Introduction

As follows from the currently existing structure of oil product consumption, more than half of the funds invested in the development of the oil and oil refining industries, it is necessary for the production of motor fuels for internal combustion engines, as that oil are practically the only source of motor fuels [1]. The development of the motor transport, using oil fuel creates a global environmental problem [2]. With the exhaust gases of vehicles about two hundred different substances, a half of which constitutes a danger to human health and environment are released into atmosphere, and the scale of air pollution increase due to the tendency of increasing the output of cars. In big cities the proportion of air pollution from vehicle exhaust in the total amount of emissions entering the atmosphere, ranges from 80 to 95% [3]. According to the World Health Organization (WHO) three-quarters of human diseases are bound to the ecological reasons caused by anthropogenous activity and motor transport is one of the most serious sources of deterioration in ecology [4].

Very relevant is the involvement in petroleum refining of the alternative sources of carbonaceous materials, such as natural gas, associated petroleum gases, heavy fuel oil, coal and its processing sludge, peat, plant biomass, etc. for the purpose, to produce high-octane gasoline components. At the same time it is very important today to obtain ecologically clean high-octane components of modern gasoline’s, complies with Euro-5 and Euro-6 standards [5-8].

The main requirements to change the hydrocarbon composition of motor gasolines consist in increasing of the amount of isoparaffins from 20 to 45, decreasing aromatic hydrocarbons from 42 to 25%, in increase in high-octane additives up to 10-12% [9].

In this regard technologies of producing iso hydrocarbons by isomerization and alkylation of paraffin gain all great value olefins importance [10,11]. The alkylation process is used for recycling C_{4}-C_{6} hydrocarbons obtained from gases of the catalytic cracking by converting their most part to alkylate and also as a possible alternative method for reducing the total sulfur content in gasoline, without losing octane in a product. There have been considered in article technologies of alkylation their prospects for the future have been given.

The impressive pace of scientific discovery in the industry demonstrate how demand alkyl benzene, which proved to the most valuable component of the fuel for carburetor aircraft and automobile engines. Alkyl benzene is one of the most important products of oil processing. For example, in the USA, about 11% of gasoline is currently being produced by an alkylation of isobutene by alkenes C_{3}-C_{5}. Alkylate approximately consists of 70% C_{6} of alkanes, mainly trimethylpentanes 15% C_{7}-C_{8} and 15% C_{9}-C_{10} hydrocarbons.

Alkylate meets the technical, operational and environmental requirements of modern European and American standards for motor fuel in internal combustion engines. Currently in the world the gasoline share on the basis of alkylate reaches proportion, about 25% of the total consumption of motor gasoline components, and in aviation gasoline’s it is a major component (more than 60%). In abroad the volume of alkylate production exceeds 70 mln. t/year. There are no doubts that as long as the vehicles are operated on a high-octane gasoline’s, alkylate will still be a desirable component of automobile gasoline [12,13].

The advantage of the alkylation of paraffins with olefins process on heterogeneous catalysts is in the stable operation of the catalyst and its multiple use of after regeneration. In this connection with this in Institute of Petrochemical Processes Azerbaijan National Academy of Sciences there have been studied the process of alkylation of paraffin’s with olefins on zeolite catalyst OMNICAT-210P modified Ni, Co, Cr.

Experimental Section

Researches on alkylation of hydrocarbons contained in the gases of a catalytic cracking carried out in the reactor in the presence of heterogeneous industrial-zeolite catalyst OMNICAT-210P modified Ni, Co, Cr. Below is a description of the principal technological schemes bigger pilot plant (Figure 1).
The raw material from the balloon 2 through the rotameter (4) is fed to the reactor (diameter of reactor -34.2 mm; height 931 mm). The catalysts (15) with diameter of pellets 3.2 mm in amount to the reactor (diameter of reactor -34.2 mm; depth of reaction zone -931 mm). Fillings (Raschig rings) have been backfilled on the catalyst layer a 64 mm high (17) and under the catalyst layer 136 mm high (16). Fillings (15) with dry ice; 13 thermocouple internal (80 mm depth of immersion in the catalyst bed); 14-external thermocouple (at the height of the catalyst length 360 mm); 15-catalyst zone (volume-270 cm³; height 437 mm layer); 16-filling (layer height 136 mm); 17-filling (layer height 64 mm); 18 insulation layer; 20-winding.

The waste gases from reaction zone come to the cooler (9). Liquid reaction products (including the condensed water, which is used for desorbing hydrocarbons from the catalyst surface) are cooled by running water and collected in the reservoir (10) but not condensed reaction products enter into the container (11) cooled by dry ice (12).

For the purpose of a desorption of the reaction products from the catalyst surface the steam is entered on the catalyst layer (15). For this purpose the spout (8) and pump (7) have been provided which supplies water from the dispenser to the reaction zone of the catalyst (15). Previously water evaporates in the filling region (17) and the steam with a temperature of 350-400°C is feed to the catalyst bed. Thus, from the catalyst surface boiling hydrocarbons are desorbed which after passing a cooler (9) is condensed in the receiving tank 10 and 11. After desorption of boiling hydrocarbons at a temperature of 200-400°C the regeneration of oxidizing catalyst is carried out in the presence of air oxygen, which is fed from the balloon (5), having a pressure gauge (19). After regeneration, the reactor is purged with an inert gas in order to release of reactionary volume from air oxygen to its absence in the exhaust gases.

### Results and Discussion

The model of industrial reactor calculated taking into account the hydrodynamic mode allows to predict with high accuracy carrying out the studied system at change of the technological regime or composition of raw materials.

The plug flow reactor (PFR) is carried in laminar hydrodynamic regime. In such reactors, the reactants stream flows in one direction longwise of the reactor without hatching.

Hydrodynamic regime in PFR is characterized by the fact that any particle of stream moves in one direction longwise of reactor, the reverse (longitudinal) hatching absent. There is also no hatching on reactor section. It is assumed that the distribution of substances on this section is uniform, i.e., values of parameters of reaction mixture are identical. Each element of volume reaction mass dVr moves along the length of the reactor without mixing up with the previous elements of the volume, and behaves as a piston in the cylinder, foxing out everything that is before it. Therefore, such driving mode of reagents is sometimes called piston or full displacement mode. The composition of each volume element sequentially changes longwise the reactor, as a result of the chemical reaction. So, for example, concentration of initial reagent varies progressively longwise the reactor from initial (Cᵣₒ) to a final value (Cᵣ). The consequence of this movement mode of the reaction mixture is the fact that the residence time of each particle in the reactor is same.

For the mathematical description of the fixed bed catalyst there have been used quasi-homogeneous model of a layer of the granular catalyst. According to this model, the catalyst layer is presented in the form of a permeable solid medium through which a gas stream flows, and the chemical reaction proceeds with a speed equal to the observed speed of conversion. In this case, the catalyst layer is considered as a homogeneous medium with a continuous distribution of concentration, temperature, pressure and a flow rate.

Reaction rates are averaged by the volume of the layer, but the heat and mass transfer is determined by the effective thermal conductivities and diffusions coefficients, which depend on physical properties of the mixture, a flow rate, grain sizes, shape and the structure of a granular layer. In the adiabatic catalyst bed there is no radial heat–mass transfer. Heat transfer inside of grains takes place, mainly through a solid catalyst bulk which volume heat conductivity on several orders is higher than the thermal conductivity of gas.

As the length of the catalyst layer in industrial reactors is usually large enough, then the effect of axial diffusion is insignificant. While the Reynolds number above 100 heat and mass transfer occurs due to turbulent diffusion. In these conditions, the molecular diffusion can be neglected and the hydrodynamic regime approaches a plug flow regime [14].

There have been studied the influence of the temperature and rate of volume flow of supply of raw materials on liquid yield reaction, there have been installed the mechanism of the process. There have been compiled the kinetic equations describing the process of alkylation of C₃–C₄ paraffins by olefinic hydrocarbons.
The catalyst is the commercial zeolite containing catalyst of modified Ni, Cr, Co in amount of about 1.5-2%. Modification of Ni, Cr and Co allows conducting the dehydrogenation reaction of paraffin’s C5-C10 to the corresponding olefins. They in their turn together with olefins of feedstock participate in reaction of alkylation of paraffin’s.

At volumetric feed rate of 50 h⁻¹ and reaction temperature 280-300°C liquid yield of reaction products stored at ~78-80 wt%. Researches of kinetic regularities have been carried out in an isothermal reactor.

The volume of the catalyst was 50 cm³. For carrying out the process in continuous conditions it is necessary to install three (3) reactors. The first reactor works in an alkylation mode (30-60 min), the second works in the mode of desorption of products from the surface of the catalyst with steam at a temperature of about 400°C and finally the third reactor works in the regeneration mode (t_reactor=550-580°C) in the presence of atmospheric oxygen.

Then there is a switching of the third reactor in the alkylation mode, the second in the regeneration mode and first in the mode of a desorption of hydrocarbons from the catalyst surface. The process test has been carried out on the enlarged pilot plant with a catalyst volume by ~300 sm³.

For carrying out the process in industry there is proposed the reactor with the volume of 20 m³ and with 2.6 m inner diameter (which is a cylindrical device). A possibility of application of model of PRF for the considered process, it is checked by the calculation of diffusion and thermal Pelet’s criterion for a stream on an entrance to the alkylation reactor. Taking into account the mean value of a volume flow of a reaction mixture of 1000 m³/h (V=50 h⁻¹) the peripheral speed of a stream in the reactor makes:

\[
w = \frac{Q_A}{3600 \pi d^2} = \frac{1000 \times 573 \times 4}{298 \times 3600 \times 3.14 \times 2.6} = 0.101 m/s
\]

where, \(w\) - flow rate in the reactor, taking into account the temperature in the reaction zone (300°C), m/s; \(Q\) - volume flow of the reaction mixture at a feed rate of 50 h⁻¹, m³/h; \(d\) - inner diameter of the reactor, m. Heat Pelet’s criterion \(Pe_t\), calculated by the formula [15]:

\[
Pe_t = \frac{w \cdot 1 \cdot C_p \cdot \rho \cdot \lambda}{\eta}
\]

Where, \(w\) - in the reactor the flow rate, m/s; \(l\) - linear size of the reactor, m; \(C_p\) - specific heat of the mixture, J/mol ∙ K; \(\rho\) - density of the mixture in kg/m³;

\[
\lambda = \frac{\lambda_{C_a,C_b}}{\eta_{C_a,C_b}} \cdot \frac{\eta_{C_a,C_b}}{\eta}
\]

- \(\eta_{C_a,C_b}\) - Thermal conductivity of the mixture, W/m ∙ K [16]

\[
The C_p = 59.7 kcal/g ∙ mol=249.9 J/mol ∙ K
\]

\[
Pe_t = \frac{0.101 \times 3.8 \times 249.9 \times 874.7}{7.393} = 24725.6
\]

- \(\lambda_{C_a,C_b}\) - thermal conductivity of the mixture, W/m ∙ K [16]

\[
The \lambda_{C_a,C_b} = 0.81 \times 104kcal/m ∙ s ∙ sm^3 = 3.39 \times 103F / m \cdot s
\]

The diffusion criterion of Pelet characterizes the mass transfer in a moving stream and is analogous to the thermal criterion of Pelet characterizing the heat transfer in a moving medium. The ratio of thermal criterion of Pelet \(Pe_t\) to the value of diffusion criterion of Pelet is within the

\[
Pe_t/Pe_d = 0.91 + 1.2
\]

where, \(\omega\) is the velocity of flow in the reactor, m/s; \(l\) - linear size of the reactor, m; D-kinematic diffusion coefficient, m²/s.

The obtained values of diffusion and thermal criterion of Pelet suggest that the transfer of heat and material flows in the reactor is significantly prevailing over diffusion. In the reactor there is observed hydrodynamic conditions close to the ideal displacement. The kinematic D diffusion coefficient of gas A in the gas B at an absolute temperature T and a pressure P can be calculated by the following formula:

\[
D = \frac{0.004310^{-7} \times d^2}{P(v_a + v_g)} \sqrt{\frac{1}{M_a} + \frac{1}{M_b} m^2 / c}
\]

Where, \(T\), is the temperature, K; \(P\)-pressure, atm; \(M_a\) and \(M_b\) the molar mass of gases A and B, kg/kmol; \(v_a\) and \(v_g\) - molar volume of gases A and B, sm³/mol [17].

\[
v = V_c \cdot n_c + V_H n_H
\]

where, \(V\) atomic volume of carbon (14.8), sm³/atom; \(n_c\) - number of carbon atoms (C); \(V_H\) - atomic volume of hydrogen (3.7) sm³/atom; \(n_H\) -is the number of hydrogen atoms.

\[
Dc_{a,c_b} = \frac{0.0043 \times 10^{-7} \times 573^{\frac{1}{3}}}{(66.6 \times 74.9 \times 10^{-7})^{\frac{1}{3}}} \times \sqrt{\frac{1}{42} + \frac{1}{44}} = 0.1894 \times 10^{-4}, m^2 / s
\]

The equations for the calculation of comparison values diffusion of paraffinic and C₅-C₁₀ olefinic hydrocarbons inside catalyst grain with a value of the rate of reaction of an alkylation are given below:

\[
D_{ab} = \frac{F}{\Delta \Gamma} \frac{K}{C_t - C_{t,0}} \Delta V
\]

Where, \(D_{ab}\) - molecular diffusion coefficient of the reactants in the gas phase, m²/s; \(\Delta \Gamma\) - the radius of the catalyst grains, m; \(F\) - the surface area of the catalyst grains, m²; \(K\) - reaction rate constant, m³/mol ∙ sec; \(C_{t,0}\), -averaged concentration of C₅-C₁₀ paraffin’s, mol/m³; \(V\) -volume of the catalyst grains, m³.

The alkylation reaction rate constants are set by solving of the kinetic equations of the process of producing liquid products from the catalytic cracking gas (Table 1).

For the calculations to determine the speed of alkylation reaction there has been chosen VI, X, XIV equations due to the fact that the activation energies of these reactions have a minimum value.
Routes, in which are formed connections with same chemical formula but different structure have been combined.

Comparison between the diffusion contribution values and the contribution of chemical reaction to change of reactants concentration in the grain with a diameter of 20 mm indicates that the internal diffusion of reactants proceeds much faster than chemical reactions.

1. Diffusion of C3H6 and C4H10.

\[
\begin{align*}
&1. \text{Diffusion of } C_3H_6 \text{ and } C_4H_{10}.
&
\end{align*}
\]

<table>
<thead>
<tr>
<th>( k_i )</th>
<th>260°C</th>
<th>300°C</th>
<th>420°C</th>
<th>( E_i ) cal/mol</th>
<th>( K_i )</th>
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<td>( k_1 ) l/mol·s</td>
<td>0.001545</td>
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<td>0.008027</td>
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<td>( k_2 ) l/mol·s</td>
<td>0.0151</td>
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<td>( k_3 ) l/mol·s</td>
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<td>( k_4 ) l/mol·s</td>
<td>0.000022</td>
<td>0.000063</td>
<td>0.0000693</td>
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<td>( k_6 ) l/mol·s</td>
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<td>0.000000408</td>
<td>0.000003554</td>
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<td>( k_7 ) l/mol·s</td>
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<td>0.455</td>
<td>1.23</td>
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<tr>
<td>( k_8 ) l/mol·s</td>
<td>0.0109</td>
<td>0.0249</td>
<td>0.167</td>
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<td>( k_9 ) l/mol·s</td>
<td>0.348</td>
<td>0.68</td>
<td>3.197</td>
<td>10145.7</td>
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<td>( k_{10} ) l/mol·s</td>
<td>22.9</td>
<td>60.6</td>
<td>571.5</td>
<td>14754.2</td>
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<tr>
<td>( k_{11} ) l/mol·s</td>
<td>4.26</td>
<td>7.58</td>
<td>28.6</td>
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<tr>
<td>( k_{12} ) l/mol·s</td>
<td>1.17</td>
<td>1.845</td>
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<tr>
<td>( k_{13} ) l/mol·s</td>
<td>0.00567</td>
<td>0.00844</td>
<td>0.0210</td>
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<td>( k_{14} ) l/mol·s</td>
<td>0.00001128</td>
<td>0.0000168</td>
<td>0.000042</td>
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<tr>
<td>( k_{15} ) l/mol·s</td>
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<td>( k_{16} ) l/mol·s</td>
<td>894.0</td>
<td>1327.0</td>
<td>3295.0</td>
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<tr>
<td>( k_{17} ) l/mol·s</td>
<td>1.156</td>
<td>2.89</td>
<td>23.9</td>
<td>13906.0</td>
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The value of the adsorption constant \( K_{ads} \) and \( Q \) heat of formation cal/mol

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<th>( K_{ads} )</th>
<th>( Q )</th>
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<td>0.364</td>
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<td>0.956</td>
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<tr>
<td>0.937</td>
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<td>0.768</td>
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<tr>
<td>0.09587</td>
<td>0.537×10^-4</td>
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<tr>
<td>0.6934</td>
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<tr>
<td>0.387</td>
<td>0.1847×10^-3</td>
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</table>

Table 1: Kinetic parameters of the process of producing liquid products from a catalytic cracking gas.

Conclusions

As a result of studies established that the alkylation process takes place in a plug flow reactor. The ratio of the thermal criteria of Peclet to the diffusion is within the 0.9-1.22. There have been provided a comparison of the values of contribution of diffusion and chemical reactions while changing of concentration of reactants in catalyst grain. At the same time, it has been found that the inner diffusion of reactants proceeds much faster than a chemical reaction.

It has been established that the internal diffusion of reagents proceeds much faster than the chemical reaction, so for C3H6 and C4H10
is within 0.172072 ×0, 00023826. The ratio of thermal Peclet criterion (Pe_{T}) to diffusion (Pe_{D}) is in the range 0.91-1.22 that characterizes the process conditions in the reactor in an ideal displacement mode. There have been determined the values of the activation energy and the rate of constants of the principal reactions that occur in an industrial zeolite catalyst OMNICAT-210P. It means that the rate of chemical reaction is not inhibited by the diffusion of hydrocarbon inside the catalyst grains.

References