 12 h subsequently specified feed was introduced in-situ, and the HDS experiments were carried out at different reactor temperatures (330 to 380 °C), at fixed pressures 5.0 MPa, LHSV 1.5 h⁻¹, and the H_2/HC ratio was 200 ml/ml. HDT reaction products were collected and stripped by slow purging nitrogen, to ensure the removal of the dissolved NH_3 and H_2S gases, and subsequent samples were analyzed for nitrogen and sulfur compounds by using gas chromatography (HP 5890) equipped with a standard FID coupled to a selective chemiluminescent detector (SCD).

3. Results and discussion

3.1. Textural properties of adsorbents

The adsorption materials (Al_2O_3 , SiO_2 , and carbon) were characterized for their textural properties using BET method where surface area is 260, 690 and 930 m²/g, respectively. The N_2 adsorption-desorption isotherms (type IV) and BJH pore distributions indicated that the

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