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Separation of Water-Oil Emulsion Using Polyethersulfone Membranes Treated With High-Frequency Low-Temperature Plasma

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Abstract---*A study of the water-oil emulsion separation by polyethersulfone membranes with a mass of cutoff particles 10 kDa was carried out. The membranes were treated with a low-temperature high-frequency capacitive reduced pressure plasma in an argon and nitrogen medium (70:30) at a voltage of U_a = 1.5-5.5 kV and processing time τ = 1 5-7 minutes. Round flat filter elements with a diameter of 47 mm were used in the capacity of membranes. The emulsion with a concentration of 3% (by volume) was prepared on the basis of Devon oil from the Tumutukskoye oil field and distilled water and was stabilized by the Kosintol-242 surfactant. The experiments were carried out on a laboratory ultra filtration separation unit. Based on the results of the studies, an increase in the separation productivity of the water-oil emulsions after plasma treatment of the membranes is shown; an increase in the studied process efficiency from 95.1 to 98.4% with the exposure by plasma at U = 3.5 kV and τ = 7 min is noted. Using electron microscopy, sedentary droplet, and IR spectroscopy methods, we have revealed an increase in the surface roughness of the membranes after plasma treatment with nitrogen argon, as a result of which the contact angle of distilled water decreased from 75.3° to 65.3°, which indicates an increase in hydrophilicity and, respectively, water absorption, and in addition, the formation of oxygen-containing functional groups and the hydrogen bonds in the surface structure of the polymer polyethersulfone membrane.*

Keywords: *Polyethersulfone, membrane, plasma, oil, emulsion*

I. INTRODUCTION

The need to increase the effectiveness of environmental protection measures is due to the continuing deterioration of the environmental conditions throughout the planet caused by increased mining volumes and expansion of human activities at all, and, as a result, exhaustion of resources and pollution of ecosystems. The prompt solution of the problem under consideration is advisable both from the standpoint of ecology and from the point of view of the economy, since it’s easier and cheaper to protect nature today than to try to restore it at exorbitant prices tomorrow, and the day after tomorrow there will be nothing left!

All the components of the biosphere: earth, water, air, animals, plants, microorganisms, and people, are affected by anthropogenic impacts from environmental and organisms degradation to habitat destruction and extinction of populations. One of the ways to prevent these phenomena is the use of effective technologies that ensure the most

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complete neutralization of hazardous waste by converting it into safe substances, and preferably into secondary material resources. Moreover, the cost of such technology should be adequate for the resulting environmental effect.

Membrane technologies are based on separation under the influence of a driving force (which is pressure used in most cases (baromembrane technologies)) of a mixture with various qualitative and quantitative composition using a membrane as a filtering element. The mixtures are separated into the permeate (filtrate) which passes filter and is less concentrated relative to the initial flow and detained and more concentrated retentate (concentrate). Upon that, varying the membrane process parameters (the membrane material, its layout, pore size, surface area and pressure) various values of productivity and separation selectivity, which are required to solve specific scientific and production problems, could be achieved.

In particular, when separating a water-oil emulsion formed as a waste in the oil industry and containing one of the ten most dangerous pollutants - oil, the use of membrane technology helps to produce purified water which, depending on the degree of purity, can be used in a technological recycling or dumped into a sewer or a reservoir, as well as to produce a hydrocarbon concentrate, which in turn can also be used as a raw material or product [1] or disposed of.

Despite the variety of membrane systems offered by domestic and, to a greater extent, foreign manufacturers the possibility of increasing the efficiency of membranes is relevant. Various methods are used for this;they can conditionally be divided into:

- Mechanical, carried out by direct contact of the processing tool and the workpiece (membrane),

- Chemical, using chemical reagents to modify the structure of membrane filter elements [2]

- Physical, based on the action of energy fields (ultraviolet, x-ray and radioactive radiation [3], plasma [4-6], heat [7], laser [8], corona discharge [9,10]).

The first method is mainly used for the manufacture of membranes and the formation of general productivity and selectivity characteristics, while the second and third methods can and shall be used for fine-tuning the membranes for the purpose of their operation in order to solve specific problems.

In the case of oil-water emulsion separation, the necessary property is the hydrophilicity of the filter element surface, which ensures a greater passage of the aqueous phase and repulsion of hydrocarbons. The plasma effect of certain gaseous media, for example, argon, oxygen, and air on the surface of the processed material, leads to its hydrophilization. This circumstance is due to the nature of the plasma consisting of charged particles of ions and electrons, which upon contact with the object being modified lead to various physical and chemical processes occurring on its surface, among which etching, oxidation, destruction and formation of chemical compounds are most likely; having combined together, they form a complex picture of changes in the structure of the object, and, accordingly, its characteristics.

II. METHODS

Based on the above, in this paper, we study the separation of a model oil-water emulsion simulating the corresponding waste with the use of plasma-treated polyethersulfone membranes.

A water-oil emulsion (WOE) was prepared by mixing 967 ml of distilled water with 3 ml of Kosintol-242 surfactant at a temperature of 40 °C, followed by mixing with 30 ml of Devonian oil from the Tumutukskoye field. The chemical oxygen consumption value of the obtained 3% oil-water emulsion was 23400 mg O / dm^3.

Polyethersulfone (PES) membranes in the form of films with a thickness of ≈ 0.1 μm, a diameter of 47 mm, and a mass of cut off particles of 10 kDa were selected as a filter element because of their thermal and chemical stability, and most importantly their surface hydrophilicity.

The experiments with membrane separation were carried out in a laboratory setup - a cell made in the form of a plastic cylinder, in the lower part of which a membrane with a magnetic stirrer armature on its surface is installed on the stand, and the divided medium in the amount of 50 cm^3 is poured on top, after which the mixing device immediately starts creating the flow in the cross-flow mode to prevent the phenomenon of concentration polarization on the surface of the filter element. The module is sealed with a clamping system, and then 2 atm pressure created by the compressor which determines the beginning of the separation process is fed through the nozzle of the upper cover.

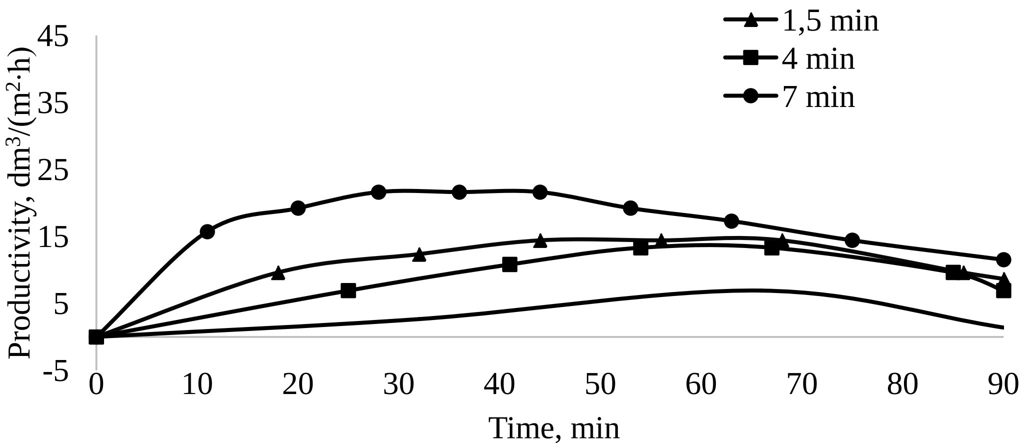
The membranes were processed with a high-frequency reduced pressure capacitive plasma in a mixture of argon and nitrogen gas media (70:30) at a voltage (U) of 1.5, 3.5, 5.5 kV and a treatment time (τ) of 1.5, 4, and 7 min, current strength was 0.5-0.7 A, pressure - 26.6 kPa, gas mixture flow rate - 0.04 g / s.

The initial stage of the study determined the main oil-water emulsion separation characteristics with the initial and plasma-treated polyethersulfone membranes:

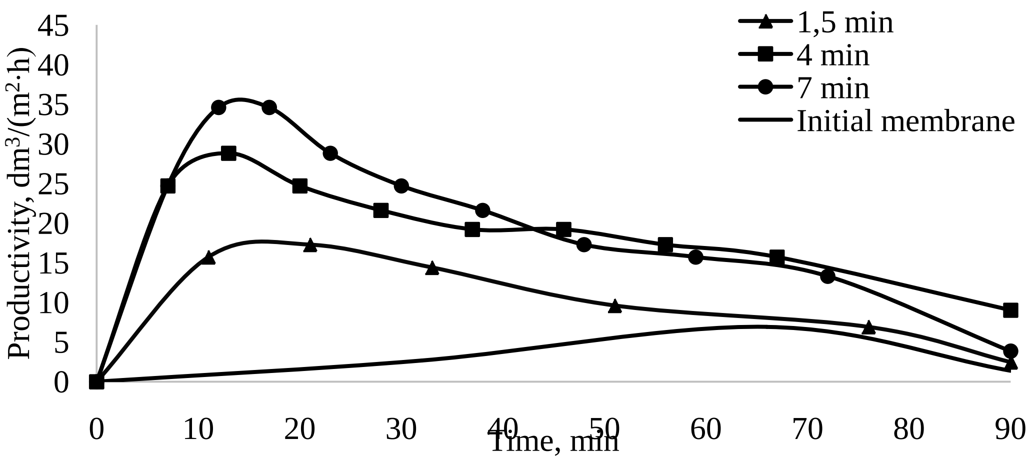
- Performance as the ratio of the mixture stream volume passed through the filter element to the product of the membrane surface area and the processing time,

- Efficiency (selectivity), determined by changing of the chemical oxygen demand (COD) value of the oil-water emulsion after membrane separation determined according to the titrimetric method. The results are presented in Figure 1 and Table 1.

III. RESULTS AND DISCUSSION



a)



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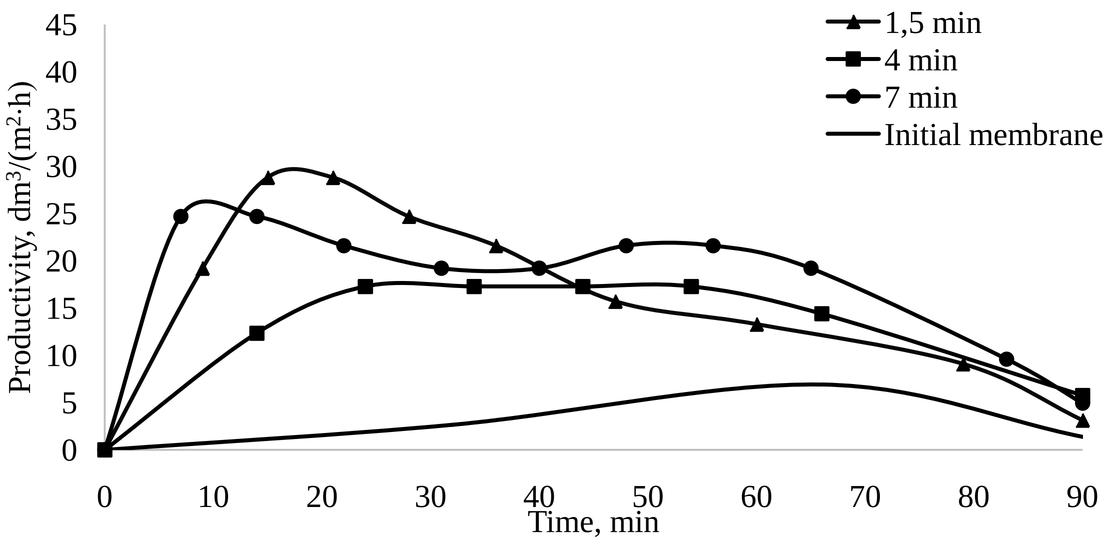

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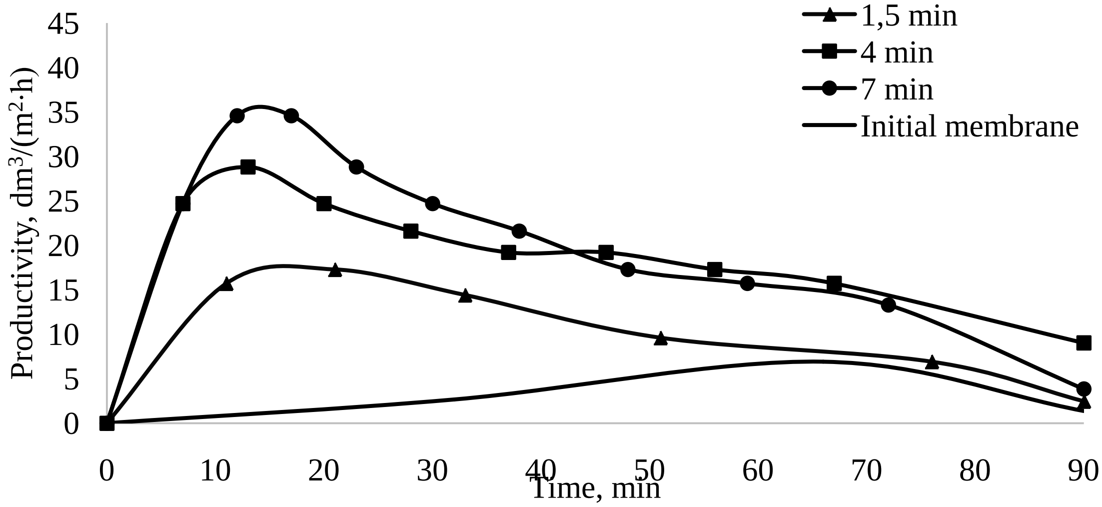

Figure 1: Productivity of VNE PES separation by membranes treated in a plasma flow at a voltage value: a) 1.5 kV; b) 3.5 kV; c) 5.5 kV.

Based on the presented graphical dependencies, an increase in the water-oil emulsion separation performance as a result of plasma treatment of polyethersulfone membranes is shown. It was not possible to identify the dependences on the voltage and processing time, which is apparently due to the complexity of both processes - plasma exposure and membrane separation, which when interacting lead to disordered results, as shown by the data in Figure 1.

Table 1: Filtrate chemical oxygen consumption values

Anodevoltage (U), kV	Chemical oxygen demand, mgO / dm^3		
	Treatment time (τ), min		
	1,5	four	7
1,5	960	1280	2880
3,5	1440	1080	360
5.5	2160	1800	2520
Initial membrane	1152		
Water-oil emulsion	23400		

Table 1 data analysis shows disordered values similar to the results for performance (Figure 1).Moreover, in most cases, the values for the chemical oxygen consumption from the filtrates by modified filter elements are greater than the initial value, which, together with an increase in productivity, is explained by etching of the surface of the functional layer of the membrane and, accordingly, the passage of larger amount of hydrocarbons. However, plasma processing at U = 1.5 kV and τ = 1.5 min, U = 3.5 kV and τ = 4 and 7 leads to an increase in efficiency, in particular, from 95.1% (for the initial membrane) to 98, 4% (U = 3.5 kV and τ = 5.5 min), while the value of the considered parameter decreases in 3 times from 1152 mgO / dm^3 to 360 mgO / dm^3. This circumstance is explained by that in

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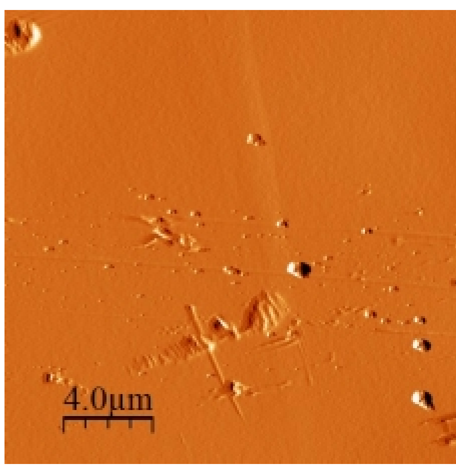
addition to the aforementioned etching, other processes occur that contribute to an increase in the separation efficiency of a 3% oil-water emulsion, the nature of which is currently difficult to clearly identify. We can only talk about the possible partial oxidation and sintering, due to which the structure of the polyethersulfone membrane can change, which leads to an increase in efficiency.

In order to qualitatively determine the surface deformations of plasma-treated filter elements during the study by electron microscopy using a probe microscope of the MultiMode V brand, we obtained images of the initial and plasma-treated polyethersulfone membranes with the corresponding histograms, shown in Figs. 2 and 3.

The image of the modified membrane relative to the original one appears rougher; this is also confirmed by histograms. As a result of plasma treatment of the polyethersulfone membrane in an argon and nitrogen medium, the number of nodes with a size of 100 nm decreases from 35000 to 1000, at the same time, protrusions up to 300 nm in size appeared, which is a consequence of burning out the main selective layer by about 100-200 nm and confirms that the etching process flows.

An increase in roughness is a prerequisite for increasing the wettability of the filter element surface, in connection with which, using the sedentary drop method with the Kruss DSA 20E apparatus, this parameter was measured. The results are shown in Figure 4.

a) 

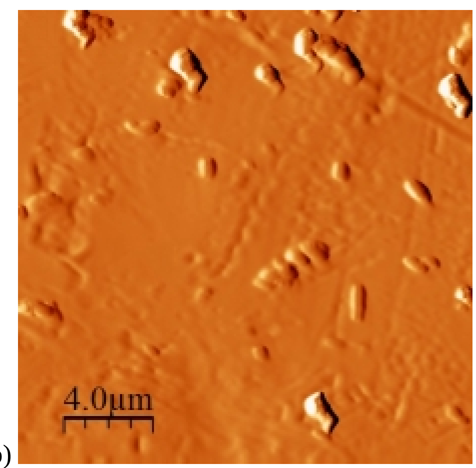
b) 

Figure 2: Images of the PES membrane surfaces: a) initial b) plasma-processed

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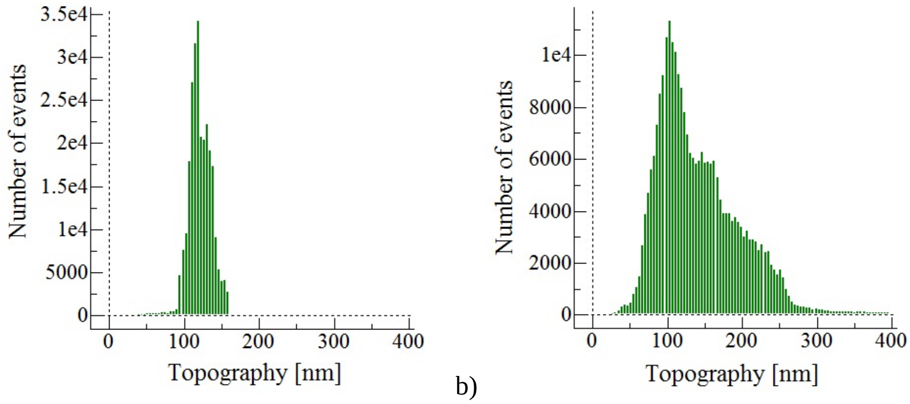
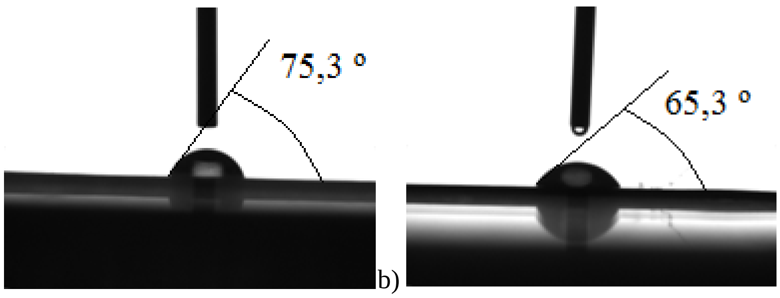


a) b)

Figure 3: Histograms of PES membrane protrusion distribution: a) initial b) plasma-processed



a) b)

Figure 4: Images of PSA membrane wettability by distilled water drops: a) initial; b) plasma-processed.

Based on the images presented in Fig. 4, an increase in wettability is shown by a decrease in the wetting angle of a distilled water drop on a polyethersulfone membrane from 75.3º to 65.3º as a result of argon and nitrogen HF plasma treatment of the latter, which confirms the above connection with an increase in roughness, and also a consequence of a possible change in the chemical structure of the polymer due to the formation of oxygen-containing functional groups on the membrane surface. In this regard, using the InfraLUM FT-08 brand Fourier infrared spectrometer, we obtained spectra of the studied membrane samples in the frequency range 600–4000 cm $^{-1}$ shown in Figure 5.

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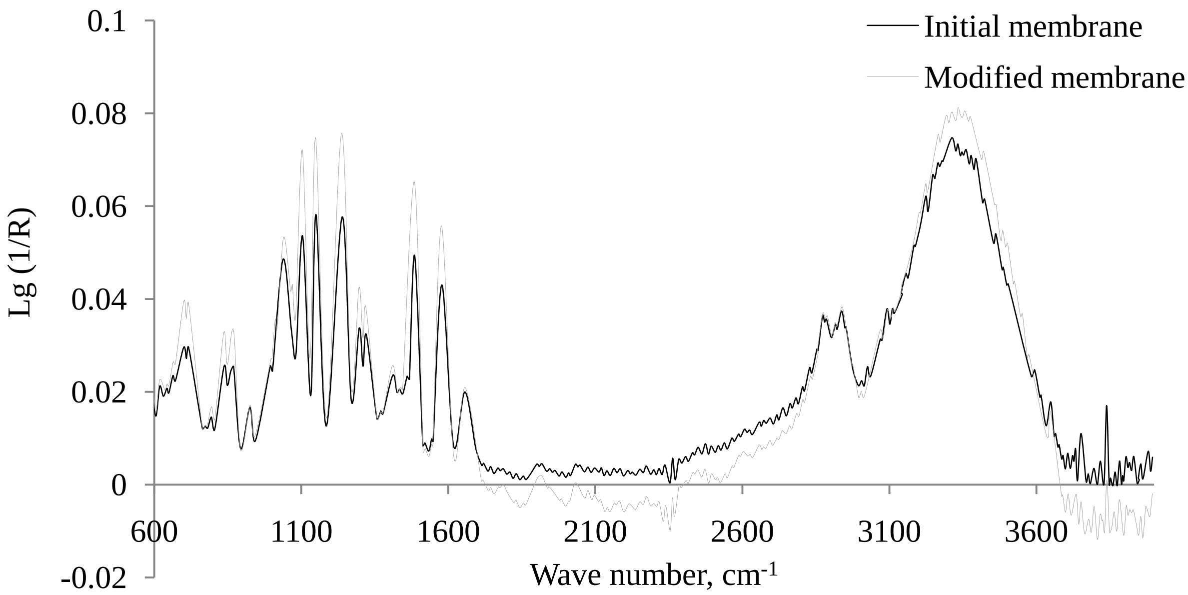

Figure 5: Infrared spectra of the membrane: a) initial, b) plasma-processed.

As a result of a comparative analysis of the presented IR spectroscopy data, in particular, an increase in the C – O stretching vibrations in the C – O – C group was observed at 1260 cm $^{-1}$.They can also make a significant contribution to increasing the hydrophilicity of the filter element surface and therefore, its performance and selectivity. An increase in the intensity of the region of a wide spectrum band of 3300 cm $^{-1}$ is also observed, which indicates an increase in the number of hydrogen bonds and, accordingly, additional cross linking of the polyethersulfone polymer chains, which can lead to a change in the pore geometry and throughput.

IV. SUMMARY

Based on the research results presented in this work, a positive effect of plasma exposure on polyethersulfone membranes was revealed, i.e. a slight increase in the selectivity and separation efficiency of the oil-water emulsion due to hydrophilization of the filter element surface due to increased roughness and partial chemical modification. However, the nature of these changes is disordered due to the complexity of the nature of interactions between plasma and membranes.

V. CONCLUSIONS

Nevertheless, the lack of full knowledge formed in viable hypotheses and theories about the mechanism according to which membranes are processed by plasma is not an obstacle to the practical use of plasma-modified filter elements. In general, it has been shown that it is possible to increase the efficiency of membrane water purification from oil by pretreating of polyethersulfone membranes in a stream of HF reduced pressure plasma in argon and nitrogen (70:30).Thus, a lesser supply of hydrocarbons to either a water body or to a subsequent purification step will result in a lower subsequent burden on the environment.

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