# Mathematical Modeling of the Process of Dehydrogenation of Ethylbenzene to Styrene

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## Abstract

*This paper concerns the development of the mathematical model of dehydrogenation of etylbenzene to styrene. The process of dehydrogenation of etylbenzene is realized in current of superheated  water steam in the presence of catalyst of mark K-22. By the experiment it's found the sceme of the mechanism of the reaction and it's calculated kinetic constants. And same time the algorithm was created  to search kinetic parameters of the process and developed equation of thermal balance of the process. By Fisher's criterion it is established that the received kinetic model adequately describes the process.*
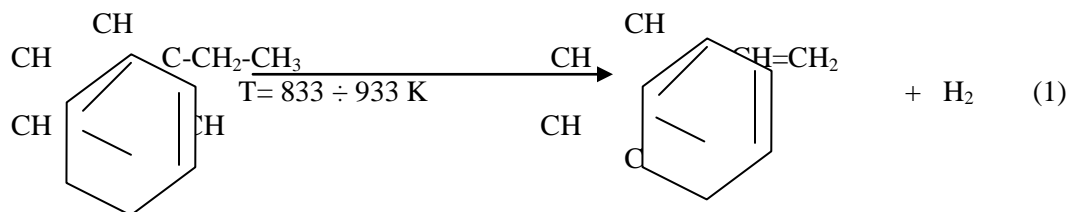
**Key words:** mathematical model, chemical process, dehydrogenation, ethylbenzene, styrene, mechanism of reaction, algorithm, kinetic parameters, method of Runge-Kutta, equation, thermal balance.

## *Introduction*

Production of synthetic rubber and plastic is one of the major branches of the petrochemical industry. Now, about 66 % of capital and operational expenses in production of these products make up the expenses, connected with the make-up of initial monomers, one of which is styrene. In this connection, of great important are the researches on increase of production of this valuable monomer, decrease in specific loss and maintenance of stability in industrial dehydrogenation of ethylbenzene in styrene.
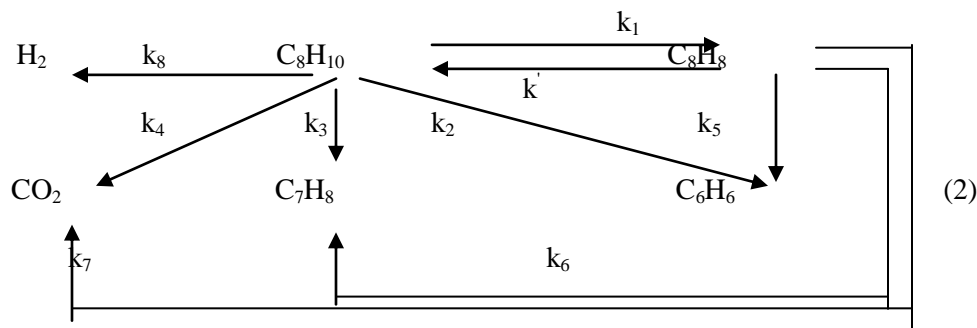
Now, styrene is made up, basically, through dehydrogenation of ethylbenzene in the adiabatic reactor. Industrial process of the make-up of styrene is a difficult technological system, the combined and cooperating devices with fractional recycling of unreacted stuff. Production consists of two technological blocks intended for dehydrogenation of ethylbenzene and division of reaction products.

The process of dehydrogenation of ethylbenzene is realized in current of superheated water steam at temperature $580 – 660$ $^0$C in the presence of the catalyst of mark K-22 on reaction:



Experimentally was established that the process takes place in the kinetic area, proved by the notable extent of energy activation. Influence of outward diffusion braking is insignificant and they can be neglected, as the process is carried out at high speed (0. 5 sec$^{-1}$) and temperature change strongly influences speed of reaction.
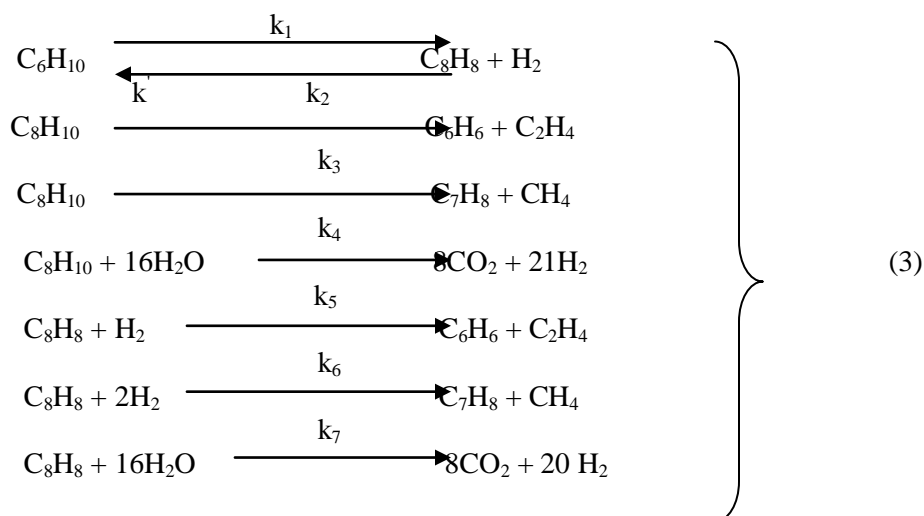
The experimental data received during studying of kinetic laws and kinetic researches, carried out on the personal computer, have allowed accepting the following prospective scheme of the mechanism of reaction:



$$(2)$$

In identification of catalytic processes by mathematical models there are two main stages:

1. Definition of functional kind of mathematical model;
2. Numerical estimation of the parameters the model of uncertain factors (kinetic constants) comprises.

Results of the theoretical and experimental researches of kinetics have shown, that process of dehydrogenation of ethylbenzene in styrene on industrial catalyst K-22 can be described in the following equations of total routes:



$$(3)$$

Starting with stoichiometric equations of separate stages of chemical reaction, it is possible to write down the following expression for definition of speeds of each stage of reacting system:

$$W_1 = -\frac{dC_{C_8H_{10}}}{d\tau} = \frac{dC_{C_8H_{10}}}{d\tau} + \frac{dC_{H_2}}{d\tau} = k_1 [C_8H_{10}]$$

$$W_2 = -\frac{dC_{C_8H_{10}}}{d\tau} = \frac{dC_{C_6H_6}}{d\tau} + \frac{dC_{C_2H_4}}{d\tau} = k_2 [C_8H_{10}]$$

$$W_3 = -\frac{dC_{C_8H_{10}}}{d\tau} = \frac{dC_{C_7H_8}}{d\tau} + \frac{dC_{CH_4}}{d\tau} = k_3 [C_8H_{10}]$$

$$W_4 = -\frac{dC_{C_8H_{10}}}{d\tau} = \frac{1}{8}\frac{dC_{CO_2}}{d\tau} + \frac{1}{21}\frac{dC_{H_2}}{d\tau} = k_4 [C_8H_{10}]$$

$$W_5 = -\frac{dC_{C_8H_8}}{d\tau} = \frac{dC_{C_6H_6}}{d\tau} + \frac{dC_{C_2H_4}}{d\tau} = k_5 [C_8H_8]$$

$$W_6 = -\frac{dC_{C_8H_8}}{d\tau} = \frac{dC_{C_7H_8}}{d\tau} + \frac{dC_{CH_4}}{d\tau} = k_6 [C_8H_8]$$

$$W_7 = -\frac{dC_{C_8H_8}}{d\tau} = \frac{1}{8}\frac{dC_{CO_2}}{d\tau} + \frac{1}{20}\frac{dC_{CH_2}}{d\tau} = k_7 [C_8H_8]$$

(4)

where $C_{C_8H_{10}}$, $C_{C_8H_8}$, $C_{C_7H_8}$, $C_{CO_2}$, $C_{H_2}$, $C_{H_2O}$ is concentration of corresponding

reagents; $k_i$ – the constants of speeds corresponding to reaction; $i$ – an index specifying number of the route of reaction; $\tau$ - contact time; $W_i$ - speed of corresponding reaction.

Experimentally had been proved the absence of influence of change of concentration of water steam and hydrogen, at wide range, on the exit of styrene, therefore, while drawing up kinetic model of process, usages on these products have been accepted as zero.

Identification of kinetic models was established through large researches. The basic stage of these researches is working out of various search algorithms for the purpose of choice and estimation of kinetic parameters. Reliability of these researches depends on efficiency of the made programs and the degree of their automation.

The essence of identification consists in the following:
  - made the nonlinear mathematical model of the contact device in which are placed all its basic constructive and physicochemical laws. For each operating mode this model allows to unequivocally define all key parameters of the process;
  - carried out identification of model on the results of research;
  - adequacy of the received models is checked by comparison of experimental data with results of machine experiment.

In solution of the task, the mathematical models should correspond to following requirements:

  1. Target parameters of model should correspond to the parameters measured during researches;
  2. The model should have sufficient number of the constants which can be changed in the process of identification;
  3. The model should be efficient at any set of entrance parameters, i.e. enough universal;
  4. Time of calculation of one mode for the computer on the model should be comprehensible;
  5. All functions entering into model should be continuous.

The developed algorithm of the search of kinetic parameters, which is one of the first problems of identification, is presented on Fig. 1. The prepared program works as below. After setting the approximate value of the constant of speed $K_{01}$ it is made a descent by the method of the quickest descent up to a minimum of the sum of squares of deviation. Descent is considered finished when all the derivatives $_{\partial F / \partial Ki}$ will become less than some fixed size of ε. Then, other approximate value of the constant of speeds are set and with a new set of constants $K_{02}$ it is made descent as a result of which result we get the second point of descent. Through two points of descent it is drawn a straight line on which on distance of ravine step there is a point named the point of deviation. From this point, again is made a descent to a minimum and there is a third point of descent. Further, it is drawn through the second and third points a straight line, is made a ravine step, found the following point of deviation from which it is made the next descent etc.

The process of calculation of the constants of speeds consists in solution of systems of the differential equations of model with minimization of the functional $F_{min}$, representing the sum of squares of deviations between experimental and calculated by means of kinetic model, value of speeds:

$$F_{\min} = \frac{1}{nm} \sum_{i=1}^{m} \sum_{j=1}^{n} B_k \left( \frac{W_{ij}^{Ex} - W_{ij}^{C}}{W_{ij}^{Ex}} \right)^2 \qquad (5)$$

where $B_k$ is the weight ratio.

Summation was carried out on all components of the mixture (Ci) and on all points on time axis (τ).

It was thus supposed that change of the constants of speeds from temperature submits to the law of Arrhenius:

$$K_i = K_{0i} \cdot Exp(-E_i/RT) \qquad (6)$$

where $K_{0i}$ - is preexponential factor; $E_i$ – energy of activation; R – Universal gas constant;
T – temperature in $^{\circ}K$; i = 1÷7.

As a result of the analysis of the experimental and theoretical representations of the process the following kinetic equations of the speeds of reaction with the account of stoichiometric basis of factors were made:

$$
\begin{aligned}
W_1 &= dC_1/d\tau = -(K_1 + K_2 + K_3 + K_4) \cdot C_1 \\
W_2 &= dC_2/d\tau = K_1 C_1 - (K_5 C_6 + K_6 C_6 + K_7 C_7) \cdot C_2 \\
W_3 &= dC_3/d\tau = K_2 C_1 + K_5 C_2 C_6 \\
W_4 &= dC_4/d\tau = K_3 C_1 + K_6 C_2 C_6 \\
W_5 &= dC_5/d\tau = 8 \cdot (K_4 C_1 + K_7 C_2 C_7) \\
W_6 &= dC_6/d\tau = K_1 C_1 + 21 K_4 C_1 - K_5 C_2 C_6 - 2 K_6 C_2 C_6 + 20 K_7 C_2 C_7 \\
W_7 &= dC_7/d\tau = -16 \cdot (K_4 C_1 + K_7 C_2 C_7) \\
W_8 &= dC_8/d\tau = K_3 C_1 + K_6 C_2 C_6 \\
W_9 &= dC_9/d\tau = K_2 C_1 + K_5 C_2 C_6
\end{aligned}
\qquad (7)
$$

where $C_1, C_2, C_3, C_4, C_5, C_6, C_7, C_8$ и $C_9$ are concentration of ethylbenzene, styrene, benzene, toluene $CO_2$, $H_2$, $H_2O$, $CH_4$ and $C_2H_4$, respectively.

As has been experimentally proved the absence of influence of the change of concentration of water steam and hydrogen, largely, on the exit, then at conformity of kinetic model of process, usages of these products have been accepted as zero.

Input of starting point:
$K_{0i}$ and $K_{0i+1}$ $(i=1)$

Quickest descent
$K_{0i} \longrightarrow K_i$

$F_{min} = F(K_i)$

Quickest descent
$K_{0i} \longrightarrow K_{i+1}$

$F_{min} > F(K_{i+1})$     No

Yes

$F_{min} = F(K_{i+1})$

$F_{min} < \varepsilon$     Yes

No

$K_{0i+1} = K_{i+1} + h(K_{i+1} - K_i)$

$K_{0i+2} = K_1 + h(K_i - K_{i+1})$

$i = i + 1$

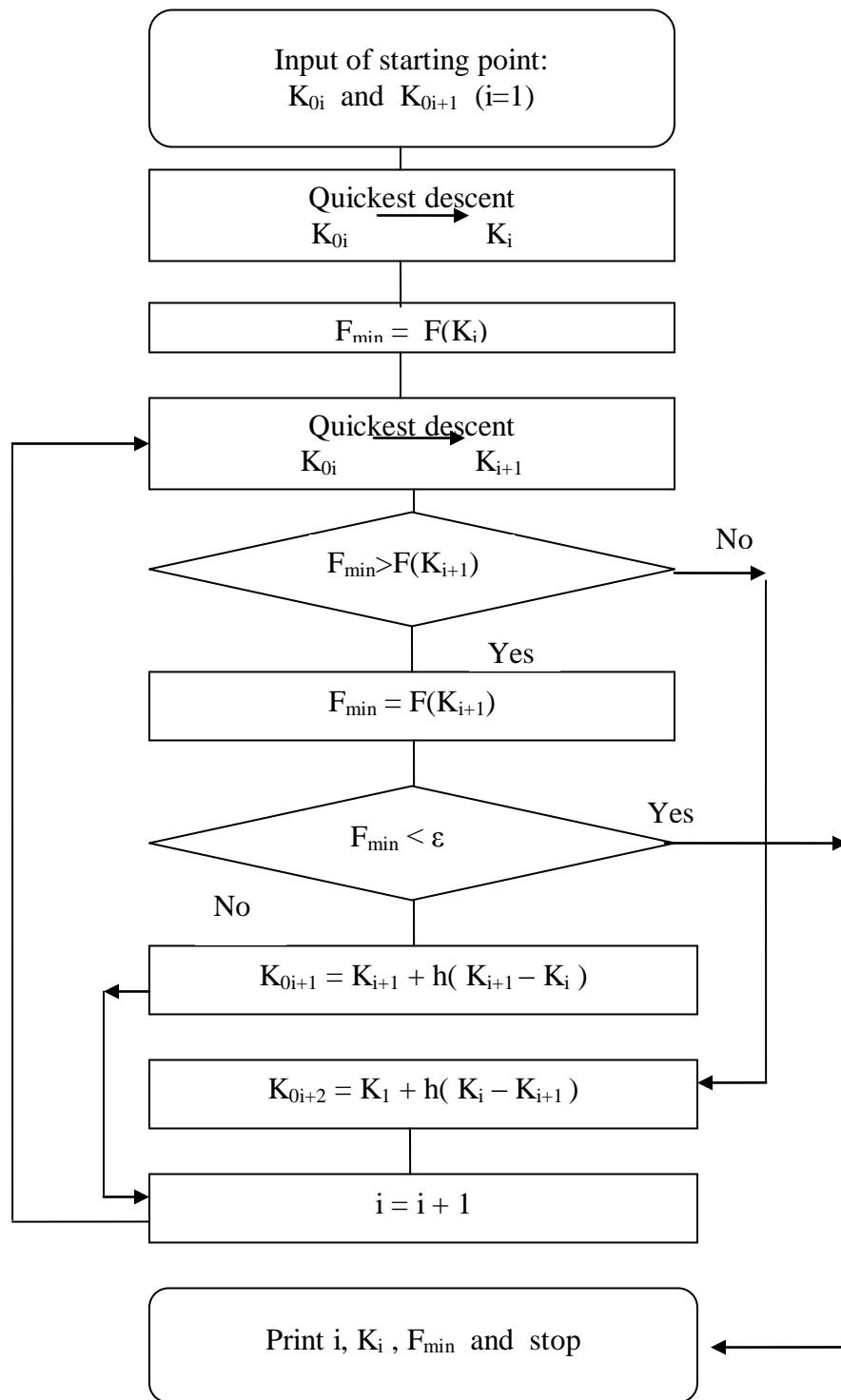Print i, $K_i$ , $F_{min}$ and stop

Fig. 1. Algorithm of the search of kinetic
parameters of the process

The kinetic model of the process of dehydrogenation of ethylbenzene in styrene has been made in the form of the differential equations describing changes of the concentration of other reacting substances and looks like:

$$W_1 = dC_1 / d\tau = - (K_1 + K_2 + K_3 + K_4) \bullet C_1$$
$$W_2 = dC_2 / d\tau = K_1 C_1 - ( K_5 C_5 + K_6 C_5 + K_7) \bullet C_2$$
$$W_3 = dC_3 / d\tau = K_2 C_1 + K_5 C_2 C_5$$
$$W_4 = dC_4 / d\tau = K_3 C_1 + K_6 C_2 C_5 \tag{8}$$
$$W_5 = dC_5 / d\tau = (K_1 + 21 K_4) \bullet C_1 - ( K_5 C_5 + 2 K_6 C_5 - 2 K_7 ) \bullet C_2$$
$$W_6 = dC_6 / d\tau = 8 \bullet ( K_4 C_1 + K_7 C_2 )$$
$$W_7 = dC_7 / d\tau = ( K_2 + K_3 ) \bullet C_1 + ( K_5 C_5 + K_6 C_5 ) \bullet C_2$$

During the following entry conditions:

$$\tau = 0; C_1 = 0.057; C_2 = C_3 = C_4 = C_5 = C_6 = C_7 = 0 \tag{9}$$

where $C_1 \div C_7$ is, respectively, concentration of ethylbenzene, styrene, benzene, toluene, $H_2$, $CO_2$ and ( $CH_4$ + $C_2H_4$) ; $K_1$ is constant of speed of the transformation of ethylbenzene in styrene; $K_2$ – constant of speed of the formation of benzene from $C_8H_{10}$; $K_3$ – constant of speed of the formation of toluene from $C_8H_{10}$; $K_4$ – constant of speed of the formation of $CO_2$ at burning of $C_8H_{10}$; $K_5$ - constant of speed of the formation of benzene from styrene; $K_6$ – constant of the speed of formation of toluene from $C_8H_8$; $K_7$ – constant of speed of the formation of $CO_2$ at burning of $C_8H_8$.

It was calculated, on the values of constants of speeds, found at three temperatures, by the Runge-Kutta method, the value of preexponential factor and energy of activation.

Values of $K_i$ , $K_{0i}$ and $E_i$ are presented in Tab. 1.

**Table 1. Value of the constants of speeds, the energy of activation, preexponential factor during dehydrogenation of ethylbenzene**

| Constants of speeds $Sec^{-1}$ | Temperature, $^{o}K$ | | | $K_i$ $Sec^{-1}$ | $E_i$ $Cal / (g \bullet mol)$ |
|---|---|---|---|---|---|
| | 853 | 883 | 903 | | |
| $K_1$ | 0.66859 | 0.87922 | 1.20721 | $1.2962 \bullet 10^4$ | $1.6726 \bullet 10^4$ |
| $K_2$ | 0.03922 | 0.04252 | 0.05485 | $1.1594 \bullet 10$ | $9.6961 \bullet 10^4$ |
| $K_3$ | 0.04272 | 0.05527 | 0.07964 | $2.2699 \bullet 10^3$ | $1.8495 \bullet 10^4$ |
| $K_4$ | 1.99818 | 4.99975 | 9.99879 | $6.8881 \bullet 10^{12}$ | $4.8959 \bullet 10^4$ |
| $K_5$ | 1.96443 | 5.23873 | 9.71612 | $6.7884 \bullet 10^4$ | $4.8932 \bullet 10^4$ |
| $K_6$ | 0.05321 | 0.08816 | 0.07123 | $3.4216 \bullet 10$ | $3.5176 \bullet 10^3$ |
| $K_7$ | 0.08024 | 0.09632 | 0.06835 | $6.8244 \bullet 10$ | $1.6457 \bullet 10^3$ |

It is necessary, that the mathematical model is enough, qualitatively and quantitatively described properties of the modeled object, i.e. it should be adequate to process. Therefore, during construction of model we inspected adequacy of the chosen kinetic model by minimization of deviation of the sum of the square of difference of experimental and rating under the formula:

$$S(\theta) = \min \sum_{i=1}^{m} \sum_{j=}^{n} \alpha_{ij} (\frac{C_{ij}^E - C_{ij}^R}{C_{ij}^E})^2 \tag{10}$$

where $C^E_{ij}$ , $C^R_{ij}$ is value of i - variable concentration in j - the point of time of contact on modeled process and values corresponding to it on the model; $\alpha_{ij}$ is weight factor; $S(\theta)$ – values of criterion function.

Check of adequacy of the model was carried out on Fisher's statistical criteria. We consider that the equation (8) adequately describes investigated process if residual variance $S^2_{res}$ of the output quantity $Y^R_u$, calculated on the equation (8) concerning experimental data $Y^e_u$ , does not surpass in statistical sense the error of experience ($S^2_o$).

The residual variance was calculated under the formula:

$$S_{res}^2 = \frac{m}{f} \sum_{i=1}^{N}(Y_u^E - Y_u^R)^2 \tag{11}$$

where $f = N \cdot m - n - 1$ is the number of DOF (degrees of freedom); N – quantity of experiences; m – number of parallel experiences; n – quantity of factors.

For each group of parallel experiences were calculated sample variances under the formula:

$$S_u^2 = \frac{1}{m-1}\sum_{k=1}^{m}(Y_{uk} - Y_u)^2 \tag{12}$$

where m - is number of parallel experiences ( m =3 ); $Y_{uk}$ - is experimental value of parameters; $Y_u = (1/m) \cdot \Sigma Y_{uk}$ - average value of out parameter on results of parallel experiences.

Check of the uniformity of variances was carried out on the Kohren criterion under the formula:

$$G_{max} = - \frac{S_{u\,max}^2}{\sum_{i=1}^{N} S_u^2} \tag{13}$$

where $S^2umax$ – is maximum from the calculated sample variances in experiences; $\Sigma\, S^2_u$ - the sum of all variances on N experiences.

The hypothesis about uniformity of variances is accepted in case the inequality is carried out:
$$G_{max} < G_T(f_1, f_2) \tag{14}$$
for value of DOF f1 = m – 1; f2 = N and the set significance value q.

The error of experience $S^2_0$ is calculated so:

$$S_0^2 = \frac{1}{N}\sum_{u=1}^{N}S_u^2 = \frac{1}{N(m-1)}\sum_{i=1}^{N}\sum_{k=1}^{m}(Y_{uk} - Y_u)^2 \tag{15}$$

The model adequately describes investigated object if it is carried out the inequality:

$$F = \frac{S_{res}^2}{S_0^2} < F_{tab}(f_1, f_2) \tag{16}$$

where $F_{tab}$ – value of Fisher's criterion (F - criterion) is presented in the table for the sample significance value q of DOF numerator $f_1 = N \cdot m - n - 1$ and the denominator $f_2 = N \cdot (m - 1)$.

In practical calculations of check of the value factors of model the following expressions are used:
$$|K_i| > |\Delta K_i| \tag{17}$$

Thus, the deviation of any factor can be written down so:
$$\Delta K_i = \pm S_{ki} \cdot t_T \tag{18}$$

where $S_{ki} = \sqrt{\dfrac{S_0^2}{Nm}}$ – variance of factors $S^2_{ki}$ .

Procedure of check of the value factors includes drawing up of relations and their comparison with value $t_T$ – criterion, which are under tables of distribution of Student's **t**-distribution (the t-distribution) for the sample value factor and freedom number.

$$\frac{|K_i|}{S_{ki}} = t_{ki} > t_T(q, f) \tag{19}$$

The calculated data resulted in Tab. 2. confirms the hypothesis about uniformity of variance since the inequality (14) is carried out at $f_1 = 7$, $f_2 = 8$,
q = 5%. $G_T = 0.3185$.

To check up the hypothesis about adequacy of the mathematical model, expressed in the form of systems of the differential equations (8) and objects, it is necessary to observe the conditions (16).

By Fisher's criterion it is established that the received kinetic model adequately describes the process.

### Table 2: The data calculated on the computer at various temperatures

| $^0K$ | $S^2_0$ | $S^2_{ost}$ | $S^2_u$ | $\Sigma S^2_u$ | F | $G_{max}$ | $S_{ki}$ | $\Delta K_i$ |
|---|---|---|---|---|---|---|---|---|
| 853 | 0.0029 | 0.0042 | 0.0141 | 0.0491 | 1.71601 | 0.14342 | 0.005983 | 0.001334 |
| 883 | 0.00259 | 0.0039 | 0.0099 | 0.0984 | 1.5002 | 0.2866 | 0.00729 | 0.00473 |
| 903 | 0.00074 | 0.00112 | 0.00196 | 0.0345 | 1.4993 | 0.1979 | 1.40602 | 0.28271 |

The mathematical description represents the equations of kinetics, material and thermal balances, and can be used not only for optimization of operating installations, but also for optimum management of chemical-technological process.

On the basis of kinetic model of the process of dehydrogenation of ethylbenzene in styrene it is possible to make mathematical description taking into account thermal balance at following assumptions:

1.  Process stationary;
2.  Process proceeds in adiabatic conditions;
3.  The hydrodynamic mode is close to the order of ideal replacement.

The equation describing change of temperature on length of the reactor looks like:

$$dT/d\tau = -\frac{1}{C_p \rho} \sum_{i=1}^{n} q_i w_{r_i} \tag{20}$$

where: T – is temperature of reactionary mix, in $^0K$; $C_p$ – average thermal capacity of reagents in the reactor, in cal/ (mol•q); $q_i$ – thermal effect i – of the reaction, in cal/mol; $\rho$ – mix density, mol/l.

The thermal capacity of gas mix for the process of dehydrogenation of ethylbenzene in styrene will be:

$$C_{p(cm)} = m_{e/b} \bullet C_{p(e/b)} + m_{water} \bullet C_{p\ water} \tag{21}$$

where: $m_{e/b}$, $m_{water}$ – are mole fraction of ethylbenzene and water steam, accordingly:
$$m_{e/b} = 1.25 \quad and \quad m_{water} = 20.$$

At temperature of $900^0K$, thermal capacities of these components will be:

$$Cp\ (e/b) = 71.27\ cal./degree/mole) \quad and \quad C_{p\ water} = 5.56\ cal./degree/mole).$$

In this case, the thermal capacity of gas mix will be
$$C_{p(cm)} = 71.27 \bullet 1.25 + 5.56 \bullet 20 = 200.2878\ .$$

Average thermal capacity of mix:
$$C_p = C_{p(cm)} / \Sigma m = 200/2878/21/25 = 9/42529\ cal./degree/mole).$$

Thermal effects are defined as enthalpy difference of products. Hence, the following equation of thermal balance is received:

$-V \cdot g \cdot C_p \cdot \rho \cdot dT / d\tau = 29824 K_1 C_1 + 24282 K_2 C_1 - 15005 K_3 C_1 - 5542 K_4 C_2 - 45361 K_5 C_2$

As a result, the mathematical model of statics of the process has the following appearance:

$$
\begin{aligned}
& dC_1 / d\tau = - (K_1 + K_2 + K_3 + K_4) \cdot C_1 \\
& dC_2 / d\tau = K_1 C_1 - ( K_5 C_5 + K_6 C_5 + K_7) \cdot C_2 \\
& dC_3 / d\tau = K_2 C_1 + K_5 C_2 C_5 \\
& dC_4 / d\tau = K_3 C_1 + K_6 C_2 C_5 \\
& dC_5 / d\tau = (K_1 + 21 K_4) \cdot C_1 - ( K_5 C_5 + 2 K_6 C_5 - 2 K_7 ) \cdot C_2 \\
& dC_6 / d\tau = 8 \cdot ( K_4 C_1 + K_7 C_2 ) \\
& dC_7 / d\tau = ( K_2 + K_3 ) \cdot C_1 + ( K_5 C_5 + K_6 C_5 ) \cdot C_2 \\
& dT / d\tau = - (29824 K_1 C_1 + 24282 K_2 C_1 - 15005 K_3 C_1 - 5542 K_4 C_2 - \\
& \qquad - 45361 K_5 C_2 ) / (C_p \cdot \rho)
\end{aligned}
\qquad (22)
$$

At the stage of laboratory researches, it was checked up the basic possibility of realization of the developed process, studied the mechanism of the major transformations, defined target and by-products, and are investigated physicochemical properties of new substances. At this stage, developed were mathematical descriptions of the reactor block of the process of dehydrogenation of ethylbenzene in styrene. The kinetic parameters entering into the equations of mathematical models were studied, as a rule, on specially created laboratory installations.

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