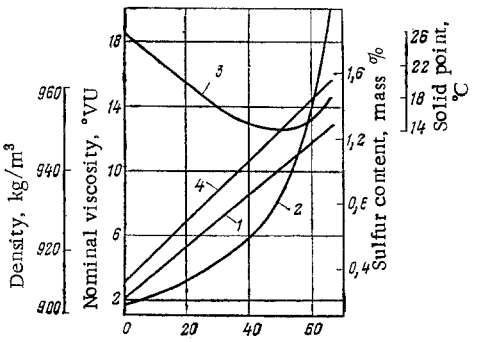

Fig. 1. Variation of most important properties of boiler fuel with the contents of vacuum resid (above 540°C) and hydrotreated vacuum gasoil (350-540°C), from Samotlor crude: 1) density at 20°C; 2) nominal viscosity at 80°C [similar to Engler viscosity]; 3) solid point; 4) sulfur content.

(0.5%), the fuel corresponds to Grade 40 boiler fuel meeting GOST 10585-75; and in the other cases corresponds to Grade 100, being classed in the latter grade mainly because of its high solid point.

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IMPROVEMENTS IN OPERATION OF DELAYED COKING UNIT AT NADVORNAYA REFINERY

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UDC 665.642.4(477.8)

The delayed coking unit at the Nadvornaya refinery is equipped with two reaction chambers, each 4.6 m in diameter, one pyramidal-type furnace, and distillation equipment of the type conventionally used in delayed coking units [1]. The coker feedstock is a cracked tar from mixed Bitkov and Eastern Ukrainian resids. This coker unit is one of the best in the petroleum industry in the USSR with respect to its basic operating indices. The coker has reached the level specified by the design with respect to the production of total coke, and the yield of electrode coke fractions amounts to 50% by mass; the feedstock capacity is 20-30% above the design level. However, the lengths of the runs in the coker unit between shutdowns for maintenance are no greater than 25-30 days, in comparison with runs of 100 days or more that are made in many delayed coking units in the USSR, and with a run of 170 days that has been made in the coker unit at the Novo-Ufa refinery.

The length of the run in a delayed coker unit between shutdowns for maintenance is affected by a number of factors, principally the feedstock quality (Table 1). We have listed in Table 2 the basic coil dimensions and the operating conditions for the cokers in the Nadvornaya and Novo-Ufa refineries. It can be seen from the data of Table 1 that the coker feedstock at the Nadvornaya refinery contains four times as much paraffinic-naphthenic hydrocarbons and only half as much polycyclic aromatic hydrocarbons and resins as the coker feedstock at the Novo-Ufa refinery. This ratio of components in the coker feedstock at the Nadvornaya refinery is responsible for a lower stability of this stock in terms of aggregation of colloidal particles, and

Bashkir Scientific-Research Institute for Petroleum Processing (BashNII NP). Translated from Khimiya i Tekhnologiya Topliv i Masel, No. 11, pp. 29-31, November, 1979.

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TABLE 1. Quality of Primary and Secondary Feedstocks for Delayed Coker Units

Indices	Nadvornaya refinery		Novo-Ufa refinery	
	primary	secondary	primary	secondary
Density, d_4^{20}	0.9378	0.9595	1.0302	1.0755
Conradson Carbon residue, mass %	6.7	4.2	14.8	16.6
Sulfur content, mass %	0.82	0.84	3.15	3.40
True boiling point distillation				
IBP, °C	175		191	246
mass % distilled				
IBP-200°C	1.37	0.38		
200-250°C	4.11	1.71		
250-300°C	9.51	4.56		0.9
300-350°C	10.50	20.46		3.16
350-400°C	17.93	31.51		11.76
below 400°C (total)	43.42	58.62	26.4	15.82
Hydrocarbon group composition, mass %				
paraffinic and naphthenic	44.27		10.59	
monocyclic	10.69		9.77	
bicyclic	9.54		9.40	
polycyclic	17.46		35.16	
resins	12.90		26.95	
asphaltenes	4.54		8.04	
carboids	0.43		0.09	

TABLE 2. Delayed Coking Unit Operating Parameters

Indices	Nadvornaya refinery	Novo-Ufa refinery
Consumption of turbulizer in secondary feed, mass %	3.9	1.7
Temperature, °C		
at inlet to reaction coil	357	360
at outlet from reaction coil	499	493
at inlet to reaction chamber	474	485
Temperature drop between chamber and furnace, °C	25	8
Pressure, MPa		
at inlet to reaction coil	2.55	2.43
at outlet from reaction coil	1.18	0.64
in chamber	0.35	0.18
Length of reaction coil, m	850	920
Outside diameter, m		
tubes	0.127	0.127
transfer line	0.152	0.152
Linear velocity of vapor in upper section of chamber, m/sec	0.136	0.09

hence faster coking of the tubes [2]. Also, the tube coking rate is very definitely affected by the hydrodynamic condition in the coil, the coil geometry, the heat load on the tube, the coil pressure, and other factors.

Certain hydrodynamic parameters in the reaction coils of the two units are listed in Table 3; these data show that the fraction of distillate and the volumetric gas content are higher in the Nadvornaya furnace coil, but the linear velocities at the furnace outlet are far higher in the Novo-Ufa furnace coil. The higher values for the fraction of distillate and the volumetric gas content are explained by the fact that the secondary feedstock in the Nadvornaya furnace is lower in distillation range, containing 58.62% by mass distilling below 400°C, in comparison with 15.82% for the secondary feedstock in the Novo-Ufa unit (see Table 1). The quantity

TABLE 3. Hydrodynamic Parameters of Reaction Coils in Delayed Coking Units

Parameter	Novo-Ufa refinery	Nadvornaya refinery
Gas content, vol. fraction	0.969	0.974
Linear velocity of product at furnace outlet, m/sec	37	21
Mass fraction of distillate at furnace outlet	0.44	0.63
Residence time of product in coil, sec		
at 430°C	97*	60
at 450°C	41	48
in last 15 tubes	13.5	17
in last 6 tubes	1.5	3

* Residence time was determined by I. M. Blokh by a technique involving the use of radioactive isotopes.

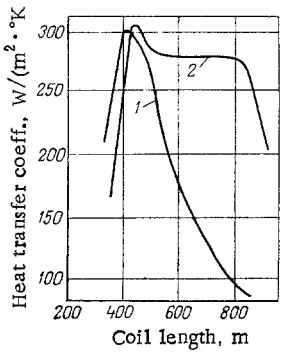

Fig. 1. Variation of heat transfer coefficient along reaction coil in furnaces of delayed coking units at the following refineries: 1) Nadvornaya; 2) Novo-Ufa.

of secondary feed in the Novo-Ufa unit is 1.5 times that in the Nadvornaya unit; hence the linear velocities at the Novo-Ufa furnace outlet are considerably higher. The higher gas content and lower velocities tend to give poorer heat transfer (Fig. 1), as can be seen from the variation in the coefficient of heat transfer from the tube metal to the flow core along the coil.

Moreover, the heat transfer process in two-phase flow through tubes is greatly affected by the structure of the flow [3]. It was established previously [4, 5] that "second-order" crisis phenomena of heat transfer are present in the delayed coker furnace at the Nadornaya refinery. From the data in Fig. 1 it can be seen that the heat transfer in both furnaces becomes much poorer in the section of the coil near the outlet; in the Novo-Ufa furnace this is observed only in the last 70-100 m, but in the Nadvornaya furnace in the last 350-400 m of the coil. Operating experience with these units has shown that in the Novo-Ufa furnace the tubes most frequently coked are the last six or seven roof tubes, whereas in the Nadvornaya furnace oil all of the roof tubes are coked, as evidenced by the number of tubes that are discarded during the course of operation. This is apparently explained by the early changeover of the disperse-annular regime to the completely dispersed regime of two-phase flow in the Nadvornaya furnace coil. The higher coking rate of the Nadvornaya furnace coil is also related to the long residence time of the feedstock in the zone of intense cracking, beginning at a temperature of 450°C (see Table 3). The furnace operating regime is greatly influenced by the geometry and layout of the transfer line. High hydraulic resistance in the transfer line gives higher pressures in the furnace coil, and this tends to suppress the vaporization process and reduces the amount of vapor and the heat content of the mixture at the furnace outlet; this, in turn, affects the thermal regime of the reaction chambers.

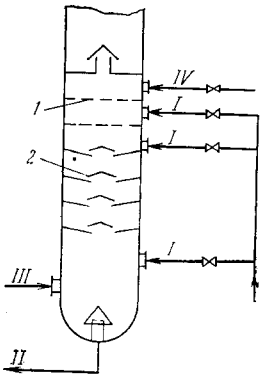

Fig. 2. Design of bottom section of T-1 tower: 1) sieve-type trays; 2) cascade trays; I) primary feed; II) secondary feed; III) vapor from reactor; IV) reflux (heavy gasoil).

The temperature drop between the furnace and reactor in the Nadvornaya coker is 25°C (see Table 2); with a furnace outlet temperature of 499°C , the temperature at the reactor inlet drops to 474°C; in the Novo-Ufa coker, with a lower temperature of the product at the furnace outlet (493°C), we find a higher temperature at the reactor inlet (485°C). This difference is explained by the lower distillation range of the coker feedstock and the greater length of the transfer line in the Nadvornaya coker (about 70 m in comparison with 45 m in the Novo-Ufa coker) and the greater number of returns (18 in comparison with 9 in the Novo-Ufa coker). Calculations have shown that if the pressure at the furnace outlet is reduced from 1.18 to 0.6-0.7 MPa, the product temperature at the furnace outlet will be lowered by 10-12°C, but the chamber inlet temperature will not be lowered; i.e., the quality of the coke will not be changed (currently, in the Nadvornaya coker, the content of volatile material in the electrode coke is 7% by mass). Moreover, higher pressures in the furnace coil tend to prevent the vaporization of the light paraffinic fractions which, remaining in the liquid phase, will precipitate the asphaltenes on the furnace tube walls and thus give rapid coking.

The length of the runs between shutdowns for maintenance and the operating efficiency of the unit depend on the vapor velocity in the reactor. The linear velocity of vapor in the free section of the reactor should be no greater than 0.09 m/sec [6]; in the Nadvornaya coker, this velocity is considerably higher (see Table 2). With this higher vapor velocity there is more carryover of coke particles from the reactors to the next pieces of equipment (distillation tower and furnace), and this represents one of the reasons for the short runs of the unit between maintenance shutdowns. At the end of each run, the lower part of the T-1 tower is found to be plugged with coke.

Thus we see that the use of a paraffinic feedstock with a relatively low distillation range, the higher hydraulic resistance in the transfer line, and the higher linear velocity of vapor in the reactor (considerably higher than the allowable value) are the principal reasons for the short runs of the Nadvornaya coker between maintenance shutdowns. It is not feasible to add any sort of materials to the feedstock to increase its aromaticity; hence, the only solution is to reexamine the entire refinery flow plan for crude oil processing. The atmospheric pipestill should be supplemented with a vacuum section; the vacuum gasoil and the coker gasoil should be directed to the thermal cracking unit; the cracked tar should be mixed with the straight-run vacuum resid for use as the coker feedstock. In order to improve the fractionation conditions in the bottom section of the T-1 tower (Fig. 2), the cascade trays should be supplemented by the installation of one or two sieve trays, and reflux should be provided in the form of heavy coker gasoil.

Calculations have shown that, when the necessary conditions for fractionation are set up, a residue distilling above 400°C can be obtained from the bottom of the tower, and this will essentially cut in half the load on on the reaction coils (see Table 1). In order to reduce the consumption of turbulizer to 1-1.5% by mass in the secondary feed, it will be necessary to replace the 0.127-m diameter tubes in the reaction coil by 0.102-m diameter tubes. The use of the heavier feed and the decrease in consumption of turbulizer will result in a much lower hydraulic resistance in the tubes. The resistance can also be reduced by changing the transfer line geometry.

The net result of these changes will be a sharp increase in the length of runs between maintenance shutdowns, an increase in the output of coke, and an increase in effectiveness of the equipment.

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EFFECT OF SULFURIC ACID CONCENTRATION ON QUALITY OF ALKYLATION PRODUCTS

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UDC 66.095.253 : 546.226-325 : 541.12.035

In the alkylation of isobutane with olefins, the catalyst (sulfuric acid) accumulates impurities that lower its concentration. The data that are available on the treatment of acid in the interest of process optimization are far from adequate [1-3]. In connection with this shortage of information, we have carried out a study of the effects of acid concentration and impurities in the acid on the quality of the alkylation products. These studies were performed in a typical commercial alkylation unit at the Novo-Groznyi refinery, equipped with vertical reactors and with an ammonia refrigeration system to remove heat from the reaction zone. The feedstock was a butane–butylene cut from catalytic cracking. The capacity of the unit remained practically constant, and was higher than the design capacity by about 30%. The process conditions were as follows: temperature −13 to −16°C, stirrer speed 380 rpm, volume ratio of isobutane to olefins at reactor inlet about 6, and ratio of acid to hydrocarbons 1.1.

Samples of the acid were drawn at the outlet of the circulating pump, and samples of the alkylation products were drawn after the acid settler and were stabilized at atmospheric pressure for 30 min at 35°C. The acid concentration was determined in accordance with GOST 4204–66, and the bromine number of the products was determined in accordance with GOST 8997–57; the contents of organic impurities, alkyl sulfates

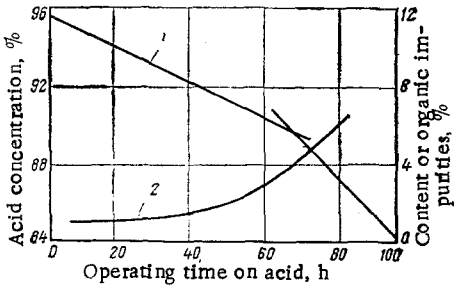

Fig. 1. Acid concentration (1) and content of organic impurities in acid (2) as functions of operating time on acid.

Groznyi Scientific-Research Petroleum Institute (GrozNII). Translated from Khimiya i Tekhnologiya Topliv i Masel, No. 11, pp. 32-33, November, 1979.

0009-3092/79/1112-0819 $07.50