Mathematical software for the synthesis of domestic catalyst of ethylene acetoxylation process

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Abstract
We have created a mathematical model of the catalyst carrier of the process of ethylene acetoxylation for synthesis of vinyl acetate take into account the physical parameters of the catalyst carrier and chemical composition of the catalyst. We have solved the following problems: the problem of optimization of the physical parameters of the catalyst carrier; the problem of multi-objective constrained optimization of chemical composition of the catalyst. This optimization allows maximizing the selectivity and the activity of the catalyst and minimizing the content of gold and palladium. These problems have been solved through nonlinear programming methods.

Keywords: catalyst for synthesis of vinyl acetate based on ethylene; mathematical model; multi-objective optimization

1. Introduction

The vinyl monomer vinyl acetate (VA) is used to produce polyvinyl acetate, polyvinyl alcohol, polyvinyl butyral, copolymers containing ethylene and propylene. Nowadays the world consumption of VA is about 7 million tons per year. At the present stage of industrial development VA is mainly produced by the catalytic synthesis of ethylene, oxygen and acetic acid (AA). In Russia there is only one enterprise (JSC "LUKOIL", OOO "Stavrolen" Budennovsk) which was purchased under the license of Bayer and was brought into production in 1987. The process heavily depends on the imported catalyst which is a porous aluminosilicate balls of a diameter of 5-6 mm with the over layer of palladium, gold and potassium acetate.

In this regard, the study of the development of a domestic catalyst of ethylene acetoxylation for the synthesis of VA is relevant.

Non-stationary process of VA synthesis from ethylene, oxygen and AA is being implemented in a tubular reactor by passing the gas mixture of the initial reagents through the catalyst bed at a temperature of 145-200 °C and a pressure of 0.81 MPa [1]. The chemical aspect of the process is approximated by the gross reactions of formation of the target and by-products [1,2]:

$$C_2H_4 + CH_3COOH + 0,5O_2 \xrightarrow{Pd} CH_3COOCH = CH_2 + H_2O + 146\ KJ;$$
$$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O + 1327.3\ KJ.$$

Besides the main by-product – carbon dioxide (CD) we also have carbon monoxide, methyl acetate, ethyl acetate, acetaldehyde, acrolein, ethylidendiacetate generated in small quantities (in an amount not to exceed 1% of the weight per the amount of VA). Over time the catalytic complex ages, its activity decreases and the output of VA decreases.

2. The object of the study

In the domestic literature there is a large observational material on the study of the process of ethylene acetoxylation. The "simplest" models to describe the influence of the carrier and the composition of the catalytic complex on its activity and selectivity were developed [3-6]. The experiments were carried out in a pilot plant at a synthesis temperature of VA 155 ° C, an absolute pressure of 0.9 MPa and the ratio of ethylene: AA is 4:1, the volumetric feed rate of the mixture of 8,000, the oxygen content in dry gas of 7.0 vol. % The amount of catalyst used is 0.001 m^3.

However, the authors of the above-described experiments have not evaluated the accuracy of the regressions; they have not studied the influence of the physical parameters of the catalyst carrier (pore mid-radius, specific surface area and volume, bulk density) on the selectivity and activity of the catalytic complex. Turning to the analysis and solution of the tasks of the optimization of the catalyst composition, the authors looked for the "optimal components", the "optimal textural character". These strict and certain concepts have little or no relation to optimization tasks, as the restrictions were not formulated, the optimality criteria were not selected and the time interval of the study of 200 h was not justified. In our opinion, the results obtained by authors are only initial approximations of structural and parametric identification of the model of the catalytic complex with an evaluated accuracy and the synthesis of its optimal composition.

On the basis of obtained experimental data we have carried out the modeling and the optimization of the catalyst composition of ethylene acetoxylation to eliminate these disadvantages.

3. Methods

We have written the obtained mathematical model of the catalyst carrier with some metal palladium deposited on its surface (without this over layer the acetoxylation reaction is not possible) as follows:

$$W_{VA}(t) = \left(a_1 r + a_2 r^2 + a_3 v + a_4 v^2 + a_5 s + a_6 s^2 + a_7 / r + a_8 rvs + a_9 \rho^{-1,5} + a_{10}\right) \cdot t \cdot \exp\left[\left(a_{11} + a_{12} t + a_{13} t^2\right) \cdot t\right]; \quad (1)$$

$$W_{CD}(t) = \left(b_1 r + b_2 r^2 + b_3 v + b_4 v^2 + b_5 s + b_6 s^2 + b_7 / r + b_8 rvs + b_9 \rho^{1,25} + b_{10}\right) \cdot t \cdot \exp\left[\left(b_{11} + b_{12} t + b_{13} t^2\right) \cdot t\right], \quad (2)$$

where $W_{VA}(t)$, $W_{CD}(t)$ is the development of the targeted VA and of the main by-product CD products during the work t of the catalyst, mole; r is pore mid-radius of the catalyst carrier, $10^{-12} \cdot m$; s is the specific surface area of the carrier, $10^3 \cdot m^2 / kg$; v is the specific volume of the carrier pores, $10^{-3} \cdot m^3 / kg$; ρ is the bulk density $10^3 \cdot kg / \mathrm{m}^3$; t – time, h; $a_1 - a_{13}$, $b_1 - b_{13}$ – regressive coefficients.

Expressions with coefficients $a_1 - a_{10}$, $b_1 - b_{10}$ represent time-independent initial speeds of the formation of target-product and by-products respectively. Expressions with coefficients $a_{11} - a_{13}$, $b_{11} - b_{13}$ are the functional parameters of the time instability of the catalyst. The average ratio error of model (1), (2) for the 9 studied catalyst carriers are shown in column 1 of table 1, amounted to: for VA from ±0.066% to ±2.32%, for CD from ±2.26% to ±of 7.03 %. The difference (1), (2) from the known equations are based on the initial formation rate dependence of the products on physical properties of the carrier and the time dependence of the coefficients of the instability of the catalyst. This allowed improving by several times the accuracy of the simulation.

The output of VA is a criterion of the optimization of the physical parameters of the catalyst carrier. The criterion is limited by the value of selectivity of catalyst C equal to:

$$C = \frac{W_{VA} \cdot M_{VA} \cdot 100\%}{W_{VA} \cdot M_{VA} + W_{CD} \cdot M_{CD} + 0.01 \cdot W_{VA} \cdot M_{VA}} \geq C^{\min}, \quad (3)$$

where $C^{\min}$ is the minimal selectivity value, at which the use of the catalyst is cost efficient, %; M_{VA}, M_{CD} are molar weight of VA and CD.

The literature data [1, 2] and the operational experience of the working plant show that the value of $C^{\min}$ should not be less than 82–85%.

In addition to (3) the limits of the maximum and minimum values of the optimized physical parameters of the catalyst carrier are imposed to the criterion:

$$r^{\min} \leq r \leq r^{\max};\ s^{\min} \leq s \leq s^{\max};\ v^{\min} \leq v \leq v^{\max};\ \rho^{\min} \leq \rho \leq \rho^{\max}, \quad (4)$$

where $p^{\min} = f(r, s, v, \rho)$ and $p^{\max} = f(r, s, v, \rho)$ are the minimum and maximum values of the physical parameters of the porous carrier respectively.

The optimization problem is to select such a catalyst of the 9 studied ones and to define such values of physical parameters for which the output of VA is maximum for the period of operating time from 0 to the moment of achievement of minimum permissible selectivity:

$$R = -W_{VA}(t) + 10^{25}\left[\left|C(t) - C^{\min}\right| - C(t) + C^{\min}\right]^2 + 10^{25}\sum_{P=1}^{4}\left(\left|p_i - p_i^{\min}\right| - p_i + p_i^{\min}\right)^2 +$$

$$+10^{25}\sum_{P=1}^{4}\left(\left|p_i - p_i^{\max}\right| + p_i - p_i^{\max}\right)^2 \longrightarrow \min_{p_1, p_2, p_3, p_4, t} \quad (5)$$

where R is the target function; 10^{25} is penalty factor; p_i i – vector p element.

The mathematical dependence of the formation rate of VA and CD on the chemical composition of the catalyst has been found in the form of a fractional-linear function:

$$W_P^0 = \frac{\left(C_{PD} + 10^{-6}\right)^{\alpha_1}\left[\alpha_2 + \alpha_3\left(C_{PA} + 10^{-6}\right) + \alpha_4\left(C_{AU} + 10^{-6}\right)\right]}{B};$$

$$B = \left[\alpha_5 + \alpha_6\left(C_{PD} + 10^{-6}\right)^{\alpha_7} + \alpha_8\left(C_{PD} + 10^{-6}\right)^{\alpha_9} \cdot \left(C_{AU} + 10^{-6}\right) + \alpha_{10}\left(C_{PD} + 10^{-6}\right) \cdot \left(C_{AU} + 10^{-6}\right) \cdot \left(C_{PA} + 10^{-6}\right) + \right.$$

$$\left. + \alpha_{11}\left(C_{PA} + 10^{-6}\right)^{\alpha_{12}} + \alpha_{13}\left(C_{AU} + 10^{-6}\right)^{-\alpha_{14}}\right]^{\alpha_{15}}, \quad (6)$$

where W_P^0 – is a mole rate of the formation of the product VA or CD, *mole/h*;

C_{PD}, C_{AU}, C_{PA} – are the catalyst weight concentrations of palladium, gold and potassium acetate respectively, %; 10^{-6} is a pre-set small quantity; $\alpha_1 - \alpha_{15}$ are the factors of the model. The model structure (6) for VA and CD is the same but the regressive factors α_i ($i = 1-15$) take different values. The range (6): $0 \le C_{PD} \le 3.0$ % of the weight; $0 \le C_{AU} \le 3.0$ % of the weight; $0 \le C_{PA} \le 20.0$ % of the weight.

The average relative error of model (6) with respect to experimental data [3-5] is (for) VA ±4.7%, (for CD) ±7.9%.

The criterion of the optimization of the chemical composition of the catalytic complex is written as the sum of the normalized values of selectivity, activity of the catalyst, content of palladium and gold:

$$R_{XC} = -\gamma_C \cdot C^* - \gamma_A \cdot A^* + \gamma_{PD} \cdot C_{PD}^* + \gamma_{AU} \cdot C_{AU}^*, \tag{7}$$

where R_{XC} – is the criterion of the chemical composition of the catalyst; $\gamma_C, \gamma_A, \gamma_{PD}, \gamma_{AU}$ –the weight factors at normalized values of selectivity, activity of the catalyst, content of palladium and gold. They are chosen while synthesizing the catalyst so that their sum was equal to 1; $C^*, A^*, C_{PD}^*, C_{AU}^*$ – are normalized values of the criterion parameters (7). The normalization is made according to the formula:

$$P_j^* = \frac{2P_j}{P_j^{\max} + P_j^{\min}}, \tag{8}$$

P_j^* – a normalized value of the criterion parameter (7); $P_j^{\max}$, $P_j^{\min}$ – maximum and minimum value of the parameter j. The catalyst activity is calculated according to the formula:

$$A = W_{VA}^0 \cdot M_{VA} / V_{CAT}, \tag{9}$$

V_{CAT} – is the catalyst volume, l; W_{VA}^0 is the rate of VA formation, *mole/h*, calculated according to the formula (6).

Criterion (7) is limited according to the maximum possible value of selectivity $C^{\max}$ of the pre-set maximum activity $A^{\max}$, maximum and minimum value of the content of palladium, gold and potassium acetate:

$$C \le C^{\max};\ A \le A^{\max};\ C_{PD}^{\min} \le C_{PD} \le C_{PD}^{\max};\ C_{AU}^{\min} \le C_{AU} \le C_{AU}^{\max};\ C_{PA}^{\min} \le C_{PA} \le C_{PA}^{\max}. \tag{10}$$

The task of optimization of the chemical composition of the catalyst is to minimize the criterion (7) at the fulfillment of constraints (10) and this task is formalized similarly (5). The solution of this multi-objective problem allows determining the optimal concentrations of palladium, gold and potassium acetate which maximize the selectivity and activity of the catalytic complex with a minimum content of precious metals.

4. The results of the discussion

The results of the solution of problem (5) are given in table 1. Analysis of table 1 shows that the best carrier of the catalytic complex is Silicagel KSS3, hydro- and heat-treated at 200 ºC in 6 hours time where the output of VA is 52.025 kg at the catalyst course time of 84 h. The optimal values of physical parameters are $r = 124.8 \cdot 10^{-10}$ *m*; $v = 0.664 \cdot 10^{-3}\ m^3/kg$; $s = 192.0 \cdot 10^3\ m^2/kg$; $\rho = 0.432 \cdot 10^3\ kg/\text{m}^3$. The optimal composition of the catalyst is $C_{PD} = 0.58$ %, $C_{PA} = 6.87$ %, $C_{AU} = 0.255$ %.

The parametric synthesis of mathematical models (1), (2), (6) was conducted by applying the method of the least squares using the configurations method of Hooke-Jives. The optimization problems were solved using a genetic algorithm with a subsequent refinement of the desired ratios using the configurations of Hooke-Jives.

The method of Hooke-Jives was modified by us. This modification consists in the automatic search of a new direction of configurations, this direction is randomly generated. When you choose a failed direction it is returned to its original state and a new direction is generated. The search will stop when decreasing of the increment value is 10^{-7}.

The genetic algorithm is based on the classical method of John H. Holland [7]. Not the regression coefficients themselves but their increments are randomly generated in a population. Each population consists of 2,000 specimens. If there are any changes of the objective function over 300 generations, generation step is reduced significantly and the increment added to coefficients of the model. Then the cycle is repeated to obtain the given accuracy. To prevent losses of effective increment, all the specimen are involved in the crossing. Then 85% of the worst specimen (according to values of the objective function) is removed from the population, and the remaining specimen move on to the next generation. The percentage of mutations in the crossing of the generated specimen is equal to 10.

The soft ware package for modeling of the synthesis of domestic catalyst for ethylene acetoxylation has been developed in the programming language C# in Microsoft Visual Studio 2010.

5. Conclusion

Thus, we have developed a software package for the simulation of synthesis of catalyst of ethylene acetoxylation process and also we have obtained a mathematical model of the catalytic complex for the synthesis of vinyl acetate based on ethylene. By applying the methods of nonlinear programming we have formulated and solved the optimization tasks of physical parameters of the catalyst carrier and multi-objective optimization of chemical composition of the catalytic complex. The developed software can be used in the synthesis of the catalyst of the ethylene acetoxylation in order to choose an optimal catalyst carrier and time of run limited by the minimum selectivity of the catalyst on the whole. The developed software is also to optimize the chemical composition of the catalyst in order to reduce the content of precious metals without sacrificing its effectiveness.

Table 1. The optimal values of the physical parameters of the studied carriers and the course time of the catalyst in the synthesis of vinyl acetate

Name of the carrier and method of its processing	Mid-radius of the pores (r), $10^{-10} \cdot m$	Specific volume of the pores (v), $10^{-3} \cdot m^3 / kg$	Specific surface(s), $10^3 \cdot m^2 / kg$	Bulk density of the carrier (ρ), $10^3 \cdot kg / \mathrm{m}^3$	Course time, h	Development of vinyl acetate, gram
MarkA1 on the basis of Al_2O_3 heat-treated at 1100 ^{0}C	660	0.4	13.2	0.496	98.6	25,061
MarkShN2on the basis of Al_2O_3	120	0.442	120	0.64	99.8	15,374
MarkShN2on the basis of Al_2O_3 heat-treated at 1050 ^{0}C	600	0.406	18	0.728	98.76	38,630
Silicagel KSK	60	0.72	420	0.384	52.72	11,445
Silicagel KSS3	36.72	0.672	660	0.416	74.61	36,838
Silicagel KSS3, hydro- and heat-treated at 200 ^{0}Cin 6 hours time	124.8	0.664	192	0.432	83.93	52,025
Silicagel KSS3, hydro- and heat-treated at 300 ^{0}Cin 13 hours time	498	0.624	39.83	0.44	99	43,576
Silicagel KSS3, hydro- and heat-treated at 250 ^{0}C in 6 hours time	108	0.48	156	0.36	87.79	18,880
Silicagel KSS3, hydro- and heat-treated at 320 ^{0}C in 4 hours time	184.8	0.454	84	0.36	52	6,366

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