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Integrated waste-free technology for the utilisation of acid tar

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Abstract. The significance of acid tar processing lies in the fact that it affects the environmental safety of both industrial regions and the planet overall. The purpose of this study was to utilise acid tar from storage ponds using conventional methods and membrane technology that uses the unique properties of pervaporation membranes. The current state of petroleum waste processing in the EU and Ukraine was reviewed and analysed. The study proposed a comprehensive waste-free disposal of petrochemical

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waste of the second class of environmental hazard – acid tar. The issue of multiple storage ponds around the world was outlined. The study addressed economically viable and promising aspects of obtaining secondary processing products. Technological stages of acid tar processing, both conventional and using membrane processes, were proposed. The physical and chemical parameters of pond acid tar and its group composition were presented in detail. A four-stage stage of acid tar utilisation was proposed. The study highlighted the physicochemical parameters after the deasphalting stage and the stage of deasphalting agent after the second deasphalting. At the stage of selective purification, a pervaporation membrane apparatus was used. The membrane technology for purification of acid tar from petroleum products with their subsequent fractional separation was presented. Based on the findings of the study on acid tar processing, the target products were obtained: lubricants, briquetted solid fuel, resins, and purified process water. It was emphasised that the specified temperature regimes for each stage should be observed: for the neutralisation and deasphalting stage, the temperature is 60-70°C; the selective purification stage requires maintenance within 50-60°C; the lubricant production stage – 100-120°C; pond water treatment stage – 30-35°C. The study proved an increase in the content of the lubricant fraction in stage-by-stage processing of acid tar for storage ponds. The study experimentally confirmed the production of pure components with the possibility of further use. The complete purification of pond water from organic impurities was demonstrated

Keywords: pervaporation membranes; target products; storage ponds; waste; recycling; petroleum waste

Introduction

Large-tonnage environmentally hazardous waste generated by petroleum refineries in the purification of medical, cosmetic, perfume, petroleum oils, paraffin, and high-quality motor fuels using sulfuric acid, the so-called acid tar, is drained and stored in "special ponds" of artificial origin in the open air. As a result, the surface of these ponds is covered with water in which sulphuric acid and sulphonic acids are dissolved. These ponds pose a major environmental threat to the environment, as they are classified as class 2 toxic. This 'burial' of acid tar causes environmental pollution, namely acidification of soil and water bodies and, as a result, the destruction of flora and fauna. The natural, spontaneous redox process causes the release of large amounts of sulphur dioxide, which pollutes the air and harms flora and fauna (Leonard *et al*., 2010)

The complexity of acid tar utilisation lies in the variable composition and changes in properties over time, the constant process of sulphuric acid emulsion generation, which requires an individual approach and selective removal from storage ponds with the reconfiguration of the neutralisation and utilisation process. Therewith, acid tar is a valuable secondary material resource.

In Romania, methods for treating sulphuric acid waste by encapsulating it with various additives have been proposed. M. Tita *et al*. (2023) observed the best results when they physically altered the waste by encapsulation and stabilisation *in situ*. The methods proposed in this study do not allow for the complete utilisation of acid tar.

A. Fedorov *et al*. (2023) proposed a comprehensive scheme for the neutralisation and utilisation of petroleum sludge, depending on its physical and chemical properties, which allows for the effective neutralisation of hazardous waste with the production of marketable products and non-toxic soil mixture. Ways of further use of the obtained substances were proposed. The presented technology of petroleum sludge utilisation does not allow processing acid tar since it contains a large variety of hydrocarbons. To process acid tar using the presented technology, it is

necessary to additionally carry out its neutralisation and deasphalting.

The possibility of mixing acid resin waste with coal as a method of beneficiation was also investigated. D. Musademba *et al.* (2022) considered different ratios of acid tar waste to coal. It was found that the acid tar waste shows high volatile and moisture content with low ash and carbon content compared to coal. It was proved that a two-component mixture of 1:3 yields a higher proportion of fixed carbon, which contributes to an increase in the calorific value of the fuel, which is an excellent factor for combustion. The utilisation of acid tar produces asphaltenes, which are excellent high-calorific fuels. The use of acid tar as an additive to coal is considered inefficient.

M.S. Lawan *et al.* (2023) analysed the wastewater treatment of petroleum refineries. Pollutants were clearly identified: oil and grease, petroleum hydrocarbons, phenols, ammonia and sulphides, their concentration, and the presence of organic and inorganic compounds. An overview of the methods and processes used for purification was given. It was proposed to use a photocatalytic process for the degradation efficiency of photocatalysts. The method of biological water treatment presented in the study does not consider the permissible concentration of harmful organic substances, the so-called "volley emissions".

Pre-treated produced water, after petroleum extraction, is increasingly being considered as an interesting resource, especially in water-scarce regions such as the Arabian Peninsula. F. Salem & T. Thiemann (2022) analysed the available methods for treating produced water, purifying it, or disposing of it after treatment. The proposed water treatment methods cannot be used to treat acidic pond water contained in the tar, as these methods are very costly for disposal.

F. Alsalem *et al.* (2024) evaluated produced water from petroleum and gas operations in Kuwait and industrial salts as a resource and alternative storage. Reverse osmosis is used to desalinate the water, using porous membranes that cannot be used for pond water treatment. This is because this water contains high amounts of finely dispersed solid asphaltenes.

The treatment of water produced from shale oil and gas is a challenging process as it contains a variety of organic compounds and inorganic impurities. L. Ogletree *et al.* (2021) outlined that conventional membrane processes, such as reverse osmosis and nanofiltration, are problematic if the produced water has high salinity. The researchers proposed the use of direct osmosis and membrane distillation to treat produced water. The use of direct osmosis and membrane distillation is very energy-intensive, and therefore these methods are ineffective for treating pond water, as it contains fine mechanical impurities.

D. Radovanovic *et al.* (2024) pointed out the hazardous properties of petrochemical waste: an emulsion of various organic compounds, sulphuric acid, and water, which persist decades after its creation. It was outlined that the specific chemical composition and physical properties stand in the way of unambiguously determining the methods and technological treatment. The researchers proposed a technology for the treatment of petroleum waste, namely acid resin, until its complete physical and chemical transformation into a dry powder with the characteristics of inorganic material. The researchers did not show the further use of this powder or its utilisation.

The purpose of this study was to dispose of acid tar from storage ponds using conventional methods and membrane technology using the unique properties of pervaporation membranes.

To fulfil the purpose, the following objectives were set:

- to perform complete neutralisation of acid tar together with pond water;
- to conduct deasphalting of tar with removal of asphaltenes, to remove resins from deasphalting agent, and to produce average industrial lubricants;
- to purify pond water from traces of asphaltenes, resins, and organic substances, and to prove that the resulting asphaltenes can be used as briquetted high-calorific solid fuel.

Materials and Methods

Experimental and practical research was conducted in 2018-2019 in four stages using specialised equipment: a unit for the utilisation of acid tar, a unit for selective treatment, a unit for the production of lubricant, and a unit for the treatment of pond water. The unit was designed and documented at the Department of Biotechnology and Engineering of Igor Sikorsky Kyiv Polytechnic Institute, and the experimental unit was manufactured at a machine-building plant in Brovary, Kyiv region. Considering that this unit is a symbiosis of conventional devices combined with structurally unique membrane modules, there is no mass production of such units. The experiment was performed in the membrane technology training laboratory at the Department of Biotechnics and Engineering, Faculty of Biotechnology and Biotechnics, National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute" (Ukraine). The use of membrane technology ensured the complete recovery of all organic solvents used in the disposal process. The fractional composition of the source tar, as well as stage products of acid tar processing (asphaltenes, resins, lubricating oil, purified pond water) were analysed in the laboratories of the Masma Research Institute in Kyiv.

The object of the study was the process of obtaining purified products of acid tar processing (asphaltenes, resins, oils, water). The subject of the study was an integrated approach to the utilisation of acid tar by combining conventional methods and unique membrane pervaporation technologies. A sample of pond acid tar was used for the study. To investigate the process of acid tar utilisation, samples were taken from storage ponds. The samples were analysed physically and chemically, and the following key parameters were determined in the initial samples: the content of oils, paraffins, asphaltenes, and sulphuric acids. The storage ponds were located in industrial areas of the western part of Ukraine.

The first stage of the study was performed using the acid tar utilisation unit. The technology of acid tar utilisation itself had the following stages: neutralisation and deasphalting stage; selective purification stage; lubricant production stage; pond water treatment stage. The technological process of the neutralisation and deasphalting stage was as follows (Fig. 1).

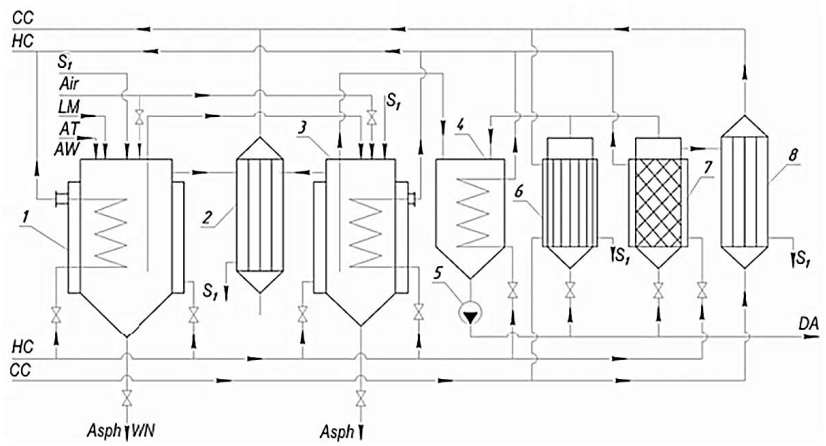

Figure 1. *Flow chart of the neutralisation and deasphalting stage*

Note: 1 – neutraliser-deasphalter; 2 – refrigerator-condenser; 3 – deasphalter; 4 – tank; 5 – pump; 6 – pervaporation apparatus; 7 – membrane adsorber; 8 – refrigerator-condenser; *AT* – acid tar; *AW* – acidic water; *LM* – lime milk; S_1 – solvent; *Air* – compressed air; *Asph* – asphaltenes; *WN* – water after neutralisation; *DA* – deasphalting agent; *HC* – hot coolant; *CC* – cold coolant

Source: developed by the authors of this study

Acid tar was loaded into the neutraliser-deasphalter *1* together with pond acid water, solvent was added, and lime milk was poured in. Solvent S_1 was added to deasphaltise and reduce the viscosity of the tar, as alkalisation of viscous lubrication systems results in stable, difficult-to-separate emulsions. Hot coolant was supplied to the jacket and coil of the neutraliser-deasphalter *1,* and the working mixture was boiled. Two processes took place simultaneously: neutralisation of acidic water and tar and asphaltene leaching. The vapour of solvent S_1, which was formed during boiling, was fed into the condenser-refrigerator *2*, where it was condensed and cooled.

After the boiling process was completed, the working mixture in the neutraliser-deasphalter was divided into three layers: the upper one was deasphalting agent; the middle one was neutralised water; and the lower one was asphaltenes. Then compressed air was supplied to the neutraliser-deasphalter and hot deasphalting agent with asphaltenes residues was fed through a transfer pipe to deasphalter *3*. Asphaltenes were discharged from the bottom of the neutraliser-deasphalter to be used for briquetting, and neutralised water with insoluble salts was drained and sent for further purification from organic impurities.

The process of deposition of asphaltene residues took place in the deasphalter *3*. For this, solvent S_1 was added to the apparatus, which was formed after the refrigerator-condenser *2*, and hot coolant was supplied to the jacket and coil, and the process of boiling and deasphalting took place. After deasphalting, compressed air was supplied to the deasphalter and the deasphalter was fed through a transfer pipe into the tank *4* and then, using the pump *5*, was fed into the membrane pervaporation apparatus *6*, where the main amount of solvent S_1 was removed. Then, the deasphalting agent was fed to the membrane adsorber *7*, where the remaining solvent S_1 was absorbed by the membrane elements and, during regeneration, was supplied in the form of vapour to the refrigerator-condenser *8*, where it was condensed and cooled. Next, the purified deasphalting agent was fed to selective purification.

At the stage of selective purification, the chemical composition of the de-asphaltising agent was improved by extracting resinous compounds with a solvent. The technological process was as follows (Fig. 2).

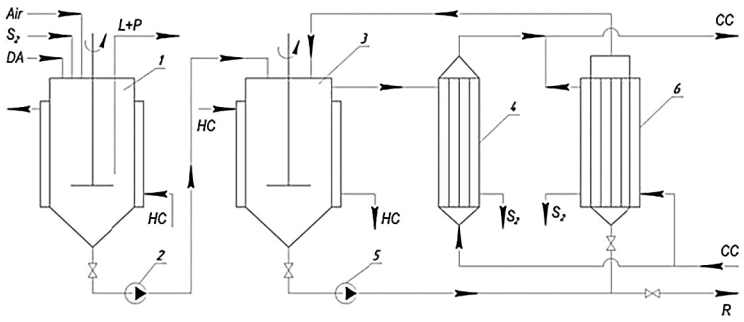

Figure 2. *Flow chart of the selective purification stage*

Note: *1* – extractor; *2*, *5* – pumps; *3* – distiller; *4* – refrigerator-condenser; *6* – membrane apparatus; *DA* – deasphalting agent; S_2 – solvent; *L+P* – lubricating fraction with paraffins; *R* – resins; *HC* – hot coolant; *CC* – cold coolant; *Air* – compressed air

Source: developed by the authors of this study

Deasphalting agent and solvent S_2 were loaded into extractor *1*. With constant stirring and heating of the mixture, the extraction of resinous substances by solvent S_2 took place. As a result, two layers were formed in extractor *1*: the upper one was a mixture of the lubricating fraction

with paraffins, while the lower one was a solution of resinous substances in solvent S_2. Then compressed air was supplied to the extractor, and the mixture of the lubricating fraction with paraffins was removed through the transfer pipe, which was fed to the stage of obtaining lubricant, while the solution of resinous substances was pumped by pump *2* to distiller *3*. In distiller *3*, solvent S_2 was distilled with constant stirring and heating, the vapour of which was fed into a refrigerator-condenser *4*, where condensation and cooling took place.

At the end of the distillation process, the resin was pumped by pump *5* to the pervaporation membrane apparatus *6*, where the residual solvent S_2 was removed. The purified resin was then sent for utilisation. In the future, it can be used in the production of bitumen.

At the third stage, acid tar was utilised to produce lubricating oil. The dewaxing process is designed to produce lubricants with the required pour point by removing paraffins from the raw materials (Fig. 3).

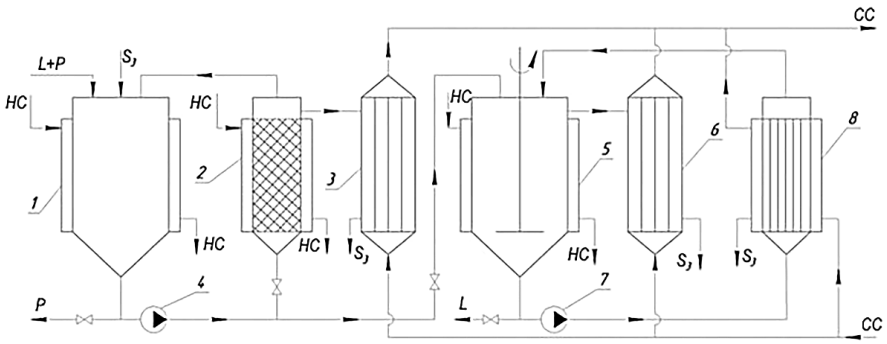

Figure 3. *Flow chart of the lubricant production stage*

Note: *1* – tank; *2* – adsorber; *3* – refrigerator-condenser; *4*, *7* – pumps; *5* – tank; *6* – refrigerator-condenser; *8* – pervaporation membrane apparatus; *L* – lubricant; *P* – paraffin; S_3 – solvent; *HC* – hot coolant; *CC* – cold coolant
Source: developed by the authors of this study

The lubricant fraction containing paraffins was loaded into tank *1*, heated and pumped through adsorber *2* by pump *4*. In adsorber *2*, the lubricant fraction was sorbed by membrane elements. After the absorption of the lubricant fraction was completed, paraffin waxes were left in the tank *1* and removed to the outside. Next, solvent S_3 was poured into tank *1*, which was pumped through adsorber *2* by pump *4*. The adsorber was used to displace the lubricant fraction from the membrane elements and fill them with solvent S_3. After the displacement of the entire lubricant fraction, the membrane elements were regenerated. For this, hot coolant was supplied to the adsorber jacket *2*, and when heated, solvent S_3 was removed from the membrane elements, which was supplied in the form of vapour to the refrigerator-condenser *3*, where it was condensed and cooled. The lubricating fraction with solvent S_3 was pumped from tank *1* by pump *4* into tank *5*, where the solvent was distilled with constant stirring and heating. Therewith, the vapour of the solvent S_3 was supplied to the refrigerator-condenser *6*, where it was condensed and cooled. At the end of the distillation process, the lubricant, together with the remaining solvent, was pumped from the tank *5* by the pump *7* through the pervaporation membrane apparatus *8*, in which the remaining solvent S_3 was removed from the grease. At the end of the pervaporation process, the purified lubricant was removed from the tank *5* and stored as a finished product.

The last stage for the disposal of acid tar was the pond water treatment stage (Fig. 4).

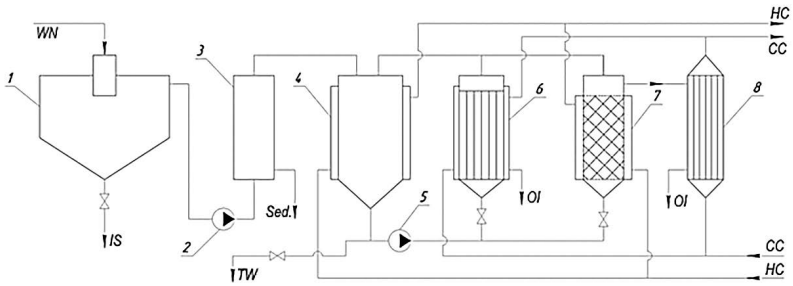

Figure 4. *Flow chart of the pond water treatment stage*

Note: *1* – settling tank; *2*, *5* – pumps; *3* – filter; *4*, *7* – pumps; *4* – tank; *6* – pervaporation membrane apparatus; *7* – membrane adsorber; *8* – refrigerator-condenser; *WN* – water after neutralisation; *IS* – insoluble salts; *Sed.* – sediment; *OI* – organic impurities; *TW* – treated water; *HC* – hot coolant; *HT* – cold coolant

Source: developed by the authors of this study

The neutralised pond water was treated as follows. The pond water containing insoluble salts and organic impurities from the neutralisation and deasphalting stage was fed into the settling tank *1*. Insoluble salts settled at the bottom of the settling tank, while water from the top of the settling tank was pumped by pump *2* through filter *3*, where the microfiltration process took place, and fed into tank *4*. From tank *4*, heated water was pumped by pump *5* through a pervaporation membrane apparatus *6*, where most of the organic impurities were removed.

Then the partially purified water from the tank *4* was pumped by the pump *5* through the membrane adsorber *7*, where the final purification from organic impurities took place. After the sorption process, the membrane elements in the adsorber were regenerated by supplying hot coolant to the jacket of the latter. The vapour of organic impurities was supplied to the refrigerator-condenser *8*, where it was condensed and cooled. The purified pond water was drained from the tank *4*.

Results and Discussion

After analysing the material from the four storage ponds for the processing of acid tar, their characteristics, composition, and volume were determined. Detailed information on the extracted acid tar is presented in Table 1.

At the neutralisation and first deasphalting stage, sulphonic acids and asphaltenic acids are neutralised and most of the asphaltenes are removed. The composition of the deasphalting agent after this stage is presented in Table 2.

Table 1. *Physical and chemical parameters of pond acid tar and their group composition*

No.	Indicators % (wt.)	Pond No.			
		1	2	3	4
1.	Lubricants fraction with paraffins	13.75	26.06	11.10	11.23
2.	Resins	29.50	17.65	30.65	31.25
3.	Asphaltenes	3.43	10.38	5.96	5.13
4.	Sulphonic acids	42.05	42.34	39.85	38.89
5.	Asphaltenic acids	1.33	1.95	1.63	1.87
6.	Carbenes, carboids, mechanical impurities	9.94	1.62	10.81	11.63
7.	Density, g/cm^3	1.238	1.090	1.201	1.302
8.	Acid number, m^2 KOH/g	41.30	67.28	40.21	41.05

Source: developed by the authors of this study

Table 2. *Physical and chemical parameters after deasphalting and their group composition*

No.	Indicators % (wt.)	Pond No.			
		1	2	3	4
1.	Lubricants fraction with paraffins	25.85	57.49	21.12	20.75
2.	Resins	49.65	35.48	53.13	52.67
3.	Asphaltenes	5.81	3.46	5.18	5.08
4.	Carbenes, carboids	18.69	3.57	20.57	21.50

Source: developed by the authors of this study

As Table 1 shows, the fractional composition of acid tar from the storage ponds was as follows: lubricant fraction with paraffins 11.10-26.06% (wt.); resins 17.65-31.25% (wt.); asphaltenes 38.89-42.34% (wt.); asphaltenic acids 1.33-1.95% (wt.); carbenes, carboids, mechanical impurities 1.62-11.63% (wt.); acid number 40.21-67.28% (wt.).

After neutralisation and the first stage of deasphalting, sulphonic acids, asphaltenic acids, and a considerable part of asphaltenes were completely removed from the tar. The mechanism of this process was as follows. Acid tar is loaded into the deasphalter together with pond water, a lime suspension, and solvent S_1. The process requires constant stirring at 10-12 rpm and heating, with the mixture beginning to boil. In this process, neutralisation occurs, and three layers are formed: the upper one is deasphalting agent with solvent S_1; the middle one is neutralised water; the lower one is asphaltenes together with salts formed during neutralisation.

These layers are formed because they have different densities. The asphaltenes released from the deasphalting agent sink into the lower layer, passing through a layer of water that forms a buffer zone separating the deasphalting agent and the asphaltenes. Composition of the deasphalting agent after the second deasphalting is presented below (Table 3).

Table 3. *Physicochemical parameters of deasphalting agent after the second deasphalting and its group composition*

No.	Indicators % (wt.)	Pond No.			
		1	2	3	4
1.	Lubricants fraction with paraffins	34.24	61.84	28.44	28.26
2.	Resins	65.76	38.16	71.56	71.74

Source: developed by the authors of this study

After the second deasphalting, a membrane apparatus is used to remove the remaining solvent S_1 from the deasphalting agent. This is because the pervaporation membranes can remove solvent S_1 from the highly viscous medium, which is the resin-derived deasphalting agent. After the second deasphalting, the working mixture has the following composition: lubricant fraction with paraffins 28.26-61.84% (wt); resins 38.16-71.74% (wt).

The composition of the lubricants fraction after selective purification is presented in Table 4.

Table 4. *Physical and chemical parameters of the lubricants fraction Wafter selective purification and its group composition*

No.	Indicators % (wt.)	Pond No.			
		1	2	3	4
1.	Lubricants fraction	78.30	90.20	84.86	81.79
2.	Paraffins	21.70	9.80	15.14	18.22

Source: developed by the authors of this study

At the stage of selective purification, resins are removed from the mixture using solvent S_2, and the pervaporation membrane apparatus is used to regenerate the solvent. The mixture after this stage has the following composition: lubricant fraction 78.30-90.20% (wt); paraffins 9.8-21.70% (wt). To remove the lubricant fraction, sorption by membrane elements of the lubricant during heating is used, because with increasing temperature, the viscosity of the lubricant decreases and the diffusion coefficient increases. Unlike mineral sorbents, which lose their sorption properties with increasing temperature, the properties of the pervaporation membrane elements increase due to their structure. Therefore, the absorption of the lubricant fraction from the mixture occurs in the membrane adsorber. To remove the lubricant fraction from the membrane elements, the method of displacing the latter with a more active sorbent-solvent S_3 is used. Therefore, after the membrane elements are saturated, solvent S_3 is fed into the adsorber, which displaces the lubricant fraction from the membranes. At the outlet of the adsorber, a highly concentrated solution of the lubricant fraction in solvent S_3 is formed, from which solvent S_3 is removed using conventional methods, for example, distillation.

The increase in the lubricant fraction content as a result of the stage-by-stage processing of acid tar is presented in Figure 5.

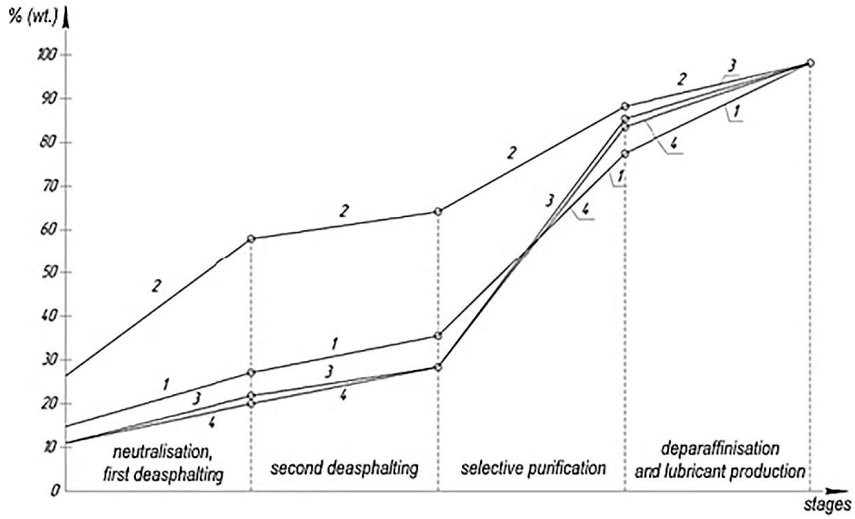

Figure 4. *Diagram of the growth of the lubricant fraction*

Note: 1, 2, 3, 4 – Numbers of the acid tar storage ponds
Source: developed by the authors of this study

As the diagram shows, after selective purification, the content of the oil fraction in the samples taken from the four storage ponds ranges within 78.3-90.2%. The difference in the lubricant content in the samples is small and equals 11.9%. Therefore, the rate of increase in the concentration of the lubricant fraction during deparaffinisation for all four experiments is approximately the same and amounts to 0.25% per 1 min (determined experimentally).

Neutralised pond water contains fine asphaltene and resin inclusions. Therefore, before the water is fed into the settling tank, a coagulant is added to it, which binds the fine inclusions, and they settle out. The water is then fed to filtration and then undergoes complete purification from organic impurities in membrane apparatus.

The asphaltenes that settled out at the deasphalting stage are briquetted and used as fuel.

The physicochemical composition of acid tar waste is important in the evaluation and development of processing options for its further utilisation. C.H. Chihobo *et al.* (2015) used gas chromatography/mass spectrometry (GC/MS), Fourier transform infrared (FTIR), and scanning electron microscopy with energy dispersive X-ray (SEM/EDX) to characterise the acid tar waste from crude benzene refining. Organic analysis of the aromatic fraction of the acid tar waste revealed a wide range of compounds, including polycyclic aromatic hydrocarbons, furans, phenols, thiophenes, and biphenyls. These findings can be useful in the design and development of technological processes that can utilise acid tar waste. Notably, these findings are encouraging, but they do not consider all the constituents of acid tar. X. Lu & U. Isacsson (2000) obtained polymer-modified bitumen by mixing bitumen with various thermoplastic polymers. It was found that the morphology and rheological properties of modified binders are influenced by the characteristics and content of the polymer and the nature of the bitumen. The rheological changes in the materials, which are associated with bitumen oxidation and/or polymer degradation, were outlined. However, the researchers relied on the structure of polymeric materials, which allows them to bind to bitumen. However, the asphaltenes that are part of the tar do not have the same structure as polymeric materials, and therefore they will not bind to bitumen and improve its structure.

According to I.A. Burtna *et al.* (2006), the utilisation of acid tar is still a serious environmental and technological problem due to its complex chemical composition, high reactivity, and corrosiveness, which complicate the development of a universal method of its treatment. The high viscosity and sulphonic acid content of tar makes it impractical to use standard diesel fuel desulphurisation technologies for their utilisation. The cracking and distillation methods discussed in D.D. Milne *et al.* (1986), specifically, using anhydrous $AlCl_3$ as a catalyst, open prospects for converting petroleum residues into volatile petrol fractions. However, these studies did not focus on the problems arising from the supply of acidic resin to the combustion nozzles.

According to I.A. Burtna *et al.* (2011), acid tar residues were previously stored in landfills near oil refineries, and their remediation has become a critical environmental issue. Meanwhile, the problem of organic impurities in acidic wastewater from storage ponds stays unresolved. I. Knapkova & D. Samesova (2017) discussed the utilisation of acid tar to reduce environmental pollution, but the problem is not completely eliminated.

The use of gas chromatography-mass spectrometry to analyse the composition of acid tar, as noted by G.V. Krymets *et al.* (2022), can reveal its S-organic content, which hinders the production of fractions that meet petroleum product standards. Researchers also pointed to the possibility of reusing polymeric waste and natural bitumen to modify acid tar, but their implementation in industry is still challenging.

Membrane technologies, including reverse osmosis, are used for water treatment in the petroleum and natural gas industry due to their resistance to aggressive environments (Le & Nunes, 2016). However, these membranes are not effective for treating acidic water from storage ponds, as fine asphaltenes can clog pores. An analysis of the environmental impacts of tar waste on groundwater by H. Xu (2007) indicates possible risks, but effective disposal methods have not yet been developed.

Thus, the available research shows a variety of approaches to the utilisation of acid tar, but the need for further investigation and development of effective methods to reduce the environmental burden stays urgent.

After analysing the methods of processing acid tar, it becomes clear that there is no single technology that can combine these processing methods and create a closed cycle of their utilisation. Therefore, instead of the four areas of acid tar processing – high-temperature thermal decomposition, low-temperature decomposition, hydrolytic decomposition with water or vapour,

and neutralisation with alkali metal hydroxides – four stages have been proposed to form a single technology for acid tar processing. These are the following stages: neutralisation and deasphalting, selective purification, lubricant production, and treatment of pond water. Let us consider the advantages of using these stages.

Increased production of petroleum-containing water and its treatment has become a challenge due to the complexity and quantity of waste generated. Such unwanted wastewater needs to be treated before final disposal or for burial in the environment. T.C. Nonato *et al.* (2018) reviewed technologies for the recovery of petroleum and other toxic agents and the treatment of produced water from petroleum. This study did not consider methods for the disposal of hazardous waste generated during the treatment of petroleum-containing water.

At the stage of neutralisation and deasphalting, two processes take place simultaneously in the apparatus called a neutraliser-deasphalter: neutralisation of acid tar with pond water and deposition of asphaltenes. The supply of solvent S_1 to the neutraliser-deasphalter reduces the viscosity of the tar, as there is tar that is almost solid, and creates conditions for the neutralisation and deasphalting processes. According to C. Danha *et al.* (2014), such conditions can considerably reduce solvent consumption by 5-7 times and carry out the process at atmospheric pressure compared to conventional technologies, where the pressure in the apparatus is maintained at 2-5 MPa. This stage produces asphaltenes that can be used as briquetted solid fuels. Membrane devices are used to completely remove solvent P_1 from the deasphalter, without which this process would be impossible.

At the stage of selective purification, the extraction is carried out using solvent S_2. A membrane apparatus is used for its complete extraction from the lubricant fraction. The use of solvent S_2 instead of forfuryl or phenol (according to conventional technology) allows reducing solvent consumption by 4-9 times.

At the stage of dewaxing or obtaining the lubricating fraction, unique membrane redistillation processes are used: adsorption of the lubricating fraction from its mixture with paraffins by membrane sorbents; the effect of displacement of the lubricating fraction from the membrane sorbents by the solvent S_3; purification of the lubricating fraction from S_3 residues by redistillation. In this case, the process of purification of the lubricating fraction from paraffins using conventional technology takes place at a temperature from -30°C to -57°C, while the sorption of the lubricating fraction by membrane sorbents takes place at a temperature within 100÷120°C, the energy costs for maintaining which are much lower.

The stage of pond water treatment was also performed using membrane pervaporation apparatuses. This became possible after the use of a coagulant proposed by the authors of the present study. Its use allows pre-treating water from mechanical contaminants – finely dispersed asphaltene particles.

The following target products were obtained during the utilisation of acid tar: briquetted asphaltenes (can be used as solid fuel); resins (used in bitumen production); lubricating fractions (used in the automotive and other industries); and purified industrial water. Thus, the stages considered allow stating that an integrated non-waste technology for the utilisation of acid tar was developed.

Conclusions

The study considered the problem of utilisation of acid tar. The existing methods of acid tar processing were analysed. These methods have many disadvantages, and therefore they are not widely used. A new non-waste technology for the utilisation of acid tar was proposed, which employs conventional and membrane processes.

The proposed combined waste-free technology with conventional extraction processing of tar and production of lubricants gave the following results: deasphalting stage: solvent S_1; process temperature 70-80°C; working pressure 0.1 MPa; solvent-tar ratio (by volume) 0.3:1; stage of

selective cleaning: solvent S_2; process temperature 15-20°C; solvent-deasphalting agent ratio (by volume) 0.4:1; stage of deparaffinisation: solvent S_3; saturation temperature 150°C with displacement 20°C; dilution ratio (by weight) 0.4:1.

Comparing the indicators of stage-by-stage processing of tar by the proposed and conventional technology, it was proved that the volume of solvent S_1 is 16-20 times less than the volume of propane, while the pressure in the apparatuses is 20-50 times less. At the stage of selective cleaning, the volume of solvent S_2 is 4-9 times less than the volume of farfurole or phenol. At the deparaffinisation stage, the mass consumption of solvent S_3 is 3.5-8 times less than that of the corresponding solvents. The saturation process at this stage takes place at 150°C, the energy consumption to maintain which is an order of magnitude less than that required to obtain and maintain the temperature of -57°C using conventional technology.

The proposed technology is much less energy-intensive and less expensive in terms of hardware design than the conventional and already known technology.

The results of the processing of acid tar were presented, which resulted in the following target products: briquetted asphaltenes that can be used as fuel; resins that can be used in the production of bitumen; lubricants that can be used in automotive equipment and other industries.

There are ways to further improve the developed utilisation technology, namely: recycling of contaminated waste (wood, leaves, etc.) on the surface of the storage ponds by pyrolysis to produce synthesis gas; use of anaerobic biological treatment of pond water after sedimentation of mechanical impurities to produce biogas using bioreactors.

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Conflict of Interest

None.

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Анотація. Важливість переробки кислих гудронів полягає в тому, що від неї залежить екологічна безпека як промислових регіонів, так і планети в цілому Метою дослідження було утилізація кислих гудронів із накопичувальних ставків за допомогою традиційних методів та мембранної технології, що використовує унікальні властивості первапораційних мембран. Розглянуто та проаналізовано сучасний стан переробки нафто відходів в країнах ЄС та в Україні Запропоновано комплексну безвідходну утилізацію відходів нафтохімічних виробництв другого класу екологічної небезпеки – кислих гудронів. Окреслено питання множинності ставків-накопичувачів по всьому світу. Акцентується увага на економічно вигідних та перспективних питаннях отримання вторинних продуктів переробки. Запропоновано технологічні стадії переробки кислих гудронів, як традиційних так і за допомогою мембранних процесів. Докладно представлено фізико-хімічні показники ставкових кислих гудронів та їх груповий склад. Запропонована чотиристадійна стадія утилізації кислих гудронів. Висвітлено фізико-хімічні показники після стадії деасфальтизації та стадії деасфальтизата після проведення другої деасфальтизації. На стадії селективної очистки використано первапараційний мембранний апарат. Представлено мембранну технологію очистки кислих гудронів від нафтопродуктів с подальшим їх пофракційним розділенням. За результатами проведених досліджень переробки кислих гудронів одержано цільові продукти: мастила, брикетоване тверде паливо, смоли, очищена технічна вода. Наголошується на дотриманні заданих температурних режимів для кожної стадії: для

стадії нейтралізації та деасфальтизації температура 60-700°C; стадія селективної очистки вимагає дотримання в межах від 50-60°C; стадія одержання мастила: 100-120°C; стадія очистки ставкової води: 30-35°C. Доведено зростання вмісту мастильної фракції в процесі постадійної переробки кислого гудрона для ставків-накопичувачів. Експериментально підтвердженно отримання чистих компонентів з можливістю подальшого використання. Засвідчено повне очищення ставкової води від органічних домішок

Ключові слова: лісокультурне виробництво; генетичні резервати; плюсові дерева; лісове господарство; відновлення лісів