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CATALYST ADVANCES PROMOTE PRODUCTION OF NEAR ZERO SULPHUR DIESEL

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Abstract

This work discusses the results of commercial test performed at the Lukoil Neftochim Bourgas, Bulgaria middle distillate hydrodesulphurization units indicating that by proper catalyst selection and optimized feed stock composition it is possible to produce near zero sulphur diesel.

Key words: ULSD; NZSD; hudrodesulphurization.

1. Introduction

The near zero sulphur diesel(NZSD) must be available at the petrol station pump as from 01.01.2009 in the whole European union according to Directive 2003/17/EC. In order to meet this requirement the European refining has been forced to plan reconstruction of the existing hydrotreatment units and construction of new high pressure hydrotreaters [1,2].

The catalyst suppliers committed great afford to help refiners to achieve the goal – near zero sulphur automotive fuels production. As a result new catalyst families appear in the market[3]. Lukoil Neftochim Bourgas (LNB) the only refinery operating in Bulgaria at present time has started a programme with the aim to search cost effective ways for meeting the requirements of the near zero sulphur fuels. Several middle distillates from different origin have been hydrotreated in the pilot unit of the research department on the most active catalysts available today in the market [4-12]. As a result knowledge was accumulated that has helped the LNB process engineers to optimize the operation of the middle distillate hydrotreaters. The transition from 0.2 to 0.05, 0.035 and 0.005 % sulphur in diesel has been achieved in the LNB refinery only on the base of feedstock composition optimization and proper selection of catalyst [9,13]. The catalyst has played major role in achieving the goal of production of ULSD. The approach of feedstock composition optimization has been also applied in the LNB refinery in its aim to start production of NZSD before the mandate date of 01.01.2009. The aim of this work is to discuss the results of commercial tests carried out at the LNB middle distillate hydrotreaters.

2. Experimental

Technological scheme of the LNB refinery is presented on Figure 1. On Figure 2 is depicted a diagram of the technological scheme for production of automotive diesel in the LNB. Properties of the streams used as feed stocks for the LNB hydrotreaters are given in Table 1. The Lukoil Neftochim Bourgas hydrodesulphurization units HDS-1 and HDS-4 treat light middle distillate fractions (SRGO 180-240, SRGO200-300, and FCC LCO) while the units HDS-2 and HDS-3 treat heavy diesel fractions: SRGO 240-360; LVGO; VBGO and the remaining part of the SRGO 200-300. The conditions at which the LNB HDS units operate are summarized in Table 2.

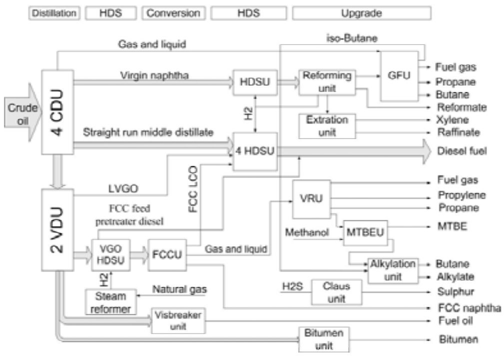

Figure 1 Simplified processing scheme of the Lukoil Neftochim Bourgas Refinery

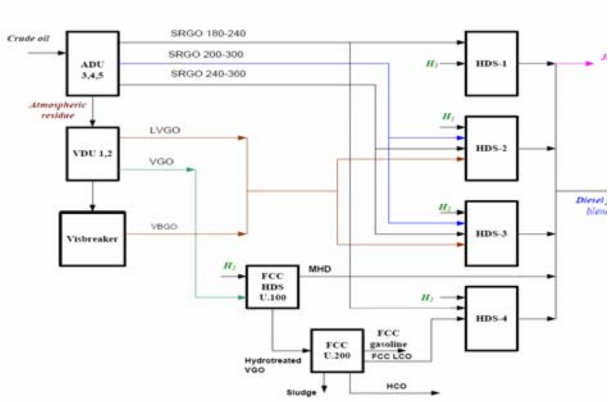

Figure 2. Simplified technological scheme for production of automotive diesel in the LNB refinery

Table I Properties of the middle distillates used as feed stocks for the LNB HDS units (HDS-1,2,3,4)

Properties	SRGO 180-240	SRGO 200-300	SRGO 240-360	LVGO	FCC LCO	VBGO
Density at 20^{o}C, kg/m3	803.2	837	857.5	864.9	915.1	816.8
Distillation according to ASTM D 86, o C						
IBP	166	188	230	247	170	132
5 % v/v distilled at		217	257	282	191	177
10 % v/v distilled at	184	224	266	288	195	186
30 % v/v distilled at	196	236	283	303	211	204
50 % v/v distilled at	207	243	298	314	223	224
70 % v/v distilled at	218	251	315	329	236	249
90 % v/v distilled at	233	265	344	361	254	289
95 % v/v distilled at	240	274	360	377	267	309
EBP	248	289	368	379	282	327
Content of fraction boiling over 340^{o}C (according TBP), % v/v	0	0	30	33	0	3
Sulfur, % w/w	0.4	0.36	0.87	1.21	0.0519	1.53
Nitrogen. % w/w		0.0068	0.012	0.026	0.0346	0.0337
Polycyclic arenes. % w/w	5.4	6.3	12.68	22.2	51.2	3
Total arenes. % w/w	22.0	20	29.4	45.4	86.9	26
Cetane index	46	44.4	52.6	54.8	16.4	46.9
Bromine number. g Br2 /100 g			3	4		

Table II Operating conditions at the LNB hydrodesulphurization units

Process parameter	HDS-1	HDS-2	HDS-3	HDS-4
Feed Rate. m^3/h	60	100	130	90
Space velocity. h^{-1}	2.9	2.1	1.6	4.9
Total pressure. MPa	2.2-2.8	3.3	3.4	4.3
H_2/feed ratio. nm^3/m^3	380	290	250	344
Fresh H_2 consumption. Nm^3/m^3 feed	14	48	40	47
H_2 content in recycle gas. % v/v	80-92	60-87	60-83	70-95
Reactor temperature. ^{0}C	310	330-400	340-400	320-400

3. Results and discussion

The light middle distillates are known to not contain the most refractory disubstituted dibenzothiophenes above 340ºC [15]. That is why the gas oils SRGO 180-240, SRGO 200-300 and FCC LGO have been hydrotreated to less then 10ppm in the LNB HDS-1 and HDS-4 without any difficulties. The most difficult heavy middle distillate fractions have been hydrotreated in HDS-2 and HDS-3 units. The selection of the Topsoe TK-576 BRIM catalyst as a result of extensive pilot plant investigation programe[9] was found to be the key driver for production of ULSD and NZSD. The use of this catalyst in the LNB has allowed 100% production of ULSD without any reconstruction of the HDS units. Now the target was to start production of NZSD much earlier than the mandate date of 01.01.2009. Based on the model developed in the research department[16] the HDS-2 and HDS-3 unit feed stocks were optimized. The optimization consisted of determining the proper ratio between heavy diesel fractions and the light SRGO 200-300 in a way to get feedstock with a definite 340ºC + fraction content. Table 3 summarizes the results of the commercial test on the LNB HDS-3 unit.

Table III Commercial test results obtained at the LNB HDS-3 unit

	Initial conditions of the tests	Test 1	Test 2	Test 3	Test 4	Test 5
LHSV. hr^{-1}	1.6	1.6	1.6	1.6	1.6	1.6
Product Sulphur. %	0.0054	0.0025	0.0015	0.0013	0.0009	0.0013
Feed Sulphur. %	0.910	0.910	0.851	0.851	0.721	0.695
WABT[1]. ^0C	360	365	370	370	370	370
340+ content in the feed. % v/v	25.5	22.1	21.3	19.9	15.3	20.3

[1]*WABT - weight average bed temperature = reactor inlet temperature + 2/3 reactor delta temperature*

It can be seen from these data that NZSD can be produced by optimizing the feedstock 340ºC + fraction content and the reactor temperature. The HDS-2 has been running for more than 12 months with once ex-situ regenerated TK-576 BRIM catalyst and its goal in this test was to produce hydrogenate with sulphur level not higher than 100ppm. This unit operated at a higher LHSV than HDS-3 and a reconstruction of it has been planned in early 2009. That is why the requirements for this unit were lower than those for HDS-3. The level of 100 ppm sulfur in the HDS-2 hydrogenate was sufficient to achieve simultaneous production of ULSD and NZSD in the LNB refinery. The results of the commercial test in the LNB refinery have indicated that NZSD is possible to produce by proper feedstock preparation and proper catalyst selection. The TK-576 BRIM catalyst selected on the base of preliminary pilot plant study has proved its ability to contribute to the production of ULSD and NZSD. In has also proved to have a high stability allowing the LNB refinery to run at high reactor temperature compensating the problems with the poor reliability the HDS unit heat exchangers[16].

4. Conclusions

The right catalyst selection and proper management of the middle distillates used as feedstock for the LNB hydrotreaters has allowed the production of NZSD to start earlier than the mandate date of 01.01.2009 year.

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