SUPERCRITICAL FLUID PROPANE-BUTANE MIXTURE IN REFINERY AND PETROCHEMISTRY

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ABSTRACT

The results of using the processes of liquid and supercritical fluid extraction to separate petroleum products from oil sludge and bituminous sand have been presented. A mixture that consists of 75 wt % propane and 25 wt % butane has been used as an extractant. The initial oil sludge is characterized by the absence of water and a content of mechanical impurities in the amount of 12.05 wt %. The content of petroleum products in bituminous sandstone is up to 7. 23%. Extraction processes are carried out in the temperature range of 85–160°C and pressure interval of 5–50 MPa.

Results of an experimental realization of the supercritical fluid impregnation process and characteristics of the impregnated crushed stone are given. The results of the process of experimental implementation and the characteristics of impregnated crushed stone, including the water absorption capacity which decreased from 3.6 to 0.21%, are presented.

INTRODUCTION

In laboratory and industrial practice, carbon dioxide has become quite a widespread supercritical fluid (SCF) solvent. Despite the doubtless merits of using carbon dioxide as a solvent, one hardly can attribute it to universal solvents.

The most preferred solvents (extractants) for petroleum refining and petrochemical industries are propane, butane as well as their mixtures. Propane and butane are hydrocarbons “affinitive” to petroleum. They are produced, mainly, from the associated petroleum gas obtained during the refining process. One more important advantage of these substances is related to relatively low values of critical parameters, especially, of pressure. In line with [1], the critical parameters of propane and butane are following: propane T_{crit}=369.82 K (96.67^{o}C), P_{crit}=4.247 MPa; butane: T_{crit} =425 K (151.85^{o}C), P_{crit} =3.797 MPa.

The following processes involving usage of the propane-butane mixture as a solvent, have been developed: oil sludge utilization [2], extraction of petroleum from petroleum-saturated sandstones [3], crushed stone impregnation [4,5]. For experimental running of these processes, a complex laboratory unit was developed that allows conducting the extraction and impregnation processes.

MATERIALS AND METHODS

The experimental setup, which combines the capabilities of the consequential implementation of the extraction and impregnation processes, is presented in Figure 1.

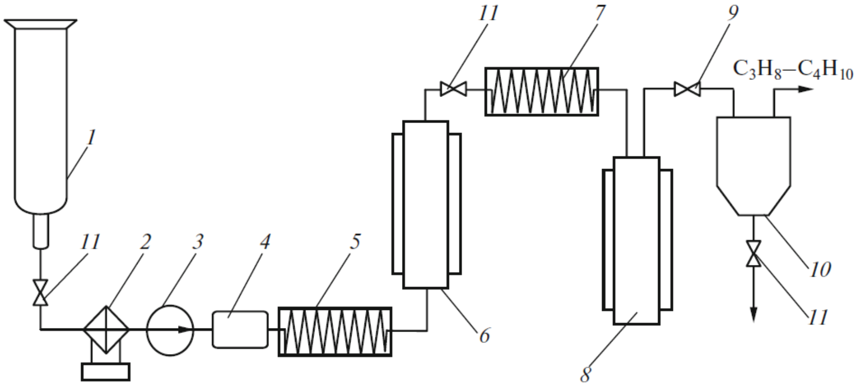


Figure 1. Scheme of the complex experimental setup of impregnating of macadam by the fraction of oil residues: *1*, balloon with propane—butane mixture; *2*, refrigeration unit; *3*, pump; *4*, receiver; *5*, *7*, heat exchangers; *6*, extractor; *7*, heat exchanger; *8*, heated vessel of impregnation; *9*, pressure regulator; *10*, heated separator; *11*, valves.

The setup includes as major elements, systems for generating and maintaining pressure, as well as adjusting and maintaining temperature. The system of generating pressure consists of the cylinder with propane–butane mixture 1, volume 40 L; refrigeration unit 2 (“Thermo Electronic Corporation”, NeslabRTE7 brand), the pump cooling operating chambers; plunger gradient pump (Thar Technology) for gas supply with a constant volumetric flow rate in the range from 0.1 to 10 mL/min and pressure regulator 9 (GoReg, VR66-1A11CJ0151). At the initial time, the propane–butane mixture is cooled and condensed by the refrigeration unit and pushed into the system by the pump plunger. Via receiver 4, a uniform supply of propane–butane mixture is fed into the system without pulsations. With the heat exchanger 5, the temperature conditions for the performance of extraction process are established and implemented in high-pressure vessel 6, volume 1L, where the oil residue is preloaded. During the extraction deasphalting process of this residue, asphalt accumulates on the bottom of the extractor. The liquid solution of deasphaltizate in the propane–butane mixture, withdrawn from the top of the extractor, passes through the heat exchanger for preheating *7*, ensuring the transfer of the solution to supercritical fluid state. Next, further on the route of the SCF solution, there is an impregnation vessel *8* with an intensive heating system in the region of the impregnated matrix (carbonate crushed stone).

As part of the process of separating oil from oil sludge and sandstone, the impregnation chamber is used to separate the extractant and extract (petroleum products), and in the impregnation of crushed stone as an impregnating vessel.

Figure 2. Photo of the experimental setup.

As an extractant, a propane–butane mixture containing 75 wt % propane and 25 wt % butane is used. According to [6], the above composition of the propane–butane mixture has the following values of the critical parameters: Tcr = 386 K (~113°C), Pcr = 4.31 MPa.

RESULTS

Figure 3 shows the yield of a petroleum product from oil sludge using a propane-butane extractant in a wide range of process parameters (pressure, temperature). The relative error of the experimental values of the yield of petroleum products from oil sludge in the course of the extraction varies in the range of 5.4–8.3%.

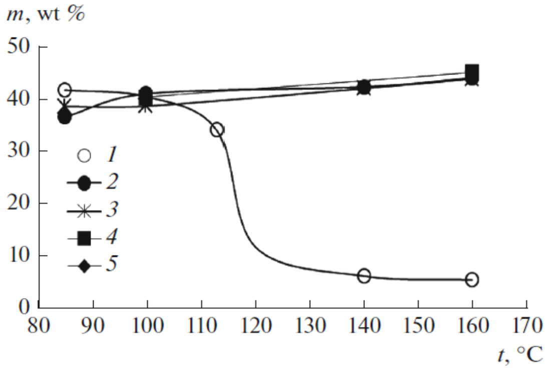


Figure 3. Dependence of the yield of petroleum product from oil sludge on temperature during extraction withdrawal, using propane–butane extractant for 30 min at different pressures: (*1*) 5; (*2*) 10; (*3*) 15; (*4*) 20; (*5*) 50 MPa.

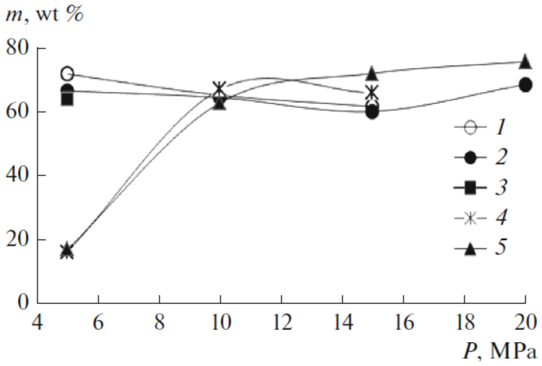


Figure 4. Dependence of the yield of oil product from oil sludge on pressure during extractive withdrawal using propane–butane extractant for 90 min at different temperatures: (*1*) 85; (*2*) 100; (*3*) 113; (*4*) 140; (*5*) 160°C.

One can state an easily visible analogy in the behavior of the solubility of naphthalene in CO_2 [7] and the yield of the product (Fig. 3) within the extraction isolation with propane–butane extractant. Namely, a sharp decrease in the solubility [7] and the yield of the oil product (Fig. 3) at low pressures (7–9 MPa for carbon dioxide and 5 MPa for propane–butane) in the region of transitioning the solvent from a liquid state to supercritical fluid lies at the base of the highly profitable and ROSE process [8].

Figure 4 shows the nature of the change in the yield of petroleum product in the extraction isolation process using propane–butane extractant in liquid (85 and 100°C) and supercritical fluid (113, 140 and 160°C) states represented as corresponding isotherms.

In Figure 4, it can clearly be seen how the temperature dependence of the yield of the oil product varies in different pressure ranges. In particular, in the range of $P = 6.5–12$ MPa, if the yield decreases with increasing temperature, the reverse trend is observed at $P > 12.5$ MPa, i.e., with increasing temperature, the yield of the oil product also increases. According to the above results, taking into account the errors in the results of measurements at pressures of ~4.5–5.5 MPa and ~11–13 MPa correspond to first and second crossover points, respectively.

Data concerning the extraction of petroleum products from oil sludge show that the pressure increase from 5 to 10 MPa hardly affects the efficiency of liquid extraction at 100°C and the potentialities of the supercritical fluid extractant exhibit a multiple increase (by a factor ranging from 6 to 8), and the isolines for 140 and 160°C coincide.

Figures 5 and 6 present the yield of hydrocarbons from the bituminous sand in the process of extractive recovery using a propane–butane extracting agent within a wide range of variations in the operating process parameters (*P* and *T*).

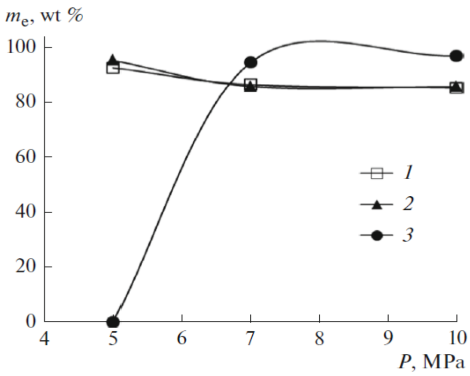


Figure 5. Dependence of the yield of hydrocarbons from the bituminous sand on the pressure during the extractive recovery using the propane–butane extracting agent at M2 : M1 = 1.5 : 1 and various temperatures: (1) 80, (2) 100, and (3) 140°C.

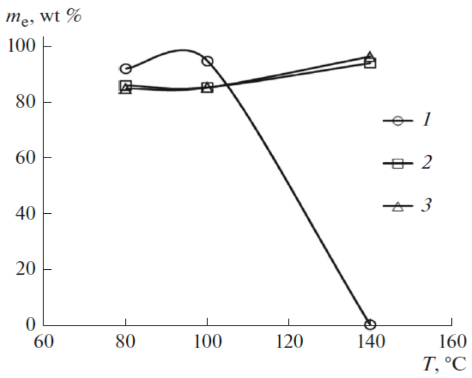


Figure 6. Dependence of the yield of hydrocarbons from the bituminous sand on temperature during the extractive recovery using the propane–butane extracting agent at M2 : M1 =1.5 : 1 and various pressures: (*1*) 5, (*2*) 7, and (*3*) 10 MPa.

The isotherms of the liquid at 80 and 100°C are close. With growth in the pressure, there is a small drop in the yield of hydrocarbons. In the case of growth in the pressure at the same temperature, the density of the extracting agent increases, which leads to an increase in the viscosity, and possibilities for treating sandstone become complicated, which in turn leads to a small decrease in the yield of hydrocarbons from the sandstone. The SCF isotherm (140°C) has a character that is traditionally inherent to isotherms for processes involving solvents in the SCF state [2]. At high pressures, the absolute value of the yield of hydrocarbons with the extracting agent in the SCF state which exceeds the yield in the case of extracting agents in a liquid state is explained by the fact that an SCF solvent possesses substantially higher penetrating capacity and treats a larger surface area of the initial sandstone. In the isobar $P = 5$ MPa, the density of the liquid is lower, which corresponds to the lower viscosity of the medium, which, in turn, is preferable for the effective treatment of the sandstone and leads to the high value of the yield of hydrocarbons. Other than that, the behavior of isobars in liquid–SCF adjacent areas is traditional and common [2].

As can be seen from the results, the technology makes it possible to extract hydrocarbons up to 96.34 wt %, while residual asphaltenes form a superstable hydrophobic film on the surface and pores of sandstones.

Table 1 presents the properties of the petroleum product obtained from the bituminous sand using the extraction process and the propane–butane extracting agent at $T = 140$°C and $P = 10$ MPa.

Table 1. Some characteristics of petroleum product obtained using propane–butane extraction process performed at T =140°C and P = 10 MPa

№	Parameters under determination	Unit of measure	Test methods	Results
1	water	wt %	GOST 2477-65	0
2	ρ при 20°C	kg/m^3	GOST 3900-85	937.7
3	sulfur	wt %	GOST P 51947-02	4.498
4	υ	mm^2/s	GOST P 33-00	511.73
5	mechanical impurities	wt %	GOST 6370-83	0.0088
6	Yield of fractions: initial boiling point at T to 100°C at T to 150°C at T to 200°C at T to 250°C end boiling point at T to 292°C	 °C wt % wt % wt % wt % °C wt %	GOST 2177-99	 63 2 3 3.5 4.0 292 16
7	m of paraffin of asphaltenes of tars	 wt %		 4.61 1.28 20.90

The process of crushed stone impregnation with deasphaltizate comes to the following technological processes: extraction of deasphaltizate (oil hydrocarbons) with liquid propane from the heavy oil residue; impregnation of crushed stone with deasphaltizate under supercritical parameters of propane-butane mixture; regeneration of propane-butane mixture and return of it to recycle.

Carbonate crushed stone was used as a raw material, mesh size 20 - 40 µm from Saltykovsky field in Republic of Tatarstan.

Deasphaltizate was used as an impregnation material, which had been gained from the heavy oil residue of conversion process of high-viscosity oil from Ashalchinsk place by thermal-steam effect method [9] and propan/butan deasphaltizing [9].

Operating parameters of providing complex process are given in Table 2.

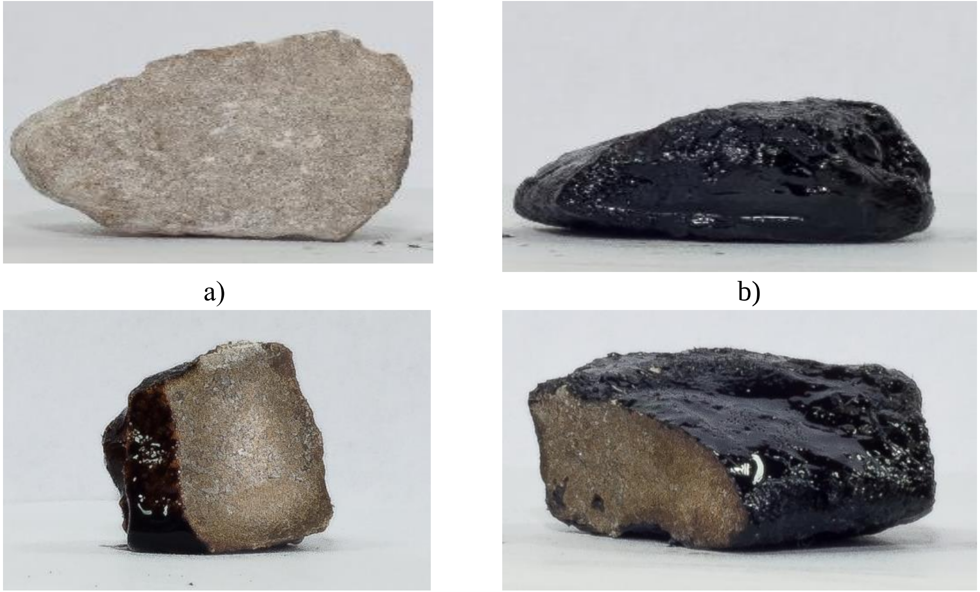
Table 2. Operating parameters of providing complex process.

No.of operating condition	$P_{extraction}$, MPa	$T_{extraction}$, ˚C	$P_{impregnation}$, MPa	$T_{impregnation}$, ˚C	Mass ratio «extractant: oil residue»	Vent of deasphaltizate,%
1	4.5	85	4.5	85	2:1	66
2	4.5	85	4.5	138	1.5:1	54
3	6.0	85	7.0	138	2:1	65.4
4	7.0	85	7.0	138	1.5:1	52
5	7.0	85	7.0	138	1:1	42

The influence of SCF impregnation process conditions on quality of crushed stone impregnation is shown on photos given in Figure 7.

Homogeneous deasphaltizate shell formed on the surface of the stone after the impregnation process (see Figure 7b, 7c, 7d), has good hydrophobic and adhesive properties. The latter has its force if applied to the asphalt coat material, which traditionally placed on the surface of crushed-stone layer during pavement forming up. Water absorption of the crushed stone sample is 0.24%.

However, during road construction process and during first years in service, crushed stone fractionizes intensively, whereby its inner part becomes bare. In case of impregnation with the traditional approach, this part usually stays untreated, it causes increasing of water uptake of the material and deterioration of its physical and mechanical properties. One of the solutions to this problem is a pass-through and uniform impregnation of crushed stone.



a) b)

c) d)

Figure 7. Photos of crushed stone samples: a) source sample; b) outer look of crushed stone sample after impregnation process; c) sample piece after impregnation in conditions No.1 (table 2); d)sample piece after impregnation in conditions No.4 (table 2).

Impregnation of crushed stone with liquid solution of deasphaltizate in propane-butane mixture (condition No.1 in Table. 2) provides peripheral preferably the so-called "crusted" impregnation (see Figure 7c). In the case of transfer of propane - butane mixture in a SCF state (conditions in Table No. 2-5. 2) impregnating of the crushed stone with deasphatizate is appears as uniform and "pass-through" (see Figure. 7d).

Table 3 shows the physical and mechanical properties of the original and impregnated samples of crushed stone, evaluated under GOST techniques [10].

Table 3. Physical and mechanical properties of the original and impregnated samples of crushed stone.

No. of operating condition	fraction, mm	True density, g/cm^3	Average density, g/cm^3	sponginess, %	Water uptake, %	Crushability rate, %/ grade	
						In dry consistence	Hydro-saturated consistence
initial sample	20-40	2.7	2.36	12.6	3.6	16.4/600	17.1/600
1	20-40	-	-	-	3.6	-	-
2	20-40	-	-	-	0.95	-	-
4	20-40	2.69	2.29	14.9	0.21	16.4/600	16.9/600

Indicators of water absorption determined after the crushing of initial and impregnated samples of crushed stone. As we can see, the rate of water absorption of the sample subjected to liquid impregnation (condition No.1 in Table 2) does not differ from the rate obtained for the initial sample of crushed stone, due to the inner part impregnation absence in this sample. In the case of impregnation of the crushed stone with a deasphaltizate solution and propane-butane mixture in a SCF state (conditions No.2 and No.4 in Table. 2), the water absorption prosperities of the samples decreases significantly.

The analysis of the histograms of pore size distribution (Fig. 8) shows that pores with a diameter from 0.032 to 0.034 mm are prevalent in the samples. The absolute number of pores decreases as their size increases. The concentration of large pores (0.192 mm) is negligible. At the same time, if in an untreated sample the absolute number of pores with a size of 0.032 mm in an untreated sample is 18620 pcs (which corresponds to their concentration amounting to 12.5 pcs/mm3), then in the sample after impregnation the number of such pores decreases more than by10 times (1687 pcs). The latter number of pores corresponds to a pore concentration of 0.74 pcs/mm^3).

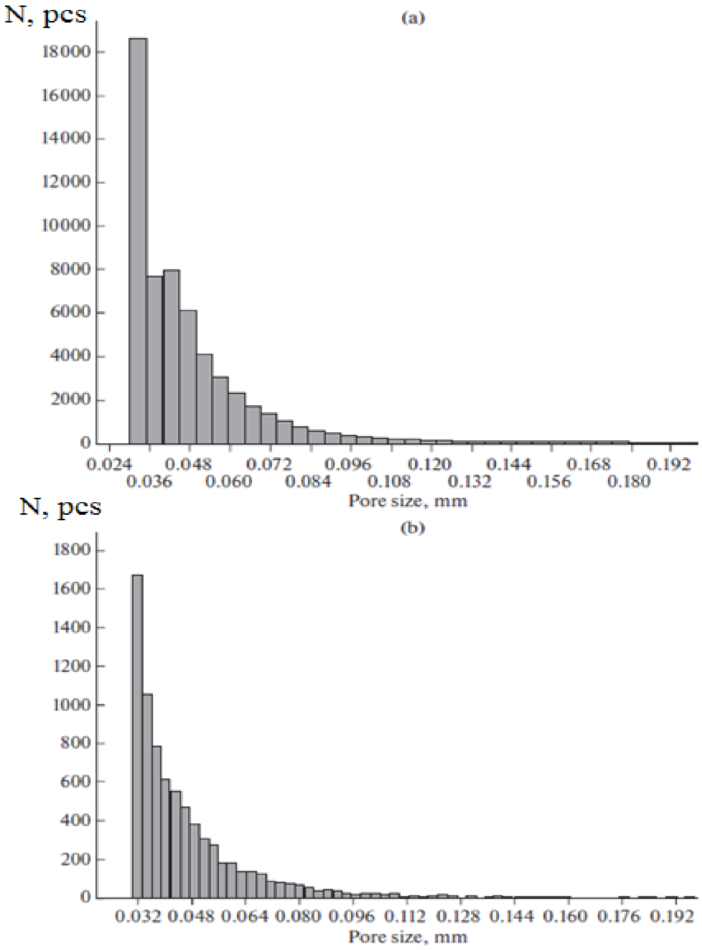


Figure 8. Histograms for pore size distribution (ordinate—the number of events N of pore detection, pcs); the upper figure corresponds to an untreated sample, the lower figure corresponds to a sample after impregnation.

CONCLUSION

1. The efficiency and preference of supercritical fluid extraction with the use of the propane-butane mixture for the extraction of petroleum products from oil sludge has been established. Results are presented concerning an indirect evaluation of pressure ranges for the first (5.0–6.5 MPa) and second (11–12 MPa) crossover points of isotherms inherent in the solubility of studied petroleum products in the propane-butane solvent.
2. A series of experiments on the processing of oil bearing sands of the Spiridonovskoe field of the Republic of Tatarstan has been conducted using processes of liquid and SCF extraction. In the course of the investigation, it has been found that supercritical fluid propane–butane extraction treatment of oil-bearing sands makes it possible to isolate up to 96.34 wt % of hydrocarbons from the sandstone. Here, the treated residual sandstone is a good raw material for preparing activated mineral flour.
3. A workable technology to improve the performance characteristics of cheap crushed stone is proposed by effectively impregnating it with cheap oil feedstock.

The uniform impregnation of macadam samples throughout the volume is achieved. By the nature of the penetration of oil products into the macadam samples, aphanitic areas of the breed with the admixture of clay matter are largely subjected to the treatment, and zones of developed porosity and weakened areas of the breed are involved.

As a result of using the proposed technology, water absorption of the macadam samples subjected to the treatment is reduced to 0.21%.

ACKNOWLEDGEMENTS

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