OIL SHALE RESOURCES AND THE WAYS FOR USE

Arzu.E. Alizadeh[13]

UDC 544.
LBC 65.304.17

Keywords:

Shale
Mineral content
Kerogen
Mazout
Gasoline
Diesel fraction

ABSTRACT

Organic and mineral content in oil shale alternative to petroleum was studied, elemental composition was determined and the studies on oil shale resources in Azerbaijan and efficient ways to use, obtaining fuel fractions from oil shale were generalized as a review. Simultaneously, the paper represents the studies on the problems of the current state of processing of heavy oil residue, catalytic processing of heavy crude oil; catalytic processes were classified and the investigations were summarized on the direction of obtaining light coloured petroleum products by heavy crude oil and also by co-processing them with oil shale via hydrocracking process that is the most effective one among catalytic processes. Technological parameters were determined for mazout and oil shale hydrocracking process: temperature - 430-440 C, pressure – 10-60 atm, maximum possible amount of oil shale – 7.5-10 wt.%. Mineral content in oil shale was found to be responsible for coke extraction preventing equipments from coking. Light coloured petroleum products (gasoline and diesel fraction) of 61% (mas.) and cracked residue of 32-34% were obtained by mazout and oil shale hydrocracking process

[13]. Y.H. Mammadaliyev Institute of Petrochemical Processes of ANAS
aalizade-sm@mail.ru
https://orcid.org/0000-0001-6761-1058

Received: 24.05.2021
Accepted: 07.08.2021

ISSN: 2790-0029 (Print)
ISSN: 2790-0037 (Online)

JOURNAL OF "HISTORY OF SCIENCE"
Cild 2, Say 3, Sıra 5, 2021, 16-30

YANAR ŞİST EHTİYATLARI VƏ ONLARIN İSTİFADƏ İSTİQAMƏTLƏRİ

Arzu.E.Əlizadə[14]
UOT 544.
KBT 65.304.17

Açar sözlər:

Yanar şist
Mineral hissə
Kerogen,
mazut
Benzin fraksiyası
Dizel fraksiyası

ANNOTASİYA

Məqalədə neftə alternativ xammal mənbəyi olan yanar şistlərin üzvi və mineral hissələri tədqiq edilmiş, element tərkibi təyin edilmiş, Azərbaycanda yanar şist ehtiyatları və onların səmərəli istifadə istiqamətləri, yanar şistlərdən yanacaq fraksiyalarının alınması istiqamətində aparılmış elmi tədqiqat işləri araşdırılaraq icmal şəklində ümimiləşdirilmişdir. Bütün bunlarla yanaşı məqalədə ağır neft qalıqlarınn emal probleminin müasir vəziyyəti araşdırılmış, ağır neft xammalının katalitik emal probleminə xüsusi diqqət yetirilmiş, katalitik proseslər təsnifatlaşdırılaraq, onlardan ən effektlisi hesab edilən hidrokrekinq prosesi vasitəsilə ağır neft xammalından, eləcə də onların yanar şistlərlə birgə emalından açıq rəngli neft məhsulları alınması istiqamətində aparılan elmi-tədqiqat proseslərinin xülasəsi verilmişdir. Mazutun yanar şistlə birgə hidrokrekinqi üçün prosesin texnoloji parametrləri təyin edilmişdir: temperatur 430-440°C, təzyiq 10-60 atm, yanar şistin əlavə edilməsinin maksimal miqdarı 7,5-10 küt.%. Müəyyən edilmişdir ki, yanar şistin mineral hissəsi aparatların kokslaşmasının qarşısını almaqla koksun çıxarılması vəzifəsini görür. Mazutun yanar şistlə birgə hidrokrekinqi prosesindən 61% (kütlə) açıq rəngli neft məhsulları (benzin və dizel fraksiyası), 32-34% krekinq qalığı alınmışdır.

[14]. Y.H. Məmmədəliyev adına AMEA Neft-Kimya Prosesləri İnstitutu
E-mail: aalizade-sm@mail.ru
https://orcid.org/0000-0001-6761-1058

Məqalə redaksiyaya daxil olmuşdur: 24.05.2021
Təkrar işlənməyə göndərilmişdir: 05.06.2021
Çapa qəbul edilmişdir: 07.08.2021

СЛАНЦЕВЫЕ РЕСУРСЫ И ТЕНДЕНЦИИ ИХ ИСПОЛЬЗОВАНИЯ

А.Э.Ализаде [15]
УДК 544.
ББК 65.304.17

Ключевые слова:

Сланец
Минеральная часть
Кероген
Мазут
Бензиновая фракция
Дизельная фракция

АННОТАЦИЯ

В настоящее время в мире существует множество конфликтов, причиной продолжительности которых является невыполнение принятых в связи с этими противостояниями решений Организации Объединенных Наций, представляющей мировое сообщество. Такого же рода причины способствовали длительному пребыванию под оккупацией захваченных территорий Азербайджанской Республики. Несмотря на то, что в свое время мировое сообщество принимало важные решения относительно очагов конфликта они не выполнялись и со временем такие вопросы как оккупация и раздробление территорий навязывались как «факт» и «реальность».

Данная тенденция не является исключением и для израильско-палестинского противостояния, которое на политической арене известно как ближневосточный конфликт. На большинстве этапов данного конфликта международное сообщество демонстрировало позицию и задокументировало их в формате различных постановлений. В 1947 году Генеральная Ассамблея ООН вынесла постановление под номером 181 о создании еврейского и палестинского государств на территории Палестины. Согласно решению, 57% территории Палестины выпадало на долю евреев, а 42% арабов. Оставшийся 1% территории, где находился город Иерусалим должен был стать международной территорией. Это было первым международным постановлением для урегулирования израильско-палестинского конфликта, которое до сих пор не выполнено.

Как видно, конфликт не остался абстрактным для взглядов мирового сообщества и было принято достаточно судьбоносных решений. Одним из самых необходимых шагов для правильной интерпретации конфликта здесь - это точное и последовательное исследование решений ООН.

[15]. Институт нефтехимических процессов имени академика Юсифа Мамедалиева
E-mail: aalizade-sm@mail.ru
https://orcid.org/0000-0001-6761-1058

Introduction

Increase in global energy consumption is accompanied by a rapid depletion of the main energy sources, primarily petroleum and gas. Inevitable depletion of traditional fuel resources leads to the search for new sources of raw materials for fuel and energy production. This feature needs to develop the technologies for production of energy and motor fuels on the basis of non-petroleum based raw material, as well as various monomers for petrochemical industry. Therefore, possibility of obtaining the products from non-petroleum based raw materials with the composition and properties identical to natural gas and petroleum products is important for petrochemical industry.

The Organization of the Petroleum Exporting Countries (OPEC) forecasts depletion of oil reserves in the next 40-50 years, and some countries in a shorter time according to the limited oil reserves in subsoil, increase in production and transport costs, current rate of consumption growth.

The modern world balance of oil consumption shows an increase in the demand for engine fuel. Increasing the part of total processing of heavy and high-sulfur oils at the same time leads to a reduction in the yield of light and medium distillates and worsening their quality. Therefore, development of oil refining industry requires deep processing and rational use of oil residues.

As one of organic raw material resources alternative to petroleum, the volume of oil shale resources is 500 million tons in our republic that is significantly important due to energetic properties and technological parameters.

The resin properties obtained on the basis of oil shale allow to accept it as an alternative source of natural hydrocarbons to petroleum and it's practical advantage of oil shales. Currently, the ways for use are intensively developed in Russia on the basis of application of deep processing technologies for the purpose of obtaining liquid fuel, high-calorie gas, semi-coke and chemical raw materials from solid fuels, especially from oil shale. Experts in this field around the world [1] unanimously believe that all types of oil shales have great potential for any country as a whole, both now and in the future, as an alternative source of petroleum. Therefore, the most important way to use oil shale in our country is obtaining liquid fuels from the organic matter of oil shale by processing via various technological processes.

One of the processing technologies of oil shale is hydrocracking process with heavy oil residue. The world leading companies are investing heavily in complex processing technology for heavy oil residues - thermal (flexicoking, deasphalting, coking) and catalytic (FCC catalytic cracking, high pressure hydrocracking H-Oil, LC-Fining, T-Star, Isocracking) [2].

Hydrocracking is one of the effective processes for obtaining motor fuels of high quality from heavy oil residue. For example, Chevron Lummus Global's recirculated two-stage hydrocracking process [3] allows for 100% conversion of raw materials, obtaining the required products with the highest quality, minimizing hydrogen consumption and processing more complex raw materials.

Shale deposits were discovered in Azerbaijan in the early twentieth century. As this period coincided with the discovery and development of large oil and gas reserves, oil shales were neglected. This, in turn, has led Azerbaijan's fuel and energy complex to rely entirely on traditional liquid and gaseous hydrocarbon fuels. For this reason, the assessment of the suitability and expediency of oil shale has not been studied until recently.

Oil shale is organic-mineral sedimentary rock belonging to the group of solid caustobiolites, that provides the separation of resin close to petroleum by dry distillation. The mineral content in oil shales (calcites, dolomite, montmorillonite, kaolinite, feldspar quartz, pyrite, etc.) predominates over the organic content consisting mainly of kerogen. The organic content of oil shale is composed of the remains of primitive seaweed, zoo- and phytoplankton undergone biochemical and geochemical transformations.

The largest source of hydrocarbon reserves in Azerbaijan after petroleum and natural gas is oil shale, a lack of studies on physicochemical and performance properties, suitability for processing, as well as the use as energy fuel and petrochemical raw materials is one of the most pressing issues of our time.

Shale deposits in Azerbaijan are located mainly in the east of the country, northern and southern foothills of the Greater Caucasus. In general, there are about 80 oil shale deposits and manifestations in Azerbaijan. The Guba, Dially and Jangichay deposits have been explored to some extent [4].

The most energetically interesting part of oil shale is its organic component - kerogen. Kerogen (or kerobitum) is generally the organic part of rocks that is insoluble in solvents. Kerogen has a very complex structure and the chemical composition consists mainly of the elements C, H, O, N and S. The C/H mass ratio in oil shale varies from 7.5 to 10. As this indicator is between the C/H ratio in coal and petroleum, the kerogen structure also occupies an intermediate position between coal and petroleum.

The mineral content in oil shale usually consists of quartz, feldspar (albite), clay, carbonates (dolomite, calcite), as well as pyrite and some mineral salts [5].

Carbonate, aluminosilicate-carbonate-based shales are distinguished according to the colorful chemical composition of inorganic content. Inorganic content of oil shale contains valuable chemical elements, including germanium, yttrium, scandium, and other metals [6].

Energetic direction is the first of the main directions for the use of oil shale. Thus, oil shale is burned as solid fuel in the furnaces of power plants [7].

The second one is the technological direction. In this case, oil shale is subjected to thermal decomposition in special aggregates to obtain gas and liquid products: resin, natural gasoline, gas and pyrogenetic water. Heavy resin fraction (about 50% of the total resin) is used as a raw material for the production of road bitumen.

The high sulfur content of bitumen is a positive factor and improves asphalt pavement quality. The middle fraction (about 25-30%) is a raw material for partial impregnation on sleepers in the production of oil and meliorative preparations. But the other part is directed to the production of furnace fuel after hydropurification process.

Natural gasoline and light fractions (15-25%) are used as raw materials for the production of thiophene and homologues. After the removal of organic sulfur compounds, the remaining part is hydropurified and used for the production of furnace fuel.

Besides, technical benzene, 99% commercial and 90% technical toluene according to the main product amount, xylene isomers and xylene concentrate consisting of ethylbenzene mixture that is used as a solvent in paint industry and also as for other purposes, are produced from the products of oil shale thermal treatment [8].

Like all solid hydrocarbon fuels, oil shale consists of two parts - organic matter and mineral components. Potential amount of resin in oil shale has been determined by Fischer analysis and the results are set into Tab. 1.

The results of oil shale Fischer analysis

Indices	Amount, % (mas.)
Resin	14.75
Solid residue	71.54
Water	5.38
Gas	8.24

Elemental composition of oil shale as well as the resin and solid residue obtained by their Fischer analysis was determined and represented in Tab.2.

Table 2

The results of oil shale elemental analysis

Sample	Amount, % (mas.)			
	C	H	N	S
Guba oil shale	21.93	2.17	0.21	2.4
Resin	77.46	11.03	0.36	0.65
Solid residue	17.76	1.12	0.18	4.37

The amount of organic and mineral components, as well as ash, moisture, volatile matter content, total sulfur and combustion temperature in oil shale (Guba) were determined by technical analysis (Tab. 3). The results of oil shale elemental analysis by fluorescent method are set into Tab. 4.

Table 3

Average values of oil shale technical analysis results (mas. %)

Indices	Amount, % (mas.)
Organic carbon	20.70
Density at 20 ºC, kg/m^3	2290
Moisture	2.84
Volatile matter	22.63
Ash	71.54
Combustion temperature, kJ/kg	3880

Table 4

The results of oil shale elemental analysis

Oil shale	Metal and metal oxides											
	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_3	SO_3	K_2O	CaO	TiO_2	MnO_2	Fe_2O_3	Loss by incand.
Amount, % mas.	1.25	2.20	13.75	43.16	0.17	0.015	2.56	2.87	0.63	0.054	7.30	25.61
Amount, ppm	Ni	Cu	V	Zr	Cr	Rb	Sr	Ba	Zn	Pb	Ti	Sc
	0.24	0.0047	0.023	0.024	0.057	0.037	0.043	0.071	0.011	0.002	$<1\cdot10^{-4}$	$<1\cdot10^{-3}$

Numerous studies have been carried out in the direction of thermocatalytic cracking of heavy oil residues together with oil shale. It has been established that organic and mineral content of oil shale have an activating effect on thermal conversion of heavy oil products [9].

The current development level of scientific research and technological processes allows to obtain large quantities of commercially available petroleum products from oil residues, as well as carbon products from high-quality carbon coke. The leading role in the solution of this problem is given to hydrogenation catalytic processes, which allow to prepare the oil residues for further processing by the processes of metal decontamination, sulfur removal, saturation with hydrogen. These processes are characterized by high flexibility and good quality of products. However, the necessity to high investments (hard conditions of the process, complexity in the design of the apparatus, the presence of hydrogen and complicated catalyst systems) can be noted as shortcoming.

In the economically developed countries (USA, Japan), where the oil is refined for import, certain successes have already been achieved in industrial implementation of these processes [10-11].

However, currently there are no qualified catalytic systems for processing of fuel oil and goudron to high-yield and high-quality products in internal oil refining and industrial scale. Desulphurization process (equipped with reactor and compressor equipment) of fuel oil and goudron has not been developed. The adsorption - catalytic cracking and thermodeasphalting processes of HOR are at the stage of pilot studies.

Worldwide, the following group of HOR treatment processes in the oil refining industry have a wide application area [12]:

- thermal and thermocatalytic processes —these processes are based on the extraction of carbon excess or carbon-rich products by comparison with primary raw materials (oil coke, coking on the catalyst of cracking process, cracked residue, catalytic cracking gas-oil, heavy pitch obtained from pyrolysis, etc.) from the composition of HOR;
- hydrothermal and hydrocatalytic — these processes are based on inclusion of hydrogen from the outside and thus, on the formation of low- and medium-molecular fuel fractions or a compound containing low sulfur, oxygen and nitrogen compounds and a rich product possessing metals;
- thermo- və catalytic oxidation processes — these processes are accompanied by the formation of carbon oxides and hydrogen via gasification of coke and HOR with oxygen vapor and/or vapor, these compounds are considered to be semi-product for the synthesis of hydrocarbon oxides (alcohols, ethers, ketones, aldehydes, etc.). This group also includes the process of carbonation by oxidative condensation for the production of bitumen.

The hydrocatalytic processes are the most effective processes in the deep processing of heavy oil residues. Hydrocracking (HC) of oil distillates and residues is a popular destructive process of oil refining for the purpose of obtaining light oil products. This process was firstly known in the United States.

The main advantage of HC is the ability of processing of distillates, also residual stocks accompanied by obtaining of high quality products: compressed gases, gasoline with high octane number, diesel with low freezing temperature and jet fuels and oils. HC is the only second oil refining process that allows a significant expand in jet fuel resources.

The authors [13] have developed the principal fundamentals for a new process of thermochemical processing of oil residues based on the experiments on thermal solubility of oil shale. The basis of the process is the unique properties of oil shale, which are natural generators of radicals, catalysts of cracking and donors of hydrogen. The process occurs at 390-440 °C temperature and 3-8 MPa pressure. The peculiarity of the Baltic's shales used in the process is the high level of hydrogen in the organic mass. Other sapropelite fuels may also be used in this process: Povolj sulfur shales, Kuzbas sapro-mixed or far east sapropelite.

The basis of the made process consist of the considerations about the mechanism of thermal destruction (thermal solubility) of the organic mass of oil shale [14, 15]. Under optimal conditions, the processes of decomposition and fluidization of organic mass of oil shale occur by the formation of liquid products containing radicals with various molecular mass and compounds, which possess donor - hydrogen characteristics (hydrogen-forming condensed aromatic hydrocarbons, nitrogen and oxygen-containing derivatives, as well as cyclic alcohols). Under thermochemical processing, these chemically active compounds formed from the organic mass of oils shale conditions the destruction (by radical-chain mechanism) of hydrocarbons with high boiling temperature contained in goudron. Mineral parts, mainly consisting of alumosilicate and ferrous salts, have a significant influence on the development of hydrogenation reactions of compounds, which are composed of initial raw material, and their decomposition products [16].

During the thermochemical processing of goudron in the presence of shale, along with the destruction of high-molecular hydrocarbons of goudron, it is also possible occurring of destruction of asphaltenes contained in it. The main part (up to 90 %wt.) of organic mass of shale converts to liquid and gaseous products [17]. In the developed process, oil shale and its conversion products are activated, as mentioned, the destruction reactions of goudron are the source for the components of the process liquid products.

The regularities for co-processing of the mazout obtained from Baku oil with oil shale were studied.

It was established, that not only physical but also chemical transformations occur on dispersed particles surface in the mixing process of mazout with oil shale. As a result of co-processing, a fraction boiling up to 360 °C is obtained, as well as an increase is observed in the amount of resin-asphalt substances on the oil shale particles.

It is known from literature [9], that organic and mineral content of oil shale have activating effect on thermal conversions of heavy oil products. These compounds actively promote hydrogenation of unsaturated compounds formed by heavy oil residue cracking and simultaneously prevent intensive coking of equipments, in other words play a role of coke extractors.

The combination of the addition of highly dispersed (10-50 μm) oil shale particles to the reaction medium by thermal process removes coke deposits to the surface and prevent coking of the reaction apparatus wall.

On the other hand, mineral content of oil shale containing aluminosilicates, iron, molybdenum, cobalt, nickel and other catalytic active metals oxides intensify cracking and hydrogenation reactions.

Technological parameters for hydrocracking process of mazout with oil shale were determined: temperature 430-440 °C, pressure 10-60 atm, maximum possible amount of oil shale addition 7.5-10%. It was established that mineral content of oil shale is responsible for coke extraction preventing equipments from coking. 61% (mas.) of light coloured petroleum products (gasoline and diesel fraction), 32-34% of cracked residue were obtained from hydrocracking process of mazout with oil shale.

REFERENCES

1. Gorlov E.G., Nefedov B.K., Gorlova S.E., Andrienko V.G. Processing of heavy oil residues in the presence of oil shale. Solid Fuel Chemistry. 2006. № 6. P. 43-56.
2. Kotov A.S., Gorlov E.G. Thermolysis of mazout and resin with activating additives for obtaining light oil fractions. Solid Fuel Chemistry. 2009. № 3. P. 30-36.
3. Zhukov V.Yu., Yakushin V.I., Kapustin V.M., Semenov V.N. Hydrocracking unit T-Star OOO Lukoil-Permnefteorgsintez. Chemistry and Technology of Fuels and Oils. 2009. № 1. P. 17.
4. Kerimov Kh.M. Study of Azerbaijan oil shales. Azerbaijan Chemical Journal. 2007. № 1. P.162-173.
5. Kerimov Kh.M. Study of physicochemical properties of oil shales. Solid Fuel Chemistry. 2004. № 1. P. 18-25.
6. Blokhin A.I., Nikitin A.N., Frayman G.B. Oil shale – alternative fuel and raw material for chemistry. Fuel-Energetic Complex. 2000. № 2. c. 19-25.
7. Kerimov Kh.M. Fast pyrolysis and determination of kinetic parameters oil shale decomposition. Journal of Applied Chemistry. 2004. V. 77. Iss. 1. P. 158-162
8. Yesavdzh V.F., Popov A.I., Shuparskiy A.I. Harmful emissions into atmosphere in burning of povolzhskiy shales. Goryuchie slantsy. 1997. V. 3. № 2. P. 205-217.
9. Maloletnev A.S., Yulin M.K., Vol-Epstein A.B. Thermal cracking of heavy oil residues mixed with shale oil. Solid Fuel Chemistry. 2011. No.4. P. 20-25
10. KotovA.S., GorlovE.G. Thermolysisof-fuel oil and goudronwith activating additives for obtaining of light oil fractions. Solid Fuel Chemistry., 2009,3,p. 30-36.
11. Zhukov V.Y., Yakushin V.I., Kapustin V.M., Semenov V.N. "T-Star LLC hydrocracking device" Lukoil-Permoilorgsynthesis. Chemistry and technology of fuels and oils. 2009. No.1. P. 17.
12. LevinterM.E., AkhmetovS.A. Deep oil refining. M.: Chemistry, 1992, 224 p.
13. Patent No.2024577, Russia, 1992.
14. Platonov V.V., Vol-Epstein A.B., Klyavina O.A. et al. Investigation of the structure of compounds of the products of thermal dissolution of kerogen-70 from the Baltic oil-shale-kukersite. Solid Fuel Chemistry, 1982,No.3,p.49-52
15. Vol-Epstein A.B., Platonov V.V., Spielberg M.B. etal. Thermocracking of oil goudron.Chemistry of solid fuel, 1990, No.5, p. 86-91
16. Vol-Epstein A.B., Shpilberg M.B., Platonov V.V., Rudensky A.B. Oil shales are hydrogen donors during the thermal dissolution of brown coal in the Kansk-Achinsk basin. Solid Fuel Chemistry. 1987, No.2, p.75-77
17. Vol-Epstein A.B., Shpilberg M.B., Gorlov E.G. Production of fuel products by thermal dissolution of enriched Baltic oil shale. Solid Fuel Chemistry. 1983, No.2, p.59-68