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Comparative investigations of hydrotreating catalysts in laboratory and process conditions

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Abstract

Hydrotreating procedures have exceptional place in modern oil refineries as the most effective way to improve oil products quality. The variation of process parameters by laboratory reactor simulation using different crudes and catalysts is a useful and economic tool for the optimisation of these processes in practice. There are presented comparative investigations of commercial industrial hydrotreating catalysts and various feeds as a support for real refinery practice. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Nowadays the refinery industry is facing a great challenge of very stringent limitation of sulphur and other contaminants. The key environmental technologies that provide product quality opportunities and cost-effective solutions are hydrotreating processes. Improved environmental performance is mostly based on update catalysts formulations [1].

These new catalysts provide active metal loadings offering higher HDS activity, specially for middle distillates. Modified pore structure improved diffusivity and gives better resistance to carbon deposition. The novel catalysts with higher selectivities using the zeolites as carrier are developed too. The new catalyst generation with silica promoted alumina having higher HDS activity and more coke tolerance has been evaluated, as well.

In spite of that the refineries often seek improved solution in existing units through small, but significant improvements in catalysts performances. Such improvements in commercial scale units are difficult to predict without responsible laboratory or pilot plant test-work.

It is known that the technological problems related to catalyst use in practice (such as effects of feed quality process conditions, catalyst performances) may be successfully solved using laboratory simulation of industrial hydrotreating process. So, the proposal of exact option for best catalyst selection and their valorisation need laboratory investigation of new catalyst samples and permanent control during their use.

This paper describes our experience in laboratory simulation of the hydrotreating process with different HT catalysts (based on CoMo, or NiMo, respectively, deposited on Al_2O_3). The various petroleum fractions (gasoline, diesel fuels and gas oils) were included in these experiments. The process parameters were simulated analogous to real Oil Refinery Pančevo hydrotreating units. The objectives of these studies were oriented to optimum contaminant reduction, depending on feed quality and used catalyst.

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2. Experimental

The experiments were realised in commercial continuous high pressure twin reactor system FOK GYEM, model OL-105 with 100 cm^3 catalyst volume, under isothermal operation [2]. The various petroleum fractions were tasted using different HDS catalysts. The process parameters used in experiments simulated the run of some real hydrotreating unit. The content of undersigned contaminants [3] was analysed before and after every set of process conditions.

The used catalysts were presulphided in situ by DMDS using catalyst producer recommendations, concerning the limits of real HT units and technical possibilities of laboratory reactor [4]. All the catalysts, before and after use in laboratory reactor, were characterised for chemical, physical and mechanical properties.

2.1. Hydrodesulphurisation of gasoline fractions

2.1.1. Straight run gasoline

Straight run gasoline from high sulphur level crudes (200–350 mass ppm sulphur content in feed) was processed to reach sulphur level below 0.5 mass ppm, proposed for platforming unit feed.

The catalysts of different commercial producers based on CoMo, or NiMo/Al_2O_3, respectively, were used. The operating conditions corresponding commercial unit and laboratory test results are summarised in Table 1.

Table 1
Hydrodesulphurisation of straight run gasoline with different HDS catalysts

	1	2	3	4	5	6
Catalyst[a]	NiMo	CoMo	CoMo	NiMo	CoMo	NiMo
Feed	Straight run gasoline					
Operating conditions						
Pressure (MPa)	5.6	5.6	5.6	5.6	5.6	5.6
Temperature (°C)	360	350	350	340	300	355
H_2/feed (mol/mol)	50:1	50:1	50:1	50:1	50:1	50:1
Product quality						
Sulphur, mass ppm	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5

[a] All the catalysts, except No. 1, were polilobe extrudates.

Table 2
Hydrodesulphurisation of straight run gasoline and visbreaking gasoline blend

Feed	SR/VR = 90/10 vol.%	SR/VR = 90/10 vol.%
Feed quality		
Density (20°C) (g/cm^3)	0.747	0.752
Sulphur (mass ppm)	1617	13800
Nitrogen (mass ppm)	3.6	
Distillation (°C)		
IBP/FBP	73/190	42/204
FIA (stabilised sample) (vol.%)		
P + N	89.4	48.5
O	2.4	38.6
A	8.2	12.9
Operating conditions		
Catalyst	CoMo	NiMo
Catalyst volume (ml)	50	100
Pressure (MPa)	5.6	3
Temperature (°C)	330	320
LHSV (h^{-1})	3.5	3
H_2/feed (Nm^3/m^3)	50:1	100:1
Product quality		
Density (20°C)	0.749	0.746
Sulphur (mass ppm)	0.5	0.02
Distillation (°C)		
IBP/FBP	75/184	
FIA (stabilised sample) (vol.%)		
P + N	92.5	90.1
O	0	0.3
A	7.5	9.6

2.1.2. Straight run gasoline and visbreaking gasoline blend

The economical and ecological valorisation of visbreaking gasoline can be attained by blending with straight run gasoline. The objective was also to reach the quality of platforming unit feed. All specifications and test results are summarised in Table 2.

2.2. Hydrodesulphurisation of middle distillates

2.2.1. LGO and LCO blend

The proposed objective of HDS test with blended LGO and LCO feed was to obtain diesel fuel with sulphur level below 0.1 mass% using CoMo catalyst existing in real unit.

The feed quality, operating conditions and test results are summarised in Table 3.

Table 3
Hydrodesulphurisation of LGO and LCO blends

Feed	LGO 100	LGO/LCO 70/30 (vol.%)	LGO/LCO 50/50 (vol.%)
Feed quality			
Sulphur (mass%)	0.76	1.23	1.49
Density (20°C) (g/cm^3)		0.862	0.884
Operating conditions			
Catalyst		CoMo	CoMo
Catalyst volume (ml)		50	50
Pressure (MPa)		4.4	4.4
Temperature (°C)		320	340
LHSV (h^{-1})		2	2
H_2/feed (Nm^3/m^3)		100:1	100:1
Product quality			
Sulphur (mass%)	0.08	0.17	0.098

Table 4
Hydrodesulphurisation of LGO and LVGO blends

Feed	LGO		LVGO	LGO/LVGO			
				90/10 vol.%		80/20 vol.%	
Feed quality							
Density (20°C) (g/cm^3)	0.828		0.868	0.832		0.836	
Sulphur (mass%)	0.23		0.533	0.266		0.29	
Nitrogen (mass%)	0.004		0.189	0.0056		0.007	
Distillation (°C)							
IBP/FBP	206/342		279/400	208/370		208/386	
FIA (stabilised sample) (vol.%)							
P + N	83.1		68	81.5		80.1	
A	16.9		32	18.5		19.9	
O	0		0	0		0	
Cetane index	56.2		58.5	55.4		55.6	
Operating conditions							
Catalyst	CoMo-1	CoMo-2		CoMo-1	CoMo-2	CoMo-1	CoMo-2
Catalyst volume (ml)	100	100		100	100	100	
Pressure (MPa)	4.5	4.5		4.5	4.5	4.5	4.5
Temperature (°C)	330	320		340	340	350	350
LHSV (h^{-1})	3	3		2.5	2	2.5	2
H_2/feed (Nm^3/m^3)	100:1	100:1		100:1	100:1	100:1	100:1
Product quality							
Sulphur (mass%)	0.056	0.026		0.036	0.046	0.043	0.057
Nitrogen (mass%)	0.0007	0.00075		0.001	0.00115	0.0016	0.057
FIA (stabilised sample) (vol.%)							
P + N	85	81.7		81.7	81.9	81.7	81
A	15	18.3		18.3	18.1	18.3	19
Cetane index	57.7	57.1		58	57.6	58.1	57.9

2.2.2. LGO and LVGO blend

The objective was to reach new proposed diesel fuels specifications of less than 0.05 mass% sulphur level in blended feeds of 80–90 vol.% LGO with 20–10 vol.% LVGO using catalysts of different producers, based on CoMo/Al_2O_3 formulation.

The feed quality, operating conditions and test results are summarised in Table 4.

3. Results

Hydrodesulphurisation of straight run gasoline (Table 1) indicate that catalyst No. 5 is the most active as the temperature of 300°C is sufficient to reach the demanded sulphur level lower then 0.5 mass ppm. However, the rapid deactivation was observed. So, the catalyst No. 4 based on NiMo was proper one to reach the proposed sulphur level at temperature 340°C, with less deactivation.

The data obtained by hydrodesulphurisation of straight run gasoline and visbreaking gasoline blend (Table 2) indicate that 320 and 330°C, respectively, is sufficient temperature for less than 0.5 mass ppm sulphur in product. As can be seen sulphur level lower than proposed is relatively accessible by using a good hydrotreating commercial catalysts, based on NiMo.

Hydrodesulphurisation of middle distillates (LGO and LCO blend) reported in Table 3 indicates that mass% sulphur in product is accessible using existing CoMo process catalyst with tested blended feed up to 50:50 vol.% LGO:LCO at suitable operating conditions.

For LGO and LVGO blend obtained results (Table 4) indicate that cleaner diesel fuels (specifications of less than 0.05 mass% of sulphur) are possible to reach using these catalysts and suitable operating conditions, especially lower LHSV.

The proposed objective is attained at the temperature level of 320, 330, 340 and 350°C but the sulphur content in product is various. For pure LGO sulphur content is double lower with catalyst No. 2. Moreover, in the case of blends with 10 and 20 vol.%, respectively, LVGO sulphur level in products is lower with catalysts No. 1. The test also confirm that both the catalysts can reduce nitrogen level too. Catalysts No. 2 shows better HDN activity on testing blends.

Almost every shown result is proven in practice. The transposition of laboratory simulated conditions in real process gave all but same results.

At all events, the way to reach proposed aim is shorter, cheaper and rather successful. It gives opportunity to make some responsible decisions with less risk. Moreover, the samples of catalysts used in experimental work are broad base for deactivation study [5].

4. Conclusion

Laboratory simulation of industrial hydrotreating unit using commercial CoMo or NiMo catalysts were carried out in the flow pressure reactor with fixed catalyst bed.

Our experience have confirmed that laboratory simulation of industrial hydrotreating process may provide the answer how some refinery can optimally utilise its existing resources; available crude oils and processing units with present or new catalysts, to realise the demand for processing heavier feedstocks and the need for high quality products.

The key operating conditions for hydrotreating unit include, beside the catalyst quality, catalyst bed temperature, hydrogen partial pressure and liquid hourly space velocity, specially for heavier fractions [6].

So the shown results made possible to solve some technological problems; the choice of proper reactor temperature and space velocity for every type of feed and catalyst used.

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