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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy
(Doctor of Science)

DEVELOPMENT OF THE TECHNOLOGY FOR OBTAINING THE OXYGENATES ON THE BASIS OF C_4-FRACTION OF PYROLYSIS PROCESS

Specialty: 3303.01 – Chemical technology and engineering

Technical science

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Introduction

The actuality of the subject. Production level of polyolefins, oils and fuels are in the crisis point in the world industrial practice. Industrialized countries are focusing more on improving qualitative properties of polyolefins, oils and fuels, than the increase of their production.

Improvement in qualitative properties depends on the correct selection of antioxidants, additives and stabilizers added to them. In this regard, chemical additives on the basis of alkylphenol and bioethanol (methanol) are important due to their environmental and economic properties. As well as they are more effective additives in polyolefins, rubbers and oils against influence of external factors simultaneously they are more effective and affordable. Their polyfunctional properties allow improve some properties of the object at the same time.

The work deals on the development of the technology for obtaining methyl and ethyl tertiary butyl ethers by etherification of C_4-fraction obtained in pyrolysis process of low-octane gasolines with methanol and bioethanol, simultaneously on obtaining alkylphenols by interaction with phenol, their N, P, S-, carbonyl-containing derivatives with the products obtained by C_4-fraction dimerization, cyclodimerization reactions and testing them.

The aim and objectives of the work: The aim of the study is investigating the efficient use of C_4-fraction [butane-isoobutylene (BIF) and butane-divinyl (BDF) fractions], which has not yet found its full use in oil refining and petrochemical industry and carrying out the scientific researches in the following directions:

- study of catalytic etherification reaction of methyl and ethyl alcohols by BIF and BDF;
- development of the technology for obtaining the process, use in industry and calculation of the process technical-economic properties;
- obtaining 3-vinylcyclohexene and C_{8-12} fraction as a result of dimerization, cyclodimerization, alkylation reactions of butane-isobutylene and butane-divinyl fractions;
- study of catalytic alkylation reactions of phenol by

vinylcyclohexene and C_8-C_{12}-fraction;

- study of interaction reactions of alkylphenols obtained on the basis of 3-vinylcyclohexene and C_8-C_{12} fractions with phosphorous 3-chloride;
- development of Mannich bases;
- finding out the methods for realization the processes on pilot device, development of production technology and substantiation of the process technical-economic efficiency;
- testing of obtained alkylphenylphosphites, benzylphenylamines, aceto-, benzophenones and methyl-(-ethyl)-tertiary butyl ethers as thermo-, photostabilizer in polyolefins, as antioxidants in rubbers, diesel fuel, oils and as additives in gasolines.

Research methods. The studies were carried out on laboratory, pilot devices and semi-industrial plants with the capacity of 12 thousand tons/year, built on the project suggested by us.

Basic provisions for defense. Producing the oxygenates as a result of etherification reactions of bioethanol and methanol by C_4-fraction (non-divinyl and divinyl-rich fractions) obtained in pyrolysis process of low-octane gasolines; carrying out phenol catalytic alkylation reaction by C_4-fraction dimerization and cyclodimerization products; producing the products with different definitions by aminomethylation, phosphitation, acylation and sulphonation of alkylphenols.

The scientific novelty of the work. For the first time, scientific bases for efficient production methods of alkylphenylphosphites, benzylphenylamines, 2,2`-thiobis-(alkylphenol)s, aceto- and benzophenones, methyl-, ethyl tert-butyl ethers, obtained on the basis of C_4-fraction; catalytic alkylation reactions of phenol with C_8-C_{12} fraction and vinylcyclohexene have been studied and efficient conditions have been determined for obtaining the target alkylphenols. Tert-(alkylphenyl)-phosphites, Mannix bases, 2, 2`-thiobis- (alkylphenols), aceto- and benzoophenones have been synthesized by interactions of alkylphenols obtained on the basis of C_4-fraction with phosphorus trichloride, formaldehyde and aniline, dichloride sulfide, acetic acid and benzoil chloride and the influence of various factors on the processes has been studied; the ethers obtained in the presence of KU-23 catalyst on the basis of methyl and ethyl alcohols with BIF and BDF and Zeolite-Y catalyst saturated by ortho-phosphate acid have been studied and scientific bases of production have been prepared for their industrial use; a new technological scheme has been developed and based for obtaining ethyl tert-butyl ether with high purity and scientifically justified.

Theoretical and practical significance of the research. As a result of the scientific substantiation of the studies carried out in the field of complex analysis of the efficient use of C_4-fractions, technological schemes have been developed for obtaining technical and industrial products from them, optimal technological parameters of the processes have been determined and their industrial application is ensured: tert-(alkylphenyl)-phosphites have been tested as antioxidants in T-46 turbine oil. 2-Hydroxy-5-alkylaceto- and benzophenones have been comparatively tested with the industrial stabilizers as photostabilizer in polystyrene, antirad in polypropylene; 2-hydroxy-5-alkylbenzylphenylamines have been tested as antioxidant for CNK-26 nitrile rubber and diesel fuel; obtaining methyl and ethyl tert-butyl ethers has been tested on the pilot device with capacity of 5 kg/h; ETBE production device with a capacity of 12.000 tonnes / year has been built for the purpose of increasing ethyl tert-butyl ether production. The process has been tested on the device and its technological and economic parameters have been determined. Technological regulations, Technical specifications and technical and economic indicators have been developed for the process.

The author's personal presence. The main ideas included in the dissertation, issues and their implementation, conducting of experimental tests, summarizing the results obtained, the report and publication were done by the author herself. The co-authored works also included the direction of the conducted research, the selection and justification of the issues and methods of the experiments.

Published scientific works. 80 papers on the dissertation work were published, including 26 monographs, thesis and 8 patents have been received.

Approbation and application. The main results of the work have been reported and discussed at the following scientific conferences: the IV, V and IX Baku International Petrochemical Conferences (Baku, 2000, 2005, 2016); the V International Scientific Conference "Ecology and Life Safety" (Sumgait, 2004, 2007); the scientific conference dedicated to the 100th anniversary of academician M.F.Naghiyev (Baku, 2008), the conference on “Socio-economic development of Sumgait city” (Sumgait, 2008), X International Conference “Chemistry and Physical Chemistry of Oligomers ”(Volgograd, 2009), the II Republican Conference dedicated to the 100th anniversary of professor A.A. Verdizada (Baku, 2014), the II Baku Economic Forum of Economic Cooperation Member States, Baku (2014), the I International Scientific Conference of Young Scientists and Specialists on “The Role of Multidisciplinary Approaches in Addressing Actual Problems of Functional and Applied Sciences” (Baku, 2014); the I International scientific conference of SOCAR (Baku, 2014), Republican scientific conference dedicated to the 50th anniversary of the Institute of Chemistry of Additives of ANAS (Baku, 2015); the III Republican Scientific Conference “Modern problems of monomers and polymers chemistry” (Sumgait, 2015, 2019); republican scientific conference dedicated to the 90th anniversary of academician T.N.Shahtakhtinsky (Baku, 2015); Scientific and practical conference on the 92nd anniversary of H.Aliyev (Baku, 2015); the International chemical conference (Turkey, Canakkale, 2015), scientific conference dedicated to the 80th anniversary of the establishment of the Institute of Catalysis and Inorganic Chemistry of ANAS (Baku, 2016); Scientific-practical conference on "Actual problems of modern biology and chemistry" (Ganja, 2015, 2016, 2018, 2019).

The size of the work. The dissertastion consists of 326 pages and includes introduction, 7 chapters, results, 464 references and appendicies. The work includes 75 tables and 34 figures.

The organization where the dissertation is performed. Institute of Petrochemical Processes of the Azerbaijan National Academy of Sciences.

In the introductory section the relevance of the topic, the purpose of the dissertation, the scientific novelty of the work, its practical significance are justified and the essence of the chapters is summarized.

Chapter 1 is devoted to the analysis of the literature on the etherification of methanol and bioethanol by the C_4 fraction of pyrolysis, alkylation reactions of phenol by olefins and cycloolefins in the presence of different acid catalysts, simultaneously aminomethylation, phosphitation, sulfurization and acylation reactions of alkylphenols. It also includes a critical analysis of the current work in this area and justification of scientific directions of the studies.

Chapter 2 is experimental part that deals on the primary raw materials, their physical and chemical parameters, the course of the experiments and the description of the used devices, the analysis methods for used crude and the target products obtained in the result of the reaction.

Chapter 3 deals on the study of methanol and bioethanol etherification by C_4 fraction of pyrolysis on the pilot device in the presence of KU-23 and Zeolit-Y catalyst impregnated by ortho-phosphate acid. Non-divinyl and divinyl-rich fractions of C_4-fraction were used for etherification.

Chapter 4 summarizes the results of the catalytic alkylation reactions of phenol with the fraction of C_8-C_{12}, which are the dimerization products of the C_4 fraction (BIF). The catalysts KU-23, ortho-phosphate acid-impregnated Zeolite-Y, zeolite-containing Zeokar-2 and Zeokar-2M were used for for the alkylation reaction. The processes were performed on batch and continuous plants.

Chapter 5 is about studying of alkylation reactions of vinylcyclohexene obtained by cyclodimerization of phenol by BDF in the presence of the catalysts KU-23, ortho-phosphate acid-impregnated Zeolit-Y, Zeokar-2 and Zeokar-2M. This chapter summarizes the results of researches on alkylation carried out on the batch and continuous plants.

Chapter 6 is devoted to the study of phosphitation of para-alkylphenols obtained by catalytic alkylation of phenol with C_8-C_{12}

and 3-vinylcyclohexene by tert-chlorine phosphorus, aminomethylation with aniline and 2,6-diisopropylaniline, sulfurization with dichloride sulfide, acylation with benzoyl chloride.

Chapter 7 is about the experiments as testing methyl- and ethyl tert-butyl ethers obtained in the results of the studies as oxygenate in automobile gasolines; tert-[para-(alkyl)-phenyl]-phosphates as antioxidant in oils and polyolefins; 2-hydroxy-5-alkylbenzylphenylamines as antioxidant for nitrile rubber and diesel fuel; 2,2'-thiobis-(para-alkylphenols) as vulkanizate in rubber mixtures; 2-hydroxy-5-alkylaceto- and benzophenones as photostabilizer in polystyrene, and as antirad in polypropylene.

The results reflecting the essence of the research, a list of references are given at the end of the dissertation.

The dissertation was performed according to the work programme of 0111Az2071 registration number at academician Y.H.Mammadaliyev Institute of Petrochemical Processes of ANAS.

SUMMARY OF THE WORK

Primary raw materials, catalysts, experimental rules and the methods for analysis of reaction products

Bioethanol, methanol, C_4-fraction (BIF, BDF) obtained by the pyrolysis of low-octane gasoline, phenol, tert-chlorine phosphorus, hexamethylenetetramine, aniline, 2,6-di-isopropylanilin, dichloride sulphide, acetic acid and benzoyl chloride were taken as raw materials for carrying out the studies.

Non-divinyl (BIF) and divinyl-rich fractions of C_4 fraction of the pyrolysis have been used for the studies.

As is seen from Table 1, non-divinyl C_4-fraction (BIF) contains up to 42.29% of isobutylene. Isobutylene of this concentration in BIF allows carrying out the reactions of etherification and dimerization with bioethanol and methanol. For this reason, we have used BIF in etherification and dimerization reactions.

Divinyl-rich C_4-fraction (BDF) contains 38.30% isobutylene and 49.90% divinyl.

KU-23 (GOST 20298-74), phosphate-impregnated Zeolit-Y, Zeokar-2 and Zeokar-2M catalysts have been used as the catalyst for alkylation reactions.

The content of non-divinyl C_4 fraction is given in Table 1:

Table 1

The composition of non-divinyl C_4 fraction

Composition	BIF, %
Propane	0.85
Propylene	0.17
Isobutane	4.14
Isobutylene	42.29
Butene-1	28.49
Butadiene-1,3	0.50
n-butane	4.67
trans-butylene	9.46
cis-butylene	9.43
Total	100.00

The phosphorous-containing Zeolite-Y catalyst is developed by the following procedure: alumogel cracking catalyst (zeolite-Y, SiO_2:Al_2O_3=4.8, ion exchange rate - 97%) is perfectly mixed. The obtained mass is passed through the sieve with a diameter of 1.6 mm, scrapped and grinded. The 10% ortho-phosphate acid (according to P_2O_5) is absorbed into the catalyst and evaporated, dried at 100 °C in the oven, and heated under the temperature from 200 °C to 600 °C. Then the catalyst is cooled down and used.

Zeokar-2 is an industrial catalyst, but Zeokar-2M is obtained by treating of Zeokar-2 with 10% hydrochloric acid.

Phenol alkylation reactions were carried out on the batch and continuous plants. The batch process was carried out in a three-necked tube equipped with a mixer, thermometer and separator lock. Phenol continuous catalytic alkylation reactions with alkylcyclens were carried out in the following order: calculated amount of phenol and alkene were transferred from the container into the mixer, and then to the bottom of the reactor. The component mix is passed over the catalyst and collected in the container after being cooled in the refrigerator and sent for rectification.

The reactions of synthesized p-alkylphenols with formaldehyde and aniline, urotropine were carried out in three-necked flask.

The process of obtaining tert-(alkylphenyl)-phosphites was realized on two methods. In the the first method, phosphitation reaction was carried out using tert-amines as acceptor to capture released HCl; in the second method, inert gas - nitrogen was used to remove HCl from the reaction zone.

The pre- and post-reaction analyses of the pyrolysis products used for the studies were carried out on Fraktovan model 2150 “Carlo Erba” (Italy) chromatograph with 50 m long, 0.2 mm internal diameter, equipped with silicone OY-101 inactive liquid phase. The condition for the analysis are: pressure at gas-helium column input - 2.4-2.5 kg/cm^2, flow allocation - 1:150, the sample volume - 0.3 µl. The starting temperature was 30 °C, but 10 min later, the system started to heat up at 2 °C/min. The analysis lasted for 40 min. Chromatographic analysis of the reaction and rectification products was carried out on chromatography LKhM-72.

Density of the synthesized products was determined by pycnometer method, but refractive coefficients - by refractometry "IRF-22" (Russia).

The spectra of the reaction products were drawn on the Se/Zn crystal on ALPHA IR-Furye spectrometer by German firm "BRUKER" at wavelength of 600-4000 cm^{-1}. ^{1}H and ^{13}C NMR spectra were drawn on Furye spectrometer of “Bruker” (Germany) at 300.18 MHz and in benzene solution deuteriumed at room temperature. The chemical displacements of the signals were taken corresponding to the tetramethylsilane. The relative compositions of different structural fragments protons are determined by integrating the peak areas in the corresponding strips of the spectrum.

Investigation of catalytic etherification of methyl and ethyl alcohols with butane-isobutylene, butane-divinyl fractions

Obtaining methyl and ethyl tert-butyl ethers by the catalyst KU-23

Etherification of BIF by methanol

The interaction reactions of methanol with BIF and KU-23 catalyst have been carried out according to the above methodology.

Methanol and BIF are transmitted to the bottom of the reactor after mixing under pressure; it is sent for rectification after cooling at the reactor output passing over the catalyst.

The effect of temperature, mol ratios of the initial components, volume velocity and pressure on the course of etherification has been studied for the purpose of finding the effective output of methyl tert-butyl ether.

The reaction temperature has been studied at 50-90 °C, mol ratio of methanol to BIF at the limits of 1:1÷5, volume velocity 0.2-1.0 h^{-1}, pressure 0.6-1.0 MPa.

The results of MTBE obtaining process in the result of etherification of methyl alcohol with BIF in the presence of catalyst KU-23 are presented in Fig. 1.

As is evident from Fig. 1, the yield of the target product at the reaction temperature of 50-60 °C amounts to 60.4-69.7%. The yield is 78.3-78.8% at the reaction temperature of 70-80 °C. Subsequent rise in temperature does not have a serious effect, as MTBE yield decreases to 73.5%. Investigation of the reaction temperature effect on the process reveals that the effective yield of MTBE is achieved at 70-80 °C of etherification temperature and in this case the yield amounts to 78.8%. Another factor effecting on the process is the ratio of the initial components taken for the reaction. As is evident from the Figure, 1:1 mol ratio of methanol and BIF in the initial components mixture taken for the reaction is unacceptable; meantime the yield of MTBE is 41.6%. The reason for the low yield is the low percentage of isobutylene in the total mixture and obtaining unwanted reaction products at the same time.

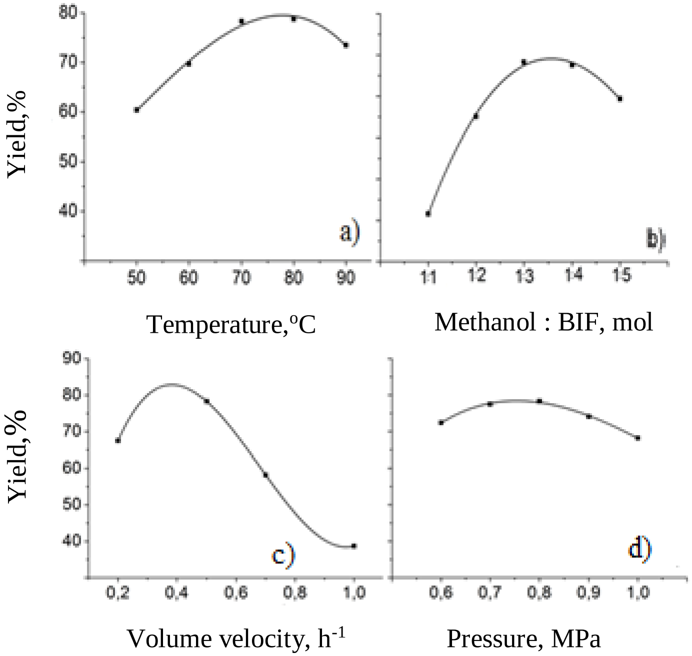


Fig. 1. Dependence curves of the yield of MTBE obtained in the presence of the catalyst KU-23 on temperature (a), mol ratios of the initial components (b), volume velocity (c), and pressure (d)

The target product yield amounts to 65.1% at 1:2 mol ratio of methanol to BIF. As BIF contains about 40-42% of isobutylene, the most favorable condition for methanol etherification should be considered 1:3 mol ratio of methanol to BIF. In this case the yield is 78.3%. MTBE yield decreases to 69.4% by 4-5-fold increase of BIF concentration in the general mixture.

This is explained by the fact that BIF, taking excessively, can be undergone dimerization, isomerization, and oligomerization reactions under pressure in liquid phase. One of the key factors effecting on the process direction and the content, yield of the obtained products is volume velocity. As is evident from the Figure, the yield of the target product according to methanol is 78.3% at 0.5 h^{-1} vol. velocity. The result is lower, according to the increase and decrease of meeting durations of initial components mixture with the catalyst; the yield is 38.7-58.2% at 0.7-1.0 h^{-1} volume velocity. As a result of the studies, it has been found that the target product yield can be considered effectively at 0.5 h^{-1}. MTBE yield is 77.5-78.3% at 0.7-0.8 MPa pressure in the system.

Pre- and post-reaction hydrocarbon compositions of BIF, taken for etherification are set into Table 2.

Table 2.

Pre- and post-reaction hydrocarbon composition of BIF with methanol

BIF h/c composition	Pre-reaction, %	Post-reaction,%
Propane	0.85	2.69
Propylen	0.17	0.49
Isobutane	4.14	9.47
Isobutylene	42.29	6.34
Butene-1	28.49	38.17
Butadiene-1,3	0.50	1.23
n-butane	4.67	9.18
trans-butylene	9.46	16.27
cis-butylene	9.43	16.16
Total	100.00	100.00

Table 2 shows that although BIF contains 42.29% of isobutylene before etherification, the amount of isobutylene in the hydrocarbon composition decreases to 6.34% after the reaction. As a result, the amount of saturated hydrocarbons in BIF after the reaction is significantly reduced, and this fraction may be suggested as household fuel.

Etherification of BIF with bioethanol in the presence of catalyst KU-23

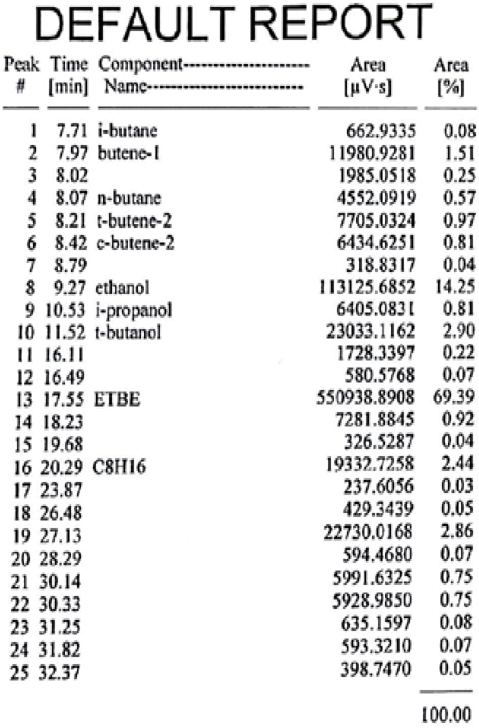
Etherification reaction has been carried out on the above methodology. Butane-isobutylene fraction containing 38-42% isobutylene, ethanol with 98.8% purity have been used as the primary raw materials for the process.

Various factors have been studied effecting on the course, direction and yield of the process. The reaction temperature has been studied at 50-90 °C, volume velocity 0.2-1.0 h^{-1}, pressure 0.7-0.9

MPa, and mol ratios of the primary components (ethanol to BIF) at 1:2÷5 mol/mol. The composition of the etherification products obtained under the optimal conditions is presented in Table 3.

Table 3

Chromatographic analysis of BIF etherification products obtained with ethanol in the presence of the catalyst KU-23



DEFAULT REPORT

Peak #	Time [min]	Component Name	Area [µV·s]	Area [%]
1	7.71	i-butane	662.9335	0.08
2	7.97	butene-1	11980.9281	1.51
3	8.02		1985.0518	0.25
4	8.07	n-butane	4552.0919	0.57
5	8.21	t-butene-2	7705.0324	0.97
6	8.42	c-butene-2	6434.6251	0.81
7	8.79		318.8317	0.04
8	9.27	ethanol	113125.6852	14.25
9	10.53	i-propanol	6405.0831	0.81
10	11.52	t-butanol	23033.1162	2.90
11	16.11		1728.3397	0.22
12	16.49		580.5768	0.07
13	17.55	ETBE	550938.8908	69.39
14	18.23		7281.8845	0.92
15	19.68		326.5287	0.04
16	20.29	C8H16	19332.7258	2.44
17	23.87		237.6056	0.03
18	26.48		429.3439	0.05
19	27.13		22730.0168	2.86
20	28.29		594.4680	0.07
21	30.14		5991.6325	0.75
22	30.33		5928.9850	0.75
23	31.25		635.1597	0.08
24	31.82		593.3210	0.07
25	32.37		398.7470	0.05
				100.00

Table 3 shows that about 69.39% of ETBE is obtained as a result of the reaction.

Obtaining MTBE and ETBE in the presence phosphorous-containing Zeolite-Y catalyst

Ortho-phosphate acid impregnated Zeolite-Y catalyst is heated to 110 °C before use for being free from the moisture contained in it.

The effect of temperature, mol ratios of primary components, volume velocity and pressure on the direction and composition of etherification reaction has been studied for the purpose of finding out the optimal conditions for methyl tert-butyl ether.

The reaction temperature is 50-90 °C, the ratio of methanol to BIF – 1:1÷5 mol, volume velocity – 0.2-1.0 h^{-1}, pressure – 0.6-1.0 MPa. The results of the studies are set into Tab. 4.

Table 4.

The results of etherification reactions of methanol with BIF in the presence of ortho-phosphate impregnated Zeolite-Y catalyst

Exp. No	Temperature, °C	Methanol:BİF, mol/mol	Volume velocity, h^{-1}	Pressure, MPa	Yield, % mas.
1.	50	1:3	0.5	0.8	54.4
2.	60	1:3	0.5	0.8	71.6
3.	70	1:3	0.2	0.7	67.5
4.	70	1:3	0.5	0.8	81.7
5.	80	1:4	0.5	0.7	82.8
6.	70	1:5	0.5	0.8	70.4
7.	60	1:5	0.7	0.8	53.3
8.	80	1:2	0.5	1.0	32.7
9.	70	1:3	0.5	0.6	72.4
10.	50	1:2	0.5	0.7	31.2
11.	70	1:2	0.2	0.8	36.8
12.	80	1:3	1.0	0.7	38.7

As is evident from Table 4, the effect of different factors on the yield of the target product is variable. As a result of the studies, the optimum conditions for the process of obtaining the MTBE have been found.

Etherification reactions of BIF with bioethanol have been carried out in the presence of ortho-phosphate-impregnated Zeolite-Y catalyst.

The influence of various factors on the direction, course of the etherification, the composition of the ether products and the yield of the target products have been studied. The reaction temperature of 50-90°C, volume velocity 0.2-1.0 h^{-1}, pressure 0.6-0.9MP, the ratio of primary components (bioethanol to BIF) have been studied at 1:2÷5 mol/mol have been studied. the ETBE yield amounts to 81.7-82.8% under the found optimal conditions.

Study of etherification reactions of methyl and ethyl alcohols with BDF in the presence of catalysts KU-23 and ortho-phosphate impregnated Zeolite-Y catalysts

Interactions of methanol with BDF in the presence of catalyst KU-23 has been carried out according to the above method.

The effect of temperature, mol ratios, volume velocity and pressure of primary components on the direction of etherification reaction and the reaction products components have been studied to find the most favorable conditions for the interaction between methanol and BDF. The reaction temperature has been determined as 60-90 °C, mol ratio of methanol to BDF – 1:1÷5, volume velocity – 0.2-1.0 h^{-1}, and pressure – 0.6-1.0 MPa.

The results of MTBE obtaining process as a result of methanol etherification with BDF ion the presence of the catalyst KU-23 are presented in Figure 2.

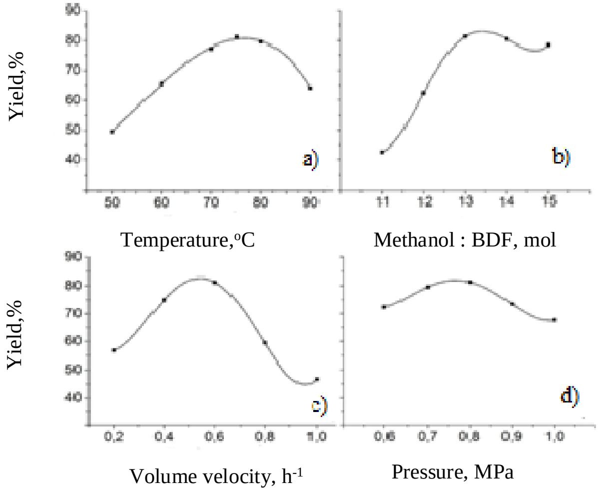


Fig.2. Dependence curves of MTBE yield on temperature (a), mol ratios of the initial components (b), volume velocity (c) and pressure (d)

As is seen from the Figure, the yield of the target product is 49.6% for taken methanol at 50°C of reaction temperature and 65.5% at 60 °C. At 70-80 °C of reaction temperature, MTBE yield is 77.2-81.3%. The yield decreases to 63.1% by the temperature increase up to 90°C. Figure 3.5 (a) shows that the effective dissolution of the etherification is obtained at 70-80°C of the reaction temperature. One of the main factors influencing the direction of the etherification is the ratio of the initial components taken for the reaction. As is evident from the Figure, the yield of the target product is 42.6% at 1:1 mol ratio of methanol to BDF. An increase in yield is also observed by increasing BDF concentration in the reactor mixture.

Thus, the yield amounts to 64.4% at 1:2 mol ratio of methanol to BDF and 81.3% at 1:3 mol ratio. There is a slight decrease (80.5-78.4%) in MTBE yield by 4-5-fold increase of BDF in the mixture. This indicates that the excess taken BDF undergoes dimerization, oligomerization, and isomerization reactions in liquid phase under pressure on the catalyst. One of the major factors having effect on the direction of etherification reaction of methanol with BDF, the composition of the products and the yield of the target product, is the time of the initial component mixing with the catalyst.

As is seen from Fig. 2 (c), the target product yield is increased from 56.8 to 81.3% by the change in volume velocity from 0.2 to 0.5 h. MTBE decreases to 59.4% by the reduction in the time of the reaction mixture with the catalyst (at 0.8 and 1.0 h^{-1} volume velosity). As a result of the researches it was found that volume velocity of 0.5 h^{-1} can be considered acceptable for etherification process because in this case the target product yield is higher than the methanol. As shown in Fig. 6, it is more expedient to accept pressure 0.7-0.8 MPa in the system.

Pre- and post-reaction hydrocarbon composition of BDF used for etherification reaction has been determined. The results are set into Table 5.

As is seen from Table 5, as BDF taken for the etherification reaction contains 38.30% of butylene, their content decreases to 7.61% after the reaction; primary raw material contains 46.90%, but after reaction 68.34% of 1,3-butadiene.

Table 5

Hydrocarbon composition of BDF with methanol before and after etherification in the presence of the catalyst KU-23

No	BDF h/c composition	Pre-reaction, %	Post-reaction, %
1.	C_3	0.05	0.10
2.	Iso-butane	3.50	4.17
3.	n-butane	3.45	6.48
4.	Butylene	38.30	7.61
5.	Cis-2-butylene	3.57	6.93
6.	Trans-2-butene	3.43	6.32
7.	1,3-Butadiene	46.90	67.06
8.	C_5	0.80	1.33
	Total	100.00	100.00

As seen, the amount of butadiene in BDF increases by 22% after the reaction. Divinil-rich BDF is recommended as an effective raw material for divinyl production.

Etherification reactions of BDF with methyl and ethyl alcohols in the presence of ortho-phosphate impregnated Zeolite-Y catalyst

Interactions of methyl and ethyl alcohols with BDF have been performed on continuous mini-unit.

Study of etherification reactions of BDF with methyl alcohol

Methyl alcohol etherification with BDF in the presence of ortho-phosphate acid impregnated Zeolite-Y catalyst have been performed according to the above method. The used catalyst reactor is filled. BDF and methyl alcohol mixture are transferred to the bottom of the reactor. The mixture is sent for rectification passing through the catalyst and after cooling in the refrigerator at the output of the reactor.

The effect of temperature, mol ratios of initial components, volume velocity and pressure on the direction of etherification reaction, the reaction products composition have been studied to find the most favorable conditions for the interaction of methyl alcohol with BDF. The reaction temperature has been studied at 60-90 °C, the ratio of methanol to BDF – 1:1÷5, volume velocity – 0.2-1.0 h^{-1}, and the pressure – 0.6-1.0 MPa.

Results of MTBE obtaining process in the result of BDF etherification with methanol in the presence of ortho-phosphate acid-impregnated Zeolite-Y catalyst are presented in Fig. 3.

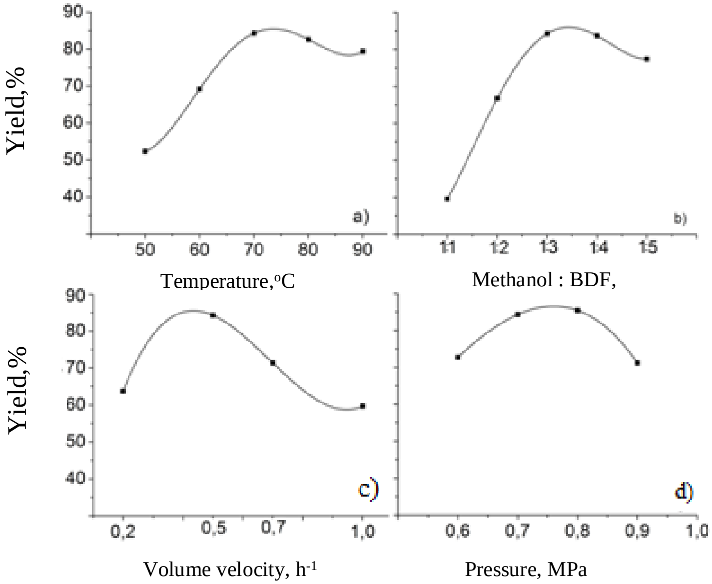


Fig.3. Dependence curves of MTBE yield on temperature (a), mol ratios of initial components (b), volume velocity (c) and pressure (d)

As is evident from the Fig., the target product yield is 52.3% at the reaction temperature of 50°C according to taken methanol and 69.2% at 60 °C. MTBE yield is 82.6-84.3% at 70-80°C of reaction temperature. The yield decreases to 79.4% by the temperature increase to 90°C.

Fig. 3 (a) reveals the effective yield of etherification reaction is obtained at 70-80 °C of the reaction temperature. One of the important factors influencing the direction of the etherification is the ratio of the initial components taken for the reaction. It’s evident from the figure that the target product yield amounts to 39.5% at 1:1 mol ratio of methanol to BDF. Increase in yield is also observed by increasing BDF concentration in the mixture given to the reactor.

Thus, methanol yield to BDF at 1:2 mol ratio is 66.8%, and 84.3% at 1:3 mol ratio. There is a slight (83.7-77.4%) decrease in MTBE yield by the increase of BDF concentration by 4-5 times.

This indicates that the excess-taken BDF undergoes dimerization, oligomerization, and isomerization reactions on the catalyst, under in liquid phase. One of the major factors effecting on the direction of etherification of BDF with methanol, the composition of the products obtained, and the yield of the target product is the time of the initial components mixture with the catalyst. Fig. 3 (c) shows that the target product yield has been increased from 63.7 to 84.3% with the change in volume velocity from 0.2 h^{-1} to 0.5 h^{-1}. MTBE yield decreases to 52.7% by the reduction of reacting time of the reaction mixture with the catalyst (at vol. velocity of 0.8 and 1.0 h^{-1}, respectively). As a result of the studies, it has been determined that the value of 0.5 h^{-1} of volume velocity can be considered acceptable for etherification process, as the yield of the target product is higher than taken methanol. According to the properties of Fig. 3, it is more expedient to accept pressure 0.7-0.8 MPa in the system.

Etherification reactions of methanol with BDF in the presence of ortho-phosphate acid-impregnated Zeolite-Y catalyst have been carried out under different conditions and these indicators are presented in Tab. 6.

Thus, as a result of the studies of Tab. 6 effective conditions have been found for etherification reactions of methanol with BDF in the presence of ortho-phosphate acid-impregnated Zeolit-Y catalyst: temperature 75-80°C, 1:3÷4 mol/mol ratio of methanol to BDF, volume velocity 0.5 h^{-1}, pressure 0.7-0.8MPa.

Table 6

The results of etherification reactions of BDF with methanol in the presence of phosphorous-containing Zeolite-Y

N	Temp., °C	Methanol: BDF, mol/mol	Volume velocity, h^{-1}	Pressure, MPa	Yield, % mas.
1.	50	1:3	0.5	0.8	52.3
2.	60	1:3	0.5	0.8	69.2
3.	70	1:3	0.5	0.8	84.3
4.	70	1:4	0.2	0.7	69.4
5.	80	1:4	0.5	0.7	83.7
6.	60	1:5	0.2	0.8	57.4
7.	80	1:3	0.7	1.0	62.4
8.	80	1:2	0.5	0.8	66.8
9.	50	1:5	0.5	0.7	47.9
10.	70	1:2	1.0	0.7	22.4
11.	90	1:5	1.0	0.7	36.7
12.	75	1:3	0.2	0.8	63.7

Table 7

Hydrocarbon composition of BDF before and after etherification with methanol in the presence of ortho-phosphate-impregnated Zeolite-Y catalyst

BDF- h/c composition	Pre-reaction, %	Post-reaction, %
C_3	0.05	0.12
Iso-butane	3.50	4.31
n-butane	3.45	6.53
Butylenes	38.30	6.72
Cis-2-butylene	3.57	6.57
Trans-2-butene	3.43	5.96
Butadiene-1,3	46.90	68.34
C_5	0.80	1.45
Total	100.00	100.00

The yield of methyl tert-butyl ether on the taken methanol is 83.7-84.3% under this condition.

Hydrocarbon composition of BDF used for etherification has been determined before and after the reaction and the results are given in Table 7.

As is seen from table 7, although BDF taken for etherification contains 38.38% butylenes, their amount decreases to about 6.72% after the reaction; they are 46.90% in the content of primary raw material and 68.34% of 1,3-butadiene after the reaction. As is seen, amount of butadiene increases about 20% in BDF after the reaction. Divinyl-rich BDF is recommended as an efficient raw material in divinyl production.

Etherification reactions of BDF with bioethanol in the presence of ortho-phosphate impregnated Zeolite-Y catalyst

Etherification reactions have been carried out according to the above methodology.

Different factors effecting on the course, direction, and the yield of the target product have been studied. The reaction temperature 50-90 °C, volume velocity 0.2-1.0 h^{-1}, and 1:1÷5 mol/mol ratios of the initial components- ethanol to BDF have been studied.

Dependence curves of the yield of ethyl tert-butyl ether obtained in the results of BDF etherification reactions with bioethanol in the presence of ortho-phosphate impregnated Zeolite-Y catalyst on the reaction temperature, initial components mol ratios, volume velocity and pressure are illustrated in Fig. 4.

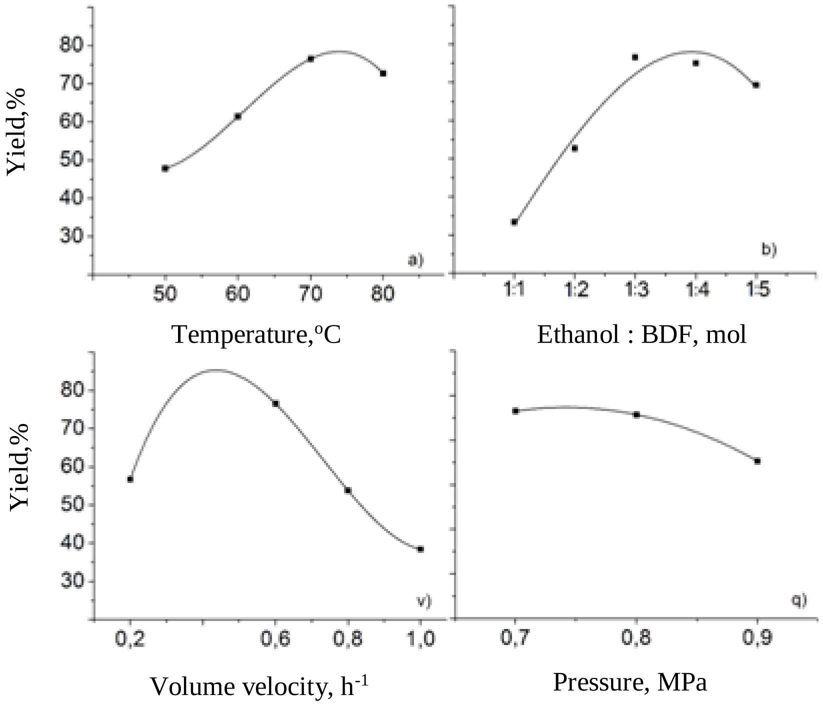


Fig. 4. Dependence curves of ETBE yield on temperature (a), initial components mol ratios (b), volume velocity (c) and pressure (d)

As is evident from Fig. 4, ETBE yield increases from 47.8% to 76.5% by increasing reaction temperature from 50 to 70°C; in this case mol ratio of methanol to BDF is 1:3, volume velocity 0.5 h^{-1}, and pressure 0.8 MPa. High yield of the target product isn't acceptable by taking ethanol in excess for etherification reaction; 1:1 and 1:2 mol ratios of ethanol to BDF results in the yield of the target product correspondingly 33.4 and 52.7%. 3-fold increase in BDF in the components mixture causes increase in the yield of ETBE up to 76.5%. The yield is relatively low (69.3-75.0%) in further increasements of BDF concentration in the mixture. Reacting time of the initial raw materials with catalyst also has a great role. As is seen from the figure, volume velocity of 0.5 h^{-1} is efficient for conducting etherification reaction; so that the yield of the target product is higher in this case (76.5%). Other values of volume velocity don't allow to have efficient yield of ETBE. As is seen from the curves, taking of 0.8 MPa pressure is more appropriate in the system.

The yields of BDF etherification reactions with bioethanol in the present of phosphorous-containing Zeolite-Y catalyst in different rejimes are presented in Table 8.

Table 8

The results of etherification reactions of BDF with bioethanol

Num. of exp.	Temp., °C	Ethanol:BDF, mol	Pressure, MPa	Yield, % mas.
1	60	1:3	0,8	61.4
2	70	1:3	0,8	76.5
3	80	1:3	0,8	72.7
4	70	1:4	0,8	75.0
5	75	1:3	0,8	73.3
6	80	1:4	0,7	69.8
7	75	1:5	0,7	69.3
8	60	1:5	0,8	61.4
9	75	1:4	0,7	75.2
10	80	1:4	0,7	72.7
11	70	1:2	0,8	52.6
12	80	1:2	0,7	53.1

The indices of Tab. 8 allow to determine that ETBE efficient yield may be achieved by changing the factors influencing the etherification reactions course, direction and composition of obtained products.

So, the efficient conditions have been found out for etherification reaction of BDF with bioethanol in the presence of phosphorous-containing Zeolite-Y catalyst: temperature – 70-75°C, mol ratio of bioethanol to BDF – 1:3, volume velocity 0.5 h^{-1}, pressure – 0.8 MPa. ETBE yield accordingn to taken alcohol amounts to 76.5% under these conditions.

According to pre- and post-reaction chromatographic analysis of the fraction hydrocarbon composition taken for BDF etherification reaction with bioethanol, it has been determined that unsaturativity of BDF is significantly lower.

Hydrocarbon composition of BDF before and after etherification is given in Tab. 9.

Table 9

Pre- and post-reaction hydrocarbon composition of BDF

Number	Hydrocarbon composition of BDF	Pre-reaction, %	Post-reaction,%
1.	C_3	0.05	0.14
2.	İsobutane	3.50	4.71
3.	n-butane	3.45	7.05
4.	Butylenes	38.30	7.74
5.	Cis-2-butylene	3.57	6.93
6.	trans-2-butene	3.43	5.81
7.	1,3-Butadiene	46.90	66.35
8.	C_5	0.80	1.27
	Total	100,00	100,00

It is seen from Table 9 that as there are 40.30% of isobutylenes in the composition of BDF taken for the reaction, their amount decreases to 8.63% after reaction; the amount of 1,3-butadiene is 46.90% in the hydrocarbon composition of initial BDF, after reaction it is 66.07%. As a result, the amount of butadiene in the hydrocarbon composition of BDF from the reaction have increased up to 18-20%.

Divinyl-riched BDF is recommended as an efficient raw material in the production of divinyl.

The study of catalytic alkylation reactions of phenol with C_8-C_{12} fraction and 3-vinylcyclohexene

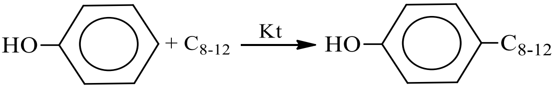
The alkylation reactions of phenol with BIF and BDF dimerization products have been realized on the batch and continuous pilot plants in the presence of catalysts KU-23, ortho-phosphate impregnated Zeolite-Y, Seokar-2 and modified Seokar-2. For example, let’s see the study of alkylation reactions of phenol with 100-190°C fraction (IDF) of dimerization products of BIF in the presence of KU-23 catalyst.

The alkylation reactions of phenol with KU-23 catalyst have been realized on the batch and continuous plant**s.**

Oligomers of isobutylene up to 40.5% are obtained from the dimerization of BIF on the zeolite catalyst. The purpose of taking oligomers of isobutylene and its 100-190°C fractions extracted by distillation is to achieve an increase in concentration of diisobutylene in composition of alkylating agent.

There is diisobutylene of 51.35% in hydrocarbon composition of 100-190°C fraction. As the alkylation reaction mainly runs with diisobutylene, the main part of obtained alkylate will consist of para-tert-octylphenol.

The alkylation reaction of phenol with IDF follows the scheme given below:



The effect of various parameters as reaction temperature, duration, molar ratios of initial components, the amount of catalyst and volume velocity on yield and selectivity of reaction products have been investigated to find the optimal condition for alkylation reaction of phenol with IDF.

Temperature of alkylation reactions of phenol on batch plant at 60-140°C, duration of experiment 2-6 h, molar ratios of phenol to IDF from 2:1 to 1:2, the amount of catalyst within the limits of 5-20% have been studied.

Under the found optimal condition the yield of TP is 80.4%, the selectivity is 95.7%.

The alkylation reaction of phenol with IDF has been realized on the continuous laboratory device.

We tried to show an assumed mechanism of alkylation reaction of phenol with C_8-C_{12} fraction generally on the bases of the references and our experimental results from the point of significancy of alkylation reactions of phenol in the presence of acid catalysts.

We offer the following mechanism by taking into consideration the available theoretical views about the alkylation reactions of phenol on acid catalysts.

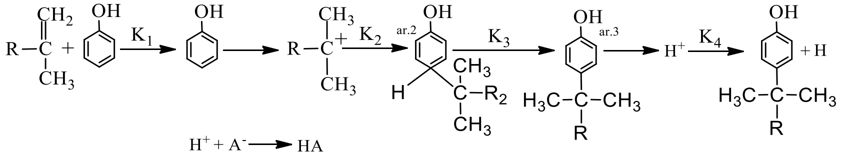
Table 10

The results of alkylation reactions of phenol with IDF in the presence of KU-23 catalyst on the pilot plant

Taken, g		Reaction condition		Yield, %	Selectivity, %
Phenol	IDF	Temp., °C	Volumetric speed, h^{-1}		
47	120	80	0.5	45.7	92.6
47	120	100	0.5	59.3	91.4
47	120	120	0.5	67.4	95.6
47	120	130	0.5	63.2	89.7
47	120	140	0.5	58.5	82.3
47	60	120	0.5	28.4	78.8
47	120	120	0.5	67.4	95.6
47	180	120	0.5	69.9	96.3
47	240	120	0.5	69.6	87.4
47	120	120	0.2	55.8	89.7
47	120	120	0.5	67.4	95.6
47	120	120	0.7	53.7	94.3
47	120	120	1.0	48.0	96.7

Note**: TP – target product**

A carbocation is obtained from the interaction of diisobutylene with HA catalyst, and this forms ɤ-complex with it by affecting the phenol molecule. During the re-transformation of ɤ -complex to π-complex, a covalent bond is formed between the carbon atom of the aromatic ring and the alkyl substituent, and meantime an electron effect of hydroxyl group generates the favorable condition for formation of ɤ-complex with para-atom of carbon. The ɤ-complex is not stable and it easily transforms to π-complex of alkyl compound. And the last one stabilizes by generating alkylphenol with giving its proton:



The differential equality system of primary raw materials and reaction products depending on time has been generated on the bases of assumed mechanism of the reaction.

The effect of reaction temperature, molar ratios of initial components and volume velocity on yield and selectivity of alkylphenols have been investigated to find the optimal condition of the alkylation process of phenol with IDF on the batch plant in presence of ortho-phosphate acid impregnated zeolite-Y catalyst.

The alkylation process has been investigated in atmospheric pressure in the continuous reactor of straight flow with unmoved layer of the catalyst in liquid phase. And the results are given in Table 11.

Table 11

The results of the alkylation reactions of phenol with IDF in the presence of phophorous-containing zeolite-Y catalyst on the continuous plant

Exp. No	Taken, g		Reaction condition		Yield of TP, %	Selectivity, %
	Phenol	IDF	Temp., °C	Volume velocity, h^{-1}		
1.	47	120	80	0.5	51.8	95.6
2.	47	120	100	0.5	65.3	95.4
3.	47	120	115	0.5	74.7	96.5
4.	47	120	130	0.5	75.1	91.1
5.	47	120	140	0.5	70.3	86.5
6.	47	60	115	0.5	47.8	93.7
7.	47	120	115	0.5	74.7	96.5
8.	47	180	115	0.5	75.4	94.2
9.	47	240	115	0.5	68.2	87.7
10.	47	120	115	0.2	70.5	85.4
11.	47	120	115	0.5	74.7	96.5
12.	47	120	115	0.7	59.3	96.7
13.	47	120	115	1.0	57.6	97.3

The alkylation reactions of phenol with IDF in the presence of Seokar-2 and hydrochloric acid impregnated Seokar-2 have been investigated.

Unlike the above-mentioned catalysts, zeolite-containing Seokar-2 and hydrochloric acid impregnated Seokar-2 (Seokar-2M) catalysts are mechanically more strong, longer-lasting catalysts.

The alkylation reactions of phenol with IDF over the Seokar-2M catalyst have been studied at temperature limits of 80-140°C, molar ratios of 1:1-1:4 of phenol to IDF, in the rate of volume velocity of 0.2-1.0 h^{-1}.

The experimental results of alkylation reactions with Seokar-2M catalyst have been presented in Table 12.

As seen from the Table, the yield of the target product for taken phenol increases from 47.2% up to 70.4% by increasing the reaction temperature from 80°C up to 110°C. The yield accordingly decreases to 72.3 and 65.8% by increasing temperature up to 120, 140°C.

It is expedient to send in molar ratio of 1:2 of phenol to IDF to the reactor. Thus, meantime the highest yield (70.4%) and selectivity (95.7%) can be achieved. There is no any positive result in increasing or decreasing of the concentration of this or that raw material in the mixture of initial components.

As seen from Table 12, if volume velocity of the process is 0.5 h^{-1}, the yield of para-alkylphenol is 70.4% (for taken phenol), and the selectivity for the target product is 95.7%. The yield and selectivity of the target product are not significant in other values of reacting duration of components mixture with catalyst.

Table 12

The results of the alkylation reactions of phenol with IDF in the presence of the Seokar-2M catalyst on the continuous plant

Taken, g		Reaction condition		Yield of TP, %	Selectivity, %
Phenol	IDF	Temp., °C	Volume velocity, h^{-1}		
1	**2**	**3**	**4**	**5**	**6**
47	120	80	0.5	47.2	96.7
47	120	100	0.5	58.7	96.1
47	120	110	0.5	70.4	95.7
47	120	120	0.5	72.3	87.0

47	120	140	0.5	65.8	84.3
47	60	110	0.5	48.4	88.9
47	120	110	0.5	70.4	95.7
47	180	110	0.5	73.6	93.4
47	240	110	0.5	62.8	85.5
47	120	110	0.2	49.9	93.1
47	120	110	0.5	70.4	95.7
47	120	110	0.7	71.7	96.0
47	120	110	1.0	66.8	95.0

The results of the conducted experimental researches show that it is necessary to take reaction temperature of 110°C, molar ratio of phenol to IDF as 1:2 mol/mol, volume velocity of the process of 0.5 h^{-1} for conducting the alkylation reactions of phenol with IDF in the presence of Seokar-2M catalyst in continuous reactor. In ths condition the yield of the para-alkylphenol is 70.4% (for taken phenol), the selectivity for the target product is 95.7%

The studies of the alkylation reactions show that more efficient results have been achieved by using the modified Seokar-2 catalyst among the used catalysts.

The interesting results have been obtained during the analysis of the composition of reaction products obtained in the catalytic alkylation reactions of phenol with IDF on the continuous plant. The results are give in Table 13.

It is seen from the Table that when the KU-23 catalyst used for alkylation, 3.0% of reaction mixture is composed of phenol, 61.2% of İDF-I, 35.8% of alkylation products. 1.2% of alkylation products consists of alkylphenyl ethers, 4.8% is ortho-alkylphenols, 93.0% is para-alkylphenols, but 1.0% is di-alkylphenols. Ratios of para- and ortho-alkylphenols are 19.4, the yield of the target product is 69.7%, and the selectivity is 93.3%.

Table 13

The results of the catalytic alkylation reactions of phenol with IDF on the continuous plant

The reaction condition:				
– Catalyst	KU-23	Zeolite-Y	Seokar-2	Seokar-2M
– Temperature, °C	120	110	125-130	110
The composition of the reaction mixture, % mas.				
– Phenol	3.0	3.8	3.8	3.3
– IDF	61.2	59.6	61.2	58.0
– Alkylation products	35.8	36.6	35.0	38.7
The composition of the alkylation products, % mas.				
– Alkylphenyl ether	1.2	1.0	–	–
– Ortho-alkylphenols	4.8	2.4	4.3	2.6
– Para-alkylphenols	93.0	96.0	93.0	96.1
– Di-alkylphenols	1.0	0.6	2.7	1.3
– The results of ortho- and para-alkylphenols	19.4	40.0	21.6	40.0
– Yield, %	67.4	74.7	63.6	75.7
– Selectivity, %	95.6	96.5	94.7	96.8

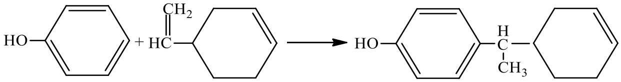
According to the data of the Table, if to use ortho-phosphate acid impregnated zeolite-Y as a catalyst in the alkylation reactions of the phenol, the composition of the reaction mixture consists of phenol of 3.8%, IDF-II of 59.6%, the alkylation products of 36.6%. But there are alkylphenyl ethers of 1.0%, ortho-alkylphenols of 2.4%, para-alkylphenols of 96.0%, di-alkylphenols of 0.6% in the composition of the alkylation products. The ratios of the para- and ortho-alkylphenols are 40.0, the yield of the target product is 73.6%, and the selectivity is 96.5%.

Alkylphenyl ethers are not obtained in the process of realizing the alkylation reactions in the presence of Seokar-2, Seokar-2M catalysts.

As a result, ortho-alkylphenols of 2.6-4.3%, para-alkylphenols of 93.0-96.1%, di-alkylphenols of 1.3-2.7% are obtained.

It is seen from Table 13 that the amount of the target product – para-alkylphenols in the composition of the alkylation products is 96.1% when the alkylation reactions of phenol with IDF on pilot plant conducted in the presence of the Seokar-2M catalyst unlike other catalysts. The yield of the target product for taken phenol constitutes 75.7%, the selectivity for the target product constitutes 96.8%.

In the same way, the cycloalkenylation reactions of phenol with 3-vinylcyclohexene (VCH) in the presence of the above-mentioned catalysts have been investigated.



As an example, let’s see the results of the cycloalkenylation reactions of phenol with VCH in the presence of the KU-23 and phosphorous-containing catalyst.

Unlike the existing catalysts when the catalytic alkylation reactions of the phenol with VCH conducted in the presence of the KU-23 catalyst, the reaction condition is mild, the yield and selectivity of the reaction products are high.

The obtaining of the final products with quality and high yield depends on the right selection of the reaction condition. For this purpose, to find the optimal condition for obtaining

The effect of temperature, reaction duration, molar ratios of initial components and the amount of catalyst on the yield and selectivity of the reaction products have been investigated to find the optimal condition for obtaining para-(cyclohexenylethyl)-phenol.

The studied reaction temperature in the interval of 60-120°C, reaction duration of 2-7 h, molar ratios of phenol to VCH from 2:1 to l:2, the amount of the catalyst of 5-20% (for taken phenol) have been investigated.

In Table 14, the results of cycloalkenylation reactions of phenol with VCH in the presence of KU-23 catalyst are given.

As seen from the Table, if reaction temperature is 100°C, then the highest yield of para-(cyclohexenylethyl)-phenol is 76.2 % (for taken phenol). If we raise the temperature of the reaction mixture up to 120°C, the yield of the target product is 70,8 %.

Table 14

The results of cycloalkenylation reactions of phenol with VCH in the presence of KU-23 catalyst

Taken, g		Reaction condition			Yield, %	Selectivity,
Phenol	VCH	Temp., °C	Time, h^{-1}	Amunt of the catalyst, %		
94	108	60	5	10	39.7	90.1
94	108	80	5	10	48.3	92.8
94	108	90	5	10	63.4	94.2
94	108	100	5	10	76.2	96.4
94	108	120	5	10	70.8	92.3
94	108	100	2	10	34.3	96.3
94	108	100	3	10	58.2	95.7
94	108	100	5	10	76.2	96.4
94	108	100	8	10	73.0	93.6
94	54	100	5	10	29.3	76.8
94	108	100	5	10	76.2	96.4
94	162	100	5	10	78.7	89.9
94	216	100	5	10	75.5	83.6
94	108	100	5	15	51.7	90.7
94	108	100	5	10	76.2	96.4
94	108	100	5	15	77.4	90.2
94	108	100	5	20	78.5	88.4

If to increase the maintaining duration of the initial components in the reaction zone from 2 h up to 5 h, during first 5 h the yield of para-(cyclohexenylethyl)-phenol increases from 34.3 % up to 76,2 %, and then decreases to 73,0 %. It is explained by the fact that long maintaining of mono-substituted cycloalkylphenols in the reaction zone are resulted with 2- and 3-substituted cycloalkylphenols obtaining.

It is possible to obtain the yield of para-(cyclohexenylethyl)-phenol of 76.2 % in the amount of molar ratio of 1:1 of phenol to VCH. The changing of the amount of phenol or cyclene in total mixture of components does not give any positive result; the amount of the target product remains at the same level.

The yield of the cycloalkenylation products depends on the catalyst amount used for this purpose. The studies have been conducted in limits of 5÷20% for taken phenol of the catalyst amount. It has been determined that such a positive result can not be achieved by increasing the catalyst amount.

Thus, has been established that the efficient yield of the target product as a result of the cycloalkenylation of phenol with VCH in the presence of KU-23 catalyst can be obtained in the condition mentioned below: reaction temperature of 80 °C, duration of experiment 5 h, molar ratio of 1:1 of phenol to VCH, te amount of the catalyst - 10 % (for taken phenol). In this condition the yield of the target product constitutes 76,2 %.

In a similar way, the study of the catalytic cycloalkenylation reactions of phenol with VCH has been conducted on the continuous plant in the presence of its catalyst.

In Table 15, the results of the cycloalkenylation reactions of phenol with VCH in the presence of the KU-23 catalyst have been given. As seen from the Table, temperature of reaction at 60-120°C, molar ratio of phenol to 3-vinylcyclohexene from 2:1 to 1:3, volume velocity of 0.2-1.0 h^{-1} limits have been studied to obtain para-(cyclohexenylethyl)-phenol with high and efficient yield. As seen from the Table, if reaction temperature is 105°C, in this case the efficient yield of para-(cyclohexenylethyl)-phenol is 68,7 % (for taken phenol) and the selectivity is 97,5 %. Despite of high selectivity at low temperatures, the yield of the target product is significantly lower and this can not be considered as optimal. The amount of 2- and 3-substituted cycloalkylphenols in the composition of the reaction products increases by raising the reaction temperature above 105°C. And this reflects in the yield and selectivity of the target product. Thus, when the reaction temperature is 120°C, the yield of the para-(cyclohexenylethyl)-phenol constitutes 59.3 %, selectivity is 88.7 %. The one of the main factors that affect the yield and selectivity of cyclohexenylethyl-phenol is the concentrations of penol and VCH in the initial raw material mixture. As seen from the Figure, when the molar ratio of phenol to 3-vinylcyclohexene is 1:1 corresponding to the stoichiometric equation, the yield of the target product is 68.7 %, the selectivity is 97,5 %.

Table 15

The results of the cycloalkenylation reactions of phenol with 3-vinylcyclohexene in the presence of KU-23 catalyst on continuous plant

Taken, g		Reaction condition		Yield, %	Selectivity, %
Phenol	VCH	Temp., °C	Volume velocity, h^{-1}		
94	108	60	0.5	38.3	93.0
94	108	80	0.5	47.8	93.4
94	108	90	0.5	56.5	96.2
94	108	105	0.5	68.7	97.5
94	108	120	0.5	59.3	88.7
94	54	105	0.5	35.5	80.7
94	108	105	0.5	68.7	97.5
94	162	105	0.5	71.2	89.4
94	216	105	0.5	65.1	84.9
94	108	105	0.2	66.4	86.3
94	108	105	0.5	68.7	97.5
94	108	105	0.7	61.2	96.7
94	108	105	1.0	53.7	96.4

Although the selectivity slightly increases by increasing or decreasing of the concentration of any of initial components, if to consider the catalyst amount of 10% (for taken phenol), the yield and selectivity of the target product are acceptable. The increasing of the catalyst amount above 10% affects slightly the composition of the final product.

Thus, the efficient condition has been found for conducting the catalytic cycloalkenylation reaction of phenol with 3-vinylcyclohexene in the presence of KU-23 catalyst on the continuous plant: temperature of 105 °C, molar ratio of 1:1 of phenol to 3-vinylcyclohexene, volume velocity of 0.5 h^{-1}. In this condition, the yield of para-(cyclohexenylethyl)-phenol for taken phenol is 68.7 %, and the selectivity is 97.5 %.

The study results of the catalytic cycloalkenylation reactions of phenol with 3-vinylcyclohexene in the presence of ortho-phosphate acid impregnated Zeolite-Y catalyst are given in table 16.

Table 16

The results of the cycloalkenylation reactions of phenol with 3-vinylcyclohexene in the presence of ortho-phosphate acid impregnated Zeolite-Y catalyst on the continuous plant

Taken, g		Reaction condition		Yield, %	Selectivity, %
Phenol	VCH	Temp., °C	Volume velocity, h^{-1}		
94	108	60	0.5	37.5	96.1
94	108	80	0.5	48.7	95.8
94	108	90	0.5	61.3	96.6
94	108	110	0.5	72.4	97.7
94	108	120	0.5	60.1	89.4
94	54	110	0.5	37.5	81.2
94	108	110	0.5	72.4	97.7
94	162	110	0.5	69.7	87.6
94	216	110	0.5	57.2	84.2
94	108	110	0.2	66.3	87.9
94	108	110	0.5	72.4	97.7
94	108	110	0.7	63.6	95.0
94	108	110	1.0	51.7	94.8

The effect of the different parameters on yield and selectivity of alkylation reactions have been investigated to achieve the efficient yield of para-(cyclohexenylethyl)-phenol. In this purpose, the reaction temperature of 60-120°C, molar ratio of phenol to VCH from 2:1 to l:2, volume velocity in interval of 0.2÷1.0 h^{-1} have been studied.

As seen from the Table, when the reaction temperature is 60-90°C, the yield of the target product is 37.5-61.3%, selectivity is 96.1-96,6 %. If to raise the reaction temperature above 90°C, the yield of the product increases; but the selectivity decreases. So that, when temperature of the reaction product is 110°C efficient yield of the target product is 72,4 % and selectivity is - 97,6%. The yield and selectivity of the target product decrease by increasing to 110°C and above.

One of the main factors affecting the yield and selectivity of the target product is molar ratios of the initial components. As seen from Table 16, the efficient yield (72.4 % for taken phenol) and selectivity (97,7%) of the target product are obtained in molar ratio of 1:1 of phenol to VCH.

The increasing or decreasing of the amount of any of the initial components does not have a positive effect. On the other hand, taking more or less of the concentrations of the initial components is profitable neither economically nor technologically.

If we pay attention to the indicators of Table 16, we can see that the yield of the target product changes from 66,3 to 51.7% by increasing volume velocity from 0.2 to 1.0 h^{-1}. But the yield of the target product is 72,4 %, selectivity is 97,7 % in the value of the volume velocity of 0,5 h^{-1} and this can be considered acceptable for the reaction.

Thus, the efficient condition has been found for cycloalkenylation reaction of phenol with VCH in the presence of phosphate impregnated Zeolite-Y catalyst on the continuous plant: temperature of 110 °C, molar ratio of 1:1 of phenol to VCH, volume velocity of 0.5 h^{-1}. In this condition, the yield of para-(cyclohexenylethyl)-phenol (for taken phenol) is 72,4 %, and the selectivity is 97.7 %. After the rectification and purification of para-(cyclohexenylethyl)-phenol again in low pressure, IR- and NMR-spectra are drawn and its chemical structure has been confirmed. Besides, the physical and chemical properties of para-cycloalkyl-phenol have been defined and there have been determined that these indicators coincide with properties mentioned in previous discussion.

The alkylation reactions of phenol with VCH in the presence of Seokar-2 and Seokar-2M catalysts have been carried out on above-mentioned pilot plant.

The effect of reaction temperature, molar ratios of the initial components and volume velocities on the target product have been investigated to achieve the efficient yield and selectivity of para-cycloalkylphenol. The reactions temperatures are 100-140°C, molar ratio of phenol to VCH from 2:1 to 1:2, volume velocity in the limits of 0.3-0.7 h^{-1} have been studied. The yield of the target product is 71.8-76.2%, selectivity is 91.7-96.3% in the found optimal condition.

The yield of the target product reaches to 72.4%, selectivity to 97.7% by taking the amount of VCH same with the amount of phenol. The yield and selectivity of the target product decrease slightly by taking phenol in excess amount in total mixture; properly 37.5 % and 81.2 %. And this fact is explained by obtaining bisphenol as a result of the reaction:

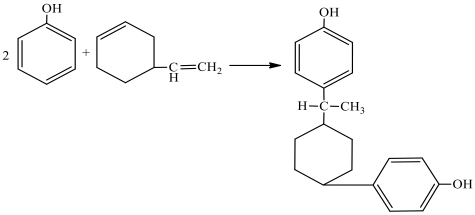
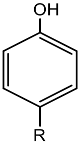
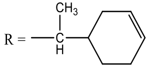


Table 17

Physical and chemical properties of para-alkylphenols obtained on the bases of IDF and VCH

Sample 	Empirical formula	$T_{boil.}$, ^oC 5 mm.Hg	n_D^{20}	ρ_4^{40}	Mol. mas.
R= C_{8-12}	$C_{15}H_{24}O$	140-160	1.4450	1.0135	280
	$C_{14}H_{18}O$	147-150	1.5445	1.0040	202

The synthesis of derivatives containing nitrogen, phosphorus, sulphur and carbonyl of p-alkylphenols obtained on the basis of C_4-fraction

The main advantage of the alkylphenol-based chemical compounds is that they have multifunctional properties. Their efficient properties can be achieved by incorporating various fragments (N, P, S) to alkylphenols. In this purpose, derivatives containing nitrogen, phosphorus, sulphur and carbonyl of para-alkylphenols that we obtained, have been synthesized and tested in different fields. In this sense, nitrogen-containing derivatives have been obtained as a result of aminomethylation reactions of para-alkylphenols with hexamethylentetramine, aniline, 2,6-di-isopropylaniline, phosphorus-containing derivatives from the phosphitation reactions with phosphorus trichloride, sulphur derivatives from the sulphurization reactions with dichloride sulfide, carbonyl-containing derivatives from the acylation reactions with acetic acid and benzoyl chloride.

The resins of para-alkylphenolamine are obtained by the known method. Para-alkylphenol, urotropin in calculated amount are poured to the three-necked flask at temperature of 140°C, and stirred during 30 minutes. Then the mixture added to the porcelain dish in hot state. The light yellow-colored resin is obtained. The resin is grindled fine by treating in mortar and pestle, and its physical and chemical properties are determined.

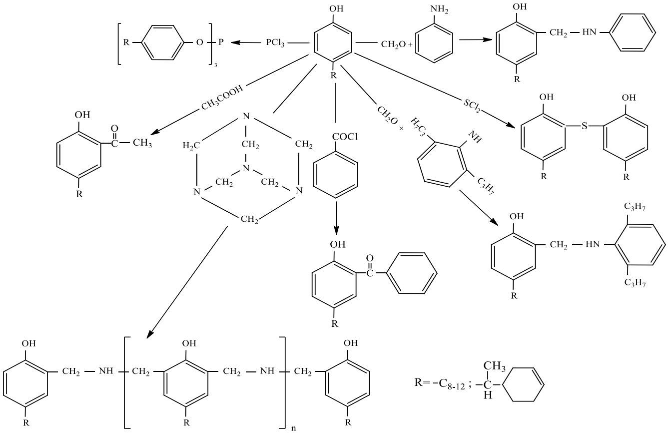


Figure 5. Scheme for the synthesis of N,P,S-containing derivatives of para-alkyl phenols

The physical and chemical properties of para-alkylphenolamine resin obtained on the basis of synthesized IDF are given below:

- Softening temperature – 98°C
- Ortho mol. mas. - 1428
- Elemental composition: C – 78.35%, H – 6.8%, N – 5.1%
- Functional composition: OH – 7.35%, N – 5.2%

The physical and chemical properties of para-(cyclohexenylethyl)-phenol amine resin are given below:

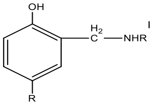
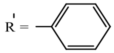
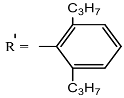
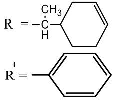
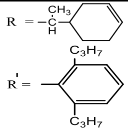
- Ortho mol mas. –1425
- Softening temperature – 103°C
- Elemental composition: C – 78.18%, H – 7.3%, N – 5.4%
- Functional composition: OH – 7.17%, N – 5.5%

The interaction reactions of synthesized para-alkylphenols with with formaldehyde and anilines have been investigated.

The physical and chemical data of 2-Hydroxy-5-alkylbenzylphenylamines are given in the Table below.

Table 18

Physical and chemical data of 2-Нудроху-5-алкулбензулрhенуламинес

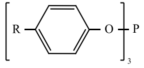
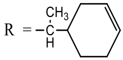
	Boiling point, ° C/10 mm.Hg	n_D^{20}	ρ_4^{40}	Mol. mas.	Calculated, % Found, %		
					C	H	N
R=C_{8-12};  $C_{22}H_{27}NO$	208-220	1.5656	0.9765	303	$\frac{82.3}{81.8}$	$\frac{7.2}{6.6}$	$\frac{4.2}{4.9}$
R=C8-12;  $C_{27}H_{41}NO$	218-226	1.5754	0.9825	395	$\frac{81.6}{80.9}$	$\frac{9.8}{9.2}$	$\frac{3.0}{2.5}$
 $C_{11}H_{27}NO$	216-218	1.5810	0.9815	307	$\frac{81.7}{81.2}$	$\frac{7.7}{7.1}$	$\frac{4.3}{3.8}$
 $C_{27}H_{37}NO$	224-228	1.5963	0.9875	391	$\frac{82.3}{81.5}$	$\frac{9.2}{8.8}$	$\frac{3.4}{2.7}$

The phosphitization reactions of p-alkylphenols with phosphorus trichloride on the bases of IDF and VCH have been conducted.

The reaction must be conducted in the following condition for achieving the efficient yield of the process (for taken para-alkylphenol): temperature of 70°C, duration of the reaction 4 h, molar ratio of 1:3 of para-(cyclohexenylethyl)-phenol to phosphorus chloride. Meantime the yield was 92.6-94.7%. The physical and chemical indicators of 3-[para-alkylphenyl]-phosphites are given below:

Table 19

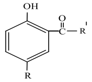
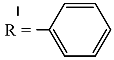
The physical and chemical indicators of 3-[para-alkylphenyl]-phosphites

	Empirical formula	Boiling point 5°C/ mm.Hg.	n_D^{20}	ρ_4^{40}	Mol. mas.
R=C_{8-12}	$C_{42}H_{39}O_3P$	315-330	1.5830	1.0855	628
	$C_{42}H_{51}O_3P$	321-324	1.5715	1.0782	634

The reactions of acylation of para-alkylphenols with acetic acid and benzoyl chloride have been conducted. The physical and chemical properties of the obtained aceto and benzophenones are given in Table 20.

Table 20

Physical and chemical properties of 2-Hydroxy-5-(alky)-aceto and benzophenones

	Boiling point 5°C/ mm.Hg.	Melting temp. °C	Molş mas.	Empirical formula
R= $-C_{8-12}$ R^1=$-CH_3$	167-171	78	232	$C_{15}H_{20}O_2$
R= $-C_{8-12}$ 	193-197	98	302	$C_{21}H_{18}O_2$

Test of the developed processes and synthesized products

Tests of p-alkylphenolamine resins as coating agents for paint and varnish materials

Coating agents for varnish have been obtained from 60%

solutions of the obtained p-alkylphenolamine in p-xylene and known resins. Physical-mechanical properties have been studied after testing on steel plates.

60% solution of proposed para-alkylphenolamin resin in p-xylene has more superior properties than the known amine resins: impact thoughness 40-45 cm, drying time 105-109 min., hardness – 0.65-0.70 sc.un., brightness is 56-60% and these properties are significantly superior than known resin used in industry.

Benzilfenilaminlərin CNK-26 nitril kauçukunda antioksidant kimi sınaqları

Tests of benzylphenylamines as antioxidants for SNK-26 nitrile rubber

The tests of 2-hydroxy-5-alkylbenzylphenylamines obtained on the basis of IDF and VCH as antioxidants in SNK-26 nitrile rubber have been compared with widely used NG-2246 antioxidant in central laboratory of Sumgait “Synthetic Rubber” Plant.

Qualitative properties of the samples as antioxidants have been determined under the conditions of thermal destruction of SNK-26 rubber (atmoshperic pressure -2 h, at 150°C) and naturally aging for 6 months.

Addition of the samples, suggested by us, into nitrile rubber, stability coefficient of rubber equals to 0.95-0.96 after thermal destruction; molecular weight of the rubber keeps its stability after 6 months under natural conditions, stability coefficient equals to 1.0.

These properties correspondingly change as 0.59 and 0.95 by addition of NG-2246, used in industry for this purpose, into nitrile rubber.

On the bases of the test results of the antioxidants, proposed by us, it may be concluded, that slight changes are observed in the rubber in thermal destruction process by addition of benzylphenylamines obtained on the basis of 2,6-diisopropylaniline into SNK-26 nitrile rubber. But the rubber isn’t subjected any destruction after 6 months under natual conditions.

Tests of benzylphenylamines as antioxidants in diesel fuel

Aminomethylation products of para-alkyl(C_8-C_{12})- and para-(cyclohexenylethyl)-phenols with aniline and 2,6-diizopropylaniline have been tested as antioxidants in diesel fuel according to GOST 9144-79.

Further, the amount of the sediments have been determined formed after the oxidation of initial diesel fuel (DF) and the antioxidants-added samples in ЛСАРТ device at 150°C during 4 h.

Unlike the known antioxidants, slight sediment (0.4mg/100 cm^3) is formed in diesel fuel by addition of the antioxidants, synthesized by us, to diesel fuel; but there isn’t any sediment by addition of 2-hydroxy-5-(cyclohexenylethyl)-benzylphenylamine on the basis of VCH to diesel fuel.

Tests of tert-[para-(arylalkyl)-phenyl]-phosphites as antioxidants in T-46 turbine oil

Synthesized tert-[para-(arylalkyl)-phenyl]-phosphites have been tested as antioxidant for T-46 turbine oil. The tests have been carried out in DK-NAMI device at 100°C for 10 h according to GOST-11063-77 and the antioxidant mas. has been determined as 0.5%.

As a result of using phosphites in turbine oil, increase in oil viscosity is 3.8-4.0% at 100°C, but the amount of the sediment formed after 10 minutes is 0.15-0.17%; these indices are correspondingly 10.76 and 2.17% for the base oil without antioxidant.

Thus, tert-[para-(arylalkyl)-phenyl]-phosphites, synthesized by us, meet all of the requirements for antioxidant additives and may be recommended as antioxidant for T-46 turbine oil.

Comparative tests of 2-hydroxy-5-alkylacetophenones as photostabilizer in polystyrene

2-Hydroxy-5-alkyl(C_{8-12})- and 2-hydroxy-5-(cyclohexenyl-ethyl)-acetophenones have been added to polystyrene (PS) in the amount of 0.5% mas. and tested comparatively with the known stabilizer (2,4,6-tert-butylphenol). PS and PS-added samples have been irradiated by PRK-2 mercury-vapor lamp. It has been determined that their optical densities stay unchanged during 8 h.

Test of 2-hydroxy-5-(cyclohexenylethyl)-acetophenone as antirad in polypropylene

The composite of 2-hydroxy-5-(cyclohexenylethyl)-acetophenone on the basis of polypropylene has been developed and its electrophysical properties have been studied; the dependence of its specific resistance on the radiation dose has been studied. It has been determined, that value of specific resistance reduces to a certain limit up to 50kGy of radiation dose. But value of specific resistance remains stable in the further doses.

Industrial tests of ETBE production process

A pilot plant with a capacity of 12 000 tons/year has been constructed on the basis of etherification reactions of BIF with ethanol carried out in pilot device.

Principial technological scheme of ethyl tert-butyl ether production device is illustrated in Fig.6 and the equipments are ranked as follows:

Butylene-isobutylene fraction (BIF) of butadiene production has been used as raw material for the synthesis of ethyl tert-butyl ether (ETBE). BIF is carried by compressed gas machines and converted to E-3 container. A drawer has been put for preventing acception in generating of high level in the container on BIF line. E-3 capacity is provided with two safety valves. Ethanol is taken into the E-l capacity, which is brought from the railroad tank by car tanks. In the case of generation of a high level of the capacity, a separator marker is placed on the ethanol line to stop the acception.

The technological scheme intends ethanol purification from oxygen in Kt-8 column, when ethanol composition contains more than 0.0005% oxygen amounts. Therefore ethanol is given to Kt-8 column through H-2-pump. The bottom of the column is heated by the boiler. Oxygen-alcohol mixture from the upper part of the column is cooled in T-9 condenser and the alcohol is condensed, but oxygen is absorbed into the air. Oxygen-free ethanol is poured to E-1 capacity from the column cube. E-1 capacity has been provided by a small window. Ethanol is given from E-1 capacity to T-5^a heater through N-1 and N-4 pumps at 0.9 t-1 limitation of ethanol:isobutylene molar ratio. Completely calculated amount of ethanol adn 85-90% of BIF are given to the heater.

The obtained mixture is heated up to 50°C by hot water in T-5^a heater and given to R-6 tube reactor. Obtaining process of ethyl tert-butyl ether is realized in the reactor tubes filled by macroporous catalyst of KU-2-8.

Obtaining process of ETBE is carried out through separation of water. Therefore, 50-80°C water is given to the section of the reactor between tubes for the purpose of providing temperature mode in the reaction zone close to isothermal mode. The water with these parameters is obtained by heating the water in T-20 boiler. Water heating is achieved by burning of natural gas in the boiler. The boiling water is supplied to the reactor with N-21 pump. Reverse water from the reactor is returned to T-20 boiler. The cycle cooling of the reactor can be realized according to the required technological scheme. The temperature of cooling water entering and leaving the reactor should be 3-5 °C. The rest of BIF (10-15% of all BIF) is mixed to the reaction products (ETBE + C_4 hydrocarbons) leaving R-6 reactor at 58-70 °C and given to R-7-positioned the 2nd reactor. The temperature is regulated by 30-70°C straight-flow hot water in R-7 reactor.

ETBE obtaining process is realized in liquid phase. Pressure is remained at 8 kg/cm^2 by control valves put at the output of R-7 positioned 2nd reactor for the purpose of turning all components of the reaction mixture into liquid state. R-7 positioned reactor has been provided by 2 protective valves against increasing pressure.

The project also provides the giving of the product to the reactors from the bottom and their parallel operation. It ensures loading of catalyst to one of the reactors and the device reliability, simultaneously doesn’t prevent obtaining process of ETBE in any of the reactors.

The reaction product (ETBE + C_4-hydrocarbons) is given directly from the R-7 reactor to the plate of Kt-8 column.

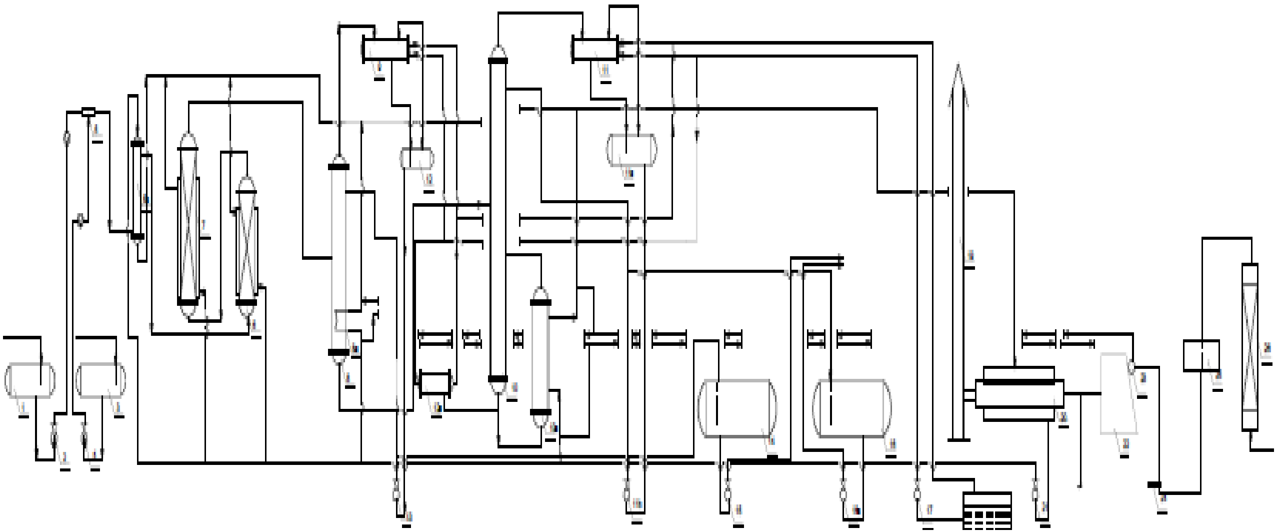


Fig. 6. 1 – Capacity for alcohol; 2 - pump; 3 – capacity for BIF; 4 - pump; 5 - mixer; 5^a - heater; 6 - reactor; 7 - reactor; 8 – rectification column; 8^a - heater; 9 - condenser; 10 – rectification column; 10^a - heater; 11 - condenser; 1 l^a – intermediate capacity; 1 l^b - pump; 12 - intermediate capacity; 12^a - refrigerator; 13 – phlegm pump; 14 - BIF tank; 15 – liquid gas pump; 16 – ether tank; 16^a - pump; 17 – water pump; 18 – circular water tank; 19 – smole pipe; 20 – water-boiler; 21 – water pump; 22 – steam boiler; 23 – steam separator; 24 – feeding pump; 25 - chemically pure water capacity; 26 – water filter.

K_t-8-positioned rectification column has been designed for the separation of the non-reacting C_4 fraction from ETBE synthesis products.

The cost of BDF and methanol amounts to 383.5 and 253.3 man/t (including VAT), raw materials expenses amount to 851,400 manat (84%), and technological process expenses amount to 160,7 thousands AZN (16%).

Total expenses amount to 1012,1 thousands AZN/month.

Developed C_4-fraction obtained in the process as a non-calculated product is got out of general expenses, other expenses represent the net cost of 1000 t MTEB.

Beləliklə, ilkin hesablamalar nəticəsində müəyyən edilmişdir ki, 1000 t/ay həcmində istehsal olunan MÜBE-nin 1 tonunun maya dəyəri I variant üzrə 513 man. 57 qəp. (~293 dol.) və II variant üzrə 563 man. 42 qəp. (~322 dol.) kimi formalaşır.

So, it has been determined, that the net cost of 1 ton of MTBE produced in 1000 t/month amounts to 513 man. 57 kopecks ((~293 dol.) according to the I variant and 563 man. 42 kopecks (~332 dol.) according to the II variant.

Fig. 7. General view of ETBE (MTBE) obtaining plant

RESULTS

1. For the first time, etherification reactions of non-divinyl C_4-fraction (BIF) and divinyl-rich C_4-fraction (BDF) with methanol and ethanol in the presence of KU-23 and ortho-phosphate impregnated Zeolite-Y catalysts have been carried out on a pilot device with capacity of 2 kg/h. As a result of the studies it has been determined that methyl(ethyl) tert-butyl ethers yield are in the limits of 68.3-84.3% under the found optimal conditions as: temperature of 70-75°C, 1:3 mol ratio of alcohol to BIF (BDF), 0.5 h^{-1}volume velocity, and 0.7-0.8 MPa pressure in the system.
2. BIF dimerization has been realized on the continuous pilot plant in the presence of ortho-phosphate impregnated Zeolite-Y catalyst at 200°C, 0.5 h^{-1} volume velocity and 0.8 MPa pressure, but BDF cyclodimerization has been carried out in autoclave at 200°C for 2 h. In the result, C_8-C_{12}fraction containing 38.78% of diisobutylene, 21.08% diisobutylene isomers and 32.76% of isobutylene trimers, and 3-vinylcyclohexene of 98.6% purity have been obtained.
3. Influence of phenol with BIF oligomerization products and BDF cyclodimerization product – VCH and different factors (temperature, time, the components mol ratios, catalyst amount, volume velocity) on the target products yield and selectivity has been studied on the batch and continuous plant in the presence of KU-23, ortho-phosphate impregnated Zeolite-Y, zeolite-containing Zeokar-2 and Zeokar-2M catalysts.
4. For the first time, aminomethylation reactions of p-alkylphenols obtained on the basis of BIF dimerization, BDF cyclodimerization products with hexamethylentetramine (urotropine) have been realized. The reaction has been carried out at 140°C for 2 h. In the result, crystalline p-alkylphenol-amine resins have been synthesized with 1425-1428 of mol ratio, 98-103°C of softening temperature, OH-7.17-7-35% functional composition and NH-5.2-5.5%.

- Mannich bases have been obtained by aminomethylation reactions of p-alkylphenols with formaldehyde and aniline (2,6-diisopropylaniline). It has been determined, that the yields of the target products – 2-hydroxy-5-alkylbenzylphenylamines amount to 84.6-92.4%, and selectivity according to the target products – 87.4-93.7%.

- Tert-[para-(alkyl)-phenyl]-phosphites have been synthesized as a result of phosphitation reactions of p-alkylphenols with phosphorous trichloride. The yields of the target products amount to 92.6-94.7% at 70-75°C, in 4 h-reaction duration, 3:1 mol ratio of para-alkylphenol to phosphorous trichloride.
- 2,2'-thiobis-(4-alkylphenol)s have been obtained at 40°C, for 4 h, 2:1 mol ratio of para-alkylphenol to sulphide dichloride with the yield of 88.6-91.7% in the result of sulphidation reactions of p-alkylphenols with sulphide dichloride. 2,2'-thiobis-(4-alkylphenyl)chlorophosphites have been obtained by phosphitation reactions of obtained 2,2'-thiobis-(4-alkylphenol)s with phosphorous trichloride at 120°C, for 5 h reaction time, 1:1 mol ratios of initial components and 92-94% yield.
- Acylation reactions of p-alkylphenols with acetic acid and benzoyl chloride have been studied in the presence of $ZnCl_2$, KU-23 catalysts. The influence of rejime parameters (temperature, time, initial components mol ratios, catalyst amount) of p-alkylphenols taken for the reaction on the yield of the target products and the reaction direction. As a result of the studies it has been determined that the yield of the target products – 2-hydroxy-5-alkylacetophenones amounts to 56.7-67.4%, and the yield of 2-hydroxy-5-alkylbenzophenones – 61.2-74.8% under the found optimal conditions.

5. P-alkylphenolamine resins have been tested as coating agents for paint and varnish materials. It has been determined that 60% solution of p-alkylphenolamine resins in p-xylene has better properties than known amine resins. Impact thougness – 40-45 cm, drying time – 105-109 min., hardness – 0.65-0.70 sc.un., brightness is 56-60% and these properties are significantly superior than known Amberol-Stamine resin used in industry.
6. 2-Hydroxy-5-alkylbenzylphenylamines have been tested as antioxidants for nitrile rubber known as SNK. As a result of the tests it has been determined that by adding some of the samples

presented by us obtained on the basis 2,6-diisopropylamine into nitrile rubber, stability coefficient is 0.95-0.96 after thermal destruction of rubber, after 6 months the rubber molecular weight remains unchanged in natural conditions, stability coefficient equals to 1.0.

7. Aminomethylation products of p-alkyl (C_8-C_{12}) and p(cyclohexene-3-yl-ethyl)-phenols with 2,6-diisopropylaniline have been tested as antioxidants on ЛСАРТ device according to GOST 9144-79. It has been determined, that adding 0.004% of synthesized antioxidants into diesel fuel at 150^0C, after 4-hour oxidation, results in forming a small amount (0.4mq/100 cm^3) of sediment in 2-hydroxy-5-alkyl(C_8-C_{12})-benzyl-2,6-diizopropylphenylamine-added diesel fuel; but it isn't observed any sediment in 2-hydroxy-5-(cyclohexene-3-yl-ethyl)-benzyl-2,6-diisophenylamine- added diesel fuel.
8. 2-Hydroxy-5-alkylbenzyl-2,6-diisopropylphenylamines have been used as ligands to catalytic precursors used in ethylene oligomerization process. Use of benzylphenylamines as ligand for catalyst used in ethylene oligomerization process causes to have higher (80-85%) yield of the target products than known catalysts (70-75%).
9. Synthesized tert[para-(alkyl)-phenyl]-phosphites have been tested as antioxidants for T-46 turbine oil. It has been determined, that adding of phosphites to the turbine oils in 0.5% is followed by the increase in viscosity – 3.8-4.0%, but sediment amount is 0.15-0.17% according to GOST 11063-77. These indices are correspondingly 10.76 and 2.17%.
10. 2-Hydroxy-5-alkylacetophenones have been tested as photostabilizer in polystyrene and antirad against radiation in polypropylene. As a results of the tests, it has been determined, that adding of alkylacetophenones to polystyrene in 0.5%, optical densities of polystyrene-specific fragments remain stable after 8 hours of photocatalyzing, unlike known stabilizers. Testing of 0.5% composites of 2-hydroxy-5-alkylacetophenones in polypropylene shows that the value of special resistance above 50 kGy of irradiation dose remains constantly.

11. A plant with production capacity of 12000 tons/year has been constructed on the basis of laboratory indices for the purpose of industrial implementation of etherification processes of methanol and ethanol with BIF and BDF. 600 tons of ethyl tert-butyl ether, 200 tons of methyl tert-butyl ether produced on the plant have been sent to Germany, Poland, Greece, Ukraine and received positive references. Technological regulations, technical specifications and technical-economic properties have been developed for the processes.

THE MAIN CONTENT OF THE DISSERTATION WORK IS PUBLISHED IN THE FOLLOWING SCIENTIFIC WORKS

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