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CATALYTIC PROCESSING OF A MIXTURE OF DISTILLATE FRACTIONS OF COAL TAR AND CRUDE COKING BENZENE

Abstract. It was shown that the yield of benzene increases by 1.4 and yield of naphthalene increases by 1.9%, respectively, due to hydrodealkylation and hydrocracking of aromatic hydrocarbons as a result of high-temperature hydrogenation of a mixture of crude benzene and naphthalene fraction after recycle of residue in the composition of products with residue recycle. It was established that the yield of a product of hydrogenation increases up to 98.2% with hydrogenation of hydrotreated feedstock with the addition of residue after naphthalene extraction compared with 97.0% with hydrogenation of hydrotreated feedstock.

Key words: coke-chemical tar, semi-coking, tetralin, tar fractions with boiling points up to 180, 180-230 and 230-280°C, naphthalene, benzene.

At present, due to the tightening of requirements for the quality of feedstock for organic syntheses, the growing need for benzene and naphthalene, research and experimental work are underway in the countries of near and far abroad to improve the hydrogenation processes of coke-chemical feedstock.

Naphthalene fractions of coal (coke-chemical) tar and technical grades of naphthalene are the objects of research aimed at developing the conditions for their hydrogenation purification of impurities of sulfur compounds, unsaturated hydrocarbons, etc., as well as at obtaining tetralin. However, the resulting tetralin is difficult to extract in its pure form with its low concentration in a product of hydrogenation. Therefore, studies are being carried out in parallel to develop the conditions for hydrogenation making it possible to purify naphthalene with a minimum depth of its hydrogenation.

Studies on the hydrogenation of naphthalene-containing products (crude naphthalene fractions, press runoffs, etc.) were aimed at developing optimal conditions for producing sulfur-free naphthalene and tetralin, as well as at increasing the yield of naphthalene as a result of hydrodemethylation of its homologues contained in the feedstock [1]. It should be noted that the processing of press runoffs by a coke plant is of particular interest, since they do not currently find qualified use.

The hydrocracking reactions of saturated hydrocarbons and hydrodealkylation of aromatic hydrocarbons are intensively developed at high-temperature hydrogenation, carried out at a temperature of 500°C and higher, along with the removal of sulfur-, oxygen-, and nitrogen-containing compounds. As a result, the

naphthalene yield and its concentration in the products of hydrogenation increases as compared with the feedstock, the technology of its extraction is simplified. In particular, it becomes possible to apply the method of precision fractional distillation to obtain 99% and cleaner naphthalene with a high degree of recovery from the potential. Hydrogenates containing 82-85% of naphthalene, 0.3-0.5% of tetralin and 0.0031-0.0017% of sulfur were obtained when hydrogenating naphthalene fractions of the Zaporozhye Coke Plant and Gubakha Coke Plant (400-550°C, 5 MPa, feed space velocity is 0.5 kg/l·h, gas supply containing 50% of H₂ is 1.5 m³/kg, Al-Co-Mo catalyst, steam supply is 15% for feedstock). The yield of a product of hydrogenation, containing 90.8% of naphthalene, 0.4% of tetralin and 0.0015% of sulfur was 96.5% when hydrogenating processing naphthalene tar fraction of the Novolipetsk Metallurgical Plant in similar conditions [1]. It was shown that, naphthalene practically does not hydrogenate at a temperature of 550°C, but demethylation reactions of methylnaphthalenes intensively proceed.

It was found in the paper [2] that catalytic hydrogenation of a mixture of crude benzene and naphthalene fraction of coke-chemical tar under a pressure of 5 MPa (hydrogen-containing gas contained 50-55% of H₂) and a temperature of 560-580 °C over the Al-Co-Mo catalyst produces a product of hydrogenation for complete extraction of aromatic hydrocarbons using precision fractional distillation. Similar results were obtained when using the MoHNaY zeolite-containing catalyst, but at a lower temperature of 475 °C [3-5]. The presence of large hydrogen resources at the Kazakhstan Coke Plant determines the prospects for the widespread introduction of processes for the production of sulfur-free naphthalene, high-purity benzene, tetralin and other hydrogenation processing of coal (coke) tar. The prospect of the implementation of this direction on an industrial scale is due to the availability of industrial equipment of the necessary capacity, produced by the enterprises of Kazakhstan, which is significant, since it does not require additional investments in the creation of the mechanical-engineering base.

This article is concentrates on the development of processes for the catalytic hydrogenation of crude naphthalene fractions of coal tar of the Kazakhstan Coke Plant to obtain high-grade sulfur-free naphthalene, high-purity benzene for organic syntheses, as well as to increase the yield of naphthalene.

EXPERIMENTAL PART

The used feedstock was a mixture in a mass ratio of 3:1 of crude coke-chemical benzene and naphthalene fraction with a boiling point of 180-230°C of coal tar obtained at the enterprise SaryArkaSpetskoks JSC (Karaganda, Republic of Kazakhstan).

Hydrogenation was carried out in a flow laboratory high-pressure unit with a hollow reactor with a volume of 0.25 dm³ with an agitator (figure 1). The feedstock in a mixture with ground up catalyst were placed in a reactor, which was previously purged with argon at an initial pressure of 4 MPa. Heating of the reactor was turned on, and upon reaching 150 °C an agitator was turned on too. The

temperature was measured with a thermocouple and automatically maintained to an accuracy of $\pm 2^{\circ}\text{C}$. The group hydrocarbon composition of the feedstock and the resulting products of hydrogenation were determined on the CHROMOTEK chromatograph (Germany), the sulfur content was determined using a POST LEKI P1437 device (Germany).

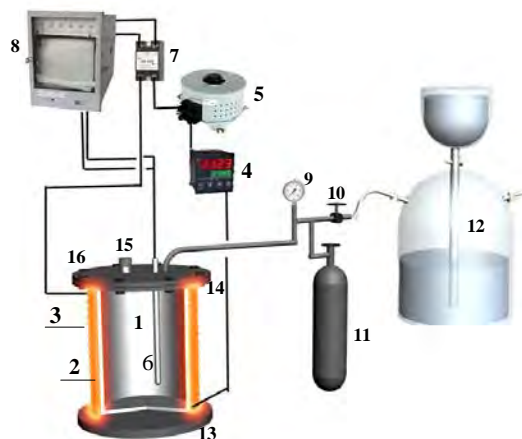


Figure 1 –
The scheme of the laboratory flow high pressure unit:
1 – reactor; 2 – insert; 3 – heater;
4 – ammeter; 5 – voltage regulator;
6 – thermocouple (chromel – copel);
7 – relay; 8 – KSP-4; 9 – pressure gage;
10 – fine adjustment valve;
11 – cylinder with hydrogen (or inert gas);
12 – gas meter; 13 – agitator;
14 – sealing device; 15 – plug;
16 – sealing bolts

RESULTS AND DISCUSSION

Experiments on the hydrogenation of a mixture of benzene: naphthalene fraction = 3:1 (characteristic of which was as follows (wt.%): saturated hydrocarbons 2.9; benzene 47.6; toluene 12.8; xylenes 3.8; ethylbenzene 0.9; C9 aromatic hydrocarbons 3.6; tetralin + methyltetraline 15.8; naphthalene 10.2; 2-methylnaphthalene 0.9; 1-methylnaphthalene 0.1; other compounds 4.1; sulfur content <0.001) were carried out at 4, 0-5.0 MPa, preferably 4.0 MPa, temperature 400-580°C, preferably 450 °C, ratio of H_2 :feedstock = 12:1 (mol), Mo-containing catalyst on HNaY zeolite. To increase the yield of a product of hydrogenation and improve the quality of benzene and naphthalene, the feedstock was preliminarily subjected to ozonation for 30, 60, 90 minutes, preferably 60 minutes, at 20°C and atmospheric pressure. Ozonation was carried out on a PV-5 laboratory ozonizer at 20°C and atmospheric pressure in a bubble-type reactor with a continuous supply of an ozone-air mixture (2.16 mol% of ozone) with rates of 0.25 and 2.0 ml/min [5]. Considering the results of studies [4] to determine the effect of ozonation on the hydrogenation process of the semi-coking tar of Shubarkol coal, 60 minutes were chosen as the duration of ozonation. Then the ozonized mixture of crude coke-chemical benzene and naphthalene tar fraction was subjected to high-temperature hydrogenation. The results of high-temperature hydrogenation of preliminary ozonated feedstock are shown in table 1.

Table 1 shows that the deposition of coke on the catalyst during the process at 450°C is 1.2% less than at 525°C. However, when hydrogenating the feedstock at 525°C, an increase in the naphthalene yield by 1.6% and a yield of a product of

Table 1 – Results of high-temperature hydrogenation of preliminary ozonated feedstock (4,0 MPa, ozonation time is 60 minutes, benzene:naphthalene fraction = 3:1, H₂:feedstock = 12:1 (mol), Mo-containing catalyst on HNaY zeolite)

Indicator	Temperature, °C	
	450	525
Liquid yield, wt. %	93.8	96.6
Gas yield (C ₁ –C ₄), wt. %	5.2	3.1
Hydrogen consumption, wt. %	1.0	0.8
Coke content on catalyst, wt. %	2.4	3.6
Yield of purified products with precision fractional distillation wt. %:		
benzene	56.0	51.2
naphthalene	22.3	23.9

hydrogenation of 96.6% compared to 93.8% at 450°C was observed. Precision fractional distillation was used to extract commercial benzene and naphthalene from a product of hydrogenation obtained at 525°C. The head fraction was distilled from the a product of hydrogenation, and then benzene, toluene, fractions with a boiling point of 120-150 and 150-180°C (solvents) and naphthalene were extracted.

The products obtained during distillation had the following quality indicators: naphthalene salts – crystallization temperature was of +78.6°C and sulfur content was less than 0.0002%. The crystallization temperature of benzene was +5.41°C, density $\rho_4^{20} = 0.8783$, iodine value was less than 0.05 g J₂/per 100 g of a product, sulfur content was 0.00014%, which meets the requirements of GOST 9572-93 for high-purity benzene for organic synthesis.

The aromatic hydrocarbons C₇-C₉ and C₁₁ should return to the process in the amount of ~ 25-30% in the form of recycled material after extraction of benzene and naphthalene, since feedstock it is not fully converted to benzene, naphthalene and gas during its one pass.

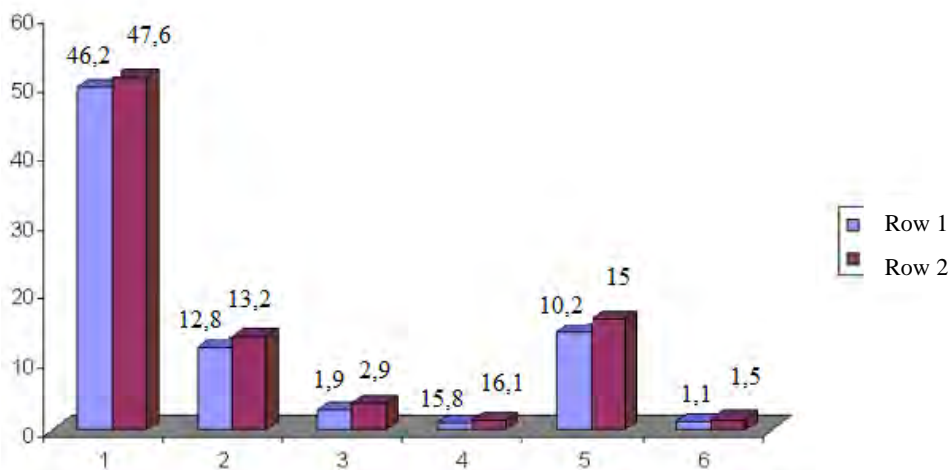
The results of high-temperature hydrogenation of a mixture of crude coke-chemical benzene and naphthalene fraction (3:1) after recycle of residue are shown in table 2 and figure 1.

Table 2 shows that an increase in the yield of a product of hydrogenation was noted – 98.2% with the hydrogenation of hydrotreated feedstock with the addition of residue after naphthalene extraction, compared to 97.0% with hydrogenation of hydrotreated feedstock. The gas yield during hydrogenation of hydrotreated feedstock with the addition of residue after naphthalene extraction is 1.2 wt. %. And also coke content on catalyst increases from 0.6 wt. to 3.6 wt. % Hydrogen consumption during hydrogenation of hydrotreated feedstock with the addition of residue after naphthalene extraction is 0.8 wt. %.

Table 2 – Results of high-temperature hydrogenation of a mixture of crude coke-chemical benzene and naphthalene fraction after recycle of residue

Indicator	Hydrotreated feedstock	Hydrotreated feedstock + residue after naphthalene extraction
Liquid yield, wt. %	97.0	98.2
Gasyield (C ₁ –C ₄), wt. %	2.2	1.2
Hydrogen consumption, wt. %	0.2	0.8
Coke content on catalyst, wt. %	0.6	3.6

Figure 2 shows that the yield of benzene increases by 1.4 and yield of naphthalene increases by 1.9%, respectively, due to hydrodealkylation and hydrocracking of aromatic hydrocarbons in the composition of products with residue recycle.



row 1 – hydrotreated feedstock; row 2 – mixture (75:25) of hydrotreated feedstock and residue after naphthalene extraction. 1 – benzene; 2 – toluene; 3 – decalin and methylindan; 4 – tetralin; 5 – naphthalene; 6 – methylnaphthalenes.

Figure 2 – Chemical composition of high-temperature hydrogenation products of a mixture of crude benzene and naphthalene fraction after residue recycle (wt. %)

Conclusion. Thus, it was shown that the yield of a product of hydrogenation increases up to 98.2% with hydrogenation of hydrotreated feedstock with the addition of residue after naphthalene extraction compared with 97.0% with hydrogenation of hydrotreated feedstock. This increase is due to hydrodealkylation and hydrocracking of aromatic hydrocarbons.

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Резюме

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ТАС КӨМІР ШАЙЫРЫНЫҢ ДИСТИЛЛЯТТЫҚ ФРАКЦИЯСЫ МЕН ШИКІ КОКСОХИМИЯЛЫҚ БЕНЗОЛ ҚОСПАСЫН КАТАЛИТИКАЛЫҚ ӨНДЕУ

Тас көмір шайырының дистилляттық фракциясы мен шикі коксохимиялық бензол қоспасын қалдықты рециркулирлеуден кейін жоғары температураларда гидроөңдеу, қалдықты рециркулирлеу арқылы алынған өнімдердің құрамында бензол шығымын 1,4 %-ға нафталин шығымын 1,9 %-ға ароматты көмірсутектердің гидрокрекингтелуі және гидроделалкилирленуі нәтижесінде артатындығын көрсетті. Нафталинді бөліп алғаннан кейінгі қалдықты, гидротазаланған шикізатқа қайта қосып гидрогендеу арқылы гидрогенизат шығымының гидротазаланған шикізатты гидрогендеумен салыстырғанда 97,0 %-дан 98,2 %-ға артатындығы орныналды.

Түйін сөздер: коксохимиялық шайыр, жартылай кокстеу, тетралин, 180 дейін, 180-230 және 230-280°C қайнайтын шайыр фракциялары, нафталин, бензол.

Резюме

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КАТАЛИТИЧЕСКАЯ ПЕРЕРАБОТКА СМЕСИ ДИСТИЛЛЯТНЫХ ФРАКЦИЙ КАМЕННОУГОЛЬНОЙ СМОЛЫ И СЫРОГО КОКСОХИМИЧЕСКОГО БЕНЗОЛА

Показано, что в результате высокотемпературной гидрогенизации смеси сырого бензола и нафталиновой фракции после рециркуляции остатка в составе продуктов увеличивается выход бензола на 1,4 и нафталина на 1,9% соответственно за счет гидроделалкилирования и гидрокрекинга ароматических углеводородов. Установлено, что при гидрогенизации гидроочищенного сырья с добавлением остатка после выделения нафталина увеличился выход гидрогенизата до 98,2 % по сравнению с 97,0 % при гидрогенизации гидроочищенного сырья.

Ключевые слова: коксохимическая смола, полукоксование, тетралин, фракции смолы с т. кип. до 180, 180-230 и 230-280°C, нафталин, бензол.