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Determining the optimal parameters of the hydrostabilization process of pyro-condensate in the presence of a nickel-chrome catalyst with the method of mathematical statistics

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The work aimed to obtain mathematical static estimates of the influence of various factors on the degree of hydrostabilization of pyrocondensate obtained during the pyrolysis of straight-run gasoline, and an attempt to determine the most optimal process mode. The experimental data obtained earlier made it possible to define the temperature range, duration, volume of the catalyst, and the ratio of hydrogen to feedstock necessary for the effective hydrostabilization of the pyrocondensate, which made it possible to narrow the range of variation of the process parameters. At the same time, the task was set to find the optimal conditions that ensure the maximum degree of hydrogenation of the condensate. The planning of the experiment was carried out according to the scheme of a full factorial experiment 2^4. The parameters on which the process of hydrostabilization of pyrocondensate depends are the following: T is the temperature of the experiment; τ is the duration of the experiment; V_{kat} is the catalyst volume; H_2:C is the ratio of hydrogen to raw material. Due to the results of an active experiment carried out using mathematical planning methods, the major role of variable factors was determined, a mathematical model was obtained, and the optimal mode for conducting the pyro-condensate hydrostabilization process with the presence of a nickel-chromium catalyst was determined: temperature - 80° C, the ratio of hydrogen volume to raw material, equal to 0.3, catalyst volume - 5 cm^3, process duration - 120 min. The temperature has the greatest influence on the degree of pyro-condensate hydrogenation. Comparison of the results of mathematical modeling with experimental data indicates a low discrepancy (0.8% rel.) and confirms the reliability of calculations using the obtained regression equation.

Keywords: hydrogenation, hydrostabilization, pyro-condensate, catalyst, experiment planning matrix, optimization, statistics.

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Introduction

Modern science and technology advancement is related with the creation of new and constant improvements in existing scientific and technological processes. Due to the rapid development of chemical technology, mathematical processing and analysis of the results of a chemical experiment are becoming significantly important. Methods for processing experimental data began to develop more than two centuries ago due to the need of solving practical problems in agrobiology, medicine, economics, and sociology. The results obtained subsequently formed the foundation of such a scientific discipline as mathematical statistics. The emergence of mathematical statistics as a science was facilitated by the emergence of probability theory, the development of its methods, and its use in practical applications. The development of statistics is associated with the names of prominent scientists, including Pierre Simon Laplace (1749–1827), Simeon Denis Poisson (1781–1840), Jean Baptiste Fourier (1768–1830), Lambert Adolphe Quetelet (1796–1874) [1-4]. They laid the foundations of modern statistical methodology and actively applied the methods obtained to establish patterns in social phenomena.

A significant rise in the efficiency of experimental research and engineering development is achieved by using mathematical methods for planning experiments. The (there should not be anything)experimentation and processing of the data obtained significantly diminishes the time for solving, reduces the cost of research, and improves the quality of the results obtained. The beginning of experiment planning was labeled by the works of the English statistician Ronald Aylmer Fisher (1935), who emphasized that rational experiment planning gives no less significant gain in the accuracy of estimates than optimal processing of measurement results [5,6]. Fisher showed for the first time that the planning of experiments and observations and the processing of their results are two inextricably linked tasks of statistical analysis. He established the foundations for the theory of experiment planning. proposed several effective statistical methods (first, analysis of variance), naturally arising from the uniqueness of the experiment and developed the theory of small samples, started by the English scientist Student (W. Gosset) [6].

At present, the use of methods of mathematical statistics is an essential condition for the optimization and modeling of all chemical-technological processes [1-3, 7-15]. The use of methods of mathematical statistics in solving problems aimed at solving the problem of rational use of by-products of oil refining is the key to its successful solution.

The work aims to obtain mathematical static estimates of the influence of various factors on the degree of photostabilization of straight-run gasoline pyrocondensate, and an attempt to determine the most optimal process mode.

I. Experimental technique

Previous experiments made it possible to determine the temperature range, duration, volume of the catalyst, and the ratio of hydrogen to feedstock necessary for the effective hydro stabilization of pyro-condensate, which made it suitable to contract the range of variation of the process parameters [16, 17]. At the same time, the task was set to find the optimal conditions which ensure the maximum degree of hydrogenation of the condensate. The planning of the experiment was carried out according to the scheme of a full factorial experiment 2^4 [2-4,6]. The parameters on which the process of phytostabilization of pyro-condensate depends on the following: T - is the temperature of the experiment; τ- is the duration of the experiment; V_{kat} is the catalyst volume; H_2:C is the ratio of hydrogen to raw material.

An industrial nickel-chromium catalyst was used as a catalyst (TU OST 113-03-4001-90; mass fraction: nickel in it - not less than 48 wt.%, chromium oxide - not less than 27 wt.%). The raw material was the pyrolysis condensate of straight-run gasoline, evaporating in the range of n.c.–200°C, obtained at the EP-300 plant of the Ethylene-propylene plant of the Azerkimya Production Association, SOCAR, Azerbaijan, Sumgait. Characteristics of straight-run gasoline: density 0.705 g/cm^3; group hydrocarbon composition (wt %): n-paraffins - 32.6; isoparaffins - 36.4; naphthenes - 24.6; aromatic hydrocarbons - 6.1; unsaturated hydrocarbons - 0.3.

The method for determining the component and quantitative hydrocarbon, as well as the group composition of raw materials and products obtained, is given in [16,17].

The degree of hydrogenation C_{hydr} was calculated based on the results of the quantitative content of olefins in the reaction mixture according to the formula:

$$C_{\text{hydrogenation}} = \frac{n_0 - n_i}{n_0} \cdot 100\%.$$

where n_0 – is the initial content of olefins, wt. %; n_i – is the final content of olefins, wt. %.

The data processing of the active experiment and the subsequent optimization of the technological process was carried out using a program written in Fortran-e.

II. The discussion of the results

An experiment planning matrix at temperatures of 80, 100, and 120°C, process durations of 30, 60, and 120 min, catalyst volumes of 5, 10, and 15 cm^3, hydrogen volume to feed ratios of 0.3, 0.5, and 0.8, and In the course of active research, data on the hydrostabilization of pyrocondensate are presented in the form of a table.

The experiment carried out on the selected matrix made it possible to obtain a mathematical model describing the influence of X_1-X_4 factors on the selected optimization parameter Y. Because the 4-parameter regression equation does not give reliable results, an equation with cross terms was used, of the form:

$$Y_{\text{hydrogenation}} = a_0 + a_1 \cdot X_1 + a_2 \cdot X_2 + a_3 \cdot X_3 + a_4 \cdot X_4 + a_{12} \cdot X_1 \cdot X_2 + a_{13} \cdot X_1 \cdot X_3 + a_{14} \cdot X_1 \cdot X_4 + + a_{23} \cdot X_2 \cdot X_3 + + a_{24} \cdot X_2 \cdot X_4 + a_{34} \cdot X_3 \cdot X_4.$$

To process the data of an active experiment and subsequent optimization of the technological process using a program written in Fortran-e, calculations of the regression coefficients were carried out. The obtained values of the regression coefficients a_1 = 2.9054,
a_2 = 2.8369, a_3 = 1.4635, a_4 = (-2.4136),
a_{12} = (-2.3533), a_{13} = (-1.5379), a_{14} = 2.0815,
a_{23} = (-2.6599), a_{24} = 0.5558, a_{34} = (-0.1239),
a_0 = 88.8215.

The resulting mathematical model makes it possible, by the value of the linear regression coefficients, to judge the degree of influence of individual process factors - the greater the regression coefficient of the corresponding factor, the greater its influence on the output parameter. S_0, for this particular case, the temperature has the greatest influence on the degree of pyro-condensate hydrogenation since the coefficient in front of the dependent variable has the highest value, the catalyst volume has the least

Table 1.

Planning Matrix and Experimental Results

Variable levels		Coded				Working matrix				Output parameter	
		X_1	X_2	X_3	X_4	T, °C	τ,сек	H_2:C	V_{kat}	Y_{hydr}, % degree of hydrogenation	
Base: 0		0	0	0	0	100	60	0.5	10		
Interval variations		Δ	Δ	Δ	Δ	20	45	0.25	5		
top: +1		+	+	+	+	120	120	0.8	15	Exper.	Calc.
bottom: -1		-	-	-	-	80	30	03	5		
Experiment	1	+	+	+	+	120	120	0.8	15	89.334	88.287
	2	+	+	+	-	120	120	0.8	5	92.977	87.766
	3	+	+	-	+	120	120	0.3	15	92.167	95.777
	4	+	+	-	-	120	120	0.3	5	94.364	96.384
	5	+	-	+	+	120	30	0.8	15	91.765	92.592
	6	+	-	+	-	120	30	0.8	5	92.534	93.120
	7	+	-	-	+	120	30	0.3	15	92.313	91.387
	8	+	-	-	-	120	30	0.3	5	88.361	90.649
	9	-	+	+	+	80	120	0.8	15	87.026	88.279
	10	-	+	+	-	80	120	0.8	5	92.511	92.691
	11	-	+	-	+	80	120	03	15	90.675	90.782
	12	-	+	-	-	80	120	0.3	5	94.213	96.927
	13	-	-	+	+	80	30	0.8	15	82.865	83.107
	14	-	-	+	-	80	30	0.8	5	93.268	93.120
	15	-	-	-	+	80	30	0.3	15	65.118	73,870
	16	-	-	-	-	80	30	0.3	5	81.653	83.403
	17	0	0	0	0	100	60	0.5	10	90.84	87.651
	18	0	0	0	0	100	60	0.5	10	90.91	88.265
	19	0	0	0	0	100	60	0,5	10	91.08	88.266

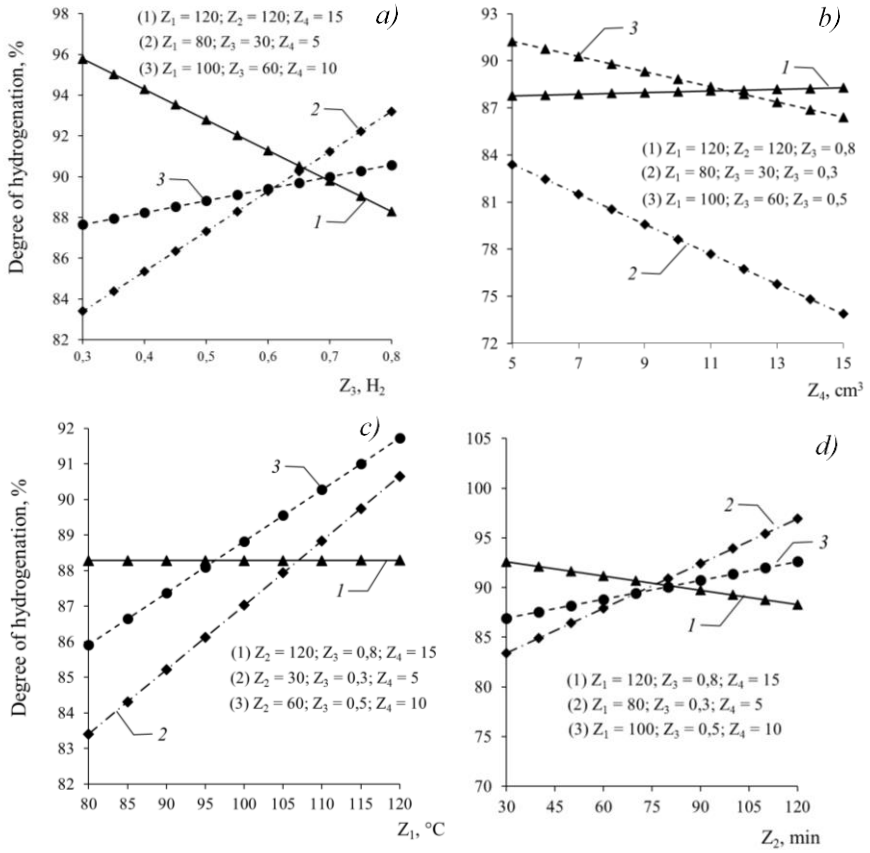

Fig. 1. Calculated profiles of the degree of pyrocondensate hydrogenation versus temperature (*a*), duration (*b*), hydrogen: feedstock ratio (*c*), and catalyst volume (*d*).

influence on the degree of hydrogenation of the pyro-condensate since the coefficient in front of the dependent variable has the smallest value.

The analysis of the regression equation showed In general, analysis of the regression equation showed that the depth of hydrogenation rises with increasing process duration, average temperatures, process duration, catalyst volume, and the ratio of hydrogen volume to feedstock.

Using the above Fortran program, we can determine the deviations of experiments, the following were also calculated: reproducibility variance $S^2_{\text{repr}} = 0.31015 \cdot 10^4$ and error variance SS = $0.55691 \cdot 10^2$. The hypothesis of the applicability of the mathematical model was tested using the Fisher criterion, the value of it was 0.0023, which is much less than the tabulated value of the Fisher criterion, equal to 19.3 [2-4,6].

To check the reliability of the obtained regression equation, control experiments were carried out in the accepted ranges of variable process factors. The results of the confirmed experiment (table) are its reliability. Also, in the table, the experimental ones are given in addition to the calculated values of the pyrocondensate hydrogenation depth, in the studied ranges of parameter variation. As can be seen, the differences between the experimental and calculated values are insignificant. This indicates that the resulting equation adequately describes the experiment.

It was done by a graphical method, building graphs for different values of 3 influencing factors (upper, lower, base) and a linear increase in the fourth factor, in total, four graphs of a family of lines were obtained with linear rises in each of the 4 influencing factors (Fig.).

The presented graphical data allowed us to determine the optimal parameters for conducting the process of hydrostabilization of pyrocondensate. According to the calculated data, to achieve the maximum degree of hydrogenation of 96.9%, the required technological regime is temperature - 80°C, ratio of hydrogen volume to feedstock equal to 0.3, catalyst volume 5 cm^3, process duration - 120 min. During the experiment under these conditions, the degree of pyrocondensate hydrogenation was 96.1%, which indicates a low discrepancy (0.8% rel.) and once again confirms the reliability of the calculations performed using the obtained regression equation.

Conclusions

Thus, the implementation of a full factorial experiment and the analysis of the results obtained by the method of mathematical statistics allowed: by the value of the linear regression coefficients, to judge the degree of influence of individual process factors - the temperature has the greatest impact on the degree of pyro-condensate hydrogenation since the coefficient in front of the dependent variable has the highest value, the catalyst volume has the least effect on the degree of pyro-condensate hydrogenation; for conducting to establish the optimal parameters for the process of pyro-condensate hydro finishing in the presence of a nickel-chromium catalyst: temperature - 80°C, the ratio of hydrogen volume to feedstock equal to 0.3, catalyst volume - 5 cm^3, process duration - 120 min; while comparing the results of mathematical modeling with experimental data, establish a low degree of discrepancy (0.8% rel.) and high reliability of calculations according to the obtained regression equation.

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Е.А. Гусейнова, Г.С. Хасанов

Визначення оптимальних параметрів процесу гідростабілізації піроконденсату в присутності нікель-хромового каталізатора методом математичної статистики

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Метою роботи було отримання математичних статичних оцінок впливу різних факторів на ступінь гідростабілізації піроконденсату, отриманого при піролізі прямогонного бензину, та спроба визначення найбільш оптимального режиму процесу. Отримані раніше експериментальні дані дозволили визначити необхідний для ефективної гідростабілізації піроконденсату діапазон температур, тривалість, об'єм каталізатора та співвідношення водню та вихідної сировини, що дозволило звузити діапазон варіювання параметрів процесу. При цьому ставилася задача знайти оптимальні умови, що забезпечують максимальний ступінь гідрогенізації конденсату. Планування експерименту проводили за схемою повного факторіалу 2^4. Параметри, від яких залежить процес гідростабілізації піроконденсату, наступні: Т – температура досліду; τ – тривалість досліду; $V_{кат}$ – об'єм каталізатора; H_2:С – співвідношення водню до сировини. За результатами активного експерименту, проведеного методами математичного планування, визначено основну роль змінних факторів, отримано математичну модель і оптимальний режим піротехніки. Визначено процес гідростабілізації конденсату за наявності нікель-хромового каталізатора: температура - 80°С, співвідношення об'єму водню до сировини 0,3, об'єм каталізатора – 5 $см^3$, тривалість процесу - 120 хв. Найбільший вплив на ступінь гідрогенізації піроконденсату має температура. Порівняння результатів математичного моделювання із експериментальними даними свідчить про низьку розбіжність (0,8% відн.) та підтверджує достовірність розрахунків з використанням отриманого рівняння регресії.

Ключові слова: гідрогенізація, гідростабілізація, піроконденсат, каталізатор, матриця планування експерименту, оптимізація, статистика.