

DOMESTIC HYDROTREATING UNITS. STATUS AND MODERNIZATION METHODS

A. I. Yelshin, R. R. Aliev, V. P. Tomin, and S. G. Krashchuk

UDC 665.644.26.097

Data on use of domestic hydrotreating units are generalized. Ways of enhancing operation of the units to improve their technical and economic indexes are indicated. The results of operation of the L-24-6 unit at Angarsk Petrochemical Co. on AGKD-205A catalyst for manufacture of diesel fuel with a sulfur content of less than 0.05% are reported.

Hydrotreating of middle distillates is primarily conducted on L-24-5, L-24-6, L-24-7, LCh-24-7, LCh-24-2000, and LK-6U units and hydrorefining of vacuum distillates – feedstock for cat crackers – is conducted on KT-1 and G-43-107 complexes. The first four units, started up in the 1960s-1970s, are double-flow. They have two serially connected reactors in each stream (version I) with a catalyst volume of approximately 14 m³ in each one. The next two, more modern units have one reactor in each with a 70 m³ catalyst volume. The average process parameters for the first four units in processing different types of feedstock are reported in Table 1 [1-9]. They ensure the required degree of desulfurization of diesel fuel: the residual sulfur content does not exceed 0.2%, which corresponds to the specifications.

The domestic catalysts GKD-202, TKD-205, GO-117, GS-168Sh, GP-497, GKD-202P, GP-534, GKD-205A, and others were initially used in hydrotreating processes [10]. It later became necessary to manufacture diesel

Table 1

Indexes	Hydrotreating unit in refining of feedstock				
	1	2	3	4	5
Feedstock space velocity, h ⁻¹	5 – 7	3	2.5	3	2.5
Temperature in reactors, °C	320	340	345	350	355
Pressure in reactors, MPa	3.3	3.2	3.3	3.4	3.4
Pressure differential over reactor, MPa	0.1	0.1	0.15	0.2	0.2
Residual sulfur content in hydrogenation product, wt. %	0.008	0.1	0.12	0.13	0.15
Time between regenerations, years	2	2	1	1	1
Total lifetime, years	7	6	5	5	5
<i>Notation.</i> 1) jet fuel cut; 2, 3) straight-run diesel fuel cut with sulfur content under 0.8 and over 0.8 wt. %; 4, 5) diesel fuel cut in mixture with up to 10 and up to 20% secondary gasoils.					

Angarsk Petrochemical Company. VNII NP Company. Translated from *Khimiya i Tekhnologiya Topliv i Masel*, No. 3, pp. 15 – 17, May – June, 2005.

fuel with a lower content of sulfur compounds. A number of studies was conducted for this purpose, and the following proposals were made:

- new catalytic compositions GKD-300 and AGKD-205A with higher hydrogenating and strength properties;
- a combined scheme for sulfuring of the initial catalyst that ensures more complete conversion of metal oxides into sulfides and disulfides;
- a special method of loading the catalyst using FOR-1 preliminary catalytic purifier as the protective layer for the catalyst.

Implementation of these proposals on the L-24-6 industrial unit at Angarsk Petrochemical Co. ensured production of diesel fuel with 0.05-0.11% sulfur at sufficiently high output in feedstock [3-5]. This facility differs from other similar domestic facilities in the parallel scheme of connecting both single-stream reactors (version II).

This scheme, combined with the load in the upper part of the reactor of hollow cylinders of FOR-1 preliminary catalyst purifier as a protective layer, increased the output of the unit and brought the feedstock space velocity to 4-5 h⁻¹ without increasing the pressure differential and without regenerating the catalyst for three years.

A fixed run of the L-24-6 unit using mixed diesel cuts as feedstock was conducted to determine the activity potential of AGKD-205A catalyst. The basic process parameters and results of the run are reported in Table 2. The

Table 2

Feedstock space velocity, h ⁻¹	Consumption of HCG (fresh) in normal conditions, m ³ /h	Temperature in reactor, °C		Excess pressure in reactor, MPa	Sulfur content in product, wt. %
		at inlet	at outlet		
3/4	2000/2500	335/335	345/345	3.3/3.3	0.08/0.12
3/4	1800/3000	340/335	360/345	3.6/3.6	0.08/0.1
3/4	2300/3000	350/335	370/345	3.6/3.6	0.04/0.09
3/4	2000/2600	350/335	360/345	3.5/3.5	0.05/0.06
3/4	2000/2600	350/335	360/345	3.3/3.3	0.08/0.1
4/4	2000/2300	350/335	360/345	3.3/3.5	0.06/0.08
4/4	2000/2500	350/335	360/345	3.6/3.6	0.08/0.1
4/4	2600/1400	350/250	360/250	3.6/3.6	0.05/0.1
4/4	3800/2200	350/250	360/250	3.6/3.6	0.07/0.09
4/5	2900/2900	350/335	360/340	3.5/3.5	0.04/0.12
4/5	2500/2500	360/335	360/340	3.6/3.6	0.04/0.04
4/5	2600/2700	360/335	360/340	3.6/3.6	0.06/0.05
4/5	2500/2300	360/335	360/340	3.6/3.6	0.03/0.08
4/5	2300/2200	360/335	360/350	3.6/3.6	0.04/0.09
4/5	2200/1800	360/335	360/350	3.6/3.6	0.03/0.1
4/5	1400/1200	360/335	360/345	3.6/3.6	0.03/0.011
4/5	1900/1800	360/335	360/345	3.5/3.4	0.04/0.1
4/5	1300/1400	360/335	360/345	3.5/3.5	0.04/0.05
5/5	2400/2400	340/335	360/345	3.4/3.4	0.04/0.08
5/5	2200/2200	340/335	360/345	3.5/3.5	0.05/0.06

Note. In the numerator: for the first stream; in the denominator: for the second stream.

content of secondary products in the feedstock – light catalytic gasoil, naphtha and diesel coking cuts – was 16-24%.

The catalytic system used produced diesel fuel with a residual content of sulfur compounds of 0.05-0.12% at a temperature of 335°C in the reactors. After increasing the temperature to 360°C, the diesel fuel obtained contained less than 0.05% sulfur.

Additional reactors (version III) were installed in a number of units during revamping to produce low-sulfur diesel fuel [7-9]. As a result, their output in feedstock almost did not change, while the feedstock space velocity decreased to 1.6-2 h⁻¹. Hydrotreating takes place in the new reactors at a maximum pressure of 3.5 MPa.

This does not allow increasing the depth of hydrodesulfurization and if necessary hydrogenating polycyclic aromatic hydrocarbons. As experience shows, decreasing the space velocity without increasing the pressure does not guarantee a product with a low content of these hydrocarbons.

In industrially developed countries, the diesel fuel quality requirements are becoming increasingly stiff. The new EU standards limit the sulfur content to 350 ppm, and beginning in 2005, it cannot be any higher than 50 ppm. The polycyclic aromatic hydrocarbon content must not exceed 11%, and decreasing it to 6% and then to 4% is planned in the future. To satisfy these requirements, it is desirable to:

- use a system of the highly active Al–Ni–Mo and/or Al–Co–Mo catalytic compositions which have high hydrogenating functions with respect to both sulfur compounds and polycyclic aromatic hydrocarbons;
- increase the partial hydrogen pressure at the maximum overall pressure and hydrogen:feedstock ratio;
- reduce the proportion of secondary kinds of feedstock;
- decrease the end point of the initial gasoil (this solution should be used in exceptional cases, since it can decrease the feedstock life);
- replace the units for stabilization and removal of hydrogen sulfide from gases;
- replace the furnaces.

Implementation of these solutions by stages guarantees:

- introduction of an almost new unit without stopping production;
- production of low-sulfur diesel fuel after the first stage;
- saving on investments due to partial use of available equipment and process communications;
- increasing the efficiency of the unit in feedstock while decreasing the content of both sulfur compounds and polycyclic aromatic hydrocarbons in the diesel fuel obtained.

However, a new unit with one-time investment of \$60-80 million must be built.

Table 3

Indexes	Hydrotreating unit operating in version				
	1	2	3	4	5
Number of reactors	4	4	6	2	2(3)
Volume of catalyst loaded, m ³	48	48	180	150	180
Output in feedstock, millions of tons/year	1.2	1.5	1.3	2.5	1.3(1.0)
Working pressure in reactors, MPa	3.4	3.7	3.5	5	5
Pressure differential over reactors, MPa	0.1	0.05	0.15	0.1	0.1(0.2)
Content in hydrogenation product, wt. %					
sulfur compounds	0.12	0.06	0.06	0.03	0.02(0.2)
polycyclic aromatics	15	13	14	5	3 – 5
Note..	In parentheses: in hydrotreating of vacuum gasoil				

Fundamental revamping (version IV) of obsolete units for hydrotreating of middle distillates with replacement of old reactors with a volume of less than 15 m³ operating under pressure of approximately 3.5 MPa by reactors with a minimum volume of 50 m³ designed to operate under high pressure (preferably 6-7 MPa) is proposed as an alternative.

A preliminary reactor (version V) can be included in front of the basic reactor in the scheme of one of the unit's streams if hydrotreating of vacuum gasoil is necessary. The preliminary reactor can be loaded with spent hydrotreating catalyst, using it to remove particulate contaminants, metal compounds, and coke from the feedstock. This is especially important in refining of vacuum gasoil with an end point of 530-560°C.

The lifetime of the catalyst in the preliminary reactor is 8-10 months. It is then regenerated or replaced. All of these proposals guarantee an increase in the degree of hydrodesulfurization and a decrease in the metal, coke, and nitrogen compound content in the product. In addition, the yield of naphtha cuts is increased by 0.9-2% as a function of the type of unit and the quality of the feedstock while decreasing the amount of sulfur in them by 30-40%.

The basic technical and economic indexes for operating the different versions of domestic hydrotreating units are generalized in Table 3. The best indexes were obtained in the case of installing new reactors and simultaneously increasing the partial pressure in them.

This version produces a better-quality product with respect to both the sulfur compound and the polycyclic aromatic hydrocarbon content. Power consumption is reduced both in operation and in regeneration of the catalyst.

REFERENCES

1. R. R. Aliev, E. D. Radchenko, and B. K. Nefedov, *Khim. Tekhnol. Topl. Masel*, No. 4, 16-18 (1988).
2. S. A. Loginov, V. M. Kapustin, A. I. Lugovekoi, et al., *Neftepererab. Neftekhim.*, No. 10, 8-10 (2001).
3. A. I. Yelshin, V. I. Anufriev, I. V. Kuks, et al., *Khim. Tekhnol. Topl. Masel*, No. 3, 36-38 (2000).
4. R. R. Aliev, A. I. Yelshin, and F. I. Seredyuk, *Neftepererab. Neftekhim.*, No. 6, 15-18 (2001).
5. R. R. Aliev, A. I. Yelshin, I. V. Kuks, et al., *Katal. v Promyshlennosti*, No. 6, 51-56 (2002).
6. A. Yu. Munirov, E. L. Talisman, D. O. Belikov, et al., *Neftepererab. Neftekhim.*, No. 1, 17-20 (2003).
7. RF Patent No. 2206396.
8. R. R. Aliev, V. A. Ovsyannikov, Roman R. Aliev, et al., *Khim. Tekhnol. Topl. Masel*, No. 6, 11-13 (1997).
9. P. R. Saifulin, V. A. Gantsev, A. M. Sukhorukov, et al., *Ibid.*, No. 2, 13-15 (2001).
10. E. D. Radchenko, B. K. Nefedov, and R. R. Aliev, *Industrial Catalysts of Hydrogenation Processes* [in Russian], Khimiya, Moscow (1987).