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# MANUFACTURE OF DESIRED END PRODUCTS BY MEANS OF FINE TREATMENT OF COAL TAR RESIN

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*The possibility of desired end product manufacture from by-product coke industry wastes is shown. A large number of valuable products can be obtained from different fractions of coal tar resin by their fine treatment. The products obtained in this way find application in medical and chemical industries and etc. Moreover, recycling of by-product coke wastes into end products solves the problem of their utilization.*

The flowsheet of chemical coke by-products recycling in the 60–70s of the previous century began undergoing significant changes. From the classical sheet with obtaining of a number of chemicals (pyridine, benzene hydrocarbons, naphthalene, phenols etc.), chemical recycling of coke by-products was substantially transformed to decontamination of coke oven gas for its further using in power engineering. The recycling of crude benzene, fractions of pitch, pyridine bases with extraction of individual substances or their mixtures was planned at special enterprises, at the devices of high unit capacity.

In the course of this tendency, in connection of startup of the powerful by-product coke industry at the West-Siberian metallurgical enterprise, there appeared the real possibility of removing workshops of crude benzene and resin recycling of the nearby by-product coke plants (Kemerovo BPCP and by-product coke industry CMP) from the flowsheet owing to the equipment excessive wear. The recycling of resin at by-product coke industry of 3CMK is of narrow directed character: naphthalene extraction, obtaining of straw oil (for needs of domestic manufacture and nearby by-product coke enterprises) and pitch [1, 2].

The same sheet of resin recycling was carried out at OAO «Altay-coke», built 20 years later. The difference is only in the fact that the end products of resin recycling are pitch and sleeper impregnation oil. Naphthalene, phenolic and significant part of anthracene fractions are sent to cognate enterprises, where there are devices for recycling to end products, or utilized by means of burning with heat release.

These «wastes» hardly bring profit to the enterprise at the existing rail transportation rates. Their marketing carries more environmental directivity than economical appropriateness.

The concept of centralized resin recycling, realized in Germany, USA and other countries in the middle of the 20th century was also seriously examined in domestic coke chemistry. Resin deep recycling into end products was partially realized in Ukraine and at phenolic plants. About 25 individual substances and about10 chemical agents (while in Rursk region in Germany more than 100 designations of end products and chemical agents) were produced [3].

In Russia such approach to resin recycling is hardly appropriate for economic reasons. Nevertheless, many chemical compounds, which are obtained as products in by-product coking industry, are deficient raw materials for many branches of chemical industry (pharmaceuticals, polymers, semi-products, colorants etc.). There is a requirement in acenaphthene, fluorene, carbazole, pyrene and many other compounds, the manufacturing of which is practically absent in Russia for a variety of reasons.

The following main components with content from 1 % and more are contained in high-boiling resin fractions [4]: acenaphthene, diphenylene oxide, fluorene, phenanthrene, anthracene, carbazole, fluoranthene, pyrene, chrysene. The first three components are concentrated in stripping fraction and influence significantly the temperature of its crystallization at conventional technology of stripping fraction extraction in one column device of rectification resin. When changing place of extraction to the side of temperature decreasing the quality of straw oil improves owing to the relative increasing of methyl naphthalenes content. Intermediate fraction 270...310 °C, where acenaphthene, diphenylene oxide and fluorene (about 60 %) are concentrated may serve as raw material for further recycling to the individual products [5, 6].

At present the quantity of resin manufactured by «Altai-coke» corporation is about 170 thous. tons a year. With start up of the fifth battery this number will increase to 200 thous. tons and resources of these valued chemical compounds in resin will be 8...10 thous. tons/year. In our opinion, this may be a stimulus for inclusion into process installation for manufacturing end products.

One more source of raw materials for production of acenaphthene, diphenylene oxide and fluorene is polymers of straw oil regeneration. Sum content of mentioned components in polymers is not less than 80...85 %. Process module of polymers recycling should include equipment for occurring the following stages:

- distillation to 305...310 °C for concentration of desired products and polymers separation (in vat residue);
- dissolving of distilled fraction in crude benzene at higher temperature (to 60 °C);
- washing with 15 % sulphuric acid and alkali for removing quinolinic bases and phenols to exclude the possibility of azeotropic compounds formation at rectification;
- cooling and crystals isolation;
- melting and mixture rectification with extraction of fractions 270...280 °C (acenaphthene), 280...290 °C (diphenylene oxide), 290...300 °C (fluorene);
- purification of technical products by means of recrystallization in complex solvents individually selected for each component.

Resources of acenaphthene (A), diphenylene oxide (D) and fluorene (F) in polymers are fluctuating by different data from 30 % for each component to 33 (A), 27 (D), 24 (F) at OAO «Altai-coke». It depends on oil quality and regeneration temperature. At recycling 10000 tons/year of a polymer in terms of 50 % extraction of these products we may produce:

- acenaphthene 1700 t.
- diphenylene oxide 1300 t.
- fluorene 1000 t.

According to the data of academician G.V. Sakovich [7] cost of fluorene, delivered from China is 25 US$. This is without taking into consideration the rest of the products which are produced simultaneously and cost less on the world market.

The next group of compounds – phenanthrene, anthracene and carbazole are concentrated in anthracene fraction. The recycling consists in isolating from this fraction crude anthracene and its further recycling in one or another way. Carbazole is rather easy separated from anthracene- phenantrene fraction by rectification. In scientific literature the techniques of anthracene and phenanthrene separation by the mixture of toluene with pyridine and maleic anhydride are described. The producing string of these compounds separation is approximately the same as at polymers recycling except some peculiarities [8].

One more group of compounds – fluoranthene, pyrene and chrysene are concentrated in heavy pitch distillates at pitch fraction recycling. When obtaining high-percentage individual compounds the same flowsheet may be applied: rectification-crystallization-centrifugation. The process module for recycling heavy pitch distillates is carried out at Gorlovskii by-product coke plant in Ukraine. Products purity after rectification and double or triple recrystallization in solvent refining agents is: fluoranthene – 96,5 %, pyrene – 97,5 %, chrysene – 96,3 % [9].

Using the suggested process module is not exhausted by 9-10 compounds mentioned above. Rectifying column may be used for development of process of production of long quinolinic fraction and extraction of end products: quinaldine, isoquinoline and high-boiling pyridine bases.

It was stated above that straw oil quality depends on extraction temperature range and regeneration. However, there is one more factor: in world and domestic experience of benzene hydrocarbons catching the best straw oil grades are considered to be depyridined and dephenoled stripping fractions. Heavy pyridine (quinolinic) bases is removed by means of washing with 15...20 % solution of sulphuric acid. Sulfates of the bases (heavy pyridine and quinolinic) turn into water solution. Sulfates extraction is carried out with benzene (or benzene fraction). Pyridines and quinolines turn into free state after having been neutralized with alkali and benzene, and water are distilled from the mixture. The bases are subjected to rectification with obtaining close-cut fractions or mixtures [10]. It should be noted that quinolinic bases are also accumulated in reverse benzene fraction, using in dissolving long distillate from polymers in washing technology. Vat residues after benzene fraction distillation are accumulated and rectified too. The following products may be obtained from quinolinic bases: quinoline, isoquinoline, quinaldine.

Close boiling temperatures do not allow extracting the components of sufficient purity by means of rectification. Nevertheless, Czech researchers suppose that quinoline and isoquinoline with concentration of base material of more than 96 % and binary mixture of 2-and-8-methylquinolines may be produced at the column. 650 tons of crude quinolinic bases may be obtained from 200 thous. tons of resin at recycling. And 235...300 tons of quinoline, 90 tons of isoquinoline, about 50 tons of 2-methylquinoline and about 15 tons of 4-methylquinoline may be obtained from 650 tons of crude quinoline bases at recycling. Taking into consideration the fact that silesian coals are worse significantly than Kuzbas ones in nitrogen content, these numbers for quinoline are supposed to be 2...3 times higher, as well as for manufacturing quinoline and high-boiling quinolinic bases (latudine, xylidine) [10].

In conclusion, it is necessary to note, that in modern conditions the organization of by-product coke enterprise is appropriate to compose of end products manufacturing for various branches of chemistry, including raw materials for pharmaceuticals synthesis, for growth of its economical efficiency. The real prerequisites for organization of such area in coke chemistry are the following:

- availability of active raw materials, in some cases the unique ones, in sufficient amount;
- manufacture does not require deficient and metal-intensive equipment and great capital investment; high price of marketable products ensures quick payback;
- availability of powerful treatment facilities solves the problem of neutralization and utilization of these industries waste.

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# IMPROVING THE PROCESS OF HIGHER PARAFFIN DEHYDROGENATION ON THE BASIS OF NONSTATIONARY KINETIC MODEL

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*Technological modelling system of the dehydrogenation process of $C_{10}$–$C_{13}$ n-paraffins, in the basis of which there is a formalized mechanism of hydrocarbons transformation on the Pt-catalyst surface has been developed. According to predictive calculation, application of the developed system allows the prolongation of catalyst life due to optimization of its operation modes as well as simulation of different variants in equipment reconstruction, in particular, at transition to operation of reactors placed in parallel.*

The potential demand of domestic market of synthetic detergents ащк a raw material base, which is linear alkyl benzenes (LAB) and linear alkyl benzene sulphanates (LABS), is about 100 thous. tons per year. Meanwhile, at present, OOO «KINEF». is only one LAB manufacturer in Russia. The production capacities are 50 thous. tons of LAB per year, the 70 % of which are orientated to export. The rest quantity of LAB is sufficient only for 3–4 domestic enterprises of more than existing thirty ones. In connection with the demand for LAB on Russian market the task of increasing this production capacity is urgent.

The main stages of LAB production by UOP (Universal Oil Products Company) technology are: 1) higher paraffins dehydrogenation at Pt-catalyst (Pacol process); 2) by-products hydrogenation (Define process); 3) benzene alkylation with obtained monoolefines with the use of HF-catalyst.

Nowadays, the only combination set for LAB production in Russia Pacol-Define Limited Company «KINEF» operates at excess rated capacity by 20 %. Probably, the reserves of productivity improvement (without equipment replacement) are not exhausted yet. One of the possible ways of the set productivity improvement