Evaluation of the possibility of separating commercial phenol from the phenolic fraction of coal tar

Y.O. Schastnyy[1], *N.A.* Romanova[1], and *R.R.* Gizatullin[2]

[1]Department of ATPP, Department of Mineral Processing, Saint Petersburg Mining University, Saint Petersburg Russia
[2]Well Drilling Department, Department of Oil and Gas, Saint Petersburg Mining University, Saint Petersburg Russia

Abstract: This article is about the possibility of concentrating commercial coal phenol with a concentration of 99% by the weight method of rectification from the phenolic fraction of coal tar. The sufficiency of phenol is ensured by the kumol method, however, the consumption of phenol increases. Modeling of the vapor-liquid equilibrium of double and triple mixtures of components using the NRTL model showed the presence of the following positive homogeneous azeotropic mixtures: phenol-indane, phenol-indene. Modeling of the vapor-liquid equilibrium of double and triple mixtures of components using the NRTL model showed the presence of the following positive homogeneous azeotropic mixtures: phenol-indane, phenol-indene. The compositions and temperatures of these azeotropes are determined. The authors propose the isolation of phenol from the fraction and its purification from indane and indene by a clear rectification method. The technological scheme consisting of four devices is based on the analysis of the component composition of the initial mixture and the existing azeotropes. Modeling of the technological scheme showed that this scheme provides the release of phenol by 99% of the mass, which meets the requirements for coal phenol. After optimizing the technological parameters of the distillation columns, the estimated extraction costs will amount to 5.64 Gcal per ton of commercial phenol.

1 Introduction

Coal tar is a by-product of metallurgical coke or oil coke production. There are many works devoted to an increased yield and improved quality of needle coke [1-5]. Coal tar has a complex composition with a high level of valuable aromatic compounds, like phenol, naphthalene, anthracene, etc. [6]. Due to its content, coal tar can be used as a rich sourcefortheextraction of its components [7]. During processing by theclassical method, coal tar is separated by rectification into several fractions, which are called by the prevailing target products: light, phenolic, naphthalene, absorption, and anthracene fractions. [8,9].

The most promising issue for research is the processing of phenolic and naphthalene fractions since phenol and naphthalene are valuable raw materials for chemical synthesis.

Phenol is widely used in the manufacture of dyes, plasticizers, polymer masses, as an agent in selective oil purification, etc. Generally, basic industrial needs in phenol are satisfied by the cumene process, which converts isopropylbenzene to synthesize phenol and acetone [10]. Russia has several large petrochemical plants with phenol production facilities, located in cities such asUfa, Kazan, Samara [11,12].

However, the demand for phenol keeps growing, therefore, its separation from coal tar has practicalinterest.Although, it should be notedthat oil and coal phenols have different degrees of purity, both in terms of the content of the main component and the required profile of possible impurities.

Currently, the separation of coal tar is conducted by distillation into fractions, and the pure phenol is obtained by extraction or by chemical methods [13-18]. The same methods are used to isolate phenol from petroleum resins. Initially, coal resin (or petroleum resin) is distilled in a distillation column, then crude phenol is isolated from phenolic fraction, from which pure phenol is extracted at the next stage using selective solvents or chemical reagents, converting phenol into phenolates. The extraction method allows obtaining phenol of sufficient purity (according to GOST 11311-76 "CoalPhenol" in Russia). However, these methods are still multi-stage, expensive, and make it difficult (harder) to solve the environmental problems associated with the treatment of large amounts of wastewater. Several works are devoted to the problem of wastewater treatment from phenol [19]

Sometimes the crystallization method is used to increase the purity of commercial phenol.

In this article, the authors do not investigate the process of phenol separation from coal tar by extraction method, because this technology is well-studied and widely known. The authors suggest the separation of phenol from the fraction and its purification from indane and indene using a precision fractional distillation method. Distillation is currently used to separate the so-called crude phenol from coal tar, which is not sufficiently pure, and the subsequent additional purification is carried out by the above-mentioned extraction method.

The article suggests a phenol separation technology that meets GOST 11311-76 "Coal phenol" (government standard) with a basic substance content of at least 99% wt. This technology does not require the use of extraneous agents, except for the available water, and in terms of energy consumption, it is commensurate with the energy consumption in the separation of contaminated dirty crude phenol.

2 Main part

Extraction of phenol from coal tar may pose difficulties, mostly, since tar is a polyazeotropic mixture of aromatic and other compounds, including heterocyclic ones. Such azeotropic mixtures as phenol-indane and phenol-indene make the concentration of the target component more complicated and expensive. Table1 shows the composition of the initial phenolic fraction.The composition of coal tar given in the article is the result of averaging the compositions of various resins at the contracting enterprise. The name of the company is a trade secret and cannot be disclosed.

Table 1. Feed composition*.

Components	Boiling temperature, C°	Mass,%
P-xylene	138.4	0.155
M-xylene	139.1	0.155
1-methyl-3-ethylbenzene	161.3	5.660
Mesitylene	164.7	2.332

Pseudocumene	169.3		1.244
Hemimellitene		176.1	2.021
Indan		178.0	2.971
Phenol		181.0	33.670
Indene		182.8	15.845
Benzonitrile		188.0	6.284
O-cresol		191.0	3.961
Durol		196.9	0.606
P-cresol		201.9	7.922
M-cresol		202.0	14.854
Prehnitene		205.0	0.606
Xylenol		216.9	0.031
Naphthalene		217.0	1.571
Thionaphthene	219.9		0.078
Methylnaphthalene		244.7	0.031

* The average composition of the phenolic fraction of coal tar

Analysis of the composition showed that phenol forms binary and ternary azeotropeswithindane and indene, naphthalene, pseudocumene, hemimellitene, mesitylene, and other compounds.Table 2 presents binary azeotropesandTable 3 presents ternary azeotropes.

Table 2. Binaryazeotropes.

Components	Boilingtemperature, C°	
Phenol- mesitylene		163.62
Phenol- pseudocumene		167.22
O-cresol-pseudocumene	169.36	
Phenol-indane		171.29
Phenol-hemimellitene		171.43
O-cresol-hemimellitene	175.09	
Indane- o-cresol	175.47	
Phenol-indene		175.98
Indane- p-cresol	177.46	
Indane- m-cresol		177.50
Indene-o-cresol	181.20	
Indene-p-cresol	182.78	
Indene-m-cresol	182.78	
Benzonitrile-hemimellitene		191.78
O-cresol-benzonitrile		193.06
Naphthalene-p-cresol		200.91
Naphthalene-m-cresol		201.19
Naphthalene-xylenol		211.12

Table 3. Ternary azeotropes.

Components	Type of azeotrope	Boiling temperature, C°
Phenol-Indane-hemimellitene	Heterogeneous	171.27
Phenol-Benzonitrile-Mesitylene	Homogeneous	191.00
Benzonitrile-hemimellitene -o-cresol	Homogeneous	191.12

Benzonitrile-hemimellitene-p-cresol 91.58	Homogeneous
Benzonitrile-hemimellitene-m-cresol 91.59	Homogeneous

Separation of such mixtures by conventional distillation is a complicated task, which, as a rule, requires special methods with PSD-technologies, described in detail in the article*Energy optimization of multi-column rectification complexes*. [20] or special separating agents.The azeotropic distillation process is described in the book*Processes and devices of oil and gas processing and petrochemistry*[21]. For example, a suitable agent that satisfies this requirement is water. Water is known to form an azeotropic mixture with phenol;this fact is widely used in the separation of phenol from alpha-methylstyrene in the above-mentioned cumene method.

Calculations showed that azeotropic mixtures of phenol-indane and phenol-indene are most problematic in terms of separation. Their type, composition, and boiling points are given in the table below.

Table 4. Existing azeotropes.

Phenol-Indan			Phenol-Indene		
Type:homogeneous boiling temperature 171.29 C°	Positive with boiling		Type: homogeneous temperature 175.98 C°.	Positive with	
Component	Mole ratio	Mass ratio	Component	Mole	ratio
Phenol	0.4011	0.3478	Phenol	0.4944	
		0.4421 Mass ratio			
Indan	0.5989	0.6522	Indene	0.5056	
0.5579					

The listed azeotropic mixtures are insensitive to pressure changes;asshowninFigure 1 forthephenol-indane mixture. To break problematic azeotropes, it is proposed to use water as a separating agent. Water forms a positive homogeneous azeotrope with phenol and can be further separated from the target product by vacuum distillation.Figure2shows equilibrium curves for the phenol-water system at normal pressure and residual pressure 20 mmHg.
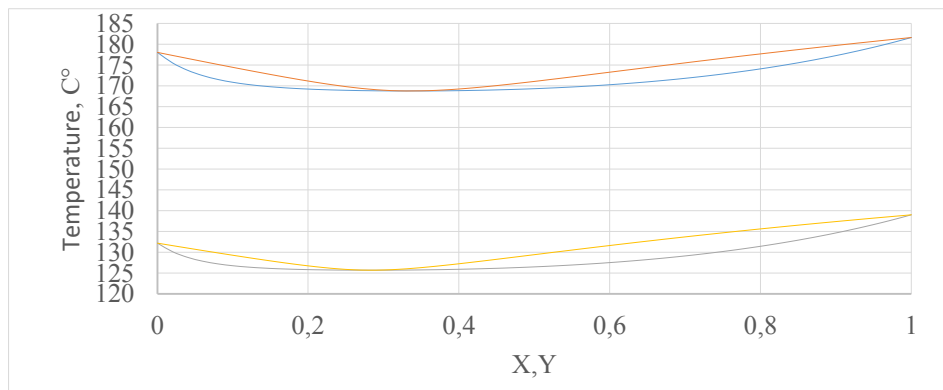

Fig. 1. The equilibrium curve in *T*-X Y coordinates for a pair of phenyl-indane at normal pressure and residual pressure in the apparatus of 200 mmHg.
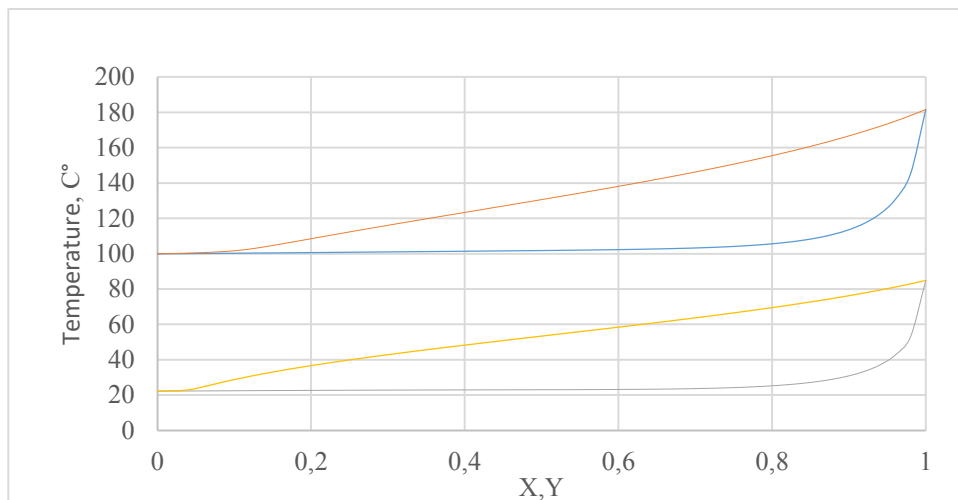
Fig. 2. The equilibrium curve in T-XY coordinates for the phenol-water pair at normal pressure and at residual pressure in the apparatus of 20 mmHg.

The separation scheme proposed herein consists of four successive distillation columns, (K-1…K-4), the first three operate under vacuum, and the fourth is under excess pressure.

The supply stream is fed to the K-1 column that separates light impurities with boiling points lower than the boiling point of azeotropic mixtures of phenol-indane and phenol-indene, such as p-xylene, m-xylene, 1-methyl-3-ethylbenzene. The bottoms product of the K-1 column together with water - 75% of the total mass to be separated -isfed to the K-2 column, which is designedto breakphenol-indane and phenol-indeneazeotropes. Indane and indene leave the K-2 column as a distillate, while the bottom product of the K-2 column - a new phenol-water azeotrope - is fed to the K-3 column. The latter operates at a residual pressure of 20 mm Hg and is designed to separate water. The K-4 column is used to separate commercial phenol from heavy impurities.
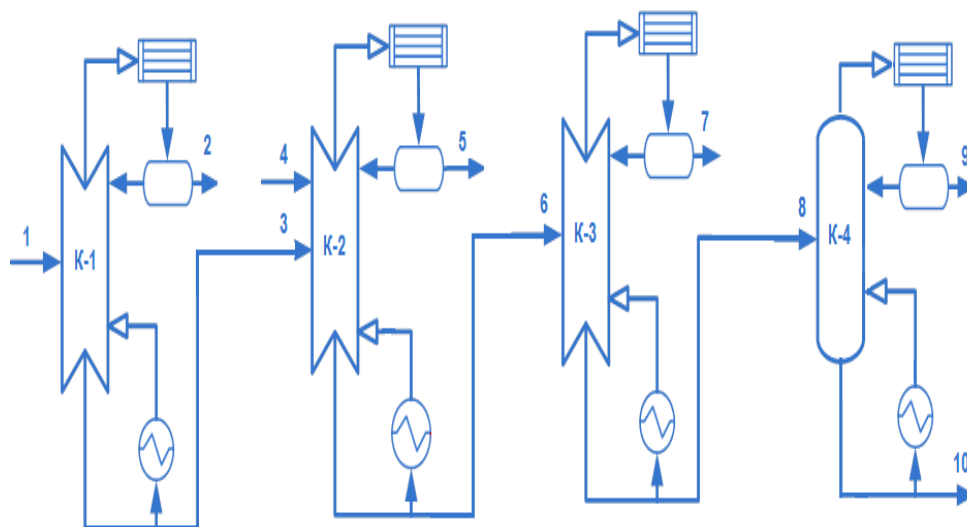

Fig. 3. Basic technological scheme of the process

The main flows of the scheme are explained below:

1. Raw supply
2. Light components
3. Fortified fraction
4. Water
5. Indane, indene
6. Phenol-water with a heavy residue
7. Water for regeneration
8. Phenol and heavy components
9. Phenol byGOST-11311-76
10. Heavy residue

To simulate the process, the authors used the ASPENHYSYS softwarewith the NRTL thermodynamic package; the missing binary coefficients were calculated by the UNIFAC method. The main technological parameters for operations of all column units are listed inTable 5.

Table 5. Technological parameters.

Column	К-1	К-2	К-3	К-4
NTR	20	15	20	40
Feedstage (topdown)	9	9	10	20
Pressure at the top. 2200 mmHg.	250	200	20	
Refluxratio	12	4	1	7
Sampling ratio 0.55	0.12	0.32	0.49	
Heatinput.Gcal/t* 1.04	0.39	2.25	1.96	

*Calculation per 1 ton of commercial phenol

The table shows that the energy costs in the proposed separation scheme will amount to 5.64 Gcal/t.

Thus, the following conclusions can be made:

•The result is that it is possible to separate the phenol from the resin by distillation at 99% by weight of the main substance without using extraction stages.

• Simulationof the vapor-liquid equilibrium of the initial mixture showed that there are homogeneous positive azeotropic mixtures of phenol-indane (at 760 mm Hg, the composition is equal to 0.3478 wt of phenol and 0.6522 wt of indane) and phenol-indene (at 760 mm Hg,thecomposition is equal to 0.4421 wt of phenol and 0.5579 wt of indene).

• The authorsproposeda principal schemeofdistillationof commercial coal phenol with a concentration of 99% wt. The separating agent to break azeotropic mixtures is water - 75% of the total coal tar to be separated.

• The scheme is optimized in terms of minimum energy costs, which amount to 5.64 Gcal/t of commercial phenol.

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