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RATIONAL REFINING OF HEAVIER CUT OF PYROLYSIS GAS OIL

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The composition of the fractions of the heavier cut of pyrolysis gas oil production was investigated by gas chromatography. In order to increase the profitability of pyrolysis units, it is recommended to organize complex technological schemes for the processing of the heavier cut of pyrolysis gas oil.

Introduction. The general power of pyrolysis processes in the world exceeds 130 million tons per year. The process of getting light olefins is accompanied by forming about 20% coproducts. The usage of these coproducts is a serious technical and economic problem that is associated with increased profitability of production. In order to remain competitive in the ethylene business for steam crackers, more effort must be made to upgrade all of the byproducts that are formed by liquid crackers. Producers who do not upgrade these by-products will face growing tension on the plant margins owing to competition from the world's low-cost regions [1].

One of these coproducts is the heavier cut of pyrolysis gas oil (PGO). The heavy distillates of the steam-cracked naphtha contain aromatic hydrocarbons that boil above 180 Celsius degrees. Only in Russia the production of PGO exceeds 325000 tons per year. Belarussian petrochemical Plant "Polymir" which is part of JSC "Naftan" is able to produce from 12000 up to 16000 tons of PGO yearly [2,3].

The issue of rational use of PGO is relevant for Belarus due to the future plans to increase the capacity of the enterprise, which will lead to an increase in the amount of by-products and amount of problems associated with their marketing.

Nowadays, PGO is used as a source of boiler heater. It is possible to obtain from the heavy pyrolysis tar not only boiler fuel but also carbon black, inactive carbon black, coke, dark petroleum resins, concrete superplasticizing agents, plasticizers, bitumen materials and to extract individual aromatic hydrocarbons (Naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, etc.).

With the increasing global market demand for naphthalene, naphthalene defining technology is extensively studied internationally. Industrial naphthalene from coal tar accounts for 85% of total naphthalene production in the world. Naphthalene is produced from a high heteroatoms content coal-tar resin. In order to remove these heteroatoms expensive cleaning operations are used [4-16].

Up to date, there is still a problem to release pure naphthalene from coal tar and from components with similar boiling point to Naphthalene (217,97°C), such as Thionaphthene (219,90°C) and 2,3-Xylenol (216,87°C). It should be noted that the PGO of a wide fraction of light hydrocarbons, in contrast to coal tar, does not contain heteroatomic compounds, including Thionaphthene and Xylenols, and therefore is the preferred raw material for producing high purity Naphthalene [1].

Task formulation. The composition of the fractions of PGO production was investigated by gas chromatography.

Methods of research. Gas chromatography identifies resin ingredients by peak area, evaluate their quantitative content with high accuracy.

Results, their discussion and perspectives.

As a result of fractional distillation of PGO according to Engler, the yield of fractions is the following: b.b.-180°C was 1.89% wt., fraction 180-210°C was 18.76% wt., fraction 210-230°C was 14.45% wt. and semi-solid non-distillable residue of polymeric nature (pitch) was 64.90% wt. We have analyzed the Belarussian heavy pyrolysis resin (tar) and identified individual substances. PGO liquid concentrate is a mixture of various groups of hydrocarbons, primarily aromatic, both monocyclic and polycyclic. Also, all fractions contain isoparaffin, unsaturated, naphthenic and paraffinic hydrocarbons.

Table 1 presents data on the group hydrocarbon composition of individual fractions of heavy pyrolysis resin, produced at the factory "Polymir".

While the content of aromatic hydrocarbons in PGO reaches to 68%wt., in particular, naphthalene is up to 18 % wt. More than 75 individual aromatic hydrocarbons were found in the PGO liquid concentrate and their content increases with the weighting of the fractional composition.

The main component of the liquid product of PGO with boiling point up to 230°C is naphthalene and its alkyl derivatives.

Table 1. – The group hydrocarbon composition of individual fractions of PGO

Groups of hydrocarbons	Fractions of PGO, % wt.			
	b.b.-180°C	180-210°C	210-230°C	Total fraction
Paraffins	2,04	0,94	0,43	0,79
Isoparaffins	10,96	13,29	14,04	13,47
Aromatics	62,82	66,30	70,47	67,82
Naphthenes	7,30	5,26	1,94	4,00
Olefins	13,09	5,26	3,43	6,70
Unknown	3,79	5,64	9,69	7,22

Naphthalene plays an irreplaceable role in Fine Chemical Industry. Naphthalene is used for the synthesis of sulfonic acids, phthalic anhydride, azo dyes, plasticizers, decalin, tetralin, naphthol and others. Sulfonic acids from naphthalene are good surface-active substances (surfactants). The way of the derivation of superplastifikators for concrete from naphthalene is actively developing now.

The output of naphthalene at the factory "Polymir" from the PGO fraction with boiling point up to 230°C can be about 1000 tons per year. Naphthalene recovery is economically feasible. The results of chromatographic analysis show that in the process of obtaining high-purity naphthalene from PGO, separation of homogeneous azeotropes (naphthalene & 1-methyl naphthalene; naphthalene & 2-methyl naphthalene; naphthalene & biphenyl and others) might be a problem.

Various product derivatives can further increase the profitability of naphthalene recovery (Xu, 2012). Methylnaphthalenes are used as insecticides, solvents and starting materials in the synthesis of dyes, to produce sulfonic acids of mono- and dimethylnaphthalenes, used as surface active substances. Besides:

– 2-Methylnaphthalene is a valuable raw material for the production of synthetic vitamin K3 (2-methyl-1,4-naphthoquinone, menadione), which is widely used in medicine as a drug to increase blood clotting.

– 1-Methylnaphthalene is a reference when determining the cetane number of diesel fuel (for 1-methyliaphthalin, it is assumed to be zero).

– 1,4-dimethylnaphthalene is used to suppress the germination of potatoes and vegetables.

– 2,6-dimethylnaphthalene is oxidized to 2,6-naphthalene dicarboxylic acid used in the production of polyesters and polyamides.

The theoretical output of 2-methylnaphthalene at the factory "Polymir" from a liquid product PGO can reach 250 tons per year, for 1-methylnaphthalene is about 170 tons per year, for 1,4-dimethylnaphthalene is about 18 tons per year, for 2,6-dimethylnaphthalene is about 15 tons per year.

Cymols of PGO liquid product can be widely used for the synthesis of cresols, highly effective antioxidants, phthalic acids (mainly isophthalic and terephthalic acids), flavors, etc. The use of cymols in petrochemical synthesis allows sprawling of the raw material base for the production of alkylaromatic hydrocarbons. The theoretical output of cymols at the factory "Polymir" from PGO with boiling point up to 230°C can be: for 1-methyl-2-isopropyl benzene is about 630 tons per year, for 1-methyl-3-isopropyl benzene is about 125 tons per year and for 1-methyl-4-isopropyl benzene is about 2 tons per year.

Indane (2,3-dihydroinden) is the starting material for the synthesis of 2-, 4- and 5-indanols, which are used in the preparation of medicines. The theoretical output of indane from the liquid fraction of PGO can be up to 80 tons per year.

Tert-butylbenzene is the starting compound in the preparation of valuable fragrances, and is also used as a solvent and raw material for alkyl polystyrenes. It is potentially possible to organize the production of tert-butylbenzene from PGO liquid product up to 68 tons per year.

Pseudocumene (1,2,4-trimethylbenzene) is used in the production of trimellitic acid and its anhydride, pseudokumidin, vitamin E. The theoretical output of 1,2,4-trimethylbenzene from the liquid fraction of PGO can be more than 55 tons per year.

Biphenyl is used as a precursor in the synthesis of polychlorinated biphenyls, as well as other compounds used as emulsifiers, insecticides and dyes. It is possible to extract about 50 tons of biphenyl per year from PGO liquid product.

It is expedient to use the residue of the distillation of PGO as a raw material for the production of pitches and carbon fibers.

Conclusion. In order to increase the profitability of pyrolysis units, it is recommended to organize complex technological schemes for the processing of PGO.

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