

As a manuscript

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**DEVELOPMENT OF A METHOD OF
PRODUCING ANTIDETONATION ADDITIVES
TO GASOLINES WITH THE USE OF A
CATALYST IN A NANOSTRUCTURED FORM**

18.04.01 – Chemical Technology

ABSTRACT
Master's Dissertation
For the award of master's degree

Tambov2017

The work was carried out at the Department of Chemistry and Chemical Technologies of the Federal State Budget Educational Institution of Higher Education "Tambov State Technical University" (FSBEIHE-"TSTU").

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The defense of the thesis will be held on 28th June, 2017 at 10.00 am at a meeting of the State Examination Commission of Tambov State Technical University at the address: 392020, Tambov, Leningradskaya street, block1, room. 17.

You can get acquainted with the thesis in the library of the FGBOU VO "TSTU".

The author's abstract was prepared on 25th May, 2017.

Secretary SAK

M.Y. Subocheva

GENERAL DESCRIPTION OF WORK

Relevance of the topic. At present, the production of motor fuels, in particular, motor gasolines, has significantly increased. In parallel with the volumes of production, the requirements to their quality are also growing. Known ways to improve the quality of gasolines due to the improvement of technological processes for obtaining high-octane hydrocarbon fractions can not be realized sufficiently and are economically unprofitable. Therefore, the most widespread methods of improving the quality of automotive fuels is with the use of octane-enhancing additives and additives of various types.

At present, additives are an indispensable element of a high technical culture of production and use of fuels.

The production and use of modern additives to fuels in many countries of the world has not yet reached the modern level, so the development of new high-performance additives in gasoline is an urgent and required topic.

The purpose of the work and the tasks of the study.

The aim of the thesis is to develop a method for obtaining an antiknock additive using nanostructures that provide an increase in the octane number, complete combustion of fuel and a reduction in the amount of harmful substances in the exhaust gases.

The tasks of experimental research:

1. To develop a composition and a method for producing an antiknock additive based on aromatic amines and oxygen-containing compounds using nanomaterials;
2. Develop an experimental setup for the composition of the additive;
3. To select the optimal composition of the antiknock additive on the basis of the results of the study of gasoline samples on the universal engine installation UIT-85;
4. To evaluate the effect of changing the octane number from the addition of additives to standard fuels and gasoline of A-80 and Regular-92 grades;
5. To assess the effect of the additive on the amount of harmful substances in the exhaust gases.
6. Develop a chemical scheme for the production of monomethylaniline;
7. To develop a conceptual and sketch technological scheme for the production of monomethylaniline;

8. To calculate the material and heat balances of the additive production.

Methods of research. For the conduction of experimental studies of the antiknock additive providing complete combustion of fuel, increasing the octane number and reducing the amount of harmful substances in the exhaust gases, the following steps were carried out:

- A technique for obtaining an antiknock additive based on aromatic amines and oxygen-containing compounds using nanomaterials was developed;

- The optimal composition of the antiknock additive was determined, based on the results of a study of gasoline samples at the universal engine installation UIT-85.

Scientific novelty. The composition of the antiknock additive with the use of nanostructures providing an increase in the octane number, complete combustion of fuel and a decrease in the amount of harmful substances in the exhaust gases is proposed.

The practical value of the work is as follows:

- An experimental setup for the composition of the additive was developed;

- A method for identifying the optimal composition of the antiknock additive was proposed, based on the results of a study of gasoline samples at the UIT-85 universal engine;

- A technique for estimating the effect of an antiknock additive on the change in the octane number from the addition of additives to standard fuels and gasoline of grades A-80 and Regular-92;

- The effect of the antiknock additive on the amount of harmful substances in the exhaust gases is estimated.

Publications. On the topic of the dissertation, 3 scientific works were published.

Structure and amount of work.

The thesis consists of an introduction, three chapters, conclusion, a list of sources used, including 35 titles. The main part is set out on 73 pages of typewritten text, contains 15 figures, 12 tables.

laboratory sample of the additive. The values found are presented in Table 1.

Table 1 - Norms of consumption of raw materials for laboratory additive synthesis

Name	Consumption rate%
Raw materials	42
N-methylaniline	9
Aniline	13
Nitrobenzene	29
Methanol	7
Isopropyl alcohol	0.008

The production of an antiknock additive using nanomaterials was carried out as follows:

In a 500 ml glass beaker, 210 ml of N-methylaniline was added, the stirrer was turned on and the number of revolutions (30 rpm) was set using LATR. A solution of 0.001 g of nanocatalysts No.1 with aniline of 22.5 ml volume was prepared, similarly to the nanocatalyst Nos. 2 and 3. The nanocatalyst is a gray powder with a particle size of 10 to 100 nm. After 10 minutes, 65 ml of nitrobenzene, 145 ml of methanol, 35 ml of isopropyl alcohol were added to the beaker, and preliminary solutions of aniline and nanomaterials were added. The resulting suspension was stirred with a laboratory stirrer for 30 minutes. At the end of the synthesis of the additive, samples were taken to determine the optimum composition of the additive by subsequently measuring the detonation resistance of the mixture at a single-cylinder UIT-85 unit. The test formulation of the additives is given in Table 2.

Table 2 - Composition of additives introduced into standard gasolines

No p/p	Compositions of additives added to standard gasolines
1.1.	Aniline-30%, methanol-70%, Nanocomposition No. 1-0.0017%
1.2.	Aniline-30%, methanol-70%, Nanocomposition No. 2-0.0017%

Continuation of table 2

1.3.	Aniline-30%, methanol-70%, Nanocomposition No. 3-0.0017%
2.1.	N-methaniline-60%, methanol-30%, Isopropyl alcohol -10%, Nanocomposition No. 1-0.0017%
2.2.	N-methaniline-60%, methanol-30%, Isopropyl alcohol -10%, Nanocomposition No. 2-0.0017%
2.3.	N-methaniline-60%, methanol-30%, Isopropyl alcohol -10%, Nanocomposition No. 3-0.0017%
3.1.	N-methaniline-45%, aniline-10%, Nitrobenzene-15%, methanol-25%, Isopropyl alcohol-10%, Nanocomposition No. 1-0.0017%
3.2.	N-methaniline-45%, aniline-10%, Nitrobenzene-15%, methanol-25%, Isopropyl alcohol-10%, Nanocomposition No. 2-0.0017%
3.3.	N-methaniline-45%, aniline-10%, Nitrobenzene-15%, methanol-25%, Isopropyl alcohol-10%, Nanocomposition No. 3-0.0017%

2) determination of the octane number of samples obtained for additives for research and motor methods;

The octane number was determined on a single-cylinder unit UIT-85 for research and motor methods.

The octane numbers of gasoline for various compositions of antiknock additives are presented in Table 3.

Table 3 - Octane numbers of gasoline for various compositions of antiknock additives

Sample name	Octane number	
	By Research method	By Motor method
Gasoline A-80	83.6	79.9
Gasoline A-80 with additive №1 in quantity,%	87.9 91.7 92.6	81.5 83.7 83.1
Gasoline A-80 with additive №2 in quantity, % 1.2. 2.2. 3.2.	86.6 90.8 94.8	80.4 83.1 84.7
Gasoline A-80 with additive №3 in quantity,% 1.3. 2.3. 3.3.	87.6 92.6 96.4	81.2 84.2 86.3
Gasoline A-80, containing N-methylaniline 1.35%, Aniline 0.3%, Nitrobenzene 0.45%, Methanol 0.75%, Isopropyl alcohol 0.3%	91.9	83.2
Gasoline Regular-92	92.8	82.6

Continuation of table 3.

Gasoline Regular-92 with additive № 1 in quantity, %		
1.1.	94.2	83.3
2.1.	95.1	84.6
3.1.	95.3	85.3
Gasoline Regular-92 with additive № 2 in quantity, %		
1.2.	95.1	84.4
2.2.	96.4	86.2
3.2.	97.6	86.9
Gasoline Regular-92 with additive № 3 in quantity,, %		
1.3.	96.1	85.2
2.3.	98.2	87.3
3.3.	99.1	88.5
Gasoline Regular-92, containing N-methylaniline 1.35%, Aniline 0.3%, Nitrobenzene 0.45%, Methanol 0.75%, Isopropyl alcohol 0.3%	95.7	85.2

From the analysis of the obtained values of octane numbers for standard fuel and gasolines A-80 and Regular-92 with added additives 1-3, it can be seen that the use of the composition of nanomaterials No. 3 in the additive enhances the anti-detonation effect of the mixture.

The presence of the effect of increasing the octane number from the introduction of nanomaterials into real gasolines can be presumably attributed to the presence of low-temperature cracking and isomerization processes.

3) determining the amount of harmful substances in the exhaust gases;

Further experimental studies were carried out with an anti-detonation additive consisting of N-methylaniline 45%, aniline 10%, nitrobenzene 15%, methanol 25%, isopropyl alcohol 10%, and nanocompositions No. 3 0.0017%.

The measurement of the content of harmful substances in the exhaust gases is presented in Table 4.

Table 4 - Results of measuring the content of harmful substances in exhaust gases

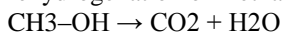
Fuel grade	Testing Mode	Distsnce travelled S, км	Estimated fuel consumption Q, l	CO g/км	CH g/км	NO g/км	CO2 g/км
Gasoline AI-92	Urban	5,5	8.2	1.82	0.094	0.303	794
	Country		5.8	11.42	0.342	0.178	944
Average value			7	6.62	0.218	0.24	869
Gasoline AI-92 + 3% weight. Supplements	Urban	5,5	7.5	0.663	0.021	0.151	737
	Country		5.87	5.97	0.1	0.09	964
Average value			6.68	3.32	0.06	0.12	850.5
Reduction of harmful emissions in exhaust gases, times			1,04	2	3.6	2	1.02

On the basis of the above experimental data, it can be concluded that its use has made it possible to reduce the content of harmful substances in the exhaust gases: CO 2 times, CH 3.6 times, NO 2 times, CO2 1.02 times and reduce gasoline consumption 1 , 04 times.

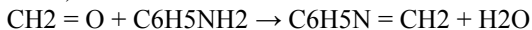
The third chapter is devoted to the development of a technology for the production of monomethylaniline, which is the main component of the antiknock additive to gasoline using a catalyst in a nanostructured form.

The following basic chemical reactions occur during the synthesis of monomethylaniline:

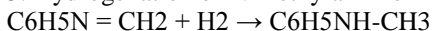
1. Dehydrogenation of methanol to formaldehyde:



2. Condensation of formaldehyde with aniline (methylenedianiline production):



3. Hydrogenation of N-methylaniline in monomethylaniline:



To implement the proposed method of production of the main component, a sketch flowchart was developed,

Consisting of the following main stages: preparation of raw materials, mixing, contacting (synthesis of MMA), separation of reaction mass, distillation of methanol, distillation of MMA crude, processing of bottoms, production of technical MMA, synthesis of additives.

Based on the chemical and sketch schemes, a material calculation of the production of monomethylaniline was carried out.

Thermal calculation was carried out for the main stages of production of monomethylaniline in order to determine the amount of coolant and refrigerant.

To implement the proposed method for the production of an antiknock additive into gasoline using a catalyst in nanostructured form, a principal technological scheme has been developed.

MAIN CONCLUSIONS AND THE RESULTS OF THE WORK

1. The composition of the antiknock additive in gasoline using a catalyst in nanostructured form is proposed.
2. The effect of increasing the octane number from the addition of additives to standard fuels and gasoline of A-80 and Regular-92 grades was evaluated.
3. Based on the results of experimental data, it can be concluded that the use of an antiknock additive can reduce the content of harmful substances, as well as the consumption of gasoline.
4. A chemical scheme has been developed for the production of the main component of the additive.
5. Principal and draft technological schemes for the production of monomethylaniline have been developed.
6. Calculations of material and thermal balances of production of monomethylaniline are given.

LIST OF WORKS PUBLISHED ON THE THEMES OF DISSERTATION

1. Leontieva AI, Vizhanov AV, Alchaabavi A.H., Egorova A.S. Development of antiknock additives to gasolines with the use of nanomaterials that ensure complete combustion of fuel / Leont'eva AI // Collected scientific papers on the materials of the XXI International Scientific and Practical Conference. - 2016. - Part 1. № 12 - 48-50 with.
2. Leontieva AI, Vizhanov AV, Alchaabavi A.H., Egorova A.S. Study of the influence of the gasoline modifier using catalysts in nanostructured form on

the environmental parameters of fuel combustion in gasoline engines / Leont'eva AI // Collection of scientific papers on the materials of the XXII International Scientific and Practical Conference. - 2017. - Part 2. No.1 - 72-75 with.

3. Leontieva AI, Vizhanov AV, Alchaabavi AH, Egorova AS Carrying out research to determine the physicochemical and antiknock properties of the gasoline modifier / Leontiev A.I. / Collection of scientific papers on the materials of the XXIII International Scientific and Practical Conference. - 2017. - Part 1. №2. - 63-67 p.