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## HYDROFINING OF THE HEAVY FRACTION OF CATALYTIC CRACKING GASOLINE, PRODUCING FROM MIXTURE OF AZERBAIJAN OIL

**Abstract:** The process of selective hydrofining of catalytic cracking gasoline by separation of the wide fraction on light – b.s.-130°C and heavy b.e.-130°C with following hydrofining of the heavy fraction on industrial catalysts have been studied. It have been determined that by mixing of the light and hydrofined heavy fractions by balance and introduction of catalytic cracking gasoline in composition of commercial gasoline content of total sulphure is decreased from 230 up to 30 ppm.

**Key words:** hydrofining, catalytic cracking, heavy fraction, Azerbaijan oils, mercaptane sulphure, thiophene sulphure.

**Language:** English

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### Intorduction.

A modern automobile gasolines must satisfy to demands of the world standards by content of sulphure no more than 30-10 ppm. benzene and aromatic hydrocarbons – no more than 1 and 35% correspondingly, olefins no more than 14%. Introduction in composition of gasolines up to 10-15% oxygen containing additives (oxyhenates) is compulsory.

For productin of gasolines, corresponding to modern ecological demands it is necessary improvement of quality of automobile gasolines base components – gasoline of catalytic cracking, riforming by content of sulphuric compounds, benzene and total aromatic hydrocarbons.

The gasoline of catalytic cracking (GCC) is related to the most high sulphuric component of commercial gasolines. For production of gasoline with low content of sulphure it is necessary or

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preliminary hydrofining of vacuum gas oil (fraction 350-500°C) being a raw material of catalytic cracking, or hydrofining of GCC directly before of mixing in block of compound-filling [1,2].

The most preferable version is hydrofining of gasoline fraction of catalytic cracking process. But in composition of GCC both a big amount of sulphuric compounds and a highoctane olefin hydrocarbons, which secure the high octane number (ON) of gasoline is contained [3].

Proceed from that, the hydrofining process of the fraction GCC leads to not only decrease of sulphuric compounds content, but also to sharp of

gasoline ON owing to saturation of highoctane olefin hydrocarbons [4].

The aim of this work is lowering of the total sulphure content in GCC by maintenance of ON by separation of gasoline on the light and heavy fractions with subsequent hydrofining only of heavy fraction of GCC.

### Experimental part

At this known that content of total sulphure is normally increased by increase of molecular mass of hydrocarbon fractions. Below the distribution of sulphuric compounds in gasoline fractions, produced from mixture of Azerbaijan oils is presented:

| Gasolines                      | Sulphure (% mass) |
|--------------------------------|-------------------|
| Straight-run gasoline          | 0.012-0.015       |
| Gasoline of catalytic cracking | 0.0220-0.0260     |
| Gasoline of coking             | 0.1450-0.1500     |

As a subject of research the GCC being a base supplier of sulphure in commercial gasoline have been used. Introduction of GCC in automobile gasoline in amount 35-45% lead to increase of sulphure content over admissible values 30-10 ppm, corresponding to international identifications.

Chromatographic analysis of GCC have been made on chromatograph Autosistem XL (Perkin Elmer) by ASTM method. Analysis of total sulphure of liquid samples was made by roentgenofluorescence method by ASTM-D4294 methodic. Content of mercaptane sulphure have been determined by adsorption of mercaptanes with solution of sodium hydroxide with following potentiometric titration of mercaptides of alkaline metals by nitrogen-acid ammoniates silver.

In hydrofining process simultaneously on a level with removal of sulphuric compounds the process hydrogenation of highoctane unsaturated hydrocarbons proceeds, that leads to decrease of gasoline octane number and change of it in sort of

low-qualitative fuel component. Hydrodesulphurization degree of sulphuric compounds (%) have been determined by relation of difference content of sulphure in raw material and hydrogenate to sulphure in raw material. Hydrogenation degree of olefin hydrocarbons (%) also have been determined by relation of difference of olefin content in raw material and hydrogenate to olefins in raw materials.

Octane numbers of GCC and its narrow fractions no M.M. and RM have been determined by motor tests at the plant UIT-65 by comparison of tested sample of fuel with standard (mixture of isooctane with n-heptane) by standard conditions (state standard R52946-2008).

### Results and its discussions

In the table 1 qualitative characteristics of base component of commercial gasoline - GCC, produced at Baku oil processing plant named after H.Aliyev are presented.

Table 1. Quality of catalytic cracking gasoline

| Indices   | Value |
|---|-------|
| Density by 20 <sup>0</sup> C, kg/m <sup>3</sup> | 747   |
| Fraction composition, <sup>0</sup> C            |       |
| b.s.  | 44    |
| 10% is boiled away by t <sup>0</sup> C          | 52    |
| 50% is boiled away                              | 148   |
| 90% is boiled away                              | 197   |
| b.e.  | 211   |
| Content of total sulphure, ppm                  | 230   |
| Content of mercaptane sulphure, ppm             | 30    |
| Group hydrocarbon composition, % mass           |       |
| paraffines                                      | 11.62 |
| Isoparaffines                                   | 48.72 |
| Aromatic  | 17.58 |

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|                      |       |
|----------------------|-------|
| Olefines             | 10.3  |
| Naphtenes            | 9.25  |
| Molecular mass       | 95.7  |
| Octane number (M.M.) | 80-81 |

In GCC the isoparaffines hydrocarbons with strongly branched structure are presented in the most amount up to 49% mass. Total content of paraffin-naphtenes hydrocarbons makes up 69,59%, nonidentified C<sub>10</sub> – up to 2,3 mass.

For maintenance of the octane characteristic GCC have been preliminary fractionated on light – s.b. – 130°C and heavy – b.e. - 130°C, yield of which on initial gasoline made up 60 and 40% vol. correspondingly. Only heavy fraction of GCC – heavy gasoline, containing 440 ppm of total sulphure have been subjected to hydrofining.

Experimentally it have been determined that in the heavy fraction – b.e. - 130°C of GCC above 76.5% of hard-removed thiophene sulphure and small amount – up to 2.8% olefines come in. It is mean, that hydrofining of heavy fraction of GCC b.e. - 130°C may be conducted practically without essential lowering of octane number [5,6]. In the table 2 distribution of sulphuric compounds and olefines in wide, light – b.s. - 130°C and heavy fraction – b.e. - 130°C of GCC are presented.

**Table 2. Distribution of sulphuric compounds in GCC**

| Indices                 | GKK  | b.s.130°C<br>GCC | b.e. 130°C<br>GCC |
|-------------------------|------|------------------|-------------------|
| 1                       | 2    | 3                | 4                 |
| Total sulphure          |      |                  |                   |
| On fraction, ppm        | 230  | 90               | 440               |
| On raw material, % mass | 10   | 23.5             | 76.5              |
| Mercaptane sulphure     |      |                  |                   |
| On fraction, ppm        | 30   | 40               | 15                |
| On raw material, % mass | 100  | 80               | 20                |
| Unsaturated:            |      |                  |                   |
| On raw material, % mass | 10.3 | 15.3             | 2.8               |
| On fraction, % mas      | 100  | 91.0             | 9.0               |
| ONM, p                  | 80   | 82               | 80                |

In light fraction of GCC content of total sulphure makes up to 23.5% and content of easily-removed mercaptane sulphure – 80%/ There are also up to 91% of highoctane unsaturated hydrocarbons from total amount of olefines in GCC that stipulated ON of this fraction – 82 point by M.M.

In heavy fraction of GCC – b.e. 130°C up to 76.5% of total sulphure from raw material – 4410 ppm and small amount of olefines – 2.8% on raw material – is contained.

Proceeding from this the heavy fraction of GCC may be subjected to hydrofining practically without lowering of ON.

As catalyst of hydrofining the industrial alumocobalt-molibdenium catalyst S-12 (Co/Mo) have been used. Catalyst have been subjected to drying in atmosphere of air, blow-down by nitrogen and reduction by hydrogen-containing gas by 480-490°C up to complete removal of moisture.

Experiments have been conducted in flowing reactor by T=200°C, V<sub>vol</sub>=1,0hour<sup>-1</sup>, correlation H<sub>2</sub>:raw material = 1:1 and pressure of hydrogen-containing gas 2,0-2,5 MPa by loading of catalyst 130 sm<sup>3</sup>.

The results by hydrofining of the wide and heavy fraction of GCC are presented in table 3.

**Table 3. Hydrofining of the wide and heavy fraction of GCC by T = 200°C**

| Indices                     | Wide fraction<br>44-211 |        | Heavy fraction 130°C b.e. |        |
|-----------------------------|-------------------------|--------|---------------------------|--------|
|                             | 2.0 MPa                 | 2.5MPa | 2.0 MPa                   | 2.5MPa |
| Sulphure, ppm               |                         |        |                           |        |
| Total                       | 98                      | 90     | 100                       | 60     |
| mercaptane                  | 3.8                     | 2.0    | 5.3                       | 4.8    |
| Degree of hydrogenolysis, % |                         |        |                           |        |
| Total sulphure              | 51.0                    | 61.0   | 77.2                      | 86.4   |

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|                            |      |      |      |      |
|----------------------------|------|------|------|------|
| Mercaptane sulphure        | 87.3 | 93.3 | 82.3 | 68.0 |
| Degree of hydrogenation, % | 95.6 | 96.7 | 10.5 | 11.4 |
| ONM                        | 76.5 | 76.0 | 79.5 | 79.2 |

Result of experiment show that by hydrofining of the wide fraction of GCC practically a full saturation of olefines takes place and loss by ON makes up 4-4.5 points.

Content of total sulphure in heavy fraction b.e. 130°C of GCC is decreased from 440 up to 60 ppm by  $P_{H_2}=2.5\text{MPa}$  and  $T = 200^\circ\text{C}$ . Hydrogenolysis degree of total sulphure makes up 86.4% and exceed a rate of mercaptane sulphure hydrogenolysis.

By mixing balance of 40% heavy fraction with content of sulphure 60 ppm and 60% of light fraction

with content of sulphure 90 ppm content of total sulphure in composition of GCC is decreased from 230 up to 78ppm practically with change of ON.

By introduction of hydrofined GCC in composition of commercial gasoline in amount 35-40% content of total sulphure is decreased up to 30-32 ppm. Hydrogenation degree of olefines in heavy fraction makes up 10.5-11.4% and loss by ON don't exceed 0.5-0.7 points.

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