

Ecological Issues Related to the Use of Petroleum Products

Miryusif Mirbabayev*

Azerbaijan Technical University in Baku, Azerbaijan

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***Corresponding author:** Miryusif Mirbabayev, Azerbaijan Technical University in Baku, Azerbaijan

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ABSTRACT

The article discusses the environmental aspects of the use of oil and oil components. The importance of studying the microelement composition of processed oils is noted both from an environmental point of view (to identify sources of environmental pollution with oil) and for applied value (to extract S, Cu, V, Ni, Hg and other metals). It is noted that the microelements (Ni, V, Co, Cr) isolated from petroleum feedstock can and should be used for microalloying steels, since the presence of these microelements in the composition of alloyed steels leads to a decrease in the weight of the structure and an increase in its strength. It is shown that for the most complete solution of applied problems in oil and gas production, taking into account the preservation of ecological biodiversity (meaning a decrease in anthropogenic environmental pollution), it is important to know the qualitative composition of the used hydrocarbon raw materials.

Keywords: High molecular weight compounds of oils, Resins and asphaltenes, Inhibiting properties, Microelements, Catalytic poisons, Waste production, Biodiversity

Introduction

As is known, the use of oil as a fuel result in the release of large amounts of carbon dioxide, oxides and sulfur compounds into the atmosphere. In addition, oil resources require complex synthesis and processing processes before it is possible to extract fuel from it. Such enterprises themselves also have a negative effect on the environment. The use of oil and gas as a fuel also poses a great danger. When these products are burned in the atmosphere, large amounts of carbon dioxide, various sulfur compounds, nitrogen oxide, etc. are released. A decrease in the amount of oxygen and an increase in the content of carbon dioxide, in turn, will affect climate change. Carbon dioxide molecules allow solar short-wave radiation to penetrate the Earth's atmosphere and trap infrared radiation emitted by the

earth's surface. Every year, for one reason or another, from 3 to 12 million tons of oil are dumped into the World Ocean. Recent studies of the surface of the world ocean have led to disappointing results - almost 30% of the surface is under an oil film. The article shows that the problem of chemical processing and rational use of heavy oil residues is currently acute. Resinous-asphaltenes substances (RAS), which make up a significant proportion (up to 40%) in oils and even more in oil components, are the main reserve for deepening oil refining and increasing the degree of qualified use of petroleum raw materials¹. Scientific information on the chemical composition of the RAS will contribute to the qualitative identification of sources of environmental pollution, especially if we consider the effect of oil properties on the pollution of the atmosphere, soil and water surface in the region of deposits.

Main Part

The oil industry of Azerbaijan is one of the main sources of pollution of the environment with toxic substances and the air is polluted not only by various gas emissions generated in the process of oil refining, but also by gaseous oil products. If we consider oil in three aspects - as a natural resource, a product of production and an environmental pollutant.

Then it is obvious that it is necessary to organize a comprehensive analysis of the impact of the properties of oil and its components on the environment. The solution to this issue is extremely important in the context of the future ecologinizing of oil producing industries.

At oil refineries, which are today industrial complexes with a high degree of mechanization and automation of production processes, raw materials are not fully used, by-products are formed and so far, not completely captured. This reduces the technological performance of production processes and sharply degrades the environment. A significant part of oil and gas emissions (carbon, sulfur and nitrogen oxides, hydrocarbon vapors, metal oxides, carcinogenic substances, dust) are highly toxic. When the atmosphere is polluted, there is an accelerated destruction of metal and reinforced concrete structures, ancient monuments, soil acidification, poisoning and death of flora and fauna and also a negative impact on human health.

Therefore, the technological perfection of oil processing methods must be assessed not only by production and economic indicators, but also by their environmental friendliness. Sources of gaseous hydrocarbons (natural and associated petroleum gases, some synthetic gases obtained during thermal and thermocatalytic processing of oil and oil products) make a certain "contribution" to the pollution of the external environment, including the air basin.

At present, a lot of attention is paid to the complex study of high molecular weight compounds, since they contain significant amounts of heteroatomic compounds that adversely affect the catalytic processes of oil refining and petrochemistry. The main part of all microelements is concentrated in the highest boiling fractions of oils (resins and asphaltenes), which allows us to consider them as the main catalytic poisons of many oils refining processes.

For example, the presence of asphaltenes in the feed reduces the hydrogenation rate by 2 ÷ 4 times and increases the rate of catalyst deactivation by several times. The RAS, which remained in the oil products, have an extremely negative effect on their operational properties^{2,3}.

Since there is a continuous exchange of microelements between oil, rocks, formation waters, oilfield and refinery equipment, the RAS can be a link through which the relationship between the oil system and the environment is carried out.

We have found that the highest concentrations in the RAS of Azerbaijani oils contain elements of the iron group and heavy halogens, especially iodine. For example, it was found that the highest concentration of iodine among the oils of Azerbaijan belongs to the oil of the Gunashli field. And halogens in all cases are concentrated mainly in the resinous components of oils.

The chemical nature of the halogenated components of oils has not yet been finally established and the relatively high

content of bromine and iodine in Azerbaijani oils indicates that these oils, especially the oil from the Gunashli field, are promising objects for scientific research. Interest in petroleum microelements increased significantly when it was discovered that the number of certain metals (in particular, vanadium and nickel) could be comparable to their content in ores.

It is characteristic that the study of metals in oils was previously mainly by geochemists, but after it became known about the harmful effects of metals on the processing technology and operational properties of fuels, they began to be dealt with by chemists-technologists and ecologists. From an environmental point of view, the study of the microelement composition of refined oils is important in order to identify sources of environmental pollution with oil.

The presence of halogen-containing compounds in low-boiling oil fractions is apparently associated with the decomposition of high-molecular halogen-containing components during the distillation process, which leads to increased corrosion of oil refining equipment. That is, the purpose of the ongoing research of petroleum metal-containing compounds is not only the rational extraction of microelements from petroleum feedstock, but also the fight against corrosion^{4,5}.

So, when burning boiler fuel containing increased amounts of heavy metals, intensive destruction of refractory masonry occurs in furnaces, with vanadium being the most aggressive component. Vanadium pentoxide and vanadium salts present in the ash are low melting compounds. Together with sulfur-containing substances, they form dense deposits that cause metal corrosion. The amount of vanadium pentoxide emitted annually with the smoke of modern power plants is measured in hundreds and even thousands of kilograms. Organic vanadium compounds have a negative effect on the performance of petroleum products and vanadyl porphyrins present in oils are effective stabilizers of petroleum emulsions that impede their destruction. Vanadium in oils, which is a part of non-porphyrin complexes, is also associated with sulfur, which leads to atmospheric pollution and sulfur oxides.

It is known that ashes of heating oil are rich sources of valuable metals (vanadium, nickel etc.), which can be effectively leached under weakly acidic reducing conditions. With the help of synchrotron radiation, arsenic in the form of pentoxide was detected in oil fly ash emitted into the atmosphere, in addition to vanadium and nickel^{6,7}.

When using fuel oil (which is to some extent a concentrate of petroleum RAS) and, therefore, microelements) as boiler fuels, the environment is polluted with significant amounts of metal oxides. According to calculations, during the combustion of 1 ton of liquid fuel in power plants and industrial facilities, 1kg ÷ 2kg of metal oxides, mainly iron and vanadium, enter the atmosphere⁸.

Knowing the microelement's composition of oils, it is possible to identify the sources of oil pollution of the environment, since microelements are present in all oil fractions, starting with gasoline and their amount, as a rule, increases with increasing boiling point of the fraction, reaching a maximum in the residues⁹.

For the qualitative extraction of metals from oils and petroleum components, we used neutron-activation analysis,

which is universal in relation to a very large number of elements and does not require preliminary preparation of samples (ashing). The application of this analysis made it possible to establish about 20 different microelements in characteristic oils of Azerbaijan, including lanthanides, which were not, determined earlier (La, Eu, Yb, Ce). The type of elements contained in all Azerbaijani (low-sulfur) oils or in the overwhelming majority of them, are Fe, Ni, Cr, V, Co, Zn, Au, Sb, Se, I, Br. These microelements (in particular, Ni, V, Cr and Co) isolated from crude oil can be used for micro alloying steels, which is very important.

In general, Azerbaijani oils are characterized by a high content of the element Fe, which is mainly concentrated in younger weakly metamorphosed oils (which are Azerbaijani oils) at the initial moment of their formation. And then, as a result of oxidation reactions and when mixed with formation waters, iron is partially washed out of the oils. We would like to note that the problem of determining a clear distribution of microelements between the isolated fractions (components) remains complex. It is difficult to predict due to the typical diversity of compounds and a significant predominance of any microelements can lead to errors due to the existence of Compton background or interference. That is, today there is no single, established point of view on the source of microelements in oils.

The study of the microelement composition of oils is used in most cases to obtain geochemical information, since the geochemical and biogeochemical processes occurring in the biosphere determine the migration, dispersion and concentration of microelements in natural processes, influencing the geochemical situation that develops in individual regions of the planet. The microelement composition of oils also has important applied significance: S, Cu, V, Ni, Hg and other metals are extracted from them.

For example, in the USA, two-thirds of vanadium production is associated with its extraction from oil and in California, gold-bearing oils are exploited. The value of oils especially increases with the presence of Pt and Pd, which are used as effective catalysts in many hydrocarbons processing processes⁵.

Some words about the practical application of oil components^{10,11}.

Petroleum RAS are natural inhibitors; they exhibit a certain inhibitory activity in reactions with a free radical chain mechanism. The total concentration of natural inhibitors in asphaltenes can reach 0.28 mol/kg of oil. They are present in high effective concentrations (0.66 ÷ 0.79) mol/kg in RAS extracted from oil of the Banka Darwin field (Azerbaijan oilfield). Natural inhibitors contained in the RAS of characteristic (low-sulfur) oils of Azerbaijan are in most cases not inferior to synthetic antioxidants in their inhibitory effect and resins from Gunashli oilfield are comparable in "strength" of action with the most effective synthetic antioxidants: naphthol and topanol.

The concentration and activity of inhibiting centers in the RAS naturally depend on the chemical type and the degree of metamorphic transformation of oil, which in turn determines the role of RAS as preservatives that stabilize the reservoir oil system and thereby ensure the preservation of oil in the bowels during geological time. RAS (0.1-2%) can be used to inhibit the polymerization of petroleum products, styrene, photo- and thermal stabilization of polyvinyl chloride and polymethyl

acrylate. It has been shown that asphaltols can serve as inhibitors of oxidation of mineral oils.

The inhibiting capacity of high-molecular heteroatomic compounds included in oils plays an important stabilizing role in reservoir systems, reducing the rate of their thermal destruction in subsurface conditions and facilitating the preservation of deposits for long periods of geological time. The concentration and activity of inhibiting centers in low-sulfur oils (which are Azerbaijani oils) decrease with increasing age and depth of deposit immersion. Catagenic transformations lead to a decrease and hyper genic ones to an increase in the inhibiting capacity of oil components.

It has been found that asphaltene concentrates increase the thermal-oxidative stability of epoxy compositions and asphaltites are accelerators in the chemical curing of epoxy resins and thermal curing of epoxy resins. Apparently, metal-containing complexes are natural catalytic systems that accelerate the curing process, since an increase in the metal content from 0.052 to 0.155% leads to a 2-fold acceleration of curing. With a 15% addition of asphaltites to phenoplasts, heat resistance and impact strength increase and the dielectric properties of the latter improve. Asphaltenes can be used in the production of cement to improve its properties; and electro photosensitivity and thermoplasticity of a number of fractions of petroleum resins allow them to be used for photo thermoplastic recording of information. Furthermore, asphaltites, due to their significant specific surface area, radiation resistance and low price, are successful fillers for some polymeric materials.

Oil residues (high-boiling oil fractions) are one of the raw material sources for the production of oil stabilizer concentrates. In particular, tar deasphalting asphalt, containing active antioxidants, is comparable in its inhibitory effect with common synthetic phenolic and naphthylamine antioxidants. The simplicity and low production cost, as well as the relatively high antioxidant properties of petroleum concentrates, consisting mainly of RAS, contribute to a more rational use of petroleum feedstock (in particular, production waste).

Various substances that have valuable practical applications in industry can be obtained from oily RAS by chemical modification using sulfonating, amination, chloromethylation, condensation, phosphorylation and thermolysis reactions. The introduction of a significant number of active functional groups into molecules of RAS leads to the production of materials with anion and cation exchange properties.

We found, that the concentration and activity of inhibiting centers in low-sulfur Azerbaijani oils decrease with an increase in the depth of the deposits, that is, catagenic transformations lead to a decrease and hyper gene transformations lead to an increase in the inhibitory ability of oil components, in particular resins and asphaltenes. Inhibitors, concentrated mainly in RAS, are represented by heteroatomic compounds and up to 10% of inhibitors are also contained in heavy residual products of oil refining (asphaltenes, tar and pitches). Therefore, it is of interest to use the residual products of oil refining as an inhibitor of the oxidation of fuels and oils instead of expensive additives. This will effectively solve the problem of maximum use of secondary resources. The practical use of petroleum RAS as stabilizers for various polymeric materials is also conditioned by their inhibiting properties. For example, chloromethylated asphaltites

are accelerators in the chemical curing of epoxy resins and reagents for sulfur less vulcanization of rubbers. When rubber mixtures are filled with asphalt, more elastic rubber is obtained than when filled with soot. Asphaltene concentrates increase the thermal-oxidative stability of epoxy compositions and petroleum asphaltene emulsions are emulsion stabilizers: their small additives (up to 1%) reduce the hydraulic resistance during the movement of oils in wells by 20% ÷ 40%. Asphaltene concentrates are also used as antifriction fillers for lubricating compositions instead of graphite.

The main carriers of the biological activity of Azerbaijani oils from the Balakhani, Naftalan and Surakhani onshore fields are naphthenic hydrocarbons with high cyclicality and optical activity; they are associated with the structures of biologically active compounds - the most important relict hydrocarbons related to steranes and triterpenes. Due to their clear association with biological products, these hydrocarbons are called biological tags. The concentration of steranes and triterpanic hydrocarbons in Azerbaijani oils does not exceed 0.3% ÷ 0.5%. The predominant amount of steranes and triterpenes is contained in oil from the Balakhani field, which determines the use of high-boiling fractions of this oil for the production of medical and perfume oils.

The main carriers of the optical activity of Azerbaijani oils are also naphthenic hydrocarbons (their highly annular representatives). The most optically active oils and their fractions were discovered from the Azeri, Balakhani and Jafarli oilfields. Optical activity is an important property of oils and their components, as it makes it possible to solve the problem of the genesis of oil and determine its age.

At present, the use of luminophores based on petroleum fractions (components) is widely developed. Among the studied samples of Azerbaijani oils from the Oil Rocks and the Banka Darwin fields, aromatic hydrocarbons isolated from the residues (fractions above 350 degrees Celsius), which have an intense yellow glow, are of greatest interest. This creates a good opportunity to use these aromatic hydrocarbons in capillary luminescent flaw detection as a luminescent component of an indicator liquid.

Here is an incomplete list of those obtained on the basis of oxidation products of resins and asphaltene: 1) a hydrophobic acid emulsion for the treatment of oil and gas formations, which is characterized by increased viability (15.6 hours), permeability and heat resistance (up to 150 °C); 2) the possibility of using resins and asphaltene as emulsifiers in the extraction of bitumen from bituminous sands directly at the extraction site.

Furthermore, chloromethylated resin-asphaltene substances are effective vulcanizing agents for sulfur-free vulcanization of rubbers and the highest vulcanizing activity is characterized by vulcanizates obtained using chloromethylated asphaltites and having higher resistance to thermal aging.

Chloromethylated asphaltites can also be used as hardeners for polycondensation monomers and polymers. For example, they are used as a hardener for alkyds; at the same time, they increase the heat resistance of the latter. The products of interaction of RAS with phosphagens are recommended as high-quality non-flammable coatings. And chlorinated asphaltene are used as binders for obtaining slabs, insulating panels, wall partitions, pipes, roofing materials, epoxy compounds from

which adhesives, laminated plastics, casting and molding compositions are made.

The authors of the works¹² consider that an additional advantage of the rational use of unoxidized bitumen in production is: 1) the ability to avoid thermal and oxidative effects on heavy components of petroleum feedstock and, accordingly, reduce the impact of polymerization and aggregation of RAS and heteroatomic components of heavy residues in the production of bitumen; 2) the absence of oxidative polymerization and destruction of raw material components, leading to the intensive formation of black diesel fuel and oxidation gases, which reduces the technogenic pressure on the environment and helps to reduce the energy intensity of production; 3) the absence of the process of oxidation of raw materials at high temperatures, due to which the polarity of the bitumen decreases and, consequently, adhesion to mineral materials remains; asphalt concretes prepared using residual bitumen are characterized by higher rates of water resistance, crack resistance, wear resistance and durability in general.

It should be especially noted that chemical transformations of oil RAS made it possible to obtain a number of previously unknown organic compounds with very valuable properties. This is a certain stage in solving an urgent national economic problem - the development of scientific foundations for the residue-free use of oil due to the involvement of a new type of oil raw material (oil RAS).

Conclusion

The presented brief review on the environmental aspects of the use of oil and oil products has shown the practical value of these substances. The range of application of oil products (components) is very wide and their potentialities are far from being exhausted, since only the chemical transformations of RAS already make it possible to obtain a number of compounds with valuable properties necessary for solving the problem of developing a technology for the non-residual use of oil. And also, oil products (components) can be used for the production of bitumen as a natural depressant for reliable insulation of pipelines. All these areas did not take into account the specific features, diverse and valuable properties of RAS. When planning the rational use of oil and its components in the future, it is possible to identify sources of oil (anthropogenic) pollution of the environment and thereby significantly reduce emissions of pollution into the atmosphere, which will generally contribute to an improvement in the environmental situation. And this is one of the measures to conserve global biodiversity.

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