DEPHENOLIZATION OF COAL TAR HEAVY FRACTIONS: A REAGENT - FREE METHOD FOR PHENOL RECOVERY

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ABSTRACT

The classical dephenolization process of the heavy fraction of coal tar involves alkaline washing to produce sodium phenolate, followed by carbon dioxide decomposition to yield crude phenols and a soda solution. The soda solution is causticized with lime, generating lime sludge contaminated with phenols - a significant environmental concern. This study explores phenol extraction technologies leveraging phenolic acidity and molecular polarity to address these limitations. A novel method for dephenolizing coal tar heavy fractions without alkali was developed, yielding wash oil suitable for capturing benzene hydrocarbons with a phenol content of 0.7 - 1.0 %. This process eliminates aqueous phenolate generation, producing a hydrocarbon residue with a composition resembling the phenol fraction, achieving a reagent-free, waste-free methodology. The proposed method employs sodium phenolate solutions with optimized sodium hydroxide concentrations to ensure minimal phenol content in oil and control impurities in the phenolate solution, maintaining non-phenolic impurities at 15 - 20 %. This reduces neutral component loss and contamination, achieved by neutralizing phenols with a 27 % NaOH solution. Additionally, methyl tert - butyl ether (MTBE) was validated as a suitable organic solvent for phenol extraction from aqueous solutions. This integrated approach simplifies the technological process while aligning the composition of neutral oil with the phenolic fraction obtained during coal tar fractionation, presenting a sustainable solution for phenol recovery and wash oil purification. <u>Keywords</u>: coal tar wash oil, phenolic extraction, methyl tert - butyl ether, technological scheme.

INTRODUCTION

Phenol plays a critical role in modern chemical technology due to its versatile applications, particularly in the production of resins, plastics, pharmaceuticals, and agrochemicals. It serves as a key ingredient in manufacturing Bakelite and formaldehyde resins. Phenol derivatives are crucial in the synthesis of drugs, including antiseptics and anesthetics. Furthermore, phenol is a precursor to produce herbicides, insecticides, fungicides, caprolactam (used to produce nylon), as well as an intermediate in the production of detergents and dyes [1 - 3].

Phenol was traditionally obtained from dehydrated coal tar [4]. However, modern industrial production has shifted to synthetic methods, with the cumene process being the predominant route. Alternative methods include the toluene oxidation process and phenol synthesis via benzene hydroxylation. These approaches are continually refined to improve environmental sustainability and efficiency [5]. Nevertheless, they rely heavily on petrochemical feedstocks. Current research focuses on developing greener methods, such as utilizing biomass - derived feedstocks [6].

The use of phenol derived from coal tar is becoming

less relevant in modern technology due to environmental concerns and the decreasing availability of coal. Nevertheless, research aimed at improving phenol extraction processes from coal tar and its fractions remains ongoing [7]. For the Ukrainian economy, which lacks domestic petroleum resources but possesses a centralized enterprise for coal tar oil processing, the production of phenolic products is economically viable. These products can also serve niche markets requiring specialized coal tar chemicals [8].

The heavy fraction, a product of coal tar rectification boiling at 230 - 300°C, is referred to as "wash oil" after phenol extraction. This wash oil is primarily used to absorb benzene hydrocarbons from coke oven gas [9]. The phenol content in the heavy fraction varies widely, depending on the degree of pyrolysis of volatile coking products, ranging from 0.7 - 1.0% to 5.5 - 6.7%. In the initial resin, phenol content typically ranges from 1.2 - 1.4% [10]. Beyond the necessity of dephenolizing the heavy fraction to meet regulatory requirements for phenol content, the extracted phenols are estimated to cost approximately three times the price of the coal tar itself [11].

The dephenolization of the heavy fraction is performed using a classical method: washing with alkali to produce a sodium phenolate solution, followed by decomposition with carbon dioxide to yield crude phenols and a soda solution. The soda solution is then causticized to regenerate alkali solution and produce lime sludge. Carbon dioxide and lime required for causticization are generated in a lime kiln using imported limestone. A significant disadvantage of this method is the need to manage lime sludge contaminated with phenols. Stricter environmental regulations have led to the closure of several such phenol production facilities in China [12].

The discontinuation of alkaline extraction for phenols has spurred the development of alternative separation methods for purifying these compounds (Table 1).

This has led to the exploration of alternative extraction methods that leverage phenol's polarity rather than its acidic properties, as evidenced by its affinity for various solvents. In general, solvents capable of forming strong hydrogen bonds are effective for extracting phenols from oil. However, the regeneration of such solvents by distillation is challenging due to the Table 1. Substances for extraction of phenolic compounds from coal tar and its fractions.

Separation agent	Source
Tetraethylammonium amino acid ionic liquids, CO2	12
Imidazolium-based dicationic ionic liquids	13 - 14
1 - propyl - 3 - methylimidazolium chloride	15
amide compounds	16 - 17
Alcohol solution or aqueous alkanolamine	18
Metal chloride, phosphoric acid salt, halogenic salt (complexation agent)	19
Glyceryl triacetate and/or sulfolane	20
Benzene, toluene, ethylbenzene, p - xylene	21
Various solvents: hexane, ethers, ketones, esters, phosphates, phthalates	22
Dimethyl sulfoxide, mixed solvent of dimethyl sulfone and sulfolane	23
Methanol and/or ethanol aqueous solution	24
Propylamine formate, propylamine acetate	25
Ethylenediamine, acetic acid, acetamide, formamide, dimethylformamide	26

strength of the complexes formed. Additionally, when selecting an extractant for dephenolization processes, its selectivity toward phenol must be carefully considered.

Alkaline washing of wash oil enables the extraction of phenols with varying acidity in the presence of excess alkali. Fig. 1 illustrates the distribution of phenolic homologues in the wash oil, categorized by their content and dissociation constants.

As indicated by the data, most phenols in the heavy fraction exhibit dissociation constants within the range of pK 10.0 - 10.5. In contrast, higher phenols, with lower pK values of 9.3 - 9.4, are more readily extracted into the aqueous alkaline layer. These phenols are more acidic, converting to phenolate ions more rapidly, although their total content in the heavy fraction is relatively low.

This analysis highlights two potential approaches for phenol extraction based on their acidic properties and molecular polarity. The first approach appears more selective, though it necessitates the development of a regeneration method that avoids by - product waste generation. The second approach requires improved selectivity for phenol extraction, as one- and two - ring aromatic hydrocarbons in the heavy fraction can form



Fig. 1. Distribution of phenolic homologues of heavy fraction of coal tar according to their concentration and dissociation constants (data are summarised from the [27, 28]).

 π - π interactions with phenolic compounds [29].

The hydroxyl groups in phenols readily form hydrogen bonds with polar solvents, enhancing the solvation of phenolic compounds and facilitating their extraction from complex mixtures, such as coal tar oils.

A prominent method for phenol extraction, combining alkaline washing with phenol separation from aqueous media, is the Lurgi Phenoraffin process. In this approach, an aqueous sodium phenolate solution acts as a selective extractant for phenols from various fractions, while diisopropyl ether is used to extract phenols from phenol - saturated solutions [30]. A similar method is described in patent, where a saturated phenolate solution serves as a polar extractant in the first stage, followed by the introduction of toluene as a non - polar extractant in the second stage [31]. The polar extractant selectively removes phenols, while the non-polar extractant separates neutral oils. Toluene is regenerated via distillation to recover neutral oils, and diisopropyl ether is employed to extract free phenols from the phenolate solution, regenerating it for reuse in subsequent extractions.

This multi-stage process addresses the challenges

posed by neutral and basic impurities that arise during phenol extraction with sodium phenolates. However, there is a clear need to enhance this process by improving the extractant's selectivity for acidic phenolic compounds and increasing its extraction capacity.

Despite significant research into phenol extraction from coal tar oils, many studies have been limited to model mixtures, which simplify the complexities of real multi - component systems. Furthermore, there is scant information on the simultaneous extraction of phenols and neutral oils using alkaline sodium phenolate solutions, highlighting an area for further investigation.

Identifying key indicators for phenol extraction technology from wash oil is crucial, particularly under the conditions of enterprises that centralize the processing of coal tar fractions. This requires consideration of existing advancements in individual stages of the process, utilizing both alkaline and organic extractants.

The objective of this study was to develop a phenol extraction technology for wash oil that leverages the benefits of both alkaline and polar extractants. A critical aspect of this development is minimizing the co - extraction of neutral oils, which necessitates an in - depth investigation into the composition of these oils and the mechanisms underlying their extraction.

EXPERIMENTAL

The heavy coal tar oil used in this study was obtained from the Ukrainian enterprise PJSC "Zaporizhkoks" and was produced using a single - column tar distillation unit. Solutions of caustic soda and sulfuric acid were purchased from "Novochem" (Ukraine), while methyl tert - butyl ether (MTBE) was purchased from Metalab (Ukraine). The key characteristics of the oil are summarized in Table 2.

Mass concentrations of coal tar heavy oil components were determined using the chromatographic method on a "Crystal 2000 M" chromatograph equipped with the "Chromatec Analytic" software. The analysis involved direct chromatography of the sample, followed by chromatogram processing and calculation of the mass fractions of hydrocarbons relative to the mass of the "internal standard" (tetradecane) added to the wash solution. For higher boiling oil components, the mass fraction was calculated relative to the "internal standard," acetophenone. The method allows the determination of wash oil components (mass fraction, wt. %) with a relative total measurement error of $\pm \delta$, not exceeding 25 % at a confidence level of P = 0.95 across the entire measurement range.

Other quality indicators of the oils were determined in accordance with the normative document [32]. Phenol content in the oils and sodium phenolate solutions was measured according to TU U 20.1-00190443-117:2017 Coal Oil Absorbent and ASTM UOP 262-99 Phenols and Thiophenols in Petroleum Products by Spectrophotometry.

Sodium phenolates were obtained from the heavy fraction of coal tar through the following procedure. The heavy fraction was dephenolized using a 15 % NaOH solution, stirred for 1 h in a water bath at 50 - 60°C. The aqueous phase (sodium phenolate solution) was carefully separated from the organic phase using a separating funnel. The aqueous solution was then filtered to obtain a clear sodium phenolate solution.

To recover the organic layer, a 20 % sulfuric acid solution was gradually added to the sodium phenolate solution under constant stirring. The amount of acid Table 2. Main quality parameters of coal tar heavy oil.

Value
1049
0.3
5
15.3
1.95
240
22
72
89
92
95
15.1
8.5
17.4
17.1
8.0
7.0
0.87

added did not exceed the stoichiometric ratio required for the decomposition of phenolates, with pH measurements used to monitor and control the process. The crude phenols (top layer) were separated from the resulting sodium sulfate solution.

The neutral components were extracted with toluene, and their composition was analysed using a chromatographic method.

RESULTS AND DISCUSSION

The results of phenol extraction from heavy oil using a sodium phenolate solution prepared from alkali solutions of varying concentrations are presented in Table 3. The results of chromatographic determination of the composition of non-phenolic aromatic hydrocarbons, which are extracted with alkaline phenolate solution are presented in Table 4.

Table 3 demonstrates that the degree of phenol extraction from heavy oil using a sodium phenolate solution depends on the concentration of the alkali solution. This solution was prepared by neutralizing

Parameters	Experiment 1	Experiment 2	Experiment 3	
sodium phenolate prepared from a 20 % NaOH solution				
Phenol content in dephenolised oil, %	1.39	1.43	1.40	
Average degree of phenols extraction, %	27.9			
Content of neutral oils in sodium phenolate solution, %	15.6	16.1	16.2	
Average value, %	16.0			
sodium phenolate prepared from a 27 % NaOH solution				
Phenol content in dephenolised oil, %	0.97	0.98	0.95	
Average degree of phenols extraction, %		50.4	-	
Content of neutral oils in sodium phenolate solution, %	23.3	23.9	22.8	
Average value, % 23.3				
sodium phenolate prepared from a 35 % NaOH solution				
Phenol content in dephenolised oil, %	0.66	0.62	0.69	
Average degree of phenols extraction, %		66.3	-	
Content of neutral oils in sodium phenolate solution, %	33.4	32.3	33.1	
Average value, %		32.9		

Table 4. Composition of neutral components of heavy coal oil extracted from sodium phenolates.

Component	Content,
	wt. %
Benzene, toluene, xylene	0.19
Indene	0.88
Naphthalene	0.65
Thionaphthene	0.005
β - methylnaphthalene	6.89
α - methylnaphthalene	2.52
Diphenyl	0.22
Acenaphthene	0.22
Acenaphthylene	0.012
Dibenzofuran	0.19
Fluorene + indole	0.25
Phenanthrene + anthracene	0.011
Total identified:	12.04

caustic soda with phenols. Phenol extraction by sodium phenolate solution beyond the stoichiometric reaction of phenol with NaOH occurs due to the formation of hydrogen bonds:



However, a significant drawback of phenolate purification of coal oil is the concurrent extraction of neutral oils and pyridine bases into the phenolate solution.

As shown by the experimental results (Table 3), the content of neutral oils in the phenolate phase increases with higher alkali concentrations due to conjugate dissolution. For instance, phenol interacts with naphthalene, forming a molecular complex, naphthalene - phenol, through the interaction between the hydroxyl group's proton in phenol and the π - electrons of naphthalene [33]. This reaction can be conventionally represented as:



Similarly, the interaction of sodium ions (Na^+) in sodium phenolates with neutral oil molecules replaces the interaction of the hydroxyl group proton (H^+) in phenols. Additionally, phenol forms complexes with pyridine, with a binding energy of 6.8 kcal mol⁻¹ [34, 35].

The goal of selecting the appropriate concentration of the phenolate solution is to ensure that the phenol content in the wash oil remains below 0.7 - 1.0 % and that the content of non-phenolic impurities in the phenolates does not exceed 15 - 20 %. This minimizes the loss of neutral components and prevents contamination of the phenolate solution. These conditions are achieved with sodium phenolates prepared by neutralizing alkali with a 27 % NaOH solution.

The ability of individual oil components to be extracted by sodium phenolates is analysed in Table 5.

The non - polar neutral components of heavy oil are effectively dissolved in non - polar solvents. In contrast, sodium phenolate, being a more polar substance, preferentially dissolves polar compounds such as phenols. Naphthalene (D = 0) and its methyl derivatives (α - MNF, D = 0.37 and β - MNF, D = 0.44) are less polar than phenol, but they are extractable due to dipole - induced dipole interactions.

Non - polar components such as naphthalene and biphenyl show low transfer coefficients, indicating weak interactions with sodium phenolate.

Highly polar components such as indole show moderate extraction efficiency due to strong interactions with sodium phenolate solution, moreover fluorene, indole, phenanthrene and anthracene are larger polycyclic aromatic hydrocarbons and should be less soluble in polar media due to their size. It should be noted that treating heavy oil with sodium phenolates results in a certain reduction in the content of valuable naphthalene homologues in the oil. Therefore, limiting the concentration of sodium phenolates is essential to minimize the excessive extraction of neutral components from the oil. Saturating the circulating sodium phenolate stream with neutral oils and selectively extracting phenols from the phenolate solution using an organic solvent also helps to prevent the intensive removal of neutral oils from the treated heavy fraction.

As shown in Table 1, the extraction of phenols from aqueous solutions is best achieved using light volatile solvents that can be removed with minimal energy consumption. These solvents include butyl acetate, 'Phenosolvan' (a mixture of butyl acetate and ethers), diisopropyl ether (DIPE), and methyl isobutyl ketone. However, their high cost has driven the development of blends based on light petroleum products. In recent years, reports have emerged on the use of MTBE (methyl tert-butyl ether) for this purpose [36]. Based on a review of studies on phenol extraction from aqueous solutions, we identified the requirements for organic solvents and evaluated the compliance of MTBE properties with these requirements (Table 6) [37].

The results of phenol extraction from a sodium phenolate solution using methyl tert - butyl ether (MTBE) demonstrated that, at an aqueous sodium phenolate solution/MTBE ratio of 1:1, the extraction efficiency of free phenols reached 99 %. Additionally,

Table 5. Component comparison for extraction efficiency by sodium phenolate.

Component:	MW	Dipole moment, D	Oil, wt. %	Phenolate, wt. %	Oil - to - extract transfer coefficient
Indene	116	0.67	1.67	0.88	0.53
Naphthalene	128	0	15.3	0.65	0.04
Thionaphthene	134	0.63	0.94	0.005	0.01
β - methylnaphthalene	142	0.44	15.1	6.89	0.46
α - methylnaphthalene	142	0.37	8.5	2.52	0.30
Diphenyl	154	0	17.4	0.22	0.01
Acenaphthene	154	0.9	17.1	0.22	0.01
Dibenzofuran	168	0.88	8.0	0.19	0.02
Indole	117	2.05	1.2	0.11	0.09
Fluorene	166	0.28	5.8	0.14	0.02
Phenanthrene	178	0.12	0.68	0.010	0.015
Anthracene	178	0	0.19	0.001	0.005

phase separation occurred immediately without the formation of emulsions.

Based on the conducted research, a technological scheme for extracting phenols from rich coal tar oil using a sodium phenolate solution was developed (Fig. 2).

The key parameters for processing 2 tonnes per hour of the heavy fraction are presented in Table 7.

In this technological scheme, the third extraction stage and the corresponding solvent regeneration stage, where neutral oils are removed, are excluded. While this simplification significantly streamlines the process, it increases the content of neutral oils in the crude phenols obtained. However, the phenol content in the phenol fraction derived from coal tar fractionation remains approximately similar. Consequently, the bottom residue from column K - 1 can be redirected to the phenol fraction. In centralized phenol processing, where most phenol - containing raw materials originate from phenol fractions, neutral oils in crude phenols are typically removed via steam stripping.

Table 6. Comparison of MTBE properties with requirements for solvents used in phenol extraction from aqueous solutions.

Parameter	Required values	Values for MTBE	
Solvent along	Alcohols, esters, chlorine and	Ethor	
Solvent class	nitrogen derivatives	Ether	
Dielectric constant	At least 2.4	2.6	
Surface tension, dyne/cm	Less than 34	18.3 (32°C)	
Calculated solubility parameter	Not less than 7.4	7.4	
Density difference between solvent	Not loss than 150	> 500	
and aqueous solution. kg m ⁻³	not less than 150	> 300	
Solubility in water	None	Low	



Fig. 2. Technological scheme of phenols extraction with sodium phenolate solution: E-1 - extractor 1; E-2 - extractor 2; K-1 - column of solvent distillation from MTBE; T-1 - condenser; P-1 - reflux tank, K-2 - column of solvent distillation from phenolate solution; T-2 - condenser, C-1 - separator, E-1 - tank with solvent; T-3 - heater of phenolate solution; T-4 - cooler of phenolate solution. Flows: 1 - phenolate solution for extraction, 2 - saturated phenolate solution; 3 - solvent for phenols extraction from phenolate solution; 4 - solvent saturated with phenols.

Table 7. Key parameters of the phenol extraction process from heavy coal tar oil using a sodium phenolate solution, followed by re - extraction with MTBE.

Parameters	Value
Productivity of the E-1 extractor for heavy oil, t h ⁻¹	2.0
Ratio 'oil : sodium phenolate solution' in extractor E - 1	1:3
Alkali concentration for preparation of phenolate solution, %	27
Extraction temperature, °C	40
Amount of extracted phenols from oil, %	1,0
Estimated composition of phenols: cresols/xylenols	1/5
MTBE extraction capacity of extractor E - 2, t h ⁻¹	9,0
Extraction efficiency of cresols and xylenols, %	99
Number of theoretical stages of E - 2 extractor	2
Extraction efficiency of neutral oils from sodium phenolate solution, %	98
Heating temperature of flow 4 upstream of column K - 1, °C	70
Reflux number of column K - 1	1
Number of theoretical stages K - 1	4
Vapour cooling temperature after condenser X-1,	30
Vapour flow rate to the bottom preheater of column K - 1, MJ h ⁻¹	3900
Temperature of column top/bottom K - 1	59/226
Composition of column K - 1 bottom residue: phenols/neutral oils	21.2/78.8
Temperature of solution upstream of column K - 2, °C	70
Temperature of the top of column K - 2, °C	88-89
Temperature at the bottom of column K - 2, °C	98-99
Flow rate of direct steam for stripping (0.6 MPa, 200°C), t h ⁻¹	0.4
Number of theoretical stages of column K - 2	4

This approach is particularly advantageous for coke - chemical plants that produce wash oil from heavy fractions through conventional alkaline washing. The process generates an aqueous solution of sodium phenolates as a by - product, which has limited commercial value. The proposed method eliminates the need for alkali procurement, ensures that the washed heavy oil meets Ukraine's regulatory standards for phenol content (0.7 - 1.0 %), and avoids the generation of additional hard - to - sell by - products.

Future research could focus on optimizing the operation of column K - 1, including the potential for side withdrawal of fractions to produce high - quality crude phenols by removing light oil components. Additionally, the application of various MTBE additives could be explored to enhance the selectivity and efficiency of phenol recovery.

CONCLUSIONS

A method for the dephenolization of the heavy fraction of coal tar without the use of alkali has been developed to produce a wash oil suitable for capturing benzene hydrocarbons with a standard phenol content (0.7 - 1.0%). Instead of generating an aqueous phenolate solution, which has limited applicability, the process yields a hydrocarbon residue with a composition similar to that of the phenol fraction. This makes the proposed method effectively reagent - free and waste - free.

The extraction of phenols from oil using an aqueous solution of sodium phenolates, with an excess of stoichiometric sodium hydroxide, requires optimizing the solution concentration. This optimization ensures that the phenol content in the oil remains below 0.7 - 1.0 %, while limiting non - phenolic impurities in the phenolate solution to 15 - 20 %. Such control minimizes the loss of neutral components and prevents contamination of the phenolate solution. These conditions are achieved by neutralizing phenols with a 27 % NaOH solution.

Experimental studies have shown that non - polar, neutral heavy oil components, such as naphthalene and biphenyl, exhibit low oil - to - solution transfer coefficients, indicating weak interactions with sodium phenolate. In contrast, highly polar components, such as indole, demonstrate moderate extraction efficiency due to their stronger interactions with the phenolate solution. Larger polycyclic aromatic hydrocarbons, such as fluorene, indole, phenanthrene, and anthracene, are less soluble in polar media, primarily due to their molecular size.

While excluding the extraction stage for neutral components simplifies the technological process, it increases the content of neutral oil in raw phenols. However, the composition of these neutral components closely aligns with the phenolic fraction obtained during coal tar fractionation.

Additionally, an analysis of MTBE properties confirmed its suitability as an organic solvent for extracting phenols from aqueous solutions.

Authors' contributions: L. Bannikov: conceptualization; D. Miroshnichenko: writing; A. Bannikov: investigation, writing; O. Borisenko: review; V. Tertychnyi: data analysis.

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