Conversion of straight-run gas-condensate benzenes into high-octane gasolines based on modified ZSM-5 zeolites

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Abstract. This paper describes the conversion of straight-run benzene of gas condensate into high-octane gasoline based on zeolite catalyst ZSM-5, modified in binary system oxide-based Sn (III) and Bi (III). It was defined that the introduction of the binary system oxide-based Sn(III) and Bi (III) into the basic zeolite results in the 2-fold increase of its catalytic activity. High-octane gasoline converted from straight-run benzene is characterized by a low benzol content in comparison to the high-octane benzenes produced during the catalytic reforming.

1. Introduction
Today one of the basic processes in petroleum refining is catalytic reforming, i.e. a technological process where high-octane benzenes are produced from straight-run gasoline. The catalytic reforming proceeds at 450-500 °C in a hydrogen-containing gas environment based on alumino-platinum catalysts. Alumino-platinum catalyst reforming is rather sensitive to different micro-impurities, therefore, raw hydrocarbons should be preliminarily subjected to high purification from sulphur-, oxygen and nitrogen compounds. Produced high-octane benzene in catalytic reforming based on alumino-platinum catalysts includes up to 50-70 % aromatic hydrocarbon and up to 7-15% benzol, which, in this case, requires additional separation of arene and especially benzol so as to produce finished motor gasoline from liquid reforming products [1-2].

In this respect, the most practical process is zeoforming[3] on zeolite-containing catalysts-ZSM-5 type for production of high-octane benzenes with low aromatic hydrocarbon content. Zeolites have a unique property [4]: they have high activity and selectivity in such reactions as dehydration, cracking isomerization, oligomerization and dehydrocyclization of various hydrocarbon source groups due to their unique microporous structure (micropore size-0.5-0.8 nm) and molecular and size analysis properties. The application of zeolite-containing catalysts excludes the preliminarily raw material hyrofining.

The conversion process of straight-run gasoline based on zeolite catalysts is quite different from that of catalyst reforming as the first produces high-octane benzene with low benzol content (not more than 1-3%), total aromatic hydrocarbon content-not more than 30-35 % and sulphur- not more than 0.05-0.10 mass %. It should also be noted that preliminarily raw hydrocarbon hydrofiningis excluded due to the application of different modified zeolite-containing catalysts [5-9].

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The target of this research is to investigate the conversion process of straight-run benzene-gas condensate into high-octane gasoline based on zeolite catalysts, modified by binary systems on complex tin and bismuth oxides.

2. Experimental procedure and applied methods
High-silica zeolites (HSZ-G) with high silic-module 50 was produced from alkaline aluminosilicic gel at 175-180°C during 3-4 days applying organic structure-forming additive hexamethylenediamine as template. After crystallization synthesized zeolites are flushed out in distilled water several times, dried at 110°C and then calcinated at 550°C for 6 hours. Reactive HSZ-G zeolites were converted in 1m NH₄NO₃ water solution at 90°C for 2 hours and further drying-out at 110°C and calcinating at 550°C for 6 hours (Na₂O content in decactionated zeolites is less than 0.01%). Modified HSZ-G is produced by liquid infiltration of 0. 1 M HCl solution, containing tin and bismuth oxides in the following element ratio: Sn/Bi = 10:1, to zeolite saturation capacity[10]. Complex tin and bismuth oxides are produced by coprecipitated hydroxide calcination. After this, zeolites with compound Sn and Bi oxide coating (1-5mass%) are dried at 110°C and calcinated at 550°C for 6 hours.

To identify the produced zeolite catalysts HSZ-G, infrared spectroscopy (infrared Fourier spectroscopy Nicolet 5700) and X-ray phase analysis (X-ray unit DRON-3-Mo-anode; Ni-filter) were applied. Infrared-spectrum was conducted within the range of 450-2000 cm⁻¹. The X-ray of synthesized samples showed lines with the following interplanar spacing (d, Å): 11.05, 10.19, 4.26, 4.07, 3.87, 3.83, 3.73, 3.66, typical for high-silica zeolites ZSM-5 type. Produced zeolite infrared -spectra showed absorption bands at 1000–1200, 795–800, 451 and 541 cm⁻¹, as in this range, the absorption bands (a,b) of the major oscillations of AlO₄, SiO₄ tetrahedron skeleton are found. Intense absorption band of 1000-1200 cm⁻¹ is conditioned by antisymmetric stretch vibrations of TO₄ tetrahedron; band of 794 cm⁻¹ is related to the valence vibration in which SiO₄ tetrahedron is the basic one, whereas, the position of this band influences the silicate module (SiO₄/Al₂O₃) in zeolite scaffold. Absorption band of 541 cm⁻¹ is stipulated by five-membered rings in the zeolite skeleton and indicates the fact that this zeolite is of the ZSM group. All synthesized HSZ-G samples according to infrared spectroscopy and X-ray phase analysis could be related to zeolite group.

Conversion of straight-run benzene fraction of gas condensate at 70–170°C based on modified zeolite catalysts was performed in a circulating catalytic unit with a fixed-bed catalyst (reactor volume 8 cm³) within the temperature interval of 350–425°C at feed space velocity of raw material2 hrs⁻¹, atmosphere pressure and exposure for each fixed temperature process was 1 hour.

The analysis of gaseous hydrocarbons was performed in the stainless steel packed column (length-3m; inner diameter-3mm), filled up with 5% NaOH to Al₂O₃ (fraction- 0.25–0.50 mm), liquid hydrocarbons- in the quartz-glass capillary column (100 m. x 0.25 mm. x 0.25 mkm) with a fixed-bed of stationary phased ZB-1. Quantitative analysis of gaseous and liquid conversion products of straight-run benzene was performed by the following method: gas chromatography via hardware and software package of gas chromatographer “Chromatek-kristall 500”, error-correcting by “Chromatek Analitik” program. Positional error of gaseous and liquid hydrocarbons by chromatography method is ±2.5%.

According to the hydrocarbon composition group, straight-run benzene fraction of 70 – 170°C gas condensate includes: 35 mass% n-paraffine,40 % isoalkane, 20 % naphthenes and 4 % arenes. The octane number of straight-run benzene fraction of 70 – 170°C gas condensate is 65 points in investigated method (IM). The catalytic activity unit was the number of produced arenes from straight-run benzene.

3. Results and discussion
The straight-run benzene conversion temperature effect on virgin zeolite catalyst HSZ-G activity showed that with a rise in process temperature from 375 to 425°C and straight-run benzene feed space velocity of 2 hrs⁻¹ high-octane gasoline yield from straight-run benzene decreases from 63.2 to 54.8 % due to the increasing conversion intensity of raw hydrocarbons (table1, figure1). Firstly, gaseous product yield increases from 34.8 at 375°C to 45.1 % at 425°C, mainly paraffins C₃–C₄, while arene
C<sub>6</sub>–C<sub>9</sub> content in liquid products increases from 23.4 to 26.7%. Toluene and xylene are predominant in the arene group, where, with a rise in process temperature from 1.5 and 1.2 at 375°C to 2.0 and 1.3% at 425°C benzol and olefine C<sub>5</sub>+ content increases, respectively; whereas, naphthene and n/isoparaffin hydrocarbon C<sub>5</sub>+ content decreases with a rise in temperature (Table 1). Among the gaseous products of the straight-run benzene conversion process the predominant products are propane and butane, where with a rise in temperature from 375 to 425°C the propane concentration among other gaseous products increases from 57.6 to 59.3%; while the total content of propane and butane among gaseous products is 93–97% and methane and ethane content- not more than 3–7%.

Introducing tin and bismuth oxides into HSZ-G (samples: 1% (Sn:Bi = 10:1)/99% HSZ-G) significantly increases the content of arenes up to 32.9–43.8% in straight-run benzene conversion process liquid products and the decreases the content of iso-paraffin and naphthene hydrocarbons from 27.4–34.9% and 18.0–21.8%, respectively. High-octane benzene yield in the straight-run benzene conversion process with a rise in temperature from 375 to 425°C and feed space velocity of 2 hrs.⁻¹, based on these catalysts, changes from 62.6 to 49.3%, while octane number increases with a rise in temperature from 93.1 to 96.3 units according to IM.

The most active of investigated samples in the conversion of straight-run benzene into high-octane gasoline was the catalyst 1% (Sn:Bi = 10:1)/99% HSZ-G. For example, based on the catalyst 1% (Sn:Bi = 10:1)/99% HSZ-G with a rise in temperature in straight-run benzene conversion process from 375 to 425°C liquid product yield decreases from 60.5 to 52.4%, while octane number of these liquid products increases from 94.6 to 95.3 units according to IM. With a rise in temperature arene and benzol content in liquid products of straight-run benzene conversion process increases from 35.0 to 43.8% and from 2.1 to 3.7%, respectively.

### Table 1. Composition of conversion products of straight-run benzene gas condensate based on catalysts:

| Item                     | Catalyst type       |
|--------------------------|---------------------|
|                          | 1                   | 2                   | 3                   | 4                   |
| Temperature, °C          | 375                 | 400                 | 425                 | 375                 | 400                 | 425                 | 375                 | 425                 |
| Gas phase, mass %        | 36.8                | 43.0                | 45.1                | 39.5                | 45.9                | 47.6                | 37.4                | 45.5                | 50.7                | 13.2                | 18.7                |
| Liquid phase, mass %     | 63.2                | 57.1                | 54.8                | 60.5                | 54.1                | 52.4                | 62.6                | 54.5                | 49.3                | 86.8                | 81.3                |
| Gas phase composition, mass% |          |                   |                     |                     |                     |                     |                     |                     |                     |                     |                     |
| Methane                  | 0.5                 | 0.9                 | 1.6                 | 0.3                 | 0.5                 | 1.0                 | 0.3                 | 0.5                 | 1.0                 | 0.2                 | 0.5                 |
| Ethane                   | 1.5                 | 2.3                 | 3.5                 | 1.3                 | 2.1                 | 3.3                 | 1.3                 | 2.1                 | 3.3                 | 1.1                 | 1.9                 |
| Ethylene                 | 0.6                 | 0.9                 | 1.3                 | 0.4                 | 0.7                 | 0.9                 | 0.4                 | 0.6                 | 1.0                 | 1.8                 | 4.4                 |
| Propane                  | 57.6                | 58.5                | 59.3                | 57.4                | 58.9                | 61.4                | 56.0                | 59.5                | 61.7                | 52.6                | 47.0                |
| Propylene                | 1.5                 | 2.0                 | 2.7                 | 0.8                 | 1.5                 | 1.8                 | 0.7                 | 1.2                 | 1.8                 | 3.9                 | 10.3                |
| Iso-butan                | 19.6                | 18.2                | 16.1                | 22.5                | 20.6                | 17.9                | 23.0                | 20.6                | 17.8                | 19.7                | 15.1                |
| n-butan                  | 17.2                | 15.2                | 13.3                | 17.3                | 15.5                | 13.3                | 18.1                | 15.3                | 13.0                | 17.1                | 13.6                |
| Iso-butene               | 1.3                 | 1.6                 | 1.8                 | 0.1                 | 0.3                 | 0.4                 | 0.3                 | 0.3                 | 0.4                 | 3.5                 | 7.1                 |
It should be noted that the produced high-octane gasoline from straight-run benzene based on zeolite catalysts modified 1–3 % (Sn:Bi = 10:1)/99-97 % HSZ-G fully complies with the corresponding motor gasoline “Evro-4 and 5”. Further increase of tin and bismuth content (catalyst 5 % (Sn: Bi = 10:1)/95 % HSZ-G ) significantly decreases the arene content from 12.6–15.0 % in liquid products of the straight-run benzene conversion, while arene formation selectivity is not more than 30 %.

| Liquid phase composition mass % | 23.4 | 26.7 | 26.7 | 35.0 | 40.0 | 43.8 | 33.8 | 32.9 | 43.0 | 13.0 | 12.6 |
|---------------------------------|------|------|------|------|------|------|------|------|------|------|------|
| Arenes                          | 1.5  | 2.0  | 2.0  | 2.1  | 3.2  | 3.7  | 1.9  | 1.9  | 4.2  | 0.4  | 0.6  |
| Benzol                          | 41.8 | 40.7 | 40.7 | 34.0 | 31.6 | 28.5 | 34.9 | 34.6 | 27.4 | 38.6 | 37.3 |
| Isoalkanes                      | 19.1 | 18.0 | 17.9 | 21.0 | 18.0 | 18.0 | 21.8 | 21.2 | 18.5 | 30.4 | 28.7 |
| Naphthenes                      | 14.5 | 13.3 | 13.4 | 8.6  | 9.0  | 8.2  | 8.4  | 10.0 | 8.2  | 15.2 | 16.3 |
| Alkanes                         | 1.2  | 1.3  | 1.3  | 1.4  | 1.3  | 1.5  | 1.2  | 1.3  | 3.0  | 2.8  | 5.0  |
| Olefines                        | 89.7 | 91.7 | 90.5 | 94.6 | 94.3 | 95.3 | 93.1 | 93.3 | 96.3 | 79.7 | 80.8 |

**Figure 1.** Yield dependence of arene from process temperature

Temperature C⁰ aromatic hydrocarbons HSZ-G

Thus, introducing tin and bismuth oxide mixture as 1–3 % (catalysts: 1–3 % (Sn:Bi = 10:1)/99-97 % HSZ-G) into zeolite ZSM-5 significantly increases the catalyst activity in the conversion process of straight-run benzene into high-octane gasoline. In this case, produced zeolites modified by complex tin and bismuth oxide mixture already show a high aromatic activity at the temperature from 375–400 °C. at the temperature reaction of 375 °C for sample 1 - 1 % (Sn:Bi = 10:1)/99 % HSZ-G , the aromatic hydrocarbon yield is 35 %, which is 1.5 times higher than in the case of catalyst HSZ-G at
the same temperature. This proves the perspective application of zeolite catalysts, modified by complex tin and bismuth oxide mixture in the conversion process of straight-run benzene into high-octane gasoline.

4. Conclusion
Thus, introducing modified complex additive based on tin and bismuth oxide mixture into zeolite ZSM-5 significantly increases the catalyst activity in the conversion process of straight-run benzene into high-octane gasoline, in comparison to HSZ-G feed. The most perspective are HSZ-G catalysts, modified 1–3 % complex tin and bismuth oxide mixture.

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