InfoMine
research group

Association of Independent Consultants and Experts in Mineral Resources,
Metallurgy and Chemical Industry

Naphthalene Market Research in the CIS

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ANNOTATION

The report is devoted to research of current standing of naphthalene in CIS and forecast of its development. The report is composed of 6 Chapters, contains 105 Pages, including 26 Figures, 47 Tables and 2 Appendices.

The first Chapter of the report presents data on methods of deriving naphthalene, and resources used in the sector of industry, and describe directions and volumes of supplies of the resources to naphthalene producers.

The second Chapter of the report is devoted to analysis of production of naphthalene for the period from 1999 to 2007 in CIS. The Chapter presents data on volumes of production, traces dynamics of production of the product by enterprises of Ukraine and Russia, and considers current standing of naphthalene producers in CIS. It presents data on available resources base, volumes of production, plans on development of the companies, as well as data on volumes and directions of supplies of the products for the latest years.

The third Chapter describes foreign trade operations in naphthalene in Russia and Ukraine with analysis of volumes and directions of the export-import supplies..

The fourth Chapter is devoted to analysis of dynamics of prices on naphthalene at domestic and export markets.

The fifth Chapter describes market of consumption of naphthalene в Russia and in Ukraine. We have analysed in detail pattern of consumption of the product, and its supply-demand balance. The Chapters offers review of the main fields of consumption of naphthalene.

The sixth Chapter of the report gives forecast of development of naphthalene market up to 2015.

The Appendices present addresses and contact information on the main company-producers and consumers of naphthalene in CIS.

This work is "desk" study, in the course of implementing of which we analysed many information sources, first of all, data of state bodies – Federal Service of State Statistics of Russia (FSSS), State Statistic Committee of Ukraine, Statistic Agencies of other CIS countries (data on production of the product), JSC "RZHD" (statistics of Russian domestic railage), Federal Customs Service of Russia and State Customs Committee of Ukraine (data on foreign trade operations). Besides, we used data of companies, own database of "InfoMine", materials of mass-media and internet.

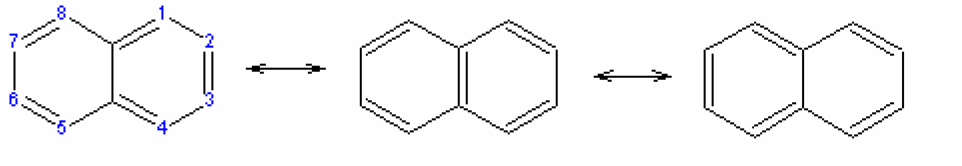
This all allowed the authors to draw actual picture of naphthalene market in the CIS and prospects of its development.

INTRODUCTION

Naphthalene (not to be confused with naphtha), also known as naphthalin, naphthaline, napthene, tar camphor, white tar, albocarbon, or antimite is a crystalline, aromatic, white, solid hydrocarbon (formila $C_{10}H_8$, molecular weight 128.2), best known as the traditional, primary ingredient of mothballs. It is volatile, forming a flammable vapor, and readily sublimes at room temperature, producing a characteristic odor that is detectable at concentrations as low as 0.08 ppm by mass.

A naphthalene molecule is composed of two fused benzene rings (in organic chemistry, rings are fused if they share two or more atoms.) Accordingly, naphthalene is classified as a benzenoid polycyclic aromatic hydrocarbon (PAH). There are two sets of equivalent hydrogens: the alpha positions are positions 1, 4, 5, and 8 on the drawing below, and the beta positions are positions 2, 3, 6, and 7.

Unlike highly-symmetrical aromatics, such as benzene, the carbon-carbon bonds in naphthalene are not of the same length. The bonds C1–C2, C3–C4, C5–C6 and C7–C8 are about 1.36 Å (136 pm) in length, whereas the other carbon-carbon bonds are about 1.42 Å (142 pm) long. This has been verified by x-ray diffraction, and is consistent with the valence bond model of bonding in naphthalene which involves three resonance structures (as shown below); while the bonds C1–C2, C3–C4, C5–C6 and C7–C8 are double in two of the three structures, the others are double in only one.



Like benzene, naphthalene can undergo electrophilic aromatic substitution. For many electrophilic aromatic substitution reactions, naphthalene is more reactive than benzene, reacting under milder conditions than benzene does. For example, whereas both benzene and naphthalene react with chlorine in the presence of a ferric chloride or aluminium chloride catalyst, naphthalene and chlorine can react to form 1-chloronaphthalene even without a catalyst. Similarly, while both benzene and naphthalene can be alkylated using Friedel-Crafts reactions, naphthalene can also be alkylated by reaction with alkenes or alcohols, with sulfuric or phosphoric acid as the catalyst.

Two isomers are possible for mono-substituted naphthalenes, corresponding to substitution at an alpha or beta position. Usually, electrophiles attack at the alpha position. The selectivity for alpha over beta substitution can be rationalized in terms of the resonance structures of the intermediate: for the alpha substitution intermediate, seven resonance structures can be drawn, of which four preserve an aromatic ring. For beta substitution, the intermediate has only six resonance structures, and only two of these are aromatic. Sulfonation, however, gives a mixture of the "alpha" product 1-naphthalenesulfonic acid and the "beta" product 2-

naphthalenesulfonic acid, with the ratio dependent on reaction conditions. The 1-isomer forms predominantly at 25OC, and the 2-isomer at 160OC.

Naphthalene can be hydrogenated under high pressure with metal catalysts to give 1,2,3,4-tetrahydronaphthalene or tetralin (C10H12). Further hydrogenation yields decahydronaphthalene or decalin (C10H18). Oxidation with chromate or permanganate, or catalytic oxidation with O2 and a vanadium catalyst, gives phthalic acid.

Most naphthalene is derived from coal tar. From the 1960s until the 1990s, significant amounts of naphthalene were also produced from heavy petroleum fractions during petroleum refining, but today petroleum-derived naphthalene represents only a minor component of naphthalene production.

Naphthalene is the most abundant single component of coal tar. While the composition of coal tar varies with the coal from which it is produced, typical coal tar is about 10% naphthalene by weight. In industrial practice, distillation of coal tar yields an oil containing about 50% naphthalene, along with a variety of other aromatic compounds. This oil, after being washed with aqueous sodium hydroxide to remove acidic components (chiefly various phenols), and with sulfuric acid to remove basic components, undergoes fractional distillation to isolate naphthalene. The crude naphthalene resulting from this process is about 95% naphthalene by weight, often referred to as 780°C (melting point). The chief impurities are the sulfur-containing aromatic compound benzothiophene (<2%), indane (0.2%), indene (<2%), and methylnaphthalene (<2%). Petroleum-derived naphthalene is usually purer than that derived from coal tar. Where required, crude naphthalene can be further purified by recrystallization from any of a variety of solvents, resulting in 99% naphthalene by weight, referred to as 800°C (melting point).

Naphthalene and its alkyl homologs are the major constituents of creosote.

Large volumes of naphthalene are used as a chemical intermediate to produce other chemicals. The single largest use of naphthalene is the industrial production of phthalic anhydride (although more phthalic anhydride is made from o-xylene than from naphthalene). Other naphthalene-derived chemicals include alkyl naphthalene sulfonate surfactants, and the insecticide 1-naphthyl-N-methylcarbamate (carbaryl). Naphthalenes substituted with combinations of strongly electron-donating functional groups, such as alcohols and amines, and strongly electron-withdrawing groups, especially sulfonic acids, are intermediates in the preparation of many synthetic dyes. The hydrogenated naphthalenes tetrahydronaphthalene (tetralin) and decahydronaphthalene (decalin) are used as low-volatility solvents.

Naphthalene sulfonic acids are used in the manufacture of naphthalene sulfonate polymer plasticizers which are used to produce concrete and plasterboard (wallboard or drywall). They are also used as dispersants in synthetic and natural rubbers, and as tanning agents in leather industries. Naphthalene sulfonate polymers are produced by reacting naphthalene with sulfuric acid and polymerizing this with formaldehyde, followed by neutralization with sodium hydroxide.

Naphthalene is also used in the synthesis of 2-naphthol, and miscellaneous chemicals and pharmaceuticals.

Naphthalene's most familiar use is as a household fumigant, such as in mothballs (although 1,4-dichlorobenzene (or p-dichlorobenzene) is now more widely used). In a sealed container containing naphthalene pellets, naphthalene vapors build up to levels toxic to both the adult and larval forms of many moths that attack textiles. Other fumigant uses of naphthalene include use in soil as a fumigant pesticide, in attic spaces to repel animals and insects, and in museum storage-drawers and cupboards to protect the contents from attack by insect pests.

It is used in pyrotechnic special effects such as the generation of black smoke and simulated explosions. It is also used to create artificial pores in the manufacture of high-porosity grinding wheels. In the past, naphthalene was administered orally to kill parasitic worms in livestock. Naphthalene vapour can also slow the onset of rust, such as the use of moth balls in a tool box.

Naphthalene is toxic. Exposure to large amounts of naphthalene may damage or destroy red blood cells. Humans, particularly children, have developed this condition, known as hemolytic anemia, after ingesting mothballs or deodorant blocks containing naphthalene. Symptoms include fatigue, lack of appetite, restlessness, and pale skin. Exposure to large amounts of naphthalene may cause nausea, vomiting, diarrhea, blood in the urine, and jaundice (yellow coloration of the skin).

Physical properties of naphthalene are as follows:

Colour: white or colorless.

State/Form: solid-crystals.

Description: Transparent prismatic plates also available as white scales, powder balls or cakes with a characteristic odour and aromatic taste. It volatilizes and sublimes at room temperature above the melting point with a characteristic moth ball or strong coal tar odour. Naphthalene absorbs ultraviolet rays.

Boiling point: 217.9°C.

Melting point: 80.2°C.

Flash point - open cup 79°C; closed cup 88°C.

Autoignition temp: 567°C.

Vapour pressure (at 25°C): 0.087 torr.

Solubility in water, alcohol and ether –

Solubility in water: 3mg/100mL at room temperature.

Solubility in methanol/ethanol: 7.7g/100 ml

Very soluble in ether.

CAS number: 91-20-3.

Other numbers. RCRA Waste Number: U165; UN1334 (DOT); UN2304 (DOT); NCI-C52904.

This compound in a petroleum ether solution will give off purple fluorescence under a mercury light.

I. Technology of naphthalene production and resources used

I.1. Obtaining naphthalene fraction when processing coal tar

In industry, naphthalene is mainly obtained from ***coal tar*** (containing 8-10% of naphthalene), as well as is derived from petroleum pyrolysis products. Petroleum-derived naphthalene is usually purer than that derived from coal tar.

Coal tar is a product of the destructive distillation of bituminous coal, when coal tar is mainly generated in the course of pyrogenetic decomposition of primary tar in coking process.

Coal tars are by-products of the carbonization of coal to produce metallurgical coke and/or natural gas. Annual global production of 400 mln t of coke is accompanied by obtaining around 16 mln t of coal tar. Notice that some coke shops (in USA, China) apply process, which doesn't provide further processing of coal tar, which is simply burnt in the process of coke production, From estimates, only around 50% of coal tar, produced in the world, are subjected to further processing to obtain additional commodity products.

Coal is converted to coke in large coke oven batteries. The coking process consists of heating crushed coal above 900ºC in the absence of air to drive off the volatile compounds; the resulting coke is a hard, but porous carbon material that is used for reducing the iron in the blast furnace. The modern by-product coke oven recovers volatile chemicals in the form of coke oven gas, tars, and oils.

Tar is released in the course of the whole coking process: initially, primary tar is released, containing mainly aliphatic compounds. With increasing temperature, formation of aromatic hydrocarbons begins. Further heating results in formation of polycyclic compounds. For instance, maximal generation of naphthalene and anthracene is reached at 1000ºC.

Coal tar is a product of thermal breakdown of primary tar. The bulk of primary products (90-95%) raises to near-roof space of oven, where it is mixed with released gases, heated and the first stage of decomposition proceeds, with the primary products conversion into high-temperature tar, benzene and other products.

Releasing of coal tar from coking gas proceeds by several stages: the first stage – when cooling the coking gas in gas collector by over-tar water from 750˚C to 80˚C, and the second – when cooling coking gas in primary gas coolers.

Coal tar is obtained in by-product recovery shops of by-product coke enterprises. The obtained tar is mixed and goes to further processing.

Composition, yield and properties of coal tar depend on composition of charge, design of ovens and coking conditions (first of all, on temperature of near-roof space of oven and period of aging volatile components in the oven).

Yield and quality of coal tar is governed by content of volatile components in charge (the higher the content the better grade of further pitch). In this connection, charge content of coals of grades G, GZhO, GZh («gas» coals) must be maximal to obtain high-quality coal tar, whereas from viewpoint of production of metallurgical coke, the former two grades of coal refer to low-coking and their suitability is limited. That is why maximizing quality pitch yield doesn't correspond sometimes to solving problem of obtaining grade metallurgical coke.

At by-product coke enterprises of CIS, yield of coal tar in per cents of metallurgical coke ranges 4.0-4.9%.

Coal tars are complex combinations of polycyclic aromatic hydrocarbons (PAHs), phenols, heterocyclic oxygen, sulfur, and nitrogen compounds. In chemical properties, all the components of coal tar are subdivided into 3 groups: neutral, acid and basic.

The neutral hydrocarbon compounds are mainly presented by naphthalene $C10H8$, anthracene $C14H10$, chrysene $C18H12$, accompanied by indole, carbazole, benzo-carbazole, styrene, indene, coumarin and their derivatives.

Sulfur-containing neutral compounds of coal tar are presented by thiophene $C4H4S$, thionaphthene $C8H6S$ (and their methylated derivatives), di-phenyl sulfide, an-benzo-thionaphthene and other. Most of the compounds occurs in washing (absorption), naphthalene and anthracene fractions. However, their separation in the course of fractionation (rectification) is not possible owing to closeness of their boiling points to those of hydrocarbons. Most of the sulfur-containing neutral compounds is harmful impurity in products of coal tar processing – distillation and so are removed from distillates (fractions, technical products) by chemical purification and other methods. The most hard-removable compound is thionaphthene.

Summarized content of the neutral compounds in coal tar reaches 42–43%. The most valuable of them are naphthalene and anthracene, which are distilled from coal tar in naphthalene and anthracene fractions, respectively.

Acid part of coal tar is presented by compounds, containing oxygen in side chain: phenol $C6H5OH$, cresols $C6H4CH3OH$, xylenols $C6H3(CH3)2OH$ and polycyclic phenols, total content of which reaches 1.2–2.0%. The most valuable components are phenol and o-, n-, m-cresols. Most of the compounds is distilled from coal tar in phenol fraction, and the rest is spread over other fractions. Phenols from fractions are separated by their treating with alkaline solutions to obtain phenolate.

Basic properties are demonstrated by nitrogen-containing compounds of coal tar – pyridine ($C5H5N$), xynolene ($C5H7N$) and their derivatives, as well as high-boiling bases. Total content of bases in coal tar reaches 0.8–1.2%. In the course of distillation of coal tar the compounds are spread over fractions depending on boiling point. Separation of bases from fractions and oils is conducted by treating with sulfuric acid.

Processing of coal tar.

Coal tar is processed in tar-processing shops of by-product coke enterprises; there are 16 such shops in the CIS territory now.

Processing of coal tar includes the following main stages:

- preparation of coal tar for processing;
- final dewatering;
- rectification (distillation) to obtain fractions (distillates);
- processing of fractions;

- chemical purification of fractions and oils from phenols and pyridine bases;
- treating of mid-temperature pitch;
- obtaining high-temperature pitch and its coking;
- obtaining purified naphthalene, anthracene and other products.

Coal tar from by-product recovery shops arrives by pipeline to a surface storage (reservoir) of tar storehouse. To tar-processing shops, coal tar arrives at moisture up to 4% and ash content up to 0.1%. Such coal tar requires purification from water, dissolved salts and ash. The tar storages provide stability of tar composition and its partial dewatering, desalting and ash removal.

The storehouse includes at least 4 reservoirs (both underground and surface), positioned in cascade order, as well as water and oil collectors. The surface storages are individual reservoirs with capacity up to 3000 m^3, equipped with bottom heaters for heating coal tar up to 70–80°C. Top part of each reservoir includes collector for periodical self-discharge of over-tar water.

Tar-processing shop at enterprises of CIS use practically a single flow chart, providing for distillation of coal tar at its one-time evaporation in continuous tube facility, equipped with one or two rectification columns. Most of large enterprises has design capacity on coal tar processing shop of 200 kt of coal tar per year. Depending on rectification apparatus and operating practice, specific quantitative yield of fractions and their various qualities are obtained.

Unlike rectifying crude benzene, conducted by successive evaporation of its individual components, in rectifying coal tar, one-time evaporation and fractional condensation principle is applied.

At the first stage of processing of coal tar in tube facilities, one-time evaporation of coal tar is conducted, determining yield and composition of resulted vapor and liquid phases, degree and quality of transfer of individual components of coal tar into fractions. The evaporation provides quick heating of coal tar in heat coils, from which coal tar goes to evaporator, in which, as a result of sharp pressure release, vapors are immediately separated from liquid, forming distillate. At the second stage, the obtained distillate is rectified in rectification column to separate it into narrow fractions depending on their boiling points. Initially, in the column bottom, high-boiling fractions are condensed – anthracene, then washing, naphthalene, phenol, which are removed as liquids by side bleeding. Light fraction is taken from the column top as vapor.

The tube heating coal tar – processing facilities are characterized by a number of important advantages, including:

high producibility and compactness;

low area of the facility;

stability of mode and reduced period of thermal action on coal tar, resulting in increasing yield of fractions;

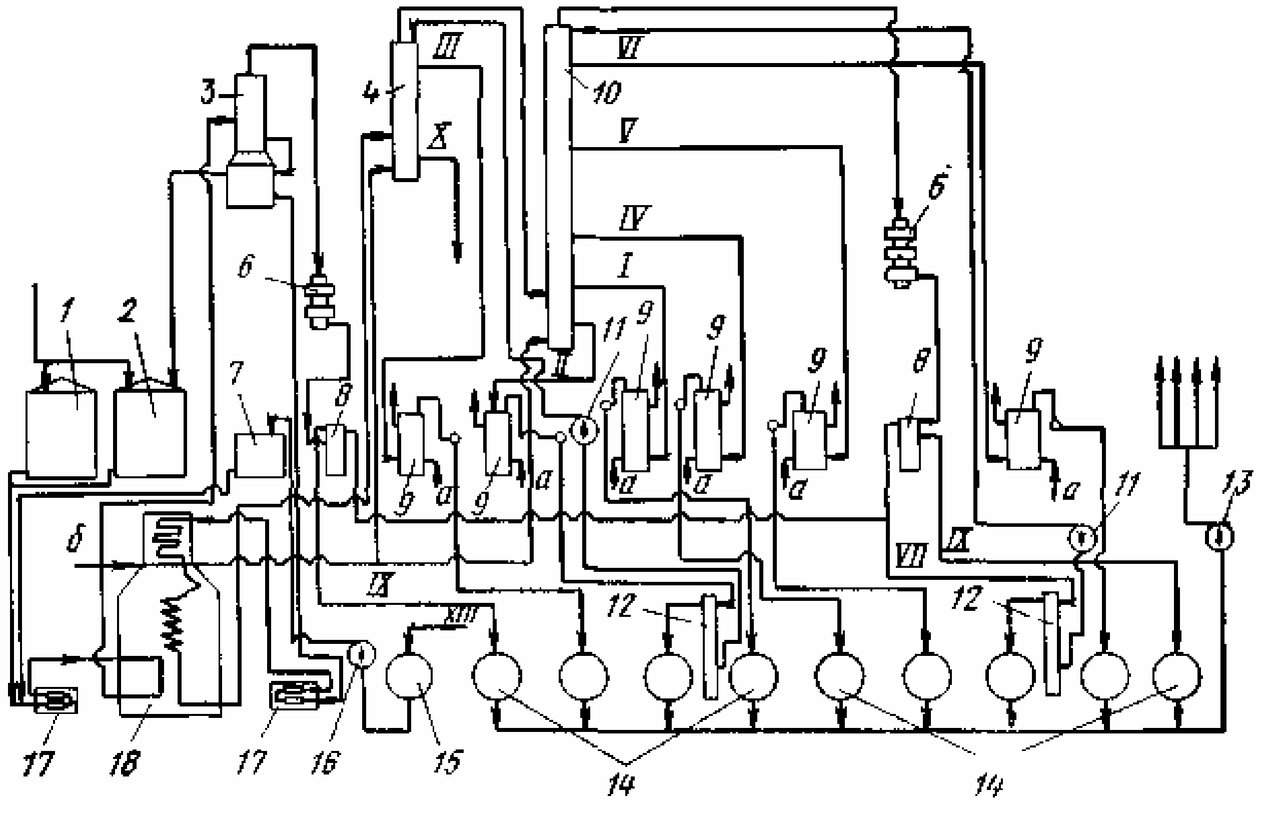
high controllability of the process;

low risk of fire (compared with periodic-type facilities).

In two-column tube facilities, heating of coal tar up to one-time evaporation temperature is conducted in radiant-convection chamber-type tube furnaces with productivity of 100–200 kt of coal tar per year. Distillate formation and its rectofiation is conducted in pitch (anthracene) and fractioning columns.

At present time, the most widespread is one-column tar-rectification facility (Fig.1). The facility is equipped with tube furnace with productivity of 200 kt of coal tar per year with heating walls, containing flame-free panel burners of system «Giproneftemash» and two-side lighting shield. The rectification column, compared with the fractioning column of two-column facilities, has more plates for distillate division into 5 liquid fractions and light oil vapor. This scheme allows to obtain 3 anthracene fractions. Change to one-column facilities allowed to simplify apparatus arrangement of facilities and to improve rectification of evaporated part of coal tar.

Figure 1: Scheme of coal tar rectification in one-column tube facility

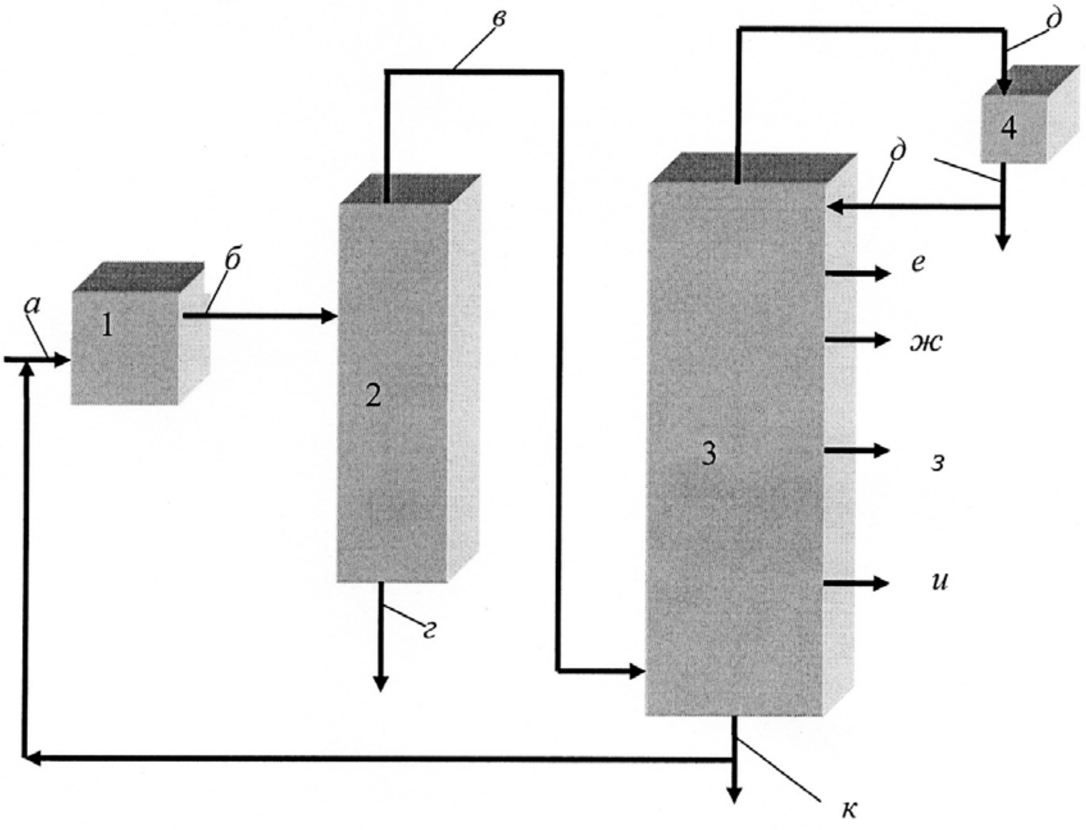


I, II, III – anthracene fractions; *IV* – washing (absorption) fraction; *V* – naphthalene fraction; *VI* – phenol fraction; *VII* – light oil; *VIII* – soda solution; *IX* – ammonia aqua; X – pitch; *a* – cooling water; *б* – super-heated steam
1, 2 – storing reservoits; *3* – 1st stage evaporator; *4* – 2nd stage evaporator; *6* – condenser-cooler; *7* – mixer; *8* – separator; *9* – cooler; *10* – rectification columns; *11, 13, 17* – pumps; *12* – reflux tank; *14*, *15* – collectors; *18* – tube furnace

Source: review of scientific and technical literature

Simplified scheme of processing of coal tar with obtaining various fractions is presented in Fig. 2.

Figure 2: Simplified scheme of coal tar processing with obtaining various fractions



1 – tube furnace; 2 – evaporator; 3 – rectification column; 4 - condenser; а - dewatered coal tar; б - vapor-tar emulsion; в - tar fractions vapors; г - coal tar pitch; д - light oil; е - phenol fraction;жс - naphthalene fraction; з - washing (absorption) fraction; и - 1st anthracene fraction; к - 2nd anthracene fraction

Source: review of scientific and technical literature

Average parameters of fractions yield and bleeding temperatures in the course of rectifying coal tar are presented in Table 1.

As seen, the highest yield in the course of processing of coal tar is reached for coal tar pitch – up to 60% of coal tar.

Fractions of rectification of coal tar are processed for separation of contained individual products. Naphthalene is derived from naphthalene and phenol fractions.

Table 1: Average parameters of fractions yield in the course of rectifying coal tar

Fraction	Bleeding temperature, °C	Yield of fraction, %	Content in fractions, %		Recovery degree, %	
			naphthalene	phenols	naphthalene	phenols
Light	Up to 170	0.6	2.0	0.5	0.12	0.17
Phenol	170-210	1	18	38	4.51	52.28
Naphthalene	210-230	10	82	6	82.19	33.01
Washing	230-300	10.8	8	1.5	7.62	7.84
I Anthracene	300-360	9.1	2.5	0.7	4.36	6.7
II Anthracene	310-440	8.4	1.5	–	1.2	–
Pitch	–	54.6-60	–	–	–	–

Source: review of scientific and technical literature

Russian and Ukrainian by-product coke enterprises, in the course of rectification of coal tar obtain concentrated **naphthalene fractions** with content of naphthalene of 79-88%; besides, the fraction contains phenols and quinoline base. That is why the naphthalene fraction can be source for obtaining of all these 3 products.

After separation of phenols and bases, content of naphthalene in residual neutral part of naphthalene fraction increases up to 90-91%. Among other components of the fraction are methylnaphthalenes, durol, isodurol, prehnitene, tetralin, bihexyl, 4-methylidene, indole, acetophenone, phenylethyl ketone, 5- and 6-methylcoumarone, di-methylcoumarones, benzonitrile, thionaphthane. Content of thionaphthene depends on content of sulfur in initial coals, which determines differences in composition of naphthalene fraction, derived from coal tar, obtained, in turn, in the process of coking of Donetsk and Kuznetsky coals (content of sulfur of 2.05-2.13% and 0.52-0.56%, respectively). In Table 2, composition of naphthalene fractions, derived at some plants in the CIS is given.

Table 2: Composition of naphthalene fractions of some plants in the CIS

Enterprise	Resources	Content of components in fraction, %			
		naphthalene	thionaphthene	bases	indole
"Avdeevka by-product coke plant", Ukraine	Coal tar from Donetsk coals	82-85	3.6-3.9	1.1-1.4	0.2-0.3
"Severstal", Russia	Coal tar from Pechora coals	83-87	2.4-2.6	2.3-2.5	–
"Nizhny Tagil steelworks", Russia	Coal tar from Kuznetsky coals	85-87	1.2-1.3	2.4-2.7	0.6
"Phenol plant" NPO "Inkor and Co^{o}", Ukraine	Oil after separation of naphthalene by crystallization	79-81	5.5-5.9	1-1.3	0.02

Source: review of scientific and technical literature

Separated, in the course of processing of coal tar, **light fraction** contains large amount of benzene hydrocarbons and light pyridine bases (40-70% depending on quality of coal tar and conditions of its fractioning). It is close in composition to heavy benzene, separated earlier, so it goes to shop of benzene rectification their joint processing.

Phenol fraction contains 25-35% of phenols, 15-30% of naphthalene, 14-19% of indene, 11-12% of benzene hydrocarbons. The fraction is used as raw material for obtaining phenol, nitric bases and naphthalene. Mix of phenols is used for obtaining phenol-formaldehyde resins, pesticides, disinfectants. After recovery of phenol, residual phenol fraction finds application in manufacture of technical oils of various designation.

Washing (absorption) fraction is mainly used for manufacture of washing oil, obtained after washing the fraction from phenols. This fraction can be also used as raw material for obtaining high-boiling phenols and heavy pyridine bases.

Washing oil is used at by-product coke enterprises of CIS for catching benzene from coke gas.

Anthracene fraction contains, as main components, anthracene, carbozole and phenanthrene, as well as large amount of other hydrocarbons. At present time, crystallization of the 1st anthracene fraction is applied for recovery of crude anthracene and anthracene oil. Crude anthracene is raw material for production of anthracene. Anthracene oil is used as antiseptic in manufacture of sleeper-impregnation oil. Besides, anthrecene oil is used as resources for production of carbon black.

Modernising available schemes of coal tar rectification provides for:

- using heat of fractions and pitch for preliminary heating of coal tar;
- providing additional heating of columns (hot spraying and heat-carrier recirculation) to concentrate in naphthalene fraction up to 90% of naphthalene and to improve quality of washing and anthracene fractions;
- application of modernized plates;
- decreasing live steam (HHPS) consumption;
- applying two-stage evaporation of coal tar (at the first and the second stages of heating of coal tar at atmospheric and elevated pressure, respectively).