DEASPHALTIZING PETROLEUM RESIDUES WITH COMPRESSED GASES IN AN EXPERIMENTAL INDUSTRIAL PLANT

T. P. Zhuze, G. N. Yushkevich,
G. S. Ushakova, A.V. Gusarev, I. Kh. Arutyunov,
E. I. Ivanov, and V. N. Mel'nikova

UDC 66.067:665.521.7

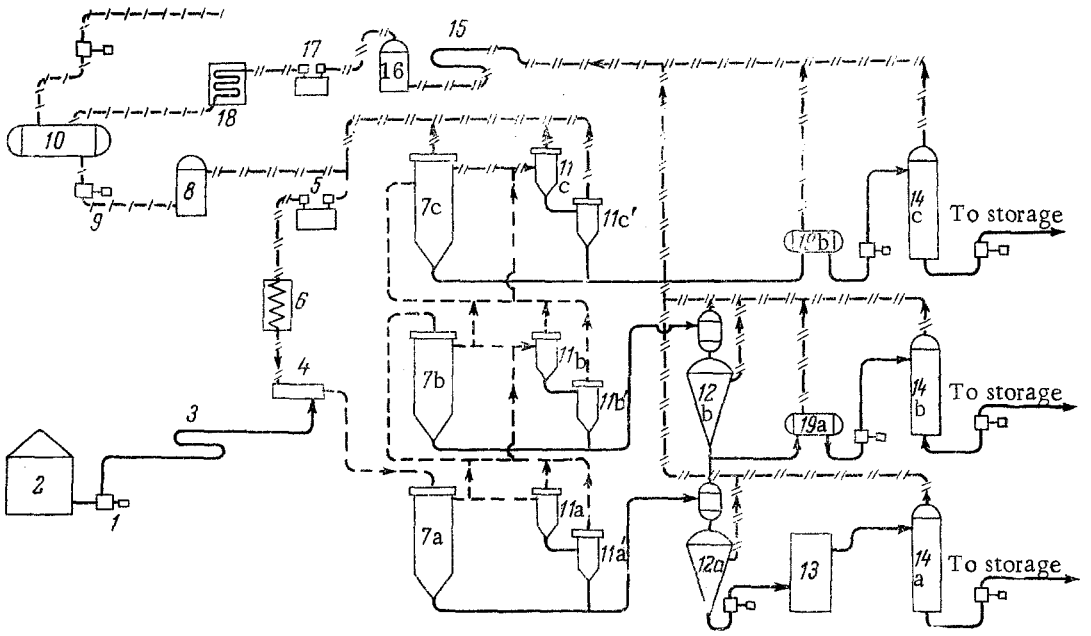
An experimental-industrial plant (EIP) was built in the Grozny oil refinery according to Giprogaztopprom design for the purpose of checking and implementing a new method of deasphaltizing heavy petroleum residues with compressed gases, which was developed at IGiRGI. The nonstandard equipment for this plant was designed at Giproneftemash and the high-pressure propane compressor—at Azinmash.

In principle the technological scheme for the EIP and for the consolidated continuous flow installation in the laboratory at IGiRGI, which was described earlier,* were similar. However, a unit for reclamation of the gas-solvent from the deasphaltizate and from the residue was included in the EIP scheme. Moreover, in view of the experimental nature of the plant, a number of duplicate nonstandard pieces of equipment of different design (separators of gravity and cyclone type, stripping equipment of the usual and film type, etc.) were installed for the purpose of selecting the most efficient types. For the same reason, provision was made for flexibility of EIP operation under different schemes. Actual processing capacity of the plant was 8-10 tons of raw material per day. A generalized flow diagram for two variants of EIP operation is given below. For operation under the first variant, three gravity separators were included in the scheme, and for operation under the second variant—three cyclone separators. To carry out only the deasphaltizing process, two separators were required: one for separating the raw material mixture and gas into gaseous mixture and residue and the second for separating the deasphaltizate from the gaseous mixture. The third separator was provided in the plant for separating the deasphaltizate into two fractions.

The original raw material is supplied from tank 2 by pump 1 to heat exchanger 3, where it is heated to 105-110°C and sent to injector type mixer 4. At the same time the gas-solvent, compressed to 100-120 atm by DSG-125P compressor 5 and cooled to 105-100°C in cooler 6, is delivered there. Selection of weight ratio of raw material to gas depends on their nature and composition. Atomization of the raw material in gas, which accelerates its solution, is accomplished in the mixer. The entire mixture then enters the first stage gravity separator 7a, which is a hollow cylinder 1.4 m^3 in volume. The temperature here is maintained at 105-110°C by means of an external steam jacket. Entry into the separator is through a central pipe lowered to approximately $^2/_3$ the length of the apparatus. Owing to the reduction of velocity of movement in this apparatus, settling of asphaltic-resinous raw material components which were insoluble in the gas under the specified conditions occurs. The residue collects at the bottom of the separator and is periodically delivered to the solvent reclamation system. The gaseous mixture leaves the first stage separator through a side pipe in the top part of the apparatus, is throttled to 65-70 atm and sent to second stage gravity separator 7b, which is also heated to 105-110°C. Dimensions of the first and second separators are similar. The first fraction of the deasphaltized product, which henceforth will be called the first deasphaltizate, falls out from the gaseous mixture as a liquid in the second separator. The remaining gaseous mixture leaves the second separator, is throttled to 40 atm, passes through a heat exchanger (not shown in the diagram) and enters the third stage gravity separator 7c, 3 m^3 in volume, and also heated to 105-110°C, where the second deasphaltizate separates out. As the products separated out in the second and third separators accumulate, they are delivered to the solvent reclamation system which is common for both schemes. The gas freed from the dissolved product leaves from the top of the third separator and enters the intake of compressor 5. Gas recompressed from 40 to 100-120 atm is cooled to 105-110°C in cooler 6 and returned to the mixer where the raw material is being continuously supplied by pump 1. The deasphaltizing stage of raw material is thus accomplished. Gaseous propane from vessel 10 by pump 9, is introduced into the gas line running from the third separator to the intake of compressor

*T. P. Zhuze, Khim. i Tekhnol. Topliv i Masel, No.9, 1966.

IGiRGI (Institute of Geology and the Development of Mineral Fuels). Translated from Khimiya i Tekhnologiya Topliv i Masel, No. 1, pp. 15-20, January, 1967.



Generalized flow diagram of the experimental-industrial plant for deasphaltizing petroleum residues. Streams: ———— petroleum raw material: products of deasphaltizing, residue; –/–/ liquid propane: –/ /–/ /– gaseous propane: – – – – gaseous mixture.

5. It is for replenishment of the small part of the gas which leaves the cycle as dissolved gas along with products removed from the separators. The vaporized propane is sent along with the remaining gas stream at 40 atm and 105-110°C to compressor 5. Removal of the residue from separator 7a is accomplished automatically with the aid of a radioactive level gauge.

In the second variant of the technological scheme of the plant, cyclone separators 11a, 11b, and 11c were used instead of the gravity separators. The mixture to be separated first enters the cyclone housing and from there it enters the cyclone proper. The volume of the cyclone is approximately 14 times smaller and its weight 7-8 times smaller than the volume and weight of the first gravity separator. According to the second variant, operation of the plant is as follows. The mixture of raw material and gas enters from mixer 4 into first cyclone 11a. From there the residue flows through an outlet pipe into intermediate collector 11a' which has the same volumetric capacity (0.1 m^3) as the cyclone housing. The gaseous mixture leaves from the top of the first cyclone and collector, is throttled to 65-70 atm and then enters second cyclone 11b. Here the first deasphaltizate fraction falls out, flowing into collector 11b'. The gaseous mixture leaves from the top of the second cyclone and its collector, is throttled to 40 atm, is heated to 105-110°C in a heater and then enters the third stage cyclone separator 11c where the second deasphaltizate fraction separates out, flowing into collector 11c'. The reclaimed gas leaves the top of the third cyclone and collector, is sent to compressor 5 where it is recompressed from 40 to 100-120 atm and returned to the mixer. The deasphaltizates and the residue accumulated in collectors 11a', 11b', and 11c' are periodically delivered to the solvent stripping system. Reclamation of gas dissolved in the residue is accomplished in the first stage stripping apparatus 12a, based on the principle of gas stripping from a thin layer of the product. The residue, heated to 150°C in the bottom part of the first separator or the intermeidate collector of the first cyclone, enters the top section of the stripping apparatus where most of the dissolved gas is separated from it, owing to pressure reduction from 100-120 atm to 0.5 atm. From here the residue continuously runs down on the distributing plate in the bottom section of the apparatus, and from there it trickles on the side walls of the apparatus where it is stripped by heating to 160-180°C. Small vertical gas heater 13 for heating the residue to higher temperatures (230°C) and a usual type stripping column 14a were also provided in the plant. Gas from the top and bottom sections of the first stripping apparatus (in a mixture with steam in the case where the stripping column is included) is successively sent to condenser-cooler 15, receiver 16, and intake of low-pressure compressor 17 where it is boosted to 20 atm. After that, the gas passes through cooler 18 and from there in liquid form it passes into vessel 10. The first deasphaltizate could be sent for stripping either into second stripping apparatus 12b, constructed similarly to the first, or into reboiler 19a and stripping column 14b. In both cases, gas leaving the top of the apparatus combines into a single stream and enters a common line for reclaimed low-pressure gas leading from all stripping

TABLE 1. Results of Deasphaltizing Concentrates (tar oils)

Indices	Runs				
	1	2	3	4	5
Weight ratio of gas to raw material	4.8:1	–	4.6:1	5.8:1	5.5:1
Yields, %:					
first deasphaltizate	51.0	47.7	41.0	58.5	61.1
second deasphaltizate	4.0	3.7	3.9	–	3.6
total yield	55.0	51.4	44.9	58.5	64.7
residue	45.0	48.0	54.6	41.0	35.0
losses	–	0.6	0.5	0.5	0.6
Characteristics of the obtained products					
First deasphaltizate:					
density ρ_4^{20}	0.905	0.903	0.898	0.908	0.913
excise tar conent, %	20.0	10.7	10.0	15.0	–
coke content, %	1.65	1.15	1.46	1.41	1.30
relative viscosity RV_{100}	3.0	2.7	2.7	3.1	3.3
Second deasphaltizate:					
density ρ_4^{20}	0.883	0.881	0.884	0.898	0.899
excise tar content, %	–	4.0	4.0	–	–
coke content, %	0.106	0.100	0.064	0.542	0.220
relative viscosity RV_{100}	1.55	1.56	1.53	–	1.7
Total deasphaltizate:					
density ρ_4^{20}	0.903	0.896	0.897	0.908	0.912
coke content, %	1.37	1.07	1.27	1.459	1.23
relative viscosity RV_{100}	2.9	1.98	2.6	3.1	3.2
Residue:					
density ρ_4^{20}	0.960	0.950	0.953	0.976	1.005
coke content, %	11.7	12.3	–	–	17.5

apparatus in the plant to the intake of compressor 17. Stripping of the second deasphaltizate takes place in reboiler 19b and in stripping column 14c.

The plan of EIP operation included a check of the method of deasphaltizing petroleum residues with compressed gases, selection of the most efficient equipment, determination of the optimal operating conditions, and obtaining technological indices of deasphaltizing certain petroleum residues. Results of the most typical tests of deasphaltizing petroleum residues from Volgograd and Grozny crudes are summarized in Tables 1–3.

The concentrate from Volgograd residual oil having 0.925 density and 7.62% coke content was used as the raw material in the first three runs (see Table 1). The tests were made with three cyclones at pressures of 110, 67 and 38 atm, respectively. Raw material used in the fourth run was the concentrate from Volgograd residual oil having density ρ_4^{20} 0.940 and 6.6% coke content, and in the fifth–the concentrate from Grozny crudes with ρ_4^{20} 0.954, coke content 8.925% and relative viscosity at 100°C of 6.8. The fourth and fifth runs were made with gravity separators at pressures of 115-117, 68-70 and 31-37 atm, respectively. The first four runs were made only to check the efficiency of the cyclone and gravity separators, and the fifth run was made at the optimal technological conditions of deasphaltizing the concentrate. In the first four runs, yields were low as a result of the pressure being too low in the first separator. They could be increased considerably by increasing the pressure to 115-120 atm, as can be seen from data for the fifth run. Coke content in the deasphaltizate obtained under the optimal conditions was 1.23%, i.e., deasphaltizing was very efficient. This is also substantiated by high density of the residue (1.005).

The results of deasphaltizing cracked residue are summarized in Table 2. From Table 2 it is seen that from 23 to 51% deasphaltizate with excellent coke content from 0.15 to 0.82%, respectively, may be obtained from cracked residue. Fractional composition of the 45% first deasphaltizate yield was as follows: init. b.p. 270°C; 4% distilled to 350°C, 80% to 500°C, 95% to 546°C (end b.p.).

TABLE 2. Results of Deasphaltizing Cracked Residue*

Indices	Runs			
	1	2	3	4
Weight ratio of gas to raw material	4.9:1	3.7:1	5.4:1	6.2:1
Yields, %				
first deasphaltizate	31	23	45	51
second deasphaltizate	–	–	2.5	–
residue	68.3	77	51.0	45
losses	0.7	–	1.5	4
Characteristics of the obtained products				
First deasphaltizate:				
density ρ_4^{20}	0.910	0.908	0.912	0.917
excise tars, %	4	6	8	10
coke content, %	0.122	0.147	0.299	0.816
relative viscosity RV_{100}	1.6	1.6	1.7	1.9
color on NPA scale	7	6.5	7	8
Second deasphaltizate:				
density ρ_4^{20}	–	–	–	0.903
coke content, %	0.024	0.024	0.060	0.025
relative viscosity RV_{100}	1.3	1.3	1.3	1.2
Residue†				
density ρ_4^{20}	1.015	1.008	1.033	1.023
coke content, %	17.64	18.04	21.16	20.46

*Cracked residue from the Grozny oil refinery had density ρ_4^{20} 0.974, coke content 12.7% and excise tars 40%. Pressure in the first, second and third separators was 115-117, 65-70, and 39 atm, respectively.

†Melting point of residues by KiSh (ring and ball method) corresponded to 35, 25 and 43°C.

Considering the capacity of compressed gases for selective extraction principally of paraffin-naphthenic hydrocarbons from raw materials, the obtained deasphaltizates could be used as the raw material for catalytic cracking and hydrocracking, despite their high end boiling point. The residues from cracked residue deasphaltizing, having high density and high coke content, could be a very satisfactory raw material for coking. As was shown by tests made in the consolidated laboratory installation at IGiRGI, the coking value of the residues from deasphaltizing the cracked residue from eastern crudes, when necessary, could be brought to 45-50%. The domestic oil refineries have had industrial experience in vacuum distillation of cracked residues aimed at obtaining residues with high coke content to be used as raw material for coking. The by-products obtained in this connection are vacuum distillates with undesirable hydrocarbon composition and high tar and coke content, which could only be used as raw material for thermal cracking or as fuel oil components. The deasphaltizing process using compressed gases makes selective separation of deasphaltizates according to the hydrocarbon content possible, and therefore during distillation of cracked residues, it could possibly fulfill two functions simultaneously: obtainment of raw material for coking and raw material for catalytic processes.

Deasphaltizing residual oil from a mixture of Zhirnovo and Korobkovo crudes (Table 3) with compressed gases in EIP yielded a total of 79.4 to 91.2% deasphaltizate and 18.3 to 8% residue; yield of the first deasphaltizate was 69.0-76.0% and of the second—3.4 to 16.6%. It was determined that by changing the process parameters (principally the drop in separator pressures and the ratio of gas to raw material), it is possible to change the quality of the obtained deasphaltizates. The residues from residual oil deasphaltizing, judging from their high density and coke content, are very satisfactory raw material for coking.

Concerning reclamation of gas in the deasphaltizing process, the following should be mentioned.

It was found experimentally that average content of gas-solvent in the residue present in the first separator at 100°C and 100-120 atm amounted to 3 wt %. The first deasphaltizate present in the second separator at 100°C and 75 atm contained about 34% gas, and the second deasphaltizate present in the third separator at 100°C and 40 atm contained about 18.5%.

TABLE 3. Results of Deasphaltizing Residual Oil from a Mixture of Zhirnovo and Korobkovo Crudes (density ρ_4^{20} 0.909, coke content 3% and excise tar content 24%)

Indices	Runs			
	1	2	3	4
Pressure in cyclones, atm:				
in first	100	100	110	100
in second	68	68	69	66
in third	37	37	38	37
Weight ratio of gas to raw material	8:1	3.5:1	5:1	5:1
Yields, %				
first deasphaltizate	74.6	76.0	71.0	69.0
second deasphaltizate	16.6	3.4	11.3	16.2
residue	8.0	18.3	17.0	14.6
losses	0.8	2.3	0.7	0.2
Characteristics of the obtained products				
First deasphaltizate:				
density ρ_4^{20}	0.901	0.900	0.901	0.903
coke content, %	1.44	1.38	1.43	1.36
relative viscosity RV_{100}	2.00	1.83	1.94	1.92
Second deasphaltizate:				
density ρ_4^{20}	0.878	0.876	0.876	0.888
coke content, %	0.042	0.047	0.025	0.749
relative viscosity RV_{100}	1.35	1.36	1.32	
Total deasphaltizate:				
density ρ_4^{20}	0.896	0.899	0.897	0.900
coke content, %	1.17	1.31	1.23	1.24
relative viscosity RV_{100}	1.88	1.81	1.85	–
Residue:				
density ρ_4^{20}	1.002	0.995	0.996	–

When the products are discharged from the separators into the stripping apparatus where pressure is atmospheric, most of the gas evolves from them and passes to the intake of the low-pressure compressor. After this, in the residue and the deasphaltizate there remains about 0.5-0.6 wt % and 2-3 wt % of gas, respectively, which is subject to stripping by heating. If the two separation stages required for the deasphaltizing process proper and the five-to-one weight ratio of gas to raw material are considered, then the total amount of gas discharged along with the products from the separators will be about 2.5 wt % of the circulating gas. The amount of gas reclaimed when it passes over into the stripping apparatus as a result of pressure reduction amounts to approximately 1.7%, and the amount of gas that is subject to stripping in the stripping apparatus is about 0.8 wt % of the gas circulating in the separators. The small amount of gas-solvent that is subject to reclamation by heating is one of the characteristic and positive features of the new method of deasphaltizing petroleum residues. For comparison, we will mention that in deasphaltizing tar oils with liquid propane, most of the propane supplied to the extraction column is reclaimed by heating. Numerous vaporizers and condensers are provided in industrial deasphaltizing plants for this purpose; reclamation is multistage and it requires large consumption of steam and water. It is well known that expenditures for steam in operating deasphaltizing plants constitute 40-45% of total production costs. The process of circulating gas-solvent through separators necessitates gas compression in a high-pressure compressor from 40 to 100-120 atm. As is well known, consumption of energy in gas compression does not depend on the absolute values of initial and final pressure but depends on their ratio, i.e., on the degree of gas compression. In the process under discussion, it is approximately three, i.e., it is small.

In checking the operating efficiency of gravity separators, the maximum flow rate of the gas-liquid stream at which complete settling-out of the liquid phase still occurs in the apparatus was determined. This rate proved to be low and it was 0.010-0.012 m/sec and therefore the use of such apparatus in the process of deasphaltizing petroleum residues with compressed gases is inadvisable. Very good separation of the phases was observed in the cyclones during deasphaltizing tests of residual oil and concentrate. Notwithstanding their small size, the cyclone

separators are much more efficient apparatus for separating the liquid phase from the gas phase then gravity separators. In the tests made, the volumetric flow rate of the gas-liquid stream in the cyclone section ranged from 300 to 550 $m^3/m^2/hr$. The volumetric flow rate of the stream in the extraction columns during deasphaltizing tar oils with liquid propane was 30 to 37 $m^3/m^2/hr$.

Operating efficiency of the stripping apparatus of Giproneftemash design, based on gas stripping from a thin layer of the heated product, was also checked in EIP. Good results were obtained in laboratory tests when heating the deasphaltizate to 150-160°C and the residue to 180°C at low vacuum (20 mm Hg). The operating efficiency of the stripping apparatus in EIP was successfully determined only for the residue. A satisfactory flash point of the residue (210°C) was obtained when it was heated to 225°C without vacuum.

Tests conducted in the experimental-industrial plant in Grozny confirmed the possibility of commerical utilization of the process and the technological indices of its basic design. It was determined that the method is applicable to deasphaltizing a great variety of petroleum residues. The change from one type of raw material to another in deasphaltizing is easily accomplished either by changing the extraction pressure or the weight ratio of gas to raw material. It was ascertained that for separating gas and liquid phases in the process of deasphaltizing petroleum residues with compressed gases, it is advisable to use cyclone separators which permit operation at high volumetric flow rates. It would now be expedient to conduct a project study of an industrial plant for deasphaltizing heavy petroleum residues with compressed gases in order to have more accurate technical and economic specifications for the process.