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Environmental pollution in the petroleum refining industry

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Abstract The petroleum refining industry has a significant influence on the total pollution of the environment by industrial discharges and wastes. In the operation of petroleum refineries, the atmosphere is polluted with hydrogen sulfide, sulfur dioxide, nitrogen oxides, carbon monoxide, hydrocarbons, and other toxic substances. The main pollutants are sulfur dioxide and hydrocarbons. The fresh water used by refineries in product cooling is returned to the original source of water containing crude oil, petroleum products, and mineral salts as contaminants. The extent of air and water pollution depends on the particular processing technology, control measures that are employed and also on the scale of the processing. In working out these measures, the primary attention of scientific-research institutes and design and planning organizations must be directed not only towards how to reduce the contaminating and poisoning action of industrial discharges on the environment, but primarily towards preventing or minimizing these discharges in the refineries.

Keywords: petroleum-containing wastes, petroleum sludges, petroleum-catching emulsions

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1. Introduction

The petroleum industry can be divided in upstream and downstream segments. Upstream refers to exploration, extraction and production of crude oil and natural gas. Downstream consists of refinery operations, distribution and retail of the petroleum fractions, mainly based activities [1].

Petroleum and sludge storage pits of petroleum production and refining companies contain millions of tons of petroleum-containing wastes which pose a threat to the environment [2].

The petroleum refining industry has a significant influence on the total pollution of the environment by industrial discharges and wastes. In the operation of petroleum refineries, the atmosphere is polluted with hydrogen sulfide, sulfur dioxide, nitrogen oxides, carbon monoxide, hydrocarbons, and other toxic substances. The principal pollutants are sulfur dioxide and hydrocarbons. The fresh water used by refineries in product cooling is returned to the original source of water containing crude oil, petroleum products, and mineral salts as contaminants. The extent of air and water pollution depends on the particular processing technology and control measures that are employed, and also on the scale of the processing [3].

It should be considered that the growth rates in petroleum refining capacity will be at least this high in the future; hence, the measures to combat the discharge of pollutants, if they remain at the present level, it will be entirely inadequate to prevent further contamination of the air and water basins of our country. In order to prevent such pollution, action is needed now in mapping out a set of measures that can be applied, with acceptable levels of capital investment, to bring about not only a relative but also an absolute reduction in the industrial discharges to the environment from refineries. They must include the introduction of basically new refining processes, improved units and equipment, and advanced methods for organizing production. In working out these measures, the primary attention of scientific-research institutes and design and planning organizations must be directed not only towards how to reduce the contaminating and poisoning action of industrial discharges on the environment, but

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primarily towards preventing or minimizing the discharges of the refineries [3].

2. Measures to prevent industrial discharges in refineries

The goals are the reduction of atmospheric pollution by hydrocarbons and sulfur dioxide and the pollution of water bodies by mineral salts and petroleum products. The proposed measures for reducing such pollution will give a significant reduction in the overall environmental pollution. They are examined in the following paragraphs.

- Improvement in quality of crude-off pretreatment before processing. The scheme for crude-oil pretreatment as it has been constituted in our country includes dewatering of the crude in the oil fields [4] and desalting in the refineries, this scheme allowing rather large amounts of residual salts (up to 1000 mg/liter) in the pretreated crudes, thus causing severe corrosion of all the process equipment. In the process of pretreating such crudes in the refineries, large quantities of wastewater are discharged, contaminated with salts and with crude oil emulsion [5, 6, 7]. Such water, as it flows through the refinery sewers and treating facilities, will contaminate the atmosphere with the evaporating hydrocarbons; discharge of waters to natural water bodies will introduce salts and oil as pollutants [3].
- It is necessary to work out a single combined scheme of pretreating crude oil in the fields and in the refineries so as to give a more complete removal of salts from the oil before processing, with minimum amounts of contaminated wastewaters. Calculations show that the amount of contaminated wastewater drawn from electric desalting units in refineries can be reduced by a factor of 6 when a single complex scheme of crude-oil pretreatment is used, in comparison with the amount of wastewater produced in the current pretreating scheme, since the oil furnished from the field to the refinery will have been treated with nonionic demulsifiers [8] down to residual-salt contents of 50-100 mg/liter.

- Use of larger process units and individual components, machinery, and structures; construction of combination units for several processes in a single process block [3]. For example, the construction of a single atmospheric-vacuum pipe still unit with a capacity of 6 million metric tons per year instead of two units with capacities of 3 million tons each, together with combining the large unit with blocks for electric desalting, diesel fuel hydro treating, VGO catalytic cracking, naphtha redistillation, reforming of narrow naphtha cuts, and fractionation of hydrocarbon gases [10] will make it possible to reduce the consumption of process fuel by 20% cooling water by 26% and non-recoverable losses of crude and products by 35% [3]. Proportional reductions will be obtained at the discharge of pollutants to the atmosphere and to watercourses.

- Use of larger tanks for storage of crude oil and commercial petroleum products, and the installation of floating roofs and pontoons in these tanks [3].

- Increase in the utilization of secondary energy resources through the introduction of effective energy-process schemes and refrigeration processes based on the heat-pump principle, operating on the heat of waste gases and petroleum products [3]. The heat can be use to produce refrigeration, steam, and hot water and can give a twofold to threefold reduction in cooling-water consumption and a 30% reduction in fuel consumption. Major economy savings in refinery cooling water can be achieved through the widespread use of air-cooled condensers [3].

- The introduction of these measures will make it possible to minimize the discharge of polluted wastewaters from the refinery to natural watercourses and will not involve any great capital investment in wastewater treating facilities.

- Desulfurization of the engine and boiler fuels produced in the refineries. Here it is necessary to persist in efforts to find cheaper and more efficient catalysts [9], to develop better desulfurization processes, particularly those for heavy residual stocks, and to install large-scale units for hydrogen production. Such new units for desulfurization of petroleum products should be combined with units for recovery of sulfur from the acid gases. This will decrease atmospheric pollution by sulfur dioxide and other sulfur compounds.

- Development of methods and monitoring instruments for industrial discharges of contaminants. Here it is necessary to speed up research efforts towards finding how the volumes of industrial discharge of contaminants depend on the refinery flow plan, the process units operating conditions and equipment [3].

- In Japanese plants, for example, detectors have been installed in all zones of possible discharge of hydrocarbons to the atmosphere or accumulation of hydrocarbons in dangerous concentrations within the plant limits, these detectors transmitting audible or visible signals to the control room. The points of discharge of flue gas from tube furnaces and boilers have been connected to instruments controlling the combustion process on the basis of the contents of sulfur and nitrogen oxides in the gases. The fuel combustion process in the firebox and the composition of the stack gases are monitored by television cameras transmitting pictures to dispatcher points and to monitoring displays for observation. In all of the final drain pits for process units, instruments are installed before and after the oil traps for continuous determination of the petroleum product content in the wastewater [3].

- For a more clear-cut accounting of process losses and non-recoverable balance losses of crude oil and products, automatic meters and computers have been installed on the process units [11]. A balance of the losses is made for each hour of facility operation. All these provide practically continuous observations of the ambient, so that prompt measures can be taken when required.

- It is extremely important to find a general index characterizing the environmental contamination by refineries.

- Organization of subsections in the refinery for environmental protection, equipped with special techniques and instruments [12]. The assignment of these subsections must include identification of the sources for environmental pollution and development of measures to eliminate it. All of the treating units and facilities now operating in the refinery should be put under this regulation. The organization of such subsections in a number of refineries has demonstrated that they are highly effective.

We have now laid all the groundwork for starting to develop a refinery in which all production wastes are recovered, all discharges are eliminated, and contamination of the environment with toxic substances is no longer a problem.

3. Methods for processing petroleum wastes

As estimated by experts, loss of petroleum with waste counts for aproximately 3% of its annual production. In view of this, priority is given for investigations designed to find ways for toxic emissions neutralization and recovering petroleum-containing waste.

Petroleum waste, just as other organic matter, is recovered or processed with industrial technologies, the most popular among which being the local combustion with utilization of the heating potential of the petroleum waste.

The composition of petroleum waste is not uniform. Petroleum waste contains smeared cleaning cloth, polyethylene film, smeared brushes, pruned branches, etc. [13]. Disposing of such waste in storage yards does not conform to the current environmental requirements, making necessary to develop more efficient and environmentally safe technologies for their utilization or detoxification [14]. This waste can be utilized most effectively in retort furnaces, which are employed to this day widely for producing charcoal [15]. Thanks to simple design, fabrication of such furnaces does not involve large investments and, as many years of experience shows, it does not require special training of service personnel. Compactness of and very small area occupied by the equipment make it possible to respond fast to changes in the demand for this type of services, shift the equipment to the sources of formation of the waste, etc. [2].

One must separate out from the problem of scale of utilization of hydrocarbon materials (petroleum sludges, used oils, household waste, etc.) a specific part, namely, processing of multicomponent mixtures formed upon elimination of the emergency situations in processes of production, transportation, and refining of petroleum [16]. The utilization (heat recovery) version of combustion is used for wastes that cannot be regenerated with production of commercial products. Before combustion, the waste is treated for dehydration, removal of mineral impurities, etc. in order to increase the efficiency of its combustion. For this purpose, it is sometimes enough to let the waste to settle. In other cases, more intensive methods are needed for its dehydration, for example by centrifuging [2].

Combustion is not ecologically safe.

Pyrolysis consists in destroying the organic part of the waste with limited excess of air at 500-550°C with formation of a solid residue and combustible gases. This process prevents conversion of the organic part of the waste into toxic combustion products and allows utilization of the products (gaseous, liquid, and solid) as fuel. The yield of gaseous pyrolysis products reaches 10 % of the original weight of the wastes. About 80 % of these products have combustion heat (calorific values) of 20934-25120 kJ/kg and are used as fuel [2]. The liquid phase, or the petroleum condensate, whose yield is 29 %, has a heat capacity (calorific value) of about 37680 kJ/kg. It can be treated repeatedly or it can be used as a fuel in the enterprise itself. About 50 % of the original weight of the sludge is constituted of powdery fraction, which contains practically no petroleum products and is represented essentially by carbon-containing material. Waste can be submitted to pyrolysis only if its moisture content is low (1-3 %), i.e., petroleum sludge can be used only after pre-drying. Drying of petroleum sludge can be used both as an independent method of utilization and as an intermediate method for preparing the petroleum sludge for other method of dehydration [2].

For drying, use is made of fluidized-bed, pneumatic, spray, aero fountain, semi suspended-bed vortex driers, etc. The two-stage drying method, where the major part of the liquid components is removed by pre-drying, is frequently used.

Some companies use liquid petroleum waste (used oil) for their own needs. In general, the simplest waste treatment technologies (settling or heating and settling, including use of reagents) are employed in these cases. Sometimes, petroleum waste is not processed at all. Liquid petroleum waste is used for lubricating low-duty mechanisms. In [17], it was proved theoretically that the structure, composition, and properties of components (solid hydrocarbons, additives, etc.) affect structurization and shaping of properties of rust-preventive hydrocarbon lubricant.

One experiment is known where petroleum waste was used to reduce formation of dispersed materials during transportation [18].

The feasability of petroleum sludge use as a lubricating additive to drilling mud instead of crude oil has been indicated in a patent [19].

Pasty petroleum waste can be used as components of drilling mud for petroleum and gas drilling to provide high stability to clay rocks when the latter come into contact with the filtrate of drilling mud. Besides utilization of petroleum sludge at the refinery for its own needs and utilization by thermal methods, their use in production of building materials (cement, kilned bricks, asphalt-concrete mixes, etc.) is also known.

Numerous publications, such as [20], were devoted to the utilization of petroleum wastes in road building.

In particular, petroleum-containing waste and petroleum-contaminated soils are used as organic binder for laying structural beds of road surfacing (including asphalt-concretes), filtration-preventing shields, and waterproofing interlayers of automobile roadbeds [2].

Since automobile roads are complex structures subject to the impact of constant dynamic loads, excessive amount of petroleum-containing materials may cause shear deformation of the roadbed, so their quantity in the structural layers of roadbed and the road surface must be controlled. Especially in the conservation and farming areas, use of such materials must be prohibited because of their adverse effect on the hydro- and biosphere. Laying vapor- and moisture-proofing interlayers in automobile roadbeds is one of the methods of preventing frost heaving. As is well known, when clayey soils, including loams, sandy loams, silty soils, etc., freeze, the free moisture moves toward the subzero temperature area. Upon freezing, the water volume increases by up to 9 %, and this process is uneven. Depending upon the freezing depth, heaving (swelling) reaches 15-20 cm, which causes considerable deformation of the roadbed and premature destruction of the road surface. Vapor- and moisture-proofing layers and interlayers are laid out in automobile roadbeds, which are composed of heaving (swelling) soils, preventing thereby ascent of moisture from the underlying layers to the freezing area [2].

There are many methods of preventing and minimizing frost heaving, but use of petroleum waste may be considered most promising in light of availability of a wide variety of petroleum waste and its abundance as well as of possibility of producing hydrophobic substances based on petroleum waste.

Test data for mixtures containing 25-75 wt. % petroleum-contaminated soil, cement, and lime show that they possess fairly high strength characteristics and hydrophobic properties, which allow water-proofing interlayers to perform under almost all conditions of road use. It was proved in [2] that such interlayers are safe for environment – for atmosphere, biosphere, and hydrosphere. Furthermore, the above-noted mix was successfully used as vapor- and moisture-proofing interlayer in construction of Category III automobile road.

Another method of using petroleum waste is construction of filtration-preventing shields for the protection of waste storage yards. ATPD and petroleum-contaminated soils (binder) compounded with mineral and polymeric materials are used as waterproofing layer intended for reducing filtration properties and enhancing chemical stability to the filtrate [2]. Organomineral and organopolymeric shields are capable of resistance to the action of filtrate for a prolonged time because addition of petroleum-containing products to clay improves hydrophobic properties of the obtained material owing to prevention of direct contact of the filtrate with the clay.

In [21], a technology was proposed for complete utilization of liquid and solid petroleum-containing waste with recovery of hydrocarbons in the production cycle and production from the solid residues, after heat treatment, of environmentally safe constructional materials, such as frothed and block silicate stones, artificial gravel having improved performance properties, etc.

For enhancing the strength and frost resistance of the concrete in the concrete mix, addition of 1.5-2.5 % sludge is recommended. Utilization of petroleum sludge for manufacturing mineral-wool tiles makes the articles hydrophobic and reduces their volume weight. Utilization of petroleum sludge for producing claydite (extended clay aggregate) reduces its volume weight, raises yield of large fraction, and reduces fuel consumption. Reduced volume weight of the claydite allows poorly swelling clay rocks to be used as a raw material [2, 22, 23].

Thus, petroleum wastes, being secondary material resources, can be utilized in the industry instead of the primary raw material.

4. Conclusions

The petroleum refining industry has a significant influence on the total pollution of the environment by industrial discharges and wastes.

The extent of air and water pollution depends on the particular processing technology and control measures, and also on the scale of the processing.

The measures to prevent industrial discharges of the refineries are related to the reduction of atmospheric pollution by hydrocarbons and sulfur dioxide and the pollution of water bodies by mineral salts and petroleum products. The proposed measures for reducing such pollution will give a significant reduction in the overall environmental pollution [24, 25, 26].

Petroleum wastes, being secondary material resources, can be utilized in the industry instead of the primary raw material.

5. References

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[1]. D. Høivik, B.E. Moen, K. Mearns and K. Haukelid, Safety Science, **47**, 992-1001 (2009)

[2]. E.R. Shperber, T.N. Bokovikova and D.R. Shperber, Chemistry and Technology of Fuels and Oils, **47**(3), 237-241 (2011)

[3]. Y.G. Sorkin, Khimiya i Tekhnologiya Topliv i Masel, **4**, 32-34 (1975)

[4]. T. Chis, Annals Computer Science Series, **5th Tome, 1st Fasc.**, 35-44 (2007)

[5]. P.V. Messina, O. Pierone, V. Verdinelli and P.C. Schultz, Colloid Polym Sci, **286**, 191 (2008)

[6]. H. Schubert and R. Engel, Chemical Engineering Research and Design, **82(A9)**, 1137 (2004)

[7]. S.L. Khil'ko and E.V. Titov, Chemistry and Technology of Fuels and Oils, **43(5)**, 437 (2007)

[8]. B.E. Elizalde, A.M.R. Pilosof, L. Dimier and G.B. Bartholomai, JAOCS, **6** (10), 1454 (1989)

[9]. ***http://web.anl.gov/catalysisscience/publications/CAT_rpt.pdf

[10]. V. Ruffier-Meray, P. Ungerer, B. Carpenter and J. P. Courcy, Oil & Gas Science and Technology, **53**(3), 379-390 (1998)

[11]. ***http://www1.eere.energy.gov/femp/pdfs/omguide_complete.pdf

[12]. E. Chirilă, S. Dobrinas, E. Paunescu and G. Stanciu, Environmental Engineering and Management Journal, **10**(8), 1081-1086 (2011)

[13]. D.S. Belozerov, *Enhancing Environmental Effectiveness of the Stage of Eradication of the Consequences of Emergency Situations in Oil Field Pipelines,* Perm State Technological University Press, Perm (2007)

[14]. I.A. Yul'timirova, Taxes, Investments and Capital (in Russian), **No. 1**, 33-37 (2004)

[15]. A.N. Volegov, N.S. Gyibadullin, A.A. Surkov and all., Zashch. Okruzh. Sreda Neftegaz Kompl., **6**, 27-30 (2010)

[16]. V.V. Bystrykh, M.V. Karyagina, A.V. Naletova and all., Zashch. Okruzh. Sreda Neftegaz Kompl. **6**, 37-39 (2007)

[17]. O.I. Ruchkinova, M.A. Tagilov and O.A. Tagilova, Izv. Vuz. Neft'i Gaz, **1**, 116-111 (2003)

[18]. V.E. Lotosh, Nauch. Tech. Asp. Okhruzh. Sredy, **2**, 2-7 (2001)

[19]. *** USSR Author's Certificate, **No. 231877**

[20]. B.S. Yushkov and A.A. Minzurenko, Zashch. Okruzh. Sreda Neftegaz Kompl., **6**, 41-45 (2010)

[21]. *** Russian Federation Claim **No. 2007126232** for Useful Model (9 July 2007)

[22]. I. Anghelache, *Petroleum and non-petroleum automobile gasoline* (in Romanian), Ed. Tehnică, București (1986)

[23]. ***http://www.environment.gov.au/settlements/transport/fuelguide/tips.html

[24]. A.E. Sterpu, D.I. Arsenie, N. Teodorescu, A.I. Dumitru and D.T. Epure, Ovidius University Annals of Chemistry, **22(1)**, 41-46 (2011)

[25]. S. Dobrinas, G. Stanciu, E. Chirilă, A.D. Soceanu, E. Păunescu and D.T. Epure, Ovidius University Annals of Chemistry, **22(1)**, 21-26 (2011)

[26]. S. Vinnakota, R.G.P.Aluru, R.K. Kakarla, S. Vahi, R. Lakshmana Rao Krishna Rao, Ovidius University Annals of Chemistry, **22(1)**, 5-10 (2011)

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