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Deep desulfurization of full range and low boiling diesel streams from Kuwait Lower Fars heavy crude

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Abstract

Information on feed quality and, in particular, various types of sulfur compounds present in the diesel (gas oil) fractions produced form different crudes and their HDS reactivities under different operating conditions are of a great value for the optimization and economics of the deep HDS process. This paper deals with deep desulfurization of gas oils obtained from a new heavy Kuwaiti crude, namely, Lower Fars (LF) which will be processed in the future at Kuwaiti refineries. Comparative studies were carried out to examine the extent of deep HDS, and the quality of diesel product using two gas oil feeds with different boiling ranges. The results revealed that the full range diesel feed stream produced from the LF crude was very difficult to desulfurize due to its low quality caused by high aromatics content (low feed saturation) together with the presence of high concentrations of organic nitrogen compounds and sterically hindered alkyl DBTs. The low-boiling range gas oil showed better desulfurization compared with the full range gas oil, however, deep desulfurization to 50 ppm sulfur was not achieved even at a temperature as high as 380 °C for both feeds. The desulfurized diesel product from the low-boiling gas-oil feed was better in quality with respect to the S, N and PNA contents and cetane index than the full-range gas-oil feed.

Keywords: Deep desulfurization; Ultra-low sulfur diesel; Feed quality effect

1. Introduction

Diesel fuel sulfur level has been identified as a major contributor to air pollution by sulfur dioxide and particulate emissions in diesel fueled vehicles. Reducing the sulfur content of diesel fuels has been found to result in a direct fuel related particulate matter reduction [1,2]. As a result, environmental rules have been introduced in many countries around the world to reduce the concentration of sulfur in diesel fuels to ultra-low levels [3–5], For example, in the USA, the acceptable level of sulfur in the diesel fuel was first reduced from 2000 ppm to 500 ppm by the Clean Air Act (CAA) amendments in the nineties and then to 350 ppm and 50 ppm, respectively, in the years 2000 and 2005. Further reduction in the sulfur limits to 15 ppm has been introduced starting June 2006. In Europe, some countries including Germany, Sweden and Switzerland are promoting low-sulfur diesel fuels containing no more than 10 ppm sulfur through a variety of incentives. Other European Union countries and Japan will introduce diesel fuel with 10 ppm to the market from the year 2008. Similar ultra-low sulfur specifications are also targeted in many other countries, and most probably will be predominant worldwide during the next decade.

Although the new environmental regulations that limit the sulfur levels of diesel and other transportation fuels to very low levels are beneficial from environmental point of view, meeting the required stringent specifications represent a major operational and economic challenge for the petroleum refining industry [6,7]. The tightening of sulfur specifications of diesel fuel to very low levels requires deep desulfurization of diesel feed-streams. The shift from normal to deep desulfurization is a very complicated technical problem. Many factors such as the catalysts, process parameters, and feedstock quality can have a significant influence on the degree of desulfurization of diesel feeds [8–11]. Among these, the feedstock quality plays an important role on deep desulfurization since the types of sulfur,

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Table 1
Experimental conditions used for gas oil hydrotreating test

Operating parameters	Values
Temperature (°C)	335, 350, 365 & 380
Pressure (bar)	40
LHSV (h^{-1})	1.3
H_2/oil (ml/ml)	200

nitrogen and aromatic compounds and their concentrations in different feedstocks are different.

Most refiners process a wide variety of crudes and routinely adjust the operating conditions of major processing units according to the changing feeds and overall product needs. Additionally, the types and volume of streams feeding into the diesel pool may change due to seasonal swing in the product demand and changes in upstream operations. These changes in upstream operations will cause the composition and quality of the diesel feedstock to vary. In Kuwait, Kuwait National Petroleum Company (KNPC) refineries have operated their gas oil desulfurization (GOD) units for many years. Total gas oil hydrotreating capacity at KNPC is 190,000 B/D and this is expected to increase in the future to fulfill the increase in the international demand for low-sulfur diesel. The sulfur content of the diesel fuel will be reduced from its current 450 ppm level to 45 and 10 ppm levels to conform the export market requirements. KNPC's experience in the GOD process to produce ULSD has been reported in some recent papers [12,13].

KNPC is planning to process heavier crudes than the Kuwait Export Crude (KEC) in future in the new refinery. Kuwaiti heavy crudes, namely Ratwai/Burgan, Eocene and Lower Fars (LF) and their blends are going to be refined by year 2010. Information on various types of sulfur compounds present in the diesel (gas oil) fractions produced form different crudes and their HDS reactivities under different operating conditions will be of a great value for the optimization and economics of the deep HDS process.

Deep desulfurization of diesel feeds has been the subject of some investigation in this laboratory [14–18]. In a previous paper, we compared the HDS kinetics of straight-run and coker gas oils under deep desulfurization conditions [15]. In another study [16], the effect of lowering 95% boiling point (T_{95}) of the above two diesel feed streams on deep desulfurization to ultra-low sulfur levels was reported. In continuation of our efforts to obtain technical data on deep desulfurization of different diesel feeds produced in Kuwait, in the present work, we have investigated the HDS of full range and low-boiling cuts of a diesel stream (straight-run gas oil) produced from new heavy Kuwaiti crude, namely, Lower Fars (LF). Published data on deep hydrotreating of gas oils from heavier Kuwait crude oils to produce ULSD is scarce.

2. Experimental

2.1. Feedstock preparation

Lower Fars crude oil was obtained from Kuwait Oil Company (KOC). The full range and low boiling diesel cuts (straight run gas oils) were prepared by fractionation of the crude oil using a pilot plant distillation unit (Fisher, Model 40992) available at the Pilot Plant Hall facility at the Petroleum Research and Studies Center of Kuwait Institute for Scientific Research (KISR). Both crude oil and the gas oil fractions were subjected to detailed characterization in order to assess the quality of the feeds.

2.2. Feed and products analysis

The total sulfur and nitrogen contents of feed and product samples were determined using an Antek 7000 sulfur analyzer equipped with a SCD detector [15,16]. Density was determined by IP 190 method. Individual sulfur compounds distribution in different feeds was determined using a high resolution gas chromatograph equipped with a 30 m×0.32 mm×0.04um SPB-I capillary column and a Flame Photometric Detector (FPD). Total aromatics content and polynuclear aromatics (PNA) content of feed and products were determined with a Supercritical Fluid Chromatography (SFC) aromatic analyzer (Berger).

2.3. Hydrotreating experiments

A high pressure fixed bed microreactor unit manufactured by Vinci Technologies, France, was used for testing and comparing the HDS of the two feeds. The micro reactor unit had a cylindrical reactor with an inside diameter of 1 cm and a volume of 16 cm^3. The reactor was equipped with a thermowell that extended along the center of the reactor. The temperature in the reactor was measured at different levels using a four point thermocouple. The feed was pumped from a stainless steel tank to the reactor using a HPLC pump (slow suction quick delivery). High purity (99.999%) hydrogen was supplied from high pressure cylinders. The desired pressure of reactor was controlled by pressure regulators and controllers. A commercial new generation $CoMo/Al_2O_3$ catalyst was used in the gas oil desulfurization experiments. For each test 6 ml of crushed catalyst (12–18 mesh), diluted with 6 ml of carborundum (12–18 mesh), and was loaded in the middle zone of the reactor. Carborundum was placed above and below the catalyst bed. Before starting a run, the reactor was purged with nitrogen (40 l/h) under atmospheric pressure for 10 min. Then the unit pressure was set at 70 bars under the flow of nitrogen (40 l/h). After reaching 70 bars, pressure was maintained for 30 min and checked for leak.

After confirming that there was no leak, the system was depressurized and the catalyst was presulfided with a sulfiding feed containing 3 wt.% DMDS in straight-run gas oil (SRGO). Straight-run gas oil was introduced into the reactor with hydrogen at 25 °C and the catalyst bed temperature was maintained at this temperature for 30 min for wetting. The bed temperature was then raised to 150 °C at a rate of 25 °C/h and stabilized at the same temperature for 5 h. The temperature was further increased to 180 °C in 2 h at a rate of 15 °C/h. The presulfiding feed was introduced into the reactor at 180 °C and the temperature was increased to 230 °C at a rate of 25 °C/h. The catalyst bed was stabilized for 12 h at the same temperature. Then, the catalyst bed temperature was further increased to 320 °C at a rate of 25 °C/h. The other conditions of presulfiding were: H_2/oil=200 ml/ml; LHSV=1.3 h^{-1}; Pressure: 40 bar. After 4 h of stabilization at 320 °C, the presulfiding feed was stopped, the test feed was introduced and the operating conditions were adjusted to the test conditions required for the run. The operating conditions used for the hydrotreating tests are summarized in Table 1. Hydrotreated product samples were collected at each condition by an auto sampler after stabilization for 24 h. H_2S dissolved in the

Table 2
Properties of Lower Fars and Kuwait Export Crude Oils

Feed properties	KEC	LF
Density @ 15 °C (g/cc)	0.8782	1.0732
API	30	14
Sulfur (wt.%)	2.6	5.3
Nitrogen (ppm)	1100	4000
Kinematics viscosity @ 40 °C (cSt)	12.82	150.1
CCR (wt.%)	6.22	11.64
Asphaltanes (wt.%)	2.7	10.1
Total metals (V+Ni) (ppm)	35	132