NOVEL W-NI/ZEOLITE CATALYSTS FOR LIGHT CYCLE OIL HYDROCRACKING TO HIGH OCTANE GASOLINE

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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.

Keywords

Light cycle oil, Hydrocracking, W-Ni catalysts, High octane gasoline, Ultra low sulfur diesel.

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 and hydrogenation , 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. 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. 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

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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.

Results and discussion

LCO properties

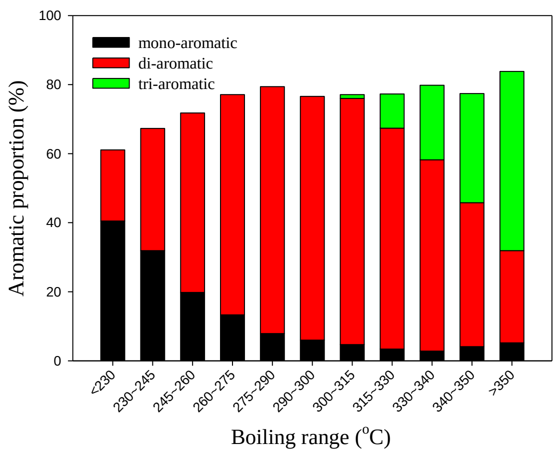

Fig. 1. Distribution of aromatics in Zhenhai LCO at different boiling range

Table 1 Densities, RON/cetane number and compositions of gasoline and diesel products

	FC-14	FC-24	FC-26
Gasoline product			
Density (g/cm^3)	0.751	0.756	0.764
RON	72.0	84.4	70.5
Alkanes content (wt%)	36.8	32.3	28.9
Cycloalkanes content (wt%)	39.5	36.2	47.8
Aromatics content (wt%)	23.7	31.5	23.3
Diesel product			
Density (g/cm^3)	0.863	0.855	0.851
Cetane number	25.0	26.3	38.0
Alkanes content (wt%)	24.7	28.7	32.5
Cycloalkanes content (wt%)	23.4	13.5	30.0
Aromatics content (wt%)	51.9	57.8	37.5

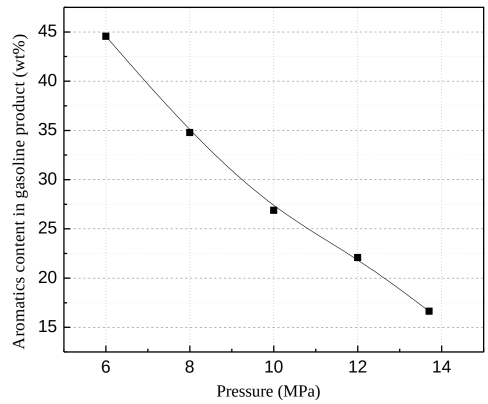

Fig. 2. Dependence of aromatics content in gasoline product on pressure (Hydrogen/oil volume ratio: 1200:1; LHSV: 0.8 h^{-1}; reaction temperature: 385 ^{o}C).

Table 2 Effects of operation type on LCO hydrocracking.

		Once through	Partial recycle	Full recycle
Pressure	MPa	8.0	8.0	8.0
LHSV (fresh feed)	h^{-1}	0.8	0.8	0.4
LHSV (freshfeed+recycle oil)	h^{-1}	-	1.16	0.8
Hydrogen/oil volume ratio		1200:1	1200:1	1200:1
Reaction temperature	^{o}C	405	415	397
One-way conversion	wt%	～51	～55	～50
Gasoline yield	wt%	54.22	53.27	89.65
Diesel yield [b]	wt%	40.81	35.95	-
Hydrogen consumption	%	3.31	3.48	3.99

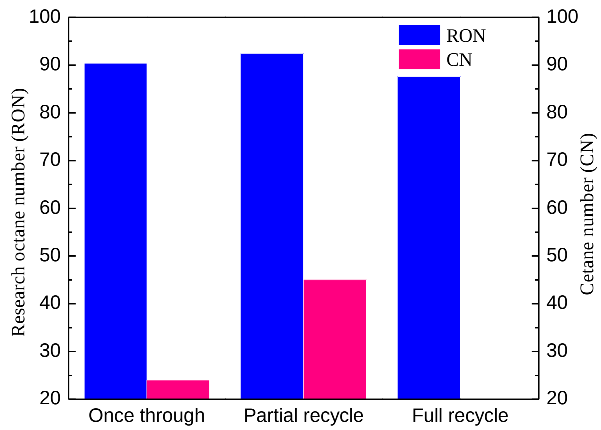

Fig. 3. Dependences of RON and cetane number on operation type.

Table 3 Operational conditions and catalytic performance of industrial-scale LCO

Item		
Fresh feed	t/h	75.1
Recycle oil	t/h	7.0
Pressure	MPa	10.7
LHSV (hydrocarcking reactor)	h^{-1}	1.33
Average temperature of hydrocra-cking reactor	℃	393.9
One-way conversion	wt%	50.95
Hydrogen consumption	%	4.31

Table 4 Physico-chemical properties of the main products.

		gasoline	gasoline	diesel
Fraction range	℃	150-210	65-210	>210
Density	g/cm^3	0.855	0.825	0.872
Distillation range				
IBP- T50	℃	121-172	79-144	229-253
T90- FBP	℃	194-210	186-204	329-365
Cetane number		-	-	31.0
RON		97.1	94.6	-
S	μg/g	0.7	2.4	16.3
N	μg/g	<0.5	<0.5	-
Aromatics content	wt %	73.28	62.01	48.5
Naphthene content	wt %	15.7	25.81	13.4
Paraffin content	wt %	11.02	12.18	38.1

Conclusions

In summary, we have demonstrated that the novel LCO hydrocracking technology (FD2G) effectively upgrades LCO for direct production of high octane number gasoline and clean low sulfur diesel blend stocks. All the three catalysts (i.e., FC-14, FC-24 and FC-26) are active for this technology, and the FC-24 catalyst is the most active and selective towards production of high octane gasoline. The medium pressure and partial recycle operation yield high-quality gasoline and diesel products. The results of industrial application of LCO hydrocracking on the FC-24 catalyst show 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 to 14 units in comparison to the feed stock, and the sulfur content is less than 10 μg/g. This technology has been industrialized in Jinling company in 2013. The insights revealed here could guide the rational design and optimization of catalytic hydrocracking of LCO.

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