HYDROCRACKING OF HEAVY DISTILLATE INTO CLEAN DIESEL OIL USING Ni-Mo/Al_2O_3 CATALYST

by

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ABSTRACT

Diesel oil is high pollution fuel and the quality of this fuel must be improved to obtain clean diesel oil. Crude oil production and its quality tend to decrease. Light fuel oil demand rate is higher than that of residual fuel.

Diesel oil produced in the refineries generally consists of predominantly straight-run diesel oil; however, compounds such as thermally and catalytically cracked diesel oils are sometimes included. The quality of straight-run diesel oil, such as hydrocarbon types and sulfur content, will in general reflect the nature of crude oil. Cracked stocks either thermal or catalytic cracked diesel oils, contain higher percentage of aromatic, olefin and sulfur contents and these cracked diesel products must be hydrogenated prior to rounting to final products.

The passage of the Clean Air Act Amendment of 1990 in the U.S.A has forced American refineries to install new facilities to comply with stricter specifications for fuels such as gasoline and diesel oil.

Hydrocracking processes are a combination of desulfurization and conversion developed primary to process feeds having a high content of unsaturated hydrocarbons (olefin and polycyclic aromatics) and non-hydrocarbon compounds (sulfur and nitrogen compounds) with a bifunctional catalyst. A variety of bifunctional catalysts and processing designs may be used commercially depending on the feedstock used and desired products.

Influence of both feedstock compositions (paraffinic and non-paraffinic vacuum distillate, and wax) and the acidity of bifunctional catalysts on the performance of hydrocracked diesel oil products are discussed briefly in this paper.

Low yield or selectivity of diesel oil products by high catalyst acidity, it is suggested that the higher secondary splitting has taken place in converting cracked products into large amounts of low-molecular weight hydrocarbons such as gasoline and LPG. High diesel index product of the paraffinic feedstock due to the high paraffin content of the produced diesel oil.

I. INTRODUCTION

Diesel oil is high pollution fuel and the quality of this fuel must be improved to obtain clean diesel oil. Crude oil production and its quality tend to decrease. Light fuel oil demand rate is higher than that of residual fuel [1-2].

Diesel oil produced in the refineries generally consists of predominantly straight-run diesel oil; however, compounds such as thermally and catalytically cracked diesel oils are sometimes included.

The quality of straight-run diesel oil, such as hydrocarbon types and sulfur content, will in general reflect the nature of crude oil. Cracked stocks either thermal or catalytic cracked diesel oils, contain higher percentage of aromatic, olefin and sulfur contents and these cracked diesel components must be hydrogenated prior to routing to final products. Sulfur content and diesel index of those diesel oil components is shown in Table 1 [3].

The passage of the Clean Air Act Amendment of 1990 in the U.S.A has forced American refineries to install new facilities to comply with stricter specifications for fuels such as gasoline and diesel oil. With these passage and other environmental legislation in the U.S.A., and abroad, refiners began installing hydroprocessing technologies to clean up cracked stocks from those thermal and catalytic crackers. Specification of clean diesel oil is given in Table 2 [4].

Hydrocracking processes are a combination of desulfurization and conversion developed primary to process feeds having a high content of unsaturated hydrocarbons (olefin and polycyclic aromatics) and non-hydrocarbon compounds (sulfur and nitrogen compounds) with a bifunctional catalyst. A variety of bifunctional catalysts and processing designs may be used commercially depending on the feedstock used and desired products.

Influence of both feedstock compositions (paraffinic and non-paraffinic vacuum distillate, paraffin and wax) and the acidity of bifunctional catalysts on the performance of hydrocracked diesel oil products are discussed briefly in this paper.

Presented in the International Workshop and Seminar on Catalyst Chemestry, Yogyakarta, 13 February 1999.

Table 1
Relation between sulfur content of diesel oil components and their feedstocks

Diesel oil components	Sulfur content, wt. %	
	Feedstock	Gas oil product
Straight-run Diesel oil	1.15	1.05
	2.01	0.90
	3.10	1.45
	3.15	1.85
Thermal-cracked Diesel oil	2.35	1.05
	3.35	2.85
Catalytic-cracked Diesel oil	1.50	0.75
	1.85	1.55

Table 2
Cetane number and specific gravity of diesel oil components

Diesel oil components	Specific gravity 60/60 °F	Cetane number
straight-run Diesel oil - Paraffinic	0.812	62.0
	0.823	57.0
	0.839	54.0
	0.845	50.5
- Intermediate	0.869	41.0
- Naphthenic	0.889	32.5
Thermal cracked - Diesel oil	0.878	45.0
Catalytic cracked Diesel oil	0.847	47.0
	0.851	39.0
	0.872	35.5
Hydrocracked Diesel oil	0.823	62.0

Table 3
Current ASEAN vs. clean diesel oil

		ASEAN	USA	EUROPE
Cetane number		45-47	48	52
Density,	kg/m^3	820-870	820-860	837
T90,	°C	-	-	350
Aromatics,	vol. %	-	10	-
Polyaromatics,	vol. %	-	1.4	6
Sulfur,	ppm	2500-8,000	500	50

II. HYDROCRACKING OF VACUUM DISTILLATE

A. *Influence of Feedstock Compositions*

Hydrocracking of paraffinic vacuum distillate (PV) non-paraffinic vacuum distillate (NPV) and paraffinic wax (WAX) with, low catalyst acidity of Ni-Mo/Al_2O_3 is presented in Table 3 [1].

By increasing conversion of both PV and NPV feedstocks, the yield and selectivities of diesel oil products decrease, but the diesel index of these products increase. PV feed gives high yield and selectivity of diesel oil products than NPV-feed. Higher diesel oil products are given by the higher paraffinic content or lower undesired aromatic content of used feedstocks. At 50% by vol. feedstock conversion with low catalyst acidity, the selectivity and diesel index of diesel oil products are 45% by vol. and 51.5; 65% by vol. and 73.5; 55% by vol. and 87.3 for NPV, PV and WAX feedstocks respectively.

Typical hydrocarbon structures present in heavy distillate consist of three groups i.e., paraffins, single-ring naphthenes and aromatics, and polycondensed naphthenes and aromatics (Table 4) [6,7].

The preferred diesel oil structures are high paraffin content and low content of both single-ring naphthenes and aromatics.

The high diesel index of diesel oil products of hydrocracking of those PV, NPV and Wax feedstocks with low acidity bifunctional catalyst suggest that undesirable polycondensed naphthenes and aromatics components of the feedstock has been converted into the preferred diesel oil molecular structures. Saturation of polyconduced aromatics, opening of some of the naphthenes rings and cracks of paraffins occurs with the following reaction mechanism. The partial hydrogenation of polycyclic aromatics over hydrogenation function catalyst, followed by rapid splitting of the saturated ring to form substitute monocyclic aromatic by both hydrogenation and acidic functions of the bifunctional catalyst.

With bifunctional catalyst, high molecular weight paraffins cracked into low molecular weight paraffins over bifunctional catalyst.

Lower diesel index of hydrocracked products of higher undesired aromatic content of feedstock, at is suggested that the higher undesired aromatic content (single and multi-ring aromatics) of its hydrocracked diesel oil.

At high feedstock conversion it appears that the cracking of products can continue to produce lower molecular weight products and also hydrodecyclization of single ring naphthenes and aromatics into isoparaffins. These reactions lead to lower yield or selectivity of diesel oil product with higher diesel index.

The heavy gas oil from petroleum coking, and catalytic cycle oil are more difficult to hydrocracked than the same fraction derived directly from crude, because of their higher content of polycyclic aromatic hydrocarbons which are alkylated (Table 4) [7].

The growing importance of processing heavier petroleum feeds raises a number of important technical and scientific questions. In particular, the effect of organically complexed metals on catalyst processes is of great significant since vanadium and nickel of ten occur in such feeds at is 100 ppm levels. Metal effects can be physical plugging catalyst pores or chemical: reacting white active sites or the support [8].

Hydrocracking of the heavy distillate feedstock may product clean diesel oil products containing sulfur impurity up to 0.005% by wt, and undesired aromatic hydrocarbons of single-ring aromatics up to 12.5% by wt and multi-ring aromatics up to 4.5% by wt [6].

B. *Influence of Catalyst Acidity*

Hydrocracking of paraffinic vacuum distillate with high catalyst acidity of Ni-Mo/Al$_2$O$_3$-SiO$_2$ is given in Table 3 [7].

By increasing feedstock conversion both low and high catalyst acidities decrease yield and selectivity but the diesel index of diesel oil products increase. Low catalyst acidity produces high yield and selectivity, and low diesel index of diesel oil products than that of high catalyst acidity.

At 50% by vol. feedstock conversion of paraffinic vacuum distillate, selectivity and diesel index are 65% by vol. and 73.5; 42% by vol. and 77.0 for low and high catalyst acidities respectively.

The low diesel index, and high yield and selectivity of diesel oil products of PV-hydrocracking with low acidity bifunctional catalyst, it is suggested that the low conversion of undesired polycondenced naphthenes and aromatics into single ring naphthene and aromatics, and also low rate of paraffin cracking into desired product of lower molecular weight by this low catalyst acidity. With catalyst of higher acidity, the secondary splitting takes place, as a consequently if the higher acidity of the catalyst converting cracked product into large amounts of low molecular weight hydrocarbons.

The highly acidic catalysts are very sensitive to nitrogen compounds in the feed, which break down under the conditions of reactions to give ammonia and neutralize the acid sites. As many heavy distillates contain obstantial amounts of nitrogen (up to approx 2500 ppm) a purification stage is frequently required to reduce up to about 10 ppm (Lepage).

Excessive acidity of bifunctional catalyst tends to cause coke, but this can be overcome by preventing the adsorption of olefinic molecules on to the catalyst with ulitization of high hydrogenation functionality.

Representative bifunctional catalysts are Ni-Mo or NiW on amorphous silica alumina for mild hydrocracking or for production of middle distillate. NiMo or NiW on zeolite can be more active and crack mainly to gasoline and jet fuel products.

Some portion of the reaction is probably thermal rather the catalytic due to the insufficient surface area and macropores to allow easy movement of large heavy distillate molecules. The amount of coke deposited has been found to be functional of catalyst pore diameter.

Catalyst coke content has been also found to decrease with increasing catalyst sulfur content, and wite increasing content of alkaly metal cations. The circulation of large quantities of hydrogen wite the feedstock prevents excessive catalyst fouling and permits long runs without catalyst regeneration.

The primary mechanisms for catalyst deactivation are pore mouth plugging, metals poisoning, and coke deposition. Catalyst composition, particle size, shape, and pore structure must be manipulated to achieve an optimum.

Table 4
Hydrocracked diesel oil of various types feedstocks

Type of feedstocks		Non-paraffinic vacuum distillate			Paraffinic vacuum distillate						Parafinic wax
Operating temperature,	C	400°	410°	420°	390°		400°				410°
		LCA	LCA	LCA	HCA	LCA	HCA	LCA	HCA	LCA	
Feedstock conversion,	vol. %	33.66	50.2	62.6	43.51	40.43	54.38	50.93	83.19	63.01	50.55
Diesel oil products,	yield vol. %	20.17	28.9	28.5	20.11	33.81	21.59	31.9	23.54	34.34	27.89
Selectivity,	yield vol. %	59.92	57.57	45.53	46.22	83.63	39.7	62.63	28.30	54.50	55.17
Diesel index		45.2	50.5	56	73	68.7	79.2	74.8	83.2	78.2	87.3

Note: LCA and HCA = Low catalyst acidity and high catalyst acidity.

III. CONCLUSION

1. By increasing feedstock conversion, the yield and selectivity of hydrocracked diesel oil products decrease, but the diesel index of these diesel oil products increase. Diesel index of hydrocracked diesel oil products increases the paraffinic content of feedstock, i.e., non-paraffinic vacuum distillate < paraffinic vacuum distillate < paraffinic wax. Low catalyst acidity gives high yield and low diesel index of hydrocracked diesel oil products than that high catalyst acidity.
2. The hydrocracking catalyst must be developed to obtain a balance between hydrogen transfer functionality and cracking functionality to achieve the decided state of product without coke deposition. The extreme versatality of hydrocracking with respect to its ability to process a wide variety of feedstocks into a wide variety of desirable products has made this hydrocracking process the leading process for production of clean diesel fuels.

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