



Direct production of high octane gasoline and ULSD blend stocks by LCO hydrocracking



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ABSTRACT

Hydrocracking of light cycle oil (LCO) is of great scientific and industrial importance to obtain high quality of gasoline and diesel. In this work, a novel LCO hydrocracking technology (FD2G) was proposed, and three kinds of hydroprocessing catalysts (i.e., FC-14, FC-24 and FC-26) were tested under different pilot-scale operational conditions and/or types. All the three catalysts are found to be active for direct production of high octane gasoline and ultra low sulfur diesel (ULSD) blend stocks, and the FC-24 catalyst is the most active and selective toward production of high octane gasoline. The quality of gasoline and diesel products is highly sensitive to pressure and operation type. Furthermore, the FC-24 catalyst was also tested in a large-scale industrial plant. It is found that the yield of gasoline blend stock reaches 30–50 wt%, the octane number of gasoline is 91–94 and the sulfur content is less than 10 µg/g; the cetane number of diesel blend stock increases 10–14 units in comparison to the feed stock, and the sulfur content is less than 10 µg/g.

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1. Introduction

Light cycle oil (LCO), having a similar boiling point to diesel, is a secondary stream from the catalytic cracking (FCC) unit, and its production is increasing with the increase in both light olefins demand and processing heavier feed stock [1]. In China, it accounts for more than 33% in the distillate pool. Because LCO has high aromatic, sulfur and nitrogen contents, high specific gravity and boiling range, as well as low API and cetane index [2,3], it is not practically used as one component of diesel blend stock. Previously, there are two main LCO upgrading technologies, i.e., catalytic cracking [5,6] and hydrogenation [7–21], for the blending of LCO into the refinery automotive diesel [4]. However, higher standards of China IV and V require further upgrading of LCO.

Hydrocracking is a secondary refining process and widely used to upgrade low-quality heavy oils. Recently, hydrocracking of LCO has been studied by using model compounds, light fractions of LCO and LCO diluted with other refinery streams [22–24]. Noble metals, such as Pt, Pd and Pt–Pd alloy, are found to be more active for this process, and the support acidity favors the ring-opening of aromatics [3,25–29]. Nevertheless, these catalysts show low stability and

undergo fast deactivation in the hydrocracking of feeds containing heteroatomic (e.g., S- and N-) aromatics, this suggests pretreatment requirements (e.g., HDS and HDN) of feed stock prior to the hydrocracking. On the other hand, their expense and scarcity are prohibitive to large-scale commercialization, calling for the development of low-cost and high efficient LCO hydrocracking catalysts.

In this work, a novel LCO hydrocracking technology (FD2G) was proposed, and three kinds of non-noble hydroprocessing catalysts (i.e., FC-14, FC-24 and FC-26) were tested under different pilot-scale operational conditions and/or types. The catalyst structure–activity relationship was correlated. Furthermore, under the optimized operational conditions, the most active and selective FC-24 catalyst was also tested in a large-scale industrial plant. The major properties of the as-obtained products were analyzed in detail. To the best of our knowledge, no similar work has yet been reported in the literature.

2. Experimental

2.1. LCO hydrocracking testing

Fig. 1 schematically illustrates a single-pass LCO hydrocracking reactor system. Three kinds of non-noble hydroprocessing catalysts (i.e., FC-14, FC-24 and FC-26) were tested. All technical parameters are precisely controlled using a distributed control system. Both the top and bottom of reactor are filled with inert particles to

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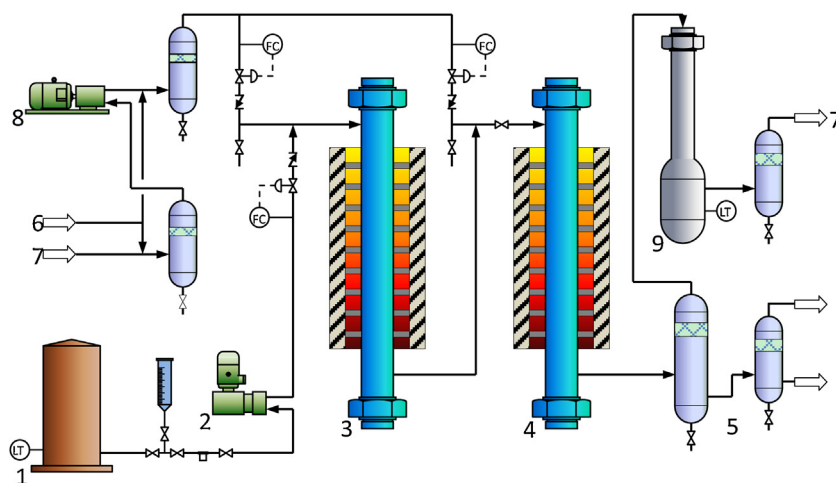


Fig. 1. Schematic flow diagram for a single-pass hydrocracking reactor system (1—feed tank; 2—oil pump; 3—hydrofining reactor; 4—hydrocracker; 5—gas-liquid separator; 6—fresh hydrogen; 7—recycle hydrogen; 8—compressor; 9—water scrubber).

maintain the uniform distribution of the fluids, and to prevent catalyst particles from entering into the pipelines. The catalysts are loaded into the hydrofining reactor and cracking reactors of $D/d_p > 18$ and $L/d_p > 350$, where D , L and d_p are the inner diameter of reactor, bed height and catalyst size, respectively. Electrolytic hydrogen obtained through high-pressure deoxygenation and dehydration using silica gel is used with a purity over 99.9 vol% and its oxygen content is less than 5 $\mu\text{L/L}$. The tail oil can be recycled back to the feed tank with this unit. Thus, the influence of different processes on the reaction can be examined.

Hydrocarbon compositions of feedstock and products were measured with an Agilent 5975C using Ar as a carrier gas according to ASTM D2425 and SH/T 0606. The nitrogen content was determined through nitrogen content analysis (ANTEK-7000), where the analysis standard was SH/T 0704-2001, and the carried gas was Ar, the burning gas was O_2 , and the burning temperature was 1050 °C. The sulfur content was determined through sulfur content analysis (ANTEK-9000), where the analysis standard was SH/T 0689-2000, the carried gas was Ar, the burning gas was O_2 , and the burning temperature was 1100 °C. The cetane number was based on the standard ASTM D4737. The specific operation was to compare the fire properties of the products with that of standard fuels whose cetane number was known under standard conditions. The research octane number was according to the standard GB/T 5487-1995. The specific operation was to compare the fire properties of the products with that of standard fuels whose research octane number was known under standard conditions. The feedstock and products density at 20 °C were according to the standard ASTM D4052. The distillation range was based on the standard ASTM D86. A 100 mL sample was distilled under suitable condition. The temperature and volume of the condensate were recorded. Then the result was calculated with the use of these data.

The conversion and chemical hydrogen consumption are defined as follows:

$$\text{The conversion} = 1 - \frac{\text{the product weight of } > 210^\circ\text{C}}{\text{fractions/the weight of feedstock}} \times 100\%$$

$$\text{The hydrogen consumption} = \frac{\text{the volume of hydrogen consumption(L)} \times 2(\text{g/mol})/22.4(\text{L/mol})}{\text{the weight of feedstock}} \times 100\%$$

Table 1
Physico-chemical properties of Qilu LCO and Zhenhai LCO.

	Qilu LCO	Zhenhai LCO
Density (g/cm^3)	0.921	0.950
Distillation range ($^\circ\text{C}$)		
IBP- T50	151–257	195–284
T95- FBP	341–354	379–389
Chemical analysis (wt%)		
C	88.32	89.14
H	10.54	9.96
S	1.05	0.79
N	0.086	0.11
Alkanes content (wt%)	14.8	13.4
Cycloalkanes content (wt%)	9.9	8.3
Aromatics content (wt%)	75.3	78.3
Cetane number	~17	~15

2.2. Catalyst characterization

The elements of the samples were analyzed by inductively coupled plasma atomic emission spectrometer (Agilent 725-ES ICP-AES). N_2 adsorption measurement of the catalysts were taken on a Micromeritics ASAP 2420 physical adsorption instrument at -196°C . Before testing, each sample was heated at 300°C under vacuum for 3 h. NH_3 -TPD experiments were conducted on an AutoChem 2920 (Micromeritics) apparatus. About 100 mg catalyst sample charged into a glass tube was heated under He flow at the rate of 30°C/min and pretreated at 485°C for 1 h. Then, the temperature was cooled down to 150°C and treated with ammonia diluted in helium for 1 h. Finally, the sample was flushed with He flow for 1 h to remove physisorbed ammonia. The temperature programmed desorption of ammonia (NH_3 -TPD) experiments was carried out from 150 to 500°C at the rate of 10°C/min .

3. Results and discussion

3.1. LCO properties

Main physico-chemical properties of Qilu LCO and Zhenhai LCO are summarized in Table 1. Both LCO have high density and aromatic content, and low cetane number, leading to low-quality of diesel. The central idea of this work is to employ a novel hydrocracking technology (FD2G) to upgrade LCO for direct production of high octane gasoline and ULSD blend stocks, and the details will be presented later. Fig. 2 shows distribution of aromatics in Zhenhai LCO at different boiling range. Clearly, as LCO narrow

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