



Effect of basic nitrogen compounds on gas oil hydrodesulfurization and deposit formed on the catalyst



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HIGHLIGHTS

- Residue desulfurization gas oil contained basic nitrogen compounds like anilines.
- Light cycle oil contained polyaromatic hydrocarbons, indoles and carbazoles.
- A low deactivation rate was observed for feed with residue desulfurization gas oil.
- The deposit from feed with light cycle oil was clarified as aromatic.

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ABSTRACT

The authors studied the effect of the composition of cracked gas oils on the hydrodesulfurization to obtain clean diesel fuel. The required reaction temperature for sulfur specification of diesel fuel using a feedstock mixed with residue desulfurization gas oil (RDS-GO) was equivalent to that using light cycle oil (LCO). RDS-GO has a high content of basic nitrogen compounds, whereas LCO has a high content of aromatic hydrocarbons that are known to inhibit the hydrodesulfurization of gas oil. Using two-dimensional gas chromatography, LCO was found to contain polyaromatic hydrocarbons and non-basic nitrogen compounds, such as indoles and carbazoles, whereas RDS-GO contained monoaromatic hydrocarbons and basic nitrogen compounds, such as anilines. In a deactivation test conducted over 2300 h, the feedstock mixed with RDS-GO showed a lower deactivation rate than LCO. Raman spectroscopy, ¹³C NMR, and electron energy-loss spectroscopy in transmission electron microscopy showed that the deposits formed on the used catalysts during the deactivation test with the feedstock mixed with LCO contained more aromatic compounds than those with RDS-GO. The coke in the deposits from the feed containing RDS-GO was expected to be more anisotropic than that from the LCO. The improved hydrodesulfurization activity observed with RDS-GO was attributed to its characteristic components, which are thought to inhibit the growth of coke on the catalyst.

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Abbreviations: LCO, light cycle oil; FCC, fluid catalytic cracking; HDS, hydrodesulfurization; SRGO, straight run gas oil; RDS, residue hydrodesulfurization; GO, gas oil fraction; VDS, vacuum gas oil hydrogenation; TEM-EELS, electron energy-loss spectroscopy in transmission electron microscopy; 2D-GC, two-dimensional gas chromatography; XRD, X-ray diffraction; LHSV, liquid hourly space velocity; XRF, X-ray fluorescence; FID, flame ionization detector; NCD, nitrogen chemiluminescence detector; HAADF, high-angle annular dark-field; 4,6-DMDBT, 4,6-dimethyldibenzothiophene.

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1. Introduction

In recent years, refineries have had to utilize many intermediate fractions from various types of refining units [1]. “Cracked gas oils” are gas oil fractions obtained from hydrotreating or cracking units using heavy feedstocks. Light cycle oil (LCO) is a cracked gas oil that is obtained as a gas oil fraction from a fluid catalytic cracking (FCC) unit, and is widely used as a component of industrial heavy fuel oil or banker fuel oil because it has a lower viscosity and sulfur content than other potential components. The recent use of LCO as a feedstock for gas oil hydrodesulfurization (HDS) units has

resulted in the upgrading of heavy industrial fuel oil into clean diesel fuel for transportation [2].

During gas oil HDS, LCO is hydrotreated by mixing it with a straight run gas oil (SRGO) fraction from crude oil [3]. However, LCO contains large amounts of aromatic hydrocarbons, which results in a highly exothermic reaction and high hydrogen consumption. Moreover, the HDS of feedstocks containing LCO results in rapid deactivation of the HDS catalyst caused by the accelerated deposition of coke on its surface [3,4]. This behavior limits the amount of LCO that can be added to a gas oil HDS unit.

Meanwhile, other intermediate gas oil fractions from various units have mainly been used as components of industrial heavy fuel oil due to their having lower viscosities and lower sulfur contents than the other residual components in industrial fuel oil [5]. A residue hydrodesulfurization (RDS) unit produces a gas oil fraction (RDS-GO) as a by-product. RDS-GO is utilized as a diluting fraction in industrial heavy fuel oil, and is expected to become a feedstock for the gas oil HDS unit as well as LCO. A vacuum gas oil hydrogenation (VDS) unit also produces a gas oil fraction (VDS-GO) that is used as a diluting fraction. RDS-GO and VDS-GO are classified as “hydrotreated gas oils”, and are considered to be good candidates for use as a feedstock for gas oil HDS units due to their having lower sulfur contents than SRGO. RDS-GO is particularly promising because it is produced in larger volumes in refineries than is VDS-GO.

The use of RDS-GO in the gas oil HDS reaction and its deactivation behavior are not well understood. When using RDS-GO as a feedstock for gas oil HDS, it is important to know the composition of the gas oil feedstock and understand the effect the components will have on HDS activity and the deactivation of the HDS catalysts during long-term operation. It has been reported that the aromatic compounds in LCO can poison the catalyst during gas oil HDS [6,7], and that nitrogen compounds also affect the catalyst's gas oil HDS activity [8]. Therefore, an investigation of the hydrocarbon and nitrogen-containing hydrocarbons in the feedstock is significant, as carbonaceous deposits on the catalyst are presumed to cause the deactivation of HDS activity in the gas oil HDS unit [9,10]. Several analytical methods have been used to characterize these carbonaceous compounds, including Raman spectroscopy [11,12], temperature programmed oxidation [12], and electron energy-loss spectroscopy in transmission electron microscopy (TEM-EELS) [13,14].

The purpose of this study is to investigate the composition of cracked gas oil and the effect of the feedstock composition on gas oil HDS. Two-dimensional gas chromatography (2D-GC) was used to clarify the types of hydrocarbons and nitrogen-containing compounds contained in the feedstock. Reactivity tests and deactivation tests were used to evaluate the effect of the feedstock composition on HDS activity and deactivation of gas oil. Furthermore, the deposits on the used catalysts were characterized using ^{13}C NMR, Raman spectroscopy, TEM-EELS, and X-ray diffraction.

2. Experimental

2.1. Feedstock

SRGO was obtained by distillation of a typical Arabian crude. LCO was obtained from a FCC unit of hydrodesulfurized residue. RDS-GO-A, -B, and -C were obtained from three different RDS units for hydrodesulfurization of atmospheric residue. VDS-GO was obtained from a vacuum gas oil HDS unit for hydrodesulfurization of vacuum gas oil. The properties of the gas oils are summarized in Table 1. For the reactivity and deactivation tests, MIX-D, -E, -F, -G, and -H were prepared by mixing 85 vol% of SRGO and 15 vol% of LCO, VDS-GO, RDS-GO-A, RDS-GO-B, and RDS-GO-C, respectively.

Table 1

Properties of the gas oil fractions used in the reactivity test and the deactivation test.

Property	SRGO	LCO	VDS-GO	RDS-GO-A	RDS-GO-B	RDS-GO-C
Density (g/cm ³)	0.8511	0.9493	0.8769	0.8738	0.8609	0.8596
90% boiling point ^a (K)	618.2	624.7	662.7	638.2	604.2	557.7
Sulfur ^b (mass ppm)	10,500	4100	870	730	180	80
4,6-DMDBT ^c (mass ppm)	155	115	105	68	80	21
Nitrogen ^d (mass ppm)	110	470	250	350	83	64
Basic nitrogen ^e (mass ppm)	50	40	100	190	56	43
Aromatic compounds ^f (vol%)	26	77	44	43	38	42
Feed name ^g	SRGO	MIX-D	MIX-E	MIX-F	MIX-G	MIX-H
Required reaction temperature for sulfur content of 8 mass ppm in product oil ^h (K)	625.7	638.4	633	638.4	627.4	629.6

^a Measured by ASTM D86.

^b Determined by X-ray fluorescence (XRF).

^c 4,6-Dimethylidibenzothiophene determined by GC-sulfur chemiluminescence detector.

^d Measured by ASTM D3228.

^e Measured by UOP 269.

^f Measured by JPI-55-49.

^g MIX-D, -E, -F, -G, and -H were prepared by mixing 85 vol% of SRGO and 15 vol% of LCO, VDS-GO, RDS-GO-A, RDS-GO-B, and RDS-GO-C, respectively.

^h The reaction conditions are: $P = 5.5$ MPaG, $\text{LHSV} = 1.5$ h⁻¹, $\text{H}_2/\text{Oil} = 250$ NL/L.

2.2. Reactivity test

The reactivity of the cracked gas oils was tested using a high-pressure bench-scale fixed bed reactor. The feedstock properties are summarized in Table 1. A CoMo catalyst (100 mL; MoO₃: 22.0 mass%, CoO: 3.0 mass%, Al₂O₃ support) for gas oil HDS was used for these tests after presulfiding with excess amount of sulfur reagent for sulfiding molybdenum on the catalyst with solvent. The following test conditions were used: hydrogen pressure: 5.5 MPaG, liquid hourly space velocity (LHSV): 1.0 h⁻¹, ratio of hydrogen to oil (H₂/Oil): 250 NL/L.

The product oil from the reactivity test was bubbled with nitrogen gas at room temperature for 8 h to remove hydrogen sulfides. The sulfur content of the product oil was measured by X-ray fluorescence (XRF) using an Axios spectrometer (PANalytical).

2.3. Deactivation test

The deactivation tests were carried out for MIX-D and MIX-F with the same catalyst and the test conditions as were used for the reactivity test after a period of about 500–2300 h. The reaction temperature was adjusted to obtain a sulfur content of nearly 8 mass ppm every 72 h. The normalized reaction temperature of hydrodesulfurization was calculated by the activation energy of 113 kJ/mol·K, which was calculated by the reactivity test.

2.4. Two-dimensional gas chromatography

The components of SRGO, LCO, RDS-GO-A, and VDS-GO were determined using 2D-GC (KT2006, ZEOX) with two columns: BPX-5 (30 m × 0.25 mm, i.d. 0.25 μm) and BPX-50 (2 m × 0.1 mm, i.d. 0.1 μm) and a flame ionization detector (FID) or nitrogen chemiluminescence detector (NCD). Helium gas was used as the carrier gas at a flow rate of 2.58 mL/min.

2.5. Used catalysts from the reactivity tests and deactivation tests

After the reactivity tests and deactivation tests, residual gas oil in the used catalysts was removed by Soxhlet extraction with

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