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PHYSICAL AND CHEMICAL PROPERTIES OF NIGERIAN OILS

AND PROSPECTIVE TECHNOLOGICAL SCHEME OF THEIR PROCESSING

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Розглянуто сучасний стан нафтопереробної галузі Нігерії, її проблеми та перспективи. Представлено результати досліджень фізико-хімічних властивостей нігерійських нафт, а також отриманих з них бензинових, дизельних фракцій, фракцій реактивного палива та мазутів. Проведено порівняльний аналіз із нафтами східних та західних регіонів України. Представлені способи переробки мазутів нігерійських нафт з отриманням бітумів та базових олив. Запропоновано перспективну технологічну схему переробки нігерійських нафт.

The current state of the oil refining industry in Nigeria, its problems and prospects are considered. The presented results of studies of the physicochemical properties of Nigerian oils, as well as gasoline,diesel fractions, jet fuel and fuel oil fractions obtained from them are compared with those obtained for oils from the eastern and western regions of Ukraine. Processing methods of fuel oils from Nigerian oils are presented with the aim of bitumen and base oils production. A promising technological scheme for the processing of Nigerian oils is proposed.

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INTRODUCTION

The relevance of the work. Nigeria’s oil industry is the backbone of its economy. Proved oil reserves in Nigeria, according to various sources, are estimated from 25 billion to 37 billion barrels (bbl).

The oil sector provides Nigeria up to 20% of GDP, up to 95% of export revenues and up to 80% of budget revenues. Nigeria is a major supplier of crude oil to Western Europe and the United States. Almost all crude oil is supplied abroad; at the peak of demand, its production reached 2.423 million bbl per day (Nigeria ranked 12th place in the world), 2.411 million bbl of which were exported (5th place). Extraction is carried out mainly in the swampy areas of the Niger Delta, as well as on the continental shelf. Interest in Nigerian oil is fueled by the fact that 65% of the whole amount is a low-sulfur oil (Bonny Light and Forcados grades). In recent years, oil companies have been focusing on offshore oil production. Almost 100% of oil extraction in Nigeria is carried out by joint ventures of the National Nigeria Petroleum Corporation (NNPC) and oil transport-national companies registered in the country. The largest company is Shell Petroleum Development Company of Nigeria Limited (SPDC). NNPC owns 55% of stocks, namely 30% – Royal/Dutch Shell, 10% – Total and 5% –Agip. The second largest company is Chevron Nigeria Limited (CNL), with 60% owned by NNPC and 40% by Chevron. Total Petroleum Nigeria Limited (TPNL) and Mobil Producing Nigeria Unlimited (MPNU) are based on the same principles. Another company, Nigerian Agip Oil Company Limited (NAOC), is owned by NNPC (60%), Agip (20%) and Conoco Phillips (20%). Texaco Overseas Petroleum Company of Nigeria Unlimited now exists as the NNPC Texaco-Chevron Joint Venture, with 60% by NNPC and 20% by Chevron and Texaco each. The expenses and income of joint ventures, after royalties and taxes, were divided accordingly. The “Big Six” (Shell, Chevron, Total, Agip, Mobil and Texaco) received almost exclusive rights to extract oil in Nigeria on more than acceptable terms.

For domestic needs Nigeria consumes about 300 thousand barrels per day, which are processed at Nigerian refineries. For a number of reasons, including equipment aging and failure, refineries operate at partial capacity. In the past 5 years, this has caused periodic acute shortages of fuel, the need to import finished petroleum products and large-scale speculation. Nigeria has not managed to establish sufficient oil refining for the population, despite huge subsidies. Petroleum products have become one of the main imports and remain so to this day: since 2008, the country has been spending more than $ 7 billion annually on fuel purchases. Aviation and land transport suffer from lack of fuel. In addition, Nigeria does not have sufficient production of oil distillates, which are a valuable raw material for the production of motor oils. Therefore, it is important and relevant to establish the possibility of obtaining marketable products, such as fuels, motor oils and bitumen from Nigerian oils, as well as attracting them for processing at Ukrainian refineries, where there is a shortage of raw materials.

Purpose of the study. To develop a technology for processing Nigerian oils, as well as substantiate the possibility of their processing at Ukrainian refineries, taking into account the availability of equipment for obtaining commercial oil products.

Research objectives:

- to investigate the physical and chemical properties of Nigerian oils and to characterize them in accordance with the accepted classification standards;
- to investigate fractions of Nigerian oils, to determine their suitability for obtaining fuels, motor oils and paving bitumen;
- to carry out a feasibility study for a Nigerian oil refining;
- to evaluate the potential content of components with a high viscosity index (VI) in oil distillates of Nigerian oils, and to purify them;
- to investigate the possibility of obtaining bitumen from Nigerian oils, to investigate their physical and chemical properties.
- to establish the possibility of processing Nigerian oils at PJSC “Ukrtatnafta” without attracting additional investments.

CHAPTER 1

THE CURRENT STATE OF THE OIL REFINING INDUSTRY IN NIGERIA. CHALLENGES AND PROSPECTS: ANALYTICAL OVERVIEW

1.1. Challenges and Prospects of Nigeria's Oil Industry

As at January 1, 2018, less than 80% of proven oil reserves are situated in eight countries. Six countries are OPEC members and two (Canada and Russia) are not. The world leader in proven reserves is Venezuela (mostly due to heavy/bituminous oil). If we take into account only light traditional oil, then the countries of the Middle East will be the undoubted leader. Together, they account for 47.3% of proven oil reserves.

In terms of world oil reserves, Nigeria ranks as second in Africa (after Libya) and 11th in the world (2.2% of world reserves) (Table 1.1).

Nigeria occupies an advantageous geographical position on the African continent. It is located in western Africa. The country is washed by the Gulf of Guinea. It has several ports that are used to transport oil across the Atlantic to importing countries. Nigeria is surrounded by states that have never been distinguished by a high level of economic development after the proclamation of independence – Niger, Chad, Cameroon, Benin. According to experts, the territory in the Niger Delta is very rich in oil. Billions of dollars are only needed to extract oil and develop the wells.

1.1.1. Nigeria's role in world oil production

The search for oil in Nigeria dates back to 1908, when the German company Nigerian Bituminous Corporation extracted oil in the Araromi region between Ijebu Ode, now Ogun State, and Okitipupa, now Ondo State, in the southwestern region of Nigeria. These pioneering efforts were halted by the outbreak of hostilities between Britain and Germany during World War I in 1914. Taking into account that Nigeria was under British territorial control and Germany lost the war, the activity of the German corporation company was not resumed after the war [2-6].

Table 1.1

Predictable world oil reserves in 2018

Country	Supplies of oil, milliard of barrels [1]	% from world supplies
Venezuela	300,9	17,6
Saudi Arabia	266,5	15,6
Canada	169,7	10,0
Iran	158,4	9,3
Iraq	142,5	9,0
Kuwait	101,5	5,9
UAE	97,8	5,7
Russia	80,0	6,4
Libya	48,4	2,8
USA	35,2	2,8
Nigeria	**37,1**	**2,2**
Kazakhstan	30,0	1,8
China	25,7	1,5
Qatar	25,2	1,5
Brazil	12,6	0,7
Other	120,7	7,1

The resumption of oil exploration in Nigeria began in 1973, when the Anglo-Dutch Consortium, a subsidiary of the Royal Dutch Shell group, received an oil exploration license covering the entire country. This initial monopoly gave Royal Dutch Shell a leading position in the exploration, development and production of oil in Nigeria [6].

At the beginning of the XXI century there were about 600 oil refineries (refineries) in the world with a total primary processing capacity of 4 billion tons. Enterprises of this industry are distributed throughout the world more evenly than oil resources, since any state seeks to have its own refineries, working for domestic consumption, and in most cases for export too. In light of this, the significant preponderance of economically developed countries in the total capacity of all refineries in the world was quite understandable: 930 million tons were concentrated in North America, 700 million tons – in Western Europe, 250 million tons – in Japan, 650 million tons – in Eastern Europe and the rest accounts for the developing countries. This ratio has developed over many decades, as it was believed that it was more economically profitable to import crude oil and process it for consumption on site. However, in the 1980-1990s the opposite tendency became more and more clearly manifested: to carry out primary processing of crude oil in the regions of its extraction, and to export commercial products. This trend is based on both the industrialization of developing countries, primarily oil-producing countries, and the policy of Western countries aimed at transferring "dirty" industries to developing countries. As a result, recently, oil refining capacities in developing countries have been increasing much faster and have already reached impressive sizes: in Latin America – 300 million tons, in the Near and Middle East – almost 300 million tons, in Africa – 150 million tons. Nowadays the share of developing countries in the world capacity of refineries is already more than 2/5, and this value continues to increase. First of all, this is about the oil-producing countries of the Persian Gulf – Saudi Arabia, Iran, Iraq, Kuwait, which already have significant oil refining capacities oriented towards export mainly. This also concerns some other oil-producing countries (Venezuela, Mexico, Indonesia), as well as Brazil, India, Argentina, Thailand, where refineries operate mainly or entirely for the domestic market. Some key points of world sea routes (Singapore), islands of the Caribbean Sea (Virginia, Netherlands Antilles, Trinidad and Tobago) have also become large centers of oil refining. Moreover, the refineries located there are distinguished by a particularly large processing capacity (20-30 million tons/year) [5].

1.1.2. Oil fields of Nigeria

The produced Nigerian oil has a low density (no more than 860 kg/m^3), the content of fractions distilled up to 350 °C is 56-59%, the amount of sulfur and resinous substances of most oils is approximately the same and is at the level of 0.1-0.3% (silica gel resins no more than 9%). There are several oils with a slightly higher concentration of sulfur and resinous substances (0.6%).

Literature sources show a negative correlation between density and sulfur content, assuming that the sulfur content is likely associated with oil degradation, but this trend is not observed in the ranges shown in Fig. 1.1.

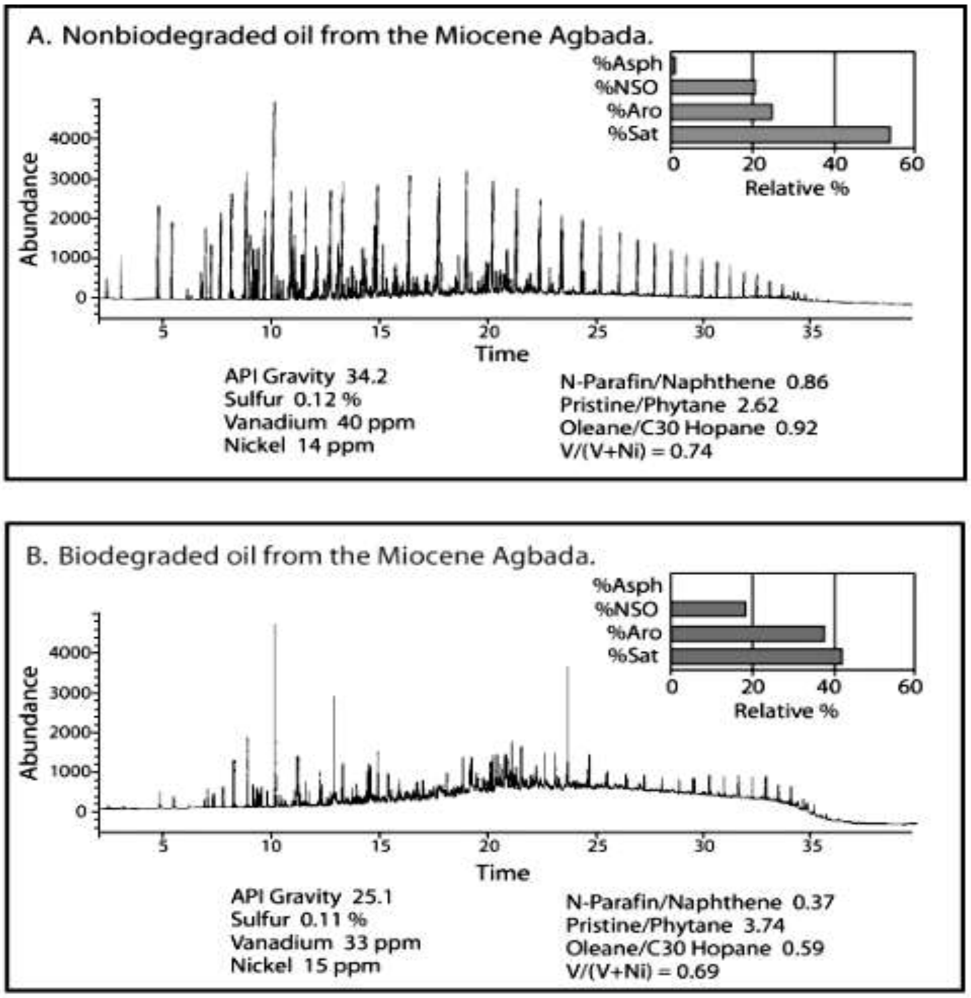

Fig. 1.1. **Geochemical data for non-biodegradable oil from the Niger Delta (data from Geomark Research, Inc. (1998).**

The spectra contain chromatograms of crude oil; the diagram shows the relative proportions of the volumetric composition: the variety of the chemical composition and the ratio of the individual components. Gasoline fractions of oil have low octane numbers (25-67) due to the high content of paraffinic hydrocarbons. Light kerosene distillates of most types of oil are characterized by low sulfur content (up to 0.10%), the absence of sour sulfur, and high-quality photometric properties. Due to the high pour point of diesel fractions, it is possible to produce mainly summer diesel fuel, which is characterized by high cetane number (45-60).

Thus, all types of Nigerian's oil are excellent raw materials for obtaining fuels and oils [7].

Most oils belong to one of two groups. The first group is light paraffin oils from deeper deposits (paraffin content is up to 20 %, but usually about 5 %; n-paraffin/naphthenes ratio is 0.86). The second group includes oils extracted from shallow deposits. They are naphthenic non-paraffinic oils with a relatively low API gravity (average API 26°) and n-paraffin/naphthenes ratio of 0.37. Biodegradation and washing in some of the Pleistocene sands of the Agbada provides the formation of heavy oils (API 8-20°). The oil density of less than 25 °API is observed for only 15 % of the reserves in the Niger Delta [7]. The concentration of sulfur in the majority of oils is low (0.1–0.3%), only for several types it is approximately 0.6 % [8].

Concentrations of Ni and V in oils of the Niger Delta is less than 100 ppm and the V/(V+Ni) ratio ranges from 0.01 to 0.41 with an average of 0.12 [7-8]. Concentrations of sulfur and V/(V+Ni) ratio depends on the natural rocks and conditions of precipitation accumulation. The traces of metals, together with organic geochemistry and physical properties of oil, indicate that rocks of the Niger Delta contain predominantly terrestrial organic matter. Organic matter is deposited in oxygen-free groundwater, where vanadium and nickel hydroxides, as well as complexes with metastable sulfide ions were present. Under these conditions, the preservation of organic matter would be promising. The presence of associated petroleum gas in the Niger Delta is due to its deep-seated origin and low content of CO_2 and nitrogen. Relatively high concentrations of mercury were observed.

Currently, 75 % of the gas produced from the Niger Delta is burned, 10% is re-injected to maintain reservoir pressure, and only 15 % is sold [9].

More than 300 continental shelf oil fields have been discovered in Nigeria. Oil in the Niger Delta is extracted primarily from the sands and sandstones of the Aghdaba Formation. The characteristics of oil fields and reservoir properties of rocks are controlled by the geological conditions and depth of the productive formations. Eocene and Pliocene oil-bearing rocks vary in thickness from 15 to 45 m; in terms of reservoir capacity - up to 10 %. Often the best reservoirs are complex deposits. The main oil-bearing structures differ in the geometry of the fields and the quality of the oil. Examples of such structures are sediments of the Niger Delta branches and coastal barrier massifs periodically cut by sandy channels. The reservoirs of the Niger Delta are composed of Miocene sandstones with porosity up to 40%, with a permeability coefficient of about 1 darcy and a thickness of about 100 m.

The lateral variability of the oily rocks thickness is largely controlled by faults, the thickness of the deposits increases towards them within the subsided block. The grain size of oily sandstones changes in the direction of the river flow, the sand becomes fine with distance from the base of the fan. This means that the sand grains of the delta channels decrease in size from the delta edge, and the sands of the barrier massifs, in turn, become more homogeneous. Most of the unconsolidated sandstones contain small amounts of mudstone cement. The porosity slightly decreases with depth due to the relative youth and "coldness" of the delta complex sediments. Computer-generated tectonostratigraphic modeling shows the presence of local shears along the inclined edge of the faults that control the thickness and lithofacies of potential deep oil sands. The most famous traps in the Niger Delta are structural, although stratigraphic traps are also found. The first of them were formed from postsedimentary deformations of the Aghdab complex. Structural complexity increases from north (early perimeters of accumulation) to south (late perimeters of accumulation) depending on the increasing instability of the lower overconsolidated shale. The variety of structural elements of traps contains simple “block-key” structures, channels filled with clay material, structures with numerical discontinuities, structures with antithetical discontinuities, and structures of destroyed uplifts (Fig. 1.2).

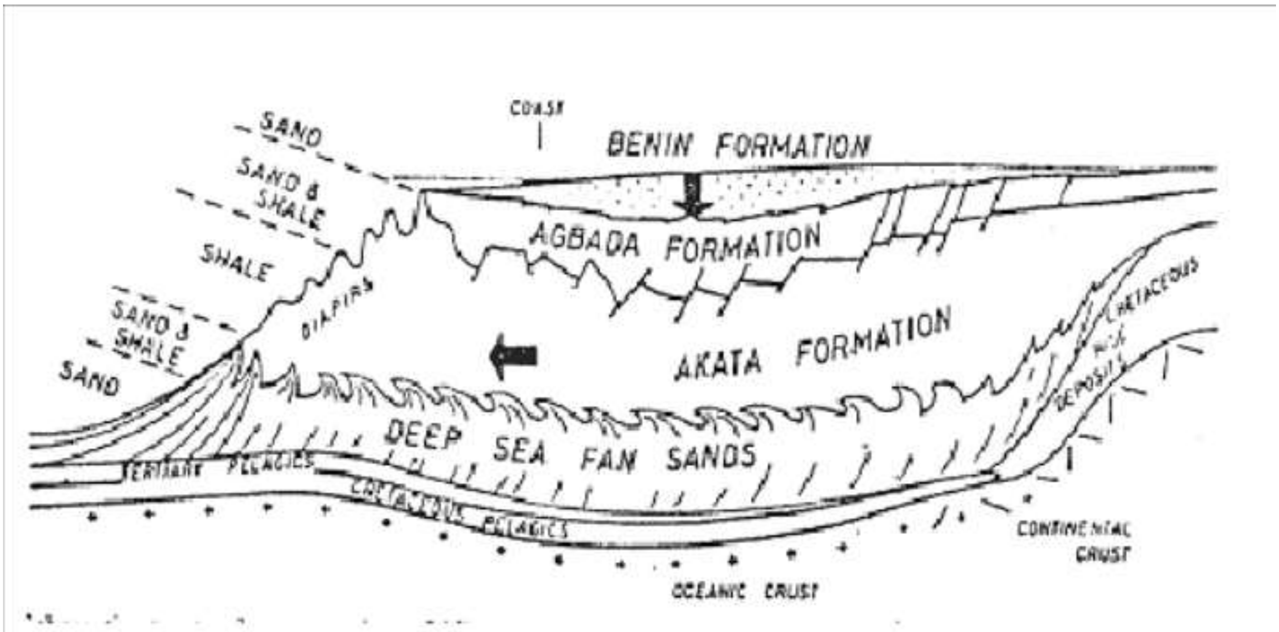

Fig. 1.2. **Schematic structural cross section of Niger Delta** *[J.N. Chukwuma-Orji, E. Okosun, A. Y.Baba Foraminiferal Biostratigraphy and Depositional Environment of Oloibiri-1 Well, Eastern Niger Delta, Nigeria/ Journal of Geography and Geology 4(4):114. October 2012]*

On the flanks of the delta, stratigraphic traps are as important and reliable as structural ones. In this zone, sandstone pockets are found between diapir structures. Towards the front of the delta (downslope from its base), this sequence of sandstone and shale gradually becomes predominantly sandstone.

The primary cover of the Niger Delta is the interbedded shale of the Aghdaba Formation. It forms three types of covers: along faults, over isolated sandstone bodies, and vertical covers. On the flanks of the delta, erosional processes of the Miocene age formed canyons filled with clay. These clays serve as covers for some offshore oil-bearing zones. The location of the basin of the early Niger Delta, oil accumulation centers and the shelf slope zone are shown in Fig. 1.3.

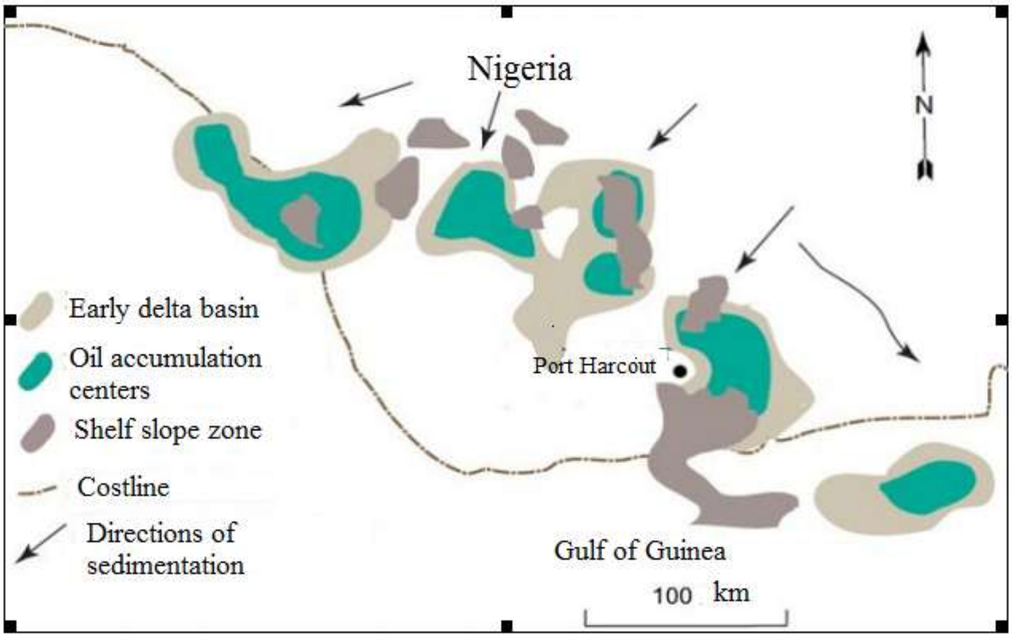

Fig. 1.3. **Map of major oil centers in Nigeria**

The structure of industry can be viewed both in sectoral and territorial aspects. The sectoral structure of industry is a set of qualitatively homogeneous groups of economic units that produce homogeneous products, provide a variety of services and carry out other socially useful activities. The territorial structure of the oil industry is the location and distribution of oil industries on the territory of Nigeria, in its individual regions and on the sea shelf. Delta of the Niger river is the main oil producing region in Nigeria which includes Abia, Akwa Ibom, Baylesa, CrossRiver, Delta, Edo, Imo with a total land area of about 75 thousand km^2 (equivalent to 7.5 % of the total land area of Nigeria) and 185 local territories [10]. Today, there are about 606 oil fields in the Niger Delta, 360 (60 %) of which are on land and 246 (40%) are on water (Fig. 1.4).

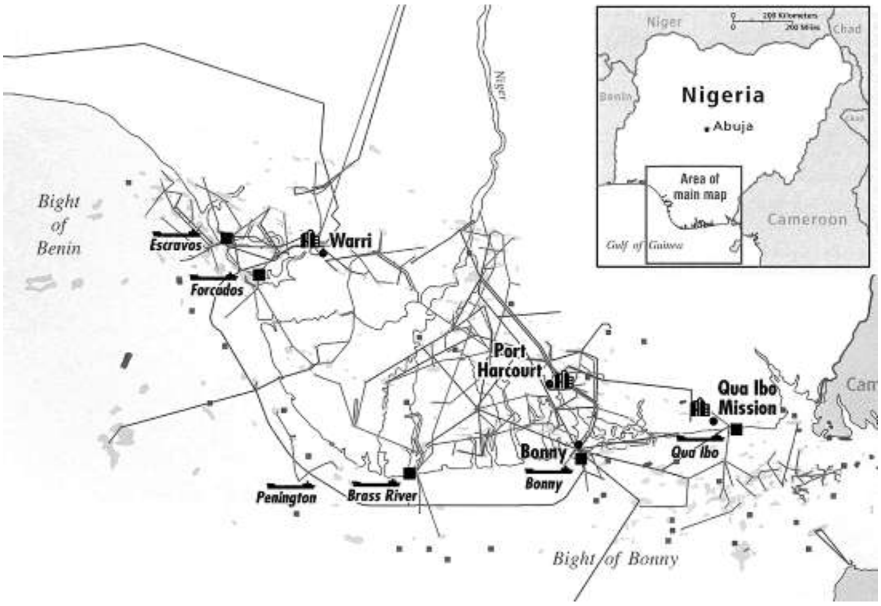

Fig. 1.4. **Location of oil derricks in Nigeria**

1.1.3. Nigeria's refining industry challenges

In the southern province of Nigeria (Rivers State), there are two refineries at Aleisa Eleim, near Port Harcourt. The refinery was first known as Port Harcourt I and Port Harcourt II.

In 1965, Port Harcourt I was built by Shell/BP as the first large oil refinery (a capacity of 3 million tons/year (60,000 bbl/day).

Port Harcourt II was built as an oil refining complex with a capacity of 7.5 million tons/year (150,000 bbl/day). It began to function in 1989. By 1993 the situation was stable and the complex developed almost without problems. The situation deteriorated sharply in 1994, when domestic prices for petroleum products decreased from 84 % to 22%, resulting in a financial crisis and virtually halting most of the maintenance work. All crude oil for both refineries was supplied via the Shell pipeline.

In 1993, Port Harcourt I was attached to the private administration. As a result of the reorganization, a new separate apparatus was created in Port Harcourt II, which began to function separately [10].

The Eleim refinery, which was built next to the Port Harcourt refinery in 1995, has a capacity of 483,000 tons/year. The plant suffered from many technological problems and functionated maximum at 40-60 % of its capacity. Moreover, like other refineries, it works intermittently.

The Warri Refinery, located in the state of Warri, is a refinery complex with a processing capacity of 6.3 million tons/year (125,000 bbl/day). The refinery started operating in 1978. A petrochemical plant operates on its basis.

Crude oil is supplied to this refinery from nearby offshore and onshore fields. Almost all deposits are controlled by Shell. The largest pipeline in Nigeria runs to the Warri plant. Products are also exported from two loading shipyards located 1 km from the plant. But this pier accepts only ships with a length of no more than 150 m. These restrictions are established due to the sharp turns of the Niger River [10, 11].

The Warri plant suffered significant losses when the government cut oil prices by 40 % in 1994. At the same time, the military government raised prices in the face of massive devaluations. Since the refinery focused on internal needs, it managed to withstand this crisis. In 1998, the new civilian government invested heavily (US $ 200 million) to solve the problems. A sharp increase in production began in early 2000. This led to significant improvements in capacity, although productivity was unstable. In 2003, the plant was at the center of military events, as a result of which its productivity decreased to 30% [1, 11].

The Kaduna refinery in northern Nigeria is a complex of refineries with a capacity of 5.5 million tons/year (110,000 bbl/day). The first unit of the refinery was built in 1980 with the capacity of 50,000 bbl/day [10, 11] and was upgraded to 60,000 bbl/day. In 1982, the refinery was expanded, new plants for lubricants production were launched; an asphalt plant, as well as other plants related to petrochemicals were opened nearby. Nigeria has ten gas processing plants and about 30 unprofitable gas fields [12]. Nigeria has six oil export terminals, including Forcados (oil storage capacity is 13 million barrels) and Bonn, which are owned by Shell. Oil produced from offshore fields is directly exported from floating storage facilities and from production platforms (Fig. 1.5) [13].

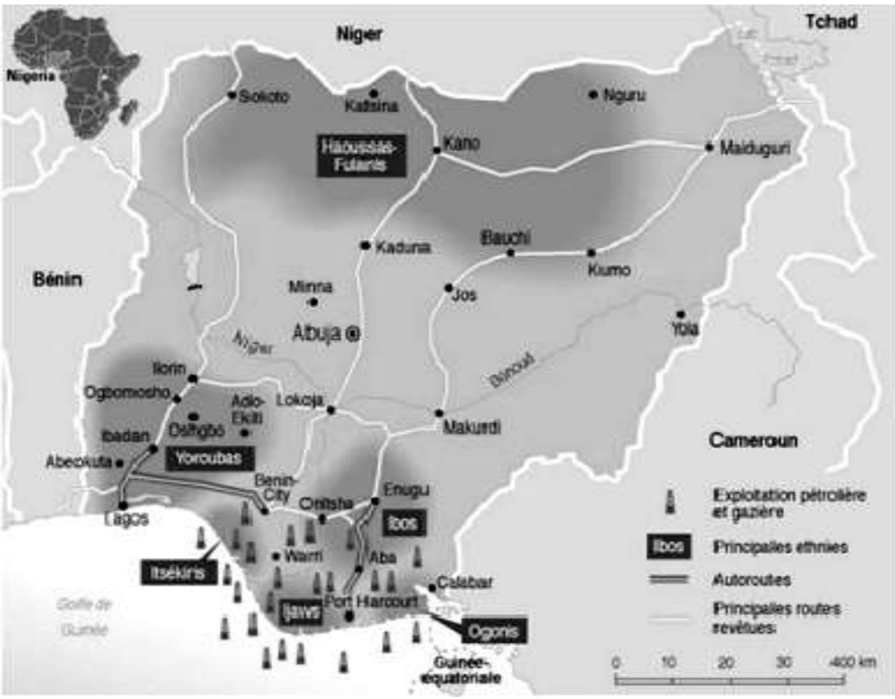

Fig. 1.4. **Location of oil derricks in Nigeria**

Primary oil refining units form the basis of all oil refineries. They produce almost all components of motor fuels, oils, raw materials for secondary processes and for petrochemical industry. The yield and quality of fuel and oil components, as well as the technical and economic indices of subsequent processing, depend on the operation of the atmospheric and vacuum distillation units (AVDU). Serious attention has always been paid to the problems of increasing their productivity and intensification. The most important problems facing modern oil refining are the following:

- further deepening of oil refining;
- increasing the octane numbers of motor gasolines;
- reducing the power consumption through the implementation of the latest achievements in the field of heat and mass transfer, the development of more advanced and intensive technologies for deep waste-free and environmentally friendly oil refining, etc.

The solution of these problems involves:

1. Improvement of the main apparatus of atmospheric and vacuum distillation units.

2. Improvement of technological schemes. When choosing a technological scheme and unit mode, it is necessary to be guided by the potential content of fractions.

3. Improvement of oil production schemes, construction of bitumen plants

1.2. Oil Refining, Production of Marketable Petroleum Products

1.2.1. Methods of oil refining

Oil and gas occupy a leading place in the fuel and energy balance of the overwhelming majority of countries in the world and play an extremely important role in their economies and politics. A wide range of different fuels is obtained from oil – from liquefied gases and gasolines to heavy fuel oils. However, the importance of oil and gas goes far beyond the leading energy carriers. Oil and gas are used as raw materials for the production of a large number of chemical products (ethylene, propylene, aromatic hydrocarbons, etc.), as well as various mineral oils, paraffins, bitumen, coke and other valuable products.

Modern commercial oil products must be of high quality. In most cases, straight-run fractions fail to meet the requirements. Therefore, there are many technological processes that can improve the properties of these petroleum products to meet all standards [14-19]. Based on the properties and quality of oil, there are three ways to process it [20]:

1 – fuel option. It is characterized by the maximum yield of gasoline, diesel fuel, jet fuels, liquefied gases. According to this option, the vacuum distillate and the residue are fed to thermal and catalytic processes in order to obtain an additional amount of fuel. The demand for light petroleum products is much greater than their potential content in crude oil. In this regard, it is necessary to correctly select secondary technological processes that would ensure the processing of heavy oil fractions into high-quality gasolines, jets and diesel fuels in the required range and quantity [21, 22]. At the present stage of oil refining development, it is possible to obtain high-quality fuels from crude oil of any quality.

2 – fuel-oil option. It is characterized by the processing of vacuum distillate and oil fractions contained in tar, in commercial oils, lubricants and lubricating

materials. The need for oils is only 5% of their potential content. However, to obtain marketable products with the desired quality, a number of processes are required to improve the properties of oil fractions and to obtain oils that meet the stringent requirements of modern technology [23].

3 - fuel-oil-petrochemical option. In this case, apart from fuels and oils, the petrochemical products are obtained.

Crude oil for processing can contain up to 1wt.% of water and salts dissolved in it. Oil and water form an emulsion and very often it is difficult to separate it. Salts, as a result of the hydrolysis reaction, form corrosive products which destroy the refinery equipment. In order to reduce the content of water and salts, oil is dehydrated and desalted at the special plants using demulsifiers [24-30].

The demineralized oil is fed to primary refining units, where it is distilled into separate fractions. In industrial practice, the distillation of oil into fractions is carried out at distillation units. Depending on the operating pressure in the columns, the units are divided into atmospheric (ADU), vacuum (VDU) and atmospheric-vacuum (ADU/VDU). This unit produces gasoline, kerosene and diesel distillates, oil fractions, fuel oil and tar [31-34].

The processes of catalytic reforming [35, 36] and catalytic isomerization [37, 38] are widely used to increase the octane number of gasoline fractions obtained at the primary distillation units or to obtain individual aromatic hydrocarbons.

Middle distillates (kerosene and diesel) are refined and purified from sulfur at hydrotreating units. Due to hydrotreating, high quality jet fuel and low-sulfur diesel fuel are obtained [39, 40].

Cracking processes, due to which an additional amount of light petroleum products are obtained, have become widespread at refineries. The improvement of the catalytic cracking technology made it possible to increase the yield of the gasoline fraction to 55-60% [41].

Thermal processes such as visbreaking, coking, and thermal contact cracking are widely used at refineries, and allow to produce tar, vacuum gas oil, bitumen, heavy resins, and other oil residues [42, 43].

The ratio of diesel fuel:gasoline (DF/G) is one of the important indices for the refinery. At the refineries with light refining scheme this ratio is not amenable to regulation, but depends only on the potential content of mentioned fractions in the processed oil. For the refineries with deep refining scheme, the required DF/G ratio is regulated by the secondary processes, which ensure the production of gasoline and diesel fuel components in appropriate proportions. To regulate this ratio, a combination of catalytic and hydrocracking processes is most often used; one of them is used for processing distillate raw materials, and another – for processing the residues. Moreover, hydrocracking can also be used to improve the quality of light distillate fractions (gasoline, kerosene, diesel). The use of hydrocracking is due to the constant improvement of the quality of commercial fuels, as well as the technological flexibility of the process itself [44, 45].

Gas flows from crude oil refining units, catalytic reforming units and other secondary processing units are directed to a gas fractionation unit. In this case, commercial liquefied gases are obtained: propane, butane and isobutene; in some cases pentane and isopentane are produced too.

Oil residues, which are used for coking processes, are often processed at deasphalting units, and for the production of bitumen.

When the refinery is oriented towards the production of commercial oils, the heavy part of crude oil (350-500 °C) is processed using such technological processes as solvent refining, dewaxing, deasphalting, as well as post-treatment processes for oil fractions.

As a result of crude oil refining, a wide range of marketable products is obtained. These products differ from each other in chemical and fractional composition, as well as in properties and application area. For convenience, all petroleum products are divided into 10 groups:

1. petroleum fuels;
2. petroleum oils;
3. lubricants;
4. paraffins, ceresins, vaselines;
5. petroleum bitumen;
6. carbon black;
7. petroleum coke;
8. additives for fuels and oils;
9. solvents and aromatic hydrocarbons;
10. other petroleum products.

The structure of an oil refinery is determined by its properties, the need for certain groups of oil products and the amount of simultaneous investment. The most capital-intensive is the processing of heavy crude oils.

In Nigeria, the total reserves of heavy oils are over 30 billion barrels with a future potential recovery of $3654 \cdot 10^6$ bbl [49, 50]. The development and production of heavy oils in Nigeria is of great importance for the development of the country's economy, because bitumen produced from it can be used in almost all processes related to the construction of houses, roads, industrial buildings, as well as to their waterproofing. All construction companies in Nigeria import bitumen and mix it with modifiers at the factories. Imported bitumen is expensive; that is why the production of bitumen from Nigerian oils is a topical issue today.

1.2.2. Base oils production

In Nigeria, there is insufficient production of oil distillates, which are a valuable feedstock for the production of motor oils. Therefore, it is important and relevant to establish the possibility of obtaining commercial oils from vacuum distillates after processing of Nigerian crude oils both in Nigeria and in Ukraine.

Although the main provisions for obtaining lubricants have been formulated a long time ago, research and improvement of even such traditional processes as solvent refining, dewaxing, deoiling, contact post-treatment (using various external influences – force fields, surfactants, etc.) are relevant [46 -48].

Oils of petroleum origin are a mixture of hydrocarbons containing 20-60 carbon atoms, with a molecular weight of 300-750 and boiling range of 300-650 °C.

Oil distillates and residues obtained after vacuum distillation of fuel oil contain:

- paraffinic hydrocarbons (n- and isocompounds);
- naphthenic hydrocarbons containing five- and six-membered rings with paraffinic chains of various lengths;
- aromatic hydrocarbons (mono- and polycyclic)
- naphthene-aromatic hydrocarbons with paraffin chains;
- resinous-asphaltene compounds;
- sulfur-, nitrogen- and oxygen-containing organic compounds.

To compare with others, paraffinic hydrocarbons have the lowest viscosity, the flattest viscosity-temperature curve and the highest viscosity index. The content and composition of paraffinic hydrocarbons in oils depends on the crude oil type and the boiling range of the fraction.

Naphthenic hydrocarbons in optimal amounts are desirable components of oils. With an increase in the boiling point of oil fractions, the number of carbon atoms in the side chains of naphthenic hydrocarbons, as well as their pour point and viscosity index increase.

Aromatic hydrocarbons are almost always present in commercial oils. Their content and structure depend on the crude oil nature and the boiling range of the fractions; the higher they are, the more amounts of aromatic hydrocarbons and the higher degree of their polycyclicity. Aromatic hydrocarbons in most cases contain naphthenic rings and side paraffinic chains of different lengths.

The chemical feature of naphthenic and aromatic hydrocarbons is their significantly higher viscosity in comparison with paraffinic ones. Therefore, to ensure good low-temperature properties of oils, apart from hard paraffinic hydrocarbons, polycyclic aromatic hydrocarbons with short side chains (low viscosity index) are also extracted from them.

However, complete removal of these hydrocarbons can impair the oxidation stability of the commercial oils.

Resin-asphalt compounds are undesirable components of oils.

Sulfides and disulfides, thiophene and thiophanes, and more complex polycyclic sulfur derivatives, which negatively affect corrosive properties and oxidation stability, can be present in oils. However, complete removal (<0.5 wt.%) impairs the protective properties of oils, especially against water.

Oxygen-containing compounds of oils contain naphthenic acids and phenol derivatives, which cause corrosion and increase carbon depositions.

The technology for the production of base oils includes a number of processes, the purpose of which is the separation of undesirable compounds (asphalt-resinous compounds, polycyclic aromatic hydrocarbons with a low viscosity index, hard paraffinic hydrocarbons) [51-53] .

These processes include:

1. Purification of raw materials – extraction (selective solvents), hydrogenation (hydrocracking, hydroisomerization), adsorption, sulfuric-acid refining.

2. Dewaxing of purified raw materials using solvents or hydrocatalytic processes.

3. Post-treatment of dewaxed oils by the contact method (contact filtration) or by hydrogenation processes.

Before solvent refining or hydrogenation the residual raw material (tar) is directed for deasphalting with propane. At some refineries a duo-sol process is used, which combines the functions of deasphalting and solvent refining processes.

Currently, the bulk of base oils are produced using extraction processes: propane deasphalting; solvent refining with phenol or furfural; dewaxing with a ketone-containing solvent. For the post-treatment of dewaxed oils on modern oil blocks, a hydrotreating process is used. Since the chemical composition of oil fractions of crude oil of different nature is different, the optimal conditions for carrying out the extraction processes of their processing are also significantly different.

To remove residual undesirable components from the deasphalted product, it is subjected to solvent refining. As a result, the target product acquires improved physic-chemical and operational characteristics in comparison with the raw material. The essence of the process is different solubility of polar and polarizable components of the raw material in a polar solvent. For oil fractions, such components are polycyclic arenes and high molecular resinous substances [54].

Oil vacuum fractions and deasphalted oil obtained during deasphalting with liquid propane are used as raw materials for this process. The resuting products are distillate or residual raffinate, which mainly contains naphthene-paraffinic and low-viscosity polycyclic aromatic hydrocarbons. A by-product of solvent refining is an extract that was used earlier as a component of boiler fuels, but now it is a scarce and valuable raw material for the production of coke, bitumen, carbon black, plasticizers for industrial rubber and other purposes [55]. Until recently, furfural was used as a solvent. However, its high toxicity is one of the main disadvantages. As a solution of this problem, another solvent was selected – N-methylpyrrolidone, which has less toxicity, greater solubility, greater selectivity with respect to aromatic hydrocarbons, and lower melting point. A comparative analysis of the processes of solvent refining with furfural and N-methylpyrrolidone showed that the raffinates of solvent refining with N-methylpyrrolidone are of better quality, and the oils obtained from them have a higher viscosity index than the raffinates of furfural purification [56]. Replacing the solvent made it possible to increase the raffinate yield by 5-7 %, improve its quality, and reduce energy consumption by 25-30 % [57]. However, and this solvent has some disadvantages, one of which is the low thermal stability of N-methylpyrrolidone, the resinification of which begins at 200 °C, i.e. below the boiling point [58].

The studies of technology for obtaining base oils led to the creation of a hydrotreating process, in which compounds of sulfur, nitrogen, oxygen and resinous asphaltene substances are removed from oil fractions, i.e. this process can fully replace the contact treatment. The hydrotreating process is a catalytic one. Aluminum-cobalt-molybdenum (ACM) and aluminum-nickel-molybdenum (ANM) are widely used industrial catalysts. They are bifunctional and contain three main components: an active component, an acid component, and a binding component. The active component, which can be sulfides and oxides of molybdenum, nickel and cobalt, performs a hydrogenating-dehydrogenating function. The amount of active component in the catalyst varied from 18 to 25 wt.%. Alumina, zeolites and amorphous aluminosilicates are used as a component performing acidic functions. The binding function can be performed by the same aluminum oxide and amorphous aluminosilicates or silicon, titanium, zirconium oxide. The main technological parameters are: process temperature 300-400 °C, pressure in the reactor 3.7-4.0 MPa, volumetric feed rate 0.5-3.0 h^{-1}, circulation ratio of hydrogen-bearing gas to feed 300-800 nm^3/m^3. Due to hydrotreating the stability, color, demulsibility and coking properties of the resulting products are improved; there is a slight increase in viscosity by 1-2 points and pour point by 1-3 °C [59].

The next process in the production of base oils is the dewaxing process, designed to remove high-melting paraffins and ceresins which deteriorate the low-temperature properties of oils. As a result of dewaxing, products with a pour point from –10 to –15 °C or even lower are obtained, depending on the process purpose [5, 6]. For the final and complete removal of unwanted components from oil fractions, including solvent residues, contact post-treatment process is used, which is based on the phenomenon of adsorption. Fine-grinding clay with a particle size of about 0.1 mm or other active substances acts as an adsorbent. Some low-tonnage and specialized oils are produced at old refineries using sulfuric acid refining process. The feedstock is fractions obtained from unique low-sulfur, low-paraffinic oils (Baku and Embensk oil fields). Due to the decline in the production of these oils and a number of disadvantages of sulfuric acid treatment processes, they are replaced by extraction and hydrogenation processes.

In modern oil production, the role of hydrogenation processes (hydrocracking, hydroisomerization, hydrocatalytic dewaxing) is increasing due to the advantages of these processes over extraction [44, 60].

Along with petroleum oils, synthetic oils have been increasingly used in recent years. They are used in extreme conditions. They have better low-temperature properties (they are mobile at temperatures lower than those for mineral ones) and withstand high operating temperatures. Poly-α-olefins, diesters, polyols and dialkylbenzenes are used as synthetic base oils.

To achieve the required quality, additives are introduced into the composition of oils. Additives are divided into ashless additives, which do not contain metal in their composition, and ash additives, in which metal is present. Predominantly oils contain several additives. Many of the additives are multifunctional, i.e., they improve several properties.

In recent years, a great attention has been paid to the development of compositions (package) of additives. In such packages, a certain combination of functional additives and their optimal ratio are selected. The effectiveness of the additives depends on the chemical composition of the base oil, i.e., on its “injectivity” to the additives.

1.2.3. Production of bitumen and their properties

Nigeria's bitumen is represented by two types depending on source: deposits of liquid bitumen (or high-viscosity oil), and tar sands. Tar sands are a mixture of wet sand and clay impregnated with bitumen (a viscous substance similar to tar); they are an alternative source of oil.

The production of liquid bitumen (or heavy, viscous oil) can be carried out in the same way as for conventional oil [61-67]. Hard bitumen from tar sands is extracted mainly by open-pit or mine methods. It should be noted that in Nigeria, the resources of heavy oil, super-heavy oil, and hard bitumen are much larger than the resources of conventional oil. This is the same type of oil found in Venezuela. In the international market, this product is much cheaper than conventional oil. Based on this, Nigeria can export bitumen, and it will not even be a part of the quota that OPEC gives Nigeria for the export of conventional oil. Moreover, apart from road construction, this heavy oil can also be used as industrial fuel for steam generation and thermal processes. This is particularly relevant for the cement and sugar industries, where a lot of hydrocarbons are burned [68-71].

Bitumen is a complex mixture of high-molecular oil compounds and their oxygen-, sulfur-, nitrogen- and metal-containing derivatives. The elemental composition of bitumen varies within the following limits (wt.%): carbon 80-85, hydrogen 2-8, oxygen 0.5-5, nitrogen – up to 1, sulfur – up to 7 %. The composition depends on the crude oil nature, the composition of the feedstock (oil residues), and on the production technology.

In industry, bitumen is obtained by deep distillation of oil fractions of tar (residual bitumen) or by oxidation with atmospheric oxygen of tar, cracking residues or extracts after solvent refining of oils and their mixtures (oxidized bitumen). Residual bitumen is a soft low-melting product, oxidized one is elastic and thermostable. Bitumen obtained by the oxidation of cracked residues contains a large amount of carbenes and carboides, which disrupt the homogeneity of bitumen and deteriorate their binding properties.

Bitumen is directly obtained in several ways by various schemes. The most common method is blowing of tar with air, resulting in oxidized bitumen. The ubiquity of oxidized bitumen is determined by the cost-effectiveness of continuous apparatuses involved in the production process. Also, bitumen (residual and precipitated) is obtained as a result of vacuum distillation of fuel oils and deasphalting of tar with propane. In addition, compounding of bitumen obtained via different processes is also used.

Vacuum distillation, oxidation and deasphalting are used for the production of petroleum bitumen. The feedstock for vacuum distillation is usually fuel oil; tar is used for oxidation and deasphalting. Commercial bitumen is obtained as a direct product or by compounding the products of different processes. The quality of the finished bitumen depends primarily on the quality of the raw material, and for oxidized bitumen also on the temperature, oxidation time and air consumption [72].

Oxidation (or blowing) with air is used for bitumen production when the feedstock contains small amount of asphalt-resinous substances and blowing can increase their content. If the amount of asphalt-resinous components in the feedstock and bitumen obtained by distillation and extraction are practically the same, then oxidation with air under certain conditions significantly changes both the qualitative and quantitative composition of the product. Oxidized bitumen is sometimes called "blown bitumen". The process of petroleum residues oxidation is of particular practical importance, since it is used now for the production of high-quality road, construction and special bitumen with various rheological and operational properties.

For the first time oxidized petroleum bitumen began to be produced in 1844 on an industrial scale. J.G. Bierley proposed to bubble air through the layer of petroleum residues at 204 and 316 °C. Depending on the temperature and the process duration, bitumen with different properties was obtained; the product was named “bierlite”. In Russia, oxidized bitumen was first obtained in 1914 in Grozny. The development of oxidized bitumen production in the former USSR began in 1925 in Baku. Modern technology consists in the oxidation of petroleum residues with atmospheric oxygen without a catalyst at a temperature of 230-300 °C for 12 hours. Air consumption is 0.84-1.4 m^3/min per 1 ton of bitumen. Air can be supplied to the reactor under pressure or sucked due to the vacuum (up to 500 mm Hg. Depending on the content of volatile substances in the feed and the oxidation depth the yield and process losses are in the range of 0.5-10 wt. % relative to the feedstock. Water vapor and carbon dioxide are removed from the system. The exothermic oxidation reaction raises the temperature in the reaction zone.

Petroleum hydrocarbons are simultaneously oxidized in two directions:

→ Acids → Hydroxy acids → Asphaltogenic acids
hydrocarbons
→ Resins → Asphaltenes → Carbens → Carboids

Depending on the oxidation conditions, mutual transformations of acidic and neutral oxidation products are possible. At high temperatures, carbon dioxide is released and asphaltogenic acids are converted to asphaltenes [61–67].

Oxidized bitumen can be obtained from oils containing 5 wt. % and more of asphalt-resinous substances, though, their desirable content would be more than 25 wt. %. The best feedstock for obtaining oxidized bitumen is the residues of high-resinous low-paraffinic oils. There is an attempt to classify oils based on the yield and quality of bitumen obtained from them. It is known that, in terms of the asphaltic-resinous substances content, crude oils can be highly resinous oils (the content of the sum of asphaltenes and silica gel resins is more than 20 wt. %), resinous oils (the content of the sum of asphaltenes and silica gel resins is 8-20 wt. %) and low resinous oils (the content of the sum of asphaltenes and silica gel resins is 6-8 wt.%). According to the content of hard paraffins, crude oils are divided into high-paraffin oils (the content of hard paraffins is more than 6 wt. %), paraffin oils (the content of hard paraffins is 2-6 wt.%) and low paraffin oils (the content of hard paraffins is less than 2 wt. %) [61-67].

The main properties of bitumen include: softening point, penetration, ductility, brittleness temperature.

The softening point of petroleum bitumen is a temperature at which bitumen passes from a relatively solid state to a liquid one under standardized conditions. When heated, the bitumen does not melt, but gradually softens. When the softening point exceeds the standard value defined for particular grade of bitumen, it passes from a viscous state to a liquid one. The softening point is determined by the ring and ball method (R&B): two horizontal discs formed of bitumen inside copper or brass rings are heated at a constant rate (5 °C/min) in a liquid medium until they withstand the mass of standard steel ball. The softening point is the average of two temperatures at which the bitumen discs soften to a degree sufficient for each ball, surrounded by the product to be tested, to move downward through the ring at a distance of 25 ± 0.4 mm. For the softening point from 30 to 80 °C, distilled (or recently boiled) or demineralized water is used as a working liquid, and glycerin is used for the softening point from 80 to 150 °C.

The penetration depth of the needle (penetration) is an indicator of petroleum bitumen consistency, characterizing the penetration depth of the cone needle vertically downward from the surface of the body material of a standard shape into semi-liquid and semisolid products under certain conditions (temperature, load, penetration time). Penetration characterizes the structural behavior and hardness (or plasticity) of bitumen. The essence of the method is to measure the penetration depth of the needle of a standard device into the product under study, which is in a brass cylinder at the temperature of 25 °C for 5 s with a load of 100 g or at the temperature of 0 °C for 60 s and the load of 200 g. Penetration unit is 0.1 mm. For bitumen, penetration can be in the range from 10 to 300 units. It is the value of penetration at 25 °C which defines a grade of petroleum bitumen. The penetration value increases with increasing temperature. A sharp decrease in the penetration temperature is observed at subzero temperatures. The higher the penetration at a given softening point, the higher the heat resistance of bitumen. To obtain bitumen with different values of penetration we may vary the initial feedstock, technologies and production modes.

The extensibility of petroleum bitumen (ductility) is a value that characterizes the bitumen ability to be extended into a thread. It is a distance over which the bitumen can be stretched into a thread before it breaks. Paving bitumen is characterized by the greatest extensibility. The greater the extensibility, the better the adhesion to dry surfaces when melted material is applied. It is impossible to draw conclusions about the quality of paving bitumen only by this indicator, since the test conditions and real loads and deformation rates of road surfaces are incomparable. The maximum value of ductility at 25 °C is achieved at the transition from the state of a Newtonian fluid to a structured fluid. The more the fluidity of the material deviates from the Newtonian, the less its ductility at 25 °C. Extensibility is not one of the functional predictive indicators of paving bitumen; therefore, it is removed from the list of mandatory indices by the norms of EN 12591.

Brittleness (brittle point, BP) of petroleum bitumen is the temperature at which a material is destroyed by a short-term applied load. BP characterizes the behavior of bitumen at low temperatures. At the same penetration the oxidized bitumen has a lower BP compared to bitumen obtained by other technologies. Paving bitumen and roofing bitumen have a lower BP on comparison with other grades.

The relative viscosity of bitumen is a value characterizing the rheological properties. The relative viscosity of bitumen is a time (s) of continuous flow of a certain volume of the investigated product through the calibration hole of the VZ-248 viscometer. It shows the ratio of the flow time of the investigated oil product (200 ml) through a calibrated hole of a standard viscometer at a certain temperature

(t) to the flow time of distilled water (200 ml) at the temperature of 20 ° C. The relative viscosity at temperature t referred to the symbol RV_t and is measured in conventional degrees.

Dielectric properties of petroleum bitumen. Bitumen is characterized by high electrical insulating properties and equals to those of the good insulators. Dielectric properties of petroleum bitumen include: breakdown voltage, electrical conductivity, dielectric loss tangent.

The dielectric strength of bitumen, or their breakdown voltage, is the value of the smallest voltage of electric current at which an electric spark jumps between two discs (25 mm in diameter) of electrodes immersed in bitumen at a distance of 2.5 mm from each other. This value is very important for all electrical high voltage devices filled with bitumen, because it determines their stable and safe operation. For bitumen, the breakdown voltage is on average 10-60 kV/mm at the temperature of 20 °C. The breakdown voltage of plastic bitumen is less than that of hard bitumen. The value decreases with increasing temperature. The breakdown voltage of bitumen depends on the method of its production and many other factors, the main of which are humidity, pollution with fibers, dust, etc., current frequency, temperature, pressure. With increasing humidity, the breakdown voltage drops sharply. Fiber or solid particles contamination also affects this value. With increasing pressure, the breakdown voltage increases linearly. Moreover, under vacuum conditions, the breakdown voltage is lower than under atmosphere pressure.

The specific electrical conductivity of bitumen is insignificant and at 50 °C it is less than 10^{-2} S/m, whereas at 80 °C it rises to 0.3 S/m. Specific electrical conductivity increases with increasing temperature and decreasing viscosity of bitumen. An increase in the electrical conductivity of bitumen solutions in benzene at 20 °C is accompanied by the increase in the coefficient of water resistance of bitumen-mineral mixtures and the increase in adhesion to mineral materials.

The tangent of the dielectric loss angle (tan δ) is very important value for assessing the insulating properties of bitumen used as insulators. The bitumen is heated under the influence of the electric field. The energy consumption for heating is called dielectric loss. The tangent of the angle of dielectric losses at 20 °C for petroleum bitumen is 0.013-0.021; losses due to hysteresis and power losses (in total) at 80 °C are within 3-5; dielectric constant at the same temperature is 2.9-3.2.

The plasticity range of paving bitumen is one of the quality indicators that is not included in regulatory documents, but has practical significance. It represents the difference between the softening point of petroleum bitumen and its brittleness. Bitumen, which is characterized by a wide plasticity range, has a higher deformation capacity, resistance to cracking at low temperatures and shear resistance at elevated temperatures. There is a relationship between the plasticity range and the penetration index, which is expressed by the formula: SP – BP = 7(10–PI), where SP is softening point; BP is brittle point; PI is penetration index. The brittle point of bitumen can be defined according to the softening point and penetration index. For paving bitumen, which is used in road construction in the mild climate, there plasticity range of 58-60 °C is sufficient, for a temperate climate it is 65-70 °C, for areas with a harsh climate it should be even wider.

Cohesion of petroleum bitumen is the adhesion of particles which form one phase. The same as adhesion, the cohesion of bitumen depends on temperature and the nature of the asphaltenes and resins included in botumen composition. With an increase in the molecular weight of resins and asphaltenes, the cohesion value increases. Cohesion decreases with an increase in the content of paraffin compounds and increases with an increase in the content of aromatic compounds. The value of cohesion increases with a decrease in the thickness of the product layer to a certain final value (about 30-40 microns), with a decrease in temperature and an increase in viscosity. With an increase in cohesion, the strength characteristics of bitumen increase, therefore, it is desirable that, under other indices being equal, the cohesion would be maximal.

Solubility and chemical resistance of petroleum bitumen. Petroleum bitumen is soluble in most organic solvents, except for low-molecular alcohols. Solvents of asphalt-resinous substances present in the composition of bitumen can be divided into three groups. The first one includes aromatic solvents, carbon tetrachloride and carbon disulfide with high solubility (83-90%) and practically zero selectivity for asphaltenes. The second group includes chloroform and trichlorethylene with high solvent ability and selectivity and the third one – aliphatic hydrocarbons C_5-C_8, lower aliphatic alcohols and acetone with moderate solvent ability and pronounced negative selectivity. According to the solubility, we may make conclusions about the ash content, the content of carbenes and carboids, as well as mechanical impurities. The solubility of bitumen is standardized at least as 99.

The harder the petroleum bitumen, the higher their resistance to chemicals. Soft bitumen with a high acid number is exposed to the action of diluted alkalis. At ambient temperatures, bitumen has high chemical resistance, but at 150 °C and higher temperatures, it reacts with oxygen, sulfur, chlorine and some other substances. This property is used to obtain various grades of bitumen. At ambient temperatures, bitumen is used to protect materials from acids and aqueous solutions of inorganic salts. Bitumen is resistant to diluted acids, but can react with concentrated acids (except for HCl, which is inert to bitumen even in the concentrated form). The diffusion rate of water into bitumen is very low.

Water absorption of bitumen during its long-term keeping in water is no more than 1-3 %. The water absorption of bitumen is significantly lower than that of rubber and other plastics.

1.2.4. Statement of the research problem

Given the fact that a sufficient number of oil and gas fields have not yet been developed, Nigeria is interested in borrowing Ukrainian experience and technologies in the field of exploration, oil and gas production. In addition, the country is interested in the participation of Ukrainian companies in the development of their oil and gas fields. In turn, at the present stage one can observe a slight activation of Ukrainian capital in the countries of the African continent. In particular, today NJSC Naftogaz of Ukraine has concessions within the framework of bilateral agreements with the companies of the Egyptian General Petroleum Corporation, as well as with the Algerian ALNAFT on the territory of the states of North Africa [73]. Therefore, the participation of Ukrainian oil and gas companies in the oil sector of Nigeria would be quite rational. It should be taken into consideration that the income from oil production is 20 % of Nigeria’s GDP, and it provides 80 % of the country's budget. Therefore, due to the activity of Ukrainian companies, Nigeria strives to increase the production of undeveloped oil and gas fields. Also, if we refer to the example of the development of a gas dialogue with Egypt and the development of a concept for the supply of liquefied natural gas to Ukraine, then theoretically it would be possible to carry out supplies of Nigerian oil by sea. It could become a source for filling the Odessa-Brody-Gdansk oil pipeline for further re-export to EU countries [73], as well as be an additional resource of oil for involving it in refining at Ukrainian refineries, in particular, PJSC Ukrtatnafta in order to obtain high-quality fuels, base oils, bitumen, etc.

To select the optimal processing option for Nigerian oils, we must first study their composition and properties using a set of standard techniques. It should be noted that the developed processing option can be applied at an existing oil refinery in Ukraine, using the necessary capacities of this plant.

In this regard, it is necessary to solve the following scientific problems:

- to investigate the physic-chemical properties of Nigerian oils and characterize them in accordance with the accepted classification standards;
- to investigate fractions of Nigerian oils, determine their suitability for obtaining fuel, motor oils and paving bitumen;
- to study the composition and properties of distillate fractions of Nigerian oils and propose options for their use;
- to assess the potential content of components with a high viscosity index (VI) in oil distillates of Nigerian oils, and to purify them;
- to study the composition and properties of the residues of Nigerian oils, to explore the possibility of obtaining bitumen from Nigerian oils, to investigate their physico-chemical properties;
- to carry out a feasibility study of processing scheme for Nigerian oil, as well as to analyze the possibility of processing Nigerian oils at Ukrainian refineries;
- to assess the impact of the refinery which processed Nigerian oils on the environmental situation.

CHAPTER 2

RESEARCH METHODOLOGY

2.1. Characteristics of Raw Materials

For the rational organization of research, we have developed a program to achieve the main goal of work in the form of an integrated step-by-step algorithm (Fig. 2.1).

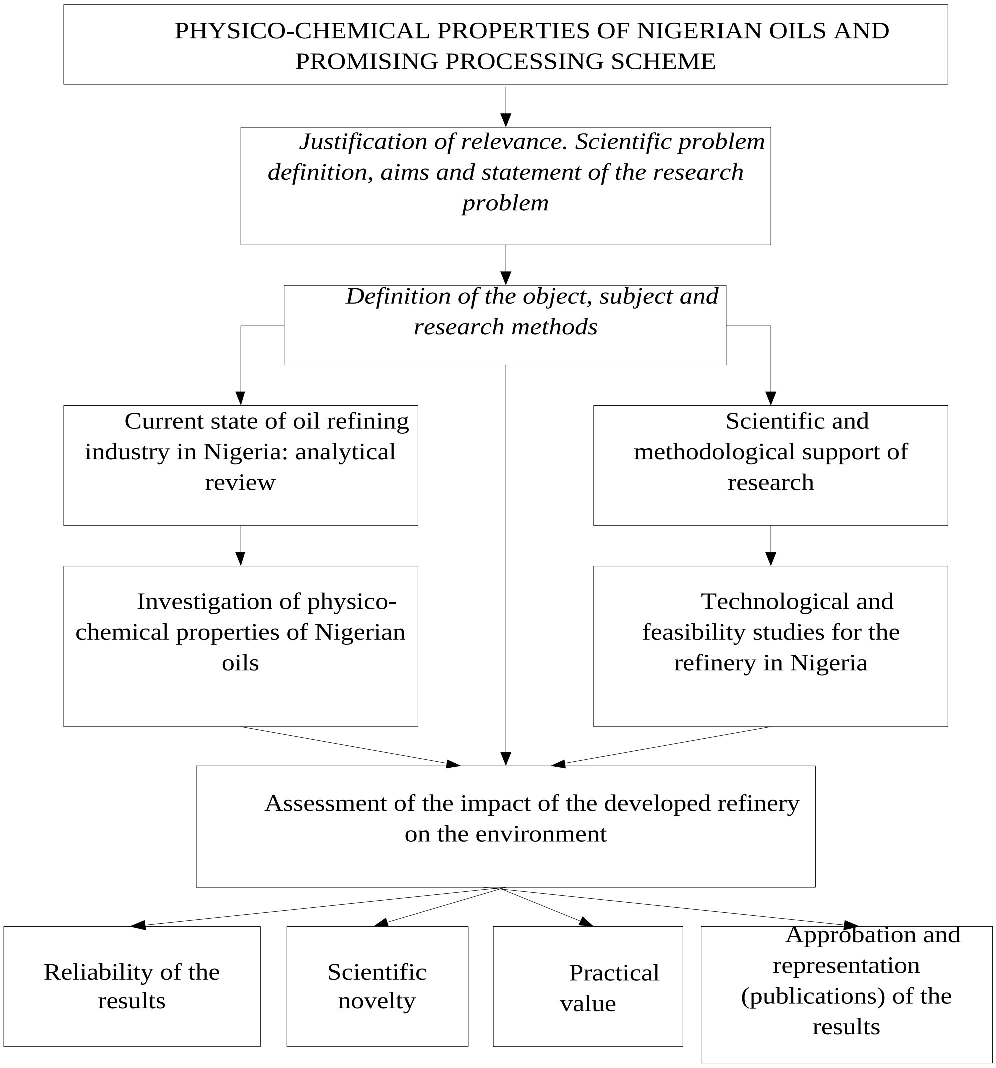

Fig. 2.1. Logical block diagram of the organization of research

Commercial grade oils Brent Dated and Bonny Light (from Nigeria) were taken for research and designated Nigeria 1 and Nigeria 2, respectively. The physico-chemical properties of these oils and products, the possibility of obtaining oils and bitumen were investigated. The mixture of oils from West Ukrainian and East Ukrainian deposits, which are processed at the PJSC "Ukrtatnafta", was analyzed for comparison.

2.2. Standard Research Methods

The fractional composition was determined according to the ASTM D86-16a method [74], the ASTM D1160 method [75], as well as by the method described in the workplace instruction of PJSC "Ukrtatnafta" 26.003.2013 "Determination of the fractional composition by the simulated distillation method according to TBP of oil, petroleum fractions and commercial petroleum products", which is analogous to ASTM D2887, ASTM D 5307 - 97 and ASTM D 6352 - 04e1 [76-78].

We used HP 7890 gas chromatograph (for light oil and fractions distilled up to 350 °C) with a flame ionization detector (FID) and the Simdis software package. The essence of the method is the chromatographic separation of hydrocarbons of oil and petroleum products on a highly effective capillary column with the subsequent registration of peaks by FID.

The density of oils and petroleum products was determined by the pycnometric method GOST 3900 [79] using an automatic DE40 density meter with a measurement range of 0–3 g/cm^3.

The coking ability of petroleum products was determined according to the standard method GOST 19932 [80]. The method consists in high-temperature evaporation of the investigated petroleum product under standard conditions and subsequent quantitative determination of the resulting residue – coke.

The ash content of petroleum products was determined according to GOST 1461 [81]. The method consists in combustion of the investigated sample and calcining the solid residue to constant weight.

The sulfur content in the oil fractions was determined according to ASTM D4294 [82].

The structural-group composition of the distillates was determined according to the standard n-d-M method [83].

The acid number of oils was determined according to GOST 11362 [84] on a Titration Excellence T70 titrator [84].

The content of mechanical impurities was determined according to GOST 6370 [85].

The content of paraffins in oil was determined according to GOST 11851 [86].

The kinematic viscosity was determined according to the EN ISO 3104: 1996 [87].

The relative viscosity was determined according to GOST 11851 [88].

The refractive index was determined using a refractometer according to GOST 18995.2 [89].

The pour point was determined according to the standard method GOST 20287 [90]. This is the temperature at which the investigated sample under test conditions solidifies so much that it does not flow for 1 min when the test jar is tilted at an angle of 45º.

The flash point of petroleum products was determined in open and closed cups according to the standard method GOST 4333 [91].

The water content in oil was determined according to GOST 2477 [92].

The content of chloride salts was determined according to GOST 21534 [93] on a Titration Excellence T70 titrator. [93]

The group composition of organosulfur compounds in petroleum fractions was determined by the method of sequential removal of individual groups using appropriate reagents. Sour sulfur was removed using an alcoholic solution of sodium plumbite. Disulfides were separated with acetic acid and zinc dust. Sulfides were separated using mercury nitrate. The content of each of sulfur compound groups was determined by the difference between the total sulfur content before and after the corresponding treatment.

The determination of the metals content in oils was carried out according to the method developed by the Center for Physical and Chemical Research of PJSC "Ukrtatnafta" (workplace instruction 26.012: 2010 "Determination of the metals content in oil and petroleum products by the atomic absorption method" (analogue of ASTM D 4628, 5863, 5184, etc.) on atomic absorption spectrophotometers

ContrAA 700, AAC-1N and C-115. The essence of the method is the mineralization of a sample when heated with concentrated sulfuric acid, followed by combustion the resulting mineralizate in a muffle furnace at 550 °C, dissolving the resulting ash in a nitrohydrochloric acid (“aqua regia”), dissolving the residue obtained after evaporation of the acid in bidistilled water and measuring the radiation intensity of the resonance lines of metals, which are excited in the spectrum of an air-gas (acetylene-air and acetylene-nitrous oxide) flame when the analyzed solutions containing these elements are introduced into it.

2.3. Obtaining Gasoline, Jet and Diesel Fractions. Research of Their Properties

Fuel fractions were obtained by distilling Nigerian oils on the ARN-2 apparatus. Fractional distillation of oils yielded gasoline fractions IBP-62 ºC, 62-105 ºC, 105-180 ºC, jet fractions 114-270 °C, diesel fractions 156-396 °C. The properties of these fractions were determined according to standard methods [79-98].

The structural-group composition of gasoline, jet and diesel fractions was determined using an Agilent-6890 gas chromatograph with a flame ionization detector, as well as by chromatography-mass spectrometry using an LKB-2091 mass spectrometer. Additionally, diesel fractions were examined on a Cary-50 spectrophotometer according to the workplace instruction PI 26.004. Aromatic hydrocarbons by groups in middle distillates were determined using UV spectroscopy.

The amount of nitrogen in gasoline and diesel fractions was determined according to the workplace instruction PI 26.011 “Determination of the total nitrogen content in oil and petroleum products”. Determination of nitrogen was carried out according to the Dumas-Pregl method, which is based on the combustion of organic matter mixed with copper oxide in an atmosphere of carbon dioxide. Carbon dioxide is passed through a quartz combustion tube before analysis (to displace air from it) and after combustion of the sample to displace combustion products from the tube: nitrogen, nitrogen oxides, water and carbon dioxide. The source of the carbon dioxide was a gas cylinder. The combustion part of the tube has a constant filling: a layer of copper oxide, a layer of reducing copper (to reduce nitrogen oxides to nitrogen), then again a layer of copper oxide.

The setup for the nitrogen determination is shown in Fig. 2.2.

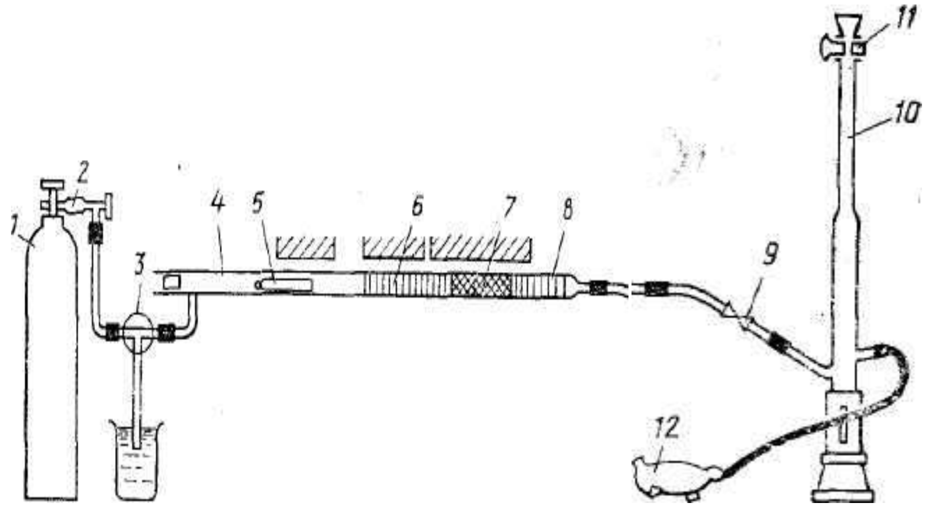

Fig. 2.2. **Laboratory setup for nitrogen determination according to Dumas-Pregl method**

1 - cylinder with solid CO_2; 2 - valve of fine adjustment; 3 – T-tap; 4 - quartz tube for combustion (length is not less than 500 mm); 5 - container for aliquot; 6, 8 - copper oxide (wire), layer lengths of 100 and 70 mm, respectively; 7 - reduced copper (wire), layer length 40-50 mm; 9 - tap with grooves; 10 - nitrogen meter, capacity of the graduated part is 1.5 or 2.5 ml; 11 - tap of the nitrogen meter funnel; 12 - pear; 13, 14 - furnaces SUOL-0.15, 0.6/1 IMP; 15 - SUOL-0.I5, 1.4/12MP

The source of carbon dioxide is a cylinder with solid CO_2, with a capacity of 3-5 liters, equipped with a shut-off valve 2 for fine adjustment of gas velocity. No more than 750 g of crushed dry ice is necessary for each liter of volume. The three-way tap 3, connecting the valve and the combustion tube, serves to roughly control the gas velocity during the working day according to the speed of the bubbles coming out of the tap into the water. The required gas velocity of 20-30 ml/min is set approximately, opening the shut-off and needle valves and passing the gas through the tap 3 into a glass of water. The correspondence between the number of bubbles and the passing volume of gas per unit time is determined for this setup once by a stopwatch using an aspirator. After filling the cylinder, a gas is venting for 30 minutes to release the air. Then the nitrogen meter is connected directly to the cylinder. Gradually opening the valve 9, one must see the appearance of microbubbles, indicating a sufficient purity of the gas. The tube for combustion 4 is permanently connected to the cylinder through the tap 3. It is made of well-fused quartz. When filling the tube, it is necessary to hold it vertically; each reagent is poured in small portions, and carefully compact by knocking.

The analysis is performed as follows. An accurately weighed sample (3-4 mg) is mixed with powdered copper oxide and placed in the combustion tube. The air is displaced from the tube by carbon dioxide until microbubbles appear in the nitrogen meter filled with 50% potassium hydroxide solution. Then the zone of constant filling is heated to 600-650 ºC by an electric furnace, and the sample is burned at a temperature of 700-750 ºC (in an electric furnace or using a gas burner).

Combustion is carried out in an atmosphere of carbon dioxide with the closed tap on a Kipp apparatus or cylinder. After combustion, the products are slowly displaced by carbon dioxide into the nitrogen meter with a velocity of not more than one bubble per second. Displacement ends when microbubbles appear in the nitrogen meter. The nitrogen content (x,%) is found by the formula:

$$x = \frac{mV}{g} \cdot 100 \tag{2.1}$$

where m is the weight of 1 ml of nitrogen under these conditions, mg, V is the nitrogen volume in the nitrogen meter, ml, g is the sample weight, mg

2.4. Obtaining Oil Fractions and Studying Their Properties

A wide oil fraction was obtained from Nigerian and Ukrainian oils using the ARN-2 apparatus at a residual pressure of 2 mm Hg. Narrow oil distillates were obtained by distilling a mixture of Nigerian oils (Nigeria 1 - 60%, Nigeria 2 - 40%). The following fractions were obtained: 350-400 °C, 400-450 °C and 450-500 °C.

The classic processes for obtaining base oils are solvent refining, dewaxing and hydro- or adsorption post-treatment. The promising ones are hydrocracking and hydroisomerization. The scheme of processing and use of oil distillate products is given in Fig. 2.3.

Oil distillates obtained in the process of vacuum distillation of fuel oil are directed to the process of solvent refining – the main process of petroleum oils production using selective solvents. The process is intended for extraction from oil distillates of resinous substances, polycyclic aromatic and naphthenic-aromatic hydrocarbons with short side chains, as well as sulfur-containing and metal-containing compounds. The important operational properties of oils such as viscosity-temperature properties and oxidation resistance are determined in this process. The efficiency of solvent refining is conditioned by the raw material quality, the nature and amount of the solvent, the process temperature, the frequency of processing and the design features of the extraction unit.

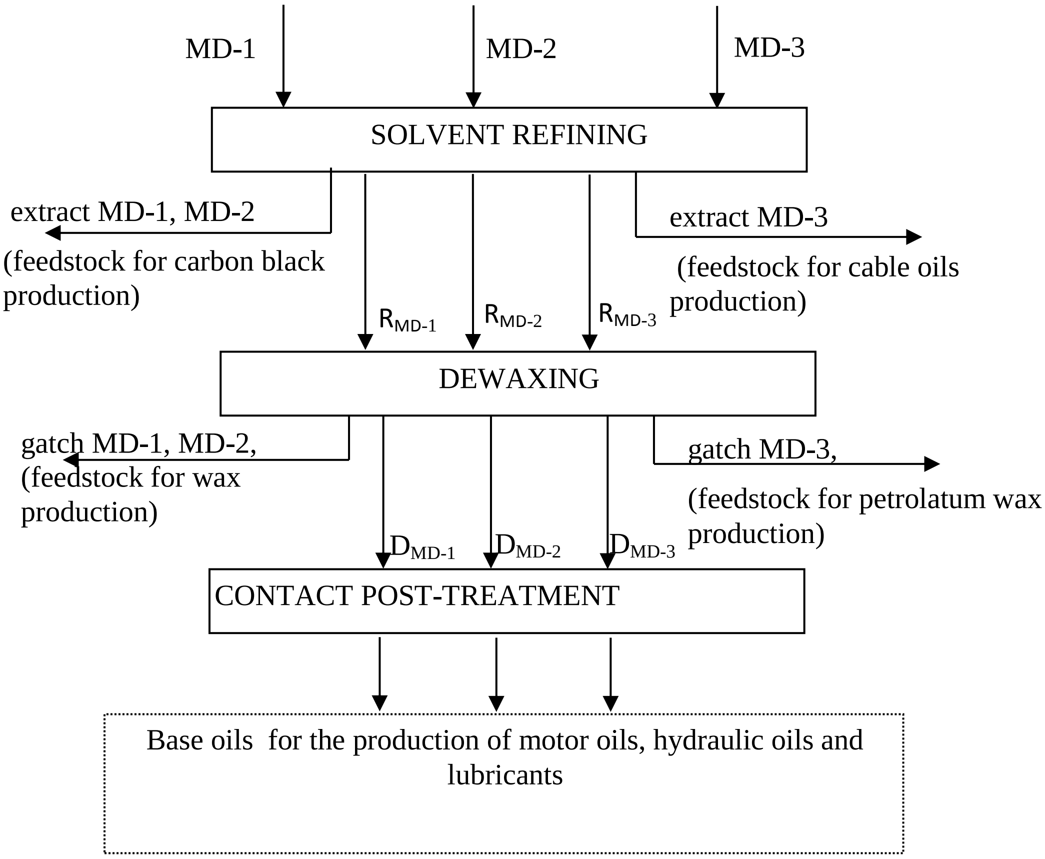

Fig. 2.3. Schematic diagram of oil distillates processing

To establish the quality of base oils all distillates under study were purified with a selective solvent N-methyl-pyrrolidone [56].

N-methylpyrrolidone (NMP) is thermally and hydrolytically highly stable, corrosive, has a high solubility, a low boiling point and can be used for oils treatment. NMP-refined oils have low cokeability, but worse viscosity-temperature properties and thermal-oxidative stability to compare with oils after phenol purification. The yield of raffinate after NMP refining is higher than that after purification by phenol [58].

The main disadvantages of NMP are its high cost and high boiling point (202 °C in comparison with 181 °C of phenol).

Solvent refining of oil distillates was performed in thermostated separating funnels. The temperature in the separating funnels was maintained by pumping water through the thermostat jackets. The mixture of oil and solvent was placed in an extractor and stirred for 20 minutes, then stirring was stopped and the mixture was held until complete transparency of the obtained phases, but not more than 20 minutes at the same temperature. After that, two formed phases were separated and their quantity was measured. Solvents were distilled off from the raffinate and extract solutions under vacuum and their yield was determined.

After solvent refining, the obtained raffinates are sent to the dewaxing process, the purpose of which is to extract solid hydrocarbons from oil raw materials. By solid hydrocarbons we mean all hydrocarbons which have a crystalline structure at room temperature. Hydrocarbons of this group are crystallized from a solution with the decrease in temperature and form a structured system that binds the liquid phase. Both solid and liquid hydrocarbons of oil fractions are a multicomponent system of paraffinic hydrocarbons (from C_{16} and above), which differ in structure, the number of carbon atoms in the molecule, the number of solid naphthenic hydrocarbons (containing 1-3 rings in the molecule and having long side chains of normal and isometric structure), as well as the number of solid aromatic and naphthenic-aromatic hydrocarbons (different in the total number of rings in the molecule, the ratio of aromatic and naphthenic rings, length and structure of side chains). The chemical composition of solid hydrocarbons in oil fractions depends on the nature of oil from which they are extracted. Dewaxing of oil distillates in the laboratory was performed using a mixture of methyl ethyl ketone and toluene.

After dewaxing, the oils were post-treated with 5% silica gel at 110 °C. The yield of refined oils after adsorption refining was about 97%. Physico-chemical properties of the resulting oil distillates were studied.

The hydrocarbon group composition of distillate oils has been studied in more detail by chromatography. The adsorption method for determining the group composition of oils is not standardized. ASK silica gel with a grain size of 0.2-0.6 mm was used as adsorbent. The oil was distributed to the fractions in a column with the length of 2500 mm and 35 mm in diameter. The column was charged with 800 g of silica gel, which was previously dried at 200 °C for 6 hours in an oven. The product : silica gel ratio is 1:8 (w/w). The oil sample was diluted twice with isooctane. The hydrocarbon fractions were sequentially eluted with isooctane, a mixture of isooctane with benzene (4:1, 1:1, 1:9) and pure benzene. The resinous substances were desorbed from the silica gel with a 1:1 alcohol-benzene mixture. The separation process was performed at elevated temperature. After distilling off the solvent in a stream of nitrogen, the obtained eluents were mixed to obtain paraffin-naphthenic and aromatic groups of hydrocarbons. We adopted a scheme of hydrocarbons grouping, developed earlier, i.e., the oil was divided into paraffin-naphthenic, three aromatic fractions and resinous substances. Paraffin-naphthenic hydrocarbons are referred to those which $n^{d}_{20}<1.49$. Aromatics are divided into groups: light aromatics with $n^{d}_{20} = 1.49 \div 1.53$, medium aromatics with n^{d}_{20} $1.53 \div 1.59$ and heavy aromatics with $n^{d}_{20}>1.59$ [99].

In addition to single-stage, three-stage countercurrent extraction was performed according to the pseudocurrent scheme. The procedure is described in the literature [100, 101].

The extraction process was considered effective when the yield of final and intermediate solutions became almost constant. For all oil distillates the following physico-chemical parameters were determined: kinematic viscosity according to GOST 33 [94], density according to GOST 3900 [79], solidification temperature according to GOST 20287 [90], flash point according to GOST 4333 [91], content of water-soluble acids and alkalis according to GOST 6307 [102], content of mechanical impurities according to GOST 6370 [103]. The refractive index was determined using a refractometer IRF-22, molecular weight was determined by cryoscopic method, acid number – by the method described in [104], the sulfur content was determined using double combustion. The Bogdanov distillation and ring analysis by the n-d-M method were performed as well.

2.5. Bitumen Obtaining and Studying its Properties

Bitumen was produced using the installation consisting of containers for feedstock, a tubular heater made of steel tubes, a reactor unit, an air supply system, a cooling system and the trap system for light oxidation products.

The laboratory setup for the production of oxidized bitumen is presented in Fig. 2.4 [105].

The feedstock from the heated container 1 is taken by the pump 7, pumped through the coil heater 2 and fed to the bottom of oxidizing column 3 or to the fitting located at ¾ of its height. The air supplied by the air compressor 9 through a tube passing inside the column enters the annular perforated manifold 11 located at the bottom of the column. Thus, the feedstock and the air can move bottom-up as parallel current or countercurrent flows.

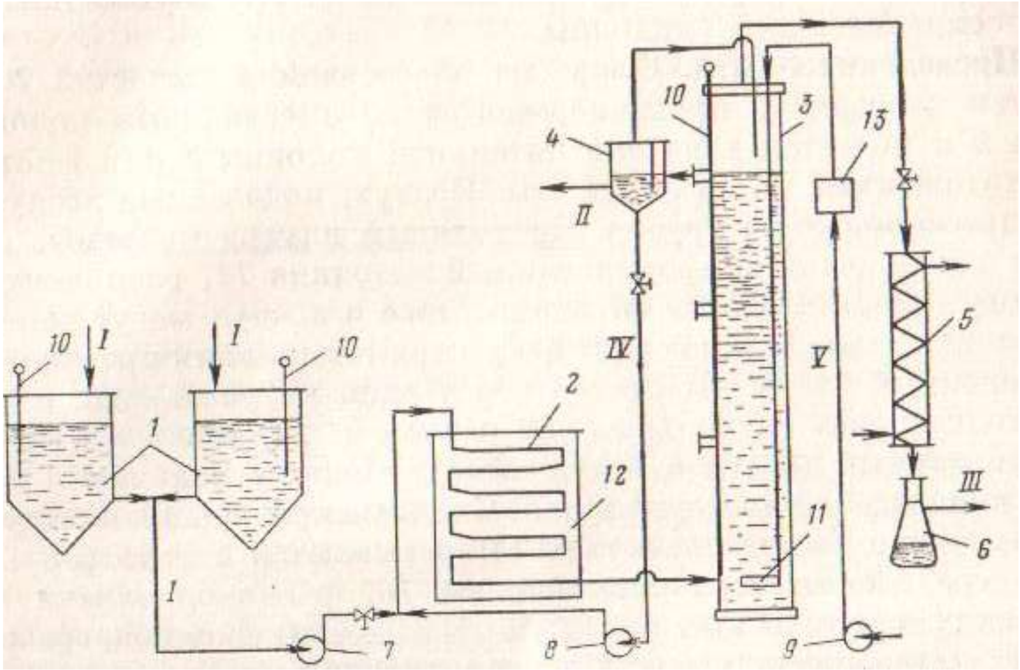

Fig.2.4. Laboratory setup for the production of oxidized bitumen

The oxidized bitumen is discharged through one of mentioned taps, passes through a hydraulic gate and enters the receiver. Exhaust air and vapors are discharged from the column top and pass through the condenser-refrigerator 5. The condensed vapors are collected in the receiver 6, and the gases are released into the atmosphere.

The temperature is measured by thermocouples 10 located at several points along the height of the column and in the coil heater. To put the unit into operation, it was necessary to do the following: to heat the feedstock in the container, tubular heater and column to the designed temperature; to fill the column with feedstock to the intended level corresponding to one of the side taps. At periodic oxidation of tar in a column it was necessary to stop supply of feedstock, begin air supply with a speed of 3-15 l/min and set a stable temperature in the column in the range of 180-250 °C.

Bitumen is a complex mixture of high molecular petroleum compounds and their oxygen-, sulfur-, nitrogen- and metal-containing derivatives. The elemental composition of bitumen varies within the following limits (% wt.): Carbon 80-85, Hydrogen 2-8, Oxygen 0.5-5, Nitrogen up to 1, Sulfur up to 7. It depends on the oil nature, the composition of feedstock (petroleum residues) and the technology of its production.

The main properties of bitumen are: softening temperature, penetration, ductility and brittle point.

Penetration for bitumen was determined by the standard method according to DSTU EN 58 [107].

The group chemical composition was determined according to the Marcuson method [108].

Ductility was determined according to GOST 11505 [109].

The brittle point (BP) was determined according to DSTU EN 12593 [110]. The conditions of determination are strictly standardized and are identical to the standards IR 80, EN 12593, JIS K2207.

2.6. Evaluation of the Effectiveness of the Developed Refinery

The indices “oil refining depth”, “yield of light petroleum products”, “share of secondary processes” and “complexity factor” (Nelson complexity index) were used to evaluate the developed refinery [112–120].

2.6.1. Calculation of the oil refining depth

Oil refining depth is a value that shows the ratio of the oil refining products volume to the total volume of crude oil. It was calculated by the following formula

$$ORD = [(CO - FO - F - L)/CO] \cdot 100\ \% \qquad (2.2)$$

where ORD is a refining depth; CO is crude oil; FO is fuel oil; F – is fuel for own needs; L is loss.

This index determines the level of crude oil conversion into motor fuel, oils and feedstock for petrochemistry.

2.6.2. Estimation of light products yield

The yield of light fractions (petrol, kerosene, diesel, etc.) was determined according to the TBP curve of the studied oil. This yield (in wt. %) is called the potential content of given fraction in oil (theoretical yield), and the total yield of the fractions boiled up to 350 °C – the potential content of the sum of light fractions in oil ($P\sum_{l.fr.}$).

In practice, when distilling oil, it does not matters how many light fractions are distilled at ARN-2, but it is important how much light petroleum products of marketable quality can be obtained from crude oil by distilling it in industrial conditions. Such properties of oil, as the content of paraffins, sulfur, etc. have an effect on the possibility of obtaining marketable products. In this case, the characteristic of oil is the actual amount of light petroleum products ($A\sum_{pet.pr.}$), which can be obtained from this oil in the industrial conditions.

We calculated the ratio $A\sum_{pet.pr.}$ / $P\sum_{l.fr.}$, which is called the potential selection, expressed either in % or unit fractions. The value of $A\sum_{pet.pr.}$ depends not only on the quality of oil, but also on the range of light petroleum products which are actually obtained from this oil. This value with a high degree of accuracy makes it possible to determine the potential content of light fractions in oil when obtaining marketable products and, therefore, makes it possible to quickly assess the future material balance of mini-refineries when working on different types of raw materials [112-120].

The light distillates yield (LDY) was determined by the formula:

$$LDY = (G + K + D + A + LP + LG + S) / C \qquad (2.3)$$

where G, K, D, A, LP, LG and S are the amounts of gasoline (automotive and aviation), kerosene, diesel fuel, aromatic hydrocarbons, liquid paraffins, liquefied gases, and solvents, respectively, thousand tons/year; C is a refinery capacity, thousand tons/year.

2.6.3. Calculation of the secondary processes share

The mentioned indices do not reflect the quality of the received petroleum products, but only indirectly allow to estimate the level of processing of residual raw materials, including fuel oil and tar. In other words, the implementation of new isomerization or alkylation plants in the scheme of the refinery will not affect the oil refining depth. Thus, the increase in the refining depth as a result of the introduction into the current scheme the processes for residual raw materials processing does not always indicate an increase in the efficiency of the enterprise. The latter requires the establishment of all technological processes, including ennobling processes, necessary to obtain marketable products of the required quality. The index “share of secondary processes” is to some extent deprived of these deficiencies.

The secondary processes include:

1) processes that deepen oil refining;
2) processes that ensure or improve the quality of petroleum products.

The first group includes hydrocracking, catalytic cracking, thermocracking, etc., which allow to obtain lighter hydrocarbon fractions due to the destructive conversion of heavy raw materials, as well as processes of production of bitumen, oils, paraffins, etc., which reduce the production of fuel oil. The second group consists of the isomerization and catalytic reforming of gasoline fractions, hydrotreating of motor fuels, processes of alkylation, production of oxygenates, hydrotreating of thermal oils and boiler fuels, etc., which determine the quality of marketable products.

The share of secondary processes was calculated as the ratio of the sum of plants capacities to the amount of refined crude oil [113].

The index “share of secondary processes”, on the one hand, characterizes the presence in the current scheme of destructive and ennobling processes aimed at the efficient use of crude oil. On the other hand, this indicator does not take into account the quality of product obtained at the individual technological stages, for example, the sulfur content in the kerosene fraction after hydrotreating, as well as the operation mode of plants, in particular for hydrocracking (“light” mode at medium and high pressures).

2.6.4. Calculation of the refinery complexity index

The coefficient of complexity (Nelson complexity index, NCI) is widely used in the world practice [112-120]. It is a measure to compare the secondary conversion capacity of a refinery with the primary distillation capacity. This concept, developed by W.L. Nelson in the 1960s, is a pure cost index that provides a relative measure of the construction costs of a particular refinery based on its crude and upgrading capacity. Based on the NCI and the shares of individual processes calculated in relation to the capacity of primary distillation, the rating of the refinery complexity is determined. The formula to calculate refinery complexity is the following:

$$CI = \sum x_i \cdot NCI_i \tag{2.4}$$

where x_i is the share of the i-th process, defined as the ratio of its capacity to the capacity of the atmospheric distillation unit; NCI_i is the Nelson index of the i-th process.

The Nelson index is a convenient indicator for comparing the investment required to build a refinery with a different set of processes, i.e., the Nelson index characterizes the measure of perfection of the refinery scheme in terms of capital intensity. The complexity factor can be used for a comparative assessment of individual refineries or in total for enterprises of the whole region.

The rating of the refinery complexity is a purely economic assessment of the enterprise construction costs and does not reflect its technological level.

Conclusions to Chapter 2

Standardized methods of analysis of oils and their fractions are described. The determination of the fractional composition by the method of simulated distillation using a gas chromatograph HP 7890, as well as determination of metals using atomic absorption spectrophotometers Contr A 700, AAS-1N and C-115 are described.

The analysis methods of distillate and oil fractions, tar and bitumen are described.

The methods of oil fractions solvent refining, dewaxing, adsorption refining and bitumen obtaining from tar are given.

CHAPTER 3

STUDIES ON PHYSICO-CHEMICAL PROPERTIES OF NIGERIAN OILS AND PRODUCTS OBTAINED FROM THEM

Oils from different fields and even different wells differ in fractional composition and physico-chemical properties. The hydrocarbon composition of oils also differs.

It is known that the properties of oils determine the direction of their processing, affect the quality of the obtained petroleum products.

To develop an option of Nigerian oil refining and, in particular, to establish the possibility of its refining at petroleum refineries of Ukraine the physico-chemical parameters of oils from in Ukrainian and Nigerian fields were investigated. Nigerian Brent Dated and Bonny Light oils (designated as Nigeria 1 and Nigeria 2) were used for the comparison. They were compared with oil mixtures of eastern and western fields of Ukraine, which are processed at Ukrainian refineries. The researches were conducted at the Chemistry Center of the National Aviation University, at the Department of Chemical Technology of Oil and Gas Refining of Lviv Polytechnic National University and in the laboratories of PJSC “Ukrtatnafta”.

When evaluating oil as an industrial raw material, the primary interest is the content of the highest quality components and the characteristics of their physic-chemical and operational properties, which will allow to judge the quality of marketable products derived from this oil.

3.1. Studies on Physico-Chemical Properties of Nigerian Oils and Oil Mixtures from the Eastern and Western Regions of Ukraine

Table 3.1 shows the main indices of physico-chemical properties of oils under study. Density is one of the important characteristics that allows, in combination with other values, to estimate the chemical and fractional composition of oil and petroleum products. Depending on this index, oils are classified as light, medium and heavy, respectively [21]. High quality oils are produced from light crude oils containing high amount of gasoline fractions and relatively small amount of tar and sulfur. Heavy oils are characterized by a high content of resins. To obtain oils from them, it is necessary to use special purification methods – treatment with selective solvents, adsorbents, and so forth. However, heavy oils are the best feedstock for bitumen production. According to the density, Nigeria 1 oil can be classified as light oil ($\rho_{15}^{15} \leq 828$ kg/m^3), Nigeria 2 oil is slightly heavier and belongs to medium oil (ρ_{15}^{15} = 828-884 kg/m^3). Ukrainian oils are similar to Nigeria 2 oil.

Table 3.1

Characteristics of investigated oils

Index	Nigeria 1 oil	Nigeria 2 oil	Mix of Eastern-Ukrainian oils	Mix of Western-Ukrainian oils
Density at 20 ºC, kg/m^3	806.8	844.0	844.7	846.6
Sulfur content, wt.%	0.37	0.18	0.87	0.43
Water content, %	absence	0.30	0.03	0.25
Salts content, mg/dm^3	2.9	21.9	8.2	40.8
Sour sulfur content, wt.%	0.0097	0.0023	0.0012	0.0005
Pour point, ºC	-18	0	-29	13
Sulfuric acid resins content, %	8	14	29	20
Acidity, mg KOH per 100 cm^3	1.77	4.92	1.33	3.88
Relative viscosity at 50 ºC, °RV	1.1	1.45	1.2	1.3
Dissolved gases content, wt.%	0.32	0.26	0.35	0.51
Yield of gasoline fraction distilled up to 180 ºC, wt.%	37.0	19.5	29.5	22.0
Yield of fraction distilled up to 360 ºC, wt.%	72.0	57.3	59.0	54.5

Sulfur content is one of the essential technological characteristics of oils. Depending on sulfur content oils are divided into 3 classes: Class I - low-sulfur oils with a sulfur content of 0-0.5%; Class II - sulfur oils with a sulfur content of 0.51-1.9%; Class III - high-sulfur oil with a sulfur content of more than 1.9% [21]. Sulfur content in the Nigeria 1 and Nigeria 2 oils is low (0.37 and 0.18%, respectively), so they belong to class I. The content of sulfur in Ukrainian oils is slightly more, so the Eastern Ukrainian oil should be classified as class II, Western Ukrainian oil – as class I. The presence of sulfur compounds (hydrogen sulfide, elemental sulfur, mercaptans, etc.) is undesirable, because they reduce the quality of petroleum products, cause corrosion of equipment and pollute the atmosphere during combustion. Sulfur compounds poison expensive catalysts of secondary processes and, resulting sulfur oxides which release into the atmosphere during combustion, create additional environmental problems. When determining the oil classification by sulfur content, it is necessary to determine its amount in products derived from oil. If the sulfur content is higher or less than the standard for oil, then oil is classified as lower or higher class. Thus, the sulfur content was determined for each narrow fraction (Table 3.2).

The content of sulfur compounds in the gasoline fractions of Nigerian and Ukrainian oils is comparable. In the jet fuel fractions of Nigeria 1 oil, the content of sulfur compounds is similar to that in the mixture of Eastern-Ukrainian oils, and sulfur compounds in Nigeria 2 oil is even slightly less than in the mixture of Western-Ukrainian oils. The content of sulfur compounds in the diesel fractions of Nigeria 1 and Nigeria 2 oils is lower than in the mixture of Ukrainian oils. The content of sulfur compounds in vacuum distillates of Nigerian oils is much lower in comparison with the mixtures of Ukrainian oils, which will improve the operating conditions of catalytic cracking plants at PJSC “Ukrtatnafta”.

According to the yield of fractions distilled up to 350 °C, all investigated oils belong to the first type [21].

Water content in Nigerian oils is relatively low (0.3% for Nigeria 2) or zero (Nigeria 1). This facilitates their transportation and preparation for processing. The water content in Ukrainian oils is similar.

The pour point of Nigerian oils is significantly lower than that of Western-Ukrainian oil and higher than the value of Eastern-Ukrainian oil. The content of sulfuric acid resins in Nigerian oils is lower in comparison with Ukrainian oils. The relative viscosity at 50 °C of all oils under study is comparable.

Table 3.2

Sulfur content in the narrow fractions of investigated oils

Fraction	Nigeria 1 oil	Nigeria 2 oil	Mix of Eastern-Ukrainian oils	Mix of Western-Ukrainian oils
IBP-62 °C	0.022	0.018	0.005	0.003
62-85 °C	0.021	0.004	0.007	0.005
85-105 °C	0.019	0.005	0.006	0.002
105-120 °C	0.027	0.012	0.006	0.004
120-140 °C	0.035	0.018	0.009	0.005
140-160 °C	0.046	0.019	0.018	0.011
160-180 °C	0.046	0.019	0.035	0.020
180-200 °C	0.060	0.024	0.057	0.034
200-220 °C	0.055	0.039	0.079	0.049
220-240 °C	0.108	0.047	0.110	0.072
240-260 °C	0.218	0.058	0.205	0.105
260-280 °C	0.362	0.070	0.385	0.184
280-300 °C	0.387	0.081	0.517	0.238
300-340 °C	0.446	0.130	0.674	0.362
340-360 °C	0.636	0.182	0.867	0.430
360-370 °C	0.654	0.210	0.942	0.437
residue, %	0.974	0.317	1.833	0.810
Vacuum distillate (vacuum distillation using ARN-2)	0.716	0.212	1.089	0.501
Residue after vacuum distillation using ARN-2	1.217	0.428	2.409	1.142

The yield of gasoline and diesel fuels from Nigeria 1 oil is high and the yield of light fractions of Nigeria 2 and Ukrainian oils is comparable.

Table 3.3 shows the fractional composition of oils, which was studied according to the method of ASTM D 86-16a.

The residue of investigated oils (> 370 ºC) was distilled according to the method of ASTM D 1160 [75], the results are given in Table 3.4.

Table 3.3

The fractional composition of the studied oils determined by the method of ASTM D 86-16a (vol.%)

Distilled temperature	Nigeria 1 oil	Nigeria 2 oil	Mix of Eastern-Ukrainian oils	Mix of Western-Ukrainian oils
IBP	50	58	51	57
80 °C	7.5	3.0	5.5	4.0
100 °C	12.0	4.0	11.5	7.0
120 °C	18.0	6.5	18.0	10.0
140 °C	26.0	10.0	23.0	14.0
160 °C	30.5	14.0	27.5	18.0
180 °C	35.0	18.5	31.0	22.0
200 °C	40.0	22.5	34.5	26.0
220 °C	44.5	27.0	38.0	29.0
240 °C	49.0	31.0	41.0	32.5
260 °C	53.0	35.0	45.0	36.0
280 °C	57.5	39.0	49.0	40.0
300 °C	61.5	44.0	53.0	44.5
320 °C	65.5	48.5	56.0	49.0
340 °C	69.0	53.0	60.0	54.0
350 °C	70.5	56.0	62.5	56.0
360 °C	72.5	58.0	65.0	57.0

Table 3.4

Fractional composition of the residue of investigated oils (vol. %)

Distilled temperature	Nigeria 1 oil	Nigeria 2 oil	Mix of Eastern-Ukrainian oils	Mix of Western-Ukrainian oils
IBP	370	380	370	373
420 °C	18,4	7,3	12,7	17,2
430 °C	23,9	15,4	17,0	22,6
440 °C	30,5	22,1	21,1	27,5
450 °C	36,0	28,4	25,9	32,1
460 °C	41,2	34,0	30,1	36,5
470 °C	46,0	39,0	34,3	40,8
480 °C	50,8	43,6	38,3	44,8
490 °C	54,7	47,8	41,6	52,1
500 °C	58,6	51,7	43,7	56,0
510 °C	62,2	55,5	46,8	57,5

Table 3.5 represents the total yield of the fractions, which was obtained by the method of simulated distillation.

Based on the results of atmospheric distillation, it can be argued that Nigeria oil 1 is light, with initial boiling point of 50 °C; Nigeria oil 2 is heavier, its IBP is 58 °C. The amount of gasoline fractions distilled up to 180 ºC is 19.5% for Nigeria oil 2 and 37% for Nigeria oil 1. The values almost coincide with those of Ukrainian oils (potential content of gasoline fractions in Ukrainian oils are 29.5 and 22%, respectively). The potential content of diesel fraction in Nigeria 1 oil is ≈35%, in Nigeria 2 oil ≈38%. The potential content of the diesel fraction in the oils of Eastern and Western Ukrainian oils is 29.5 and 32.5 wt.%, respectively.

Table 3.5

The total yield of fractions (TBP) (wt. %)

Distilled temperature	Nigeria 1 oil	Nigeria 2 oil	Mix of Eastern-Ukrainian oils	Mix of Western-Ukrainian oils
to 69	**2,8**	**2,6**	**1,7**	**1,4**
80	8	4,4	6,0	3,5
90	12	5,9	9,5	5,5
100	15	7,3	12,5	8,0
110	18	8,6	15,5	10,0
120	21	10,0	18,0	11,5
130	23	11,5	20,0	13,0
140	26	13,1	22,0	14,5
150	29	14,8	24,0	16,5
160	32	16,4	26,0	18,5
170	34,5	17,9	28,0	20,0
180	**37**	**19,5**	**29,5**	**22,0**
190	39,5	21,2	31,0	23,5
200	42	22,7	32,5	25,0
210	44	24,4	34,0	26,5
220	46,5	26,3	36,0	28,0
230	48,5	28,0	37,5	29,5
240	50,5	30,1	39,0	31,5
250	53	31,9	41,0	33,5
260	55	33,8	42,5	35,5
270	57	36,0	44,5	37,0
280	59	38,4	46,0	39,0
290	61	40,7	48,0	41,0
300	62,5	42,8	49,5	43,0
310	64	45,0	51,0	45,0
320	66	47,7	53,0	47,5
330	67,5	50,3	54,5	49,0

340	69	52,9	56,0	51,0
350	71	55,0	57,5	53,0
360	**72**	**57,3**	**59,0**	**54,5**
370	73,5	58,8	60,5	56,5
380	75	60,3	62,0	58,0
390	76,5	62,3	63,5	60,0
400	78	63,8	65,0	62,0
410	79	64,3	66,5	64,0
420	80,5	65,3	68,0	65,5
430	82	67,8	69,5	68,0
440	83,5	70,3	71,0	70,0
450	85	73,0	72,5	72,0
460	86	75,0	74,0	73,5
470	87,5	77,0	75,5	75,5
480	88,5	79,0	76,5	77,5
490	90	80,5	78,0	79,0
500	**91**	**82,0**	**79,0**	**80,5**
510	92	84,0	80,5	82,0
520	93,5	85,0	81,5	83,0
530	95	86,0	83,0	85,0
540	95,6	86,7	83,5	85,7
Residue >540 °C	4,4	13,3	16,5	14,3

The yield of jet fuel fractions of Nigeria 1 and Nigeria 2 oils is 24.5 and 17.0%, respectively, which is significantly higher than for the mixtures of Ukrainian oils. The yield of a broad oil fraction (360-540 °C) for Nigerian oils is 23.6-29.4%, for Ukrainian oils is 24.5-31.2%.

The microelement composition of oil is an important characteristic. It contains geological and geochemical information, indicating, in particular, the age of oil, ways and directions of its migration and accumulation. In the near future, oil may become a feedstock for the production of vanadium, nickel, copper, precious metals. Moreover, the metals in crude oil can have a significant impact on oil refining processes, taking into accout the poisoning of catalysts, corrosion of equipment and the ingress of significant amounts into the resulting petroleum products. It is established that the concentrations of metals in oil vary in a relatively wide range, and their average values decrease from nx10^{-3} to nx10^{-8} (wt.%) in the sequence: V, Fe, Ca, Ni, Na, K, Mg, Al, Hg, Zn, Mo, Cr, Cu, Co, Mn, Ba, Ge, Ag, Hf, Pb, Au, Be, Ti, Sn. In total, more than 60 microelements were found in oil [20-23]. The technological regulations of the relevant industries regulate the content of metals-catalyst poisons, including the content of copper for raw materials (gasoline fractions) of reforming, isomerization, etc.; content of V, Ni, Fe for raw materials (vacuum gas oils and oil residues) of catalytic cracking and hydrotreating of high-boiling oil fractions. Table 3.6 presents data on the metal content in oils.

It should be noted that vanadium and nickel present in oils have a negative effect on the catalysts used for their processing, which creates great difficulties in the implementation of cracking, pyrolysis, etc. The content of vanadium does not affect the properties of bitumen. Vanadium is completely concentrated in resin-asphaltene hydrocarbons, so vanadium oxide is formed when fuel oil is combusted. The oxide strongly corrodes the fuel equipment and poisons the environment. The amount of vanadium in the studied oils of Nigeria 1 is 0.24 ppm, Nigeria 2 - 1.28 ppm, in the mixture of Western-Ukrainian oils its amount is 1.91 ppm, and in the mixture of Eastern-Ukrainian oils - almost 11 ppm. The amount of vanadium is associated with sulfur compounds in oil, as it provides the reduction of sulfates to hydrogen sulfide and free sulfur. Indeed, in Eastern-Ukrainian oil with the highest vanadium content, the amount of sulfur (0.87%) exceeds its amount in other oils. Fuel oil produced from Nigerian oil can be used as a high quality boiler fuel.

Table 3.6

Metals content in the investigated oils, mg/kg

Metal	Nigeria 1 oil	Nigeria 2 oil	Mix of Eastern-Ukrainian oils	Mix of Western-Ukrainian oils
iron	**2.96**	**1.3**	**41.35**	**4.6**
zinc	0.72	0.38	4.21	1.79
nickel	**0.18**	**3.18**	**10.9**	**3.67**
vanadium	**0.24**	**1.28**	**10.99**	**1.91**
copper	**4.73**	**0.08**	**0.59**	**0.1**
manganese	not found	not found	0.13	0.21
cromium	not found	not found	0.22	0.07
calcium	6.52	5.07	1.64	7.47
magnesium	2.05	1.27	1.17	5.91
sodium	5.77	6.05	**10.14**	**58.49**
potassium	0.63	0.36	0.43	0.92
cobaly	0.15	not found	not found	not found
lead	not found	0.1	0.59	not found
barium	not found	not found	0.25	14.6
molibdenum	0.02	0.841	0.11	traces
aluminium	not found	2.346	6.44	3.42
silicon	0.24	5.752	1.48	0.25

Nickel is also mainly found in high-molecular components of oil in the amount of 10^{-4} to 10^{-3}%, and in small quantities it is also found in the oil fractions of heavy oil. Nickel, like vanadium, is present in porphyrin complexes of oil. Its amount in the studied oils of Nigeria 1 and Nigeria 2 is 0.18 and 3.18 ppm, respectively, in Eastern-Ukrainian oil the amount of this metal is 10.99 ppm, in Western-Ukrainian oil it is three times less - 3.67 ppm.

Nigeria 1 oil belongs to the vanadium type of oil because the ratio of V/Ni > 1 [121].

Iron is present in relatively small amounts in Nigeria 1 and Nigeria 2 oils. During distillation, iron is distributed throughout all fractions. The nature of its compounds has been insufficiently studied; it is assumed that Fe is present in the form of porphyrin complexes. The largest amount of iron was found in Eastern-Ukrainian oil (41.35 ppm), a relatively small amount in other oils (2.96, 1.3 and 4.6 ppm).

The amount of alkali and alkaline earth metals (sodium, potassium, magnesium, calcium) in oil is usually from 10^{-3} to 10^{-4}%. These elements are an integral part of stratal water. Even the most thorough preparation of oil will not result in complete purification from these micro-impurities. Studies show that all alkali and alkaline earth metals are in the form of petroleum acid salts, phenolates, thiophenolates, etc., and are found in all fractions. Among the alkaline earth metals found in the studied oils, sodium has a largest share. In Western-Ukrainian oil its share is the largest one (58.49 ppm), in Eastern-Ukrainian oil it is almost 6 times less (10.14 ppm). In Nigerian oils, sodium is present in small amounts - 5.77 and 6.05 ppm. The content of calcium in Nigerian oils is comparable to the Eastern Ukrainian oil (5-7 ppm), in the mix of Western Ukrainian oils its content is the lowest (1.64 ppm). The potassium content is insignificant in all oils - less than 1 ppm.

Copper is found in all oils under study. The largest amount was found in Nigeria 1, in other oils its amount is insignificant (less than 1 ppm).

3.2. Studies on Gasoline Fractions of Nigerian Oils

The main parameters for assessing the quality of gasoline fractions are: density, acidity, total sulfur content, fractional composition, octane number, copper corrosion test, existent gum, saturated vapor pressure, mechanical impurities and water [122-125].

The gasoline fraction is characterized by boiling points of IBP-200 °C and is obtained as the upper distillation product of atmospheric distillation. Since the octane number of the straight-run gasoline fraction does not meet the requirements of commercial gasoline, it is divided into narrow fractions at the secondary distillation unit. To determine the properties of gasoline fractions the following fractions were isolated: IBP-62 ºC, 62-105 ºC, 105-180 °C.

The results of the study of straight-run gasoline fractions are presented in Table 3.7.

Table 3.7

Physico-chemical properties of gasoline fractions

Index	Units	Nigeria 1 oil	Nigeria 2 oil	Mix of Eastern-Ukrainian oils	Mix of Western-Ukrainian oils
IBP-62 °C					
Initial boiling point	°C	50	58	51	57
Sulfur content	%	0.022	0.016	0.005	0.003
Sour sulfur	%	0.0147	0.0121	0.0003	absence
Acidity	mg KOH per 100 cm^3	0.22	0.21	absence	0.22
Fraction 62-105 °C					
Sulfur content	%	0.020	0.0092	0.004	0.005
Sour sulfur	%	0.001	0.00049	0.00043	0.00071
Acidity	mg KOH per 100 cm^3	0.40	1.15	0.09	0.40
Nitrogen content	ppm	0.14	0.18	0.48	0.84
Toluene-forming					
methylcyclohexane	%	7.52	11.23	12.76	13.37
toluene	%	5.25	4.37	6.43	8.27
heptane	%	15.91	9.50	9.16	12.66
cis-1,3-dimethylcyclopentane	%	1.67	1.44	1.79	2.47
trans-1,3-dimethylcyclopentane	%	1.56	1.39	1.62	2.30
trans-1,2-dimethylcyclopentane	%	3.47	3.05	3.08	5.00

Total of toluene-forming	%	35.38	30.98	34.84	44.07
Benzene-forming					
methylcyclopentane	%	3.96	6.59	6.12	6.62
cyclohexane	%	4.74	6.83	10.16	7.82
hexane	%	12.92	9.67	11.46	7.78
benzene	%	2.27	1.85	4.69	4.42
Total of benzene-forming	%	23.89	24.94	32.43	26.64
Fraction 105-180 °C					
Sulfur content	%	0.039	0.019	0.016	0.011
Sour sulfur	%	0.0030	0.00115	0.0007	0.0006
Acidity	mg KOH per 100 cm^3	0.89	14.23	0.44	1.11
Nitrogen content	ppm	0.17	0.18	0.40	0.45
Group composition					
Light hydrocarbons including C_4	%	-	0.01	-	-
Aromatic	%	22.39	22.99	24.09	25.83
Naphthenic	%	20.38	22.96	28.18	23.19
Paraffinic	%	57.23	54.04	47.73	50.98
Unsaturated	%	-	-	-	-
Benzene	%	0.19	0.01	0.10	0.09
Toluene	%	3.46	1.89	5.39	3.63

The following fractions were obtained:

- Fraction IBP-62 °C is a feedstock for the isomerization plant of light gasoline fraction or a component of commercial gasoline. The fraction is characterized by low sulfur content of 0.022 and 0.016%, and sour sulfur content of 0.0147 and 0.0121% for Nigeria 1 and Nigeria 2 oils, respectively. These values are slightly higher than values of Ukrainian oils, however, they will be a good feedstock for the isomerization process and production of high-octane gasoline component.

- Fraction 62-105 °C (benzene-toluene fraction) is a feedstock for the production of benzene and toluene at the catalytic reforming plant in order to obtain individual arenes or a component of commercial gasoline (in the absence of corresponding plant). The amount of toluene-forming and benzene-forming hydrocarbons was determined in this fraction. Thus, in Nigeria 1 and 2 oils the amount of toluene-forming compounds is 35.38 and 30.98%, respectively, while in the mixture of Western-Ukrainian oil their amount is 44%, in Eastern-Ukrainian oil it is almost 35%. The amount of benzene-forming hydrocarbons in Nigerian oils is about 24-25%, in Ukrainian oils their amount is slightly higher (32.43 and 26.64%). The amount of sulfur and sour sulfur in these fractions is insignificant.

- Fraction 105-180 °C is a feedstock for fuel catalytic reforming. As this process uses an expensive catalyst of new generation, special attention should be paid to the content of sulfur and nitrogen in the feedstock. Thus, in Nigeria 1 and 2 oils, the sulfur content is 390 and 190 ppm, respectively; nitrogen content is 0.17 and 0.18 ppm, respectively. This is a large enough quantity and these compounds can poison the catalyst of reforming. Therefore, in this case the process of preliminary hydrotreating under stringent conditions must be carried out.

Aromatization of gasoline during reforming is carried out due to dehydrogenation of six-membered naphthenes and dehydrocyclization of paraffins. Therefore, special attention should be paid to the hydrocarbon composition of the fraction 105-180 ºC. The largest amount of naphthene-paraffins in this fraction is contained in Nigeria 1 and Nigeria 2 oils (77.61 and 77 %, respectively), in Ukrainian oils the amount of mentioned components is slightly less. At the same time, the amount of aromatic hydrocarbons in Ukrainian oils is higher by 2-3 % in comparison with Nigerian oils. The obtained results show that Nigerian and Ukrainian oils will be a good feedstock for the reforming.

3.3. Studies on Jet Fuel Fractions of Nigerian Oils

The determined physico-chemical properties of jet fuel fractions of Nigerian and Ukrainian oils are presented in Table 3.8.

One of the main requirements for jet fuel is the content of corrosive components [126-129]. Low corrosion activity (aggressiveness) is determined by the content of total sulfur (content of heteroatomic compounds), which should not exceed 0.1-0.2% and the content of sour sulfur (not more than 0.003%). The jet fuels obtained from Nigerian and Ukrainian oils do not meet this requirement, so purification from sulfur compounds is mandatory here. The content of acids, alkalis and mechanical impurities in jet fuel is unacceptable. The ash content of jet fuels should not exceed 0.003%. All jet fuels under study meet this requirement.

One of the necessary requirements for jet fuels is a low ability to form deposits. The content of aromatic hydrocarbons in jet fuel for subsonic aircrafts should not exceed 22%, for supersonic aircrafts – not more than 10%, for the fuel of grade T-6 and T-8B – not more than 22% [129]. In this case, the amount of aromatic hydrocarbons in jet fuels derived from Nigerian and Ukrainian oils are in the range of 17.6-20.4%.

Table 3.8

Characteristics of jet fuel fractions

Parameter	Nigeria 1 oil	Nigeria 2 oil	Mix of Eastern-Ukrainian oils	Mix of Western-Ukrainian oils
1. Fractional composition				
IBP	134	135	136	136
10 %	145	148	151	151
20 %	160	164	166	166
30 %	171	175	176	176
40 %	178	183	185	185
50 %	**189**	**195**	**197**	**196**
60 %	198	203	204	203
70 %	209	214	215	213
80 %	218	224	224	221
90 %	234	237	237	236
95 %	243	249	**248**	245
98 %	263	265	269	270
Sulfuric compounds content, wt.%	0,063	0,030	0,060	0,037
Flash point (closed cup), ºC	34	36	35	37
Viscosity at 20ºC, mm^2/s	1,40	1,30	1,46	1,50
Aromatic compounds content, wt %	18,2	17,6	20,4	19,2
Ash content, wt.%	0,002	0,001	0,003	0,002

3.4. Studies on Diesel Fractions of Nigerian Oils

The results of determining the physico-chemical properties and group composition of the diesel fractions of the studied Nigerian oils are given in Table 3.9.

Table 3.9

Characteristics of diesel oil fractions

Parameter	Nigeria 1 oil	Nigeria 2 oil	Mix of Eastern-Ukrainian oils	Mix of Western-Ukrainian oils
1. Fractional composition				
IBP	181	183	185	184
10 %	215	216	219	222
20 %	235	236	240	244
30 %	253	254	265	259
40 %	268	269	271	274
50 %	**286**	**286**	**288**	**291**
60 %	302	302	304	306
70 %	318	317	321	323
80 %	341	337	343	344
90 %	348	349	349	348
95 %	**354**	**356**	**358**	**357**
EBP	396	402	397	403
2. Polycyclic aromatics content, wt.%;	8,4	8,4	7,2	6,4
3. Flash point (closed cup) ºC	56	57	59	58
4. Pour point, ºC	-12	-8	-16	+5
5. Coking	0,23	0,24	0,25	0,24

ability 10 % wt% .				
6. Viscosity at 40 ºC, mm^2/s (no less)	3,645	3,53	4,21	3,92
7. Sulfuric compounds content, wt.%	0,29	0,08	0,36	0,18

Diesel fuels derived from Nigerian oils are similar to those derived from mixtures of Eastern and Western Ukrainian oils in terms of flash point, pour point, coking ability, viscosity, and sulfur content. The content of monocyclic, bicyclic, total aromatic hydrocarbons, polycyclic hydrocarbons in diesel fractions of all oils are comparable (Table 3.10). Nitrogen content in diesel fuels from Nigerian oils is 2-3 times lower than in diesel fuel derived from Ukrainian oils.

Table 3.10

Content of aromatic hydrocarbons and total nitrogen in the diesel fuel

Place and date of sampling	Agilent 1200 liquid chromatograph. DSTU EN 12916-2006. Determination of aromatic hydrocarbons in middle distillates by high performance liquid chromatography with a refractive index detector					Spectrophotometer Cary-50. PI 26.004. Determination of aromatic hydrocarbons according to groups in middle distillates by UV spectroscopy;				PI 26.011. Determination of the content of total nitrogen in oil and oil products, wt.%
	mono-A, %	di-A, %	tri-A, %	poly-A, %	total A, %	mono-A, %	di-A, %	poly-A, %	total A, %	wt%.
Nigeria 1 oil	15,3	7,1	1,3	8,4	23,7	19,8	5,5	1,9	27,2	0,0138
Nigeria 2 oil	15,2	7,1	1,3	8,4	23,6	18,5	5,3	1,8	25,6	0,0124
Mix of Eastern-Ukrainian oils	14,9	6	1,2	7,2	22,1	16	4	1,2	21,2	0,0380
Mix of Western-Ukrainian oils	14,1	5,5	0,9	6,4	20,5	16	3,8	1,2	21	0,0234

3.5. Characteristics of Lubricating Oil Fraction

For the lubricating oil fraction, the operational quality indicators, as well as the fractional composition were determined [130] (Table 3.11). As the results showed, the oil fraction of Nigeria 1 and Nigeria 2 oils is characterized by low sulfur content - 0.72 and 0.22%, respectively. The pour point of the oil fraction from the mixture of Western-Ukrainian oil is +12 ºC and this is the highest temperature of all investigated oils. The oil fraction obtained from all oils under study should be sent to the dewaxing process, as they have a low pour point: -1 ºC and +3 ºC for Nigeria 1 and Nigeria 2, respectively; -5 ºC and +12 ºC for Ukrainian oils.

For further refining, oil fractions of Nigerian oils should be sent to catalytic cracking, hydrocracking processes or used for the production of base oils.

Conclusions to Chapter 3:

For the first time, studies of the physico-chemical properties of two commercial Nigerian oils and mixtures of Eastern- and Western-Ukrainian oils were conducted, and their comparative analysis was performed.

It has been established that Nigerian oils are low-sulfur ones, with a fairly low pour point, offering their easy transportation. Oils have a low viscosity and contain 57-72% of light fractions.

The content of metals, namely nickel, vanadium and iron, in Nigerian oils is much lower than that in Ukrainian oils. This is important when using fractions of Nigerian oils as a feedstock for catalytic reforming, catalytic cracking, as well as when using fuel oil as a boiler fuel.

A comparative analysis of gasoline fractions of Nigerian and Ukrainian oils shows that the amounts of sulfur, toluene-forming, benzene-forming, paraffinic, naphthenic and aromatic hydrocarbons in them are similar.

The results of the work described in Chapter 3 have been published [131, 132] and reported at international conferences [133, 134].

Table 3.11

Characteristics of lubricating oil fractions

Parameter	Nigeria 1 oil	Nigeria 2 oil	Mix of Eastern-Ukrainian oils	Mix of Western-Ukrainian oils
1. Fractional composition				
IBP	281	292	295	302
10 %	350	370	371	374
20 %	389	395	395	399
30 %	407	412	413	415
40 %	422	426	427	429
50 %	435	440	440	442
60 %	449	452	453	455
70 %	463	466	467	468
80 %	480	484	485	485
90 %	502	507	506	507
95 %	519	526	523	525
EBP	571	592	563	576
2. Sulfuric compounds content, wt.%.	0,72	0,22	1,12	0,53
3. Flash point (open cup) ºC	74,0	73,0	77,0	78,0
4. Pour point, ºC	-1	+3	-5	+12
5. Relative viscosity at 80 ºC, °RV	3,4	3,6	3,2	3,0

CHAPTER 4

FUNDAMENTALS OF NIGERIAN OILS PROCESSING TECHNOLOGY

4.1. Obtaining Base Oils from Fuel Oil of Nigerian Oils

One of the priorities of any refinery is the production of base oils. They are the basis for the production of high-quality commercial oils and make up 90% of the mixture of oil components, 10% are additives that improve antioxidant, detergent, viscosity-temperature and other properties of the lubricants [135].

Factors that determine the oil quality is its content in the feedstock, which enters the vacuum column [51, 99, 100, 122], as well as processes that regulate the properties of oil distillates [101, 136, 137].

To improve the quality of commercial oils, such processes as selective treatment, dewaxing, deoiling, contact treatment by means of various external influences (force fields, surfactants) and others are used [99, 100, 101, 138].

In this work, we received base oils from a mixture of fuel oils obtained from Nigeria 1 and Nigeria 2 oils (with the ratio of 2:3) and improved their quality by post-treatment of oil distillates. The raw materials of the research were oil distillates MD-1 (350-400 ºC), MD-2 (400-450 ºC) and MD-3 (450-500 ºC).

To determine the market value of oil distillates MD-1, MD-2, MD-3, their detailed analysis was carried out in the laboratories of the Department of Chemical Technology of Oil and Gas Processing of Lviv Polytechnic National University and Chemotological Center of the National Aviation University.

The characteristics of oil distillates are given in Table 4.1. Based on the different fractional composition of oil distillates, their density and viscosity are somewhat different. Thus, among investigated distillates MD-1 has a smallest density, viscosity at 100 °C and sulfur content (888 kg/m^3, 8.19 mm^2/s, and 0.38%, respectively); its initial boiling point is 342 °C. Oil distillate MD-2 has a slightly higher viscosity, density and sulfur content (13.61 mm^2/s, 909 kg/m^3 and 0.49%, respectively). The distillation temperature range of this distillate is 396÷457 °C. Distillate MD-3 has the highest values (viscosity of 16.09 mm^2/s, density of 920 kg/m^3 and sulfur content of 0.59%).

The group composition of distillate oils was studied by chromatography. The adsorption method for determining the group composition of oils is not standardized, therefore it is used by different researchers in different ways: different grades of silica gel, different types of columns, different solvents are used, hydrocarbon fractions are grouped differently, etc.

Table 4.1

Characterization of oil distillates from a mixture of Nigerian oils

Index	MD-1	MD-2	MD-3
The kinematic viscosity, mm^2/s at 100 ºC	8,19	13,61	16,09
Flash point, °C	190	265	273
Pour point, °C	-3	+8	+15
Sulfur content, %	0,38	0,49	0,59
Group composition determined by chromatography over silica gel, wt.%;			
– paraffin-naphthenic hydrocarbons	56,38	54,99	52,57
– aromatic hydrocarbons,	41,33	42,16	43,89
including:			
– monocyclic aromatics	18,02	16,40	13,13
– bicyclic aromatics	14,75	13,61	14,14
– polycyclic aromatics	8,56	12,15	16,62
– resins	2,29	2,85	3,54
Density at 20 ºC, kg/m^3	888	909	920
Refractive index (n_D^{20})	1,4883	1,5021	1,5062
Molecular weight	353	446	507
Fractional composition			
– IBP	342	396	449
– 50% distilled temperature, °C	383	428	481
– EBP, °C	409	457	512
Acid number, mg KOH per 100 cm^3	0,026	0,021	0,022
Coking ability	0,14	0,47	0,62

The largest amount of paraffin-naphthenic hydrocarbons (56.38%) is present in MD-1 distillate. The amount of aromatic hydrocarbons and resins is less in comparison with MD-2 and MD-3. The latter distillate contains the largest amount of resins (3.54%) and polycyclic aromatic hydrocarbons (16.62%). The coking ability of the distillates increases from 0.14% for MD-1 to 0.62% for MD-3.

Oil distillates obtained in the process of fuel oil vacuum distillation are sent to the solvent refining. A selective solvent - N-methylpyrrolidone was used. The material balance of the process is shown in Table 4.2.

Table 4.2

Material balance of solvent refining of oil distillates with N-methylpyrrolidone

Parameter	wt.% relative to feedstock		
	MD-1 (refining temperature is 50 ºC)	MD-2 (refining temperature is 70 ºC)	MD-3 (refining temperature is 80 ºC)
<u>Feed</u>			
Feedstock	100.00	100.00	100.00
N-methylpyrrolidone	99.04	129.14	162.43
Total	**199.04**	**229.14**	**262.43**
<u>Products</u>			
Raffinate solution:			
Raffinate	86.57	82.95	80.86
N-methylpyrrolidone	10.38	9.23	11.29
Total	**96.95**	**92.18**	**92.15**
Extract solution:			
Extract	13.43	17.05	19.14
N-methylpyrrolidone	88.66	119.91	151.14
Total	**102.09**	**136.96**	**165.28**
Grand total	**199.04**	**229.14**	**262.43**

Raffinates MD-1, MD-2 and MD-3, obtained by treatment with N-methyl-pyrrolidone, have a viscosity of 5-11 cSt at 100 ºC, a density 0.864-0.897 and consist mainly of paraffin-naphthenic hydrocarbons.

The dewaxing of oil distillates under laboratory conditions was carried out using a mixture of methyl ethyl ketone and toluene solvents. After dewaxing, the oils were further post-treated with 5% silica gel at a temperature of 125-130 °C. The yield of purified oils after adsorption post-treatment of waxed distillates was about 97%.

Before dewaxing, the raffinates were dissolved in a MEK: toluene mixture taken in a ratio of 3:2, the solvent:raffinate ratio was 2.5:1. The oil distillates with the solvent were cooled to -20 °C and then filtered. The material balance of the process is presented in Table 4.3.

Table 4.3

Material balance of dewaxing process of raffinates treated with N-methylpyrrolidone

	wt%, to raffinate		
Product	MD-1	MD-2	MD-3
Feed: Raffinat	100	100	100
Product:			
Dewaxed oil	79,5	72,4	65,4
Gatch	18,4	24,8	32,3
Losses	2,1	2,8	2,3

As a result, dewaxed oils were obtained, and their yield was 79.5% for MD-1, 72.4% for MD-2 and 65.4 % for MD-3.

Characteristics of products obtained after solvent refining and dewaxing are shown in Tables 4.4 and 4.5.

As a result of solvent refining with N-methylpyrrolidone, the amount of paraffin-naphthenic hydrocarbons in purified oil distillates increased by approximately 20 %, the amount of monocyclic aromatics decreased by 5-6 %, bicyclic aromatics decreased by 7-8%, polycyclic aromatics - by approximately 4-9 %. At the same time, the amount of resins decreased from 2.5-3.5 % to 1 % for MD-2, 1.4 1% for MD-3, less than 1 % for MD-1.

Table 4.4

Characteristics of extracts and raffinates after solvent refining of oil fractions with N-methylpyrrolidone

Parameter	MD-1	MD-2	MD-3
Extract			
Refractive index at 50 °C	1,5556	1,5726	1,5765
Relative density at 50 °C	0,964	0,979	0,988
Raffinats			
Kinematic viscosity, mm^2/s at 100 °C,	5,94	10,45	12,64
Refractive index at 20 °C	1,4787	1,4836	1,4917
Relative density ρ_4^{20}	0,864	0,8973	0,8970
molecular weight	333	414	435
Group composition determined by chromatography over silica gel, wt.%;			
– paraffin-naphthenic hydrocarbons	73,97	73,37	72,30
aromatic hydrocarbons, including:			
– monocyclic aromatics	12,10	11,90	10,13
– bicyclic aromatics	8,75	7,65	9,02
– polycyclic aromatics	4,56	5,96	7,14
– resins	0,62	1,06	1,41

Table 4.5

Characteristics of oils after dewaxing of oil fractions treated with N-methylpyrrolidone

Parameter	MD-1	MD-2	MD-3
After dewaxing oils			
Kinematic viscosity, mm2/s at 100 °C	6,71	11,02	13,61
Kinematic viscosity, mm2/s at 50 °C,	23,93	60,95	84,31
Viscosity index	>120	105	110
Refractive index at 20 °C	1,4849	1,4932	1,4955
Relative density at 20 °C	0,8797	0,8915	0,8980
Molecular weight	341	412	432
Pour point, °C	-14	-10	-8
Group composition determined by chromatography over silica gel, wt.%;			
– paraffin-naphthenic hydrocarbons	62,10	58,60	54,45
aromatic hydrocarbons, including:			
– monocyclic aromatics	20,26	21,55	20,14
– bicyclic aromatics	11,75	11,46	14,04
– polycyclic aromatics	5,24	7,30	9,92
– resins	0,65	1,09	1,45

As a result of dewaxing (Table 4.5), the kinematic viscosity of oils increased by 5-10%, the amount of paraffin-naphthenic hydrocarbons decreased from 73 to 62.1%

for MD-1, from 73.4 to 58.6 % for MD-2 and from 72.3 to 54.45% for MD-3. The pour point of raffinate solutions decreased from 25 to minus 14 ºC for MD-1, from 32 ºC to minus 10 ºC for MD-2, and from 37 ºC to minus 8 ºC for MD-3. Raffinates MD-1, MD-2, MD-3 have a viscosity at 100 ºC of 6-18 cSt, a viscosity index of 105-120.

After dewaxing, the oils were further purified with bleaching clay in the amount of 5 % for raw materials (contact filtration) for all oil distillates; the process temperature was 125-130 ºC. The material balance is presented in Table 4.6.

The yield of purified oils after contact filtration was about 94-97 %.

Table 4.6

Contact filtration of oils

Name of product	MD-1, %	MD-2, %	MD-3, %
Feed:			
Dewaxed oil	100	100	100
Clay	5	5	5
Total:			
Product:			
Purified oil	97	95	94
Spent clay	8	10	11
Total	105	105	105

4.2. Obtaining Bitumen from Fuel Oils of Nigerian Oils

To obtain bitumen of BND 60/90 and BND 90/130 grades from commercial oils extracted from fields located in the Port Harcourt area in Nigeria, it was necessary to determine methods for the production of paving bitumen. The quality of bitumen must meet the requirements of DSTU 4044 “Viscous paving bitumen. Specifications” [140]. Required bitumen parameters for BND 60/90: softening point (R&B) 47-53 °C, ductility at 25 °C – not less than 55 cm, ductility at 0 °C – not less than 3 cm, penetration at 25 °C - 61-90 and brittle point – not higher than -12 °C. Required characteristics for BND 90/130: R&B softening point 41 °C, ductility at 25 °C - not less than 80 cm, penetration at 25 °C - 91-130 and brittle point – not lower than -10 °C.

To carry out the research, a tar sample was obtained from a mixture of Nigerian oils. In this sample, according to standard methods, the following parameters were determined: softening point, penetration, ductility at 25 °C, ductility at 0 °C and brittle point. We also determined the content of asphaltenes and the group hydrocarbon composition according to GOST 11244, and the content of paraffins according to the method described in workplace instruction of PJSC "Uktatnafta" at the temperature of -28 °C. The analysis results are shown in Table 4.7.

Table 4.7

Characteristics of the obtained tar

Parameter	Tar
R&B softening temperature, ºC	37
Penetration, 0.1 mm	260
Relative viscosity, ºRV	97.78
Ductility at 25 ºC, mm	59
Ductility at 0 ºC, mm	5.6
Brittle point, ºC	-21
Asphaltenes, wt.%	8.3
Hydrocarbon composition:	
Paraffin-naphthenic hydrocarbons ($n_d^{20} < 1.49$), %, including paraffines	22.9 8.9
I group of aromatics ($n_d^{20} = 1.49 \div 1.53$)	9.3
II group of aromatics ($n_d^{20} = 1.53 \div 1.55$)	8.1
III group of aromatics ($n_d^{20} = 1.55 \div 1.59$)	32.0
IV group of aromatics ($n_d^{20} > 1.59$)	
Resins, %	19.4

It is known from literary sources [141-143] that bitumen with increased quality indices is produced preferably from tar with a relative viscosity of 60-80 °RV, content of paraffin-naphthenic hydrocarbons 20.0-22.0 wt.%, heavy aromatic hydrocarbons – not less than 34.0 wt.%, resins – not less than 35.0 wt.% and asphaltenes – no more than 8.5%.

Analyzes have shown that the asphaltene content in tar from Nigerian oils is 8.3%. The tar is characterized by a high content of paraffin-naphthenic hydrocarbons (22.9%) and a high paraffin yield (8.9%), as well as a relatively low content of heavy aromatic hydrocarbons (3 and 4 groups) and resins, which in the future should have a positive effect on low-temperature bitumen properties – brittleness and ductility at 0 °C. The total content of heavy aromatic hydrocarbons (3 and 4 groups) and resins in tar is 51.4%.

It is obvious from Table 4.7 that tar obtained from a mixture of Nigerian oils is not the best feedstock for obtaining bitumen with increased quality indices. Therefore, the work on obtaining oxidized bitumen was carried out in several stages. The scheme of the research is shown in Fig. 4.1.

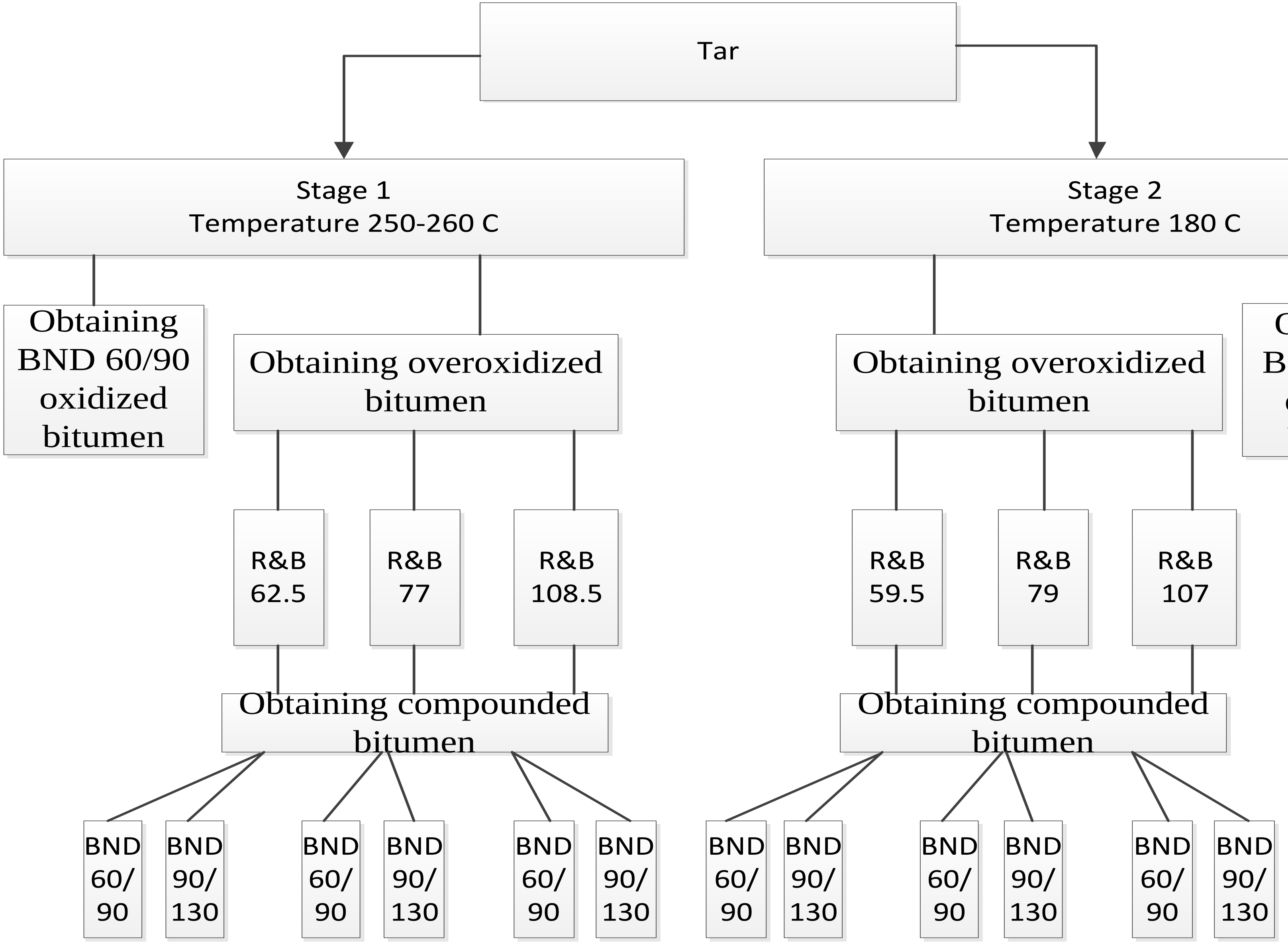

Fig. 4.1 **Obtaining oxidized bitumen**

4.3. Obtaining Bitumen by Tar Oxidation at 250-260 ºC

In the first part of stage 1, we studied the possibility of obtaining paving bitumen of BND 60/90 grade by tar oxidation with air at a temperature of 250-260 °C. The experimental conditions and the quality indices of the resulting bitumen are shown in Table 4.8.

Table 4.8

Characteristics of paving bitumen BND 60/90, obtained by tar oxidation with air at 250-260 ºC in laboratory conditions

(sample weight - 80 g, air consumption - 80 cm^3/min.)

Sample number	Oxidation temperature °C	Oxidation time, min	Penetration at 25 ºC, 0,1 mm	R&B softening point, °C
1	260±5	30	68	45,5
2	260±5	30	64	46
3	260±5	45	46	57
4	260±5	45	44	59,5
5	260±5	75	40	59,5
6	260±5	80	22	75
7	250±5	45	70	51
8	250±5	45	64	53
9	250±5	45	88	51
10	250±5	60	60	51
11	250±5	90	40	62
12	260±5	120	17	92
13	260±5	210	9	113
7+8+9	250±5	45	**55**	**52,5**

Bitumen samples No. 7, 8, and 9, obtained by tar oxidation for 45 min. at a temperature of 250 °C, meet the requirements for bitumen BND 60/90 grade in terms of softening point and penetration. Due to the small amount of bitumen obtained, samples No. 7, 8 and 9 were mixed at a laboratory setup to obtain compounded bitumen (mixing time 15 min., temperature 140 °C) to determine brittleness and ductility at 25 °C and 0 °C. The softening point of resulting bitumen was 52.5 ºC, but penetration at 25 °C did not correspond to the expected value of 61-90, it was only 55. The decrease in penetration is obviously associated with the unstable chemical composition of the obtained bitumen, and the additional oxidation, which took place during the mixing of the bitumen mixture.

Thus, it can be concluded that it was not possible to obtain BND 60/90 bitumen at a process temperature of 250-260 °C by oxidizing the tar of Nigerian oils, so further studies were carried out according to the scheme shown in Fig. 4.1.

4.4. Obtaining Bitumen by Tar Oxidation at 180 ºC

At the next stage, tar oxidation was carried out at 180 °C in order to exclude the possibility of coking reactions with the formation of carbenes and carboides, which increases the bitumen hardness. The experimental conditions and characteristics of the obtained oxidized bitumen are presented in Table 4.9.

The sample weight was 80 g, the air flow rate was 80 cm^3/min. When obtaining oxidized bitumen, maintaining the oxidation temperature regime is of great importance. So (Table 4.9) at the same time (120 min.), a change in the oxidation temperature from 180 to 187 ° C causes a decrease in the penetration value from 82 to 60 units and an increase in the softening point from 49.5 to 51.5 °C.

Table 4.9

Characteristics of paving bitumen BND 60/90, obtained by tar oxidation with air at 180 °C in laboratory conditions

Sample number	oxidation temperature, ºC	oxidation time, мин.	Penetration at 25 ºC	R&B softening point, °C	ductility at 25 ºC sm	ductility at 0 ºC sm	brittleness temperature, ºC	Relative viscosity, ºRV
1	-	-	260	41	59	5,6	-21	97,78
2	180±5	60	110	46	-	-	-	-
3/1	180	120	82	49,5	-	-	-	-
3/2	186	120	65	51,5	-	-	-	-
3/3	187	120	60	51,5	-	-	-	-
3/4	183-185	120	61	50	-	-	-	-
3	Average, obtained by mixing samples 3/1+3/2+3/3+3/4		61	51,5	65	1,0	-9	-
4	180±5	180	47	56	-	-	-	-
5	180±5	240	32	63	-	-	-	-
6	180±5	300	28	75	-	-	-	-
7	180±5	360	19	84	-	-	-	-
8	180±5	420	21	85,5	-	-	-	-
9	180±5	510	15	107	-	-	-	-
10	DSTU-4044	-	61-90	>50	>55	3	-12	-

Dependence of the softening point and penetration on the oxidation time is shown in Fig. 4.2, and the relationship between the softening point and penetration – in Fig. 4.3.

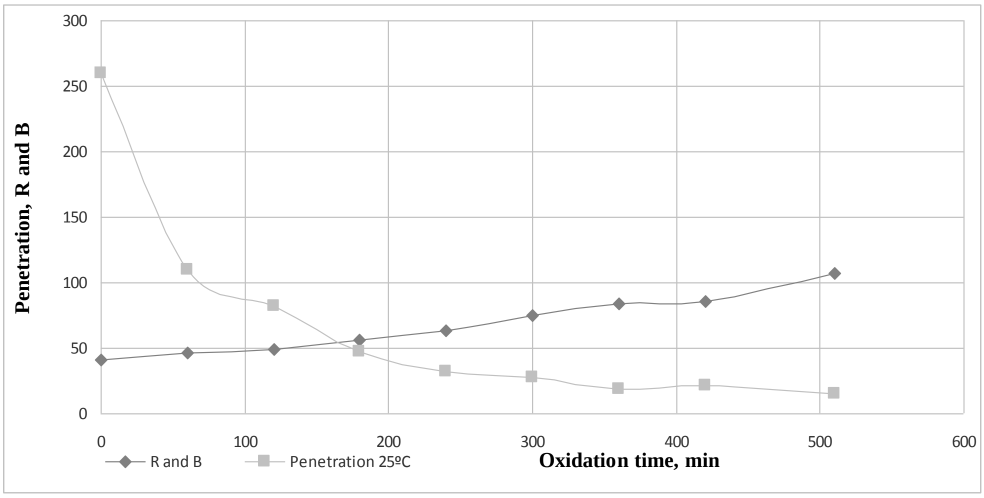

Fig. 4.2. **Quality indices of bitumen obtained at oxidation temperature of 180 ° C versus oxidation time.**

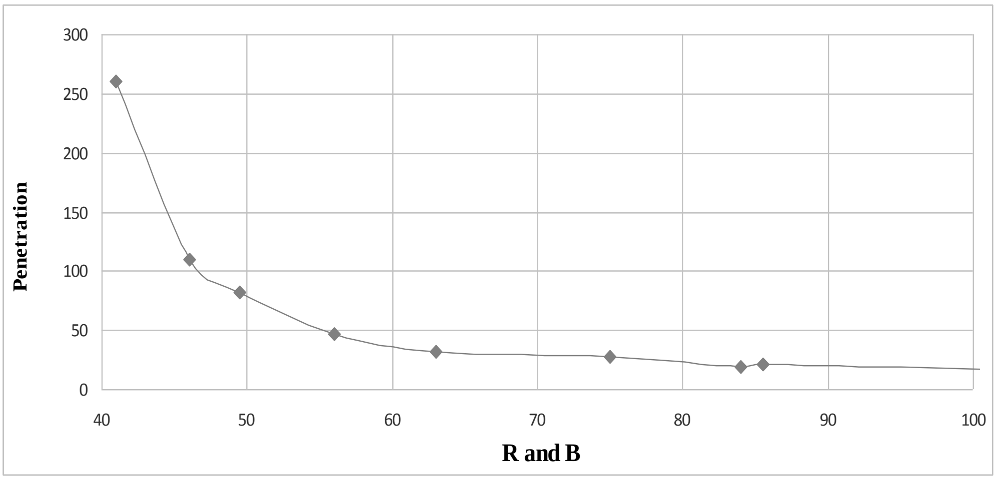

Fig. 4.3 **Relationship between the softening point and penetration for bitumen obtained at oxidation temperature of 180 °C.**

When analyzing the data of Figs. 4.2 and 4.3, one can see that within the range of oxidation time from 100 to 160 minutes it is possible to obtain bitumen with softening point of 47-53 °C and penetration of 61-90. These values meet the requirements of DSTU 4044.

With an increase in the oxidation time to 180 minutes, penetration sharply decreases by 5 times and the softening point increases by 15 ºC.

The starkest dependence is penetration-softening point is observed in the 50-250 penetration range and softening point range of 41-60 ºC.

Laboratory samples of oxidized bitumen No. 3/1, 3/2, 3/3 and 3/4 (oxidation time 120 min.), which meet the requirements for BND 60/90 bitumen regarding penetration at 25 °C and softening point, were mixed and the average sample No. 3

was obtained. The characteristics determined for this sample showed that it was not possible to obtain bitumen, which meets the requirements for BND 60/90 bitumen in terms of ductility at 0 °C and brittle point.

4.5. Obtaining Compounded Bitumen Based on Tar and Overoxidized Bitumen at 250-260 °C

Overoxidized bitumen were prepared on a laboratory plant for obtaining oxidized bitumen, under the conditions specified above. Overoxidized bitumen species with following characteristics were obtained:

- Softening point 62.5 ºC and penetration 30 (0.1 mm),
- Softening point 77 ºC and penetration 23 (0.1 mm),
- Softening point 108.5 ºC and penetration 13 (0.1 mm),

Then these samples were mixed with tar at 140 °C for 15 minutes at the laboratory plant for bitumen compounding and following samples were prepared:

- compounded bitumen based on overoxidized bitumen with softening point of 62.5 °C;
- compounded bitumen based on overoxidized bitumen with softening point of 77 °C;
- compounded bitumen based on overoxidized bitumen with softening point of 108.5 °C.

The characteristics of the resulting compounded bitumen are given in Tables 4.10, 4.11 and 4.12.

Table 4.10

Characteristics of compounded bitumen based on tar and overoxidized bitumen with softening point of 62.5 °C

Sample number	Tar content , wt%	Content of bitumen with softening point of 62.5ºC, wt%	Penetration at 25 ºC	R&B softening point, °C	ductility at 25 ºC sm	ductility at 0 ºC sm	brittleness temperature, ºC
1	100	0	260	41	-	-	-
2	80	20	176	41	-	-	-
3	70	30	118	44	82	-	-
4	62,5	37,5	110	48	81	-	-
5	60	40	106	44.5	55	0,7	-19
6	50	50	84	50	74	0,5	-17
7	37,5	62,5	71	53	-	-	-
8	0	100	30	62,5	-	-	-

Table 4.11

Characteristics of compounded bitumen based on tar and overoxidized bitumen with softening point of 77°C

Sample number	Tar content, wt%	Content of bitumen with softening point of 77 ºC, wt%	Penetration at 25 ºC	R&B softening point, °C	ductility at 25 ºC sm	ductility at 0 ºC sm	brittleness temperature, ºC
1	100	0	260	41	-	-	-
2	90	10	202	45	-	-	-
3	80	20	161	46	-	-	-
4	70	30	95	47	67	4,0	-15
5	60	40	83	49	85	3,5	-21
6	50	50	78	51	83	3,1	-19
7	40	60	51	56	-	-	-
8	0	100	23	77	-	-	-

Table 4.12

Characteristics of compounded bitumen based on tar and overoxidized bitumen with softening point of 108,5 ^{o}C

Sample number	Tar content, wt%	Content of bitumen with softening point of 105 ºC, wt%	Penetration at 25 ºC	R&B softening point, °C	ductility at 25 ºC sm	ductility at 0 ºC sm	brittleness temperature, ºC
1	100	0	260	41	-	-	-
2	90	10	206	42	-	-	-
3	80	20	126	45	57	1,9	-19
4	70	30	90	48,5	65	3,2	-22
5	60	40	55	53	-	-	-
6	50	50	38	59,5	-	-	-
7	40	60	35	60	-	-	-
8	0	100	13	108,5	-	-	-

Based on the data obtained, the dependence of the quality indices of the obtained bitumen on the tar content (see Figs. 4.4–4.6), as well as the relationship between the softening point and penetration (Figs. 4.7–4.9) were plotted.

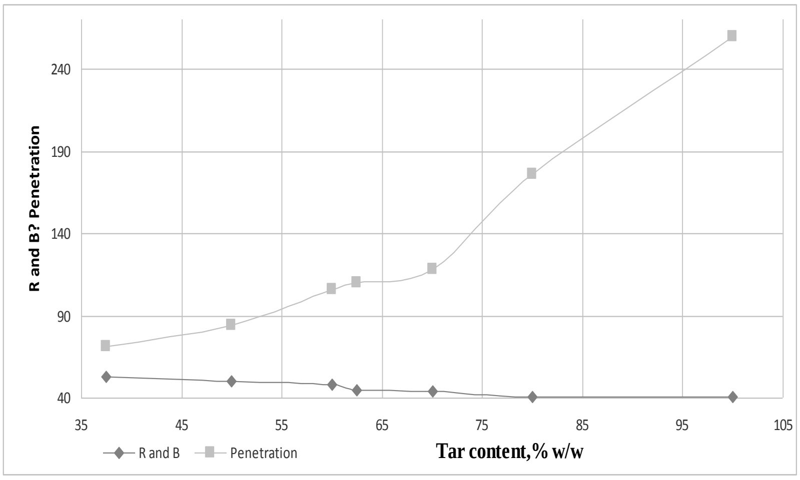

Fig. 4.4 **Quality indices of the compounded bitumen vs. tar content (the base is bitumen with softening point of 62.5 °C).**

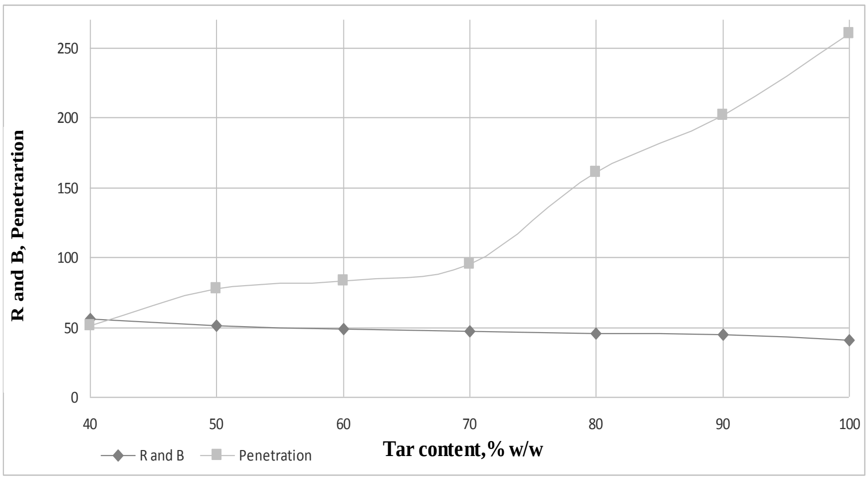

Fig. 4.5 **Quality indices of the compounded bitumen vs. tar content (the base is bitumen with softening point 77 °C).**

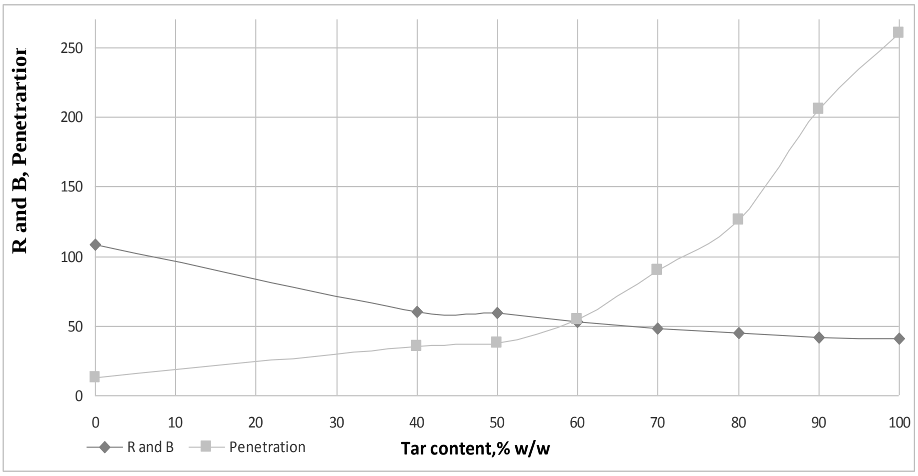

Figure 4.6 **Quality indices of the compounded bitumen vs. tar content (the base is bitumen with softening point 108.5 °C).**

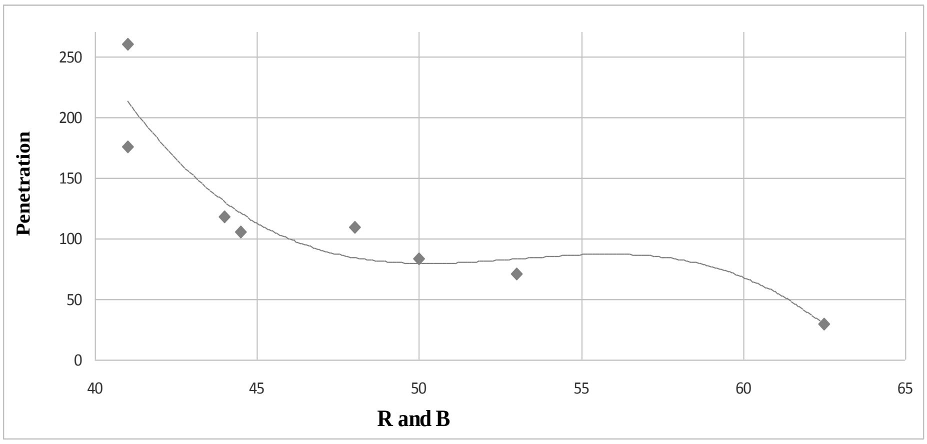

Fig. 4.7 **Relationship between the softening point and penetration of the compounded bitumen (the base is bitumen with softening point of 62.5 °C).**

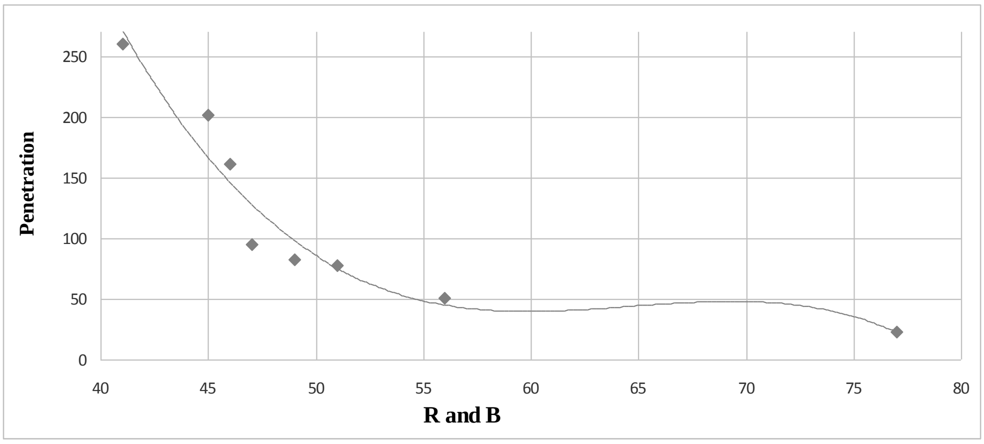

Fig. 4.8 **Relationship between the softening point and penetration of the compounded bitumen (the base is bitumen with softening point of 77 °C).**

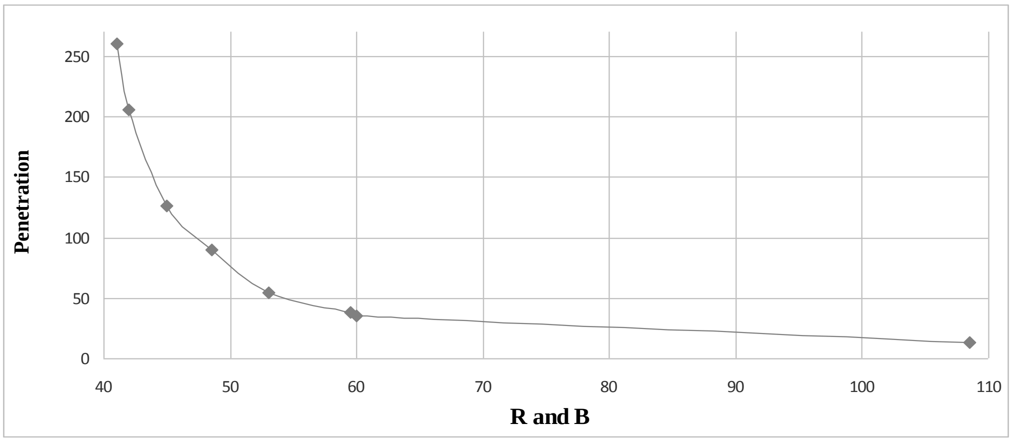

Fig. 4.9. **Relationship between the softening point and penetration of the compounded bitumen (the base is bitumen with softening point of 108.5 °C).**

One can see from Table 4.10 that the samples No. 6 and 7, which contain bitumen with softening point of 62.5 °C in amount of 50 and 62,5 wt.%, respectively, meet the requirements for BND 60/90 bitumen in terms of penetration and softening point. The samples No. 3, 4, 5 with the amount of bitumen 30-40 wt% meet the requirements for BND 90/130. Samples containing 40 and 50 wt.% of the oxidized bitumen were analyzed for ductility and brittleness. It was found that these samples do not meet the standards regarding ductility at 0 °C.

Samples No. 5 and 6, which contain oxidized bitumen with the softening point of 77 °C (Table 4.11) in the amount of 40 and 50 wt%, meet the requirements for BND 60/90 regarding penetration, softening point, ductility at 25ºC, ductility at 0 ºC and brittle point. Sample No. 4 with bitumen content of 30 wt.% meets the requirements for BND 90/130 bitumen on all indices.

Compounded bitumen was also obtained on the basis of oxidized bitumen with softening point of 108.5 °C (Table 4.12). Sample No. 4 (30 wt.% of oxidized bitumen) meets all requirements for BND 60/90. Sample No. 3 (20 wt.% of oxidized bitumen) meets some requirements for bitumen BND 90/130 but does not correspond to the standard values of ductility at 25ºC, ductility at 0 °C and brittleness.

Figs. 4.10 and 4.11 show the quality indices of the compounded bitumen depending on the tar amount.

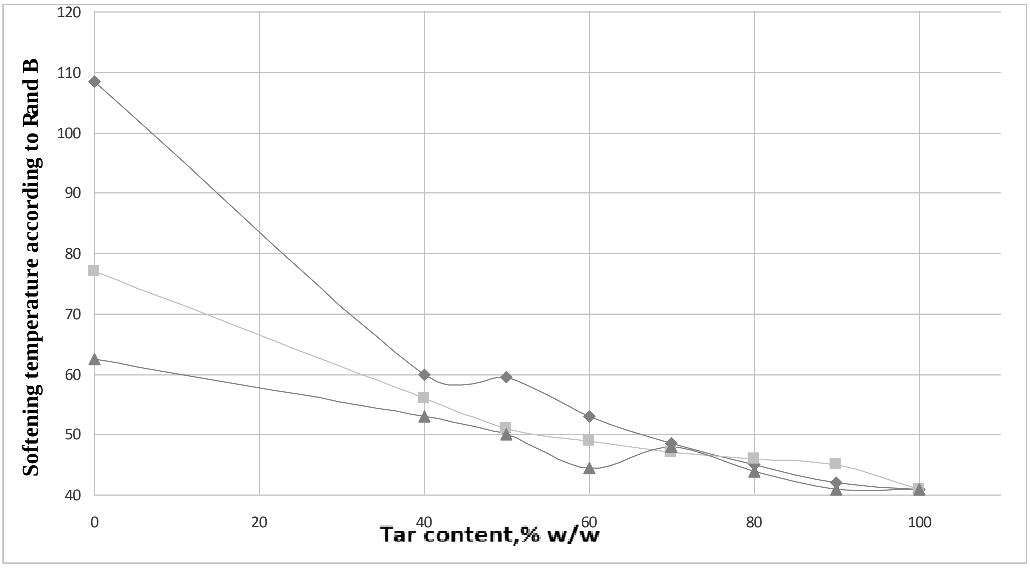

Fig. 4.10 **Softening point of compounded bitumen depending on the tar content**

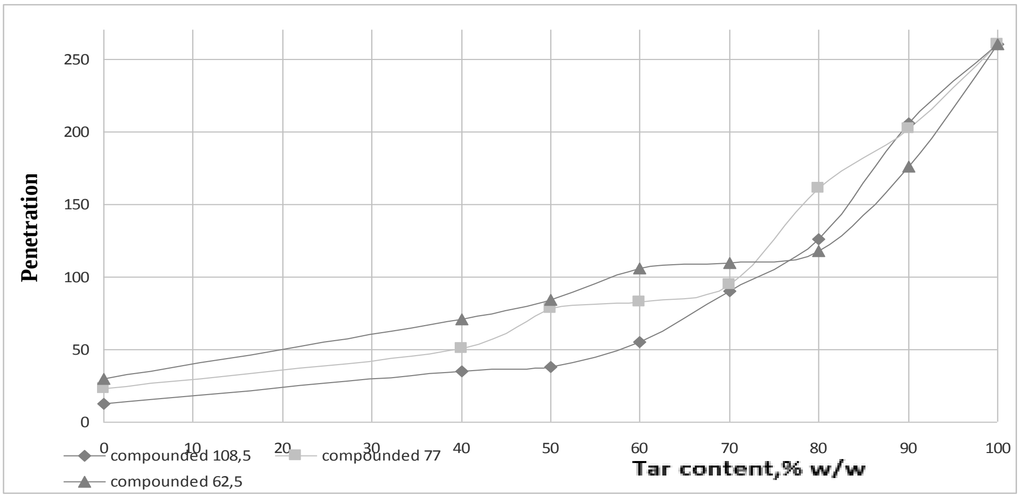

Fig. 4.11 Penetration of compounded bitumen depending on the tar content

4.6. Obtaining Compounded Bitumen Based on Tar and Overoxidized bitumen at 180 ºC

We also examined the possibility of obtaining BND 60/90 and BND 90/130 bitumen by compounding tar and overoxidized bitumen at a temperature of 180 °C. Oxidized bitumens with the following characteristics were prepared from tar at a temperature of 180 °C :

- Softening point 59.5 ºC and penetration 37 (0.1 mm)
- Softening point 79 ºC and penetration 31 (0.1 mm)
- Softening point 107 ºC and penetration 15 (0.1 mm),

After mixing with tar at 140 °C for 15 min. the following compounded bitumen were prepared:

- compounded bitumen based on overoxidized bitumen with softening point of 59.5 °C;
- compounded bitumen based on overoxidized bitumen with softening point of 79 °C;
- compounded bitumen based on overoxidized bitumen with softening point of 107 °C.

Their characteristics are given in Tables 4.13, 4.14 and 4.15. Based on the data obtained, the dependence of the obtained bitumen indices on the tar content (Figs. 4.12, 4.13 and 4.14), as well as the relationship between the softening point and penetration (Figs. 4.15, 4.16 and 4.17) were plotted.

Table 4.13

Characteristics of compounded bitumen based on tar and overoxidized bitumen with softening point of 59.5 °C

Sample number	Tar content, wt%	Content of bitumen with softening point of 105 ºC, wt%	Penetration at 25 ºC	R&B softening point, °C	ductility at 25 ºC sm	ductility at 0 ºC sm	brittleness temperature, ºC
1	100	0	260	41	59	5,6	-21
2	30	70	71	50	60	1,0	-20
3	40	60	78	50	74	1,2	-19
4	50	50	96	49			
5	60	40	119	44,5	63	1,0	-18
6	70	30	178	41			

Table 4.14

Characteristics of compounded bitumen based on tar and overoxidized bitumen with softening point of 79 °C

Sample number	Tar content, wt%	Content of bitumen with softening point of 105 ºC, wt%	Penetration at 25 ºC	R&B softening point, °C	ductility at 25 ºC sm	ductility at 0 ºC sm	brittleness temperature, ºC
1	100	0	260	41			
2	50	50	71	53	66	0,6	-19
3	60	40	90	49	54	0,6	-19
4	70	30	126	45,5	53	1,5	-7

Table 4.15

Characteristics of compounded bitumen based on tar and overoxidized bitumen with softening point of 107 °C

Sample number	Tar content, wt%	Content of bitumen with softening point of 105 ºC, wt%	Penetration at 25 ºC	R&B softening point, °C	ductility at 25 ºC sm	ductility at 0 ºC sm	brittleness temperature, ºC
1	100	0	260	41	-	-	-
2	95	5	218	42	-	-	-
3	90	10	123	46	70	1,9	-19
4	80	20	96	47,5	-	-	-
5	70	30	83	48,5	97	3,2	-17
6	60	60	59	54	-	-	-

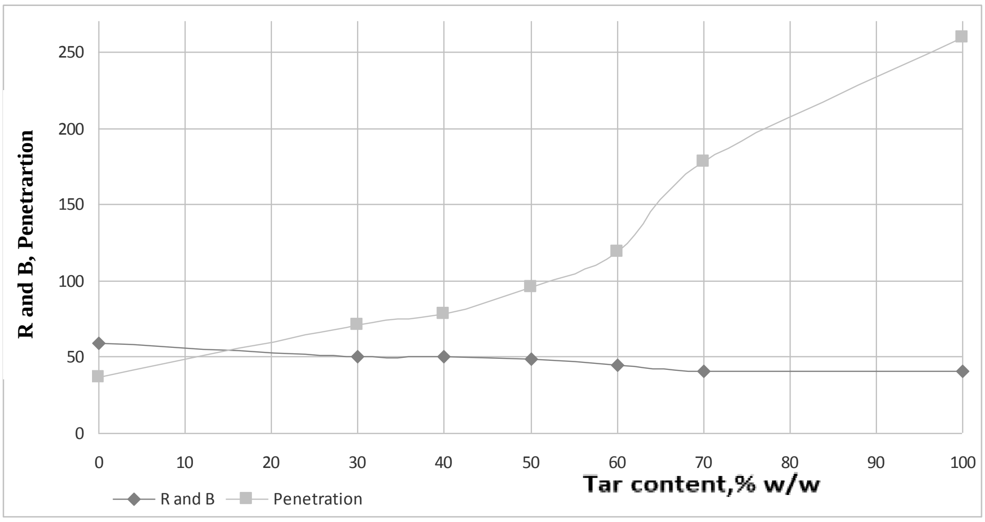

Fig. 4.12 **Quality indices of the compounded bitumen vs. tar content (the base is bitumen with softening point of 59.5 °C).**

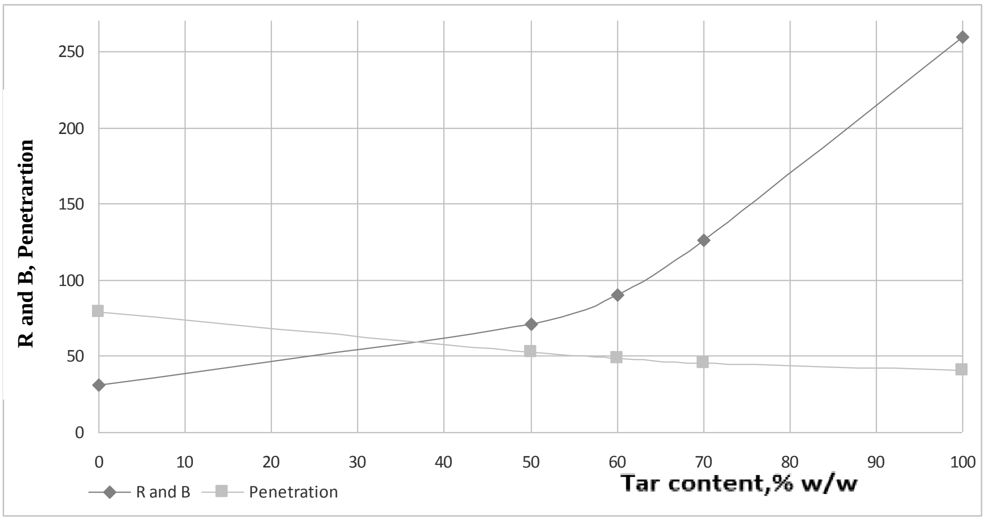

Fig. 4.13 **Quality indices of the compounded bitumen vs. tar content (the base is bitumen with softening point 79 °C).**

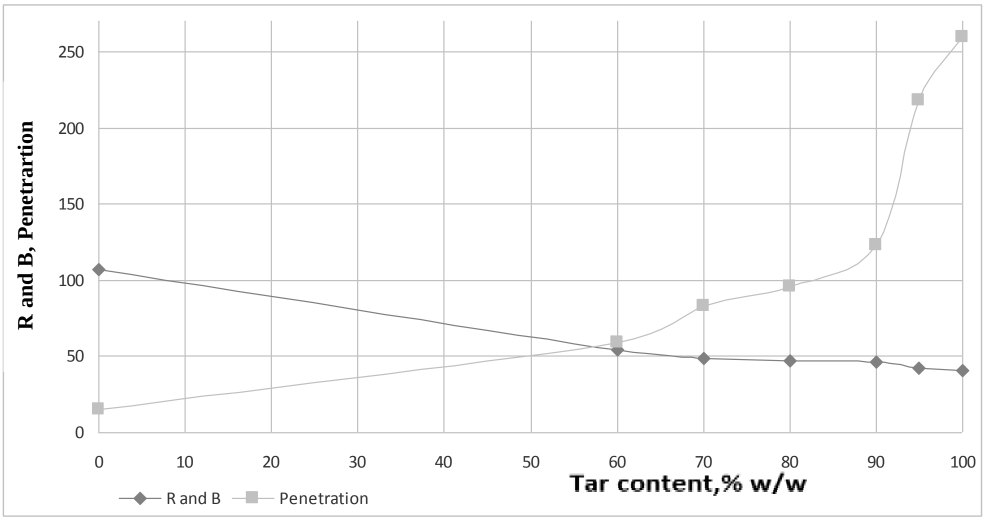

Fig. 4.14 **Quality indices of the compounded bitumen vs. tar content (the base is bitumen with softening point 107 °C).**

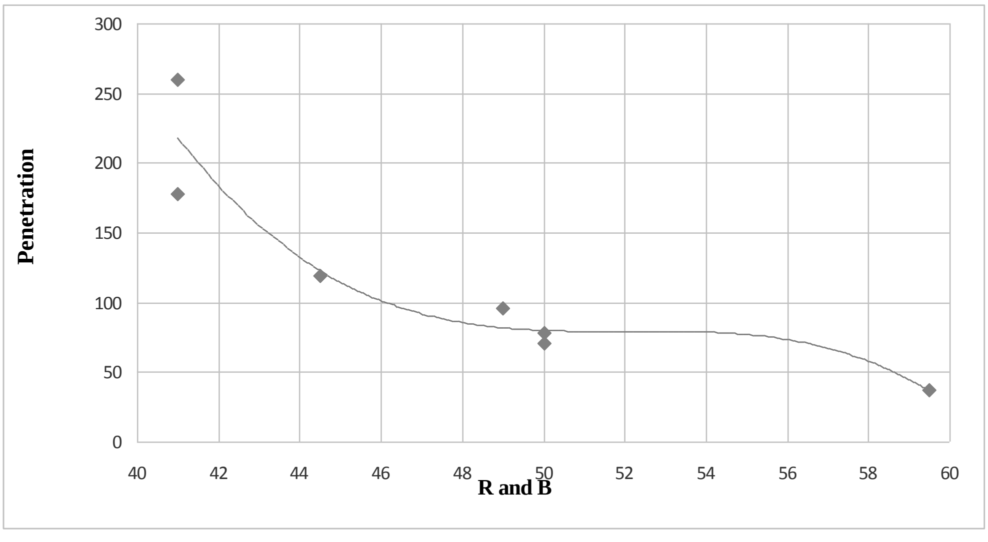

Fig. 4.15 **Relationship between the softening point and penetration of the compounded bitumen (the base is bitumen with softening point of 59.5 °C).**

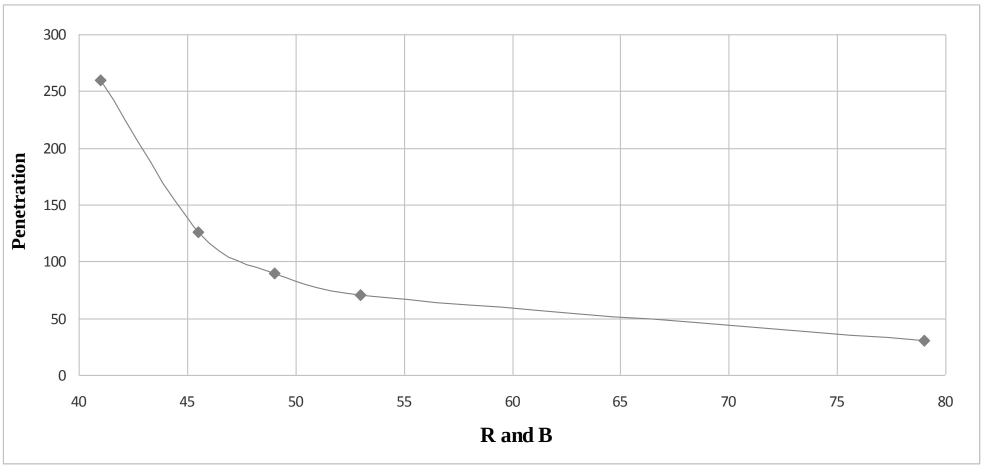

Fig. 4.16 **Relationship between the softening point and penetration of the compounded bitumen (the base is bitumen with softening point of 79 °C).**

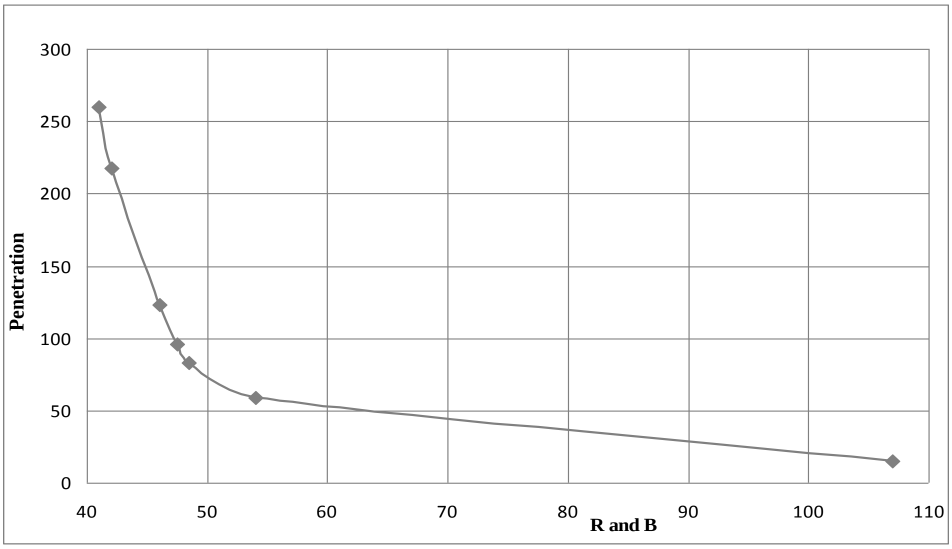

Fig. 4.17 **Relationship between the softening point and penetration of the compounded bitumen (the base is bitumen with softening point of 107 °C).**

One can see from Table 4.13 that the samples No. 2 and 3, which contain bitumen with softening point of 59.5 °C in amount of 70 and 60 wt.%, respectively, meet all requirements for BND 60/90 bitumen except for ductility at 0 ºC. Sample 5 containing 40 wt.% of bitumen meets all requirements for BND 90/130 except ductility at 0 ºC.

Values of penetration, softening point, ductility at 25 ºC and brittleness of the samples No. 2 and 3, which contain oxidized bitumen with the softening point of 79 °C in the amount of 50 and 40 wt% (Table 4.14), are consistent with the standards for BND 60/90. The value of ductility at 0 ºC does not meet the standards. The quality indices of the sample No. 4 (with bitumen content of 30 wt.%) corresponds to those of BND 90/130, except ductility at 0 ºC and brittleness.

Table 4.15 presents characteristics of compounded bitumen obtained on the basis of oxidized bitumen with softening point of 107 °C (Table 4.12). All values of the sample No. 5 (30 wt.% of oxidized bitumen) are consistent with the standards for BND 60/90. None of the samples meets the requirements for BND 90/130 bitumen.

Conclusions to Chapter 4

The possibility of obtaining base oils from Nigerian oil distillates is shown. After solvent refining, dewaxing and absorption post-treatment, base oils with a viscosity index of 90-110 and a pour point within the range of minus (8-14) °C were obtained. Using these oils, commercial engine and hydraulic oils can be produced after addition of necessary additives; distillates can be used for lubricants production. Oil distillates obtained from Nigerian oils can be recommended for Ukrtatnafta PJSC to obtain base oils from them.

Tar obtained from a mixture of Nigerian oils contains 8.9-9.6 wt.% of asphaltenes, 22.2-22.9 wt.% of paraffin-naphthenic hydrocarbons, 9.3 wt.% of 1st group aromatics, 8.1 wt.% of 2nd group aromatics, 32.2-32.6 wt.% of heavy aromatic hydrocarbons (the sum of 3rd and 4th group aromatics) and 19.4 wt.% of resins. The obtained tar is not preferable for obtaining bitumen with improved quality parameters.

We failed to obtain paving bitumen BND 60/90 with necessary characteristics by oxidation at a temperature of 250-260 °C and 180 °C. The obtained bitumen does not correspond to the value of ductility at 0 °C, which indicates a high content of paraffin- naphthenic hydrocarbons and low resin content.

Bitumen BND 90/130 was obtained by compounding bitumen overoxidized at 250-260 °C (softening point 77 °C).

Bitumen corresponding to all quality indices for BND 60/90 bitumen was obtained only by compounding tar and bitumen overoxidized at 250-260 °C (softening points 77 °C and 108.5 °C), as well as from tar and bitumen overoxidized at 180 °C (softening point 107 °C).

To obtain paving bitumen that meets all standards, it is necessary to introduce into feedstock the components containing a large amount of resins and a small amount of paraffins.

The results of the work described in this chapter were published [139] and presented at international scientific conferences [144, 145].

CHAPTER 5

TECHNOLOGICAL ASPECTS OF OIL REFINING IN NIGERIA

Based on the results of studies of the composition and properties of Nigerian oils, it can be concluded that it is possible to process them, both on the territory of Nigeria and on the territory of other states. In the first case, the most expedient is the fuel option, since the studied oils are low-sulfur light oils. In another case, it is necessary to analyze a specific refinery for the possibility of processing Nigerian oils without significantly changing the current processing scheme at this enterprise.

5.1. Reasons for the Choice of Nigerian Oils Processing by the Fuel Option

The fuel option of oil refining provides for the presence of those technological units at the enterprise, which ensure the maximum yield of oil fuels (gasoline, diesel fuel, etc.). At the same time, it is necessary to use the minimum number of technological processes, since this will affect the cost of the obtained commercial petroleum products.

The flow diagram of Nigerian oil processing is shown in Fig. 5.1. When developing the scheme, the characteristics of Brent Dated oil (Nigeria 1) were used. The scheme is designed for a new refinery located in Nigeria or any other country where it is possible to process this type of Nigerian oil.

Crude oil is sent to the units, where oil is desalted and dehydrated. Then treated oil is directed to atmospheric distillation, and the obtained straight-run gasoline fraction is sent to secondary distillation in order to obtain narrower gasoline fractions. As a result of processing, we get the following fractions:

– fraction IBP-85 ºC;
– fraction 85-180 ºC;
– fraction 180-350 ºC;
– fraction> 350 ºC (fuel oil).

Fraction IBP-85 ºC has a low octane number, therefore it is directed to the catalytic isomerization unit. The obtained isomerate is used as a high-octane component of commercial gasolines. It is advisable to use the Penex (UOP) low-temperature isomerization technology at the projected enterprise.

Fraction 85-180 ºC is sent to the catalytic reforming process to increase the octane number. The reforming catalysate is also used as a high-octane gasoline component. The optimal reforming technology in this case is CCR technology with a moving catalyst bed and its continuous regeneration.

Diesel fraction 180-350 ºC should be sent to a hydrotreating to reduce the total sulfur content. The hydrogenated product obtained as a result of processing is the basic component of commercial diesel fuel, and distillate is a component of gasoline.

The fuel oil obtained in the process of primary oil refining is most profitable to send to the catalytic cracking process RCC with a hydrotreating unit. As a result of such processing, the gasoline yield is high and a particularly valuable C_3-C_4 fraction is obtained. Light gas oil is sent to the hydrotreating unit of diesel fuel, and heavy gas oil is used as boiler fuel.

Hydrogen sulfide-containing gas from catalytic reforming and diesel fuel hydrotreating unit is sent for elemental sulfur production.

Gasoline stabilization head is sent from the catalytic reforming and catalytic cracking units to the gas fractionation unit (GFU), where individual hydrocarbon fractions of a narrow composition are obtained. The propylene fraction is sent to a polymerization unit to produce polypropylene. The iso-butane and butylene fractions are sent to the alkylation unit. The obtained high-octane light alkylate is used as a component of commercial gasolines, and heavy alkylate – as a component of diesel fuel.

Dry gases of all technological processes, as well as gas from ADU/VDU are used as gaseous fuel at the technological units of the refinery, and remove its excess amount as marketable fuel gas.

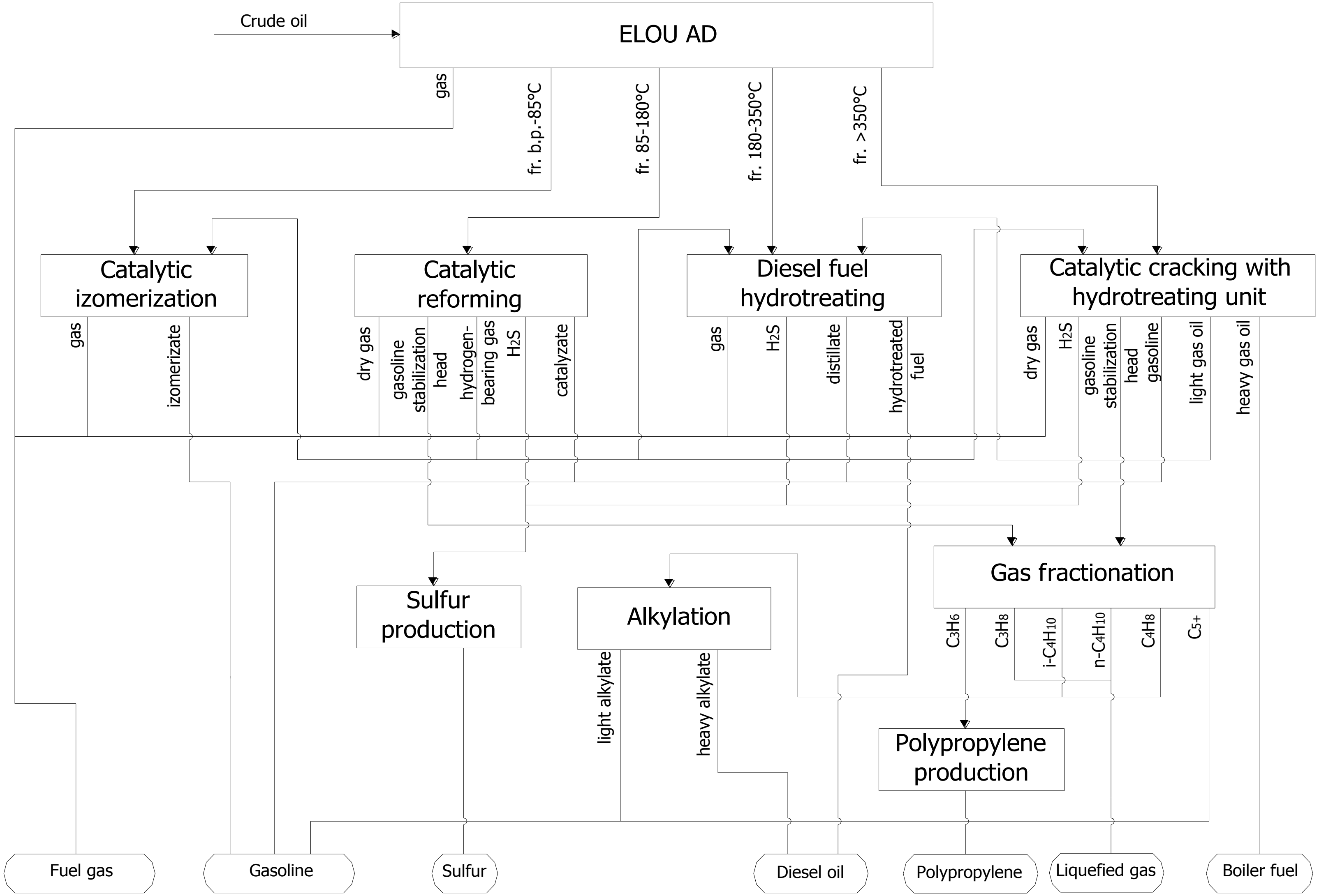

Fig. 5.1. Flow diagram of Nigerian oil processing (fuel option)

5.2. Material Balances of Technological Processes

Using the materials of the previous Chapters 3-4, as well as data from the literature [146-148], we calculate the material balances of technological units included in the flow diagram of oil refining according to the fuel option. For the calculations, we assume the 8 million tons/year refinery capacity, since it is the optimal value from the standpoint of the studied oils availability.

Material balances of technological processes and the total material balance of the refinery are presented in Tables 5.1-5.10.

Table 5.1

Material balance of the atmospheric distillation unit

Product	wt.% relative to feedstock	thousand tons/year
Feed:		
Dewatered and desalted crude oil	100	8,000
Products:		
IBP–85 °C	7.8	624
85–180 °C	26.8	2144
180–350 °C	35.4	2832
> 350 °C	29.4	2352
Losses	0.6	48
Total:	100	8,000

Table 5.2

Material balance of the catalytic isomerization unit

Product	wt.% relative to feedstock	thousand tons/year
Feed:		
IBP–85 °C	100,00	624,00
Hydrogen-bearing gas	0,20	1,25
Total:	100,20	625,25
Products:		
Gas	1,00	6,24
Isomerizate	98,70	615,89
Losses	0,50	3,12
Total:	100,20	625,25

Table 5.3

Material balance of the catalytic reforming unit

Product	wt.% relative to feedstock	thousand tons/year
Feed:		
85–180 °C	100,00	2144,00
Products:		
Dry gas	4,50	96,48
Stabilization head	5,00	107,20
Sulfurous gas	0,03	0,64
Hydrogen-bearing gas	5,00	107,20
Catalysate	84,67	1815,32
Losses	0,80	17,16
Total:	100,00	2144,00

Table 5.4

Material balance of the catalytic cracking unit

Product	wt.% relative to feedstock	thousand tons/year
Feed:		
Fuel oil (>350 ºC)	100,00	2352,00
Hydrogen-bearing gas	1,80	42,33
Total:	101,80	2394,33
Products:		
Dry gas	6,90	162,29
Sulfurous gas	0,70	16,46
Stabilization head	10,50	246,96
Petrol	41,40	973,73
light gas oil	22,30	524,50
Heavy gas oil	14,00	329,27
Burned-out coke;	6,00	141,12
Total	101,80	2394,33

Table 5.5

Material balance of the diesel oil hydrotreating unit

Product	wt.% relative to feedstock	thousand tons/year
Feed:		
180-350 °C	84,37	2832,00
Catalytic cracking light gas oil	15,63	524,50
Hydrogen-bearing gas	1,60	53,70
Total:	101,60	3410,20
Products:		
Gas	2,50	83,91
Sulfurous gas	0,32	10,74
Distillate	2,30	77,20
Hydrotreated product	96,08	3224,92
Losses	0,40	13,43
Total:	101,60	3410,20

Table 5.6

Material balance of the gas fractionating unit

Product	wt.% relative to feedstock	thousand tons/year
Feed:		
Catalytic cracking stabilization head	69,73	246,96
Catalytic reforming stabilization head	30,27	107,20
Total:	100,00	354,16
Products:		
Propane fraction	25,30	89,60
Propylene fraction	23,60	83,58
iso-Butane fraction	19,80	70,12
n-Butane fraction Фракция н-бутана	13,20	46,75
Butilen fraction	16,10	57,02
Casing head gasoline	1,60	5,67
Losses	0,40	1,42
Total:	100,00	354,16

Table 5.7

Material balance of polypropylene production unit

Product	wt.% relative to feedstock	thousand tons/year
Feed:		
Propylene fraction	100,00	83,58
Products:		
Polypropilen	97,00	81,07
Losses	3,00	2,51
Total:	100,20	83,58

Table 5.8

Material balance of alkylation unit

Product	wt.% relative to feedstock	thousand tons/year
Feed:		
iso-Butane fraction	55,15	70,12
Butylene fraction	44,85	57,02
Total:	100,00	127,14
Product:		
Light alkylate	82,50	104,89
Heavy alkylate	14,50	18,44
Losses	3,00	3,81
Total:	100,00	127,14

Table 5.9

Material balance of sulfur production unit

Product	wt.% relative to feedstock	thousand tons/year
Feed:		
Sulfurous gas	100,00	27,84
Product:		
Sulfur	94,10	26,20
Losses	5,90	1,64
Total:	100,00	27,84

Based on the obtained experimental data and using formula (2.2) and (2.3), we calculate the depth of oil refining and the yield of light petroleum products:

ORD = (8000000- (329270 + 358840)) / 8000000 100 = 91.3%

LDY = (3592700 + 3243360 + 81070 + 26200) / 8000 100 = 86.7%

Table 5.10

General material balance of Nigerian oil processing by fuel option

Product name	% масс. на сырье	тыс. т/год
Received:		
Dewatered and desalted crude oil	100,00	8000,00
Received:		
Fuel gas	4,48	358,84
Liquified propane-butane	1,70	136,35
High-octane gasoline	44,91	3592,70
Low-sulfur diesel fuel	40,55	3243,36
Fuel oil	4,12	329,27
Polypropylene	1,01	81,07
Sulfur	0,33	26,20
Losses	2,90	232,21
Total:	100,00	8000,00

Crude oil refining according to the developed scheme allows reaching a refining depth of 91.3% and yield of light petroleum products of 86.7%. The relatively large losses are due to the process of residual feedstock catalytic cracking, in which large quantities of burned coke are formed.

5.3. Reasons for Processing Nigerian Oils at PJSC “Ukrtatnafta”

PJSC “Ukrtatnafta” is an oil refinery with a 60-year history. The nominal capacity of this enterprise was 18.6 million tons/year. The refinery was focused on the processing of Ukrainian oils, high-sulfur and highly resinous Tatar oil, as well as oils that were supplied by the Druzhba pipeline.

Due to the cessation of Russian oil supplies, an increase in environmental requirements for manufactured products, physical wear and tear of equipment, the refinery capacity fell to 5-6 million tons/year, but even this amount is not supplied to the enterprise. Therefore, the prospect processing of Nigerian oils is relevant and economically profitable. Even if 3-4 million tons are supplied, this will lead to a sharp decrease in the production cost, as well as an increase in the production of gasoline, jet and diesel fuels, base and commercial oils, bitumen.

The structure of PJSC "Ukrtatnafta" includes 4 production facilities (fuel, gas-catalytic, oil, commodity transport) and 20 plants.

The general flow diagram is shown in Fig. 5.2.

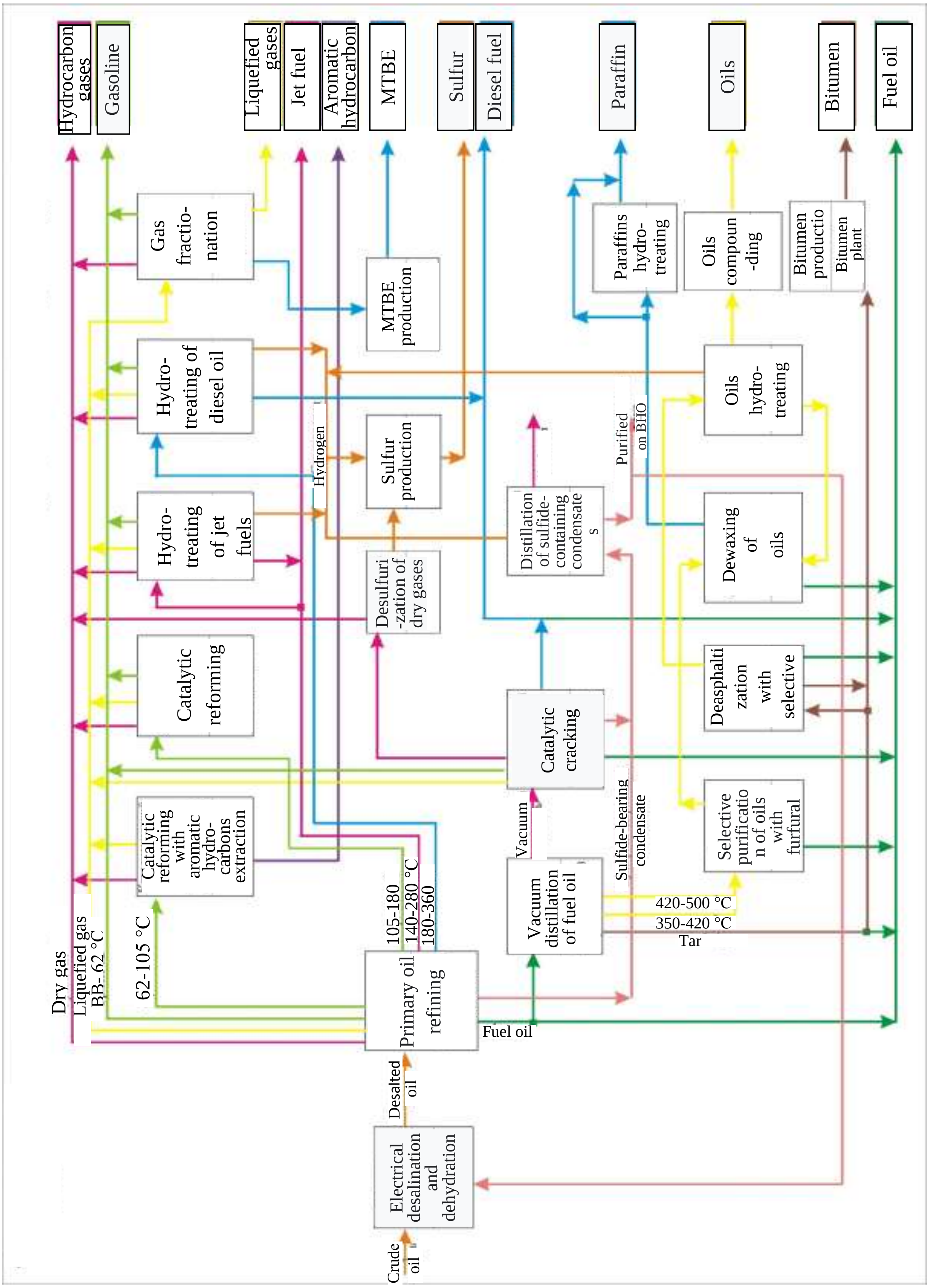

Fig.5.2 Key processes at PJSC “Ukrtatnafta”

5.4 Analysis of Nigerian Oils Possible Processing at PJSC “Ukrtatnafta”

Based on the characteristics of two Nigerian oils and two blends of Ukrainian oils (Table 3.4.), it can be argued that Nigerian oils are good feedstock for processing at PJSC “Ukrtatnafta” in addition to processing Ukrainian oils.

Crude desalter unit will operate normally, since the content of water and salts is comparable with that in Ukrainian oils. ADU/VDU will operate with insignificant temperature changes, since the content of gasoline and diesel fractions in Nigerian oils differs from Ukrainian ones by 3-10 %.

Catalytic reformers L-35-11/30, LCh-35-11/600, section 200 LK-6U will operate in a routine mode, since the content of sulfur, sour sulfur, toluene-forming, benzene-forming, paraffin-naphthenic hydrocarbons in Nigerian oils does not significantly differs from the content of the above compounds in Ukrainian oils. Circulation rate of the hydrogen-bearing gas, the temperature regime, and the pressure will remain unchanged.

The technological regime of jet fuels hydrotreater will also remain unchanged. All fractions of Nigerian and Ukrainian oils are comparable regarding the content of sulfur compounds, viscosity, mass fraction of aromatic compounds, and ash content. In terms of sulfur content in diesel fractions 180-360 °C, Nigerian and Ukrainian oils are identical, which means that it will not be a problem to obtain diesel fuel of Euro-5 class.

Taking into account an acute shortage of quality oils in Ukraine, it is possible to obtain high-viscosity index oils using the processes existing at PJSC “Ukrtatnafta” (see experimental results in Chapter 4).

Straight-run fuel oil from Nigerian oils can serve as a high quality boiler fuel.

The lubricating oil fraction after hydrotreater will serve as a feedstock for catalytic cracking units, since the content of sulfur and metals that have been transferred from crude oil is low.

It is possible to obtain high-quality bitumen from the tar of Nigerian oils by refining the technology and using a modifier.

Conclusions to Chapter 5

The choice of the fuel option for Nigerian oils processing has been justified. A set of petroleum products has been proposed to be obtained.

Material balances of all plants at the prefinerylant with a capacity of 8 million tons/year have been calculated.

The technical and economic indicators of the developed refinery have been substantiated. The payback period and profitability of the refinery are about 2 years and 49%, respectively. The implementation of a catalytic cracking unit will make it possible to increase the oil refining depth to 91.3%, while the yield of light petroleum products will be 87.6%.

The complexity rating of the developed refinery is ≈5.25, which is a fairly high indicator among the leading European oil refineries.

The conducted research and comparative analysis of the quality indices of Nigerian and Ukrainian oils allows to tell with absolute certainty that the studied Nigerian oils can be processed at PJSC “Ukrtatnafta” without major changes in the technological scheme.

GENERAL CONCLUSIONS

1. An important scientific and technical problem was solved, which is characterized by scientific novelty and has practical significance, namely: the physico-chemical properties of oils from the Port Harcourt area in Nigeria were studied; the option of their processing and involvement in processing at a Ukrainian oil refinery was proposed.

2. Nigerian oils were found to be light and low-paraffinic oils with a density of 850 kg/m^3, a low sulfur content of 0.37 and 0.18 wt.% and a low content of water and chloride salts. Taking into account the fractional composition, the investigated oils will be a good raw material for obtaining light distillate fractions.

3. The obtained gasoline fractions of Nigerian oils (boiling point 62 °C) will be a good feedstock for the light gasoline isomerization or a component of commercial gasoline. Fraction 62-105 °C is a good feedstock for the catalytic reformer, since in Nigerian oils the amount of toluene-forming components is 35.38 and 30.98%, the amount of benzene-forming hydrocarbons is 24-25%, the amount of sulfur and sour sulfur is insignificant. Fraction 105-180 °C is a good feedstock for the fuel catalytic reformer.

4. The jet fuels obtained from Nigerian oils meet the requirements of the state standards on main indices, but they must be preliminary desulfurized.

5. Diesel fractions obtained from Nigerian oils, in terms of sulfur content, are similar to diesel fuels obtained from mixtures of Eastern- and Western-Ukrainian oils. Therefore, these fractions after the dewaxing process will be a qualitative feed for the production of commercial diesel fuel Euro-5.

6. Base oils obtained after solvent refining with N-methylpyrrolidone and dewaxing of oil distillates of Nigerian oils had a high viscosity index (> 120 in the case of MD-1 oil distillate) and low pour point - minus (8-14) °C. Due to the experimental results the production methods for paving bitumen BND 60/90 and BND 90/130 were developed using a mixture of commercial oils extracted from fields located in the Port Harcourt region of Nigeria. For this purpose the tar obtained from Nigerian oils was oxidized at temperatures of 250 and 180 °C. But we were unable to obtain paving bitumen BND 60/90 and 90/130 meeting all standards.

8. Nigerian oil tar was overoxidized at a temperature of 250 °C and bitumen with softening point of 62, 77 and 108 °C were obtained. By compounding bitumen with softening point of 62 and 77 °C and tar in the ratio of 40:60 or 50:50, BND

60/90 bitumen was obtained. By compounding bitumen with softening point of 62, 77 and 108 °C and tar in the ratio of 30:70, BND 60/90 bitumen was also obtained.

9. Bitumen with a softening point of 107 °C was obtained from tar overoxidized at a temperature of 180 °C. After its compounding with tar in a ratio of 30:70, bitumen of the BND 60/90 grade was obtained.

10. When using overoxidized bitumen we failed to obtain a product meeting all standards for BND 90/130 bitumen.

11. The scheme of Nigerian oil processing according to fuel option is substantiated on the example of Brent Dated oil. The material balances of all technological processes and the total material balance of oil refinery with a capacity of 8 million tons/year were calculated. The technical and economic parameters of the refinery under development have been substantiated. The payback period and profitability of the refinery were found to be about 2 years and 49%, respectively.

12. The conducted studies and comparative analysis of quality indices of Nigerian and Ukrainian oils allow to assert that the investigated Nigerian oils can be processed at PJSC “Ukrtatnafta” without significant changes of the technological scheme.

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