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## GENERAL DESCRIPTION OF WORK

**Relevance of the topic.** One of the main tasks of the oil refining industry is to produce environmentally friendly automobile gasolines that meet Euro-4, Euro-5 standards, as well as increase their resources due to a sharp increase in demand for motor fuels and environmental pollution problems.

The solution to these problems is possible by creating alternative fuels containing oxygen-containing compounds (oxygenates), among which ethers and low molecular weight aliphatic alcohols occupy a special place, which can be synthesized from virtually any hydrocarbon feedstock - natural gas, coal, etc.

The use of oxygenates in the composition of hydrocarbon fuels increases the efficiency of the engine and reduces the toxicity of exhaust gases. However, a mixture of gasolines with alcohols is characterized by low phase stability and the need to introduce stabilizers into their composition, which leads to increased fuel consumption due to reduced heat of combustion.

It is more economical to use additives in the form of low molecular weight high-octane ethers - methyl tert-butyl (MTBE), methyl tert-butyl (ETBE), isopropyl tert-butyl (iso-PTBE) and diethyl and dimethyl, as a means of oxygenating automobile gasolines - and lowering the temperature of automobile, and gasoline savings in this case reaches 6-7 %. This is explained by a more uniform distribution of detonation resistance among fractions and an increase in the road octane number of gasoline. In addition, when mixing ethers with gasolines, phase separation is not observed, toxic products are not formed, significant engine modification is not required.

The use of the above esters in gasoline makes it possible to obtain high-octane gasoline of promising quality with an octane rating of at least 85 p. by the motor method and 95 p. by the research method based on catalytic cracking and mild reforming gasolines, which will reduce the content of aromatic hydrocarbons, especially benzene, and increase the yield of gasoline, i.e. will provide an opportunity to expand the volume of production of motor gasoline.

Currently, the above esters are prepared on the basis of isobutylene and BBP of catalytic cracking and methanol in the presence of acidic ion-exchange resins, mainly Amberlit-15, which are characterized by thermal instability, non-regeneration, leaching of acids from the catalyst surface, and a high ratio of isobutylene: methanol, which leads to the need for recycling of unreacted components.

When using zeolite-containing catalysts in this process, the above disadvantages are absent. In addition, the use in the synthesis of oxygenates of hydrocarbons with a conjugated double bond (dienes), characterized by significant reactivity compared to hydrocarbons containing one double bond (alkenes), and having characteristic abilities in addition reactions due to the mutual influence of unsaturated carbon atoms in coupled systems will allow to obtain new high-octane ethers - additives to motor gasolines.

In light of the foregoing, the problem of improving the economic indicators of the process for producing high-octane oxygen-containing additives to motor gasolines by using the butane-butylene fraction of catalytic cracking and butane-divinyl fractions of pyrolysis and C<sub>1</sub>-C<sub>3</sub> monohydric alcohols and their mixtures using industrial zeolite catalysts Zeocar-2 and Zeocar-600 is highly relevant, easy to regenerate.

**The object and subject of research** is the preparation of compounds of motor gasoline Euro-4 and Euro-5 with the use of enriched gasoline components and synthesized oxygen-containing additives.

**The aim of the work** is to expand the resources of the raw material base for the production of high-octane additives for motor gasolines by involving the butane-butylene fraction of the catalytic cracking process and the butane-divinyl fractions of the pyrolysis process and C<sub>1</sub>-C<sub>3</sub> monohydric alcohols and their mixtures, developing a formulation of marketable gasolines corresponding to environmental Euro-4, Euro-5 standards using synthesized oxygenates.

**Research Methods.** When performing the work, the following methods were used: chemical (qualitative determination of gasoline fuel indicators in accordance with GOST and ASTM), spectral (IR, NMR), x-ray phase (RF, DTA).

### **The main provisions for the defense:**

- Developed a process for obtaining motor gasolines that meet the environmental standards Euro-4 and Euro-5;
- selected effective catalysts for the synthesis of high-octane additives (oxygenates) to motor gasoline;
- the butane-divinyl pyrolysis fraction is involved in the synthesis of oxygenates in order to expand the raw material resources;
- selected the optimal conditions for the alkoxyalkylation of technical isobutylene, butane-butylene fraction of catalytic cracking and butane-divinyl fraction of pyrolysis with saturated monoatomic alcohols C<sub>1</sub>-C<sub>3</sub> to obtain high-octane additives;
- improved quality of commercial gasoline components - catalytic cracking, reforming, straight-run and coking gasolines;
- formulations of commercial gasolines have been developed that meet the environmental standards Euro-4 and Euro-5, based on gasoline components and synthesized oxygenates.

### **The scientific novelty of the work is:**

- for the first time, the possibility of involving butane-divinyl fractions of pyrolysis in the process of producing a high-octane additive to motor gasoline by alkoxyalkylation with monohydric alcohols C<sub>1</sub>-C<sub>3</sub> has been shown, which will increase its yield (by 3.0-5.2 %), and the octane number (by 8-10 p.) compared with the involvement of catalytic cracking in the butane-butylene fraction;
- the effect of the molecular weight of alcohol on the octane number of the additive from the process of alkoxyalkylation by the butane-butylene fraction of catalytic cracking and the butane-divinyl pyrolysis fraction with C<sub>1</sub>-C<sub>3</sub> alcohols was studied;
- the influence of the conditions of the alkoxyalkylation process of butane-butylene and butane-divinyl fractions with C<sub>1</sub>-C<sub>3</sub> monohydric alcohols on the yield and quality of high-octane additives was studied;
- the possibility of a significant increase in the octane number of the additive due to the involvement of the butane-divinyl pyrolysis fraction with a mixture of C<sub>1</sub>-C<sub>3</sub> alcohols in the alkoxyalkylation process was established;
- the injectivity of high-octane additives obtained in the process of alkoxyalkylation of butane-butylene and butane-divinyl fractions with

C<sub>1</sub>-C<sub>3</sub> monohydric alcohols to gasoline of direct race and catalytic cracking was studied;

– the possibility of expanding raw materials to obtain high-octane additives to motor gasolines through the use of a mixture of C<sub>1</sub>-C<sub>3</sub> alcohols and the butane-butylene fraction of catalytic cracking and the butane-divinyl fraction of the pyrolysis process has been established.

– studied the process of alkoxyalkylation of narrow fractions of GCC, GC and GR with monohydric alcohols.

**Practical value.** The results obtained in the thesis can form the basis of the industrial process for producing high-octane oxygen-containing additives, which will expand raw materials and increase the octane number of motor gasolines by involving the C<sub>1</sub>-C<sub>3</sub> alcohols and butane-butylene and butane-divinyl fractions from catalytic cracking processes and pyrolysis. The introduction of the obtained oxygenates in an amount of 10-15 % will improve the environmental characteristics of gasoline fractions and obtain, on their basis, commercial automobile gasolines of the A-93 and A-95 grades that meet the environmental standards of Euro-4, Euro-5.

**Publications.** Based on the materials of the dissertation, 40 scientific papers were published, including 26 articles and 14 theses.

**Approbation of work.** The main results of the work were presented and reported at the following conferences, symposia and meetings: IX Conference of Young Scientists on Petrochemistry dedicated to the 100<sup>th</sup> Birth Anniversary of Academician Kh.M. Minachev, Zvenigorod, October 7-10, 2008; VII Baku International Mamedaliyev Petrochemical Conference on Petrochemistry, dedicated to the 80<sup>th</sup> anniversary of the Institute of Petrochemical Processes of the National Academy of Sciences of Azerbaijan, September 29-October 2, Baku, 2009; Doc. Symposium “Catalysis in solving the problems of petrochemistry and oil refining”, Baku, September 28-30, 2010; Republican Scientific Conference, dedicated 100<sup>th</sup> anniversary of academician A.M.Quliyev, June 14, 2012; VIII Baku International Mamedaliyev Conference on Petrochemistry, October 3-6, 2012; VIII Baku International Mamedaliyev Conference on Petrochemistry, October 3-6, 2012; 1<sup>st</sup> International Chemistry and Chemical Engineering

Conference, Baku, Azerbaijan, April 17-21, 2013; Materials of the republican scientific-practical conference dedicated to the 100<sup>th</sup> anniversary of academician S.D. Mehdiyev, Baku, II volume, 2014; IX Baku International Mamedaliyev Conference on Petrochemistry, October 4-5, 2016, International scientific and technical conference “Petrochemical synthesis and catalysis in complex condensed systems” dedicated to the 100<sup>th</sup> anniversary of academician B.K. Zeynalov, Baku, June 29-30, 2017; Akademik Vahab Əliyevin 110 illik yubileyinə həsr olunmuş “Neft emalı və neft kimyasının innovativ inkişaf perspektivləri” adlı Beynəlxalq elmi-praktiki konfrans, 9-10 oktyabr 2018, Bakı; The International Scientific Conference “Actual Problems of Modern Chemistry” Dedicated to the 90<sup>th</sup> Anniversary of the Academician Y.H. Mammadaliyev Institute of Petrochemical Processes, October 2-4, 2019, Baku.

**Place of dissertation work.** The dissertation was carried out in accordance with the research plan of the Institute of National Economy and Politics of the National Academy of Sciences of Azerbaijan (State registration number 0106 Az 00012).

**Personal participation of the author.** The author outlines the main goals of the study and the tasks for their achievement, defines the areas of research, carried out processing, systematization and discussion of the results. The author also took a direct part in the formulation and conduct of laboratory and pilot tests.

**The structure and scope of the dissertation.** The dissertation is presented on 336 pages, consists of an introduction, 7 chapters, including 130 tables, 14 figures, 13 charts, a list of references from 319 items and is 352575 characters (without tables, figures, charts and list of literature) (introduction 18973, chapter I 89239, chapter II 13971, chapter III 22760, chapter IV 32686, chapter V 67905, chapter VI 53615, chapter VII 52280).

**The introduction** substantiates the urgency of the problem of producing high-octane gasoline with the involvement of oxygen-containing compounds based on monohydric alcohols C<sub>1</sub>-C<sub>3</sub> and BBF CC and BDF of pyrolysis, formulates the purpose and objectives of the study, presents the scientific novelty and practical value of the results obtained in the dissertation.

**The first chapter** provides a review of the scientific and patent literature, reflecting the current state of production of oxygenated motor gasolines, the main trends in the production of oxygen-containing compounds in connection with new requirements for the quality, production and use of alternative motor fuels.

Based on the analysis of the presented literature data, the purpose and objectives of the dissertation are outlined.

**The second chapter** describes the experimental procedure and analysis of the feedstock and reaction products. The description of the setup schemes used in the laboratory studies, the characteristics of the raw materials – BBF CC and BDF of pyrolysis, phase compositions of the used catalysts, as well as analysis methods according to GOST used in the research process are given.

**The third chapter** presents the results of a study of the production of oxygen-containing compounds – ethers based on technical isobutylene and butane-butylene fraction of catalytic cracking and C<sub>1</sub>-C<sub>3</sub> monohydric alcohols using industrial zeolite-containing catalysts Zeocar-2 and Zeocar-600. The optimal conditions for the synthesis of MTBE, ETBE, iso-PTBE and other esters were determined. The physicochemical and motor characteristics of the obtained oxygen-containing additives were studied.

**The fourth chapter** presents the results of a study of the process for producing oxygen-containing compounds – ethers based on the butane-divinyl fraction of pyrolysis and monohydroxy alcohols C<sub>1</sub>-C<sub>3</sub>.

The optimal conditions for the synthesis of MTBE, ETBE, iso-PTBE and other oxygen-containing compounds were determined: 1,3-dimethoxybutane (DMB), 2-methoxyethylcyclohexene, 1,3-diethoxybutane (DEB), 2-ethoxyethylcyclohexene. The physicochemical and motor characteristics of the obtained oxygenates were studied, and the fuel compositions were proposed.

**The fifth chapter** presents the results of a study to improve the environmental performance of gasolines in order to reduce sulfur compounds using hydrogenation and alternative (IL, cavitation) desulfurization methods. Selective hydrotreatment undergoes heavy fr. GCC 120 °C-end.b., which allows to reduce the sulfur content without changing the ON of gasoline.



The effect of ultrasonic cavitation on the alkoxyalkylation of light fractions of GC start.b.-85 °C with ethanol was studied. At the same time, the yield of liquid products increased by 4.6 %, of alkyl ethyl ethers – by 5.54 %, and the ON increased by 6 p.

**The sixth chapter** presents data on the process of reducing aromatic hydrocarbons and benzene in marketable gasolines by hydrogenation and hydroisomerization of fractions with st.b.-90 °C, isolated from a stable platform and straight-distillated gasoline using a Ni-Cr catalyst at 180 °C and  $P_{H_2} = 2-4$  MPa, while the benzene content is reduced to zero.

The process of 2-stage hydrotreating of coking gasoline for use as reforming feedstock on the GKD-205 catalyst ( $P = 3-5$  MPa and  $T = 400$  °C) was studied, while the total sulfur content decreases from 0.145 % to 0.0041 %.

**The seventh chapter** presents the recipe for the production of commercial gasolines by compounding in the necessary proportions the components of motor fuels - direct race gasoline, reforming, catalytic cracking, and oxygenates to improve the quality of gasolines in accordance with the requirements of Euro-4, Euro-5 standards.

The thesis concludes with conclusions on the work done, in which the main research results are summarized, and a list of cited literature.

## MAIN CONTENT OF WORK

### **1. Development of a process for producing high-octane oxygen-containing additives based on technical isobutylene, butane-butylene fraction of catalytic cracking and methanol using industrial zeolite-containing catalysts**

The modern formula of gasolines requires the presence of high-octane oxygen-containing additives – oxygennates, containing up to 2.4-2.7 % of the mass. bound oxygen, which will increase both the resources and the octane number of gasoline without increasing the content of carcinogenic aromatics. The most accessible oxygenates include methyl, ethyl, isopropyl alcohols and esters based on them – MTBE, ETBE, i-PTBE, etc.

Both technical isobutylene and the butane-butylene fraction (BBF) of the catalytic cracking process were used as raw materials in the synthesis of high-octane oxygen-containing additives – oxygenates (MTBE), and methanol (with the ratio of isobutylene: methanol = 1 : 1 and BBF : methanol = 6 : 1).

The resources of isobutylene for the production of MTBE can also be increased due to n-butane contained in associated petroleum gases or gas condensates, using the processes of dehydrogenation and subsequent isomerization of butylene. Gases of thermo-destructive and petrochemical processes can also be a source of isobutylene. In addition, given that the resources of isobutylene at the refinery are insufficient to obtain the required amount of oxygen-containing compounds with improved environmental properties, it is possible to carry out alkoxyalkylation of fractions of C<sub>5</sub> or C<sub>4</sub>-C<sub>7</sub> gasoline catalytic cracking, coking, pyrolysis by-products with the aim of obtaining mainly MTBE.

MTBE, in comparison with other high-octane additives (alkylates, isomerizates), has a higher octane number and lower boiling point, which together allows increasing the octane number of mainly head fractions of base gasoline.

Methyl tertiary butyl ether is a more valuable high-octane component of motor gasoline, while methyl esters of C<sub>6</sub>-C<sub>7</sub> isoolefins are considered mainly as a source of oxygen in gasolines.

Tert-alkyl esters are prepared by alkoxyalkylation of isoolefins having a double bond at the tertiary carbon atom in the presence of solid acid catalysts.

The process of obtaining high-octane additives for gasoline based on methanol and technical isobutylene was carried out in a laboratory unit with a capacity of 250 g/h.

As catalysts, industrial zeolite-containing easily regenerated catalysts Zeocar-2 and Zeocar-600 were used.

The synthesis of high-octane ethers can be carried out both in the vapor (atmospheric pressure) and in the liquid phase (pressure 1.0-2.5 MPa) at temperatures of 80-150 °C. But in the liquid phase the yield of esters is much higher. The reaction is equilibrium, and the

degree of conversion increases with decreasing temperature and dilution of isobutylene with methanol. The target reaction for producing MTBE on solid catalysts proceeds as an electrophilic addition.

Studies on the synthesis of a high-octane additive based on methanol and isobutylene were carried out on a Zeocar-2 industrial catalyst in the temperature range of 80-150 °C, an overpressure of 1.0-2.5 MPa, and a mass feed rate of  $V = 1.0 \text{ h}^{-1}$ . The results of the studies are presented in Table 1.

**Table 1**  
**The material balance of the synthesis**  
**of high-octane additives based on methanol**  
**and isobutylene on the industrial catalyst Zeocar-2**

Indices	V = 1,0 h <sup>-1</sup>											
	P = 1,0 MPa				P = 2,0 MPa				P = 2,5 MPa			
	80 °C	100 °C	120 °C	150 °C	80 °C	100 °C	120 °C	150 °C	80 °C	100 °C	120 °C	150 °C
Yield of catalyzate, % mass.	84,0	86,3	88,6	80,4	85,8	86,4	88,7	86,5	86,1	87,6	88,9	86,1
including												
isobutylene	3,0	2,7	2,1	1,8	2,7	2,1	1,4	1,3	2,4	1,9	1,2	1,0
methanol	5,8	5,3	5,0	4,3	5,3	4,8	4,0	3,7	5,1	4,7	3,8	3,5
TBA	8,6	9,5	10,1	12,5	6,3	7,1	7,2	12,4	5,8	6,8	7,0	8,8
MTBE	64,8	67,1	69,8	60,6	69,7	71,3	75,4	67,6	71,1	73,4	76,3	72,4
diisobutylene	1,8	1,7	1,6	1,2	1,8	1,1	0,7	0,5	1,7	1,0	0,6	0,4
Yield of gas, % mass.	14,7	12,5	10,1	18,1	12,8	12,4	10,0	13,1	12,4	10,8	9,8	11,9
Yield of coke and losses, % mass.	1,3	1,2	1,2	1,5	1,4	1,2	1,3	1,4	1,5	1,4	1,3	2,0
Including coke	0,1	0,1	0,2	0,3	0,2	0,2	0,3	0,4	0,3	0,3	0,3	0,5

From the Table 1 shows, that with increasing pressure at a constant temperature, the yield of catalysis naturally increases and the highest yield of catalysis and methyl tert-butyl ether (MTBE) in it is 88.9 and 76.3 % of the mass. respectively, at a temperature of 120 °C and a pressure of 2.5 MPa.

The optimal conditions for conducting the process using isobutylene are: temperature 120 °C, pressure 2.5 MPa and a mass feed rate of  $1.0 \text{ h}^{-1}$ , at which the yield of catalysis reaches 88.9 % of the mass. with

an oxygen-containing compound content of 83.3 % by mass, and unreacted isobutylene and methanol, respectively, 1.2 % and 3.8 % by mass. The octane number of catalyzate without isolation of MTBE from it reaches 112-114 points according to the research method.

In order to expand the raw material resources for the production of high-octane esters, the butane-butylene catalytic cracking fraction purified from dienes and sulfur-containing compounds that poison the alkoxyalkylation catalyst and reduce the selectivity of the process was used as a source of isobutylene.

The optimal process conditions using the butane-butylene fraction of CC are: temperature 120 °C, pressure 2.5 MPa and mass feed rate of 1.0 h<sup>-1</sup>.

The yield of catalyzate (high-octane additives) in this case reaches 45.4 % of the mass. with the content of methyl tertiary butyl ether in it – 33.6 % of the mass. The octane number of catalyzate without isolation of methyl tertiary butyl ether is 112 points by the research method. When catalyzate is added to catalytic cracking gasoline in the amount of 15 % of the mass. the octane number of gasoline rises from 90.3 p. to 93.5 p. according to the research method, i.e. more than 3 points.

Therefore, to obtain a high-octane additive based on methanol, technical isobutylene and the butane-butylene fraction of catalytic cracking, it is advisable to carry out the process using a catalyst with the largest number of strong acid sites. In this regard, subsequent studies aimed at studying the activity and stability of the catalyst in the synthesis of methyl tertiary butyl ether based on methanol, isobutylene and butane-butylene fraction of catalytic cracking were carried out using the industrial catalyst Zeocar-600. The results of the study on the production of high-octane additives based on methanol and technical isobutylene using the Zeocar-600 catalyst are presented in Table 2-3.

In the Table 3 shows the composition of a high-octane oxygen-containing additive. The maximum yield of MTBE was 85.87 % of the mass. under optimal conditions: temperature 120 °C, P = 2.5 MPa, V = 1.0 h<sup>-1</sup>.

**Table 2**  
**The material balance of the synthesis**  
**of high-octane additives based on methanol**  
**and technical isobutylene on the industrial catalyst Zeocar-600**

Indices	V = 1,0 h <sup>-1</sup>											
	P = 1,0 MPa				P = 2,0 MPa				P = 2,5 MPa			
	80 °C	100 °C	120 °C	150 °C	80 °C	100 °C	120 °C	150 °C	80 °C	100 °C	120 °C	150 °C
Yield of catalyzate, % mass.	87,0	89,3	91,6	83,4	88,8	89,4	91,7	88,5	89,1	90,6	91,9	89,1
including												
isobutylene	3,1	2,8	2,2	1,9	2,8	2,2	1,5	1,4	2,5	2,0	1,3	1,1
methanol	6,0	5,5	5,2	4,5	5,5	5,0	4,1	3,8	5,3	4,9	3,9	3,6
TBA	8,9	9,8	10,4	12,9	6,5	7,3	7,4	12,9	6,0	7,0	7,2	9,1
MTBE	67,1	69,4	72,1	62,8	72,1	73,7	77,9	69,9	73,5	75,7	78,9	74,9
diisobutylene	1,9	1,8	1,7	1,3	1,9	1,2	0,8	0,5	1,8	1,0	0,6	0,4
Yield of gas, % mass.	11,7	9,5	7,1	15,1	9,8	9,4	7,0	10,1	9,4	7,8	6,8	8,9
Yield of coke and losses, % mass.	1,3	1,2	1,2	1,5	1,4	1,2	1,3	1,4	1,5	1,6	1,3	2,0
Including coke	0,1	0,1	0,2	0,3	0,2	0,2	0,3	0,4	0,3	0,3	0,3	0,5

**Table 3**  
**The composition of the catalysis obtained in**  
**the synthesis of high-octane additives based**  
**on methanol and isobutylene on a Zeocar-600 catalyst**

Indices, % mass.	V = 1,0 h <sup>-1</sup>											
	P = 1,0 MPa				P = 2,0 MPa				P = 2,5 MPa			
	80 °C	100 °C	120 °C	150 °C	80 °C	100 °C	120 °C	150 °C	80 °C	100 °C	120 °C	150 °C
Isobutylene	3,56	3,14	2,40	2,28	3,15	2,46	1,64	1,58	2,81	2,21	1,41	1,23
Methanol	6,90	6,16	5,68	5,40	6,19	5,59	4,47	4,29	5,95	5,41	4,24	4,04
TBA	10,23	10,97	11,35	15,47	7,32	8,17	8,07	14,68	6,73	7,73	7,83	10,22
MTBE	77,13	77,71	78,71	75,30	81,20	82,44	84,95	78,99	82,49	83,55	85,87	84,06
Diisobutylene	2,18	2,02	1,86	1,55	2,14	1,34	0,87	0,55	2,02	1,10	0,65	0,45

Further studies on the synthesis of oxygen-containing additives were carried out on the basis of catalytic cracking BFF and methanol using the industrial catalyst Zeocar-600 (Table 4).

**Table 4**

**The material balance of the synthesis of high-octane additives based on methanol and butane-butylene fraction of catalytic cracking at Zeocar-600**

Indices	V = 1,0 h <sup>-1</sup>						V = 2,0 h <sup>-1</sup>					
	P = 1,0 MPa		P = 2,0 MPa		P = 2,5 MPa		P = 1,0 MPa		P = 2,0 MPa		P = 2,5 MPa	
	100 °C	120 °C	100 °C	120 °C	100 °C	120 °C	100 °C	120 °C	100 °C	120 °C	100 °C	120 °C
Yield of catalyzate, % mass.	44,7	45,3	46,3	47,9	47,4	48,4	46,4	47,5	47,8	48,3	48,2	48,3
including												
isobutylene	2,30	2,10	1,49	1,50	1,04	0,68	2,85	2,66	2,40	2,10	1,78	1,47
methanol	2,76	2,26	1,83	1,74	1,44	1,26	3,25	3,06	2,46	2,22	1,90	1,70
n-butane	2,76	3,68	3,31	4,52	3,69	4,64	3,25	4,50	4,58	5,41	4,94	5,43
isobutane	10,75	7,13	10,69	7,24	8,32	2,69	11,47	9,02	11,39	8,75	9,54	3,79
isopentane	0,57	0,91	0,80	1,10	0,86	1,14	0,46	0,64	0,92	1,02	0,92	1,02
n-pentane	0,11	0,12	0,12	0,12	0,12	0,12	0,05	0,12	0,12	0,11	0,12	0,11
TBA	1,13	1,36	1,03	1,28	0,93	1,14	1,03	1,15	0,92	1,02	0,79	0,96
MTBE	23,90	26,67	25,95	29,35	30,02	35,82	23,29	25,65	24,38	27,16	27,63	33,37
diisobutylene	1,12	1,07	1,08	1,05	0,98	0,91	0,75	0,70	0,63	0,51	0,58	0,45
Yield of gas, % mass.	53,2	52,7	51,7	50,5	50,4	49,5	52,2	50,7	50,1	49,7	49,7	49,6
Yield of coke and losses, % mass.	2,1	2,0	2,0	1,6	2,2	2,1	1,4	1,8	2,1	2,0	2,1	2,1
Including coke	0,3	0,4	0,4	0,5	0,4	0,5	0,2	0,4	0,3	0,5	0,4	0,5
Octane number by m.m.	100	102	101	103	104	105	100	103	100	101	102	104
by i.m.	108	110	109	111	112	113	107	110	108	109	110	112

As can be seen from the Table 4, the maximum yield of catalysis is 48.4 % of the mass. obtained at a temperature of 120 °C, a pressure of 2.5 MPa and V = 1.0 h<sup>-1</sup>.

The composition of the catalyzate from the synthesis process of the high-octane additive obtained on the basis of methanol and the butane-butylene fraction from the catalytic cracking process on the Zeocar-600 industrial catalyst is presented below. The synthesis was carried out at a mass feed rate of 1 h<sup>-1</sup>, an optimum temperature of 120 °C, at various pressures (1.0 MPa, 2.0 MPa, 2.5 MPa).

Isobutylene	4,64	3,13	1,4
Methanol	4,99	3,63	2,6
n-butane	8,12	9,44	9,59
iso-butane	15,74	15,11	5,56
iso-pentane	2,01	2,30	2,36
n-pentane	0,26	0,25	0,25

TBA	3,00	2,67	2,36
MTBE	58,87	61,27	74,00
Diisobutylene	2,37	2,20	1,88
Octane number by M.m.	102	103	105
Octane number by i.m.	110	111	113

As can be seen from the presented results, the maximum yield of methyl-tertiary-butyl ether is 74 % of the mass. obtained under optimal conditions at a temperature of 120 °C, a pressure of 2.5 MPa, a mass feed rate of feedstock  $V = 1 \text{ h}^{-1}$ . Unreacted isobutylene and methanol were 1.4 and 2.6 %, respectively.

## 2. Development of a process for producing high-octane oxygen-containing additives based on technical isobutylene, butane-butylene fraction of catalytic cracking and ethanol on a Zeocar-600 catalyst

Further studies on the synthesis of oxygenates were carried out using ethanol, technical isobutylene and BBF CC (Table 5-6).

**Table 5**  
**The material balance of the synthesis of high-octane additives based on ethanol and isobutylene on the industrial catalyst Zeocar-600**

Indices	V = 1,0 h <sup>-1</sup>											
	P = 0,1 MPa			P = 2,0 MPa			P = 2,5 MPa			P = 3,0 MPa		
	60 °C	120 °C	130 °C	60 °C	120 °C	130 °C	60 °C	120 °C	130 °C	60 °C	120 °C	130 °C
Yield of cataly- zate, % mass.	62,3	67,4	68,9	77,4	79,6	79,9	81,5	92,6	92,8	84,3	93,2	93,0
including												
isobutylene	8,2	8,0	7,5	7,3	6,7	6,2	6,0	5,4	5,2	5,3	5,0	4,8
ETBE	17,4	23,1	24,9	39,0	41,5	42,5	48,4	63,6	63,6	53,2	65,3	64,9
TBA	5,7	7,1	7,9	5,4	6,7	7,5	5,3	6,0	6,8	5,1	5,8	6,6
diisobutylene	1,8	1,6	1,4	1,7	1,5	1,3	1,5	1,3	1,1	1,2	1,0	0,8
Ethanol	29,2	27,6	27,2	24,0	23,2	22,4	20,3	16,3	16,1	19,5	16,1	15,9
Yield of gas, % mass.	34,9	29,4	28,2	19,9	18,7	18,3	15,7	4,8	4,2	13,4	4,6	4,4
Yield of coke and losses, % mass.	2,8	3,2	2,9	2,7	1,7	1,8	2,8	2,6	3,0	2,3	2,2	2,6
Including coke	0,2	0,3	0,5	0,3	0,5	0,6	0,4	0,6	0,8	0,5	0,7	0,9
Octane number												
by M.m.	103	103	104	105	105	105	106	107	107	106	107	106
By R.m.	115	115	117	117	117	117	117	119	118	118	119	118

The maximum yield of catalysis is 93.2 %, including ETBE 65.3 % obtained at a temperature of 120 °C, a pressure of 3.0 MPa and  $V = 1.0 \text{ h}^{-1}$  using technical isobutylene. In this case, the ON of catalyzate amounted to 107 p. by m.m. and 119 p. by r.m.

The composition of the catalyzate obtained in the synthesis of high-octane additives based on ethanol and technical isobutylene using the industrial catalyst Zeocar-600 is presented below. The synthesis was carried out at a mass feed rate of  $1 \text{ h}^{-1}$ , an optimum temperature of 120 °C, at various pressures (1.0 MPa, 2.0 MPa, 2.5 MPa, 3.0 MPa).

Isobutylene	11,9	8,4	5,8	5,4
ETBE	34,3	52,1	68,7	70,0
TBA	10,5	8,4	6,5	6,2
Diisobutylene	2,4	1,9	1,4	1,1
Ethanol	40,9	29,2	17,6	17,3
Octane number according to m.m.	103	105	107	107
Octane number according to i.m.	115	117	119	119

From the presented data it is seen that the yield of ethyl- tertiary-butyl ether under various conditions is from 34.3 to 70.0 %. The octane numbers of catalysate were 103-107 points by the motor method and 115-119 points by the research method.

**Table 6**  
**The material balance of the synthesis of high-octane additives based on ethanol and the butane-butylene fraction of catalytic cracking on an industrial catalyst Zeocar-600**

Indices	$V = 1,0 \text{ h}^{-1}$					
	T = 100 °C			T = 120 °C		
	1,0 MPa	2,0 MPa	2,5 MPa	1,0 MPa	2,0 MPa	2,5 MPa
Yield of catalyzate, % mass.	90,9	93,1	96,5	86,4	92,1	95,0
including						
isobutylene	10,5	10,0	9,8	12,6	12,1	11,8
iso-PTBE	41,5	45,7	51,3	38,0	45,6	50,0
TBA	6,9	6,3	5,6	5,2	4,9	4,6
isopropanol	30,8	30,1	29,0	29,6	28,7	28,0
diisobutylene	1,2	1,0	0,8	1,0	0,8	0,6
Yield of gas, % mass.	6,3	5,1	2,2	10,9	5,0	2,5
Yield of coke and losses, % mass.	2,8	1,8	1,3	2,7	2,9	2,5
Including coke	0,5	0,6	0,7	0,6	0,8	0,9
Octane number						
by M.m.	111,5	113	116	111	113	116
by R.m.	122,6	124	125	122	124	125



The maximum yield of catalyzate and ETBE at a temperature of 120 °C, P = 3.0 MPa and V = 1.0 h<sup>-1</sup> is 71.6 and 34.6 %, respectively, in the case of using BBF catalytic cracking.

The composition of the catalyzate obtained on the basis of ethanol and the butane-butylene fraction from the catalytic cracking process using the Zeocar-600 industrial zeolite catalyst is presented below. The synthesis was carried out at a mass feed rate of 1 h<sup>-1</sup>, an optimum temperature of 120 °C, at various pressures (1.0 MPa, 2.0 MPa, 2.5 MPa, 3.0 MPa, 3.5 MPa).

ΣC <sub>4</sub>	31,1	26,6	24,1	23,6	23,7
ETBE	35,1	42,5	47,2	48,3	47,5
Diisobutylene	1,1	1,0	1,7	2,1	2,7
TBA	2,1	1,2	0,4	0,3	0,3
Ethanol	30,6	28,7	26,6	25,7	25,8

In addition to the main component, ethyl tertiary butyl ether, the catalyzate contains dissolved C<sub>4</sub> gases, as well as diisobutylene, tertiary butyl alcohol and unreacted ethanol.

### **3. Development of a process for producing a high-octane oxygen-containing additive based on technical isobutylene and isopropanol using a Zeocar-600 catalyst**

To obtain oxygenate additives used technical isopropyl alcohol. In the Table 7 presents the results of studies on the synthesis of oxygenates based on isobutylene and isopropyl alcohol on a Zeocar-600 catalyst.

When using isopropanol as an alcohol, the yield of i-PTBE ester is less than when using ethanol as an alcohol. The maximum yield of catalyzate, including i-PTBE ether, was 96.5 and 51.3 % of the mass. respectively, at T= 100 °C and a pressure of 2.5 MPa.

The octane number of catalyzate is 116 points by m.m. and 125 points by r.m. The use of the Zeocar-600 catalyst allows one to lower the temperature of the maximum yield of isopropyl tert-butyl ether to 100 °C (V = 1.0 h<sup>-1</sup>).

**Table 7**

**The material balance of the synthesis  
of high-octane additives based on isobutylene  
and isopropyl alcohol on a Zeocar-600 catalyst**

Indices	V = 1,0 h <sup>-1</sup>					
	T = 100 °C			T = 120 °C		
	1,0 MPa	2,0 MPa	2,5 MPa	1,0 MPa	2,0 MPa	2,5 MPa
Yield of catalyzate, % mass.	90,9	93,1	96,5	86,4	92,1	95,0
including						
isobutylene	10,5	10,0	9,8	12,6	12,1	11,8
iso-PTBE	41,5	45,7	51,3	38,0	45,6	50,0
TBA	6,9	6,3	5,6	5,2	4,9	4,6
isopropanol	30,8	30,1	29,0	29,6	28,7	28,0
diisobutylene	1,2	1,0	0,8	1,0	0,8	0,6
Yield of gas, % mass.	6,3	5,1	2,2	10,9	5,0	2,5
Yield of coke and losses, % mass.	2,8	1,8	1,3	2,7	2,9	2,5
Including coke	0,5	0,6	0,7	0,6	0,8	0,9
Octane number by m.m.	111,5	113	116	111	113	116
by R.m.	122,6	124	125	122	124	125

Below is the composition of the catalyzate obtained on the basis of isobutylene and isopropyl alcohol on an industrial Zeocar-600 catalyst at various pressures (1.0 MPa, 2.0 MPa, 2.5 MPa):

Isobutylene	11,6	10,7	10,2
iso-PTBE	45,7	49,1	53,2
TBA	7,6	6,8	5,8
Isopropanol	33,8	32,3	30,0
Diisobutylene	1,3	1,1	0,8
O.n. by M.m.	111,5	113	116
O.n. by I.m.	122,6	124	125

The synthesis of a high-octane additive based on isobutylene and isopropyl alcohol was carried out at a mass feed rate of 1 h<sup>-1</sup>, an optimum temperature of 100 °C, at various pressures (1.0 MPa, 2.0 MPa, 2.5 MPa).

Thus, in connection with the tightening of the requirements for gasoline for the content of toxic components and the improvement of the environmental characteristics of fuels, processes have been developed for the production of high-octane oxygen-containing additives based

on C<sub>1</sub>-C<sub>3</sub> alcohols and olefin-containing petroleum feedstock - technical isobutylene and BBF CC. Additives of these oxygenates can increase the octane number of gasolines by 3-5 points, improve the combustion of fuels and reduce the concentration of toxic substances in exhaust gases.

It should be noted that when using Zeocar-600 as a catalyst, better results were obtained compared to the Zeocar-2 catalyst, due to its higher acidity and, hence, activity.

Based on the studies, it was found that in the alkoxyalkylation reaction based on isobutylene and C<sub>1</sub>-C<sub>3</sub> monohydric alcohols on the Zeocar-600 catalyst, in the case of iso-propanol, ethanol and methanol used as alcohols, the yield of catalyzate was 96.5; 93.2 and 91.9 % of the mass. respectively. It should also be noted that in the case of iso-propanol, ethanol and methanol used as alcohols, the yield of esters – iso-PTBE, ETBE and MTBE was 51,3; 65,3 and 78,9 % of the mass., respectively.

The octane numbers of the catalyzate obtained on the basis of the above alcohols reach 116, 107, 106, 125, 119 and 117 points by motor and research methods, respectively.

#### **4. Development of a process for producing a high-octane oxygen-containing additive based on a butane-divinyl fraction of pyrolysis and methanol using industrial zeolite-containing catalysts**

In order to obtain a high-octane additive to motor gasolines based on methanol and the butane-divinyl fraction of the pyrolysis process, studies were performed on a laboratory setup in the temperature range 80 : 130 °C, pressure 2.0 : 3.0 MPa, mass feed rate 1.0 h<sup>-1</sup> using a Zeocar-2 catalyst. The results of the studies are presented in Table 8.

Table 8 shows that with increasing pressure from 2.0 MPa to 3.0 MPa at a constant temperature and mass feed rate, both the yield of catalysis and the content of esters in it: methyl tert-butyl ether and 1,3-dimethoxybutane increase. At the same time, the gas yield decreases, and the coke yield increases slightly.

The optimal conditions for the process are: pressure 3.0 MPa, temperature 120 °C and the mass feed rate of 1.0 h<sup>-1</sup>, while the yield of

high-octane additives reaches 55.7 % by weight, including MTBE – 26.3 %, 1,3-dimethoxybutane – 17.2 %, tertiary butyl alcohol (TBA) – 2.9 %, diisobutylene – 1.3 %, 2-methoxyethylcyclohexene – 1.7 %.

**Table 8**

**The material balance of the synthesis  
of high-octane additives based on methanol  
and the butane-divinyl fraction of pyrolysis on a Zeocar catalyst**

Indices	V = 1,0 h <sup>-1</sup>											
	P = 2,0 MPa				P = 2,5 MPa				P = 3,0 MPa			
	80 °C	100 °C	120 °C	130 °C	80 °C	100 °C	120 °C	130 °C	80 °C	100 °C	120 °C	130 °C
Yield of catalyzate, % mass.	45,7	50,8	52,6	51,0	46,0	49,0	54,9	53,9	50,6	54,0	55,7	54,5
including												
ΣC <sub>4</sub>	8,3	7,1	5,3	4,7	8,6	7,3	4,7	4,3	10,2	5,9	3,7	3,5
methanol	10,7	9,8	5,8	4,4	9,9	7,0	3,5	3,0	8,3	6,2	2,6	2,7
MTBE	13,7	16,3	22,5	20,6	14,1	17,5	24,6	23,0	16,4	19,6	26,3	24,3
1,3-dimethoxybutane	6,7	11,4	12,9	14,8	6,9	11,3	16,2	16,7	8,4	16,0	17,2	17,8
TBA	2,9	3,5	3,9	4,7	2,2	2,8	3,3	4,8	2,3	2,6	2,9	3,8
diisobutylene	1,9	1,1	0,8	0,6	2,7	1,4	1,0	0,8	3,0	1,8	1,3	0,9
2-methoxyethylcyclohexene	1,5	1,6	1,4	1,2	1,6	1,7	1,6	1,3	2,0	1,9	1,7	1,5
2 Yield of gases, % mass.	52,6	47,4	45,6	47,3	52,0	49,0	43,1	44,1	47,4	43,9	42,1	43,0
3. Yield of coke, %	0,5	0,5	0,6	0,7	0,6	0,6	0,7	0,8	0,8	0,9	1,0	1,3
4. Losses	1,2	1,3	1,2	1,0	1,4	1,4	1,2	1,2	1,2	1,2	1,2	1,2
5. Octane number, p.												
m.m.	103	105	107	106	104	106	108	107	106	108	110	108
r.m.	113	115	117	116	114	116	118	117	116	118	120	118

The octane number of the additive according to the research method is 120 p.

Below is the composition of the high-octane additive obtained by the interaction of methanol and the butane-divinyl fraction from the pyrolysis process on an industrial Zeocar-2 catalyst at a mass feed rate of 1 h<sup>-1</sup>, temperature = 120 °C, various pressures (2.0 MPa, 2.5 MPa, 3.0 MPa):

ΣC <sub>4</sub>	10,0	8,5	6,7
Methanol	11,0	6,3	4,7
MTBE	42,7	45,0	47,3
1,3-dimethoxybutane	24,6	29,5	30,8

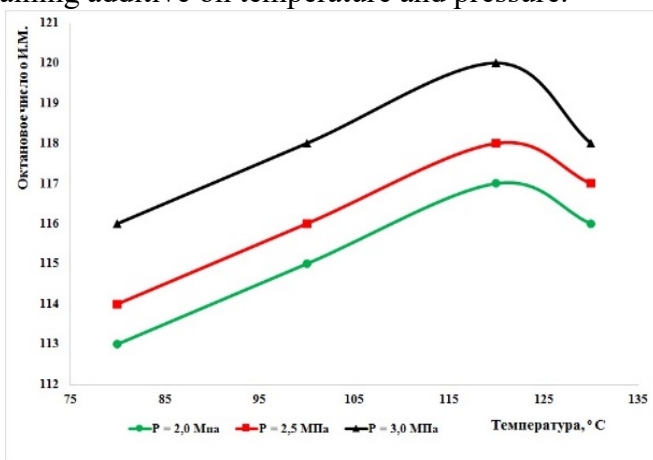
TBA	7,4	6,0	5,2
Diisobutylene	1,5	1,8	2,2
2-methoxyethylcyclohexene	2,8	2,9	3,1
Octane number according to M.m.	107	108	110
Octane number according to I.m.	117	118	120

The main components of the oxygen-containing additive are methyl tertiary-butyl ether – 47.3 %, 1,3-dimethoxybutane – 30.8 % and 2-methoxyethylcyclohexene – 3.1 %.

The composition of unreacted gas obtained during the synthesis of a high-octane additive based on methanol and a butane-divinyl fraction from the pyrolysis process using an industrial catalyst Zeocar-2 at a temperature of = 120 °C, a mass feed rate of 1.0 h<sup>-1</sup>, and various pressure (2.5 MPa, 3.0 MPa):

$\Sigma C_2$	0,06	0,06	$(\alpha+i)C_4H_8$	29,57	35,32
$C_3H_8$	0,33	0,34	$\beta_{\text{тр.}}C_4H_8$	7,2	7,8
$C_3H_6$	0,64	0,88	$\beta_{\text{цис.}}C_4H_8$	5,4	6,3
n- $C_4H_{10}$	25,8	18,5	$C_4H_6$	22,8	22,3
изо- $C_4H_{10}$	8,2	8,5			

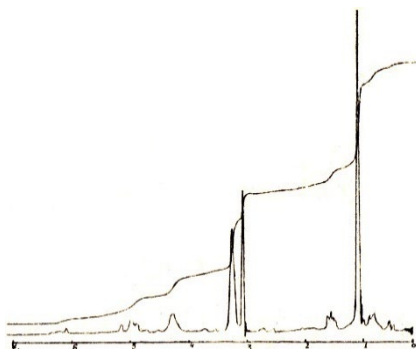
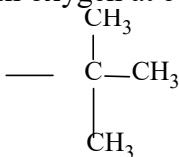
In Chart 1 shows the dependence of the octane number of an oxygen-containing additive on temperature and pressure.



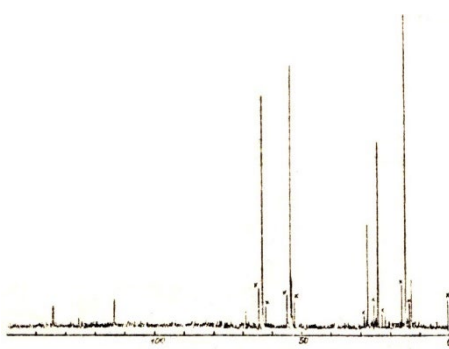
**Chart 1. The dependence of the ON of oxygen-containing additives on temperature and pressure**

To identify oxygen-containing compounds obtained during the interaction of methanol with the butane-divinyl fraction of pyrolysis,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were taken (Figures 1 and 2), which show that the main reaction product is MTBE, whose signals are located as follows:

a) protons of methyl groups at the tertiary carbon atom are observed at  $\delta = 1.10$  ppm, and the chemical shift of the  $\text{CH}_3$  groups associated with oxygen at  $\delta = 3.0\text{-}3.25$  ppm:



**Figure 1.  $^1\text{H}$  NMR spectrum of a high-octane additive based on methanol and butane-divinyl fraction**



**Figure 2.  $^{13}\text{C}$  NMR spectrum of a high-octane additive based on methanol and butane-divinyl fraction**

b) in addition to the MTBE resonance signals, proton signals in the region of chemical shifts  $\delta = 4.8\text{-}5.2$  ppm also appear in the mixture and  $\delta = 6.05\text{-}6.6$  ppm, which can be attributed to the group  $\text{CH}_2 = \text{CH}$ . In the region  $\delta = 0.8\text{-}0.95$  ppm there is a weak signal from the  $\text{CH}_3$  group, apparently associated with the  $\text{CH}_2$  group, and at  $\delta = 1.4\text{-}1.7$  ppm, a signal from a  $\text{CH}_3$  group bound to a hydrocarbon group at a double bond;

c) signals in the region  $\delta = 3.28$  ppm and  $\delta = 4.3$  ppm belong to the  $\text{CH}_3$ - and  $-\text{OH}$  groups of the starting methyl alcohol, which has not reacted.

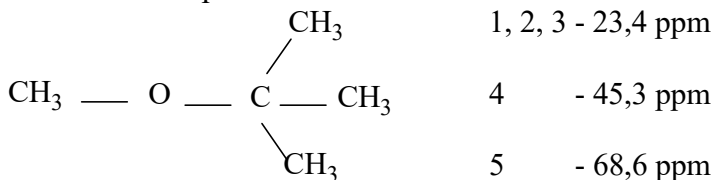
The  $^{13}\text{C}$  NMR spectrum revealed:

a) signals from the  $-\text{CH}=\text{CH}_2$  group located at  $\delta = 1.34$  ppm and 163.4 ppm and tertiary carbon atom of MTBE at  $\delta = 6.9$  ppm. The resonance absorption of  $\text{CH}_3$  groups associated with the tertiary carbon atom corresponds to a signal at 23.5 ppm, and the  $\text{CH}_3$  group associated with oxygen corresponds to 45.1 ppm. In this case, there is also a signal of the  $\text{CH}_3$  group of the starting methyl alcohol, which appears at 45.9 ppm.

In the  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra, there are two unidentified peaks near MTBE.

To identify these peaks, the obtained high-octane additive was repeatedly washed with water from alcohols, after which it was again examined by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy.

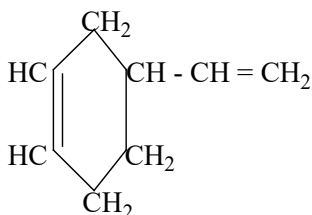
Five resonance signals appeared in the  $^{13}\text{C}$  NMR spectrum, of which three correspond to the structure of the MTBE molecule:



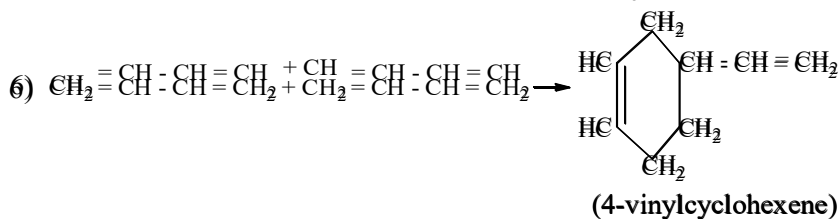
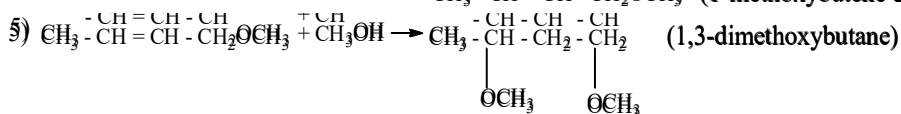
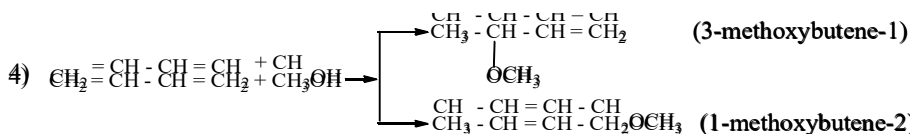
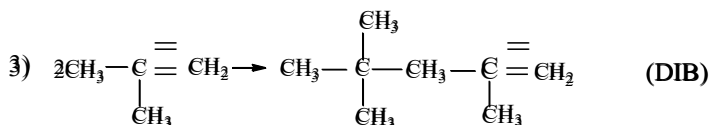
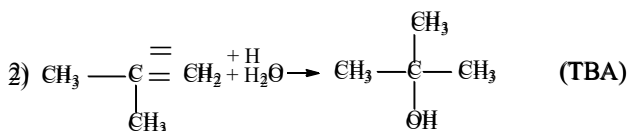
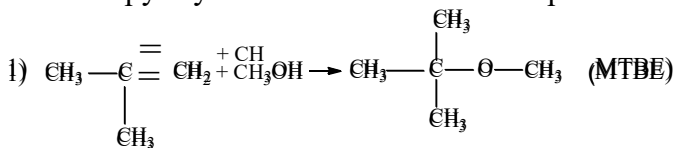
The other two signals at  $\delta = 113.6$  ppm and 134.6 ppm can be attributed to the absorption of olefin groups. These assignments are also confirmed by the  $^1\text{H}$  NMR spectra, where the signals of the  $(\text{CH}_3-)$  3 groups are clearly visible at  $\delta = 1.1$  ppm. and  $-\text{O}-\text{CH}_3$  groups at  $\delta = 3.05$  ppm. In addition, in a relatively weak field, in the region of  $\delta = 4.5-6.4$  ppm, signals of protons of conjugated double bonds are detected.

It should be noted that in the region of chemical shifts  $\delta=1.5-2.6$  ppm. and  $\delta = 1.8-2.2$  ppm. additional signals appeared that can be assigned to the protons of the  $\text{CH}_3$  and  $\text{CH}_2$  groups at a double bond. There is also a very weak signal  $\delta = 0.9$  ppm, which can be attributed to the  $\text{CH}_3$  groups associated with the methylene group.

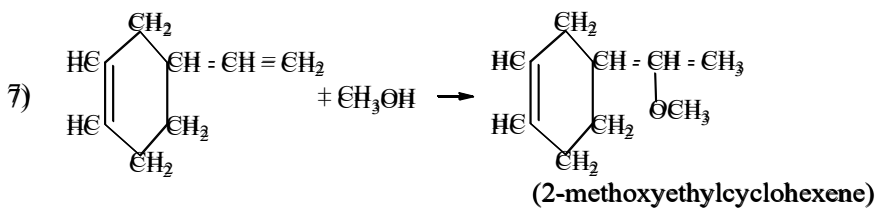
The presence of a isobutylene dimer and an olefin of cyclic structure was found:



Based on the foregoing, the chemistry of the process of the interaction of BDF pyrolysis and methanol can be represented as follows:







Based on the presented chemistry of the reaction between BDF pyrolysis and methanol, compiled on the basis of chromatography data,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR, unidentified products are 1,3-dimethoxybutane and 2-methoxyethylcyclohexene.

Further studies on the production of a high-octane additive based on methanol and BDF pyrolysis were carried out using the Zeocar-600 catalyst. The results of the studies are presented in Table 9.

**Table 9**

**The material balance of the synthesis of high-octane additives based on methanol and the butane-divinyl fraction of pyrolysis on the Zeocar-600 catalyst**

Indices	V = 1,0 h <sup>-1</sup>											
	P = 2,0 MPa				P = 2,5 MPa				P = 3,0 MPa			
	80 °C	100 °C	120 °C	130 °C	80 °C	100 °C	120 °C	130 °C	80 °C	100 °C	120 °C	130 °C
Yield of catalyzate, % mass.	48,7	53,8	55,6	54,0	49,0	52,0	57,9	56,9	53,6	57,0	58,7	57,5
including												
ΣC <sub>4</sub>	8,8	7,5	5,6	5,0	9,2	7,7	4,9	4,5	10,8	6,2	3,9	3,7
methanol	11,4	10,4	6,1	4,7	10,5	7,4	3,7	3,2	8,8	6,5	2,7	2,8
MTBE	14,6	17,3	23,8	21,8	15,0	18,6	25,9	24,3	17,4	20,7	27,7	25,6
1,3-dimethoxybutane	7,1	12,1	13,6	15,7	7,4	12,0	17,1	17,6	8,9	17,0	18,1	18,8
TBA	3,2	3,6	4,1	5,0	2,3	3,0	3,5	5,1	2,5	2,7	3,1	4,0
Diisobutylene	2,0	1,2	0,9	0,6	2,9	1,5	1,1	0,8	3,2	1,9	1,4	1,0
2-methoxyethylcyclohexene	1,6	1,7	1,5	1,2	1,7	1,8	1,7	1,4	2,0	2,0	1,8	1,6
2 Yield of gases, % mass.	49,6	44,4	42,6	44,3	49,0	46,0	40,1	41,1	44,4	40,9	39,1	40,0
3. Yield of coke, %	0,7	0,8	0,8	0,7	0,8	0,9	0,9	1,0	0,8	1,0	1,0	1,2
4. Losses	1,0	1,0	1,0	1,0	1,2	1,1	1,1	1,0	1,2	1,1	1,2	1,3
5. Octane number, p.												
M.m	105	106	108	107	105	107	110	108	107	109	111	110
R.m.	115	116	118	117	115	117	120	118	117	119	121	120

The optimal process conditions are: T = 120 °C, P = 3.0 MPa, V = 1.0 h<sup>-1</sup>. In this case, the yield of catalyzate was 58.7 %, MTBE

27.7 %, 1,3-dimethoxybutane 18.1 %, and 2-methoxyethylcyclohexene 1.8 %, the losses did not exceed 1.2 % of the mass. The octane number of catalysis was 121 p.

The composition of the high-octane additive obtained by the interaction of methanol and a butane-divinyl fraction from the pyrolysis process on an industrial Zeocar-600 industrial catalyst at temperature = 120°C, mass feed rate = 1.0 h<sup>-1</sup> and different pressures (2.0 MPa, 2.5 MPa, 3.0 MPa). is presented below.

ΣC <sub>4</sub>	10,1	8,5	6,6
Methanol	11,0	6,4	4,6
MTBE	42,8	44,7	47,2
1,3-dimethoxybutane	24,5	29,5	30,8
TBA	7,4	6,1	5,3
Diisobutylene	1,6	1,9	2,4
2-methoxy-ethylcyclohexene	2,7	2,9	3,1
Octane number according to M.m.	108	110	111
Octane number according to I.m.	118	120	121

Below is the composition of the gas obtained during the synthesis of a high-octane additive based on methanol and a butane-divinyl fraction from a pyrolysis process using an industrial Zeocar-600 catalyst at a temperature of = 120 °C, a mass feed rate of 1.0 h<sup>-1</sup> and various pressures (2.5 MPa, 3.0 MPa).

ΣC <sub>2</sub>	0,06	0,06	(α+i)C <sub>4</sub> H <sub>8</sub>	29,37	34,32
C <sub>3</sub> H <sub>8</sub>	0,35	0,32	β <sub>тр.</sub> C <sub>4</sub> H <sub>8</sub>	7,4	8,8
C <sub>3</sub> H <sub>6</sub>	0,62	0,90	β <sub>инс.</sub> C <sub>4</sub> H <sub>8</sub>	5,9	6,7
н-C <sub>4</sub> H <sub>10</sub>	25,2	18,0	C <sub>4</sub> H <sub>6</sub>	21,8	21,9
изо-C <sub>4</sub> H <sub>10</sub>	9,3	9,0			

### **5. Development of a process for producing a high-octane oxygen-containing additive based on the butane-divinyl fraction of pyrolysis and ethanol, isopropanol using an industrial zeolite-containing catalyst**

In order to expand the assortment of alcohols used in the production of high-octane additives to motor gasolines, studies were conducted

on the synthesis of ethers based on ethyl alcohol and the butane-divinyl pyrolysis fraction.

The studies were carried out on the Zeocar-600 catalyst in the temperature range of 80-130 °C and pressure of 1-3.0 MPa, and the mass feed rate of 1.0 h<sup>-1</sup>, the results of which are summarized in Table 10.

**Table 10**

**The material balance of the synthesis of high-octane additives based on ethanol and the butane-divinyl fraction of pyrolysis on the Zeocar-600 catalyst**

Indices	V = 1,0 h <sup>-1</sup>							
	P = 2,5 MPa				P = 3,0 MPa			
	80 °C	100 °C	120 °C	130 °C	80 °C	100 °C	120 °C	130 °C
Yield of catalyzate, % mass.	52,1	52,9	59,8	59,0	54,8	55,3	60,7	60,1
including								
ΣC <sub>4</sub>	11,7	10,6	6,8	5,8	11,8	10,0	5,2	5,9
ethanol	16,9	9,3	2,0	1,8	15,6	6,2	2,9	1,8
ETBE	12,8	16,1	30,3	28,9	17,7	20,1	31,7	28,5
1,3-DEB	6,5	13,4	15,8	15,2	6,1	15,3	16,0	16,3
TBA	2,0	2,1	4,0	6,4	1,9	2,1	3,8	6,6
Diisobutylene	1,6	0,9	0,6	0,6	0,9	0,9	0,6	0,6
2-ethoxyethylcyclohexene	0,6	0,5	0,3	0,3	0,8	0,7	0,5	0,4
2 Yield of gases, % mass.	45,6	45,1	38,4	38,9	44,0	42,6	37,3	37,8
3. Yield of coke, %	0,8	0,6	0,8	0,9	0,6	0,8	0,8	1,0
4. Losses	1,5	1,4	1,0	1,2	0,6	1,3	1,2	1,1
5. Octane number, p.								
M.m	108	110	113	113	110	111	114	112
R.m.	118	120	123	124	120	122	124	123

As can be seen from the Table. 10, the yield of ETBE and 1,3-DEB is 31.7 % and 16.0 %, respectively, under optimal conditions: a temperature of 120 °C, a pressure of 3.0 MPa and V = 1 h<sup>-1</sup>, and the octane number of the additive is 124 p. by research method.

The composition of the oxygen-containing high-octane additive obtained on the basis of ethanol and the butane-divinyl fraction from the pyrolysis process on an industrial Zeocar-600 catalyst at a temperature = 120 °C, a mass feed rate = 1.0 h<sup>-1</sup> and pressures of 2.5 MPa and 3.0 MPa is presented below:

ΣC<sub>4</sub> 11,4 8,6

Ethanol	3,3	4,8
ETBE	50,7	52,2
1,3-DEB	26,4	26,4
TBA	6,7	6,3
Diisobutylene	1,0	0,9
2-ethoxyethylcyclohexene	0,5	0,8
Octane number according to M.m.	113	114
Octane number according to I.m.	123	124

The yield of ethyl tertiary butyl ether and 1,3-diethoxybutane is 52.2 % and 26.4 %, respectively, under optimal conditions: temperature 120 ° C, pressure 3.0 MPa and  $V = 1 \text{ h}^{-1}$ , and the octane number of the additive 124 points by research method.

Below is the component composition of gas from  $C_2$  to  $C_4$  obtained during the synthesis of a high-octane additive based on ethanol and a butane-divinyl fraction from the pyrolysis process on an industrial Zeocar-600 catalyst.

$\Sigma C_2$	0,04	0,07
$C_3H_8$	0,23	0,35
$C_3H_6$	0,68	0,97
изо- $C_4H_{10}$	8,37	8,13
n- $C_4H_{10}$	24,94	24,45
( $\alpha+i$ ) $C_4H_8$	30,35	29,73
$\beta_{tr.}C_4H_8$	8,27	9,63
$\beta_{cis.}C_4H_8$	4,35	5,35
$C_4H_6$	22,77	22,32

In the process of producing high-octane additives for motor gasolines, isopropyl alcohol was also used.

The studies were carried out in the temperature range of 80-130 °C, a pressure of 2.5-3.0 MPa and a mass feed rate of  $1.0 \text{ h}^{-1}$ .

In the Table 11 shows the material balance of the synthesis of a high-octane additive based on isopropanol and the butane-divinyl fraction of pyrolysis using a Zeocar-600 catalyst.

The optimal process conditions are a temperature of 120 °C, a pressure of 3.0 MPa and a mass feed rate of  $1.0 \text{ h}^{-1}$ . The yield of catalyzate

is 62.1 %, of isopropyl-tertiary-butyl ether – 26.8 %, 1,3-diisopropoxybutane – 10.0 %.

**Table 11**  
**The material balance of the synthesis of high-octane additives based on isopropanol and the butane-divinyl fraction of pyrolysis on the Zeocar-600 catalyst**

Indices	V = 1,0 h <sup>-1</sup>							
	P = 2,5 MPa				P = 3,0 MPa			
	80 °C	100 °C	120 °C	130 °C	80 °C	100 °C	120 °C	130 °C
Yield of catalyzate, % mass.	53,3	55,9	61,7	59,1	55,6	57,9	62,1	61,2
including								
ΣC <sub>4</sub>	18,2	17,2	12,1	11,6	15,4	12,7	11,3	11,1
isopropanol	14,7	11,9	10,9	11,8	12,3	10,9	10,7	10,7
iso-PTBE	12,0	17,9	25,3	23,8	17,1	22,3	26,8	24,9
1,3-diisopropoxybutane	6,8	7,0	10,6	7,3	8,9	9,9	10,0	8,7
TBA	0,1	0,3	1,3	3,2	0,2	0,4	1,6	4,3
2-isopropoxyethylcyclohexene	1,1	1,2	1,2	1,1	1,3	1,4	1,4	1,3
diisobutylene	0,4	0,4	0,3	0,3	0,4	0,3	0,3	0,2
2 Yield of gases, % mass.	44,8	42,0	35,9	38,8	42,4	40,2	36,0	36,9
3. Yield of coke, %	0,4	0,5	0,7	0,9	0,5	0,7	0,7	0,8
4. Losses	1,5	1,6	1,7	1,2	1,5	1,2	1,2	1,1
5. Octane number, p.:								
m.m	106	108	110	109	108	110	116	112
r.m.	116	118	120	119	118	120	126	122

Below is the composition of the oxygen-containing high-octane additive obtained on the basis of isopropyl alcohol and butane-divinyl fraction from the pyrolysis process on a Zeocar-600 catalyst at a temperature = 120 °C, a mass feed rate = 1.0 h<sup>-1</sup> and pressures of 2.5 MPa and 3.0 MPa.

ΣC <sub>4</sub>	19,6	18,2
Isopropanol	17,7	17,2
iso-PTBE	41,0	43,2
1,3-DiisoPB	17,2	16,1
TBA	2,1	2,6
2-isopropoxyethylcyclohexene	1,9	2,2
Diisobutylene	0,5	0,5
Octane number according to m.m.	110	116
Octane number according to i.m.	120	126

The composition of the gas obtained during the synthesis of high-octane additives based on isopropyl alcohol and butane-divinyl fraction from the pyrolysis process on an industrial Zeocar-600 catalyst at

a temperature = 120 °C, a mass feed rate = 1.0 h<sup>-1</sup> and pressures equal to 2.5 MPa and 3.0 MPa are presented below:

ΣC <sub>2</sub>	0,05	0,05	(α+i)C <sub>4</sub> H <sub>8</sub>	27,4	26,4
C <sub>3</sub> H <sub>8</sub>	0,20	0,24	β <sub>тр.</sub> C <sub>4</sub> H <sub>8</sub>	6,98	6,1
C <sub>3</sub> H <sub>6</sub>	0,86	0,85	β <sub>цис.</sub> C <sub>4</sub> H <sub>8</sub>	3,43	3,2
изо-C <sub>4</sub> H <sub>10</sub>	5,84	5,2	C <sub>4</sub> H <sub>6</sub>	22,06	22,56
н-C <sub>4</sub> H <sub>10</sub>	33,18	35,4			

The involvement of isopropanol allows you to get high-octane additive with a yield of 62.1 % of the mass. and an octane rating of 126 p. by the research method.

In order to expand the raw material base of the process for producing high-octane oxygen-containing additives to motor gasolines, studies were conducted to select the optimal ratios of the compositions of monohydric alcohols.

For this, studies were conducted using a mixture of methanol and ethanol, methanol and isopropanol, as well as methanol, ethanol and isopropanol in a ratio of 1 : 1: 1 and the butane-divinyl fraction of pyrolysis.

Studies on the synthesis of a high-octane additive based on a mixture of methanol, ethanol and the butane-divinyl fraction of pyrolysis were carried out on a Zeocar-600 catalyst. The results are presented in Table 12.

**Table 12**

**The material balance of the synthesis of high-octane additives based on a mixture of methanol, ethanol and the butane-divinyl fraction of pyrolysis on a Zeocar-600 catalyst**

Indices	V = 1,0 h <sup>-1</sup>							
	P = 2,5 MPa				P = 3,0 MPa			
	80 °C	100 °C	120 °C	130 °C	80 °C	100 °C	120 °C	130 °C
Yield of catalyzate, % mass.	51,3	52,0	58,9	57,3	54,4	55,7	59,4	58,3
including								
ΣC <sub>4</sub>	14,5	8,4	3,5	2,5	15,3	8,5	3,3	2,5
methanol	6,3	3,6	1,6	1,4	5,5	2,3	1,5	1,3
ethanol	8,6	6,9	6,7	6,6	8,6	7,0	5,6	5,4
ΣMTBE + ETBE	15,4	22,7	30,1	28,9	16,9	23,6	31,3	30,1
Σ1,3-DMB + 1,3-DEB	3,1	8,0	14,2	13,1	5,0	11,8	15,1	14,5
TBA	0,2	0,5	1,4	3,6	0,2	0,6	1,3	3,3
Diisobutylene	3,2	1,9	1,4	1,2	2,8	1,9	1,3	1,2
2 Yield of gases, % mass.	46,7	45,9	39,1	40,5	43,5	42,2	38,4	39,4
3. Yield of coke, %	0,5	0,6	0,6	0,7	0,5	0,6	0,6	0,7
4. Losses	1,5	1,4	1,4	1,5	1,6	1,5	1,6	1,6
5. Octane number by m.m.	109	112	114	114	110	113	114	114
by r.m.	119	122	124	124	120	123	124	124

As can be seen from the Table 12, under optimal conditions ( $T = 120\text{ }^{\circ}\text{C}$ ,  $P = 3.0\text{ MPa}$  and  $V = 1.0\text{ h}^{-1}$ ), the yield of high-octane additive with an octane number of 124 p. By the research method reaches 59.4 % by weight, the content in her ethers MTBE + ETBE – 31.3 % of the mass. and 1,3-DMB + 1,3-DEB – 15.1 % of the mass.

The composition of the high-octane additive obtained on the basis of a mixture of methanol, ethanol and a butane-divinyl fraction from the pyrolysis process using industrial Zeocar-600 as a catalyst, pressures of 2.5 and 3.0 MPa, a temperature of  $120\text{ }^{\circ}\text{C}$  and a mass feed rate of  $1.0\text{ h}^{-1}$  is presented below:

$\Sigma\text{C}_4$	5,9	5,6
Methanol	2,7	2,5
Ethanol	11,4	9,4
$\Sigma\text{MTBE} + \text{ETBE}$	51,1	52,7
$\Sigma 1,3\text{-DMB} + 1,3\text{-DEB}$	24,1	25,4
TBA	2,4	2,2
Diisobutylene	2,4	2,2
Octane number according to M.m.	114	114
Octane number according to I.m.	124	124

It is seen that the yield of the sum of methyl tertiary butyl and ethyl tertiary butyl ethers under optimal conditions is 52.7 % of the mass. The sum of 1,3-dimethoxybutane and 1,3-diethoxybutane under optimal conditions is 25.4 % of the mass.

The composition of the gas obtained in the synthesis of a high-octane additive based on methanol, ethanol and a butane-divinyl fraction from the pyrolysis process using industrial Zeocar-600 as a catalyst, a pressure of 3.0 MPa, a temperature of  $120\text{ }^{\circ}\text{C}$  and a mass feed rate of  $1.0\text{ h}^{-1}$  is presented below:

$\Sigma\text{C}_2$	0,4	$(\alpha+i)\text{C}_4\text{H}_8$	21,8
$\text{C}_3\text{H}_8$	0,4	$\beta_{\text{tr.}}\text{C}_4\text{H}_8$	10,8
$\text{C}_3\text{H}_6$	0,9	$\beta_{\text{cis.}}\text{C}_4\text{H}_8$	6,5
iso- $\text{C}_4\text{H}_{10}$	14,1	$\text{C}_4\text{H}_6$	15,8
n- $\text{C}_4\text{H}_{10}$	29,1		

In the Table 13 presents the results of studies on the production of a high-octane additive to motor gasolines based on a mixture of methanol and isopropanol and a butane-divinyl fraction from the pyrolysis process.

As can be seen from the Table 13, the optimal conditions for conducting the process are: a pressure of 3.0 MPa, a temperature of 120 °C and a mass feed rate of 1.0 h<sup>-1</sup>.

**Table 13**  
**Synthesis of high-octane additives based on a mixture of methanol and isopropanol and a butane-divinyl fraction from the pyrolysis process (Zeocar-600)**

Indices	P = 3,0 MPa, V= 1,0 h <sup>-1</sup>		
	80 °C	100 °C	120 °C
Yield of catalyzate, % mass.	57,0	59,1	60
including			
ΣC <sub>4</sub>	7,3	6,1	5,5
methanol	7,1	6,0	5,4
isopropanol	9,5	8,3	6,8
ΣMTBE + iso-PTBE	20,7	23,3	25,5
Σ1,3-DMB + 1,3-DiisopB	9,6	12,4	13,4
TBA	2,0	2,3	2,8
Disobutylene	0,8	0,7	0,6
Yield of gas, % mass	40,4	38,4	37,5
Yield of coke, % mass	0,6	0,6	0,7
Losses, % mass.	2,0	1,9	1,8

As can be seen from the Table 13, in the case of using a mixture of methanol, isopropanol and a butane-divinyl fraction from the pyrolysis process, the yield of the high-octane additive reaches 60.0 mass %, and the octane number rises sharply to 133 points by the research method in the case of adding catalytic cracking to gasoline, which, according to apparently, due to the formation of four high-octane esters - methyl tertiary butyl, iso-propyl tertiary butyl ether – 25.5 % of the mass. and 1,3-dimethoxybutane and 1,3-diisopropoxybutane – 13.4 % of the mass.

Below is the composition of a high-octane additive based on a mixture of methanol and isopropanol and a butane-divinyl fraction from the pyrolysis process using a zeolite-containing industrial catalyst Zeocar-600, a pressure of 3.0 MPa, a temperature of 120 °C and a mass feed rate of 1.0 h<sup>-1</sup>:

ΣC <sub>4</sub>	9,2
methanol	9,0



isopropanol	11,3
$\Sigma$ MTBE + iso-PTBE	42,5
$\Sigma$ 1,3-DMB + 1,3-DiisoPB	22,3
TBA	4,7
diisobutylene	1,0
Octane number according to M.m	123
Octane number according to I.m	133

The obtained high-octane additive is mixed with primary and secondary treated gasolines in any proportions without delamination.

Studies on the synthesis of high-octane additives to motor gasolines based on a mixture of three alcohols (methanol, ethanol, isopropanol) in ratios of 1 : 1 : 1 and the butane-divinyl pyrolysis fraction were also carried out under optimal conditions ( $T = 120\text{ }^{\circ}\text{C}$ ,  $V = 1.0\text{ h}^{-1}$  and  $P = 3.0\text{ MPa}$ ). The research results are presented below.

The material balance of the synthesis of high-octane additives based on a mixture of methanol, ethanol, isopropanol and the butane-divinyl fraction of pyrolysis is shown in Table 14.

**Table 14**

**The material balance of the synthesis of high-octane additives based on a mixture of methanol, ethanol, isopropanol and the butane-divinyl fraction of pyrolysis (Zeocar-600)**

Indices	$V = 1,0\text{ h}^{-1}$ , $T = 120\text{ }^{\circ}\text{C}$ , $P = 3,0\text{ MPa}$
Yield of catalyzate, % mass.	57,1
including	
$\Sigma\text{C}_4$	6,3
methanol	2,8
ethanol	5,1
isopropanol	4,7
$\Sigma$ MTBE +ETBE + iso-PTBE	19,8
$\Sigma$ 1,3-DMB + 1,3-DEB + 1,3-DiisoPB	12,5
TBA	3,2
Diisobutylene	2,7
Yield of gases, % mass.	41,2
Yield of coke, %	0,5
Losses	1,2

The composition of the high-octane additive obtained on the basis of a mixture of methanol, ethanol, isopropanol and the butane-divinyl

fraction of pyrolysis using Zeocar-600 as a catalyst, a pressure of 3.0 MPa, a temperature of 120 °C and a mass feed rate of 1.0 h<sup>-1</sup>, as follows:

ΣC <sub>4</sub>	11,0
Methanol	4,9
Ethanol	9,0
Isopropanol	8,2
ΣMTBE + ETBE + iso-PTBE	34,7
Σ1,3-DMB + 1,3-DEB + 1,3-DiisoPB	21,9
TBA	5,6
Diisobutylene	4,7
Octane number according to r.m.	140

The composition of the gas obtained in the synthesis of a high-octane additive based on methanol, ethanol, isopropanol and a butane-divinyl fraction from the pyrolysis process using industrial Zeocar-600 as a catalyst, a pressure of 3.0 MPa, a temperature of 120 °C and a mass feed rate raw materials – 1.0 h<sup>-1</sup>, is presented below:

ΣC <sub>2</sub>	0,2
C <sub>3</sub> H <sub>8</sub>	0,4
C <sub>3</sub> H <sub>6</sub>	0,5
iso-C <sub>4</sub> H <sub>10</sub>	5,2
n-C <sub>4</sub> H <sub>10</sub>	16,1
(α+i)C <sub>4</sub> H <sub>8</sub>	42,4
β <sub>тр.</sub> C <sub>4</sub> H <sub>8</sub>	9,6
β <sub>иис.</sub> C <sub>4</sub> H <sub>8</sub>	1,4
C <sub>4</sub> H <sub>6</sub>	24,2

Using a mixture of three monohydric alcohols C<sub>1</sub>-C<sub>3</sub> allowed to obtain 57.1 % of the mass. high-octane additives containing 34.7 % of a mixture of esters of MTBE + ETBE + iso-PTBE and 20.1 % of a mixture of esters of 1,3-DMB + 1,3-DEB + 1,3-Diiso-PB, with an octane rating of 140 points research method in the case of adding to the gasoline catalytic cracking in an amount of 10 %.

Fuel compositions based on GCC and a high-octane additive based on methanol and butane-divinyl fraction of pyrolysis (Table 15) and on the basis of a mixture of C<sub>1</sub>-C<sub>3</sub> monohydric alcohols and butane-divinyl pyrolysis and GCC fraction (Table 16) were compiled.

**Table 15**  
**Compositions of motor fuels based on GCC**  
**and high-octane additives based on methanol**  
**and butane-divinyl fraction of pyrolysis**

Components	Composition of additives, %	Ratio of GCC and high-octane additives		
Gasoline of catalytic cracking (GCC), % mass.		94	91	89
Amount of additive, % mass.		6	9	11
Composition of additive, % mass.:				
ΣC <sub>4</sub>	6,6	0,4	0,6	0,7
Methanol	4,6	0,3	0,4	0,6
MTBE	47,2	2,9	4,3	5,3
1,3-DMB	30,8	1,8	2,7	3,4
TBA	5,3	0,3	0,5	0,5
Diisobutylene	2,4	0,1	0,2	0,2
2-methoxyethylcyclohexene	3,1	0,2	0,3	0,3
Octane number by r.m.	121	92	93	95
by m.m	111	83	84	85

**Table 16**  
**Compositions of motor fuels based on GCC**  
**and high-octane additives based on a mixture of monohydric**  
**alcohols C<sub>1</sub>-C<sub>3</sub> and butane-divinyl fraction of pyrolysis**

Components	Composition of additives, %	Ratio of GCC and high-octane additives		
Gasoline of catalytic cracking (GCC), % mass.		95	93	89
Amount of additive, % mass.		5	7	11
Composition of additive, % mass.:				
ΣC <sub>4</sub>	11,0	0,55	0,8	1,21
Methanol	4,9	0,24	0,3	0,54
Ethanol	9,0	0,45	0,63	1,0
Isopropanol	8,2	0,41	0,6	0,9
ΣMTBE + ETBE + iso-PTBE	34,7	1,73	2,43	3,81
Σ1,3-DMB + 1,3-DEB + 1,3-DiisPB	21,9	1,1	1,52	2,41
TBA	5,6	0,28	0,4	0,62
Diisobutylene	4,7	0,24	0,32	0,51
Octane number by m.m.	125	84	85,5	88
by r.m.	140	93,5	94,5	97

Thus, to obtain high-octane gasoline A-95 based on catalytic cracking gasoline with an octane rating of 80.8 p. for the motor and 90 p.

for the research method, it is necessary to use 11 % vol. additives obtained by the interaction of methanol and butane-divinyl fraction of pyrolysis or 7 % vol. additives obtained by the interaction of a mixture of alcohols C<sub>1</sub>-C<sub>3</sub> and butane-divinyl fraction of pyrolysis. It should be noted that the resulting fuel composition in all respects meets the requirements of AGS 059-2001 for A-95 gasoline.

## **6. Study of the process of selective hydrotreating of catalytic cracking gasoline on industrial catalysts GKD-205 and S-12**

For the production of high-quality automobile gasolines, a process has been developed for the removal of sulfur compounds in a hydrogen-containing gas medium using special hydrotreating catalysts: aluminum-cobalt-molybdenum (ACM), aluminum-nickel-molybdenum (ANM), etc.

Catalytic cracking gasoline is a high-sulfur component of commercial gasoline. In addition to the high content of sulfur compounds, GCC contains high-octane olefinic hydrocarbons, which, along with aromatic ones, provide a high ON of gasoline.

As its known, when hydrotreating a wide fraction of GCC, the olefin saturation reaches 96.7 % and the loss in ON is 4.0-4.5 p. for m.m. and 9-10 p. for r.m.

In order to preserve the octane characteristics, the GCC was divided into light st.b.-120 °C and heavy en.b. 120 °C. fractions, the yield of which on the initial gasoline was 50 % vol. Only the heavy fraction of GCC, heavy gasoline with a total sulfur content of 380 ppm, was hydrotreated.

It was determined that in the heavy fraction of GCC 120 °C-en.b. falls to 82.6 % of the mass. hard-to-remove thiophene sulfur and 2.2 % olefins. This allows you to hydrotreat the heavy fraction of GCC in fairly harsh conditions with virtually no change in the ON of gasoline.

Industrial catalysts GKD-205 and S-12 were used as catalysts for the GCC hydrotreating process.

Heavy fr. 120 °C- en.b. GCC with a sulfur content of 380 ppm was subjected to hydrotreatment on an S-12 catalyst at a temperature of 250 °C and P = 2.0-2.5 MPa (Table 17).

The total sulfur content decreases from 380 to 90 ppm, the degree of hydrodesulfurization reaches 76.3 %. Losses on ON make 0,5-0,8 points.

**Table 17**  
**Hydrotreating heavy fractions GCC at T = 250 °C**

Indices	Fr. 120 °C-en.b.	
	Pressure, MPa	
	2,0	2,5
ON	79,5	79,0
Hydrogenolysis degree, %		
total sulfur	71,1	76,3
Mercaptan sulfur	79,0	85,0
Sulfur, ppm:		
total	110	90
mercaptan	4,2	3,0
Saturation degree, %	10,5	11,4

Thus, the selective hydrotreating of the heavy fraction 120 °C-en.b. GCC practically does not lead to a decrease in ON due to the low content of olefins in its composition - up to 2.2 % of the mass.

When mixing the light and hydrotreated heavy fraction of GCC according to the balance (1 : 1), the total sulfur content decreases to 90 ppm. With the introduction of hydrotreated GCC in commercial gasoline in an amount of 35-40 %, the total sulfur content decreases to 30-35 ppm, which corresponds to the environmental standard Euro-4.

## 7. The use of ionic liquids for the desulfurization of gasoline fractions

IL-s are a class of organic salts with melting points below 100-150 °C, which are in a liquid state in a wide temperature range.

ILs are generally not miscible with organic solvents. Immiscibility with water and organic solvents is an important technological property of IL, allowing the creation of two-phase systems that are used in many fields.

In the Table 18 shows the results of the desulfurization of GCC using IL based on formic, acetic, benzoic acids and aniline, piperidine and dimethylamine. The resulting mixture, after mixing with IL, was easily stratified into raffinate (sulfur-purified gasoline) and extract,

which consists of an ionic liquid and sulfur-containing and aromatic hydrocarbons dissolved in it. The extraction duration was 2 hours.

The highest extracting ability is shown by IL obtained on the basis of formic acid and aniline, which allows to reduce the total sulfur content in GCC from 240 to 66 ppm and aromatic hydrocarbons from 25.6 to 19 % of the mass. The degree of desulfurization of GCC IL with anilinium formate was 72.5%.

**Table 18**  
**The content of aromatic compounds and sulfur in gasoline**  
**(initial sulfur 240 ppm)**

Components of IL	Content of aromatic hydrocarbons in gasoline, %	Content of sulfur in gasoline, ppm	Degree of sulfur treatment, %
Formic acid and aniline	19	66	72,5
Acetic acid and piperidine	24	110	54,2
Acetic acid and diethylamine	21	80	66,7
Benzoic acid and aniline	22	90	62,5

The degree of desulfurization of gasoline also depends on the multiplicity of the process. In the Table 19 presents the results of three-fold cleaning GCC IL. The total sulfur content decreased from 240 to 30 ppm, mercaptan sulfur from 36.0 to 7.8 ppm, aromatic hydrocarbons from 25.6 to 14.0 % with a slight decrease in the octane number.

**Table 19**  
**Three-time purification of GCC IL (initial sulfur 240 ppm)**

Indices	After treatment		
	single	double	three-time
Content of aromatic hydrocarbons, % mass.	19	16	14
Content of total sulfur, ppm	66	48	30
Content of mercaptan sulfur, ppm	30	18	7,8

### **8. The study of the process of hydroisomerization of light fr. GPG st.b.- 90 °C in order to obtain a high-octane component of gasoline**

Despite the restrictions on the content of aromatic hydrocarbons, the catalytic reforming process remains the determining process for the production of gasolines, as it is the main source of high-octane

components, as well as hydrogen for hydrotreatment plants. In this regard, the reforming process of straight-run gasoline in order to obtain reformat should be combined with the processes of benzene removal and isomerization of the gasoline fraction of st.b.-90 °C GSD.

The reforming process proceeds at a high temperature of 500-510 °C and a significant negative thermal effect. In the Table 20 presents a qualitative characteristic of the wide and narrow fractions of straight-distillated gasoline isolated from a mixture of Azerbaijani oil.

Yield of fr. st.b.-90 °C GSD is 16.2 % of the mass. The content of total and mercaptan sulfur is insignificant and amounts to 120 and 32 ppm, respectively.

**Table 20**  
**Qualitative characteristic of a wide and narrow fraction of BPG**

Indices	Fr st.b.-180°C GPG	Fr st.b.-90°C GPG
Fraction composition, °C:		
st.b., °C	42	41
10 % distilled at T, °C:	67	47
50 %	102	61
90 %	154	78
к.к., °C	173	89
Boiling away % tot.	97	98
Content of sulfur, ppm:		
total	120	32
mercaptan	6	8
ON	60	63
Yield of fr st.b.-90 °C, %		16,2
Content of hydrocarbons, % mass.:		
parafines	32,6	23,2
iso-parafines	28,1	32,2
naftens	30,2	40,0
aromatics	9,1	4,7

Due to the fact that the raw material of the reforming process is the heavy fraction of straight-run gasoline 90-185 °C, the selected head benzene-forming fraction st.b.-90 °C of straight-distillated gasoline is either added to the composition of marketable gasoline to improve its starting properties, or is sent to isomerization process to obtain a high octane gasoline isocomponent. The hydroisomerization of low-octane GPG was carried out on industrial catalysts: Al-Co-Mo, S-12, GKD-205 at temperatures of 200-400 °C, overpressure of H<sub>2</sub> P = 2-3 MPa

and  $V$  about =  $1 \text{ h}^{-1}$ . The studies were carried out both on a wide and a narrow fraction of GSD. The results of these studies are presented in Table 21.

As you can see, when using the Al-Co-Mo catalyst, the octane number of the narrow fraction of st.b.-90 °C GSD increases by only 1 point, while the content of total and mercaptan sulfur decreases from 31 to 26 ppm and from 8 to 5.6 ppm, respectively.

The octane number of gasoline obtained using the S-12 catalyst rises by 10 points – from 59 to 69 p. by m.m., the total and mercaptan sulfur content decreases to 10 and 1 ppm, respectively. The increase in the octane number of the obtained gasoline fractions occurs mainly due to the isomerization of n-paraffin hydrocarbons and the dehydrocyclization of naphthenic hydrocarbons.

**Table 21**  
**Hydroisomerization of fr. st.b. 90 °C GSD on various catalysts**

Indices	Fr.st.b.- 90° GPG	$V = 1,0 \text{ h}^{-1}$				
		Catalyst S-12		Catalyst Al-Co-Mo	Catalyst GKD-205	
		P= 2,0 MPa		P= 2,0 MPa	P= 3,0 MPa	
		T = 200 °C	T = 400 °C	T= 200 °C	T = 200 °C	T = 400 °C
Content of sul- fur, ppm:						
total	31	16	10	26	12	11
mercaptan	8	1,8	1,0	5,6	4,9	4,5
ON, p.	59	65	69	60	72	73

The use of catalyst GKD-205 allows you to increase ON by 14 points – from 59 to 73 m.m. The content of total and mercaptan sulfur is reduced by 64.5 % and 43.8 %, respectively, and is 11 and 4.5 ppm, respectively.

Thus, the GKD-205 catalyst is the best catalyst for hydroisomerization of a narrow fraction of st.b.-90 °C GSD with the aim of increasing the ON by 14 points.

The obtained isomerizates are high-octane components of motor gasolines with a low content of sulfur compounds and are introduced into the composition of marketable gasolines in an amount of 10-15 % vol.



## **9. The study of hydrogenation processes refining to enoble gasolines secondary origin (coking gasoline)**

In connection with a significant increase in the share of sulphurous oils in the total number of refined oils and a continuous increase in the consumption of low-sulfur fuels – aviation, automobile and diesel, hydrogenation processes are widely used. The application of these processes allows to increase the production and improve the quality of gasolines, to regulate the ratio of the produced amounts of motor fuels at the refinery, as well as to obtain raw materials for various processes (reforming, alkylation, etc.).

Hydrogenation processes include:

- hydrotreating, the purpose of which is to remove sulfur compounds, unsaturated hydrocarbons, and in a more severe regime, hydrogenation of aromatic hydrocarbons to naphthenes;
- hydrodesulfurization of heavy oil residues, boiler fuels;
- own hydrocracking – catalytic cracking of a deeper conversion of raw materials of various fractional composition, mainly heavy sulfur distillates and residues in order to obtain light petroleum products – jet gasoline and diesel fuel.

In the schemes of oil refineries of the fuel and chemical profile, there are hydrotreating and hydrocracking units, which allows the processing of vacuum gas oils, secondary products of thermal and thermal contact processes, as well as residual types of raw materials. In this case, hydrotreating can be the head process of combined plants.

The use of these processes allows the addition of hydrogen to both the raw materials and the cleavage products, which sharply reduces the course of polymerization, polycondensation, coke formation, which can be brought to zero.

The direct addition of hydrogen to the molecules of the feedstock can occur only if they have double and triple bonds. Acetylene, then diene, and then olefin hydrocarbons of aliphatic and cyclic structures are most easily saturated. To saturate aromatic hydrocarbons, a higher partial pressure of hydrogen is required.

Hydrotreating of distillates from sulfur compounds proceeds more deeply and less selectively. Sulfur compounds inhibit the hydrogen

saturation reaction of unsaturated hydrocarbons as a result of the capture of active sites of the catalyst.

Removal of sulfur compounds leads to an increase in engine life, reduction or complete elimination of corrosion of equipment during processing and transportation of hydrotreated oil fractions, improvement of color, odor, their stability to gum formation during storage, and prevents air pollution.

The hydrogenolysis of sulfur compounds is characterized by a breaking of the carbon-sulfur bond and hydrogen saturation of olefinic bonds. The basis of the process is that the C-S bond energy (227 kJ/mol) is significantly less than the C-C bond energy (332 kJ/mol). In addition to the above reactions, partial decomposition of hydrocarbons and hydrogen saturation of the resulting unsaturated hydrocarbons to paraffins occur. However, the proportion of these reactions is small. At the same time, hydrogenation of resins, nitrogenous and oxygen-containing compounds, destruction of organometallic compounds, isomerization of paraffinic and naphthenic hydrocarbons are observed. These reactions, depending on the properties of the catalyst, are observed to one degree or another under any desulfurization conditions. However, it should be noted that with deep desulfurization, a relatively small degree of hydrogenation occurs. So, at  $T = 340\text{ }^{\circ}\text{C}$ ,  $P = 20\text{ atm}$ , and a mass feed rate of  $5.0\text{ h}^{-1}$ , only 20 % of unsaturated hydrocarbons are saturated at 80 % desulfurization depth. Under more severe conditions and the same mass feed rate, the hydrogenation depth of unsaturated hydrocarbons rises to 85 % with a relatively small change in the hydrogenation depth of sulfur compounds.

The correct selection of the conditions of hydrogenation processes can completely prevent coke formation, stabilize the activity and selectivity of the catalysts for hydrogenation processes.

The deepest form of hydrogenation processes is hydrocracking, the purpose of which is to obtain light petroleum products. Moreover, depending on the consumption of hydrogen and the mode, the process can be oriented towards obtaining the maximum yield of gasoline or jet and diesel fuel. The process, as a rule, is two-stage: in the first stage, sulfur-resistant catalysts such as hydrotreating catalysts are used, and

at the same time hydrofining of the raw material occurs during its partial decomposition. At the second stage, on hydrocracking catalysts containing group VI and VIII metals (Co, Ni, W, Mo, Pt) on supports (amorphous type aluminosilicates or zeolites), the raw materials are converted to the required depth. Both stages are characterized by high partial pressure of hydrogen (15-20 MPa) and temperature 400-450 °C. Conventional hydrotreating catalysts are aluminum-cobalt-molybdenum (ACM) and aluminum-nickel-molybdenum (ANM), as mentioned above. The hydrogenating components are cobalt, nickel and molybdenum, deposited as oxides on alumina. The aluminum-cobalt-molybdenum catalyst contributes to deep desulfurization and desalting of straight-run distillates and distillates of secondary origin under relatively mild conditions: temperature 400-420 °C, pressure 15-20 atm. This removes not only sulfur compounds, but also a significant part of unsaturated hydrocarbons, the content of aromatic hydrocarbons decreases by 5-10 %.

The cleaning conditions depend on the nature of the feedstock and the quality requirements of the product being cleaned. So, lighter distillates, for example, gasolines, are more easily hydrotreated in accordance with the nature of the sulfur compounds contained in them (mercaptans, sulfides), and a lower content of low molecular weight unsaturated hydrocarbons. With the weighting of the raw materials, more stable sulfur compounds (thiophenes) and difficultly hydrogenated unsaturated hydrocarbons appear in it, if these are raw materials of secondary origin. At the same time, with the weighting of raw materials, the requirements for the sulfur content in the hydrotreated product are reduced. The hydrogen consumption for hydrotreating is also associated with the origin of the feed and its sulfur content. The sulfur content in straight-run gasolines of even high-sulfur oils is relatively small – 0.12 %, and in delayed coking gasolines is 0.6 %, so the hydrogen consumption in the first case is 0.05-0.07 %, and in the second – 0.54-0.64 %.

Gasolines of secondary origin, in particular coking gasoline, can be used as reforming feedstock after deep refinement.

In this regard, the process of the two-stage hydrotreating of coking gasoline as a feedstock for the reforming process to increase raw materials using industrial hydrotreating catalysts (GKD-205 and S-12) was studied in order to minimize unsaturated and sulfur compounds, as well as other undesirable components.

Coking gas produced at the Heydar Aliyev Oil Refinery is mainly used as a component of commercial gasoline. However, due to the shortage of straight-run gasoline used as reforming feedstock, it is advisable to use coking gasoline after preliminary hydrofining as a reforming feedstock.

It is known that hydrotreating gasoline thermal processes (coking, catalytic cracking) is much more difficult to carry out in comparison with straight-run fractions, since they contain a large amount of unsaturated hydrocarbons, including diene, as well as sulfur and nitrogen-containing compounds.

The sulfur content in coking gasoline (batch 1), obtained from a mixture of low-sulfur oils, is 0.145 %, olefins – 34 %, which does not allow the use of this gasoline as a reforming feed, since the permissible sulfur content in hydrotreated gasoline should not be more than 0.003 % (30 ppm).

To reduce the content of sulfur and unsaturated hydrocarbons in coking gasoline, hydrotreating was carried out on an industrial aluminum-nickel-molybdenum catalyst GKD-205.

As is known, the stability of sulfur compounds increases with increasing molecular weight of distillates, and since coking gasoline (batch 1) has a low molecular weight (107) and it contains mercaptans – RSH – and disulfides –  $R^1-S-R^2$  – this will allow carry out the hydrotreatment process in fairly mild conditions - a temperature of 350-400 °C and a pressure of 3.0-5.0 MPa.

The process of hydrotreating coking gasoline (batch 1) was carried out by a flow-through installation in an atmosphere of circulating hydrogen-containing gas on a stationary catalyst bed GKD-205. The catalyst was calcinated at a temperature of 450 °C, then reduced at the same temperature with hydrogen at  $P = 2.0$  MPa. In industrial conditions, the preparation (calcination) and regeneration of this catalyst

was carried out under the conditions: regeneration  $P = 2.2$  MPa,  $T = 500$  °C, calcination  $P = 1.9$  MPa,  $T = 500$  °C.

Hydrotreating of coking gasoline (batch 1) was carried out at different temperatures (350-400 °C) and pressures of a hydrogen-containing gas (3.0-5.0 MPa). It was found that the optimal pressure is 5.0 MPa. The material balance of the hydrotreatment process of coking gasoline (batch 1) at  $P = 5.0$  MPa,  $V = 1.0$  h<sup>-1</sup> is presented below:

	350 °C	380 °C	400 °C
Taken:			
Coking gasoline, %	100,0	100,0	100,0
H <sub>2</sub> contain gas	1,2	1,2	1,2
Total:	101,2	101,2	101,2
Received:			
Hydrotreated gasoline	98,0	97,0	96,0
Hydrocarbon gas	1,8	2,0	2,3
Loss:	1,4	2,2	2,9
Total:	101,2	101,2	101,2

After the hydrotreating process, the composition of gasoline identified the composition of olefins and determined the total sulfur content by X-ray fluorescence method on the apparatus.

As you can see, the yield of hydrotreated gasoline decreases by 1-2 % with increasing temperature, and the amount of hydrocarbon gas increases slightly. Analysis of the gas shows that it contains mainly ethane, propane, butane and some other components.

The material balance of the process of hydrotreating coking gasoline (batch 1) at a pressure of hydrogen-containing gas  $P = 4.0$  MPa and  $V = 1.0$  h<sup>-1</sup> is presented below:

	350 °C	380 °C	400 °C
Taken:			
Coking gasoline, %	100,0	100,0	100,0
H <sub>2</sub> contain gas	1,4	1,4	1,4
Total:	101,4	101,4	101,4
Received:			
Hydrotreated gasoline	98,5	98,2	97,8
Hydrocarbon gas:	1,0	1,5	1,9
C <sub>2</sub> H <sub>6</sub>	6,35	5,15	4,48

C <sub>2</sub> H <sub>4</sub>	4,12	6,54	8,89
C <sub>3</sub> H <sub>8</sub>	26,20	30,13	33,14
C <sub>3</sub> H <sub>6</sub>	2,7	3,1	3,24
i-C <sub>4</sub> H <sub>10</sub>	6,73	10,7	11,95
n-C <sub>4</sub> H <sub>10</sub>	38,05	26,95	22,90
i-C <sub>5</sub> H <sub>12</sub>	9,22	10,85	10,88
n- C <sub>5</sub> H <sub>12</sub>	6,63	6,58	4,52
Loss:	1,9	1,7	1,7
Total:	101,4	101,4	101,4

With a decrease in hydrogen pressure from 5.0 to 4.0 MPa, the yield of hydrotreated coking gasoline (batch 1) increases slightly. Below is a qualitative characteristic of hydrotreated coking gasoline (batch 1) at P = 5.0 MPa and V = 1.0 h<sup>-1</sup>.

	350 °C	380 °C	400 °C
Missed:			
Raw materials, ml	400	200	200
H <sub>2</sub> -containing gas, l	204	215	100
Received:			
Catalyst, g	143.2	141.8	140.6
Yield, %	98.0	97.0	96.0
Molecular Weight	103.7	100.2	94.6
Density, $\rho_4^{20}$	0.725	0.729	0.727
Iodine number, g J <sub>2</sub> /100 g gasoline	0.79	0.75	0.71
Unsaturated content	0.32	0.29	0.26
The degree of hydrogenation of unsaturated compounds	98.93	98.98	99.03
The sulfur content in % of the mass.	0.0041	0.0042	0.0044
The degree of desulfurization, %	97.17	97.18	96.97
Lead content, g/cm <sup>3</sup>	0.0019	0.0018	0.0017
Demetallization, %	71.21	72.72	74.24
Octane number according to m.m.	64	63.5	63

As you can see, unsaturated hydrocarbons are almost completely hydrogenated at a temperature of 350-400 °C, while the degree of hydrogenation of coking gasoline (batch 1) is 99.03 %.

It should be noted that the hydrogenolysis of sulfur compounds most fully proceeds at a temperature of 350 °C and amounts to 97.17 %.

Therefore, the selected hydrotreating conditions in this range favorably affect both the hydrogenation process of unsaturated compounds and the hydrodesulfurization process, that is, they can reduce the content of unsaturated and sulfur compounds within acceptable limits.

In the hydrotreatment process, demetallization of coking gasoline also occurs.

Due to the hydrogenation of olefin hydrocarbons, the octane number of gasoline is reduced by 4 points, from 67 points by the motor method to 63 points by the motor method, since the obtained paraffin hydrocarbons have lower octane numbers than olefin hydrocarbons.

## **10. The effect of physical effects (cavitation) on the alkoxyalkylation process**

For the intensification of petrochemical processes, various types of physical effects are currently used, in particular ultrasonic cavitation. The effect of ultrasonic cavitation on the alkoxyalkylation of the light fraction of coking gasoline with ethanol was studied.

Raw materials – fr. st.b.-85 °C GC containing 26.33 % olefins and 875 ppm total sulfur with 70 ppm ON with the number of carbon atoms C<sub>4</sub>-C<sub>8</sub>.

The alkoxyalkylation of a narrow fraction of GC with ethanol in a volume ratio of 5 : 3 was carried out on a Hungarian flow-type plant with a stationary layer of a zeolite-containing catalyst (NaY filler) at T = 80-90 °C, V = 0.5 h<sup>-1</sup>, P = 0.2-0.3 MPa. The maximum yield of liquid products – 93.6 % was observed at a temperature of 80 °C and V = 0.5 h<sup>-1</sup>. The resulting catalyzate is the product of alkoxyalkylation of ethanol and fr. st.b.-85 °C GC is the alkyl ethyl ethers of the corresponding olefinic hydrocarbons

In order to intensify the process of alkoxyalkylation – increasing the yield of esters, reducing coke formation, increasing ON, the effect of ultrasonic cavitation on this process was studied.

Cavitation treatment of the reaction mixture (st.b.-85 °C CG and

ethanol) was carried out on a UP 200 st “hielsher” instrument, operating frequency 26 Hhz, temperature range 5-40 °C, power 32-44 W, processing time 50 min. In the Table 22 shows the material balance of alkoxyalkylation.

**Table 22**  
**The material balance of the process**  
**of alkoxyalkylation st.b.-85 °C GC with ethanol**

Temperature °C	70	80	90
Taken (% mass.):			
Fr. st.b.-85°C GC	62,5	62,5	62,5
ethanol	37,5	37,5	37,5
Total:	100	100	100
Received (% mass.):			
Catalyzate, % macc.	94,3	98,2	94,0
Gas	5,35	1,44	5,55
Coke + losses	0,35	0,36	0,45
Total	100	100	100

It was found that the yield of liquid products obtained by cavitation processing of the feedstock increased by 1.8-4.6 %, coke formation decreased by 50-55 % compared to processes without cavitation. The total sulfur content in the catalyzate before and after cavitation remained virtually unchanged at 547 ppm.

### **11. Improving the environmental and motor characteristics of commercial gasoline components by introducing oxygenates into their composition**

It is known that one of the largest areas of energy use is transport, which is mainly focused on the use of liquid fuels from oil, which are characterized by high energy characteristics and relatively simple production technology. But the reserves of liquid energy carriers (oil) are not as large as the resources of solid organic raw materials, which leads to the search for alternative energy sources based on raw materials of non-oil origin.

In this regard, the process of alkoxyalkylation of GCC with bioethanol (ethanol content of 97.8 %) obtained by fermentation of agricultural waste was studied.

The results of alkoxyalkylation of fractions st.b.-130 °C and st.b.-200 °C are presented in Table 23.



**Table 23**

**Material balance of the alkoxyalkylation process  
of the fraction st.b.-130 °C (2 : 1) and fractions  
st.b.-200 °C (3 : 1) GCC with bioethanol**

Indices	Temperature, °C / pressure, MPa					
	70/0,1	70/0,2	80/0,1	80/0,2	90/0,1	90/0,2
Crude – fraction st.b.-130 °C						
Received, % mass..						
catalyzate	99,8	97,3	99,7	97,0	99,7	96,8
Including alkylethers	14,43	15,65	13,08	15,98	13,00	16,37
losses	0,2	2,7	0,3	3,0	0,3	3,2
Degree of conversion of unsaturated hydrocarbons, %	44,25	48,0	40,1	49,0	39,87	50,2
Сыр'е – fraction st.b.-200 °C						
Received, % масс.						
catalyzate	97,9	97,1	97,2	96,8	96,4	95,7
Including alkylethers	9,34	6,5	9,76	6,27	7,04	5,95
losses	2,1	2,9	2,8	3,2	3,6	4,3
Degree of conversion of unsaturated hydrocarbon, %	40,2	28,0	42,0	27,0	30,3	25,6

A higher yield of alkylethers is achieved when using the st.b.-130 °C fraction due to the higher content of unsaturated hydrocarbons in it - up to 23.3 % of the mass.

Thus, it is advisable to carry out alkoxyalkylation of the fraction st.b.-130 °C GCC. The octane number of the product alkoxyalkylation in this case is 86 p. by m.m. When this fraction is mixed with a GCC fraction of 130-200 °C with an octane rating of 83 p. by m.m., gasoline is obtained with an octane number of 85 p. by m.m.

Currently, due to environmental degradation and an increase in demand for high-quality motor fuels, there is an acute problem of using alternative sources for producing motor fuels, which include natural, associated and refinery gases containing low molecular weight C<sub>2</sub>-C<sub>5</sub> hydrocarbons.

The results of a study on the joint conversion of a narrow fraction of st.b.-85 °C with GR gases C<sub>3</sub>-C<sub>4</sub> CC on an Omnikat-210P catalyst at temperatures of 250-480 °C and V = 1.0 h<sup>-1</sup> are presented in Table 24.

With increasing temperature, the growth of liquid products decreases from 16.8 to 5.7 %. The maximum increase in gasoline fractions of 16.8 % was observed at a temperature of 250 °C.

**Table 24**

**The process of turning fr. st.b.-85 °C GR  
with gases C<sub>3</sub>-C<sub>4</sub> CC (Omnikat-210P)**

Taken, % mass.	Temperature, °C						
	200°C	250°C	300°C	350°C	400°C	450°C	480°C
fr. st.b. 85°C GR	65,4	65,4	65,4	65,4	65,4	65,4	65,4
gases C <sub>3</sub> -C <sub>4</sub> CC	34,6	34,6	34,6	34,6	34,6	34,6	34,6
Received (% mass.):							
gas	26,5	21,6	23,7	24,6	26,0	27,4	28,9
catalyzate	71,3	76,4	74,2	72,3	71,9	70,4	69,1
coke + losses	2,2	2,0	2,1	2,0	2,1	2,2	2,0
Liquid product growth	9,0	16,8	13,5	10,6	9,9	7,6	5,7

The octane number of gasoline obtained by the interaction of fr. st.b.- 85 °C reforming gas with C<sub>3</sub>-C<sub>4</sub> CC gases increased in comparison with the initial gasoline fraction of GR by 1.5 points according to m.m.

The results of studies of the interaction of fr. st.b.-85 °C GC with gases C<sub>3</sub>-C<sub>4</sub> CC on Omnikat-210P are presented in Table 25.

**Table 25**

**The material balance of the interaction process fr. st.b.-85 °C GC  
with gases C<sub>3</sub>-C<sub>4</sub> CC on the Omnikat-210P catalyst**

Indices	Temperature, °C						
	200 °C	250 °C	300 °C	350 °C	400 °C	450 °C	480 °C
Taken, % mass:							
fr. st.b. 85°C GR	65,4	65,4	65,4	65,4	65,4	65,4	65,4
gases C <sub>3</sub> -C <sub>4</sub> CC	34,6	34,6	34,6	34,6	34,6	34,6	34,6
Received (% mass.):							
gas	30,9	25,6	26,5	27,9	28,6	29,8	31,4
catalyzate	67,0	72,4	71,5	70,0	69,2	68,0	66,3
coke + losses	2,1	2,0	2,0	2,1	2,2	2,2	2,3
Liquid product growth	2,5	10,7	9,3	7,0	5,8	3,9	1,4
ON growth	1,0	2,0	2,0	1,5	1,5	1,0	1,0

As can be seen from the Table 25, the yield of catalyzate – gasoline fraction – passes through a maximum (72.4 %) at 250 °C, while the increase in liquid products amounted to 10.7 % of the mass.

Fuel compositions were compiled based on the basic components of gasoline and oxygenates obtained by the interaction of methyl alcohol and a butane-divinyl fraction of pyrolysis under optimal conditions: T = 120 °C, P = 3 MPa and V = 1 h<sup>-1</sup>. The octane number of the

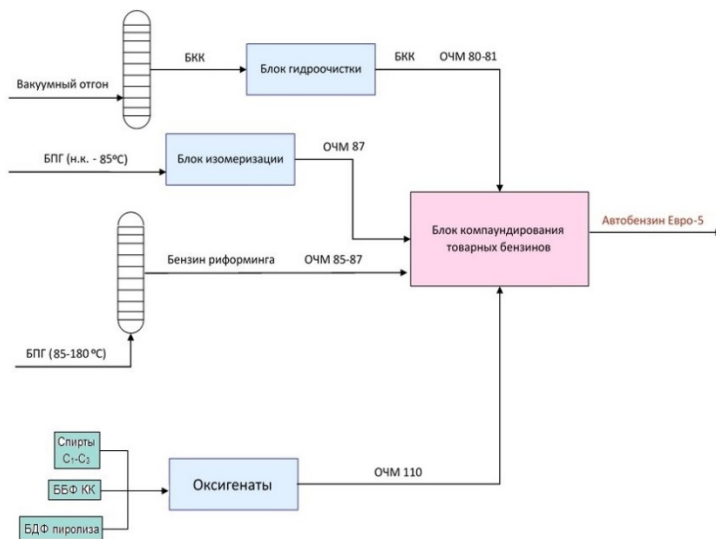
obtained additive is 140 p. according to the research method (Table 26).

**Table 26**

**Composition of marketable gasolines involving oxygenates  
obtained by reaction of methyl alcohol  
and a butane-divinyl fraction of pyrolysis**

Composition, %	Mixture № 1	Mixture № 2	Mixture № 3	Mixture № 4	Mixture № 5
GCC	45	45	45	43	40
GR	45	42	40	40	40
GSD (straight-distilled) isomerizate	4	5	5	5	5
Oxygenates	6	8	10	12	15
ON of gasoline by R.m.	93,6	94,4	95,3	96,3	97,8
ON of gasoline by m.m.	83,6	84,4	85,3	86,3	86,7

Based on the results of the research, a block diagram of the production of Euro-gasoline is presented below (Figure 3).



**Figure 3. Block scheme for producing Euro-5 gasoline**

Thus, various options for the production of high-octane commercial gasolines with the involvement of basic components (GCC, GR,

GSD), alkylates, isomerizates, and oxygen-containing compounds in their composition were presented above.

At present, Azerbaijan has facilities for the production of oxygen-containing compounds – isopropyl alcohol and methanol (AzMeCo plant, with a capacity of 2000 tons per day). The use of these oxygenates and ethers based on C<sub>1</sub>-C<sub>3</sub> alcohols, butane-butylene fraction of catalytic cracking and butane-divinyl fraction of pyrolysis (MTBE, ETBE, i-PTBE, etc.) makes it possible to produce gasolines that comply with the environmental standards Euro-4, Euro-5.

## CONCLUSIONS

1. A process has been developed for the production of high-octane oxygen-containing additives (oxygenates) for motor gasolines based on C<sub>1</sub>-C<sub>3</sub> monohydric alcohols, technical isobutylene, BBF CC and BDF of pyrolysis using industrial zeolite-containing catalysts.
2. The optimal conditions for the synthesis of oxygenates based on isobutylene and methanol on the Zeocar-600 catalyst were determined: T = 120 °C, P = 2.5 MPa, V = 1 h<sup>-1</sup>, at which the maximum yield of catalyzate and MTBE was 91.9 and 78.9 % of the mass. respectively. It was found that when GCC and GSD are added to the composition, up to 11 % of the synthesized additive of ON gasoline increases by 3-4 and 6-7 points, respectively.
3. For the first time, the possibility of obtaining oxygen-containing additives based on monohydric alcohols C<sub>1</sub>-C<sub>3</sub> and BDF pyrolysis with a butylene content of up to 56.77 % by mass was established. The effect of the main technological parameters of the process on the yield and quality of additives was studied. It is determined that the maximum yield of the additive is 58.7 % of the mass., Including 27.7 % of the mass. MTBE and 18.1 % of the mass. 1,3-dimethoxybutane under optimal conditions: T = 120 °C, P = 3 MPa and V = 1 h<sup>-1</sup>, while the octane number of the additive is 121 points according to r.m. [21].

4. A formulation has been developed for the production of high-octane gasoline with an ON of 92-95 points involving 7-11 % of the additive synthesized based on methanol and BDF pyrolysis. In the case of introducing into the composition of gasolines 7-11 % of the additive obtained on the basis of a mixture of alcohols C<sub>1</sub>-C<sub>3</sub> and BDF pyrolysis, it is possible to obtain high-octane gasolines with an ON of 95-97 points.
5. It was found that with an increase in the molecular weight of monohydric alcohols, both the yield from 89 to 95 % by mass and the octane numbers of the oxygenate additive increase (117 p. to 125 p. r.m.).
6. Alternative methods for desulfurization of gasolines using IL with the preservation of ON gasolines have been developed. The highest extraction ability under identical conditions is shown by IL obtained on the basis of formic acid and aniline, which allows reducing the total sulfur content in GCC from 240 to 66 ppm and aromatic hydrocarbons from 25.6 to 19 % of the mass. The degree of GCC desulfurization by anilinium formate ionic liquid was maximum and amounted to 72.5 % [4].
7. A method has been developed to reduce the total sulfur in BCC without reducing the ON by selective hydrotreating of heavy fr. GCC 120 °C-en.b. to on industrial hydrotreating catalysts. The content of total sulfur in heavy fr. GCC decreases from 380 to 90 ppm. When the light and heavy fractions were mixed according to the balance, the sulfur content in CC gasoline decreased to 85 ppm. Losses on ON make no more than 0,5-0,8 points.
8. The effect of ultrasonic cavitation on the alkoxyalkylation of fr. st.b.-85 °C CG with ethanol at T = 70-90 °C, V = 0.5 h<sup>-1</sup> and processing time 50 min. It was established that the yield of alkylethyl ethers increased by 50.8 %, ON by 6 points, coke formation decreased by 50-55 % compared with processes without cavitation [26].
9. The process of hydroisomerization of light fr. GSD st.b.-90 °C to obtain a high-octane gasoline component on the GKD-205 catalyst at 200-400 °C, H<sub>2</sub> pressure P = 2-3 MPa and V<sub>rev.</sub> =

- 1 h<sup>-1</sup>. At the same time, the isomerizate ON increased by 14 points, from 59 to 73 points.
10. The process of alkylation of BBF CC on the Omnikat-210P catalyst was studied to obtain high-octane components of motor fuels at T = 200-300 °C and V<sub>ob.</sub> = 100-150 h<sup>-1</sup>. The yield of alkylate in this case amounted to 82.2% of the mass. with an ON of 85-86 points. When using a cation exchange resin (KU-2) as a catalyst at T = 100 °C, the octane number of the alkylate was 108-109 points according to r.m.
  11. The cost of high-octane oxygenate additives obtained on the basis of methanol with BBF CC and BDF pyrolysis is 406.04 man./tons (based on BBF) and 735.42 man./tons (based on BDF).

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