Topical Issues of Rational Use of Natural Resources 2019 – Litvinenko (Ed)
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PGO Processing with azeotropic rectification to extract naphthalene

Y.A. Bulauka & S.F. Yakubouski
Polotsk State University, Novopolotsk, Belarus

ABSTRACT: In this study, azeotropic rectification method was attempted to extract industrial naphthalene from fractions of liquid pyrolysis' products of the hydrocarbon feed and obtain refined naphthalene. Extraction of naphthalene from fractions of liquid pyrolysis products (LPP) from hydrocarbons including the atmospheric and then the vacuum distillation of heavier cut with the extraction of naphthalene concentrate that is having azeotropic rectification and then it is coming for the stages of crystallization and pressing. In order to obtain condition for industry naphthalene purification using azeotropic rectification method, the Belarussian heavier cut's chromatography were studied. The optimization of the process of azeotropic rectification to obtain refined naphthalene is mainly discussed to provide a theoretical for the actual production and technology improvement

1 INTRODUCTION

The general power of pyrolysis processes in the world exceeds 130 million tons per year (Nakamura, 2007). 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 by products 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 (Paliashkevich, 2017).

One of these coproducts is the heavier cut of pyrolysis gas oil (PGO). The heavy distillates steam-cracked naphtha contains aromatic hydrocarbons that boils above 180 Celsius degrees (Apicella, 2003.). 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 (Bulauka, 2018).

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 degradation of problems associated with their marketing.

Nowadays, PGO uses 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 (Kershaw, 1993; Gargiulo, 2015; Granda, 2003; Gargiulo, 2016; George, 2010).

Up to date, there is still a problem to release of pure naphthalene from coal tar which related with its separation from components close to boiling point 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 hetero atomic compounds, including Thionaphthene and Xylenols, and therefore is the preferred raw material for producing high purity Naphthalene.

There is a method for producing naphthalene from liquid pyrolysis products in two vacuum columns (Gentry, 2009; Apicella, 2017; Petlyuk. 1965). Naphthalene separation process is shown in Figure 1.

The first column is designed to remove the lighter fraction than naphthalene with the column overhead. In the second column, the heavy fraction of liquid pyrolysis products are removed by the bottom product, and the naphthalene fraction is separated from the top of the column, which is sent to crystallization. The disadvantage of this process is not a high degree of purity of the product.

There is a method for separating naphthalene from the C_9-C_{11} fraction of liquid pyrolysis products. The fraction is exposed to catalytic hydrostabilization and then the C_{10}-C_{11} aromatic fraction is separated by means of rectification. The obtained product is subjected to thermal hydrodealkylation together with a hydrostabilized and hydrotreated C_6-C_8 aromatic fraction. Hydrodealkylate is processed to rectification with the release of naphthalene as one of the products. The disadvantage of the process is the complicated technological scheme of processing liquid pyrolysis products and the use of expensive catalysts.

There is a method of producing naphthalene from naphthalene-containing fractions of liquid pyrolysis products by hydro-purification of unsaturated hydrocarbons in the presence of an aluminum palladium sulphide catalyst. The disadvantages of this method of producing naphthalene are high pressure, the use of hydrogen for the hydrogenation of unsaturated compounds and expensive catalysts.

There is a method of producing naphthalene from naphthalene-containing fractions of liquid pyrolysis products by purification of unsaturated hydrocarbons by the method of their polymerization in the presence of an aluminum-cobalt-molybdenum catalyst. The process of

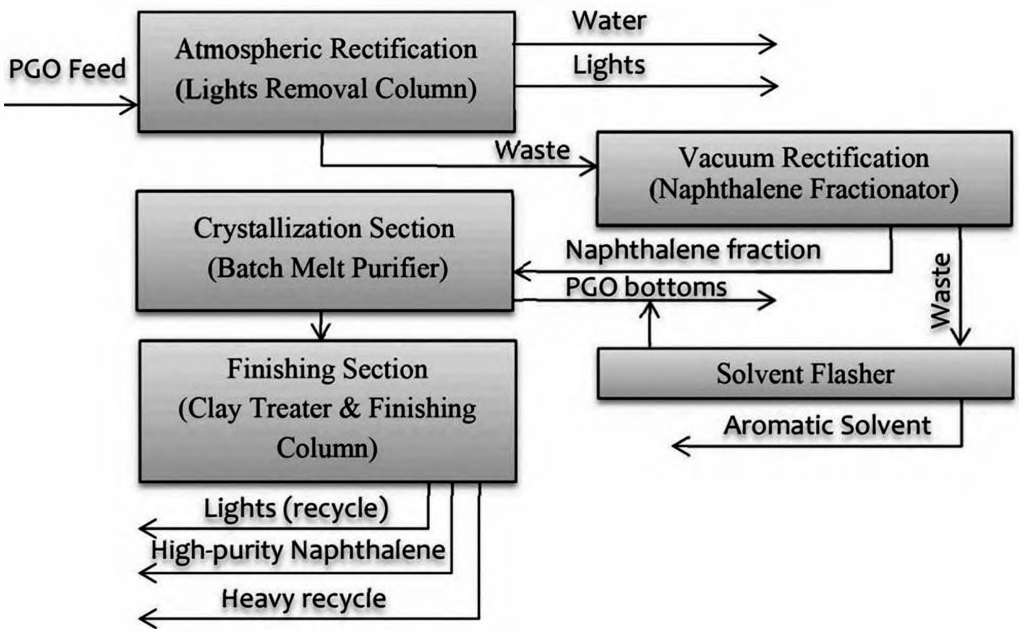

Figure 1. Naphthalene separation process.

polymerization of unsaturated hydrocarbons is carried out at a temperature of 150-210°C, pressure up to 0.1 MPa, for 0.5-2 hours. The main disadvantage of this method is the need to use hydrogen and expensive catalyst, low degree of purity of naphthalene.

There is a method of separating naphthalene from a fraction of 190-250°C of liquid pyrolysis products, which is previously subjected to catalytic polymerization in the presence of an aluminum-cobalt-molybdenum catalyst. The disadvantage of this method is the need to use a catalyst, which loses activity during the process, which leads to the need for regeneration and, as a consequence, the use of complex technological schemes, including the regeneration of the catalyst.

There is a method of separating naphthalene from the fraction that maintained at a temperature of 200-300°C, a pressure of 0.1-1.0 MPa for 2-10 hours, the treated fraction sent to atmospheric & vacuum simple distillation. The distillate is sent to the separation of naphthalene by crystallization in a known manner. The disadvantage of this method is the need for preliminary heat treatment in the reactor for liquid pyrolysis products at high temperatures up to 300°C and pressures up to 1.0 MPa, and involving expensive initiators or unsaturated individual aromatic hydrocarbons in the case of polymerization of reactive non-saturated compounds and high-boiling resins at low temperatures 200-280°C.

Current methods for the naphthalene extraction are not used in manufacture because of the high energy inputs, expensive catalysts, or low naphthalene purity.

2 PURPOSE AND OBJECTIVES OF THE STUDY

The purpose of the research is to develop an efficient method for obtaining pure naphthalene by azeotropic distillation of naphthalene-containing fraction of liquid products of pyrolysis of hydrocarbons. The proposed method of separation of naphthalene from liquid products of the pyrolysis of hydrocarbons is made in laboratory conditions using PGO produced at the factory "Polymir" with a naphthalene content of more than 18% wt.

3 RESEARCH METHODS

The composition of the fractions of PGO production was investigated by gas chromatography. Gas chromatography identifies resin ingredients by peak area, evaluate their quantitative content with high accuracy. The possibility of extracting naphthalene by the method of azeotropic distillation with ethylene glycol has been studied.

4 RESULTS AND DISCUSSION

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 containing of aromatic hydrocarbons in PGO reaches to 68%wt., in particular, naphthalene 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. Table 2 shows the main individual aromatic components that make up the liquid concentrate of PGO boiling up to 230°C.

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	5,27	3,43	6,70
Unknown	3,79	5,64	9,69	7,22

Table 2. Individual composition of aromatic hydrocarbons of separate fractions of PGO.

Individual aromatic hydrocarbon	Fractions of PGO, % wt.			
	b.b.-180°C	180-210°C	210-230°C	Total fraction
naphthalene	2,98	14,97	23,91	18,00
1-methyl-2-isopropylbenzene	4,16	13,69	9,28	11,36
2-methyl naphthalene	0,44	2,62	7,53	4,52
4-methylindane	1,23	4,03	4,91	4,24
1-methyl naphthalene	0,30	1,69	5,24	3,08
1-methyl-3-isopropylbenzene	1,19	3,02	1,35	2,23
n-pentylbenzene	0,00	1,48	1,98	1,61
2,3-dihydroindene	8,12	1,25	0,74	1,41
tert-butylbenzene	1,03	1,88	0,37	1,21
1,2,3-trimethylbenzene	0,62	1,56	0,51	1,08
1-methyl-3-n-propylbenzene	0,54	1,40	0,59	1,02
1,2,4-trimethylbenzene	0,69	1,49	0,45	1,02
biphenyl	0,08	0,50	1,63	0,94

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

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 superplatifikators 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.

The objective of this investigation is to develop a method for the separation of naphthalene of a high degree of purity from the liquid products of PGO while reducing energy consumption and material resources.

The problem is solved by the fact that method of obtaining naphthalene includes atmospheric and then vacuum distillation of PGO with separation of naphthalene concentrate, which is subjected to azeotropic distillation, and then sent to the crystallization and pressing steps.

Scheme of PGO Processing with azeotropic rectification to extract high purity naphthalene is shown in Figure 2.

The inventive method of naphthalene extraction from liquid pyrolysis products of hydrocarbon raw materials in industrial conditions can be realized as follows: naphthalene concentrate is released in a known way by atmospheric and vacuum-intelligent distillation, naphthalene concentrate is mixed with ethylene glycol in a mass ratio of 1:1 and sent to the column of azeotropic distillation. In the azeotropic distillation column ethylene glycol-naphthalene azeotrope is separated as a distillate, and the balance of the upper product (azeotrope) is mixed in a mixing tee with wash water to dissolve ethylene glycol. Subsequently, naphthalene is subjected to crystallization and pressing on a vacuum filter press in a known method.

A distinctive feature of the proposed method of extracting naphthalene from the fraction of PGO from the existing ones is the use of an additional stage of azeotropic distillation of naphthalene concentrate, the absence of a stage of polymerization of reactive unsaturated compounds.

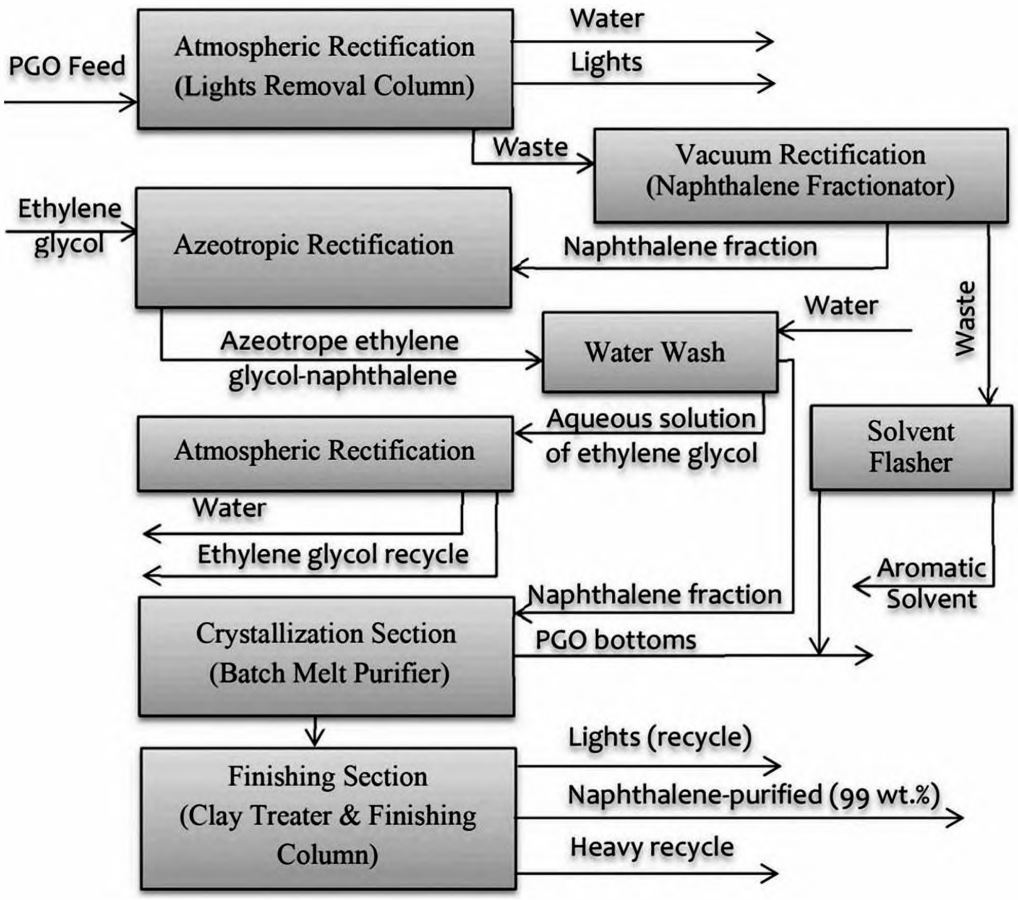

Figure 2. Scheme of PGO Processing with azeotropic rectification to extract naphthalene.

As a result of this method, naphthalene is obtained with a purity of 99% wt. (solidifying point more 79,6°C). The purity degree of naphthalene meets the requirements of GOST 16106 for "Naphthalene-purified", and the naphthalene can be used as a feed for petrochemical synthesis.

Table 3 presents the assessment of the competitiveness of naphthalene production from different manufacturers from CIS countries according to the price factor.

Table 3. Assessment of the competitiveness of naphthalene producers.

Manufacturer name	Qualification (purity, wt.%)	Price per ton, USD
Phenolic plant LLC Inkor and Co.	99	4500
West-Siberian Metallurgical Plant	99	4200
Avdeevsky Coke Chemical Plant	99	3800
Gubakhinsky Coke Chemical Plant	100	4100
Magnitogorsk Metallurgical Plant	100	3700
Nizhny Tagil Metallurgical Plant	99	4500
Novolipetsk Metallurgical Plant	99	4000
Enakievsky Coke Chemical Plant	99	4050

As it can be seen from Table 3, the price for 1 ton ranges from $ 3,800 to $ 4,500.

The State Organization SO «BELISA» has developed a business plan for the project of this processing station with a planning horizon for 5 years, investment costs are about $ 3.1 million net present value is $ 6.9 million, internal rate of return is 74%, dynamic payback period is 2.67 years, product profitability is 28%. These facts prove the rationality of investing in this project.

5 CONCLUSION

In order to increase the profitability of pyrolysis units, it is recommended to organize complex technological schemes for the processing of PGO, including the processes of primary fractionation into narrow fractions and pitches, azeotropic rectification, water washing and crystallization of the resulting distillate in order to obtain pure naphthalene.

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PROCEEDINGS OF THE XV[TH] FORUM-CONTEST OF STUDENTS AND YOUNG RESEARCHERS UNDER THE AUSPICES OF UNESCO, SAINT-PETERSBURG, RUSSIA, 13 – 17 MAY 2019

United Nations
Educational, Scientific and
Cultural Organization

International Competence Centre
for Mining-Engineering Education
under the auspices of UNESCO

Topical Issues of Rational Use of Natural Resources 2019

Volume 2

Editor

Vladimir Litvinenko

Saint-Petersburg Mining University, Saint-Petersburg, Russia

CRC Press
Taylor & Francis Group
Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an **informa** business

A BALKEMA BOOK

CRC Press/Balkema is an imprint of the Taylor & Francis Group, an informa business

Typeset by Integra Software Services Pvt. Ltd., Pondicherry, India

Library of Congress Cataloging-in-Publication Data

Applied for

Published by: CRC Press/Balkema
Schipholweg 107C, 2316XC Leiden, The Netherlands
e-mail: Pub.NL@taylorandfrancis.com
www.crcpress.com – www.taylorandfrancis.com

ISBN: 978-0-367-85713-4 (Set Hbk)
ISBN: 978-1-003-01452-2 (eBook)
DOI: https://doi.org/10.1201/9781003014522

Volume 1:
ISBN: 978-0-367-85719-6 (Hbk)
ISBN: 978-1-003-01457-7 (eBook)
DOI: https://doi.org/10.1201/9781003014577

Volume 2:
ISBN: 978-0-367-85720-2 (Hbk)
ISBN: 978-1-003-01463-8 (eBook)
DOI: https://doi.org/10.1201/9781003014638