

ЕҢБЕК ҚЫЗЫЛ ТУ ОРДЕНДІ
«Ә. Б. БЕКТҰРОВ АТЫНДАҒЫ
ХИМИЯ ҒЫЛЫМДАРЫ ИНСТИТУТЫ»
АКЦИОНЕРЛІК ҚОҒАМЫ

ҚАЗАҚСТАННЫҢ ХИМИЯ ЖУРНАЛЫ

ХИМИЧЕСКИЙ ЖУРНАЛ КАЗАХСТАНА

CHEMICAL JOURNAL of KAZAKHSTAN

АКЦИОНЕРНОЕ ОБЩЕСТВО
ОРДЕНА ТРУДОВОГО КРАСНОГО ЗНАМЕНИ
«ИНСТИТУТ ХИМИЧЕСКИХ НАУК
им. А. Б. БЕКТУРОВА»

1 (61)

ЯНВАРЬ – МАРТ 2018 г.
ИЗДАЕТСЯ С ОКТЯБРЯ 2003 ГОДА
ВЫХОДИТ 4 РАЗА В ГОД

АЛМАТЫ
2018

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HIGH-TEMPERATURE HYDROGENATION (HYDRODEALKYLATION) OF THE MIXTURE OF COAL TAR PITCH DISTILLATE FRACTIONS AND RAW COKE-CHEMICAL BENZENE

Abstract. New basic process parameters for carrying out the high-temperature hydrogenation (hydrodealkylation) of the mixture of coal tar pitch distillate fractions and raw coke-chemical benzene were developed. Optimal conditions of the process of hydrogenation of preliminarily hydrotreated mixture of tar fractions with boiling temperature 180-230⁰C and raw coke-chemical benzene in the presence of water vapor were defined. By high-temperature hydrogenation of hydrotreated mixture in the presence of catalyzer 5 % MoO₃ + zeolite HNaY high-purity benzene with crystallization temperature +5.35-5.45⁰C, sulfur content 0.002%, was obtained.

Key words: coke chemical resin, catalysts, benzene, naphthalene, hydrogenation.

Introduction. The main source of benzene yield increase are raw material alkylaromatic hydrocarbons (toluene). This circumstance is proven by the production practice of raw benzene treatment abroad, and the results of research, design and construction and development work carried out in CIS. Nowadays, with the purpose of transforming toluene or gasoline pyrolysis liquid products into benzene on an industrial scale, imported hydrodealkylation catalysts are used. At hydrodealkylation of aromatic carbohydrates and hydrocracking of saturated carbohydrates into gas, which is required for subsequent obtaining of high-purity benzene with precise fractionation, decontaminating coke settles on the catalyst surface which reduces the catalyst activity and requires its frequent regeneration because the process is carried out at high temperature – to 650⁰C.

Nowadays, in connection with the toughening of requirements to the quality of raw material for organic syntheses, increase of need for benzene and naphthalene, studies and development work on the improvement of coke-chemical raw material hydrotreatment processes are carried out actively. The experimental and theoretical data obtained formed the basis for the development of technology and new technical solutions of the process of high-temperature hydrogenation (hydrodealkylation) of preliminarily hydrotreated mixture of tar fractions with boiling temperature 180-230⁰C and raw coke-chemical benzene for production of benzene and naphthalene high-purity sorts at treatment of 95 ths. t of raw material annually.

The goal of this paper is to define basic production parameters of the conduct of high-temperature hydrogenation (hydrodealkylation) of the mixture of coal tar pitch distillate fractions and raw coke-chemical benzene.

Experiment. With the purpose of producing high-quality benzene and naphthalene, experimental studies on high-temperature hydrogenation mixture (4:1) of raw coke-chemical benzene and tar fractions with boiling temperature 180-230°C, obtained at devolatilization of coal from Shubarkolskii deposit at the enterprise Sary-ArkaSpetskoks JSC, were carried out.

Raw material hydroforming was carried out on the high-pressure laboratory installation under hydrogen pressure of 4.0 MPa in the system of two reaction areas operating in series. In the first zone, hydrogenation of non-saturated high-reactive compounds (styrolene, indene, etc.) was carried out in the presence of the production catalyst 0.5 % PdS + Al₂O₃ (MA-15) in order to provide the possibility to heat raw material to higher temperature (280-300°C) without polymerization. Deep removal of S, N, O heteroatoms and methylnaphthalenes to the corresponding tetrahydro derivatives – H-donor source for hydrodealkylation stage occurred in the second zone in the presence of Mo/Ni-Raney catalyst.

Results and discussion. Characteristic of raw coke-chemical benzene by Sary-Arka Spetskoks JSC is given in table 1.

Table 1 – Material composition of raw coke-chemical benzene by Sary-Arka Spetskoks JSC

Compound	Content, % wt.
benzene	58,00
toluene	8,30
naphthalene	0,40
methylnaphthalene	2,85
xylenes	2,45
styrene	2,03
indene	2,14
hydrindene	0,30
thiophen and methylthiophens	0,18
ethylbenzene	0,15
pseudocumene	0,25

As it is seen from table 1, the content of benzene in raw coke-chemical benzene by Sary-ArkaSpetskoks JSC is 58 % wt., toluene - 8.3 % wt., naphthalene - 0.4 % wt.

The results of hydrotreatment of the mixture of raw benzene and coke-chemical tar fraction with boiling temperature 180-230°C are given in table 2.

It is seen from table 2 that in comparison with starting material, benzene concentration in the hydrotreated product increased from 40.5 to 49.0 % wt., and naphthalene concentration decreased from 24.2 to 10.0 % wt.

Table 2 – The results of hydrotreatment of the mixture of raw benzene and coke-chemical tar fraction with boiling temperature 180-230°C (conditions: 4.0 MPa, 150°C, 0.5 % PdS + Al₂O₃ catalyst in the first zone; 380°C, Mo/Ni-Raney catalyst in the second zone, weight hour space velocity 2.0 kg/l·h)

Parameter	Initial mixture of raw benzene and tar fraction with boiling temperature of 180-230°C	Hydrotreated Product
Liquid products yield, % wt.	–	97,5
Gas (C ₁ -C ₄ , H ₂ S, NH ₃) yield, % wt.	–	2,5
Water yield, % wt.	–	0,8
Hydrogen flow, % wt.	–	1,0
Characteristic of liquid products:		
Density, ρ ₄ ²⁰	0,9356	0,9296
Chemical composition, % wt.:		
saturated hydrocarbons	0,6	3,2
Benzene	40,5	49,0
thiophen and methylthiophens	0,7	No
Toluene	13,1	13,5
Xylenes	4,0	4,9
Ethylbenzene	0,7	0,9
C ₉ aromatic hydrocarbons	3,5	4,0
tetralin + methyltetralins	–	17,2
naphthalene	24,2	10,0
2-methylnaphthalene	2,2	1,0
1-methylnaphthalene	2,0	0,5
Tionaphthen	0,35	No
Phenols	0,9	No
basic nitrogens	0,7	No
Elemental composition, % wt.:		
C	92,06	92,15
H	6,65	7,85
S	0,15	<0,001
N	0,58	<0,003
O	0,56	No

With the purpose of increasing the high-purity benzene and naphthalene yield, and for destruction of saturated carbohydrates that prevent their complete isolation at fractionation, the obtained hydrotreated mixture was exposed to high-temperature hydrogenation (Table 3). 5 % MoO₃ + zeolite HNaY was used as a catalyst, in the presence of which the process proceeds at temperature 475-500°C,

instead of 600-650°C for known production catalysts containing chrome compounds. Temperature decrease prevents the formation of carbonaceous deposits on the catalyst surface. The results of high-temperature hydrogenation of hydro-treated raw material are given in table 3.

Table 3 – The results of high-temperature hydrogenation of hydrotreated raw material (conditions: 4.0 MPa, 500°C, weight hour space velocity 1.0-1.2 kg/l·h, catalyst 5 % MoO₃+HNAY)

Parameter	Tetralin concentration in raw material, %	
	17,2	6,5
Liquid products yield, % wt.	95,7	96,6
Gas (C ₁ -C ₄) yield, % wt.	6,3	4,2
Hydrogen flow, % wt.	1,0	0,8
Coke content on the catalyst, % wt.	2,4	3,6
Pure product yield at precise fractionation, % wt.		
Benzene	56,1	51,2
Naphthalene	22,1	23,7
<i>Note.</i> Benzene concentration in raw material 40,5-49,0 %.		

It is seen from table 3 that the yield of hydrogenates for both raw material types is rather close (95.7 and 96.6 %, respectively) but coke settling in the raw material catalyst containing the reduced amount of tetralin (6.5 %) is 1.5 times higher in comparison with raw material containing 17.2 %.

At hydrogenation of raw material with higher tetralin content, slight H-donor destruction is observed and naphthalene yield is decreases by 1.6 %. Although, it is not so significant when taking into account the effect of coke formation reduction on the catalyst. Benzene, isolated from hydrogenate by precise fractionation, has crystallization temperature 5.4°C, density $\rho^{20}_4 = 0.8878$, refractive index $n^{20}_D = 1.5011$, sulfur content – less than 0.002 % which conforms to the requirements of standard for high-purity benzene for organic synthesis; naphthalene has crystallization temperature 80°C, sulfur content – less than 0.001 %. For the reason that no full transformation of raw material into benzene, naphthalene and gas per one raw material run occurs, aromatic carbohydrates C₇-C₉ and C₁₁ should return to the process into the amount from 30% as recycle benzene and naphthalene after benzene and naphthalene isolation. At this, benzene and naphthalene yield increases by 1.4 and 1.9% for both raw material types, respectively, due to hydrodealkylation and hydrocracking of aromatic carbohydrates.

Thus, it can be said on the basis of the completed studies on studying high-temperature hydrogenation (hydrodealkylation) of the mixture of coal tar pitch distillate fractions and raw coke-chemical benzene that adding the catalyst (0.5 % PdS + Al₂O₃ in the first zone; 380°C, Mo/Ni-Raney catalyst in the second zone) has a positive impact on benzene formation but does not contribute to naphthalene yield.

REFERENCES

- [1] Pevneva I.A., Gorelova O.M., Komarova L.F. Creation of resource-saving technology of processing of stone benzene steel cheese // Polzunovskiyvestnik. 2006. N 2. P. 237-240.
- [2] Romanova N.A., Khrekin A.S., Leontiev V.S. Selection of naphthalene from residues of stone-coal resin by method of re-extract refraction // International Scientific-Research Journal. 2008. N 3(57). Part 4. P. 80-85.
- [3] Voloshchuk T.G. Analysis of the influence of various factors on the quality of stone-coal resin // Science and production of the Urals. 2017. N 13. P. 9-13.
- [4] Kairbekov Zh.K., Maloletnev A.S., Smagulova N.T., Sabitova A.N. High-temperature hydrogenation of coke chemical raw materials // Chemical Journal of Kazakhstan. 2016. N 3(55). P. 187-192.

Резюме

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ТАС КӨМІР ШАЙЫРЫНЫҢ ДИСТИЛЛЯТТЫ ФРАКЦИЯЛАРЫ МЕН ШИКІ КОКСОХИМИЯЛЫҚ БЕНЗОЛ ҚОСПАСЫН ЖОҒАРЫ ТЕМПЕРАТУРАДА ГИДРОГЕНИЗАЦИЯЛАУ (ГИДРОДЕАЛКИЛДЕУ)

Тас көмір шайырының дистилляты және шикі коксохимиялық бензол қоспасының жоғары температуралық гидрогенизациясын жүргізудің негізгі технологиялық параметрлері жасалды. Су буы қатысында алдын ала тазаланған шайырдың қ.т. 180-230 °С фракциясы мен шикі коксохимиялық бензол қоспасының гидрогенизациялық процесінің қолайлы жағдайлары анықталды. 5 % MoO_3 + цеолит HNaY катализаторы қатысында гидротазаланған қоспасын жоғары температуралық гидрогенизациялап кристаллдану температурасы +5,35-5,45⁰С, күкірт мөлшері 0,002% болатын тазалығы жоғары бензол алынды.

Түйін сөздер: коксохимиялық шайыр, катализаторлар, бензол, нафталин, гидрогенизация.

Резюме

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ВЫСОКОТЕМПЕРАТУРНАЯ ГИДРОГЕНИЗАЦИЯ (ГИДРОДЕАЛКИЛИРОВАНИЕ) СМЕСИ ДИСТИЛЛЯТНЫХ ФРАКЦИЙ КАМЕННУГОЛЬНОЙ СМОЛЫ И СЫРОГО КОКСОХИМИЧЕСКОГО БЕНЗОЛА

Разработаны основные технологические параметры проведения высокотемпературной гидрогенизации (гидродеалкилирования) смеси дистиллятных фракций каменноугольной смолы и сырого коксохимического бензола. Определены оптимальные условия процесса гидрогенизации предварительно гидроочищенной смеси фракций каменноугольной смолы и сырого коксохимического бензола с т. кип. 180-230 °С в присутствии водяного пара. Путем высокотемпературной гидрогенизации гидроочищенной смеси в присутствии катализатора 5 % MoO_3 + цеолит HNaY получен высокочистый бензол с температурой кристаллизации +5,35-5,45⁰С, содержанием серы 0,002%.

Ключевые слова: коксохимическая смола, катализаторы, бензол, нафталин, гидрогенизация.