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Commercial analysis of catalytic hydroprocessing technologies in producing diesel and gasoline by light cycle oil

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ABSTRACT

Four main catalytic hydro-processing technologies of light cycle oil (LCO) were investigated in detail under typical pilot-scale operations aiming to provide industrial analysis of oil quality upgrading and to meet the various end-use applications. It is found that ultra-deep hydrodesulfurization (HDS) technology can effectively remove sulfur and nitrogen, however its performance on the improvement of cetane number and decreasing of density is limited. The property makes it suitable for production of fuel oils. Maximally improving LCO cetane number (MCI) technology is favorable for producing diesel with high cetane number by partial ring-opening of aromatics without side-chain cleavage. Medium-Pressure Hydro-upgrading (MHUG) technology partially converts LCO into naphtha for production of diesel with low density and high cetane number at medium pressure. Meanwhile, the by-product-heavy naphtha with high potential aromatic content occurs. Moreover, LCO hydrocracking (FD2G) technology employs relatively higher temperature with varied pressure, avoiding thermodynamic limits, to promote the conversion of di- and tri-aromatics into monoaromatics. This technology not only produces high octane number gasoline, but also upgrades the quality of diesel. The industrial analysis here could guide the design and optimization of LCO hydro-processing technology for fuel quality upgrading.

1. Introduction

Environmental awareness has highlighted the need for significant enhancement of fuel quality to satisfy newly established and stricter automotive emission standards. Reduction of polycyclic and total aromatic hydrocarbon contents, as well as improvement of cetane number (CN) of diesel fuel, are potential measures that must be undertaken to diminish gas emissions from diesel engines [1]. The current legislations in the EU, USA, and China limit the total sulfur content to 10, 15, and 50 μg/g respectively. Moreover, the China V standard legislation on fuel quality has established the maximum polycyclic aromatic hydrocarbon (PAH) content of 11 wt% and the minimum CN of 51 for diesel fuel [2]. However, a proposal to set the maximum PAH limit to 8 wt% is being evaluated.

Light cycle oil (LCO) accounts for approximately 10–20 wt% fluidized catalytic cracking (FCC) products. It is always used as low-grade fuel additive because of its low CN (15–25) and high amounts of sulfur (0.2–1.5 wt%), nitrogen (100–950 μg/g), and aromatics (75–90 wt%) [3]. New or revamped hydrotreating and hydrocracking units, along with novel catalytic systems, have been investigated and applied to maximize the production of ultra-low-sulfur diesel fuel (ULSD) using available crude oils and refinery process units [19]. LCO is commonly used as blend stock for home heating oil, industrial fuel oil, and diesel. Nevertheless, the increasing adoption of natural gas for home heating and energy production has reduced the demand for LCO. Although it has been an important source of diesel pools [4], its application as blend stock to meet the demand for automotive fuels is restricted by its low CN (approximately 20) as well as high sulfur and aromatic contents in the resultant fuel product [5]. Hence, enhancement of LCO quality has attracted increased research attention.

LCO can be treated by catalytic cracking [9,10,16] or hydrogenation [1–3,6–8,11–15,20–27]. Aromatic saturation and hydrocracking are commercial refining technologies used to improve the quality of high aromatic content LCO [1]. LCO is typically upgraded by hydrotreating units under mild conditions to produce the feed of FCC units or through severe hydrotreatment to produce the stocks of gasoline and diesel pools. Hydrocracking is frequently used in upgrading LCO, which is important to maximize the

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Table 1
Properties of Zhenhai LCO.

Parameter	Unit	Zhenhai
Density at 20 °C	kg/m^3	9.611
Cetane number (ASTM D 4737)		<21.5
Cetane index (ASTM D 4737-96a)		22.94
Solidifying point	°C	−20
Sulfur content	%	1.36
Nitrogen content	μg/g	1088
Hydrogen content	%	9.31
Distillation range (ASTM D1160)	°C	191–382
95% (ASTM D1160)	°C	377
Hydrocarbon types		
Paraffins	wt%	9.6
Total cycloparaffins	wt%	6.9
Noncondensed cycloparaffins	wt%	3.4
Condensed dicycloparaffins	wt%	2.1
Condensed tricycloparaffins	wt%	1.4
Total aromatics	wt%	83.1
Monoaromatics	wt%	21.5
Diaromatics	wt%	50.1
Tricyclic aromatics	wt%	11.5

economic profit of a refinery and increase the utilization efficiency of crude oil resource.

In this paper, newly developed commercial hydroprocessing concepts and technologies for LCO upgrading were critically compared. The reaction mechanism and typical reaction laws of different LCO upgrading technologies are discussed. This paper provides information about the applicability of different LCO upgrading technologies and serves as a reference for different needs of users.

2. Experimental

2.1. Materials

Commercial LCOs from Daqing, Dagang, Shengli and Zhenhai were used. The physical and chemical properties of LCO from Zhenhai Refinery (SINOPEC, China) were shown in Table 1, and those of other LCO samples are shown in Table 4. Six commercial catalysts developed by Fushun Research Institute of Petroleum and Petrochemicals (FRIPP) (SINOPEC, China) were applied (Table 2). Electrolytic hydrogen (>99.9 vol% purity and oxygen content ≤5 mL/L) was obtained through high-pressure deoxygenation and dehydration using silica gel.

2.2. Process scheme

Different LCO upgrading tests were performed in a fixed bed reactor in continuous operating mode (Figs. 1 and 2). Feedstock entered the vaporizer through a double-plunger micro-pump, mixed with hydrogen, and placed in a preheating chamber prior to entering the stainless steel reactor. Gas and liquid product samples were collected with a gas–liquid separator. The gas products were analyzed using gas chromatograph with a packed column, whereas the liquid product was distilled to obtain different fractions.

2.3. Catalytic activity

Dimethyl Disulfide (DMDS) was used as a vulcanizator. The catalysts were pre-sulfided before each run using a mixture of straight jet fuel (1.45 wt% sulfur content) and 1.5 wt% DMDS. The reactor was pressurized with hydrogen to the reaction pressure and heated to 180 °C. The pre-sulfided oil was introduced and heated to 230 °C and kept for 8 h. After this, it was heated to 290 °C and kept for 4 h, and then heated to 320 °C and kept for another 4 h. The liquid hourly space velocity (LHSV) of the feed was maintained at 1.0 h^{-1}, and the volume ratio of H_2 flow rate to feed flow rate was 1000:1. After sulfidation, the pre-sulfided oil was switched to LCO for hydrotreating or hydrocracking.

2.4. Analytical methods

- The obtained products were analyzed according to the following suitable standards:
- product density at 20 °C according to ASTM D 1298,
- hydrocarbon composition according to ASTM D 2425 and SH/T 0606,
- cetane number according to ASTM D 4737,
- cetane index (CI) according to ASTMD 4737-96a,
- research octane number according to GB/T 5487–1995,
- solidifying point according to ASTM D 2500,
- sulfur content according to ASTM D 4294, and
- distillation according to ASTM D1160.

2.5. Ultra-deep hydrodesulfurization technology

HDS technology, which usually adopts one reactor, is designed to produce ULSD from straight-run and cracked distillates. The feed and hydrogen-rich gases are heated in exchangers and a fired heater and then are allowed to flow into the fixed-bed reactor, in which hydrodesulfurization (HDS), hydrodenitrification (HDN), and olefin saturation reactions occur. The reactor effluent is separated in a separator and distilled in a distillation tower to produce clean diesel. The process flow diagram is shown in Fig. 1.

This paper investigates the influence of pressure and temperature on LCO HDS and HDN by using FHUDS-6 commercial catalyst under the following reaction conditions: pressure, 8.0–12.0 MPa; H_2/LCO volume ratio, 600:1; and LHSV, 1.5 h^{-1}.

2.6. MCI technology

LCOs have the properties of high density, unsatisfactory color, low CN, instability, as well as high contents of sulfur, nitrogen and aromatic compounds et al. MCI technology was developed to maximize the LCO CN to produce high-quality clean diesel. The MCI technology employs special catalysts and single-stage once-through process to remove sulfur and nitrogen in diesel distillates from FCC, realize partially aromatic saturation, and selectively control the ring-opening reaction. This process produces high-quality

Table 2
Properties of commercial catalysts.

		FHUDS-6	FF-46	FC-20	FC-46	FF-36	FC-24
Chemical composition	wt%						
MoO_3		23.5	24.5	–	–	24.0	14.5
WO_3		–	–	25.0	22.5	–	–
NiO		3.5	4.0	7.7	5.0	3.9	5.0
Surface area	m^2 g^{-1}	200	160	200	260	160	350
Pore volume	mL g^{-1}	0.25	0.30	0.30	0.26	0.32	0.28
Diameter	mm	1.2	1.3	1.3	1.3	1.2	1.3
Shape		trilobe	trilobe	column	column	trilobe	column

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