INTENSIFICATION OF CATALYTIC REFORMING PROCESS

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The catalytic reforming process occupies the leading place in the scheme of a refinery; it is the main source of the high-octane component of automotive gasolines, and also technical hydrogen for diesel fuel hydrotreating units. At the Ufa refinery, a reformer was put into service without any provision for preliminary hydrotreating of the feed; the reformer initially operated on a wide-cut naphtha (IBP-180°C) from high-sulfur crudes, with sulfur contents up to 0.15% and naphthene contents of 20-22%.

The octane number of the stabilized reformate was 72-73, with an aromatics content of 25%; AP-56 catalyst was used in the process. Feedstock specified by design (85-180°C) was not supplied to the unit, owing to the lack of any process section for naphtha redistillation. The reforming process was accompanied by considerable formation of gas. The vessels and piping, particularly the furnace coils, were severely corroded.

The poor efficiency of catalytic reforming of the naphtha cut was due mainly to the high content of organic sulfur compounds in the feed, deactivating the platinum catalyst. As a result, the naphthene dehydrogenation reaction was suppressed; hydrocracking reactions predominated, with considerable formation of gas. Corrosion products were deposited in the upper layer of catalyst in the first reactor, forming a dense cake consisting mainly of iron oxides.

These deposits contributed to a rapid rise in pressure drop across the reactors, up to 0.3-0.6 MPa, along with overheating of the reactor walls. In order to eliminate these phenomena, dust traps (baskets) were installed in the reactors (this extended the reaction cycle to some degree), provisions were made for feeding cold hydrogen to the inner wells of the reactors, and part of the gas—feed mixture was bypassed around the first reactor.

In the interest of more efficient utilization of the catalyst, a scheme of stepwise-countercurrent cross-loading of the catalyst was put into effect. The most thoroughly exhausted catalyst from Stage I was withdrawn from the cycle; the Stage II catalyst was unloaded, screened, and recharged to Stage I; fresh catalyst was charged to Stages II and III. This gave a more thorough utilization of the catalyst and made it possible to carry out the reforming process in the required direction. However, these measures did not eliminate the increase in pressure drop across the reactors. Oxidative regeneration was performed two or three times per year, and it did not completely restore the catalyst activity and stability.

In order to "intensify" the catalytic reforming process, a unit was put into service for preliminary hydrotreating of the feed. The typical hydrotreating scheme was modified in part.

TABLE 1

Run no.	Chemical composition of feed, %				Octane number of reformate	Sulfur content, wt. %	Temp. in reactors (inlet/outlet), °C		
	unsatur.	aromatics	naphthenes	paraffins			Stage I	Stage II	Stage III
1	0,16	8,23	28,45	77,3	77,3	0,0031	505/455	505/485	512/505
2	0,16	11,16	31,27	57,47	83,45	0,0029	496/446	499/474	505/495
3	0,13	10,06	36,75	53,06	83,1	0,001	501/442	505/483	483/478
4	0,22	9,9	35,7	54,4	81,4	0,0016	506/445	507/496	500/494
5	0,10	11,2	35,2	53,5	82,6	0,0004	509/485	511/491	509/493
6	0,20	10,6	35,53	53,69	80,7	0,00056	510/485	511/491	509/493
7	0,10	10,62	32,68	56,6	82,0	0,005	508/469	504/500	495/491
8	0,11	10,14	36,16	53,89	80,9	0,0007	495/470	499/476	497/496
9	0,20	9,3	36,7	53,8	81,1	0,0003	497/437	485/460	496/496
10	0,14	9,42	37,1	53,8	80,4	0,00021	494/433	494/466	489/467
11	0,14	9,41	33,65	56,9	80,0	0,0016	489/434	489/467	488/488

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TABLE 2

Index	Before reconstruction			After reconstruction		
	feed	hydrotr. prod.	platformate	feed	hydrotreated product	platformate
Distillation, °C						
IBP	97	99	36	107	110	36
10 %	169	111	64	—	118	80
50 %	127	129	116	—	160	126
90 %	155	156	159	—	—	163
EP	174	181	187	180	181	192
Yield, % on feed	—	—	—	98	98	96
Content, %						
Water	0,03	0,0026	—	0,029	0,0017	—
Sulfur	0,00	0,0004	—	0,066	0,0005	—
Chemical composition, %						
Unsaturates	0,63	0,49	0,58	0,18	0,23	0,55
Aromatics	9,82	9,45	48,0	11,12	10,97	58,95
Naphthenes	37,2	38,3	8,29	37,48	38,54	4,61
Paraffins	52,35	52,66	42,23	51,22	60,26	35,89
Octane number	43,5	—	79,7	44—66	—	85

TABLE 3

Index	Before reconstruction		After reconstruction	
	start of cycle	end of cycle	start of cycle	end of cycle
Pressure at outlet from Stage III, MPa	3.79	3.88	3.81	3.74
HRG circulation ratio, m^3/m^3	1230	1230	1100	1260
Feedstock space velocity, h^{-1}	2.1	1.8	1	1.3
Temperature of gas–feed mixture at reactor inlet, °C				
first	495	502	485	501
second	495	502	487	499
third	500	506	458	490
fourth	-	-	489	499
fifth	-	-	484	504
Temperature drop in reactors, °C				
first	50	50	62	48
second	24	19	29	9
third	15	11	3	7
fourth	-	-	5	–5
fifth	-	–3	–3	1
Average temperature of process, °C	495–506	495–506	480–498	480–498
Hydrogen concentration, vol. %	89.4	73.8	84.9–73.6	84.9–73.6
Distribution of catalyst among process stages	1:1.08:1.09		1:2:4	

This resulted in higher productivity of the unit; and feed with the distillation curve specified by design could be obtained, with a considerable reduction of the moisture content. This made it possible to use the more effective chlorinated platinized alumina catalyst AP-64 and to increase the capacity of the unit.

In the section for preliminary hydrotreating of the naphtha cut, the stripping tower was reconstructed: In order to increase its throughput capacity, valve trays were installed. The heat duty of the furnace was brought up to approximately 21 million kJ/h by retrofitting with panel burners, screening the bridgewall, and increasing the number of tubes in the convection chamber. In the interest of safe and trouble-free operation, and a reduction of harmful discharges, the feed pumps in the preliminary hydrotreating section were replaced by higher-capacity pumps, and glandless pumps were installed to handle the reflux in the stripping tower.

TABLE 4

Product	Bef. reconstruction	Aft. reconstruction
Taken, wt. %		
Feed	100,00	100,00
Obtained, wt. %		
Stabilized reformate	87,90	85,60
Hydrogen-rich gas	3,80	4,10
100% hydrogen	0,77	0,89
Hydrocarbon gas	1,80	1,40
Reflux	5,40	8,00
Loss	1,10	0,90
Total	100,00	100,00

TABLE 5

Feed: 85-180°C cut	Chemical composition			
	unsaturates	aromatics	naphthenes	paraffins
From West Siberian crude	0,23	10,07	36,4	53,3
From mixed Carboniferous crudes	0,2	9,49	25,94	64,47
From Karachaganak condensate	0,18	11,58	20,8	67,44

For operation on the AP-64 catalyst, more rigid requirements were imposed on the reformer feed. With the aim of reducing the moisture content in the gas—feed mixture to 20-40 ppm, an absorber section was installed for drying the circulating hydrogen-rich gas. Equipment was installed for feeding organic chlorine compounds in order to maintain the catalyst activity. In the interest of saving energy resources and curtailing harmful discharges, the feed pumps were equipped with face seals.

Gas/feed heat exchangers and air-coolers were installed in the gas, reflux, hydrotreated product, and stabilized reformate streams. The reactors were changed over to radial feed injection, which lowered the resistance in the hydrogen-rich gas circulation system from 0.3-0.6 to 0.2-0.3 MPa. These measures made it possible to increase the productivity of the unit and to bring the octane number of the stabilized reformate up to 77-79.

Then, a five-reactor (three-stage) scheme was developed for the catalytic reforming. The catalyst was distributed among the stages in a 1:2:4 ratio. In accordance with this scheme, two additional reactors were installed, with volumes of 20 m^3 each, as well as gas/feed heat exchangers; these were connected in a parallel—series network with two streams, each with three heat exchangers. An additional furnace section was installed, with a multipass coil and a pile-supported foundation. The header of the spider coil was shifted from the roof screen to the floor.

In the naphtha hydrotreating section, an additional 20.8-m^3 reactor was installed with radial feed inlet, this reactor being connected in series with the existing reactor. With this installation, it became possible to reduce the feedstock space velocity from 7.5 to 2.5 h^{-1}. Also installed was a new furnace with a duty of 31.4-37.6 GJ, as well as air-coolers for the hydrogen-rich gas and the hydrotreated naphtha. These measures made it possible to increase the capacity of the unit, and also to reduce the discharge of water into the water circulating system and the discharge of harmful substances to the atmosphere.

Data on the chemical composition of the feed and on the operating conditions of the reactors in the different stages (Table 1) show that as the content of naphthenes in the feed is increased, the octane number of the stabilized reformate also increases, while maintaining a content of organic sulfur compounds that does not exceed the standard. Under these conditions, with a charge of fresh catalysts to the reactors, the reformer operated without catalyst regeneration for 17 months. Then a regeneration was performed, restoring the catalyst activity.

The feed was a naphtha cut from West Siberian crudes, obtained in the atmospheric—vacuum tubestill unit, with the following distillation curve: IBP 95-105°, 10% 110-115°, 50% 125-130°, 90% 160-165°, and EP 170-180°C. The sulfur content was 0.03-0.07% before hydrotreating, 0.0001-0.0006% after hydrotreating. Data on the composition of the feed and products obtained before and after the reconstruction (Table 2) show that with an identical content of naphthenes in the feed before and after reconstruction, the residual content of naphthenes was lowered from 8.29% to 4.61%, and the octane number was raised from 79.7 to 81-85.

Moreover, as a result of reconstruction, the feedstock space velocity could be lowered to 1.0-1.3 h^{-1} (Table 3). However, the hydrogen concentration dropped to 84.9-73.6% by volume. The yield of 100% hydrogen increased to 0.89%, and the losses decreased from 1.1% to 0.9%. The material balance of the process is shown in Table 4. The economic advantage due to the reconstruction was 2.2 million rubles. The content of sulfur compounds in the hydrotreated naphtha was greater than that allowed by the standard. The chlorine content in the straight-run naphthas increased periodically (more than 5 ppm), and this led to catalyst deactivation, so that regeneration was required. In order to avoid these phenomena, additional heat must be supplied between the second and third reactors.

In order to ensure that the reforming process is supplied with high-quality feed, the following measures must be put into effect in the hydrotreating section: Install a new stripping tower with a diameter of 2000 mm and a working pressure of 2 MPa, equipped with a thermal siphon preheater; connect the compressors for autonomous circulation of hydrogen-rich gas (HRG) in the naphtha hydrotreating section, so that the circulation can be brought down to 200 m^3/m^3 of feed and so that stabilized, hydrotreated naphtha can be obtained with a sulfur content below 0.0001% by weight.

Measures have also been taken to ensure safe and trouble-free operation of the unit: improvements in heat transfer, saving of water, and curtailment of harmful discharges. In particular, feed pumps with face seals have been installed, giving a very marked reduction of the amount of harmful discharges. In the reforming section, a new stabilizer tower with valve trays has been installed, so that stabilized reformate with the required quality can be obtained, as well as a higher operating capacity of the unit.

Currently, the reformer has begun to receive from the hydrotreating section 85-180°C cuts from three different types of feed: West Siberian crudes, mixed high-sulfur Carboniferous crudes, and Orenburg and Karachaganak gas condensates (Table 5). In terms of the content of naphthenes, the naphthas from the mixed Carboniferous crudes and from the Karachaganak condensate are considerably inferior to the naphtha from the West Siberian crudes.

When 15-20% of the naphtha from the Karachaganak condensate is incorporated in the reformer feed, the yield and octane number of the stabilized reformate are lowered, as is the hydrogen concentration. After regeneration, the initial activity of the catalyst is completely restored. In order to obtain a high-octane component of gasoline, strict constancy must be maintained in the total load on the unit and in the ratio of components in the feed. Future reconstruction will make it possible to improve the operation of the unit, in particular to use the more effective, stable, and selective catalyst KR-110.

Thus, as a result of changing over the reforming process for operation on AP-64 catalyst, the output of high-octane component of gasoline has been increased. The reaction cycle has been lengthened by a factor of 2-3.