Prospects for the use of oil shale in the Republic of Uzbekistan

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Abstract. Oil shale is widespread throughout the world. The world resources of organic carbon accumulated in oil shale are enormous. However, despite significant reserves, the development of the oil shale industry in various countries was characterized by periodic ups and downs. The article considers the analysis of the current state of the existing reserves of oil shale in the deposits of the Republic of Uzbekistan, provides brief information about the deposits of oil shale. The features of oil shale are presented, which make it possible to consider them as an energy, chemical, technological, as well as mineral raw material for use in various industries, which is an urgent problem. Technological possibilities in the processing of oil shale are considered.

1 Introduction

Oil shale is widespread throughout the world. The world resources of organic carbon accumulated in oil shale are enormous [1-3]. However, despite significant reserves, the development of the oil shale industry in various countries was characterized by periodic ups and downs [3]. This was due to a number of reasons: the high ash content of oil shale and the lack of acceptable technologies for their integrated use with high economic and environmental efficiency [4, 5]. In addition, the pace of development of the shale industry depends on the conditions for the extraction and processing of shale, the state of the fuel and energy complex, oil prices, as well as world politics [6, 7].

However, the use of shale not only as energy carriers, but also as a source of valuable chemical products, as well as solid mineral residues, can become a new step in the development of the petrochemical industry, so they should be considered not only as a cheap and widespread solid fuel, but also as a raw material for obtaining motor fuels, oils and solvents, as well as a potential source of rare metals, most of which are present in small quantities, while uranium, nickel, molybdenum, vanadium and rhenium can form industrial concentrations [8-10].

Oil shale is one of the promising types of organic raw materials that can largely compensate, and in the future even replace oil products and gas. Unlike other types of solid fossil fuels (SFOs), oil shale contains significant amounts of hydrogen in organic matter. The possibility of obtaining liquid and gaseous hydrocarbons from oil shale, similar in

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composition and properties to oil products and natural gas, makes it possible to consider them as important strategic resources [11, 12].

Oil shale is a mineral from the group of solid caustobioliths, which, during dry distillation, gives a significant amount of resin (similar in composition to oil). There are huge reserves (47.0 billion tons) of oil shale on the territory of the Republic of Uzbekistan. Only in the Kyzylkum basin there are deposits with predicted reserves of oil shale in the amount of 24.6 billion tons. The study of the characteristics of oil shale allows us to consider them as an energy, chemical, technological, as well as mineral raw material for use in various industries [13-15]. At the Baysun, Sangruntau, Aktau, Uchkyr, Kulbeshkak, Urtabulak deposits, oil shale reserves are about 1 billion tons. Promising manifestations of oil shale have also been identified in other areas of the Republic of Uzbekistan.

2 Materials and Methods

The Sangruntau oil shale occurrence is located in the core and limbs of a fold gently dipping to the east, framing the Paleozoic Sangruntau and Nura uplands. The angles of incidence of the wings of the fold are from 2 to 10°. The shale layer has been traced for 25 km along an eroded alpine structure [1-3, 5-6].

The layer of metal-bearing shales is confined to the lower Eocene, which are represented by clays, sandstones and siltstones. The reservoir thickness ranges from 0.8 to - 4 m, averaging 1.0 m. The reservoir has a simple structure.

Shales, as a rule, are accompanied from above and below by a rim of bituminous clays, having a thickness of RO-Q-S-M and, in places, significantly enriched in metals. The oxidation zone in the Sangruntau occurrence area varies from 0 to 20 m.

Oil shale is black, homogeneous, slightly calcareous. The structure is massive, schistose. It burns from a match, emitting the smell of burnt rubber. The organo-mineral base is a dispersed carbonate-clay mixture with a structureless sapropelic substance of a colloalginite nature [8, 9].

In addition to the main components that make up oil shales, inclusions of mineral terrigenous and authigenic impurities and organic detritus are observed.

Oil shales belong to the calcareous-argillaceous vitrinite-colloalginite petrographic type and are of sapropelic origin. The oil shales of the Sangruntau occurrence consist of (%): insoluble residue up to 84.1; chloroform bitumen "A" up to 0.096; organic matter - up to 17.4. They have an ash content of 65.0-93.73% (on average 74.2%), humidity - 4.4%.

The ash of oil shale contains vanadium pentoxide - 0.1-0.33%; nickel - 0.02-0.03%; cobalt - 0.001-0.002%; molybdenum - 0.01-0.073%; tungsten trioxide - 0.01-0.06%; rhenium - 0.0001-0.0002%, titanium - 0.30-0.49%. Oil shales of Uzbekistan, in addition to carbon raw materials, contain U, Mo, Au, W, Ag, Re, Cd, Se, Cu, Ni, Pb, S, including rare earth metals and platinum group metals.

3 Results and Discussion

To determine the directions of industrial use of oil shale, it is necessary to have information about their chemical and mineralogical composition, the structure of organic matter, the presence of organomineral compounds, as well as the changes that the original substance undergoes at various stages of thermal or chemical exposure.

According to chemical analysis (Table 1), some fluctuations in their composition have been established in oil shale, which is primarily caused by different amounts of quartz, silicon and clay minerals.

Table 1. Analysis of oxides in different variants.

Oxides	Average content	Samples				
		B-1	B-2	B-3	B-4	SN-1
SiO_2	39.43	48.24	33.95	30.86	54	40.36
Al_2O_3	15.36	14.98	10.15	12.18	23	16.39
K_2O	1.4	1.21	0.86	1.28	1.6	1.59
CaO	13.32	7.57	16.16	14.23	19.2	9.29
Na_2O	0.42	0.66	0.29	0.29	0.6	0.28
MgO	2.6	3.57	1.63	2.07	3.6	2.14
P_2O_5	2.44	0.79	4.02	3.8	n/d	1.25
TiO_2	0.62	0.76	0.48	0.58	n/d	0.68
MnO	0.038	0.036	0.046	0.04	n/d	0.029
$S_{general}$	8.8	6.57	10.33	10.97	8.3	8.24
$Fe_{general}$	6.5	4.78	6.26	7.49	n/d	7.36

Note to Table 1. The analyzes were performed on an ISP mass spectrometer Elan DRC II F protected by the Republic of Uzbekistan; n/a – the element is not defined. Samples B-1, B-2, B-3, B-4 - Baysun, SN-1 - Sangruntau.

In addition, the unique composition of the organic matter of shale makes it possible to use them not only as energy carriers, but also as a source of valuable chemical products.

It should be noted that in addition to carbon, hydrogen, nitrogen and oxygen, the organic part of oil shale contains sulfur, chlorine and phosphorus may also be present. The presence of these elements negatively affects the equipment during the processing of shale, since the oxidation of organic substances produces sulfur oxides and hydrogen chloride, which are strong corrosive agents. The elemental composition of the organic part of shale is shown in Table 2; it can be seen that shale contains more sulfur than standard thermal coal grades. It should be noted that the high sulfur content and the presence of halogens require special measures when building boiler houses using such raw materials, however, given the initial low cost and low transportation costs, even the use of special boilers and flue gas cleaning systems is most often justified.

Table 2. The elemental composition of the organic part of shale.

Country field	Elementary Composition, %				
	C (carbon)	H (hydrogen)	O (oxygen)	N (nitrogen)	S (sulfur)
Sangruntau (Navoi region)	56-82	5-10	10-40	0.2-0.8	0.2-11
Baysun (Surkhandarya region)	64.5	7.7	20.3	2.3	5.2
Urtabulak (Bukhara region)	60-70	7-8	up to 20	2.6	8-11

Shale organic matter is called kerogen, and its chemical composition includes: carbon, hydrogen, oxygen, nitrogen and sulfur. Carbon is the main element that determines the heat of combustion of fossil fuels. Hydrogen is the second most important calorific element, which plays a significant role in the energy potential of kerogen. Compared to other solid fossil fuels, the organic matter of oil shale is characterized by a high hydrogen content and, thus, a better ability to transform into liquid and gaseous products during thermal catalytic destruction.

In addition, oil shale contains a wide range of non-ferrous and rare metals (Baysun deposits) (Table 3).

Table 3. The list of rare metal oil shale contains.

Metal	**Ore, g/t**	**In 1 million tons of ore, t**	**Reserves by field thousand tons**
Molybdenum	2800	2800	155.4
Vanadium	2160	2160	119.9
Selenium	106	106	5.9
Uranus	266	266	14.8
Nickel	2100	2100	116.6
Cobalt	600	600	33.3
Cadmium	200	200	11.1
Copper	400	400	22.2
Zinc	480	480	26.6
Yttrium	103	103	5.7
Scandium	6.1	6.1	0.338
Rhenium	0.2	0.2	0.011
Tungsten	1100	1100	61.0

Thus, oil shales can serve not only as an energy source, but also as a potential resource base for the industrial extraction of both rare and scattered, and industrially valuable associated components. The presence of, for example, uranium, molybdenum, germanium or other elements in them in industrially significant quantities can have a significant impact on the economics of the cost of production and processing. In such cases, the development and processing of even OM-poor shales (15–20% organic matter, resin yield 4–6%) can be profitable.

When considering the processing of oil shale, the following areas should be divided:

a) extraction with subsequent combustion as boiler fuel;

b) mining with further processing to produce cement, as well as energy;

c) mining for processing into valuable chemical and energy raw materials.

No matter which of the above methods is used in various enterprises, the products of oil shale processing are always constant and they are shale tar, high-calorific gas, water and solid product. The first processing option has been actively used in Estonia, where most of the extracted oil shale was used as boiler fuel in thermal power plants, but this use of oil shale is already limited due to stringent environmental requirements. The second way of processing can be followed in the case when oil shale contains a small amount of kerogen (organic part) in its composition, and the mineral component makes it possible to produce cement of the required quality. The third direction of oil shale processing is the most efficient - in this case, the target product of processing will be shale tar, which can be transported and processed both individually and at refineries after mixing with oil. Also, with this method of processing, an ash residue will be formed, which is a fairly cheap raw material for the production of building materials. Thus, the use of oil shale can be different and is divided into two areas:

a) fuel and energy (as a fuel for generating heat and electricity);

b) technological (target products are gas and shale tar, which can be used to produce liquid fuels and valuable chemical products).

When oil shale is heated to a temperature above 500 °C without oxygen, shale tar, gas and water begin to be released. For oil shale processing, it is cost-effective to have a resin yield of at least 6%. In total, at the present time there is another classification of oil shale processing methods (thermal processes are divided into coking, semi-coking and gasification):

a) semi-coking (the goal is to obtain oil shale resin, from which liquid fuels or chemical products are subsequently obtained);

b) high-temperature processing (the goal is to obtain shale gas, which includes energy gas and synthesis gas, as well as liquid shale tar products;

c) direct burning of shale for energy.

The disadvantages of thermal processes include the use, most often, of periodic furnaces, which requires significant capital costs for their construction and low productivity of such devices; nevertheless, their reliability and durability are known (the service life of such batteries is often at least 40 years).

Development and implementation of technology for obtaining gaseous and liquid hydrocarbons from the organic part of oil shale and obtaining on their basis chemical compounds for economic sectors and energy carriers with improved environmental and operational performance with the presence of methanol and ethanol in the composition, while simultaneously increasing the yield of gasoline of composite origin, eliminating the need to add co side of synthetic oxygenates in commercial gasoline to ensure improved environmental and performance characteristics, naturally reduce the cost of commercial gasoline products.

The oil shales of Uzbekistan are distinguished by a considerable content of the organic part. This circumstance will undoubtedly interest consumers, which stimulates the classification for the development of technology and processing of shale raw materials to obtain energy carriers of various consistency, which positively affect the technological, economic, and overall strategic indicators of the republic.

The predicted situation of potential reserves of traditional hydrocarbon raw materials is the reason for the growing interest in alternative raw materials such as natural shale and other materials of organic origin.

Based on the results of the analytical work carried out, oil shale of local republican origin is considered as a fine mineral mixture of organic and inorganic components. The organic part is also divided into bitumen and creogen. The latter consists of polycyclic subgroups linked together by long chain alkanes and isoprenides. The inorganic part, unlike other deposits, is rich in oxides, molybdenum, nickel, cobalt and tungsten, as well as the presence in the composition of both the organic and inorganic parts of significant amounts of sulfur, nitrogen and phosphorus compounds, which can also without any obstacle pass into the composition of the resulting processing of combustible shale of the hydrocarbon part, regardless of their processing conditions. Therefore, the idea of the possibility of obtaining energy carriers of gaseous and liquid consistency by simple pyrolysis of oil shale is only superficial when it comes to qualified processing of oil shale to obtain commercial products - fuel and energy materials for a wide range of consumers. In addition, the analytical material produced by the relevant qualified services shows that simple pyrolysis thermally decomposes, in addition to the organic part of the minerals contained in the composition of the inorganic part of the raw material, and is accompanied by a pyrolysis process with a rapid release of carbon dioxide, with the content of nitrogen oxides of sulfur, which are emitted into atmosphere, which is an additional load on the atmosphere, and without this it is polluted with emissions from industry, thermal power engineering and transport. At the same time, the technological process that ensures the qualified processing of oil shale with the production of gaseous and liquid energy carriers must maintain environmental safety, which today is one of the main parts of the republic's strategic security as a whole.

The technology developed by us for obtaining liquid and gaseous hydrocarbons from oil shale provides for the prevention of gases with harmful acidic properties and greenhouse effects from entering the atmosphere.

The technology represents the thermochemical destruction of the high-molecular part of organic substances, using the method and technology of compounding raw materials, creating a technological possibility of activating the catalytic properties of metal oxides that make up the inorganic part of oil shale, stimulating the catalytic destruction of molecules with partial oxidation in the presence of atmospheric oxygen and water vapor taking place in the reaction - technological zone of the reactor. At the same time, at the initial stage of the technological transformation of the organic part of oil shale, low-molecular hydrocarbons of a mixed paraffinic and olefinic structure with the corresponding oxygenates are obtained. With an increase in the temperature of the reaction-technological process, mixtures of metal oxides that occur in the composition of the raw material begin to show their catalytic properties, and in the presence of atmospheric oxygen, the technological transformation of high-molecular mono and polycyclic hydrocarbons, as well as hydrocarbons of the heterocyclic structure of the oxidizing catalytic pyrolysis.

It is known that with the implementation in the Republic of Uzbekistan of international standards for combustion in internal engines "Euro-3" and "Euro-4" and "Euro-5", a reform of the hydrocarbon composition of fuel mixtures is being carried out, which is an energy carrier - energy consumption raw material for internal combustion engines, which strictly regulates the content of aromatic hydrocarbons in the fuel mixture and completely exclude the use of ethyl fluid, which over the past 40 years has been the hegemon in the list of fuel additives used in internal combustion engines.

Instead of tetraethyl lead, oxygen-containing hydrocarbons, oxygenates, alcohols, ethers, etc., are successfully used. In the products of oxidative autocatalytic pyrolysis of oil shale, alcohols of normal and iso-structures and other chemically oxygen-containing reactive-passive substances take place in the form of raw materials. In the case of the formation of organic alcohols, the technological scheme put forward for the implementation of the technological process provides for catalytic etherification in the vapor phase of oxidative pyrolysis products. As is known, ethers also have high activity as additives that improve the environmental and performance properties of fuels. The resulting pyrocondensate, a product of oxidative autocatalytic pyrolysis, also undergoes the process of thermo-catalytic chemisorption desulfurization in an associated technological process and is sent in the form of a wide light oil fraction, together with processing with traditional hydrocarbon feedstock, to refineries. The performed analytical work stimulates the development of the above-mentioned technology, since the chemical composition of local oil shale, in contrast to not numerous objects of this kind, requires processing precisely according to such a complex multifunctional complex technology. Given that the Republic of Uzbekistan has large reserves of oil shale, the development of technology for producing synthetic fuel mixtures based on them is a sufficient promising direction. In the Republic of Uzbekistan, it is also planned to process shale from the Sangruntau deposit in the near future. It should be noted that without own developments, taking into account the specifics of the chemical composition and other local conditions, blind copying and replication of technology is not promising, as shown by many years of practice. Therefore, the development of our own technology, taking into account the peculiarities of local conditions and the characteristics of raw materials, is a guarantee of ensuring efficient, both in technological, environmental and operational terms, which is very necessary. The Republic of Uzbekistan is located in the arid zone. Therefore, blind copying of successfully operated technologies in the humid zone as TadA3 functioning in the city of Tursunzade of the Republic of Tajikistan. Whereas the Siberian aluminum smelter located in the humid zone of Russia does not show and does not cause any environmental problems, unlike the Tajik aluminum smelter located in the arid zone.

In the technological process of production of processing, the stages of obtaining organic materials of commercial quality are provided. In addition, in contrast to the thermal technological solution, which is aimed at obtaining an organic product by the destruction of the organic part, the present technological process provides for the development of pyrolysis of the resinous bituminous part by gasification of the residual carbonaceous part.

The practical value of the developed technology is the development of obtaining light naphtha with the presence of methanol and ethanol from a mixture of alternative and renewable raw materials, which simultaneously improves the environmental and operational characteristics of light oil and, consequently, the resulting commercial gasoline based on it, which is one of the most urgent problems of energy and chemical technology. Therefore, it can be confidently noted that the developed technology and the development of an environmentally safe complex-coupled technology for the processing of oil shale with the production of gaseous and liquid hydrocarbons on their basis from a compound of raw materials consisting of a mixture of oil shale with wood-bioplant material with the production of a compound fraction of light hydrocarbons with improved environmental and performance indicators is not only important, but necessary. The light naphtha compound containing methanol and ethanol, which improves the environmental and operational performance of fuels, does not contain sulfur compounds and aromatic hydrocarbons, which is very important in the production of fuels for internal combustion engines, which will improve the environmental and operational characteristics of commercial automotive fuels. Solving at the same time the problems of environmental safety in general and as one of its important components - the issue of rational use of natural and secondary raw materials. The latter is of great ecological and economic nature due to the depletion of natural traditional reserves of oil and gas potential.

4 Conclusions

It should be noted that shale oil (residue of atmospheric distillation of tar) can be used both directly, replacing sulphurous and high-sulphurous fuel oils, and mixed with petroleum products for processing. Distillate resin fractions are used as components of solvents and thinners in the absence of requirements for the product on the sulfur content, and gas oils - as process fuels, heat transfer fluids or as mixed feedstock for hydrotreating. Such separate use allows not only to increase profits for processing enterprises, but also to consider resin processing products as a partial alternative to oil refining, which may be relevant in case of a significant increase in the cost of oil or its shortage on the world market.

Thus, the extraction and use of shale in the republic cannot be considered as archaic processes that live out their lives due to the low cost of raw materials. Oil shale processing, taking into account its advantages and disadvantages, will stand firmly on its feet, responding flexibly to the global market conditions and pricing of energy resources.

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