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Application of Software Package “OptimMe” for the Study of the Process of Partial Oxidation of Propane

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Abstract

This paper presents the results of the application of the software package OptimMe developed by us for the study of process of partial oxidation of propane. The optimal parameters of the process were determined by the method of statistical planning of experiment. Catalyst activity rating was carried out on percentage of acetic acid in products of model reaction. It is obtained regression model of the process and the optimal regime of flow of this process is defined.

1. Introduction

Application development software for computation and optimization of catalytic processes are one of the most important areas in chemical engineering. Since most chemical processes take place with the participation of the catalysts, the program should be problem-oriented, modular and generalized. In processing the experimental data have to deal with large amounts of data and without application software package to solve specific problems is impossible [1-4].

As a rule, the same method was used for most tasks without properly accuracy evaluation of the obtained results and the possibility of achieving the same goals using different methods of experimental design. In addition, possibilities of the computer for automation of procedure of a choice of the experimentations methods accepted for a concrete case, formations of an initial matrix of planning, processing of results and other possible operations with orientation to work of the researcher who doesn't have special preparation and knowledge of mathematics and programming aren't fully used.

The best solution of the specified problem is creation of dialogue systems with the package of applied programs (PAP), during the work with which the researcher is exempted from studying of programming languages.

Such system not only offers the user a set of software modules for the solution a wide range of tasks, but also helps him make the right choice of a method for solution of tasks, an assessment of the accuracy of the results obtained, to control and prevent errors, etc.

1.1. Software Package “OptimMe”

We have developed a software package OptimMe for the solution of the kinetic and thermodynamic problems of chemical technology. The package includes a program module type iteration methods, optimization, numerical differentiation of linear and

nonlinear differential equations, numerical integration, etc.

The programs of the Runge-Kutta 2nd and 4th order for solving systems of differential equations, both ordinary and partial derivatives, are developed. For solution of optimization tasks in hard systems in package included numerical Adams and Gear methods. As well as the software package includes applications for calculation of hardware of chemical production, in particular algorithms for computing the

parameters of the adsorber, for motors, fans and other hydraulic devices. The developed software package is executed by the modular principle that allows to improve and expand it with the introduction of new programs.

The software package has been based on the algorithmic language C#. Fig. 1 shows the operator interface of software package OptimMe.

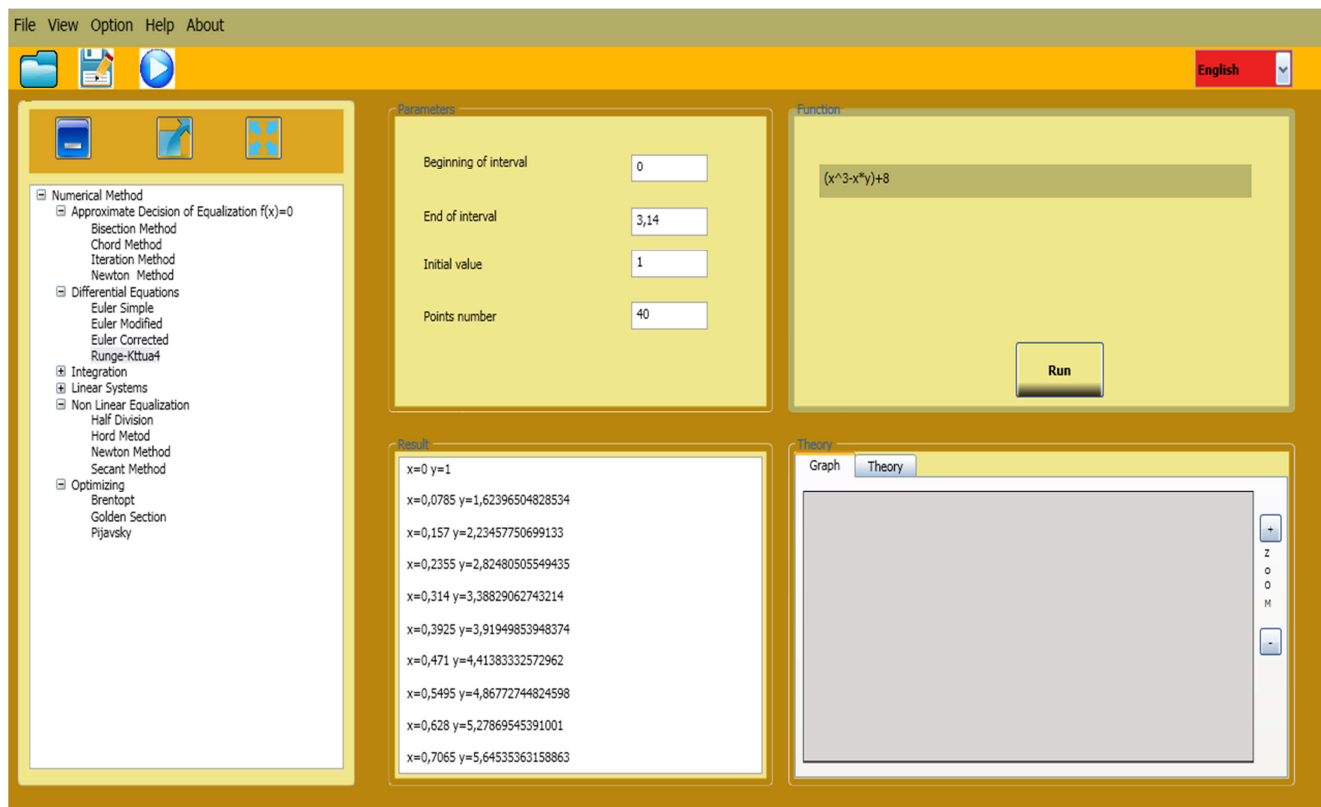


Fig 1. The operator interface of software package OptimMe.

Improving the efficiency of catalysts and reducing the time of their research are of great scientific and practical importance. Development of technology for the preparation and selection of the optimal composition of the catalyst is a complex multidisciplinary research involving certain difficulties [5-7]. One of the ways of intensification of such research is to optimize the organization and automation of experimental work. [8].

Presented software package was used to develop and optimize and the search process of active catalysts. For this process have been studied metal-zeolite catalyst properties of the catalysts prepared by ion exchange of the natural zeolite – klinoptilite.

1.2. Experimental

Experiments were performed at a flow apparatus at

atmospheric pressure in the temperature range 270-320°C, space velocity 500-2500 h⁻¹, a molar ratio of propane: oxygen = 0.4-1.2 using the metal- zeolite catalyst - natural klinoptilite (Ai-Dag field, silicate modulus = 10.8) modified with cations Ca⁺² (8%), Sn⁺¹ (7%) and Li⁺¹ (7%) [5]. Assessment of the activity of the catalyst based on the percentage content in the acetic acid reaction products of the model. For each of the catalyst samples for rapid entry into the region of optimum yield of acetic acid experiments were in accordance with the plan of full factorial experiment. From the response values of the y and normalized independent variables x were determined coefficients of the regression equations, assess their significance and checked the adequacy of the obtained experimental data modules.

In the future, the user is given the possibility of establishing and conducting experiments on a given plan.

Table 1. Dependence of the reaction for synthesizing acetic acid from partial oxidation of the propane content of the metal ions on the catalyst and the silicate modulus values.

№	Catalyst	Silicate modulus	T, °C	contact time, h ⁻¹	Composition of the reaction mixture, l/h		Conversion mol. %		Yield CH ₃ COOH mol. %
					C ₃ H ₈	O ₂	C ₃ H ₈	O ₂	
1	Ca(7%)Sn(7%)Li(8%)Kl	8.68	350	2000	1.0	1.0	77.3	50.9	9.3
2	Ca(7%)Sn(7%)Li(8%)Kl	9.8	350	2000	1.0	1.0	75.1	50.0	7.4
3	Ca(7%)Sn(7%)Li(8%)Kl	10.7	350	2000	1.0	1.0	76.4	53.6	6.9
4	Ca(7%)Sn(7%)Li(8%)Kl	10.8	350	2000	1.0	1.0	75.0	55.2	6.4
5	Ca(7%)Sn(7%)Li(8%)Kl	10.8	350	2000	1.0	1.0	77.5	62.9	10.3
6	Ca(7%)Sn(7%)Li(8%)Kl	10.8	350	2000	1.0	1.0	75.8	55.2	9.1
7	Ca(7%)Sn(7%)Li(8%)Kl	10.8	350	2000	1.0	1.0	67.2	75.7	5.9
8	Ca(7%)Sn(7%)Li(8%)Kl	10.8	350	2000	1.0	1.0	80.7	64.3	10.0
9	Ca(7%)Sn(7%)Li(8%)Kl	10.8	350	2000	1.0	1.0	69.7	64.3	6.4
10	Ca(7%)Sn(7%)Li(8%)Kl	10.8	350	2000	1.0	1.0	87.1	34.5	10.2
11	Ca(7%)Sn(7%)Li(8%)Kl	10.8	350	2000	1.0	1.0	77.1	51.9	13.1
12	Ca(7%)Sn(7%)Li(8%)Kl	10.8	350	2000	1.0	1.0	80.3	46.4	13.7
13	Ca(7%)Sn(7%)Li(8%)Kl	10.8	350	2000	1.2	1.2	78.4	35.2	6.8
14	Ca(7%)Sn(7%)Li(8%)Kl	10.8	350	2500	1.5	1.5	82.6	38.8	7.4
15	Ca(7%)Sn(7%)Li(8%)Kl	10.8	350	1000	0.5	0.5	83.7	38.8	13.5
16	Ca(7%)Sn(7%)Li(8%)Kl	10.8	350	2400	1.2	1.2	67.3	88.1	6.0

1.3. Development of Statistical Mathematical Model of Process

As a rule, because of the insignificance interaction of the coefficients regression equation reduces to an equation of the first degree[9-10]. In the next phase of experimental studies conducted search for the optimal yield area of acetic acid. The experimental data show that the best results are achieved at dealuminum types of zeolites with silicate module 10.8 and the content of calcium, lithium and tin. Increasing the Sn content from 5% to 7% by weight of zeolite significantly increases its activity. However, further increase to 10% has little effect on catalyst activity of this type. Found that adding calcium and lithium ions increases the selectivity of oxidation of propane with an increase the yield of the target product. Characteristic indicators of model process of oxidation of propane using of some samples of the studied zeolites as catalysts are given in table 1. The highest activity has klinoptilit (Cl) with the silicate modulus 10.8 modified by ions of calcium, lithium and tin, the content of which are

respectively 7%, 8% and 7% by weight of zeolite.

1.4. Second Order Rotatable Plan

To identify the optimal area of the reaction with the selected type of catalyst, subsequent experiments were carried out using a second order rotatable planning. Matrix planning and results of experiments on the selected program are shown in Table 2. If the number of factors $n = 3$, the number of experiments equal to 20. The core of the plan is a full factorial experiment 23, and the magnitude of the star shoulder $\alpha = 1.682$ when the number zero points $n_0=6$, corresponding conditions $T=300^{\circ}\text{C}$, $S=0.8$, $V=1500\text{ h}^{-1}$.

The rotatable planning matrix of experiments for the investigation of the activity of metal zeolite catalysts in the partial oxidation reaction of propan where x_1 , x_2 , x_3 -normalized values respectively temperature T , $^{\circ}\text{C}$, the molar reactant ratio S , the product feed rate V , h^{-1} , y - acetic yield acid, % shown in table 2.

Table 2. Matrix rotatable experiment planning for the investigation of the activity metalltzeolite catalysts in the partial oxidation of propan.

Product Name	T, °C	S	V, h ⁻¹	y
Basic level	300	0.8	1500	Yield CHCOOH mol %
The interval of variation	50	0.2	500	
Top +1	350	1	2000	
Lower level -1	250	0.6	1000	
Experiment number	X ₁	X ₂	X ₃	X ₄
1	+1	+1	+1	9.5
2	+1	+1	-1	8.7
3	+1	-1	+1	7.0
4	+1	-1	-1	10.7
5	-1	+1	+1	8.9
6	-1	+1	-1	6.1
7	-1	-1	+1	11.1
8	-1	-1	-1	5.9
9	+1.682	0	0	11.2
10	-1.682	0	0	13.3
11	0	+1.682	0	13.9
12	0	-1.682	0	7.1
13	0	0	+1.682	8.2

Product Name	T, °C	S	V, h ⁻¹	Y
Basic level	300	0.8	1500	Yield CHCOOH mol %
The interval of variation	50	0.2	500	
Top +1	350	1	2000	
Lower level -1	250	0.6	1000	
Experiment number	X ₁	X ₂	X ₃	X ₄
14	0	0	-1.682	13.7
15	0	0	0	6.2
16	0	0	0	7.1
17	0	0	0	6.5
18	0	0	0	8.2
19	0	0	0	7.2
20	0	0	0	6.1

It takes into account the following technological constraints for variables in this reaction:

$$\left\{ \begin{array}{l} 250^{\circ}\text{C} < T < 350^{\circ}\text{C} \\ 0.6 < S < 1 \\ 1000\text{h}^{-1} < V < 2000\text{h}^{-1} \end{array} \right\}$$

At the same time it is assumed that for a temperature variation interval T - 50°C, the basic level

- 300°C; for a molar ratio range of variation S - 0.2, the basic level - 0.8; for product feed rate variation V interval - 500 h⁻¹, the basic level - 1500 h⁻¹.

2. Result and Discussion

The coefficients of the normalized regression equation found by the method of [3] amounted to

$$b_0 = 20,85; b_1 = 0,22; b_2 = -1,69; b_3 = 0,17;$$

$$b_{12} = 0,20; b_{13} = 0,10; b_{23} = -0,30; b_{11} = -1,84; b_{22} = -2,07; b_{33} = -1,35;$$

The variance of reproducibility S_{repr} , determined by experiments put in the center of the plan was the amount of 0,45 when the number of degrees of freedom $f_{repr} = 5$. Assessment of the significance of the coefficients of the regression model determined by Student t-test with

$$S_b = 0,35; S_{bj} = 0,12; S_{bju} = 0,16; S_{bjij} = 0,12; (j = 1, 2, 3, \dots u=j).$$

At the 5% significance level of p and the number of degrees of freedom $f_{repr} = 5$, $t_{tabl} = 2,57$.

After dropping out of insignificant coefficients for which the ratio is less than tabulated, obtained by regression equations in dimensionless form:

$$y = 20,85 - 1,69x_2 - 1,84x_1^2 - 2,07x_2^2 - 1,35x_3^2 \quad (1)$$

The adequacy of the model tested using F - Fisher criterion. To this end was calculated estimate of the variance of the adequacy

$$S_{ad}^2 = (S_{ost}^2 f_{ost} - S_{repr}^2 f_{repr}) (f_{ost} - f_{repr})$$

$$\text{At } S_{repr}^2 = 0,20; f_{repr} = 5 \text{ obtained } S_{ad}^2 = 0,86.$$

$$\text{Therefore, } F = S_{ad}^2 / S_{repr}^2 = 4,3$$

The obtained value F is less than $F_{tab} = 4.8$ at the significance level $p = 0.05$ and degrees of freedom $f_{ad} = 10$ and $f_{repr} = 5$. This indicates that the equation adequately describes the studied process. Using the formula for the transition from the normalized units to natural and representing the values of the variables corresponding to the optimal value, we find that the maximum yield of acetic acid is 13.9% at the optimal value, we find that the maximum yield of acetic acid is 13.9% under optimal conditions for conducting a reaction temperature of 350°C, reagents ratio of 1:1 and the volumetric feed rate of reactants 2000 h⁻¹. Experimentally determined maximum yield of acetic acid at these values of the control parameters is 13.7%.

3. Conclusions

Thus, as a result of multivariate experiment planning was found optimum conditions for the reaction of partial oxidation of propane over a catalyst selected type.

In conclusion, it should be noted that the use of software package OptimMe in the selection of the active catalyst for propane oxidation to acetic acid reduced the volume of the experiments, improve the quality and reliability of the results.

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