Catalytic processing of the acid tars

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Acid tars are wastes from the processing of coal, petroleum, and petrochemicals (oil refining, benzene refining and petroleum fractions refining and alkylation of isobutane with butenes). Acid tar compositions include resinous substances, organic matter, and polymerization products of unsaturated hydrocarbons. The presence of free sulfuric acid in acid tars often reaches 70 % by weight. Almost all metals from oil are concentrated in tars, and the content of vanadium and nickel can reach 0.046 and 0.014 %, respectively. A lot of countries keep acid tar in the open air in spent quarries, storage ponds, barns, lagoons or near landfills. It poses a risk or even potential threat to people and to the environment nearby due to soil, water, and air pollution. Thus, disposal of the acid tars is a very important eco-logical and industrial task. In this study, we have researched catalytic cracking and distillation as the utilization methods for acid tar. Anhydrous $AlCl_3$ was used as a catalyst during the cracking of petroleum residues to obtain volatile gasoline fractions due to its catalytic activity in many organic reactions. The catalyst ratios (0.15 g/g of tar or 0.1 g/g of tar) had a very significant influence on the number of volatile fractions and boiling temperature in the acid tar cracking process. According to the results of ^1H NMR research, the main components of volatile fractions in the case of catalytic cracking were alkanes CH_3-$(CH_2)_n$-CH_3. The compositions of these fractions were similar to the compositions of gasoline and diesel fuel. A series of distillation experiments (distillation of previously deacidified and centrifuged tar, acid tar without deacidification and centrifugation, and previously deacidified tar without centrifu-gation) gave different results for each type of material. Aliphatic hydrocarbons were the main components of volatile fractions (~ 80, ~ 60 and ~ 90 %, respectively) and the contents of aliphatic S-organic compounds were also signifi-cant (~ 10, ~ 30 and ~ 8 %). Thus, both for catalytic cracking and for tar distillation, aliphatic hydrocarbons were the main component of volatile fractions. Deacidification of tar increased the yield of aliphatic hydrocarbons during tar distillation and decreased production of S-organic compounds due to its reactions with calcium carbonate. It is perspective in the context of fuel production.

Keywords: acid tar, catalytic cracking, oil processing, fuel, utilization

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Introduction

Acid tars are hazardous, non-utilizable solid wastes with resinous and viscous characteristics and varying flowability. It is waste from the processing of coal, petroleum and petrochemicals (oil refining, ben-zene refining, petroleum fractions refining and alkyla-tion of isobutane with butenes) [1]. Sulfonation tech-nologies are among the oldest technological processes of oil processing that are still used today due to their high efficiency of removing undesirable substances and improving the oxidative stability [2]. In the petro-leum and petrochemical industries sulfuric acid is used for the removal of metal impurities from spent lubrica-tion oils, for the removal of unsaturated hydrocarbons and sulfur-containing compounds from heavy lubricant fractions, and for the sulfonation of undesirable impu-rities in benzene (also toluene and xylene) separation [1, 3]. Thus, acid tars are produced as a result of these processes.

Acid tars compositions include resinous substan-ces, organic matter, and polymerization products of unsaturated hydrocarbons. The presence of free sulfu-ric acid in acid tars often reaches 70 % by weight [4]. Almost all metals from oil are concentrated in tars and contents of vanadium and nickel can reach 0.046 and 0.014 %, respectively [4]. For example, tars stored at the Lviv city landfill contain 20.6 % of carbohydrates, 78.2 % of such components as resins, carbon, carboids, ash, and oxidation products. The content of sulphuric acid and sulfonic acids is about 1.2 % [5]. In the case of the Kozinske forestry the total concentration of sul-fonic acids in the aqueous extract from the acid tar is 8.9 %. Derivatives of benzene and naphthalene are among the main species of sulfonyl chlorides in these acid tars [6].

A lot of countries keep acid tar in the open air in spent quarries, storage ponds, barns, lagoons or near landfills. The USA, UK, Netherlands, Belgium, Ger-many, Latvia, Slovenia, Slovakia, China, Ukraine, and

Zimbabwe are among these countries [7, 8]. Storage of acid tars in open areas (ponds, lagoons, etc.) causes an increase in regional environmental hazards [7, 9]. It poses risk or even potential threat to people and to the environment nearby due to soil, water and air pollution [1, 8]. The leaching of the acid tars components affects the ground water and the evolution of gaseous compounds from the acid tars also affects the atmosphere, which might cause acid rains, which will in turn affect surface water, flora, and fauna. During storage in open-air ponds, the chemical composition of the acid tar changed as a result of the leaching of the acid from the tar by rainfall, the evolution of SO_2, and condensation of the different substances [1]. There are elevated concentrations of total organic carbon (TOC), chemical oxygen demand (COD), chlorides and sulphates in groundwater in the indication area of these storage places [8]. Thus, disposal of the acid tars is a very important ecological and industrial task.

There are a lot of disposal methods for acid tars, especially thermal (combustion, gasification, etc.), biological (usage of microorganisms and enzymes), physico-chemical (separation of different fractions) and chemical methods (extraction and other approaches with usage of chemical reagents) [10].

Combustion is the most widely used process for acid tar disposal, but this method has some disadvantages, including a high concentration of SO_2 in produced gases and a significant content of heavy metals in the ash [2]. In this case, disposal of one type of waste leads to the production of polluting gas emissions and another type of toxic waste. Also, deacidification is necessary before the combustion due to the high corrosive activity of acid tars.

Acid tar disposal by biodegradation in natural conditions also has some disadvantages, especially significant duration of the degradation process; different biodegradability due to possible toxicity; the need for appropriate nutrients; large area requirements; and complex control of the biodegradation process [2, 11].

Chemical and physico-chemical processes are very perspective in the context of acid tars disposal because they produce a lot of important substances (liquid fuel, coke, asphaltic binders, surfactants, controlled low-strength materials for landfill liner and landfill daily cover, polycondensates used as basic stocks for adsorbents, etc.) [3, 12-14]. But chemical disposal is often relatively expensive due to the use of chemical reagents and can produce different wastes.

This research is about catalytic cracking and distillation of the acid tar for fuel production.

Materials and methods

We chose catalytic cracking and distillation as the utilization methods for acid tar. The acid tar sample was characterized by the following parameters: free acid content - 12%, mineral component - 21.3%, organic component - 66.7%. The main elements of the organic component are C-62%, H-17%, O-13%, N-1.5%, S-6.5%. The aim was to obtain the maximum quantity of volatile fractions from tar. $AlCl_3$ (anhydrous) was used as a catalyst during the cracking of petroleum residues to obtain volatile gasoline fractions due to its catalytic activity in many organic reactions. Although the use of aluminum chloride as a catalyst cannot be called environmentally friendly, it is still quite popular due to its high efficiency.

Figure 1 demonstrates lab-scale equipment for tar cracking. Acid tar and anhydrous $AlCl_3$ were put into a two-necked flask and heated to a temperature of about 200 °C. The obtained volatile compounds were concentrated in condensers. The activated carbon tube was used to hold emitted gases. For cooling and condensation, we used water in the Liebig condenser and air in the Dimrot condenser.

Two different catalyst ratios (0.15 g/g of tar and 0.1 g/g of tar) were used to study the effect of the amount of catalyst on the acid tar cracking process. We also carried out a series of distillations of previously deacidified and centrifuged tar, acid tar without deacidification and centrifugation, and previously deacidified tar without centrifugation. For the first distillation experiment, acid tar was deacidified by calcium carbonate ($CaCO_3$) to pH 6 and centrifuged (7000 rpm) for 20 min to separate solid and liquid phases. After centrifugation, 107.6 mL of liquid fraction was put into a round-bottomed flask and inserted into a flask heater for distillation experiment
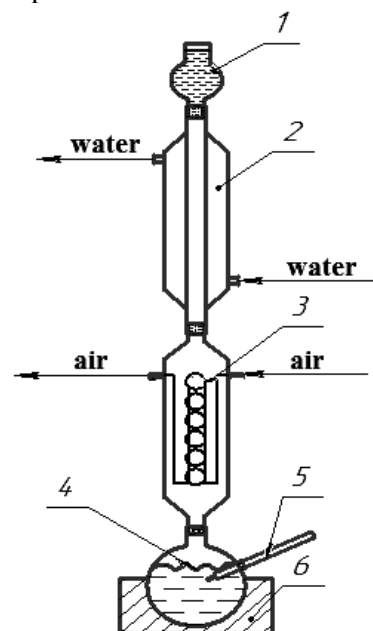

Fig 1. Tar cracking lab-scale equipment: 1 - tube with activated carbon; 2 - the Liebig condenser with ground glass joints; 3 - the Dimrot 3-way air condenser with ground glass joints; 4 - two-necked flask with ground glass joints; 5 - thermometer; 6 - flask heater.

^{1}H NMR technique was used to characterize the structures of volatile compounds after cracking and distillation experiments. The spectra were recorded in $CDCl_3$ solution (the peak at 7.02 ppm) on a Varian Gemini-2000 (400 MHz) spectrometer using tetramethyl silane as an internal standard.

Results and Discussion

The catalyst ratios (0.15 g $AlCl_3$/g of tar or 0.1 g/g of tar) had a very significant influence on the number of volatile fractions and boiling temperature in the acid tar cracking process. At the catalyst ratio of 0.15 g/g of tar at the temperature range of 170-220 °C, we observed the beginning of intensive production of white-yellow vapors, which condensed in the Liebig condenser. During massive condensation, the temperature decreased from 210-220 °C to 180-190 °C. The process duration was 2 hours. In this case, the content of volatile fractions was 14 %. In the experiment with a catalyst ratio of 0.1 g/g of tar, the content of volatile fractions was 5.5 % and the boiling temperature was about 120-140 °C. According to the findings of ^{1}H NMR research, the main components of volatile fractions in the case of catalytic cracking were alkanes CH_3-$(CH_2)_n$-CH_3 (peaks at 0.91 and 1.30 ppm). The compositions of the volatile fractions were similar to the compositions of gasoline and diesel fuel. Table 1 demonstrates information about the interpretation of ^{1}H NMR spectra.

Table 1. **The interpretation of ^{1}H NMR spectra of volatile fractions**

Peak, ppm	Characteristic group
0.91	CH_3 at the tertiary atom
1.30	CH_2 in the aliphatic chain
2.23	CH_3S in the aliphatic chain
2.29	CH_3 in aromatic compounds
2.52	CH_3S in the aliphatic chain
2.70	CH_2 in aliphatic heterocycles
7.02	$CDCl_3$
10.60	COOH

A series of distillation experiments (distillation of previously deacidified and centrifuged tar, acid tar without deacidification and centrifugation, and previously deacidified tar without centrifugation) gave different results for each type of material (Table 2). In the first case, we observed signals at 0.91, 1.31, 2.23, 2.29, 2.52, 2.70, 7.02, and 10.60 ppm, which were assigned to CH_3 at the tertiary atom, CH_2 in the aliphatic chain, CH_3 in aromatic compounds, CH_3S in the aliphatic chain, CH_2 in aliphatic heterocycles, $CDCl_3$, and COOH. In the second experiment the ^{1}H NMR spectrum had peaks at 0.92, 1.30, 2.23, 2.29, 2.54, 2.70, and 7.02 ppm, which were the signals of CH_3 at the tertiary atom, CH_2 in the aliphatic chain, CH_3 in aromatic compounds, CH_3S in the aliphatic chain, CH_2 in aliphatic heterocycles, and $CDCl_3$. In the third ^{1}H NMR spectrum, we also observed peaks at 0.92, 1.30, 2.23, 2.29, 2.54, 2.70, and 7.02 ppm. But the intensities of these peaks were different for various samples.

Table 2. **The compositions of volatile fractions**

Sample	Component	Content, wt. %
Distilled organic phase obtained at the temperature of 120 ºC from deacidified and centrifuged tar	Aliphatic (saturated) hydrocarbons (gasoline fractions)	~ 80
	Aliphatic sulfur-containing compounds of CH_3-S- and CH_2-S-types	~ 10
	Saturated heterocycles	~ 3
	Aromatic compounds	~ 4
	Acid compounds (aliphatic carboxylic acids)	~ 3
Distilled organic phase from acid tar at the temperature of 170 ºC (without deacidification and centrifugation)	Aliphatic hydrocarbons	~ 60
	Aliphatic S-organic compounds	~ 30
	Saturated heterocycles	~ 4
	Aromatic compounds	~ 6
Distilled organic phase obtained at the temperature of 150 ºC from deacidified tar (without centrifugation) with adding of 50 mL of distilled H_2O	Aliphatic hydrocarbons with a predominance of long-chained hydrocarbons	~ 90
	Aliphatic S-organic compounds	~ 8
	Aromatic compounds	~ 2

Thus, in distillation experiments (distillation of previously deacidified and centrifuged tar, acid tar without deacidification and centrifugation and previously deacidified tar without centrifugation) aliphatic hydrocarbons were the main component of volatile fractions (~ 80, ~ 60 and ~ 90 %, respectively) and aliphatic S-organic compounds were also present (~ 10, ~ 30 and ~ 8 %).

Conclusions

Acid tars are hazardous, non-utilizable solid wastes with resinous and viscous characteristics and varying flowability. This type of waste is produced in the processing of coal, petroleum, and petrochemicals (oil re-refining, benzene refining, and petroleum fractions refining).

Catalytic cracking and distillation were effective utilization methods for acid tar due to the significant amounts of volatile fractions obtained from the tar. $AlCl_3$ (anhydrous) was used as a catalyst during the cracking of petroleum residues to obtain volatile gasoline fractions due to its catalytic activity in many organic reactions. The catalyst ratios (0.15 g/g of tar or 0.1 g/g of tar) had a very significant influence on the amount of volatile fractions and boiling temperature in the acid tar cracking process. According to the findings of ^{1}H NMR research, the main components of volatile fractions in the case of catalytic cracking were alkanes $CH_3-(CH_2)_n-CH_3$. The compositions of these fractions were similar to the compositions of gasoline and diesel fuel.

A series of distillation experiments (distillation of previously deacidified and centrifuged tar, acid tar without deacidification and centrifugation and previously deacidified tar without centrifugation) gave different results for each type of material. The first sample of the distilled organic phase contained 80 % aliphatic (saturated) hydrocarbons (gasoline fractions), 10 % aliphatic sulfur-containing compounds of the CH_3-S and CH_2-S types, 3 % saturated heterocycles, 4 % aromatic compounds, and 3 % acid compounds (aliphatic carboxylic acids). The distilled organic phase of the second sample contained aliphatic hydrocarbons (60 %), aliphatic S-organic compounds (30 %), saturated heterocycles (4 %), and aromatic compounds (6 %). And the third sample contained aliphatic hydrocarbons with a predominance of long-chained hydrocarbons (~ 90 %), aliphatic S-organic compounds (~ 8 %) and aromatic compounds (~ 2 %).

Thus, both for catalytic cracking and for tar distillation aliphatic hydrocarbons were the main component of volatile fractions. According to ^{1}H NMR spectra of distilled organic phases, deacidification of tar increased the yield of aliphatic hydrocarbons during tar distillation and decreased production of S-organic compounds due to its reactions with calcium carbonate. It is very relevant in the context of fuel production.

References

1. Leonard S. A., Stegemann J. A., Roy A. Characterization of acid tars. *Journal of Hazardous Materials*. 2010. **175**(1-3). 382-392.
2. Knapcová I., Samešová D. Problems of waste acid tars (Goudrons). *Acta Facultatis Ecologiae*. 2017. **36**(1). 29-37. [in Slovakian]
3. Danha C., Chihobo C. H., Musademba D., Simbi D. J., Kuipa P. K., Jonathan E. Characterization and utilization of acid tar waste from crude benzol processing for environmental sustainability. *IOSR Journal of Environmental Science, Toxicology and Food Technology*. 2014. **8**(1). 16-21.
4. Frolov A. F., Titova T. S., Karpova I. V., Denisova T. L. About the composition of acid tars in the sulfuric acid treatment of petroleum oils. *Chemistry and technology of fuels and oils*. 1985. **6**. 37-38.
5. Khromyak U. Tarnavsky A. The impact of the Zbyranka LUE on the environment and the basic principles of creation of a new landfill. *Scientific Bulletin of UNFU*. 2016. 227-232. [in Ukrainian]
6. Zhebryakov E. V., Zorin A. D., Zanozina V. F., Gushchina, E. A. Identification of Water-Soluble Sulfonic Acids Isolated from Acid Tars by Gas Chromatography-Mass Spectrometry. *Journal of Analytical Chemistry*. 2020. **75**(1). 90-94.
7. Popovych V., Malovanyy M., Prydatko O., Popovych N., Petlovanyi M., Korol K., Lyn A., Bosak P., Korolova O. Technogenic impact of acid tar storage ponds on the environment: a case study from Lviv, Ukraine. *Ecologia Balkanica*. 2021. **13**(1). 35-44.
8. Jelinek R., Kordik J., Slaninka I., Mikusova J. Monitoring the impact of the acid tars lagoons arising from the former petrochemical industry in the Central Slovakia. *SGEM International Multidisciplinary Scientific GeoConference EXPO Proceedings*. 2019. **19**(5.2). 547-556.
9. Popovych V., Stepova K., Prydatko O. Environmental hazard of Novoyavorivsk municipal landfill. *MATEC Web of Conferences*. 2018. 247. 00025.
10. Ivashina V. V. Budyonny O. P. Modern methods of oil refining waste disposal - acid tars and oil sludges. *Modern technologies in industrial production: materials of the scientific and technical conference of teachers, staff, graduate students and students of the Faculty of Technical Systems and Energy Efficient Technologies (Sumy)*. 2011. **3**. 51-52.
11. Ollerová H., Samešová D. Revitalization of gudrons lanill with the emphasis on the choice of plant species. *Studia Oecologica. Zvolen: Technická Univerzita vo Zvolene*. 2017. 75.
12. Zorin A. D., Karataev E. N., Zanozina V. F., Knyazev A. V., Zhebryakov E. V. Thin-film cracking of acid tars. *Petroleum Chemistry*. 2012. **52**(4). 245-252.
13. Leonard S. A., Stegemann, J. A. Stabilization/solidification of acid tars. *Journal of Environmental Science and Health. Part A*. 2010. 45(8). 978-991.
14. Nikitchenko Yu. S. Obtaining surfactants on the basis of secondary raw materials for waste processing. *Eastern European Journal of Advanced Technology*. 2014. **4** (10). 26-30.

Каталітична переробка кислих гудронів

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Кислі гудрони – це відходи переробки вугілля, нафти та нафтохімічних продуктів. До складу кислих гудронів входять смолисті речовини, різноманітні органічні речовини та продукти полімеризації ненасичених вуглеводнів, а присутність вільної сульфатної кислоти у кислих гудронах часто досягає 70 % за масою. Майже всі домішки сполук металів, які містяться у нафті, концентруються у гудронах, а вміст ванадію і нікелю може досягати відповідно 0,046 і 0,014 %. Багато країн зберігають кислі гудрони під відкритим небом у відпрацьованих кар'єрах, ставках-сховищах або поблизу сміттєзвалищ. Це створює ризики або навіть потенційну загрозу для населення та оточуючого середовища внаслідок забруднення ґрунту, води та повітря. Таким чином, утилізація кислих гудронів є дуже важливим екологічним і промисловим завданням. У цій статті досліджено каталітичний крекінг та дистиляцію як методи утилізації кислого гудрону. Безводний $AlCl_3$ було використано у якості каталізатору крекінгу гудронів з метою одержання летких бензинових фракцій. $AlCl_3$ було обрано завдяки його каталітичній активності у багатьох органічних реакціях. Співвідношення маси каталізатору до маси гудрону (0,15 г/г гудрону або 0,1 г/г гудрону) мало дуже значний вплив на кількість летких фракцій і температуру кипіння суміші в процесі крекінгу. За результатами ЯМР встановлено, що у випадку каталітичного крекінгу основними компонентами летких фракцій були алкани $CH_3-(CH_2)_n-CH_3$. Склад цих фракцій схожий на склади бензину та дизельного палива. Серія дослідів по розгонці (попередньо розкисленого та відцентрифугованого гудрону, не розкисленого та не від центрифугованого кислого гудрону та попередньо розкисленого, але не від центрифугованого гудрону) дала різні результати для кожного типу матеріалу. Аліфатичні вуглеводні були основним компонентом летких фракцій (~ 80, ~ 60 і ~ 90 % відповідно), а вміст аліфатичних S-органічних сполук також був доволі високим (~ 10, ~ 30 та ~ 8 %). Таким чином, як для каталітичного крекінгу, так і для розгонки гудрону аліфатичні вуглеводні були основним компонентом летких фракцій. Розкислення гудрону підвищувало вихід аліфатичних вуглеводнів при розгонці та зменшувало утворення S-органічних сполук за рахунок їх реакцій з кальцієм карбонатом. Це робить метод доволі перспективним в контексті виробництва палива.

Ключові слова: кислий гудрон, каталітичний крекінг, нафтопереробка, паливо, утилізація