REPUBLIC OF AZERBAIJAN

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ABSTRACT

of the dissertation for the degree
of Doctor of Sciences

DEVELOPMENT OF ENVIRONMENTALLY SAFE TECHNOLOGIES FOR PROCESSING OF AZERBAIJANI OILS TO PRODUCE OILS FOR VARIOUS PURPOSES

Speciality: 3321.01 - Technology of petroleum, gas and stone-coal refining

Field of science: Technical sciences

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GENERAL CHARACTERISTIC OF THE WORK

Relevance of the topic. The development of the petroleum refining industry is aimed at increasing the efficiency of petroleum utilization, deepening its processing, improving the quality of petroleum products, including oils for various purposes.

The main direction is the development of environmentally safe technologies for the processing of Azerbaijani petroleums, including their heavy oil residues and the introduction of highly efficient technological processes that provide high-quality products with high yields.

Development of technologies in supercritical conditions is effective for solving the problem of creation of waste-free technology of deasphaltenization, demetallization, desalting, dehydration of oil and for purification of its heavy residues from asphaltenes and metals in order to obtain purified residues (deasphalticates) - feed for secondary processes and valuable metals - concentrate of valuable organometallic compounds, which are good raw materials for synthesis of catalysts.

Residual oils (brightstocks) from Azerbaijani petroleums by existing and supercritical technology are produced according to the scheme: vacuum residue→ deasphalting → selective purification → dewaxing → hydrogen treating.

It is known that one of the promising technological processes in oil production is the hydrocracking process, which helps to process raw materials very efficiently and obtain high-quality products without waste. This process is radical for rational processing (destructive hydrogenation) of raw materials with changes in the structure of molecules and obtaining petroleum products with new qualities absent in the raw feedstock.[1]

With the development of technology and the aggravation of ecological problems, the requirements for the quality of lubricating oils used in machines and mechanisms operating under harsh operative

[1] Хавкин, В.А. Гидрогенизационные процессы переработки нефтяных остатков / В.А. Хавкин, Л.А. Гуляева, П.А. Никульшин, Г.В. Битиев // Нефтепереработка и нефтехимия, - М.: - 2018. № 6, - с. 9-11.

conditions have become more stringent. Existing oil production processes do not allow for manufacturing oils that meet long-term requirements.[2]

In this situation, the development of new environmentally safe and energy-saving (hydrogenation, supercritical extraction) technologies that ensure the production of a wide range of lubricating oils that meet long-term requirements is relevant.

Object and subject of the research. The object of the study is oil production in the oil refining industry of the fuel and energy complex, and the subject is the development of innovative technologies that ensure the production of quality oils based on Azerbaijani oils and heavy fractions.

Purpose of the work. Creation of a new environmentally safe, low-stage, energy-saving technology for purification of oil and its heavy residue from asphaltenes, metals, salts, water and other impurities using CO_2 in its supercritical parameters, construction of a pilot plant and issuing recommendations for implementation in industry.

The purpose of this research is also the development of technology for obtaining oils from oil and heavy residue of a mixture of low-paraffin oils by using CO_2 in its supercritical parameters and hydrocracking (at a pressure of 5-6 MPa) of heavy residue and distillate D-11 from a mixture of low-paraffin and paraffin oils in the presence of oxides of metals of groups VI and VIII of the periodic system on aluminum oxide. Development of technology for obtaining semi-synthetic oils with improved viscosity-point properties, as well as improvement of technology for obtaining white oils.

Methods of research. When performing the work of the thesis to study the physicochemical and operational properties of the use of raw materials (petroleum, fuel oil, distillate, vacuum residue, etc.) and products obtained from them were determined by methods in accordance with GOST and ASTM, spectral (IR, UV, NMR, adsorption chromatography, mass spectrometry and atomic adsorption) methods.

[2] Аббасов, В.М. Разработки базовых основ моторных масел из бакинских нефтей / В.М. Аббасов, Ф.И. Самедова, Р.З. Гасанова [и др.] //Нефтегазовые технологии и аналитика, - Москва: - 2016. № 6, - с. 69-72.

Main points presented for defense:

-Using the process of supercritical extraction of SC-CO_2 an environmentally friendly technology of oil and its heavy residues purification from water, salts, mechanical impurities, metals, asphaltenes has been developed. Optimal regime parameters of oil and heavy oil residues (fuel oil, vacuum residue) processing with high technical and economic indicators of the process have been established.

- A new technology and scheme of purification of distillate and residual oil fractions meeting modern quality requirements on the basis of supercritical fluid extraction process using two-phase solvent system (SC-CO_2 and IL) is developed.

-A general scheme of producing brightstocks - residual oils from heavy residues (vacuum residue) according to the classical scheme using deasphalting, selective purification, dewaxing and hydrogen treating processes is proposed.

- INCP MSE AR has developed technologies for obtaining high quality white oils using selective purification and hydrogenation processes (hydrogen treating, hydrogenation and hydrocracking), as well as a combined process (dewaxing and selective purification using a single solvent) and oleum refining.

-Studies of the process of hydrocracking of oil deasphalticates and heavy petroleum residues, selection of optimal conditions in order to obtain fuels, working fluids and oils for various purposes.

Scientific novelty. For the first time, the scientific and practical foundations of oil production intensification technologies have been developed, providing for the creation of new advanced technologies (CO_2 fluid, combined dewaxing – selective purification, hydrotreating – hydrocracking) that ensure the production of a wide range of promising quality oils based on Azerbaijani oils and their heavy residues.

Using the unique properties of CO_2 in supercritical state a new environmentally safe process of purification of distillate and residual oil fractions meeting modern quality requirements has been created.

Processing of purified petroleum and its residues by hydrocracking at pressure of 4-6 MPa and points of 400-425 °C in turn creates the

possibility of obtaining environmentally safe fuels, oils and other petroleum products from them.

The influence of point and pressure of the process on the degree of destruction of feedstock, quality and assortment of obtained oils has been established. The modes of obtaining low-viscosity and high-viscosity oils and liquids have been worked out.

Using a set of modern physicochemical methods of analysis, including spectral methods, the structure-group composition of petroleum fractions of petroleums and oil blends was studied for the first time.

The chemistry of transformation of hydrocarbons of petroleum residue deasphalticate at hydrocracking under pressure of 5 MPa and points of 400-450 °C has been studied. It is shown that hydrocracking of deasphaltic residue at 400 °C and 425 °C leads to enrichment of oil fractions of hydrogenated residue with saturated (methane-naphthenic) hydrocarbons. The structure-group composition of hydrocarbons changes: the amount of condensed aromatics increases in the oil fractions due to the transformation of resinous substances.

Under the studied hydrocracking conditions, condensed aromatic and hybrid hydrocarbons of feedstock are subjected to hydrogenation and splitting, along with resinous substances, turning into low-molecular-weight hydrocarbons. Hydrocracking and isocracking of deasphaltizate and its raffinates using industrial catalysts were also carried out.

Residual oils are obtained using existing and supercritical technology from heavy residues according to the scheme:

deasphalting → selective treating → dewaxing → hydrogenation.

The possibility of using oil fractions of the studied Azerbaijani petroleums as feedstock for white oil production has been scientifically substantiated and experimentally proved:

- For the first time white oil meeting all the requirements of the standard for medical vaseline oil was produced from oil fractions of Balakhanskaya heavy and Naftalan petroleum using the technology of the Yaroslavl Refinery;

- INCP technology of white oil production from Azerbaijani petroleums by combination of highly effective technological processes

- selective treating, combined purification developed in of the Ministry of Science and Education of the Azerbaijan Republic (MSE AR), hydrogenation processes (hydrodistillation, hydrogenation, hydrocracking) and oleum after-treatment was developed;

-the influence of individual processes on the quality and structure-group composition of intermediate products and finished oils was studied;

experimentally substantiated data were obtained and corresponding scientific conclusions were made on selection of feedstock and method of its purification for obtaining white oil of medical vaseline type;

- the possibility of waste reduction in white oil production was scientifically substantiated and experimentally proved.

Practical value. Application of supercritical extraction with participation of CO_2 provides a high degree of purification of petroleum treating from asphaltenes and metals, increases the yield of deasphalted product - feedstock for subsequent secondary processes in order to obtain fuels, base oils and other petroleum products. Supercritical extraction process was also applied for oil preparation for distillation and tested as a substitute for the existing technology of oil electrotreatment (EDP AVD) from water, salts and mechanical impurities before atmospheric-vacuum distillation.

Preliminary calculations have shown that energy requirements of the process of extraction of petroleum and its heavy residues at supercritical parameters of CO_2 are much less than in known processes.

Comparative technological and economic indicators of dehydration and desalting process at processing of 6 mln. tons of petroleum can make up to 2,3 mln. manat per year.

Scientific and technological developments are the basis of recommendations for obtaining white oil from oil fractions of Azerbaijani petroleums.

Various variants of white oil production by combination of processes of selective and combined purification of step hydrogenation and oleum purification have been developed. In this case it is possible to increase the yield of the target product, sharply reduce the consumption of reagents and hard-to-dispose of wastes

polluting the environment.

The economic effect of obtaining residual oil (brightstock) when processing 89419 tons of tar to produce 50 thousand tons of oils by the proposed technology is 7138 thousand manat.

Publications. On materials of the dissertation 63 works were published, including 1 monograph, 27 articles in leading foreign and republican scientific and branch editions, 32 theses, 1 author's certificate, 2 patents of Azerbaijan.

Approbation of the work. Sections of the work were reported and discussed at: II Republican Conference dedicated to the 25th anniversary of the Institute of Additives Chemistry (Baku, 1990); IV Scientific and Technical Conference of Young Scientists and Specialists dedicated to the memory of Y.G. Mammadaliyev (Baku, 1992); I Baku International Conference on Petrochemistry, 1994; II Baku International Petrochemical Conference dedicated to the memory of Academician Y. G. Mammadaliyev, 1996; Fourth Baku International Congress, Baku, Azerbaijan Republic, 1997; III International Conference, Tomsk, 1997; III, IV, V, VIII, IX Baku International Mammadaliyev Petrochemical Conferences, 1998, 2000, 2002, 2012, 2016; VI International Conference "Chemistry of Petroleum and Gas", Tomsk, 2006; VII Baku International Mammadaliyev Conference on Petrochemistry, dedicated to the 80th anniversary of the Institute of Petrochemical Processes of NAS of Azerbaijan, 2009; VII Scientific and Practical Conference with international participation, p. Listvyanka, Lake Baikal, 2011; Scientific-Republican Conference dedicated to the 100th anniversary of Academician A.M. Kuliyev, Baku, 2012; I International Chemical and Chemical Engineering Conference, Baku, 2013; Republican Scientific and Practical Conference dedicated to the 100th anniversary of Academician S.D. Mehdiyev, Baku, 2014; Republican conference dedicated to the 50th anniversary of the Institute of Additives Chemistry named academician A.M. Kuliyev, Baku, 2015; Republican scientific conference dedicated to the 80th anniversary of the Institute of Catalytic Inorganic Chemistry named academician M. Nagiyev, Baku, 2016; International scientific and technical conference dedicated to the 100th anniversary of academician B.K. Zeynalov,

Baku, 2017; Scientific and technical republican conference dedicated to the 90th anniversary of professor S.A. Sultanov, Baku, 2017; International Conference dedicated to the 110th anniversary of Academician M. Nagiyev, Baku, 2018; International Scientific Conference dedicated to the 90th anniversary of the Institute of Petrochemical Processes named after Academician Y.G. Mammadaliyev, Baku, 2019; International Scientific and Practical Conference "Science and texnology research", Russia, Petrozavodsk, 2022; XII International Scientific Conference "Chemistry of Petroleum and Gas" (Tomsk, 2022); International Conference dedicated to the 95th anniversary of Academician A.H. Mirzajanzadeh, Russia, Ufa, 2023; XIII International Conference "Chemistry of Petroleum and Gas" (Tomsk, 2024).

Place of dissertation work. The dissertation work was carried out at the Institute of Petrochemical Processes named Academician Y.G. Mammadaliyev (INCP MSE AR) in accordance with the working programs 3/86, 6/91, 6/96, 3/2001, 3/2004, 3/2006, 2/2013 (state registration № 01880011926, 0194Az00145, 0101Az00089, 0104Az00006, 0106Az00014, 0113Az2037).

Personal participation of the author. The author determined the main purpose of research, directions and tasks for its implementation, carried out systematization, processing and discussion of the obtained results. The author was also directly involved in setting up and conducting laboratory, pilot and pilot-industrial tests.

Structure and scope of the work. The dissertation work is set out on 383 pages, consists of an introduction, 7 chapters, including 157 tables, 30 figures, 7 graphs, conclusions, list of literature, consisting of 414 names. Excluding figures, tables, list of used literature and appendices the thesis is 345385 characters (including introduction 15772, first chapter 98115, second chapter 13556, third chapter 59775, fourth chapter 19276, fifth chapter 38971, sixth chapter 30679, seventh chapter 61996 and conclusions 7245 characters).

The introduction substantiates the relevance of the topic, purpose and objectives of the dissertation work, scientific novelty and practical value of the results obtained in the process of work. The results of the research presented in chapters I-VII are briefly characterized.

The first chapter presents a review of scientific and patent literature reflecting the current state of oil production and methods of processing of oils and their residual fractions in Azerbaijan and in advanced foreign countries. Based on the analysis of the presented literature data the aim and objectives of the dissertation work are outlined.

In the second chapter the methodology of experiments is described, characterization and methods of analysis of petroleums, residual fractions and oils are presented. The schemes of installations used during laboratory, pilot and pilot-industrial tests are described.

The third chapter of the dissertation presents the results of research on the development of environmentally safe supercritical technology for processing of Azerbaijani petroleums and their heavy residues for dehydration, desalting, deasphalting, demetallization.

In the fourth chapter the results of obtaining high quality waste-free products of hydrocracking of petroleum and its residues purified in the process of supercritical extraction, recommendations for a new processing scheme are given, the economic indicators of oil production are evaluated.

The fifth chapter of the thesis is devoted to the topic of expanding the resources of raw materials for obtaining residual oils - brightstocks. It also shows the possibility of improving the quality of petroleum base oils by compounding with various synthetic oils.

In the sixth chapter the resources and selection of feedstock for production of white oils from Azerbaijani petroleums are expanded. Results of researches devoted to improvement of technology of white oil production are given.

In the seventh chapter the results of research of hydrocracking process of distillate

D-11 under pressure of 4-5 MPa and deasphaltizates of mixture of low paraffin and paraffin petroleums under pressure of 5-10 MPa at points of 400-450 °C with the purpose of obtaining oils of different purpose are presented. Hydrocracking and isocracking of deasphaltisate and its raffinates of a mixture of low-paraffin oils using industrial catalysts were also carried out.

The thesis concludes with the conclusions of the work done, in

which the main results of the research are presented, and a list of used literature. Documents confirming the results of the industrial tests carried out on this work are also presented.

THE MAIN CONTENT OF THE WORK

1. Dehydration, desalting, deasphalting and demetallization of petroleums and their residues using a supercritical extraction process

It is known that petroleum reaching the surface of the earth carries associated gas, sand, silt, salts and water in the form of saturated chloride solution. Water content in petroleum transported through trunk pipelines is up to 1 %, and in the oil coming to refineries should be no more than 0,3 %.

The salt content of petroleum delivered to OR should be no more than 50 mg/l, while petroleum with a salt content of no more than 5 mg/l should be delivered for refining.

At distillation of oil under atmospheric pressure salts accumulating in fuel oil deteriorate the quality of it and vacuum residue obtained from it.

At present, the refining industry AVD uses electric dehydrator sections to purify oil from water, salts and mechanical impurities, which requires large energy inputs.

As a result of anthropogenic human activity, large amounts of gases (CO_2, CH_4, etc.) are emitted into the atmosphere, creating a thermal effect, global warming and related climate changes pose a serious threat to all humanity. Excessive point increase leads to acceleration of a number of undesirable processes in the atmosphere and on the Earth.

According to the UNO protocol “On Climate Change”, which calls on the countries of the world to reduce emissions of heat-emitting gases into the atmosphere, since carbon dioxide and methane have a great impact on the acceleration of global warming, the decision to

gradually reduce their emissions into the atmosphere has been reflected.

At the International Forum COP-29, which was held in Azerbaijan in November 2024, this problem became the subject of discussion of the world scientific societies.

IPCP MSE AR has developed and patented an environmentally safe, energy-saving research development in the direction of petroleum dehydration and desalting using CO_2 as a solvent for preparation for petroleum refining. Utilized gases from catalytic cracking units G-43-107M (regenerator 202) and EDP-AVD-6 furnace of Heydar Aliyev Petroleum Refinery were used for CO_2 production.

Figure 1 shows an alternative version of the technology of petroleum treatment from water, salts and mechanical impurities in electric dehydrators EDP together with the device AVD.

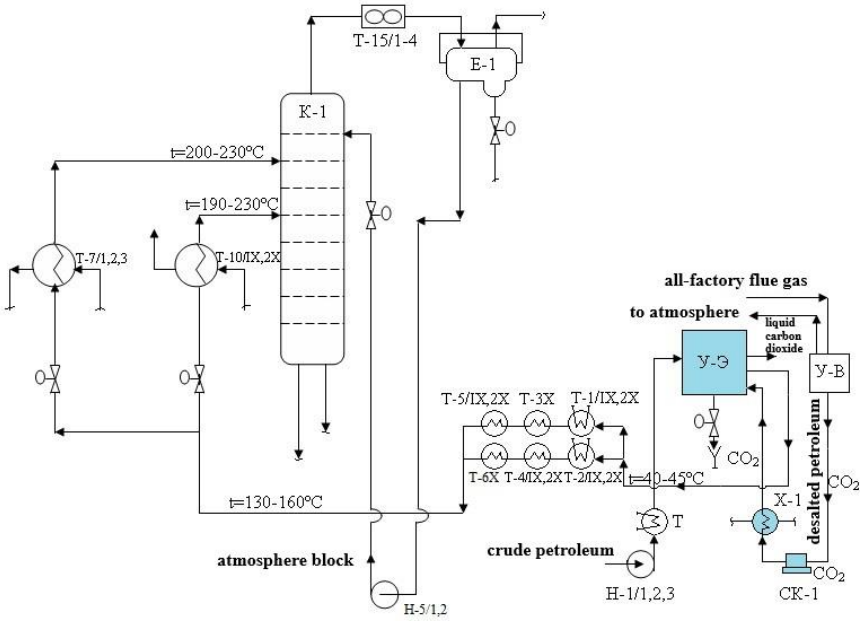

Figure 1. Principal flow diagram of a new alternative technology of OR at the AVD Refinery's EDP units. K-1 – primary evaporator (evaporation column); T-1÷T-10 – heat exchangers; T-15/1,4 – air condensers-coolers; E-1 – capacity of K-1 column; H-5/1,2 – pumps supplying irrigation from E-1 to K-1; H-1/1,2,3 – pumps; U-E – extraction unit; U-B – unit of CO_2 extraction from plant flue gases; SC-1 – CO_2 compressor; X-1 – refrigerator

The scheme of the ABT unit with the proposed extraction unit instead of EDP is given in Figure 1. CO_2 is extracted from the general plant flue gases. For CO_2 extraction, flue gases from catalytic cracking unit G-43-107 M are fed to the lower part of the absorber. Water is fed to the upper part of the absorber to extract CO_2 from the gas mixture.

At the content of CO_2 in the amount of 25-30 % in the smoke gas mixture, absorption is carried out at the pressure of 1,6-3,0 MPa. A mixture of gases N_2, O_2, CO, SO_2, NO_x is released from the upper part of the absorber. From the bottom of the absorber, CO_2 with water enters a water turbine, where the pressure is reduced and the mixture enters a separator where CO_2 is separated from water.

From the bottom of the separator, water with residual CO_2 enters the desorber, where air is supplied. From the top of desorber the air with CO_2 is discharged into the atmosphere, and water is supplied to the absorber. CO_2 from the separator in the volume of 90-93 % is supplied to the compressor SC-1 and further to the extraction unit.

In compressor SC-1 CO_2 is compressed to supercritical pressure (> 7,35 MPa), cooled in cooler X-1 to point 40-45 °C and enters the bottom of extraction column EC-1.

Oil by pump H 1/1, 2, 3 is supplied to the heat exchanger T, where it is heated to the point of 50 °C and fed to the upper part of the extraction column (EK-1). At supercritical conditions (point > 31 °C and pressure >7,35 MPa) in the extraction column the process of extraction of undesirable components of oil with the help of CO_2 is carried out.

In separators C-1 and C-2 at pressure of 4-5 MPa hydrocarbons C_1-C_5 and CO_2 are in gas state. From the top of separator C-1 CO_2 enters the CO_2 outlet line from separator 3 and together with separated CO_2 from catalytic cracking gases enters compressor SC-1. Under high pressure hydrocarbons C_1- C_5 in liquid state yield from the bottom of separator C-2.

Dewatered, desalted and cleaned from mechanical impurities petroleum from the bottom of separator C-1 by two streams is supplied for heating to heat exchangers: T_{tream} /T-1/1x, 2x, T-3x, T-5/1x, 2x and II stream – T-2/1x, 2x, T-4/1x, 2x, T-6x, where it is heated to 130-160 °C due to passing hot streams – petroleum fractions from AVD-6 unit.

After heating in heat exchangers two streams of purified oil are mixed, then again divided into two streams, pass through heat exchangers T-10/1x, 2x and T-7/1,2,3, where respectively heated to 190-230 °C and fed into the atmospheric column C-1.

Technological parameters of the process of petroleum preparation for refining at EDP- AVD units using supercritical CO_2 are given in table 1.

Table 1.

Technological parameters of petroleum treatment process with application of SC-CO_2

Parameters	Indicators
Point in EC-1, °C	40-45
Pressure in EC-1, MPa	7,4-7,8
Pressure in separator C-1, MPa	4-5
CO_2 ratio: petrolum	1 : 1
Extraction duration, hour	4
Settling time, hour	4
Absorber pressure (block B-1), MPa	1,6-3,0
CO_2 yield after water separation, % wt. (block B-1)	75

Characteristics of the mixture (sample I-III) of Neft Dashlari, Shirvan and Surakhani petroleums processed at the Heydar Aliyev Oil Refinery before and after treatment with SC-CO_2 are presented in table 2.

Also, mixtures of low-paraffin oils and oils from Azeri fields, VII horizon of Bulla-deniz, wellsite 55 of Absheron were subjected to treatment with SC-CO_2.

As it can be seen from the obtained data, as a result of realization of the process with application of SC-CO_2, besides reduction of asphaltenes content, the content of mechanical impurities, ash, pitch, and water and chloride salts (NaCl) decreases to their complete absence.

The scheme of the laboratory unit for deasphaltenization of petroleum and its heavy residues using CO_2 under conditions of its supercritical parameters is shown in Figure 2.

Table 2.

Characterization of feedstocks and extraction products

Indicators	Petroleum samples					
	I		II		III	
	initial	after extraction	initial	after extraction	initial	after extraction
Density at 20 °C, kg/m^3	887,6	886,8	891,7	890,8	886,5	885,7
Kinematic viscosity at 20 °C, mm^2/s	49,28	49,08	54,68	54,50	51,65	51,50
Pour point, °C	-22	-23	-14	-14	-11	-10
Content, % wt:						
Resins	6,74	6,28	9,22	8,03	10,2	8,55
Asphaltenes	0,30	0,05	0,43	0,10	0,40	0,12
Paraffin	4,29	3,57	4,33	4,55	4,20	4,19
mechanical impurities	0,0704	0,0169	0,0548	0,0112	0,0348	0,0102
Ash	0,036	0,030	0,027	0,024	0,026	0,020
Water	0,5	absent	0,3	absent	0,2	absent
chloride salts mg NaCl/1 dm^3 petroleum	50,4	absent	40,5	absent	54,9	absent
petroleum acids	0,9796	0,6444	0,7500	0,6106	0,5210	0,3724
Acid number, mg KOH/g	0,9880	0,8105	0,9080	0,7819	0,5850	0,4551

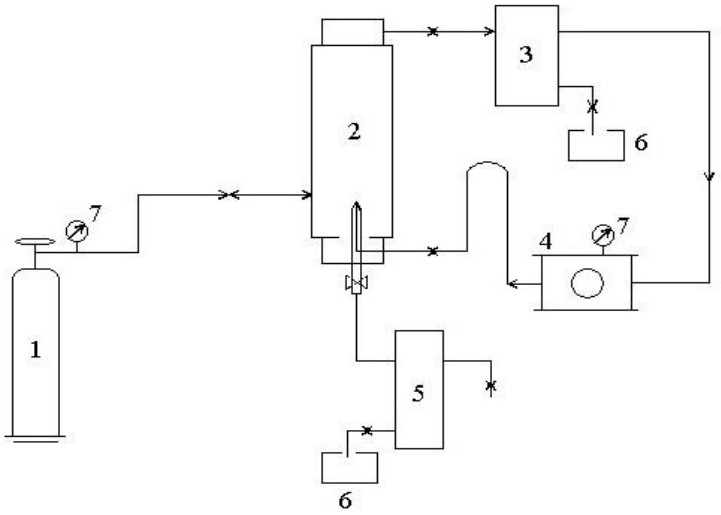

Figure 2. Scheme of the laboratory installation for deasphaltenization of petroleum and its heavy residues with participation of CO_2 under conditions of its supercritical parameters: 1 – CO_2 cylinder; 2 – extractor; 3 – gas filter; 4 – compressor; 5 – separator; 6 – product trip tanks; 7 – pressure meters

Carbon dioxide is fed into the lower part of the extractor (2) from a cylinder by means of a reducer (7) and the extraction is carried out under supercritical carbon dioxide parameters (at a point of 40 °C and a pressure of 7,5-7,8 MPa) at a mass ratio of feedstocks: CO_2 1 : 1.

At the given supercritical parameters during 4 hours CO_2 circulation is carried out according to the scheme: extractor → separator → compressor → extractor. Then CO_2 circulation is stopped and asphaltenes precipitation from the solution starts within 4 hours. At critical parameters of CO_2 the solution of deasphaltenized product from the extractor descends to the separator, where it is freed from CO_2 and fed to the tank of deasphaltenized product.

Table 3 shows the characteristics of petroleum and its heavy residues before and after deasphaltenization using CO_2 in supercritical conditions, as well as the yield of asphaltenes before and after extraction by the proposed and known methods. The amount of precipitated asphaltenes in petroleum, fuel oil and vacuum residue according to the proposed method is 1,5; 1,8 and 1,47 % counting on petroleum, respectively, that is more than at extraction by the known method according to GOST 11858-85.

As a result of deasphaltenization there is also demetallization of initial raw feedstocks, as evidenced by the data of trace element composition of petroleum, fuel oil and vacuum residue, as well as asphaltenes isolated from them (table 3,4).

Using the unique properties of CO_2 in supercritical state, a preparative method for determination of asphaltenes in petroleum and its heavy oil residues was created and patented in IPCP MSE AR. The developed new method in comparison with the known ones allows to increase the amount of the test product suspension from 5-10 to 100 g, to reduce the amount of solvent for its dilution from 40 to 1-2-fold, to improve the clarity of asphaltene precipitation, to reduce the duration of analysis.

The proposed method can be used to improve the existing standard – GOST 11858-85 and apply it not only for quantitative determination of asphaltenes in petroleum and petroleum products, but also for isolation in sufficient quantity to study their composition and properties.

Table 3.

Results of deasphaltenization of oil and its heavy residues using CO_2 at its supercritical parameters

Name		Density at 20 °C, kg/m³	Viscosity at 50 °C, mm²/s	Point, °C		Coking capacity, %	Asphaltene yield in % wt. by the method			
				Pour	flash		proposed	known	proposed	known
							Before	after	before	after
							Extraction		extraction	
Petroleum	initial	865,9	7,11	-10	5	1,91	-		-	
	same after deasphaltenization	859,0	6,33	-10	5	0,88	1,50	1,07	0,87	0,58
Fuel oil*)	initial	909,5	43,22	+8	146	3,51	-	-	-	
	same diluted in n-heptane	783,0	1,82	-	-	-	-		-	
	same after deasphaltenization	907,4	42,0	+6	148	3,30	3,10	2,57	1,0	0,79
Vacuum residue*)	initial	947,3	181,1**)	49	280	4,67	-		-	
	same diluted in n-heptane	787,0	4,19	-	-	-	-		-	
	same after deasphaltenization	940,3	105,6**)	48	280	4,10	4,50	3,96	1,46	0,89

Separation of asphaltenes from oil occurs only with the help of CO_2-due to the influence of dispersion forces, low-molecular fractions of oil act as an intermediate solvent, increasing the solubility of high-boiling and resinous substances in CO_2.

Table 4

Microelement composition of raw materials and asphaltite, ppm

Name	Raw petroleum	Asphaltite separated from petroleum	Raw fuel oil	Asphaltite, isolated from fuel oil	Raw vacuum residue	Asphaltite isolated from vacuum residue
Al	56,84	78,6	63,6	94,0	70,52	110,0
Ba	2,3	4,96	5,5	9,0	8,77	13,3
Cd	0,19	0,63	0,3	0,64	0,42	0,65
Cr	20,39	25,09	22,7	57,1	25,0	89,2
Cu	11,79	19,2	12,2	21,6	12,74	24,0
Fe	8,50	243,6	90,7	473,6	181,08	703,7
K	44,8	52,2	48,0	89,9	54,08	125,6
Mg	0,1	201,0	0,06	206,5	-	214,8
Mn	2,82	4,4	2,95	13,35	3,28	22,3
Na	335,6	890,2	220	864,9	120,6	839,6
Ni	10,66	24,4	14,3	80,2	18,0	136,16
Pt	-	-	-	traces	-	traces
Pb	1,61	<8,0	2,09	6,6	2,99	5,22
Sn	-	<4,89	-	<4,0	-	Traces
V	0,22	0,39	0,4	1,28	0,63	2,17
Zn	3,7	5,6	20,5	26,5	37,47	46,71
Se	-	8,57	-	3,5	-	-
Co	1,2	1,29	-	-	-	-
Sb	-	-	-	traces	traces	traces
Au	-	-	-	traces	traces	traces
As	-	-	-	1,11	-	2,89
Hg	-	-	-	9,67	-	10,96

Optimization of the process, namely the influence of the degree of dilution of feedstock with hydrocarbon solvent, pressure and point on the results of purification of a mixture of low-paraffin oils and its heavy residue was studied.

As a result of researches the following optimal process parameters were established: T – 56-80 ºC; P – 7,3-8,0 MPa; ratio of hydrocarbon solvent to feed (wt.) 0,7 : 1; ratio of SC-CO_2 : feedstock 1 : 1. Time of

staying of the mixture in the extractor and precipitation of asphaltenes, trace elements, water, salts and mechanical impurities is 4 hours.

The use of co-solvents such as n-heptane, toluene, acetone and their mixtures with ethanol in the process of SC-CO_2 extraction increases the efficiency of the process. The proposed method with the use of co-solvents provides better precipitability of asphaltenes and metals from petroleum and vacuum residue, while improving the quality of deasphaltenized product.

The use of two-phase system SC-CO_2 + IL allows to reduce the amount of selective solvent IL from 1:3 to 1 : 0,5 ÷ 1, without affecting the quality of raffinate. The use of two-phase solvent allowed to reduce the process point from 80 to 31 ºC and the contact time to 2 hours.

Selective purification of viscous distillate by mixture of SC-CO_2 with co-solvents LMP+MF at the ratio of distillate : solvent 1:0,5:0,5 respectively allows to improve the clarity of separation and quality of raffinate, reduce the yield of extract at lower multiplicity of solvents.

The process of vacuum residue deasphaltenization at supercritical parameters of CO_2 was carried out according to the technological scheme (Figure 3).

The use of a biphasic solvent promotes the precipitation of heavy aromatics together with resins and asphaltenes, i.e. the ionic liquid easily dissolves low-ring aromatics and precipitates condensed heavy aromatics. The ionic liquid morpholine formate remains in the deasphaltenizate solution and is blown out of it in a carbon dioxide current at 120 ºC. Purification of IL from aromatic compounds is carried out by decomposition of the complex with water at 80 ºC.

In the IR spectra (Figure 4) of asphaltenes isolated from deasphaltenizate using two-phase solvent SC-CO_2 + IL, the bands at 1377 and 1731 cm^{-1} appear with lower intensity than in asphaltenes isolated from initial tar, and the bands at 907, 1039, 1072, 1269 and 1599 cm^{-1} disappear.

This gives grounds to assert that deasphalting with the use of two-phase solvent SC-CO_2+IL allows to involve completely or partially aliphatic, cyclic or aromatic compounds with C=O and/or C-O-C groups.

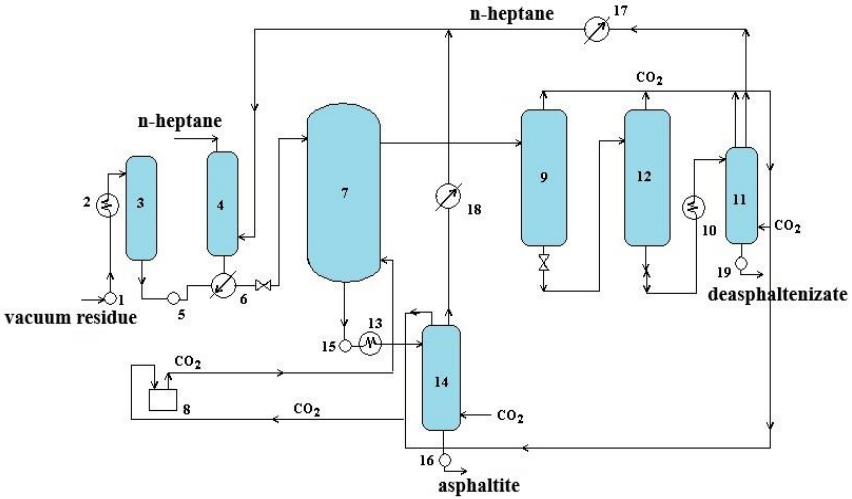

Figure 3. Principal scheme of vacuum residue deasphaltenization process at supercritical parameters of CO_2.

1, 5, 15, 16, 19 – pumps; 2, 10, 13 – heaters; 3, 4 – receivers; 6 – mixer; 7 – extractor; 8 – compressor; 9 – separator; 11, 14 – evaporators; 12 – gas filter; 17, 18 – condenser-refrigerator

Analysis of the data in table 5 shows that during SC extraction using two-phase solvent SC-CO_2 + IL in the presence of n-heptane at equal ratios of feedstock : SC-CO_2

1 : 1, the density of deasphaltenizate decreases from 945,2 to 911,4 kg/m^3, pour point increases from +16 to +23 ºC, which according to the studies is associated with the dissolution of high-molecular-weight solid hydrocarbons adsorbed on the surface of RAM in the solvent containing IL; at the same time, the clarity of RAM precipitation improves.

Deasphalting of tar with SC-CO_2 and SC-CO_2 + n-heptane + IL leads to decrease of metal content in deasphalticate, and to a greater extent – after vacuum residue treatment with SC-CO_2 + n-heptane + IL mixture.

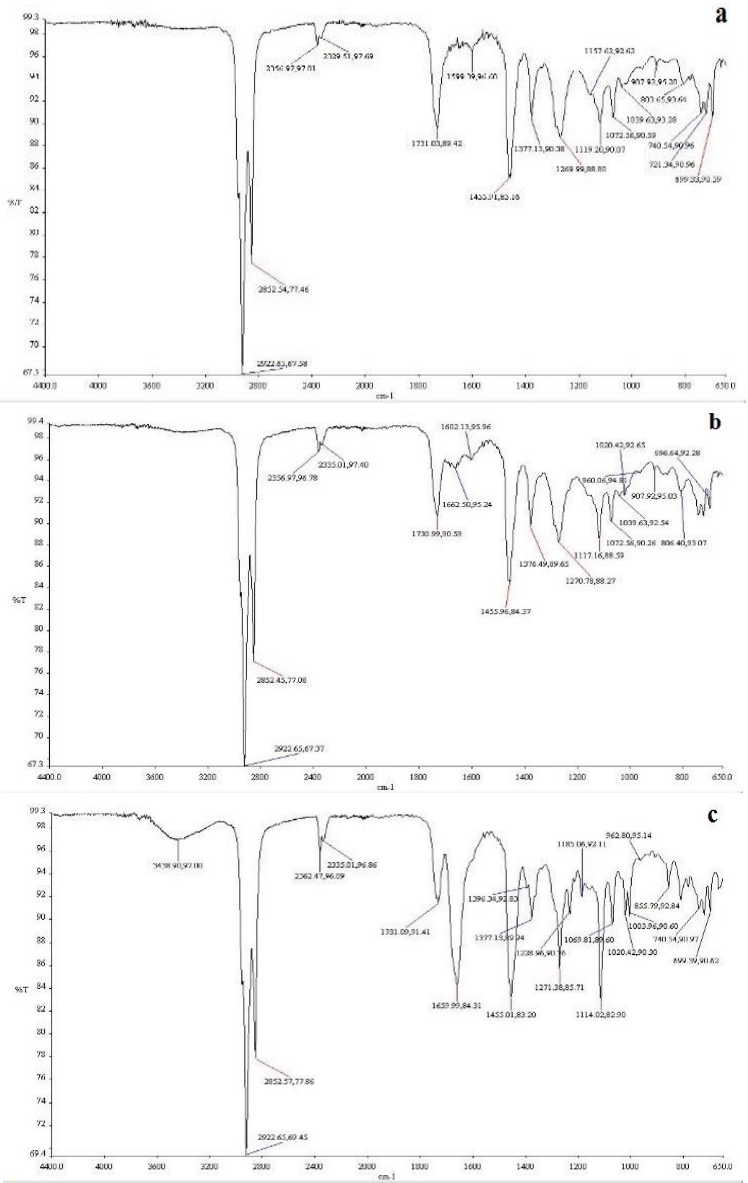

Figure 4. Spectra of asphaltenes: a – from feedstock-vacuum residue; b – from SC extraction from vacuum residue using SC-CO_2; c – from SC extraction from vacuum residue using two-phase solvent SC-CO_2 + IL

In the process of deasphaltenization with the use of two-phase solvent provides higher speed and completeness of deasphaltenization of feedstock and obtaining deasphaltenizate with optimal component composition and low density, as well as with a reduced content of metals in it.

Table 5

Characteristics of feedstocks and products of their processing

Indicators	Vacuum residue		$SC\text{-}CO_2$		$SC\text{-}CO_2$ +IL*)	
Feedstock to solvent ratio (n-heptane)	-		1 : 1,3		1 : 1,3	
Viscosity at 100 °C, mm^2/s	187,0		115,6		131,6	
Density at 20 °C, kg/m^3	955,9		945,2		911,4	
Point, °C						
Flash	278		277		276	
Pour	+40		+16		+23	
Yield, % wt:						
deasphaltenizate	-		96,0		95,8	
Asphaltite	-		4,0		4,2	
Content, % wt:						
Paraffinonaphthenic	33,75		38,25		34,74	
Aromatic						
light I	14,37		22,20		13,82	
medium II	21,45		16,08		17,24	
heavy III	16,86	30,43	12,21	23,47	25,58	33,37**)
Resins	13,57		11,26		7,79	
IL	-		-		0,83	
Asphaltenes	0,29		0,28		0,35	

*) IL – 15 wt. %.

**) are deposited together with asphaltenes

Though at application of two-phase solvent the quantity of separated asphaltite is only
0,2 % more (4,2 vs. 4,0 %), than in case of single-phase solvent, but this small share includes a part of tar (their content decreases from 11,26 to 7,79 %), which are the most undesirable components of vacuum residue.

For the first time on the basis of supercritical fluid extraction

process with the use of two-phase solvent system (SC-CO_2 and IL) for purification of distillate and residual oil fractions a new environmentally friendly technology was created, providing the highest yield of oil fractions meeting modern quality requirements. The general scheme of oil production from petroleum is presented in Figure 5.

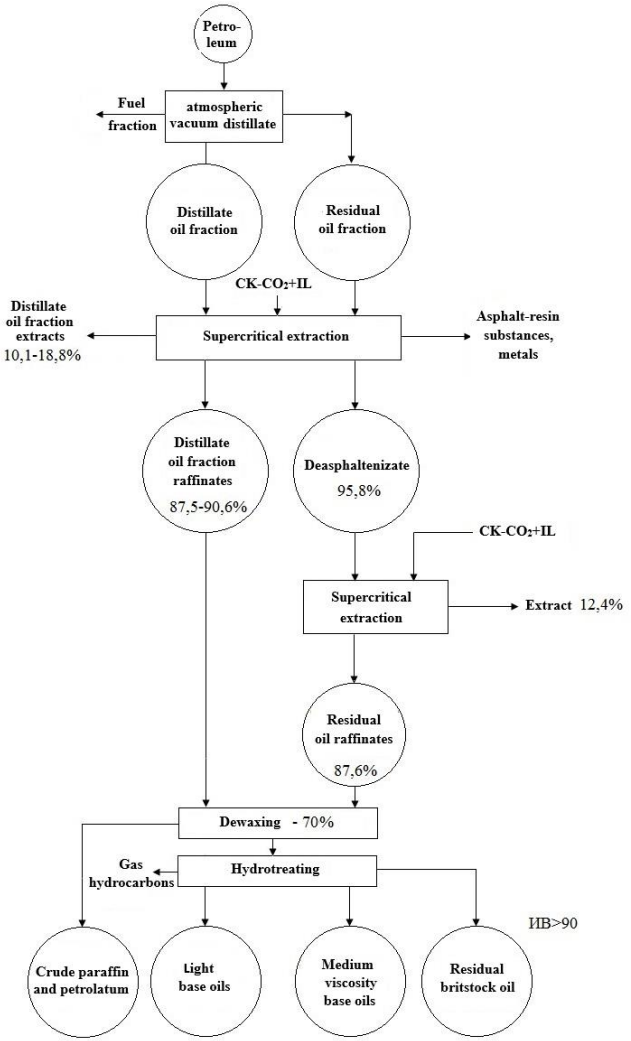

Figure 5. General scheme of oil production new technology

Supercritical purification of tar and its deasphaltisate in the

presence of CO_2 or two-phase solvent (SC-CO_2 + solvent) leads to production of residual oils according to the scheme:

$$\text{vacuum residue} \xrightarrow{CK-CO_2} \text{deasphaltization} \xrightarrow{CK-CO_2}$$

purification in 1 or 2 steps → dewaxing → hydrogenation.

From hydrogenated raffinates the oils meeting the requirements of GOST 6411-76 for heavy cylinder oil-52 and ISO 6480-2019 for P-28 oil, TU-3810131278 – for P-40 oil are obtained, brightstocks according to TU 38101361-73 are obtained light oils vapor 30.

2. Hydrocracking of supercritical extraction product

Hydrocracking of deasphaltized petroleum and its heavy residues was studied in order to create a new refining scheme. The purpose of creating a new refining scheme in the presence of environmentally safe processes is to ensure the production of environmentally safe fuels and oils.

To study the application of supercritical petroleum extraction to influence its effect on hydrocracking firstly, direct hydrocracking of petroleum was carried out.

Hydrocracking of low-paraffin petroleum mixture was carried out at points 380-425 °C, pressure 3-5 MPa, feedstock volumetric feed rate V – 0,3-1,0 h^{-1}, hydrogen flow 1000 *l/l* feedstock using industrial catalyst Al-Ni-Mo.

Hydrocracking at 380 °C and pressure of 5 MPa with decreasing volume velocity V from 1,0 to 0,3 h^{-1} results in decreasing kinematic viscosity at 50 °C from 7,11 mm^2/s to 5,13 mm^2/s, density from 865 kg/m^3 to 856,1 kg/m^3 and increasing the viscosity index of hydrogenated products from 103 to 121.

At a point of 400 °C and pressures of 3-5 MPa viscosity at 50 °C decreases to 3,28 mm^2/s, density at 20 °C to 845,7 kg/m^3, pour point decreases from minus 10 °C to minus 16 °C. When increasing the process point to 425 °C there is a further decrease in viscosity at 50 °C to 1,82 mm^2/s, density at 20 °C to 826,8 kg/m^3, pour point decreases from minus 16 °C to minus 18 °C. It is established that at points of 400-425 °C the quality of hydrogenizates improves due to changes in the composition of raw materials. At point 425 °C along with

hydrogenation isomerization occurs.

Supercritical purification of petroleu and its heavy residues was carried out at the pilot plant of the Institute at a point of 40-55 °C and pressure of 7,4-8,0 MPa. Unlike petroleum, fuel oil and vacuum residue were dissolved with n-heptane in the ratio of 1 : 1 in order to reduce the viscosity of feedstocks and improve the possibility of precipitation of asphalt-resinous substances.

After deasphalting of petroleum and fuel oil the kinematic viscosity at 50 °C from 7,11-43,22 to 6,33-42,0 mm^2/s, density at 20 °C from 865,9-909,5 kg/m^3 to 859,0-907,4 kg/m^3, coking ability from 1,91-3,51 to 0,88-3,3 % wt. % decrease.

The kinematic viscosity at 100 °C of vacuum residue I and II after deasphalting from 181,11-223,36 mm^2/s decreases to 105,64-116,52 mm^2/s, the density at 20 °C from 947,7-961,6 kg/m^3 to 940,3-954,2 kg/m^3 decreases. The yield of asphaltenes after the process increased from 0,725-1,10 wt % to 1,5-4,5 wt %.

Deasphaltized oil, fuel oil and tar sands from a mixture of low-paraffin oils were subjected to hydrocracking at points of 400-425 °C, pressure of 5-6 MPa, feedstock volume feed rate V – 0,5 h^{-1} , hydrogen flow of 1000 *l/l* feedstock using industrial catalysts Al- Ni- Mo and Al- Co- Mo.

Carrying out hydrocracking of deasphalted petroleum (table 6) in contrast to straight petroleum under the same conditions allows to improve the quality of hydrogenizates (Figure 6). Since the kinematic viscosity at 50 °C decreases from 3,28-1,82 mm^2/s to 2,9-1,17 mm^2/s, density – from 845,7-826,8 kg/m^3 to 821,0-819,0 kg/m^3.

Hydrocracking of deasphaltized fuel oil was carried out on catalyst Al-Ni-Mo, feedstock feed rate V – 0,5 h^{-1}, at point 425 ° C, pressure 5 MPa, hydrogen flow 1000 *l/l* feedstock. The hydrocracking results showed that the kinematic viscosity of fuel oil decreases from 42 mm^2/s to 8,03 mm^2/s, density at 20 ° C from 907,4 kg/m^3 to 884,4 kg/m^3 and other indicators decreased.

The vacuum residue I was obtained in the laboratory after atmospheric-vacuum distillation (above 500 °C) of a mixture of low-paraffin petroleums. As shown in table 6, hydrocracking on Al- Ni- Mo catalyst at 425 ºC of deasphaltized vacuum residue sands

I leads to a decrease in kinematic viscosity at 100 °C from 105,64 mm^2/s to 20,5 mm^2/s, density at 20 °C from 940,3 kg/m^3 to 907,6 kg/m^3.

Table 6

Physicochemical properties of deasphaltized hydrogenated hydrogenates

Name	Al-Ni-Mo				
	Petroleum, P - 5 MPa		Fuel oil, P - 5 MPa	Vacuum residue I, P - 6 MPa	Vacuum residue II, P - 6 MPa
	T - 400 °C	T - 425 °C	T - 425 °C	T - 425 °C	T - 425 °C
Viscosity, mm^2/s, at:					
100 °C	1,15	-	-	-	-
50 °C	2,9	1,17	8,03	20,5	22,3
40 °C	-	-	-	907,6	-
20 °C	-	-	-	-	912,8
Density at 20 °C, kg/m^3	821,0	819,0	884,4	-	-
Refractive index n_D^{20}	1,4653	1,4612	1,4860	1,4990	1,5010
Color in NPA grades	8	8-	8+	dark	dark
Point, °C:					
Flashes	-	-	148	-	-
Pour	-16	-18	+2	+25	+28
Coking capacity, % wt.	0,7	0,6	-	-	-
Total sulfur, % wt.	0,2	0,2	0,23	0,28	0,30
Yield, % wt:					
in the process	96,53	96,53	94,1	93,5	93,5
for petroleum	-	-	66,92	29,08	24,0

The vacuum residue II was obtained under plant conditions and after deasphaltenization was subjected to hydrocracking on Al-Co-Mo catalyst at 425 °C, P – 6 MPa.

Hydrocracking of deasphalted vacuum residue II allows a reduction in kinematic viscosity at 100 °C from 116,52 mm^2/s to 22,3 mm^2/s, density at 20 °C from 954,2 kg/m^3 to 912,8 kg/m^3.

Hydrogenizates were distilled to fuel fractions boiling at d.p.-180 °C and 180-300 °C, oil fractions at 300-400 °C and above 400 °C.

It is revealed that hydrocracking of straight petroleum is more favorable than hydrocracking of its residues, because processing does not require atmospheric-vacuum unit and dilution of feedstock with solvent.

Thus, the general scheme of petroleum refining is simplified (Figure 6).

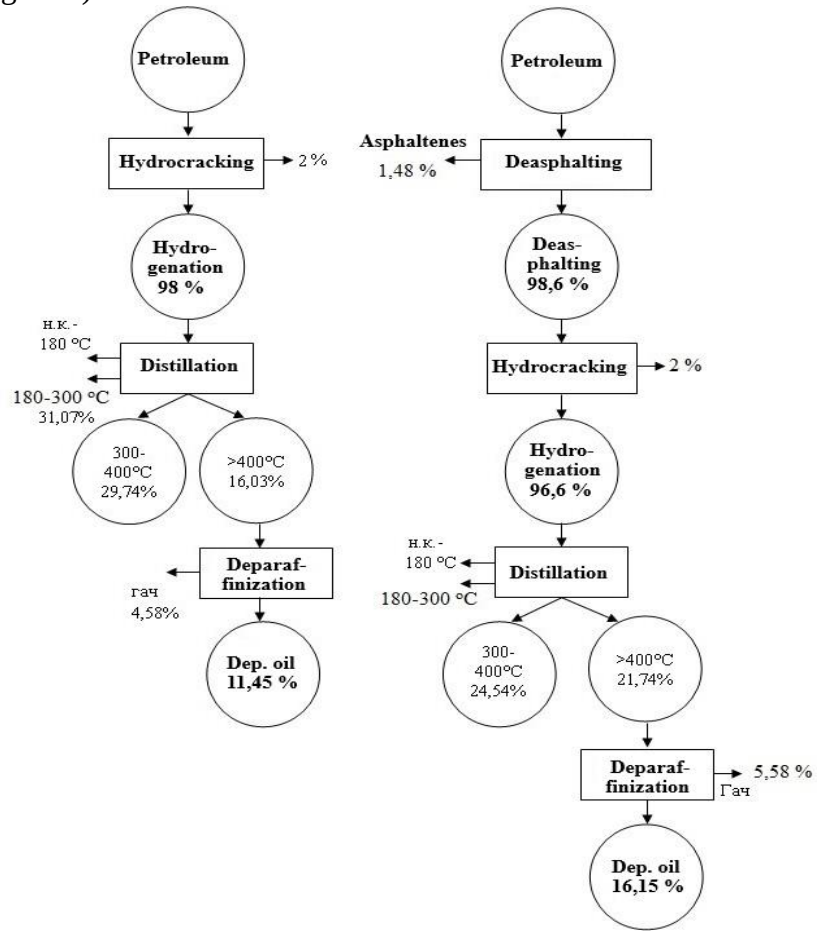

Figure 6. Scheme for obtaining products from oil and after its deasphaltenization

Comparison of the obtained products of petroleum hydrocracking and its after deasphalting showed that from hydrocracking of deasphalting petroleum at 425 °C oil oils have a higher viscosity index (ES 94-205) than oils of hydrocracking of straight petroleum (ES 90-112). This is due to rational use of the catalyst, because deasphalting before hydrocracking leads to dehydration and release of asphalt-

resinous substances, which positively affects the increase in the duration of the catalyst.

Material balance of oil production in the process of petroleum hydrocracking without and with deasphalting:

Raw material – oil (100 %)

Received:		
Gas	2,00	2,00
Gasoline (d.p.-180 °C)	21,16	24,33
Diesel fuel (180-300 °C)	31,07	25,92
Low-viscosity oil (300-400 °C)	29,74	24,54
High-viscosity oil (> 400 °C)	11,45	16,15
Gach	4,58	5,58
Asphaltite	-	1,48
Total (%):	100,00	100,00

Oil fractions boiling at 300-400 °C from petroleum hydrogenysate and after deasphalting meet the requirements of the standard (TU 38101308-97) for industrial oils of type ES-4 and ES-6.

Oil fractions boiling above 400 °C after dewaxing with yield of 71,4-74,3 % wt. per process meet the standards for motor oils M-10 and M-12 according to GOST 17479.1-2015 and base oil AC-9,5 of I and higher category according to TU 38101511-74. Also, the fractions obtained from fuel oil, boiling above 400 °C, meet the requirements for gear oil according to TU 38101529-75 and lightweight vaporizers according to TU 38101361-73.

Evaluation of the quality of fuel fractions boiling within the range of d.p.-180 °C and 180-300 °C from petroleum hydrogenisates, as well as after deasphalting of petroleum and its heavy residues showed that they can be used as a solvent of liquid PF-3 according to TU 38101964-83. These fractions can also be used as components of JF, T-2 jet fuels (GOST 10227-86) and diesel fuels (GOST 305-82). The yield of these fractions is 6-52,24 % wt. per hydrogenizate, 4,02-31,07 % wt. per petroleum.

A new petroleum refining scheme involving supercritical extraction and hydrocracking processes to produce environmentally

safe high-index oils is proposed (Figure 7).

After supercritical extraction, the obtained purified petroleum (II) is subjected to hydrocracking. Hydrocracking of feedstock, preheated in heat exchangers 8 and 9, in a mixture with H_2 -gas is carried out in a multizone reactor 10 with a downward flow of feedstock mixture. Liquid, separated from gas in separators 11 and 12, is heated in the heat exchanger 13 and enters the rectification column 17 for the separation of light gasoline (d.p.-180 ^oC). In the bottom of the column 17 is introduced water vapor VII. The fraction boiling above 180 ^oC is heated in the furnace coils 18 and separated in the vacuum column 19 into fractions (180-300 ^oC), light oil fraction (300-400 ^oC) and heavy oil fraction (above 400 ^oC). In the amine purification unit 24 hydrogen sulfide is removed from the circulating gas. Air-cooled condensers and coolers are widely used at the plant. Between units 8 and 20, water is injected into the hydrocracking product stream to wash off deposits. The obtained fractions are collected in receivers 27.

Technical-economic evaluation of the process of supercritical purification of 3 samples of petroleum mixture using SC-CO_2, showed that comparative technological and economic indicators of the process of dehydration and desalting are lower than in the existing process under production conditions at the operating units of the refinery.

At petroleum purification in the presence of CO_2 the yield of light fractions also increases, and also actually decreases the yield of vacuum residue in addition to increasing the depth of petroleum refining, which also reduces the cost of target products.

Reduction of processing costs by 2320 thousand manat/year, reduces the cost price of 1 ton of target product by 89 gyapik. Economic effect at processing of 6 mln. tons of petroleum can make 2,3 mln. manat.

At reception of 50 thousand tons of residual oil (brightstock) on the offered technology in comparison with existing technology economic effect makes 7138 thousand manat at processing of 89419 tons of vacuum residue.

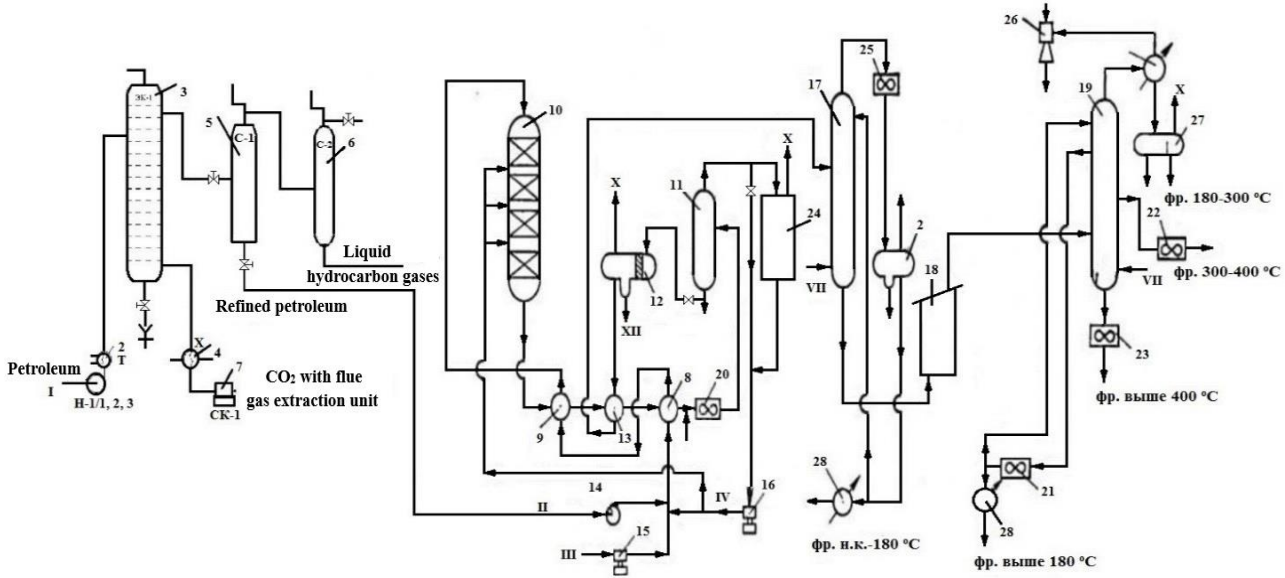

Figure 7. Proposed new scheme (hydrocracking of oil purified by supercritical extraction). 1 – pumps; 2 – petroleum heating heat exchanger; 3 – EC-1 extraction column; 4 – X-1 refrigerator; 5, 6 – separators; 7 – compressor; 8, 9 – heat exchangers for heating purified petroleum; 10 – reactor; 11, 12 – separators; 13 – heat exchanger; 14 – raw material pump; 15 – fresh gas compressor; 16 – compressor of circulating hydrogen-containing gas; 17 – atmospheric column; 18 – tube furnace in fractionation section; 19 – vacuum column; 20-23 – air coolers; 24 – block of circulating gas purification from hydrogen sulfide; 25 – condenser-cooler; 26 – ejector; 27 – receiver; 28 – cooler. I – feedstock – petroleum; II – purified oil; III – fresh hydrogen-containing gas; IV – circulating hydrogen-containing gas; V – fraction n.k.-180 °C; VI – liquid hydrocarbons; VII – water vapor; VIII – water; IX – fraction 180-300 °C; X – gas to flare; XI – hydrogen sulfide; XII – aqueous solution

3. Processing of heavy residues from Azerbaijani petroleums according to the classical scheme in order to produce brightstocks – residual oils

To obtain quality oils with high antioxidant, viscosity-point and other properties such undesirable components as resinous substances, sulfur- and nitrogen-containing compounds, polycyclic aromatic and naphtheno-aromatic hydrocarbons with short side chains, as well as paraffin hydrocarbons should be extracted from oil residues.

Studies have shown that residual petroleum fractions of Azerbaijani petroleum contain 2-3 times more oil fractions than residual fractions of petroleum from other regions. Therefore, Azerbaijani petroleum are in great demand in refining, as they provide an opportunity to obtain more petroleum products.

The technical base of the plant producing residual oil for rolling mills (P-28) from the mixture of Surakhani and Karachukhur petroleum due to limited resources of feedstocks and strict requirements to ecology was liquidated. Taking this into account, researches on expansion of raw material resources and improvement of technology of producing brightstocks from Azerbaijani petroleums were carried out. As a feedstocks were used tar sands of paraffinic oil Sangachal-deniz and mixtures of low-paraffinic petroleums of offshore fields from "Azerneftyag" plant. Concentrate – vacuum residue sands of paraffinic petroleum Sangachal-deniz, characterized by the highest content of residual fraction, were obtained at the pilot plant BHT IPCP, and vacuum residue sands from the mixture of low-paraffinic oils – at the industrial and pilot plants.

Oil for rolling mills P-28 from vacuum residue sands was produced according to the scheme: deasphalting → selective purification → dewaxing → hydrotreating.

Deasphalting of vacuum residue to reduce asphalt-resinous substances was carried out at the BHT with propane at the rate of 500 % wt. per tar at the point in the extraction column: top – 76 ^{o}C, bottom – 50 ^{o}C. Characteristics of vacuum residue and their deasphaltisates are presented in table 7.

Table 7
Characterization of tar sands and their deasphaltisates

Name	Yield on petroleum, %	Density at 20 °C, kg/m³	Viscosity at 100 °C, mm/s²	VU_{100}	Coking capacity, %	Point,° C		Acid but number, mg KOH/g
						flashs	pour	
From a mixture of low-paraffin petroleums								
Azernefteyag Production Association vacuum residue	-	994,2	-	23,54	13,38	320	+42	0,098
The same after deasphalting under industrial conditions	-	926,6	32,62	-	0.92	290	+26	0.057
BHT İNCP vacuum residue	34,69	960,4	90,24	10,80	6,64	290	+35	0,05
Same after de- of asphalting at the BHT İNCP	50,8	937,0	38,81	-	1,27	308	+39	0,49
From Sangachal Deniz paraffinic petroleum								
BHT İNCP vacuum residue	26,82	954,1	87,77	9,34	5,34	298	+48	0,21
Same after de-asphalting								
I	73	915,5	24,04	-	0,92	298	60	-
II	69	917,7	27,83	-	1,09	300	60,8	0,18
III	70,6	919,1	26,78	-	0,93	290	62	0,32

Then deasphaltisates from a mixture of low-paraffin oils were subjected to selective purification with furfural (150, 200, 300 %) on a continuously operating pilot plant BHT at point (°C) in the extraction column: top – 130-135, middle – 115-118, bottom – 95-98.

At purification of deasphaltisate from paraffinic petroleum the point in the extraction column corresponded to: top – 125, middle – 105, bottom – 85 °C (KTR 150-155 °C). Comparison of the quality of raffinates of different purification depths obtained from deasphalticates showed that with increasing amount of furfural the yield decreases, but their quality improves.

Studies have shown that at dewaxing of residual raffinate from low-paraffinic and paraffinic petroleums of different degree of purification with furfurole (200 and 300 %) oil yield was 73-90 % wt. per feedstock.

The general scheme of residual oil (brightstock) production by existing and proposed technologies is shown (Figure 8).

P-28 brightstock oils from Azerbaijani petroleums, unlike West Siberian petroleum, are rich in paraffinonaphthenes by hydrocarbon composition (35,1-72 %), which provides their high performance properties (table 8).

4. Development of technology for obtaining white oils

To obtain white oil the process of dewaxing and selective purification using a single solvent was used, i.e. a combined process. As a feedstock we used raffinates of oil fractions M-4 and I-40A from a mixture of low-paraffin petroleums of offshore fields with viscosity at 50 °C 15,9 and 42,2 mm/s^2.

Raffinates were obtained by purification of distillates with 300 % furfural to the content of aromatic hydrocarbons and resins 7,38 and 8,90 %, respectively. Combined purification of raffinate was carried out by mixed solvent furfural-alcohol.

White oils were obtained from the product of the combined method by two methods: oleum purification according to thetechnology used at the Yaroslavl OR, and two-stage hydrogenation and contact aftertreatment.

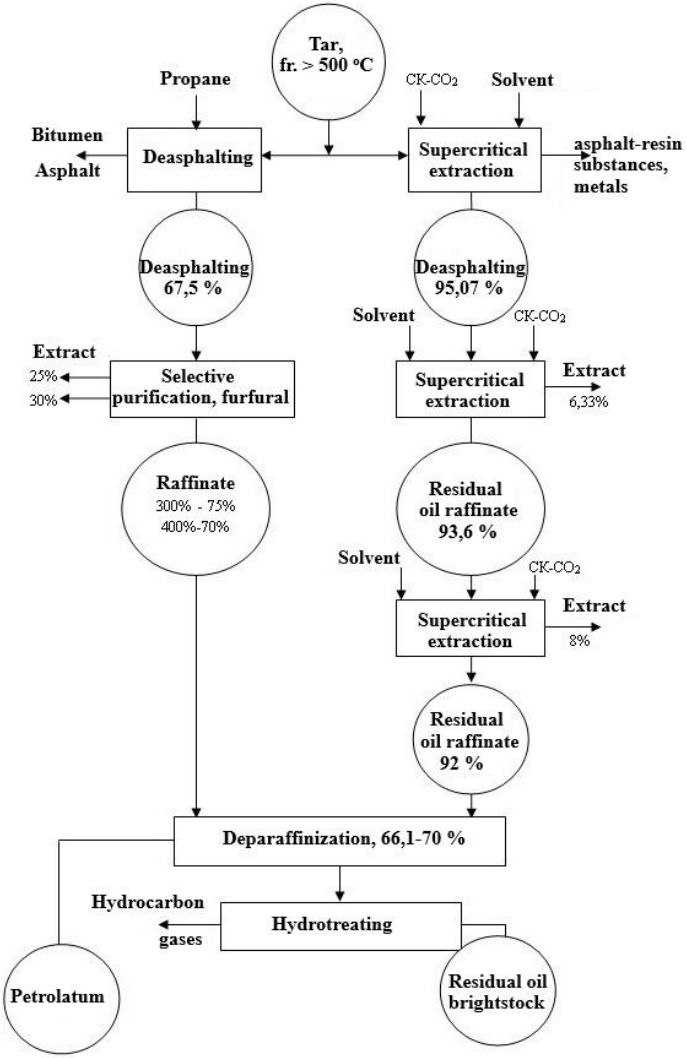

Figure 8. General scheme of residual oil production by known and new technologies

According to the first variant of the combined method raffinate was treated with oleum in two stages with supply of 5 % of oleum to each stage, followed by neutralization of sour oil with alcohol-water solution and contact aftertreatment with gumbrin (40-50 %) at 120 °C.

Table 8
Comparison of suggested brightstocks

Indicators	Brightstocks from the oils					
	low-sulfur				sulfurous	
	Oils offered	low-paraffin petroleum blend	Sangachal-Deniz petroleum	Blend of Surakhan and Karachukhur petroleums	PS-28 GOST 174794-87	Mobil Vacuoline 144 (foreign oil)
Kinematic viscosity at 100°C, mm^2/s	28,9	31,75	30,15	29,63	26-30	28,12
Viscosity index	80	87	85	85	80	95
Density at 20°C, kg/m^3	905,0	907,5	906	901	930	902
Acid number, mg KOH/g	0,02	0,015	0,03	0,02	0,02	0,03
Coking capacity, % wt.	1,0	0,62	0,60	0,81	-	0,61
Sulfur content, % wt.	0,2	0,2	0,25	0,14	1,5	1,37
Hydrocarbon group composition, % wt. %:						
Paraffinonaphthenes	35,1	59	60,2	72,0	33,6	34,9
Aromatic hydrocarbons:						
I lights	21,6	23,8	28,0	5,7	20,1	32,6
II medium	19,1	10,1	9,6	0,8	17,7	26,8
III severe	19,8	4,5	0,2	17,9	20,8	0
Resin	4,4	2,6	2,0	3,6	7,8	5,7

The second variant provides for obtaining white oil from raw materials of combined purification using two-stage hydrogenation and contact after-treatment. Due to the elimination of oleum purification, the consumption of reagents is significantly reduced, hard-to-utilize wastes are eliminated and the oil yield increases by 6-12% compared to the adopted oleum after-treatment.

Studies have shown that inclusion of the process of combined purification in the scheme of white oil production allows to reduce by 16 % the amount of required oleum and to obtain oil with aromatic hydrocarbons content of 0,47-0,95 % wt. %. (table 9).

Table 9

Quality of experimental white oils obtained using combined purification, domestic and foreign oils

Indicators	Oil NMR-12			Medical vaseline oil		
	Experience	ТУ-38101737-78	foreign oil	Experience	GOST 3164-78	foreign oil
Density at 20 °C, kg/m^3	858,5	858,0	867,1	874,9	882,0	856,3
Viscosity at 50°C, mm^2/s	13,5	10,0-13,5	9,91	30,53	28,0-38,5	31,4
Point, °C:						
flash	187	160	155	186	190	180
pour	-42	-40	-50	-16	-5	-8
Color in NPA grades	uncolored	270*	270*	uncolored	270*	270*
Refractive index n_D^{20}	1,4718	1,4720	1,4753	1,4778	-	1,4723
Acid number	0,0058	0,0040	0,0080	-	-	-
Mass fraction of aromatic hydrocarbons by adsorption separation method	0,47	2,00	10,20	0,95	1,70	-
Mass fraction of aromatic hydrocarbons by UV absorption spectra	0,50	0,76	6,00	0,62	0,50	0,45
Sample for the presence of organic impurities	endured	-	couldn't take it	endured	endured	endured

Optimization of two-stage hydrogenation of raffinate of oil fraction of Balakhani heavy petroleum on aluminocobaltmolybdenum catalyst and GR-3 has been carried out. As a result of solving the problem the following optimal mode parameters of hydrogenation process were obtained: for I stage T = 323 °C, P = 5 MPa, Q = 1200 m^3/m^3, W = 0,5 h^{-1}; for II stage T = 350 °C, P = 5 MPa, Q = 1150 m^3/m^3, W = 0,5 h^{-1}.

White oil was obtained by two-stage selective purification of 300 wt % of AC-6 oil furfurol containing up to 81,9 % of naphthene-paraffin hydrocarbons from Sangachali-Deniz petroleum. As a result of further two-stage hydrogenation on catalysts Al-Co-Mo and GR-3, the content of aromatic hydrocarbons in the oil decreased to 4,69 % wt. and to 0,75 % wt. after treatment with aluminosilicate sorbent in

the presence of oleum (3 %). As a result, a white oil meeting the requirements of the standard for perfume oil was obtained.

The possibility of obtaining medical vaseline oil from distillate raffinate of heavy Balakhani petroleum using hydrogenation processes according to three variants has been investigated. Processing of raffinate according to the considered schemes allows to obtain raw materials for production of white oils with the content of aromatic hydrocarbons and resins from 5,57 to 11,7 %. Purification of hydrogenated oils obtained according to the three schemes was carried out according to the technology operating at the Yaroslavl OR, using oleum with 19-20 % of free SO_3: feeding each stage with 5 % of oleum at 45 °C followed by neutralization with alcohol-water solution and aftertreatment with adsorbent (gumbrin or aluminosilicate) at 120 °C with inert gas supply. The obtained white oils meet the requirements of GOST 3164-78 and are not inferior in physical and chemical properties to commercial medical vaseline oil, as well as oils from West Siberian and foreign petroleums (tables 10, 11).

Studies of group chemical composition of petroleums showed that the saturated part of the oil fraction from Balakhani heavy petroleum contains 14,2 % of isoparaffinic, 84,5 % of naphthenic hydrocarbons and 1,3 % of alkylbenzene admixture. Paraffin hydrocarbons of normal structure are absent. The oil fraction of Neftyanıye Kamni petroleum contains 16,35 % of paraffin hydrocarbons. Along with isoparaffin hydrocarbons there are also paraffin hydrocarbons of normal structure. Isostructure paraffinic hydrocarbons predominate among paraffinic hydrocarbons. Naphthenic hydrocarbons make up 82,45 %, alkylbenzenes impurities – 1,2 % of the saturated part of the oil fraction.

In the oil fraction from paraffinic petroleum Sangachaly-deniz the amount of paraffin and naphthenic hydrocarbons is close.

After dewaxing of the oil fraction naphthenic hydrocarbons also prevail – 78,75 %. Paraffin hydrocarbons compared to oil fractions from low-paraffin oils are more, their amount is 19,77 %. The admixture of alkylbenzenes is 1,48 %.

Table 10

Properties of medical vaseline oil obtained by three schemes

Indicators	Medical vaseline oil						Requirements GOST 3164-78
	derived from the scheme			commodity	from west-siberian oils	Foreign	
	first	second	third				
Density at 20 °C, kg/m^3	884,2	884,5	882,6	882,8	860,0	862-893	870-890
Viscosity at 50, mm^2/s	31,99	31,92	28,76	30,40	29,5	47-545**	28-38,5
Point, °C:							
flash	185	182	185	192	195	176-262	at least 185
pour	-29	-31	-25	-10	-10	-	no higher than -8
Color, unit. KNS-1	colorless*			4	-	-	no more than 6
Zonality	absent			0,003	0,002	-	no more than 0,005
Content, %:							
sulfur compounds	absent			0,03	0,04	-	absent
reducing agents	absent					-	absent
light boiling fractions up to 360 °C	absent					-	absent
Sample for the presence of organic impurities	Withstands						
Refractive index n_D^{20}	1,4818	1,4800	1,4800	1,4817	1,4730	-	-
Yield, %:							
per product	70	78,5	83,5	-	-	-	-
per distillate	35,25	36,32	39,3	-	-	-	-

Table 11

Aromatic hydrocarbon content

Content (%) of aromatic hydrocarbons: by UV-visible absorption spectra at wavelength, nm	Medical Vaseline oil			
	third scheme	commodity	from West Siberian oils	Foreign
275	0,35	0,42	0,43	0,31-0,69
295	0,10	0,08	0,07	0,09-0,24
300	0,05	0,004	0,003	0,06-0,15

Since (according to mass spectrometric analysis data) the oil fractions of the studied oils are rich in high-ringed naphthenic hydrocarbons – carriers of therapeutic properties, it is possible to predict the possibility of using them as a raw material for obtaining white oil of medical vaseline type. It should be noted that the largest amount of tetra- and pentacyclic naphthenes is contained in the oil fraction of Balakhani heavy petroleum, which was subsequently selected as the main raw material for white oil production.

It has been established that naphthenic hydrocarbons of a number of petroleums, including those from offshore fields, are also characterized by the fact that they contain structures related to steranes and triterpans – biological tags that play an important role in the processes occurring in the body and have therapeutic properties.

Studies of the structure-group composition showed that in the saturated part of the oil fraction from Balakhanskaya heavy petroleum the content of naphthenic hydrocarbons with the number of rings more than three is 26,7 (table 12).

Oil fraction 300-450 °C obtained from naphthalan petroleum was also used as a raw material for white oil production. This fraction contains 51,5 % of naphtheno-paraffin hydrocarbons determined by chromatographic separation on silica gel according to GOST 11244-2018. Concentrates of naphthene-paraffin hydrocarbons from the studied fraction were isolated by several methods: the first two samples - by oleum purification of the oil fraction and its raffinate of furfural purification, respectively, and the next two – by stepwise hydrogenation of the oil fraction and its raffinate.

Table 12

Structure-group composition of white oils

Hydrocarbons	Saturated part of the oil fraction	White oleum refined oil		
		distillate	raffinate (400 % furfural)	Hydrogenisate
Paraffin	7,10	4,79	6,30	4,96
Naphthenic:				
monocyclic	6,4	4,43	5,10	4,18
bicyclic	9,3	7,09	6,69	4,41
tricyclics	9,5	6,24	5,19	5,50
tetracyclic	10,2	5,07	3,96	5,10
pentacyclic	5,6	2,15	1,65	2,23
hexacyclic	1,4	0,89	1,05	1,47
Alkylbenzenes	0,6	0,06	0,09	0,18

In all samples, except for sample 3, the content of aromatic hydrocarbons (according to UV-spectra) was up to 1 %.

White oils for use in other areas of national economy can be obtained from any petroleum using various refining technologies.

5. Hydrocracking of deasphaltisates under pressure of 5-10 MPa in order to obtain multigrade oils

Azerbaijani petroleums are unique in that they are low-sulfur and rich in oil fractions, especially residual oil. Oils from these petroleums are characterized by high stability, but have low viscosity indices. Improving the quality of base oils is achieved by various methods. As a result of hydrogenation treatment (hydrocracking) the chemical hydrocarbon composition of oils changes. Increasing the share of isoparaffin hydrocarbons in base oils leads to improvement of viscosity-point properties.

With the use of hydrocracking process under pressure 5-10 MPa, point 400-450 °C the technology of obtaining a wide range of oils, including high-index oils (VI-4, VI-6 and M-4_3/$6B_1$), on the basis of heavy residues from Azerbaijani petroleums, which have large resources and not found qualified application has been developed.

For this purpose, deasphalting with liquid propane (500 %) from tar sands of a mixture of low-paraffin petroleum and paraffin petroleum Sangachal-deniz was carried out for hydrocracking process at BHT IPCP. The deasphaltenesate from the mixture of low-paraffin oils was subjected to hydrocracking under pressure of 5-10 MPa and point

range of 400-450 ºC at feedstock feed rate of 0,5 h^{-1} on Al-Co-Mo catalyst (tables 13 and 14). The study of the qualities of hydrogenated oils obtained at different points and pressures from a mixture of low-paraffin petroleums showed that increasing the process pressure at the same point leads to an improvement of viscosity-point properties and refractive index of oil fractions, a decrease in density and pour point. The viscosity index of oil fractions increases from 94 to 119 units.

Table 13

Physicochemical parameters of residue and deasphaltizate of petroleum blends

Name	Residue above 500 °C	Deasphalticate
Yield, % wt per vacuum residue	-	45,0
Density at 20 °C, kg/m^3	994,2	926,6
Viscosity:		
relative at 100 °C	23,5	-
kinematic at 100 °C, mm^2/s	-	32,62
Acid number, mg KOH/g	0,10	0,06
Coking capacity, %	6,68	0,92
Point:		
Flashes	320	290
Pour	+42	+26
Refractive index n_D^{20}	-	1,5050
Color in NPA grades	-	8

In order to evaluate the quality of oils obtained by hydrocracking at different points and pressures, oil fractions boiling above 300 °C from hydrogenated oils of a mixture of low-paraffin petroleums were isolated and dewaxed (table 14).

Thus, dewaxing of oil fractions of hydrogenizates obtained at different points and pressures can produce oils of different viscosity levels and purposes, which are not inferior in quality to oils of selective purification from the specified mixture of petroleums.

Having established the possibility of obtaining oils and liquids from deasphaltizate hydrocracking products, the insignificant difference in the qualities of hydrocracking products carried out under pressure of 5-10 MPa and taking into account the dependence of process efficiency on pressure, further studies on hydrocracking of deasphaltized residue were carried out under pressure of 5 MPa.

Table 14

Characteristics of base oils obtained from hydrogenated oils boiling above 300 °C and after their dewaxing

Hydro-cracking point	Pressure, MPa	Name	Density at 20 °C, kg/m³	Viscosity, mm²/s, at		Index viscosity	Point, °C:		Refractive index n_D^{20}	Yield, %:	
				100 °C	50 °C		flashes	pour		process	diasphalticate
400	10	hydrogenisate	899,6	17,34	114,49	94	205	+20	1,4968	90,4	-
		same after dewaxing	907,7	18,28	137,0	79,5	213	-20	1,4975	84,7	78,7
	5	hydrogenisate	909,0	18,70	134,64	86,5	208	+22	1,5010	94,8	-
		same after dewaxing	917,0	19,53	160,86	70,0	208	-20	1,5030	85	75,3
425	10	hydrogenisate	892,8	9,13	46,25	98	172	+20	1,4938	86,5	-
		same after dewaxing	899,1	9,08	48,1	89,5	183	-18	1,4940	85	73,5
	5	hydrogenisate	898,0	7,91	36,13	106,5	155	+20	1,4970	88,3	-
		same after dewaxing	906,0	8,01	38,0	98	157	-20	1,5045	83,0	71,8
450	10	hydrogenisate	902,8	4,49	15,7	119,0	162	+18	1,4990	65,0	-
		same after dewaxing	903,6	4,59	16,64	108	163	-16	1,4998	83,5	53,2
	5	hydrogenisate	900,3	3,42	10,97	95,6	160	+14	1,4895	60,1	-
		same after dewaxing	901,1	3,47	11,91	68,0	170	-20	1,5050	85,0	45,1

Since the most acceptable pressure for hydrogenation processing of deasphaltenizate of petroleum mixtures is 5 MPa, the developed technology of obtaining high-index oils from deasphaltenizate hydrocracking products was based on the following scheme: atmospheric-vacuum distillation of hydrogenizate - dewaxing of oil fractions of hydrogenizate.

Deasphaltisate hydrogenated fractions obtained at 400, 425 and 450 °C were distilled to 50 °C fractions up to 500 °C and above 500 °C after distillation of fuel fractions boiling at d.p.-240 °C and 240-300 °C.

Also, deasphaltisate hydrogenates obtained from Sangachaly-deniz at 450 °C and P = 5 MPa, after distillation of fuel fractions boiling at d.p.-240 °C and 240-300 °C were distilled to 50 °C fractions up to 500 °C and above 500 °C (table 15).

Two variants of obtaining fuels and oils from hydrogenizates were developed. The first variant provided for obtaining oil fractions from hydrogenizates boiling at 300-400 °C and > 400 °C, the second variant - at 300-500 °C and > 500 °C, including atmospheric-vacuum distillation of hydrogenizate → daparaffinization of oil fractions of hydrogenizate.

In conditions of raw materials processing, containing mainly components with low viscosity index, the introduction of hydrocracking allows to obtain high-index low-viscosity (fr. 300-450 °C) and medium-viscosity (fr. 450-500 °C) base oils. Fractions boiling out within 300-450 °C meet the requirements of TU 38101308-97 standard for high-index industrial oils VI-4 and VI-6. Oils VI-4 and VI-6 can be used as base oils for production of alloyed oils of IOA series. The base oil obtained from hydrogenated fraction of low-paraffin petroleum mixture with boiling point 300-400 °C after contact refining and addition of depressant ASRI 0,3-0,5 % wt. and additive composition (0,5 % ionol + 0,15 % B-15/41 + 1,2 % DF-11 + 0,003 % PMS-200A) corresponds to the requirements for industrial oil of IOA series according to TU 381011191-97. The oil yield is 18,8 % wt. %, counting on deasphaltizate (table 16).

Table 15
Characterization of 50 °C fractions obtained from hydrogenysate deasphaltisate at 450 °C

Boiling point limits, °C	Yield, %	Density at 20 °C, kg/m^3	Kinematic viscosity, mm^2/s, at				VI	Point, °C		Refractive index n_D^{20}	Color in NPA grades
			20 °C	40 °C	50 °C	100 °C		flash	pour		
b.s.-70-240	19,10	793,6	1,43	-	-	-	-	95	-54	1,4482	1
240-300	12,2	846,3	3,16	-	-	-	-	110	-29	1,4770	1 ½
300-350	6,85	855,0	5,54	3,93	3,10	1,38	254	160	-15	1,4824	1 ½+
350-400	9,55	864,0	8,78	4,91	3,92	1,72	193	170	0	1,4896	2-
400-450	7,65	880,0	-	10,51	7,87	2,72	102	187	+16	1,4976	2 ½
450-500	10,9	900,2	-	19,07	13,37	4,08	121	202	+27	1,5112	3-
> 500	33,85	924,5	-	-	-	8,8	-	270	+33	-	8+

Table 16

Physicochemical parameters of 300-400 °C fraction obtained from hydrogenizate

Indicators	Fr. 300-400 °C	After cont. before cleaning (type VI-4)	pilot oil + additive compositions*)	TU 381011191-97 at IOA-4 (I-L-S-5)
Density at 20 °C, kg/m^3	870,0	869,0	869,6	no more 880
Kinematic viscosity, mm^2/s at:				
100 °C	1,85	1,88	-	-
40 °C	5,72	5,81	-	-
Index viscosity	-	135		
Point, °C:				
Pour				
Depressorless	-8	-8	-17	no higher -15
with 0,3 % depressant ASRI		-17		
Flashes	152	152	152	at least 110
Refractive index n_D^{20}	1,4882	1,4880	-	-
Color in NPA grades	1 ½	1 ½ -	1½	1½
Acid number, mg KOH/g				
before oxidation			0,27	no more 1,0
after oxidation			0,53 (increase of 0,26)	increase of no more than 0,5
Surface tension	-	-	20,54	< 28
Yield, % per deasphaltizate	19,2	96,5	18,8	

After dewaxing with urea of the oil fraction from a mixture of low-paraffin petroleums boiling at 300-400 °C, transformer oil with pour point -56 °C, meeting the requirements of TU 38101281-80 was obtained. The oil yield is 8,6 % per deasphaltizate (table 17).

The fraction of hydrogenysate boiling within 450-500 °C from paraffinic petroleum, having high viscosity index (VI – 121) can be used as a low-viscosity base for production of M-4 motor oils (table 15).

In comparison with oils from low-paraffin petroleums, the similar

fraction has a low viscosity index (VI – 77,5).

Table 17

Characteristics of transformer oil

Indicators	Fraction 300-400°C	After urea purification	TU 38101281-80
Density at 20 °C, kg/m^3	873,1	890,3	-
Kinematic viscosity, mm^2/s, at:			
100 °C	2,09	2,24	-
50 °C	5,3	6,42	6,5-9,0
40 °C	6,93	8,04	-
20 °C	-	17,04	no more than 30
-30 °C	-	683,2	no more than 1150
Viscosity index	104,6		
Point, °C:			
pour	-2	-56	no higher than -50
flashes	152	156	not lower than 135 in closed crucible
Refractive index n_D^{20}	1,4912	1,5022	-
Yield, % per deasphaltizate	12,8	8,6	-
Color in NPA grades	2½	2½+	-

Oil fractions boiling within 300-500 °C and yielding up to 43 %, counting on deasphalted vacuum residue, can be used as a basis for obtaining thickened motor oil of grade M-4$_3$/6B$_1$. After urea dewaxing and contact refining and introduction of 5 % polymethacrylate (PMA "D") and composition of additives ISC group B$_1$ oil, providing a high level of viscosity-point properties and meeting the requirements of OCT 3801370-84 for oil M-4$_3$/6B$_1$ (table 18) was obtained.

The advantage of the hydrocracking process is that from deasphatltisate of heavy petroleum residue under relatively mild conditions of 5 MPa it is possible to obtain the base of all-season oil with a yield of 33,6 % wt., counting on deasphatltisate.

Studies have shown that fractions 300-350 and 350-400 °C or their mixtures obtained from paraffinic petroleum Sangachaly-deniz in the process of hydrocracking at 450 °C can be used as a basis for technological viscosity PF-8 according to TU 38101883-83.

Table 18
Characterization of thickened oil base -$M4_3$ /$6B_1$

Indicators	fr. 300-500 °C	after carb. dep. and cont. before treatment	after carb. dep. and cont. before treatment + 5 % PMA "D"	practice oil + additive composition*)	GOST 3801370-84 for oil -$M4_3$ /$6B_1$
Density at 20 °C, kg/m^3	888,0	902,0	902,3	901,0	-
Viscosity, mm^2/s, at:					
100 °C	3,53	3,71	5,50	6,50	
40 °C	15,71	19,13	27,70	37,0	
-18 °C	-		1738	2398	
-30 °C	-		8481	10121	
Viscosity index	110	66	138	128	125
Point, °C:					
flashes	165	167	168	168	165
Pour	+14	-16	-50	-50	-42
Yield, % per process for dewaxing	42,53	79			
to deasphaltizate	41,68	-	33,6	-	
Corrosion on lead plates, g/m^3, not more				0,45	5,0
Stability by induction period of precipitation (IPP), hr				15	Not standardized, optional.

*) 7 % PMS «A» + 0,5 % ASK + 2,5 % DF-11 + 2,25 % A-9250 + 0,003 % PMS-200A

Fractions d.p.-300 ºC from a mixture of low paraffinic petroleums, d.p.-350 ºC from paraffinic petroleums are recommended to be used as raw materials for obtaining instrument liquid MZ-52 according to GOST 21 748-76 with the purpose of application in spiral potentiometers.

Characterization of products obtained from hydrogenysate boiling above 400 °C shows that they produce viscous and high-viscosity industrial oils of general purpose (I-40 A, etc.) such as cylinder 24, lightweight vaporizers. When increasing the boiling of hydrogenated residues up to 500 °C, it is possible to obtain industrial oil type cylinder 38. The residue boiling above 500 ºC was investigated to obtain bitumen BN 60/90 or BND 90-130.

The study of hydrogenisates obtained by hydrocracking of deasphaltenesates of heavy residue of a mixture of low-paraffin and paraffin peütroleums Sangachali-Deniz on aluminocobalt-molybdenum catalyst has shown the presence of a significant amount of medium-boiling fractions with a high content of isostructures, which allows us to consider them as a possible raw material source for obtaining low-viscosity low-fatigue bases of high-index industrial, transformer and thickened motor oils.

The possibilities of using oil fractions (320-560 ºC), D-11 distillate, mixture of Baku low-paraffin petroleums as raw materials for base oils production, including high-index components of fuels and liquids have been studied.

D-11 distillate from "Azerneftyag" BNZ was hydrocracked at continuous-operating pilot plant Shuikin BHT, on industrial catalyst QKD-205 at point 420 °C, pressure 4-5 MPa, feedstock feed rate 0,5-1,0 h^{-1} and hydrogen flow 1000 *l/l* feedstock.

It is determined that increasing the process pressure leads to improvement in the color, density and other parameters of the hydrogenizate. The color of hydrogenizates improves from 8 to 5 grades by NPA. Decreasing the volumetric rate of the process from 1 to 0,5 h^{-1} at the same point (420 °C) leads to intensive destruction of raw materials, viscosity, flash point, density and other indicators of hydrogenizates sharply decreases (table 19).

Table 19

Qualities of distillate D-11 from a mixture of low-paraffin petroleums and its hydrogenates obtained at 420 °C, different pressures and volume rates

Name	Pressure, MPa	Volumetric velocity, h^{-1}	Density at 20 °C, kg/m^3	Kinematic viscosity, mm^2/s, at:			Viscosity index VI	Point, °C		Color in NPA grades	Refractive index n_D^{20}
				100 °C	50 °C	40 °C		flashes	pour		
Distillate D-11	-	-	916,7	11,74	75,3	-	72,0	208	-8	8	1,5072
Hydrogenisate	4	1,0	909,3	8,47	47,0	77,58	74,0	178	-12	6	1,5050
Hydrogenisate	4	0,5	904,2	5,02	20,62	30,9	82,0	104	-17	6	1,4998
Hydrogenisate	5	0,5	902,1	6,26	25,73	39,58	110,0	104	-12	5	1,5010

Fractions extracted from hydrogenated distillate of distillate D-11 (P = 5 MPa, V = 0,5 h^{-1}), boiling at 300-350 ºC and 300-400 ºC are low-viscosity oils with high viscosity index (100) and meet the requirements of standard TU -3810130878 for high-index industrial oils of type VI-4 and VI-6.

These oil fractions do not need dewaxing and, as a result, the cost of production of such oils can be halved. They can be used for production of alloyed oils of IQP series.

In order to obtain the basis of high-index all-season oil of M-4 type, hydrogenated industrial distillate D-11 obtained at 420 °C, feedstock feed rate 0,5 h^{-1} and hydrogen feed rate 1000 *l/l* of feedstock, fuel (up to 320 °C) and oil fractions boiling at 320-400 °C are separated, which are thickened with 2,48-4 % viscosity (T-26/70) additive (PMA with olefin copolymer). In this case a high level of viscosity-point properties of thickened oils is provided, which meet the requirements of OST 3801370-84 for M-4_3/$6B_1$ oil, OST 3801370-84 for M-6_3/10B oil (table 20).

Table 20

Characterization of the base of thickened motor oils

Indicators	Fraction 320-400 °C		OST 3801370-84 for M-4_3/$6B_1$ oil	OST 3801370-84 for M-6_3/10B oil
	+2,48 % T-2-670	+4 % T-2-670		
Density at 20 °C, kg/m^3	906,3	907,5	-	890,0
Kinematic viscosity, mm^2/s, at:				
100 °C	6,24	9,5	5,5-6,5	9,5-10,5
50 °C	23,81	32,28	-	-
40 °C	31,86	47,73	-	-
-18 °C	2091	7809	1100-2600	≤ 9000
-30 °C	10392	-	≤ 11000	
Viscosity index, not less	133	145	125	115
Point, °C				
flashes	173	183	at least 165	at least 190
pour	-42	-37	no higher than -42	no higher than -40/-30
Color in NPA grades	4-	4	-	-
Refractive index n_D^{20}	1,5041	1,5041	-	-
Yield, % per process	18,83	18,83	-	-

The advantage of the hydrocracking process is that from D-11

distillate under relatively mild conditions it is possible to obtain the base of all-season oil with a yield of 18,83 % wt. %, counting on distillate and compounding of oil fractions it is possible to obtain various base low-fatigue oils.

Summary material balance of the process of obtaining fuels, oils and liquids from industrial distillate D-11 by hydrocracking under optimal conditions (T – 420 °C, P – 5 MPa, V – 0,5 h^{-1}, H_2 – 1000 *l/l* of feedstock):

Taken, % wt:		
Distillate	100	100
Received, % wt:	I mode	II mode
fraction up to 300 °C	5,8	-
fraction up to 320 °C	-	6,97
including:		
D.p.-180 °C (PF-3 or fuel component T-2)	1,4	1,40
180-300 °C (diesel fuel component "Z")	4,4	-
180-320 °C (diesel fuel component "Z")	-	5,57
Lubricating oil fraction		
including:		
300-400 °C (industrial VI-6)	20,0	-
320-400 °C (base of M-4 multigrade engine oil)	-	18,83
> 400 °C (cylinder light 11)	74,2	74,20
Total	100,0	100,0

Thus, in the process of hydrocracking of distillate D-11 and deasphaltized vacuum residue at points of 400-450 °C and pressure of 5 MPa hydrogenated fractions and fractions separated from them undergo certain changes in physical and chemical properties and hydrocarbon composition. Polycyclic naphthenic and aromatic hydrocarbons undergo the greatest transformations, as a result of which the fractions are enriched with mono- and bicyclic naphthenic hydrocarbons, as well as light aromatic hydrocarbons, which has a positive effect on their properties and application as oil bases.

In order to study the chemistry of transformation of resinous substances of deasphaltisate and its hydrogenisate, a number of

methods of physicochemical analysis were used – elemental analysis, PMR spectroscopy, etc. The obtained results were used to calculate the structure-group parameters of the average molecules of the investigated products. The elemental composition of substances was determined using a Perkin-Elmer-240 analyzer. Molecular masses of hydrocarbons were measured by cryoscopy in naphthalene at the concentration of the analyzed substance 0,25 % (wt.). PMR spectra were recorded on a BS 487 «Tesla» instrument at 80 MHz (Figure 9), hexamethyldisiloxane was taken as an internal standard.

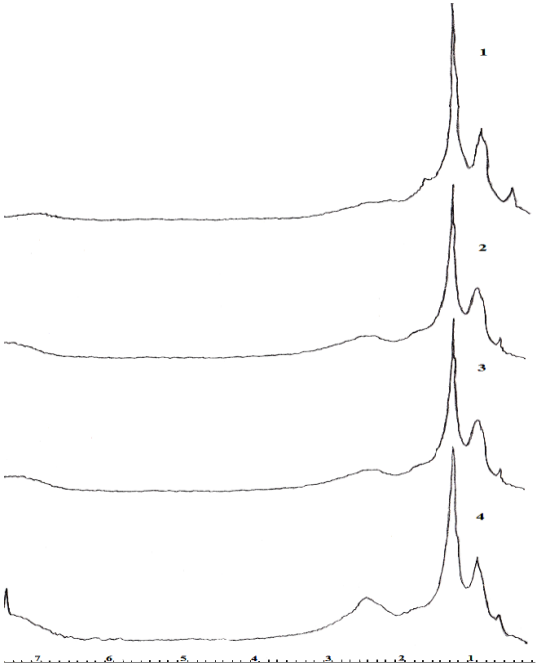

Figure 9. PMR spectra of resins isolated from deasphaltisate (1) and hydrogenisates obtained at hydrocracking points of 400 (2), 425 (3) and 450 °C (4)

Table 21 shows the molecular weights, elemental composition, atomic ratio (H/C), empirical formula, values (proton-deficiency) of the resins of deasphaltisate and its hydrogenates (> 400 °C), the average values of molecular weights are relatively small and vary within narrow limits of 420-503 a.u.m. in hydrogenates.

Table 21
Physico-chemical characteristics of resins from deasphaltisate and it′s hydrogenates boiling > 400 °C

Resins isolated from	Molecular weight	Elemental composition, % wt.					Atomic ratio H/C	Empirical formula $C_nH_{n-z}N_pS_qO_z$	Z
		C	H	N	S	O			
Deasphaltisate	635	89,98	8,04	0,14	0,50	1,34	1,07	$C_{47,6}H_{50,5}N_{0,06}S_{0,1}O_{0,53}$	44,7
Hydrogenates:									
400 °C	503	90,57	8,20	0,22	0,38	0,63	1,08	$C_{37,9}H_{40,8}N_{0/0,8}S_{0,06}O_{0,20}$	35,0
425 °C	456	90,81	8,50	0,17	0,29	0,23	1,12	$C_{34,5}H_{38,4}N_{0,06}S_{0,04}O_{0,07}$	30,6
450 °C	420	90,99	7,99	0,37	0,30	0,35	1,05	$C_{31,8}H_{33,2}N_{0,11}S_{0,04}O_{0,09}$	30,4

The average molecules of resins contain 32-48 atoms of C, 34-51 atoms of H, less than one atom of N, S, O. The value of Z (degree of proton deficiency) varies in the range of 30-35.

The concentration of paramagnetic centers in resins is 1,24-2,70·10^{18} kpc and depends largely on the value of the molecular weight of resins, the degree of aromaticity, the method of extraction, as well as on the content of heteroatomic compounds, especially oxygen-containing ones. The lower the atomic H/C ratio, the higher the aromaticity and the higher the concentration of paramagnetic centers. As shown in Table 21, aromaticity is lower in the resins obtained from deasphaltisate hydrogenated at 425 °C.

As the process point increases from 425 °C to 450 °C during hydrocracking of deasphaltisate, the atomic H/C ratio decreases from 1,12 to 1,05, i.e. it leads to aromatization of naphthenic rings, as well as detachment of the latter from the resin molecule.

The decrease in molecular weight occurs as a result of alkyl radicals detachment. The content of nitrogen from heteroatoms in resin molecules increases with the point of the hydrocracking process from 0,14 to 0,37 %. The sulfur content of the deasphaltizate is 0,5 %. The hydrogenated resins are characterized by lower sulfur content (from 0,5 to 0,3 %) apparently due to lower stability of elutriated compounds containing SO-, SO_2 -groups in the composition of the resins. Every fourth-fifth "average" molecule of resins obtained at 450 °C contains a sulfur atom.

At this point, low molecular weight components (420 a.u.m.) are characterized by increased nitrogen content, decreased oxygen 0,35 % and sulfur 0,3 %, and minimal proton-deficiency Z (30,4).

The degree of proton deficiency decreases in hydrogenated resins with increasing hydrocracking point and in comparison, with deasphaltisate. The decrease of this index indicates a decrease in the proportion of condensed aromatic structures. At the same time polycyclic structures are destroyed with formation of mono- and bicyclic hydrocarbons and conversion of naphthenes into aromatic hydrocarbons. This is confirmed by the data of Table 4,10, where the number of protons of aromatic structures (H_a) increases in hydrogenated hydrogenates compared to deasphaltisate, especially

with increasing hydrocracking point. Hydrogen unsaturation (H/C ratio) changes insignificantly.

At the process point of 450 °C hydrogenated resins contain more unsubstituted protons bound to aromatic carbon atoms (18,1 vs. 4,3 %), as well as protons belonging to groups in α-positions to aromatic nuclei (27,5 vs. 14,5 %) than deasphaltenized resins. In addition, they are characterized by a lower proportion of hydrogen atoms in the remaining saturated fragments of molecules more distant from the aromatic nucleus. This confirms the higher aromaticity of hydrogenysate resins obtained at 450 °C, which is also clearly seen in Figure 9 (spectrum 4). Aromatic compounds are registered in the region of the spectrum 6,5-8,0 m.d.

Average structural parameters of deasphaltizate resins, hydrogenated resins and aromatic blocks contained in them were calculated. The number of carbon atoms in aromatic structures increases, in naphthenic and paraffin chains - decreases. At the same time, the number of carbon atoms in the substituted groups located in the β- and γ-position with respect to the aromatic ring decreases, which indicates a decrease in the side chain length and its branching.

Deasphaltizate resin molecules contain 17-18 rings, of which 2-aromatic and 16-saTUrated. With increasing of the hydrocracking process point in hydrogenated resins the content of rings decreases to 8,22, of which 3,36 - aromatic, 4,86 - saturated. According to calculated data, the molecules of the studied resins contain on average one (m_a = 1,29-1,68) or two structural blocks, in each of which one or two aromatic rings (K_a^* = 1,06-2,18), including heterocycles, are condensed.

With increasing point the amount of saturated compounds $K_{нас}^*$ decreases from 12,34 in deasphaltisate to 3,1 % in hydrogenisate obtained at hydrocracking point of 450 °C, as well as the number of C atoms in paraffin fragments. The degree of aromaticity (C_a) increases from 20,0 to 49,1 %.

Thus, the structural characteristics and chemistry of transformation of resinous substances of deasphaltizate in the process of hydrocracking in the point range of 400-450 °C have been studied by

PMR spectroscopy with the use of elemental analysis and molecular weight data.

Hydrocracking of deasphaltisate of heavy residue of oil blend provides its residual processing: gachy and petrolatum obtained during dewaxing can be used for production of paraffin and ceresins. Studies of paraffin composition were also carried out. For this purpose oil fractions 300-350 °C, 300-400 °C, obtained at the optimal mode of 425 °C hydrocracking, were investigated on a gas chromatographic apparatus.

To study the isocracking of residual oil fraction from a mixture of low-paraffin petroleums, industrial deasphalticate obtained from the concentrate of a mixture of low-paraffin petroleums from offshore fields, boiling above 500 °C, was used.

Hydrocracking of deasphaltisate was carried out on a continuous pilot plant of the BHT IPCP under pressure of 5 MPa and point of 400 °C, at a feedstock feed rate of 0,5 h^{-1} in a hydrogen stream of 1000 *l/l* feedstock using an aluminocobalt-molybdenum catalyst. The fraction boiling above 400 °C was extracted from the deasphaltisate hydrogenated fraction and subjected to hydrogenation (II stage) using industrial catalyst SQK-1 at the Hungarian plant at point 420 °C, pressure 5 MPa, volumetric rate 0,5 h^{-1} and hydrogen supply of 1000 *l/l* feedstock. The oil fraction of hydrogenizate boiling above 400 °C was hydrogenated at the III stage at point 400 °C, pressure 5 MPa, volumetric rate 0,8 h^{-1} and hydrogen supply 1000 *l/l* feedstock on the double-layer catalyst QM-85 and KDM-2. It was found that along with hydrogenation reactions hydroisomerization reactions take place, cyclicity decreases, an increase in the proportion of carbon atoms in paraffin chains is observed, which leads to a decrease in oil viscosity from 32,62 to 16,06 mm^2/s at 100 °C and an increase in viscosity index to 84 units. At the same time solidification point decreases from +26 °C to 0 °C. When adding 0,5 % of Viscoplex 5309 depressant to hydrogenizates, the solidification point is reduced from 0 to minus 12 °C. The yield of this oil is 73,8 % perdeasphaltizate.

Increasing the isocracking point from 400 °C to 420 °C sharply affects pour point, viscosity, VI and other parameters.

To obtain oils with very low pour point and wax, catalytic

dewaxing is used in combination with selective dewaxing and dewaxing with selective solvents. In this process it was possible to obtain API group I and II base oils.

Also, one of the ways to improve the quality of base oils is compounding them with isoparaffin hydrocarbons or synthetic oils.

CONCLUSIONS

1. Methods of desalting and dehydration, as well as deasphaltenization and demetallization of petroleums and their heavy residues using supercritical extraction process were developed. Petroleum blends – Neft Dashlary, Shirvan and Surakhany, low-paraffin oil blends from Azeri field, VII horizon of Bulla-deniz and well 55 of Absheron, as well as heavy residues (fuel oil and vacuum residue) from low-paraffin petroleum blends were used for the research. The conditions of the regime for purification of oil samples from water, salts, mechanical impurities, asphaltenes were revealed. The process was carried out in the presence of CO_2 at point 35-40 °C and pressure 7,5-7,8 MPa. Energy consumption of this process is much lower than in the existing process in production conditions.
2. Supercritical extraction of oil and its heavy residues (fuel oil, vacuum residue) was carried out using SC-CO_2 and co-solvents (n-heptane, alcohol, ketone, ionic liquids (IL), aromatic hydrocarbons).

   Supercritical purification of vacuum residue and its deasphaltisate in the presence of CO_2 or two-phase solvent (SK-CO_2 + solvent) leads to production of residual oils according to the scheme: vacuum residue $\xrightarrow{CK-CO_2}$ deasphaltization $\xrightarrow{CK-CO_2}$ purification in 1 or 2 steps → dewaxing→ hydrogenation.

   The obtained oils meet the requirements of GOST 6411-76 for cylinder heavy 52, GOST 6480-78 for P-28 and TU 38101312-78 for oil P-40 – brightstocks.
3. The chemical composition of raw materials before and after purification, as well as the products isolated in the process of purification of SC-CO_2 was studied. Application of two-phase

solvent promotes dissolution of PAU in the product together with resins, but at the same time asphaltenes are isolated more clearly, i.e. ionic liquid easily forms a complex with monocyclic and bicyclic aromatic compounds and dissolving condensed PAU the yield of raffinate is 87,67 % (wt.), and the amount of solvent is reduced by 2 times.

4. The technology for obtaining oils, fuels and liquids using supercritical refining of petroleum and its heavy residues has been developed. The hydrocracking of the mentioned raw materials under pressure 3-6 MPa and point 380-425 °C on industrial catalysts Al- Ni- Mo and Al- Co- Mo has been studied. It is shown that oils obtained in the process of hydrocracking of deasphaltized oil have a higher viscosity index (VI 94-205) than hydrocracking oils of non-deasphaltized oil (VI 90-112) and residue hydrocracking oils (VI 110-147).
5. Technical-economic evaluation of the process of supercritical petroleum purification with the help of SC-CO_2, which showed that the comparative technological and economic indicators of the process of dehydration and desalting are lower than in the existing process in production conditions at the existing units of the refinery. The effect at processing of 6 million tons of oil can make 2,3 million manat. The scheme of obtaining residual oil (brightstock) by the existing and proposed technologies is shown. The economic effect is 7138 thousand manat at processing of 89419 tons of vacuum residue for production of 50 thousand tons of oils.
6. Scientific bases of selection of raw materials and method of their purification for the purpose of obtaining white oil of medical vaseline type have been developed. Chemical composition of oil fractions of Baku petroleums (Balakhani heavy oil, mixtures of low-paraffin and paraffin petroleums) of industrial production has been studied in order to select raw materials for white oil production. The degree of purification and transformation of aromatic hydrocarbons at the stages of white oil production using different technological processes (oleum, selective purification, two-stage hydrogenation) has been studied by means of УФ-

spectroscopy. he amount and structure of aromatic hydrocarbons included in white oil were determined.

7. The technology of obtaining technical white oil from raffinates by two-stage hydrogenation on catalysts Al- Co- Mo and QR-3 at 340-350 °C, pressure 5 MPa, V – 0,5 h^{-1} and hydrogen amount 1000 *l/l* of feedstock with subsequent step-by-step contacting with aluminosilicate adsorbent has been developed. Optimization of the process of obtaining technical white oil in the process of two-stage hydrogenation has been carried out, the mathematical model has been constructed and optimal technological parameters of the process have been determined, providing achievement of the required quality of white oil.
8. The technology of obtaining white oils NMR-12 and medical vaseline using raffinate of a new combined process including dewaxing and selective purification using a single solvent has been developed. It is shown that this method considerably simplifies the technology of white oil production, increases the yield of the target product and reduces the amount of hard-to-utilize waste. Inclusion of the process of combined purification in the scheme of white oil production allows to reduce by 16 % the amount of required oleum and to obtain oil with aromatic hydrocarbons content of 0,47-0,95 % wt. %. It is shown that at obtaining white oil of medical vaseline type, the development of technology of its obtaining should be carried out on the basis of the structure-group composition of the saturated part of the initial raw material in order to maximize the preservation of high-ringed, biologically active - relict hydrocarbons.
9. The technology for production of high-viscosity oils has been developed:
   - type P-28 and P-40 from vacuum residue sands of low-paraffin petroleum mixture and Sangachaly-deniz petroleum under the scheme of deasphalting → selective purification → dewaxing → hydrodistillation. The general scheme of residual oil (brightstock) production by existing and proposed technologies is given. Optimum conditions of all stages of the process are determined.
   - oils from heavy residue of low-paraffin petroleum mixture,

distillate D-11 (Neftyaniye Kamni, Guneshli and Gryazevaya Sopka) and heavy residue of paraffin petroleum Sangachali-Deniz using hydrocracking under pressure of 5-10 MPa and point of 400-425 °C on catalyst containing metals of groups VI and VIII. The presence of valuable components for oil production in hydrogenizates has been established.

10. The influence of hydrocracking process conditions - pressure, point and hydrogen flow rate on the yield and quality of the oil fraction has been investigated using the method of experiment planning. The optimum conditions of the process of hydrocracking of deasphaltizate from Baku petroleums for obtaining oil fractions with maximum yield were determined – P = 5,0 MPa; T = 400 °C; H_2 – 800 *l/l* of feedstock.
11. The group chemical composition of the oil fractions of hydrogenizates and the structure-group composition of the components of oil fractions were studied by mass-, PMR- and UV-spectroscopy. It is shown that while at 400 °C mainly reactions of hydrogenolysis and hydrodealkylation take place, with increasing point the process of destruction of raw material molecules intensifies. Naphtheno-aromatic and paraffin hydrocarbons undergo the greatest transformations, as a result of which the fractions are enriched with mono- and bicyclic naphthenic hydrocarbons, as well as light aromatic hydrocarbons, which has a positive effect on their properties. The hydrogenated resin molecules contained, on average, one or two structural blocks represented by aromatic rings with heterocycles.
12. Two technological schemes for obtaining oils from hydrocracking products have been developed: the first one provides obtaining low-viscosity high-index oils (VI-4, VI-6) and high-viscosity industrial oils (I-40, cylinder oil 11, turbine oil, etc.) from hydrogenated working fluids (RJ-3), (RJ-8).
13. Low-viscosity oils VI-4 and VI-6 are obtained from the fraction 300-400 °C by adding depressant ASRI in the amount of 0,3 % without the use of selective purification and dewaxing processes. On the basis of base industrial oils of VI-4 and VI-6 series and additive compositions IOA-4 and IOA-6 oils are developed and

after urea purification transformer oil with pour point minus 56 °C is obtained.

14. The second is the base of all-season motor oil and high-viscosity industrial oil (cylinder oil 38). The low-viscosity base of M-4 engine oil is obtained from the oil fraction of hydrogenysate boiling at 300-500 ° C after its dewaxing with urea and contacting the dewaxed oil with bleaching earth, as well as M-4 oil and additive compositions developed all-season thickened oil M-4_3/6B_1 , the quality of which is at the level of requirements of the relevant standards.
15. Hydrocracking of D-11 distillate yields all-season motor oils M-4_3/6B_1 and M-6_3 /10B along with base oils VI-4, VI-6. Dewaxing of oil fractions of hydrogenated oils boiling above 400 and 500 °C produced high-viscosity oils - vapor oils, which significantly exceed the quality of oils from unique Baku oil petroleums.

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