Optimization of the Reaction Parameters of Epoxidation of Allyl Alcohol with Hydrogen Peroxide on TS-1 Catalyst

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The epoxidation of allyl alcohol with a 30 % hydrogen peroxide in the presence of methanol over the TS-1 catalyst has been investigated. The optimum parameters of the glycidol synthesis have been established. The epoxidation of allyl alcohol was carried out using a mathematical method of experiment planning. The optimization of technological parameters was performed according to rotatable-uniform design. The magnitudes describing the process are: selectivity of transformation to glycidol in relation to consumed allyl alcohol and H_2O_2, the degree of conversion of allyl alcohol and H_2O_2. The course of variation of mentioned magnitudes during the changes of two parameters at the remaining parameters determining the maximum of function is presented. The results of parameters optimization have been confirmed by a series of the verifying syntheses.

Glycidol is a bifunctional compound with a wide application. This compound is used, among others, for the manufacture of the surface-active agents, which are included in the composition of the cosmetic formulations for moistening and cleansing of skin, shampoo, bath fluids, toothpastes, mouthwash, detergents for washing and disinfectants [1]. These agents also comprise food emulgators used for the production of margarines, ice creams, and vegetable butter [2, 3]. Other groups of applications of glycidol include dispersing agents, plasticizers for resins and rubbers [4], and the detergents in the petroleum industry [5]. One of the methods of chlorine-free preparation of glycidol is the epoxidation of allyl alcohol with hydrogen peroxide over the titanium silicalite catalysts [6—10]. This method has not been considered in the literature from the technological point of view. In this work the optimal technological parameters of the process are presented. They allow to achieve the maximum yield and selectivity of the transformation to glycidol in relation to consumed alcohol and H_2O_2. Simultaneously, the degree of conversion of allyl alcohol and H_2O_2 is high.

EXPERIMENTAL

The following reagents were used in the epoxidation process: allyl alcohol (purity 98 %, Fluka), hydrogen peroxide (30 % aqueous solution, P.O.Ch. Gliwice), methanol (anal. grade $\geq$ 99.8 %, P.O.Ch. Gliwice), a titanium silicalite TS-1 catalyst (prepared at the Department of Organic Chemical Technology, Technical University of Szczecin). The quantitative GC analyses were performed with the use of glycidol (2,3-epoxypropan-1-ol, 90 % pure, Fluka) as a reference.

Measurement Methods

The determined amounts of the reagents were introduced into the autoclave equipped with PTFE insert of 8 cm^3 capacity in the following order: allyl alcohol, hydrogen peroxide, methanol, and the catalyst. The amount of reagents was selected in such a way that the degree of autoclave filling did not exceed 80 vol. % under retaining the process parameters. The autoclave was screwed, then it was placed in a handle of a shaker and subsequently immersed in an oil bath with the temperature controlled by a thermostat. The shaker was started and the reaction was carried out over the appropriate time. After the reaction was completed, the autoclave was cooled and emptied. A post-reaction solution was subjected to analyses and the mass balance was performed.

Analytical Methods

Chromatographic analysis of the post-reaction mixture was carried out on a Chrom 5 apparatus equipped with a flame-ionization detector (FID) with the application of a column packed with 10 % Triton 100 on Chromosorb W 60/80 mesh. The column temperature was programmed in the following way: constant 50 °C for 6 min, followed by the increase to 140 °C at the rate of 15 °C min^{-1}, isothermal for 6 min, with the subsequent increase to 142 °C at the rate of 20 °C min^{-1} and finally isothermal for 2 min. The quantitative calculations were performed by the external stan-

dard methods. Glycerol was determined by means of periodate titration [11], whereas hydrogen peroxide by iodometric titration [12].

RESULTS AND DISCUSSION

The epoxidation process of allyl alcohol (AA) with hydrogen peroxide over the TS-1 catalyst can be described by the following reaction equations

$$CH_2{=}CH{-}CH_2OH + H_2O_2 \xrightarrow[-H_2O]{\text{TS-1}}$$

$$\xrightarrow[-H_2O]{\text{TS-1}} CH_2{-}\underset{\diagdown\,\diagup}{\overset{\overset{O}{}}{CH}}{-}CH_2OH$$

$$CH_2{-}\underset{\diagdown\,\diagup}{\overset{\overset{O}{}}{CH}}{-}CH_2OH + H_2O \longrightarrow$$

$$\longrightarrow CH_2OH{-}CHOH{-}CH_2OH$$

The major products were glycidol and glycerol depending on the technological parameters. The other products formed in minor amounts include: diallyl ether and the products of methanolysis of the epoxide ring. The previous investigations [13, 14] indicated that the highest yield of glycidol (64.5 mole %) in this process was achieved at the following technological parameters: temperature 20℃, the mole ratio of AA : H_2O_2 = 1 : 1, the methanol content 80 mass %, TS-1 content 1 mass %, time 1 h. Under these conditions the selectivity of transformation to glycidol in relation to consumed AA amounts to 93.6 mole %, in relation to H_2O_2 67.5 mole %. The degree of conversion of AA amounts to 68.9 mole %, H_2O_2 100 mole %. It results from these studies that interesting ranges of parameter variations are: temperature 20—120 ℃, the mole ratio AA : H_2O_2 = (1—10) : 1, the solvent content 10—80 mass %, the catalyst content 0.1—2.0 mass %, time 1—8 h.

The optimization of technological parameters of the epoxidation of AA with H_2O_2 over the TS-1 catalyst was performed with the application of rotatable-uniform design [15—18]. The planning of experiments and all calculations were performed with the application of a computer program Cadex: Esdet 2.2. The plan was realized for five input variables x_1—x_5 (independent factors), where x_1 is the temperature 15—90℃, x_2 the mole ratio AA : H_2O_2 = (0.5—5) : 1, x_3 methanol content 5—90 mass %, x_4 TS-1 content 0.1—2.0 mass %, and x_5 reaction time 15—120 min. The total number of the plan systems (experiments) amounted to 32. The real values of the input variables x_1—x_5 were recalculated on the normalized values (dimensionless) according to the equation

$$X_k = [2\alpha x_k - x_{k\ min})/(x_{k\ max} - x_{k\ min})] - \alpha$$

where $X_k \in [-\alpha, \alpha]$ is the normalized input variable, k = 1—5; α is the star level ($\alpha = 2$); x_k real input variable, $x_{k\ max}$, $x_{k\ min}$ maximum and minimum value of real input variable.

As a result of normalization a universal plan of experiments was achieved with the values of input variables (independent factors) in the dimensionless range $[-2, 2]$. In Table 1 the true values and the input variables normalized technological parameters on the levels resulting from the design of experiments are presented. As the response functions characterizing the epoxidation the following quantities were assumed: z_1– the selectivity of transformation to glycidol in relation to allyl alcohol consumed ($S_{glc/AA}$), z_2 – the selectivity of transformation to glycidol in relation to H_2O_2 consumed (S_{glc/H_2O_2}), z_3 – the degree of allyl alcohol conversion (C_{AA}), z_4 – the degree of H_2O_2 conversion ($C_{H_2O_2}$). The design matrix according to which the experiments were realized and the experimental results of the response functions z_1—z_4 are shown in Table 2.

The influence of normalized independent factors X_1—X_5 of the epoxidation process of AA on the value of response functions was presented in the form of a polynomial of the second order containing the linear components, square and dual products.

$$Z = Z(X_k) = b_0 + b_1 \cdot X_1 + \cdots + b_i \cdot X_i + b_{11} \cdot X_1^2 + \\ + \cdots + b_{ii} \cdot X_i^2 + b_{12} \cdot X_1 X_2 + \cdots + b_{i-1,i} \cdot X_{i-1} X_i$$

Table 1. Levels of Examined Factors

Level	Coded factor	Temperature	AA : H_2O_2 mole ratio	Methanol content	TS-1 content	Reaction time
		℃		mass %	mass %	min
	X_i	x_1	x_2	x_3	x_4	x_5
Basic	0	53	2.8	48	1.1	68
Higher	1	71	3.9	69	1.5	94
Lower	−1	34	1.6	26	0.6	41
Star higher	2	90	5	90	2.0	120
Star lower	−2	15	0.5	5.0	0.1	15

x_1—x_5 – independent factors.

Table 2. Design Matrix and Experimental Results

Exp.	X_1	X_2	X_3	X_4	X_5	z_1 / mole %	z_2 / mole %	z_3 / mole %	z_4 / mole %
1	−1	−1	−1	−1	−1	100	0	1	98
2	1	−1	1	−1	−1	100	0	25	91
3	1	−1	−1	−1	1	22	78	4	98
4	1	−1	−1	1	−1	30	70	4	97
5	1	1	−1	−1	−1	100	0	1	97
6	−1	1	1	−1	−1	100	0	25	94
7	−1	1	−1	−1	1	100	0	1	97
8	−1	1	−1	1	−1	50	50	3	98
9	1	−1	1	1	1	79	20	42	91
10	−1	−1	−1	1	1	8	92	9	99
11	−1	−1	−1	1	−1	75	25	23	80
12	−1	−1	1	−1	1	93	7	39	63
13	−1	1	1	1	1	100	0	1	91
14	1	1	−1	1	1	20	80	2	98
15	1	1	1	1	−1	70	30	6	95
16	1	1	1	−1	1	95	5	24	93
17	−2	0	0	0	0	73	27	8	97
18	2	0	0	0	0	80	20	25	93
19	0	−2	0	0	0	12	87	28	97
20	0	2	0	0	0	68	33	2	92
21	0	0	−2	0	0	1	89	4	98
22	0	0	2	0	0	83	7	41	100
23	0	0	0	−2	0	18	82	7	97
24	0	0	0	2	0	77	23	15	97
25	0	0	0	0	−2	21	79	5	97
26	0	0	0	0	2	86	14	20	96
27	0	0	0	0	0	93	7	43	100
28	0	0	0	0	0	85	15	12	96
29	0	0	0	0	0	85	15	12	96
30	0	0	0	0	0	85	15	12	96
31	0	0	0	0	0	85	15	12	96
32	0	0	0	0	0	85	15	12	96

for $X_k \in [-2, 2]$, where b_i are the normalized coefficients of approximation function. Number of polynomial coefficients for number of input variables 5 was $N_b = 0.5 \cdot (i+1) \cdot (i+2)$; $N_b = 21$.

In order to obtain the response function containing the true coefficients of approximation function and the true input variables x_k, the normalized values of input variables X_k were recalculated into the true values using the equations: $X_1 = 0.0533 \cdot (x_1 - 15) - 2$, $X_2 = 0.8889 \cdot (x_2 - 0.5) - 2$, $X_3 = 0.047 \cdot (x_3 - 5) - 2$, $X_4 = 2.105 \cdot (x_4 - 0.1) - 2$, $X_5 = 0.0381 \cdot (x_5 - 15) - 2$. However, the statistical calculations were performed using the response function Z containing the normalized coefficients and normalized input variables (parameters), since this allows to simplify the statistical calculations and diminishes the calculation errors. The regression equation coefficients (approximation functions, Table 3) for the normalized input variables were determined by the least-squares method. A verification of function adequacy was performed by means of the Fisher—Snedecor test [19] by a comparison with the critical value of the quotient $F(\alpha)$ read from the statistical tables [20]. The relative errors of approximation and the multidimensional correlation coefficient R (Table 3) for the respective functions were also calculated. All the calculations were carried out for the significance level $\alpha = 0.05$.

The maximum values of the regression equation were determined numerically by the utilization of the methods of Hook—Jeeves and Gauss—Seidel [18, 19]. Similar results were obtained in each method. The highest values of the response function and corresponding to them parameters are presented in Table 4. The overriding functions in establishing the optimum technological parameters of the epoxidation are $S_{glc/AA}$ and S_{glc/H_2O_2}. The examination of the function maxima performed by the method of experiment planning reveals that the function z_1 ($S_{glc/AA}$) achieves the highest value at the following process parameters: temperature 89 °C, the mole ratio AA : H_2O_2 = 2.9 : 1, CH_3OH content 90 mass %, TS-1 content 0.9 mass %, reaction time 115 min. A comparison of the maxima of functions z_1 and z_2 ($S_{glc/AA}$ and S_{glc/H_2O_2}) determined by the mathematical method indicates that the parameters determining them are similar: temperature 89—90 °C, the mole ratio AA : H_2O_2 = (1.0—2.9) : 1, CH_3OH content 90 mass %, TS-1 content 1 mass %, reaction time 120 min. However,

Table 3. Coefficients of the Regression Equation and Statistical Parameters

Coefficient	Z_1	Z_2	Z_3	Z_4
b_{00}	88.07	41.77	17.69	97.1
b_{01}	−3.94	3.58	1.6	1.36
b_{02}	9.93	1.67	−5.72	1.47
b_{03}	18.67	23.26	9.78	−3.28
b_{04}	−6.62	−6.12	−0.43	0.81
b_{05}	0.91	7.49	2.60	−0.98
b_{11}	2.61	−0.78	−0.58	−1.05
b_{12}	−1.33	−0.71	0.07	−1.99
b_{13}	3.90	0.94	0.75	2.69
b_{14}	2.64	7.40	1.93	−0.91
b_{15}	−3.66	6.31	2.47	1.19
b_{22}	−6.42	−8.80	−0.97	−1.13
b_{23}	−5.76	0.96	−4.05	3.13
b_{24}	−2.03	−5.90	−2.95	−0.97
b_{25}	6.12	−7.85	−2.97	0.75
b_{33}	−5.96	0.64	1.01	−0.06
b_{34}	9.45	−15.68	−3.31	0.95
b_{35}	9.53	6.38	1.22	−1.56
b_{44}	−4.60	−3.11	−2.02	−0.56
b_{45}	4.50	0.19	0.16	2.20
b_{55}	−2.97	−3.83	−1.59	−0.66
$R(\alpha)$	0.79	0.88	0.91	0.84
S^2_{rep}	54	628	157	3
f_{rep}	5	5	5	5
S^2_{adeq}	1013	475	19	41
f_{adeq}	10	10	10	10
F	1.88	0.75	0.12	13.62
$F(\alpha)$	3.66	*	*	4.82

S^2_{rep}, S^2_{adeq} – variance of inaccuracy and adequacy, respectively; f_{rep}, f_{adeq} – freedom degree number of the inaccuracy and adequacy, respectively; R – coefficient of multiple correlation; F – Fisher—Snedecor test value; $F(\alpha)$ – critical value of the F quotient of the Fisher—Snedecor adequacy test.
*When $F < 1$, the function is adequate and $F(\alpha)$ is not calculated.

Table 4. Maximum Values of the Response Function and their Parameters

	$S_{\mathrm{glc/AA}}/C_{\mathrm{AA}}$ (z_1)	$S_{\mathrm{glc/H_2O_2}}/C_{\mathrm{H_2O_2}}$ (z_2)	$C_{\mathrm{AA}}/S_{\mathrm{glc/AA}}$ (z_3)	$C_{\mathrm{H_2O_2}}/S_{\mathrm{glc/H_2O_2}}$ (z_4)
	Mole %			
Maximum function value	100/20	100/98	95/70	100/41
Temperature/°C	89	90	90	20
AA : H_2O_2 mole ratio	2.9	2.6	0.5	2.6
CH_3OH content/mass %	90	90	90	5
TS-1 content/mass %	0.9	0.1	1.4	0.1
Reaction time/min	115	120	120	15

the preliminary investigations reveal that the process can be carried out at the lower temperature (20 °C) and at lower mole ratio (AA : H_2O_2 = 1 : 1 [13, 14]. In that case the obtained values of functions describing the process were slightly lower: $S_{\mathrm{glc/AA}} = 94$ mole %, $S_{\mathrm{glc/H_2O_2}} = 68$ mole %, $C_{\mathrm{AA}} = 69$ mole %.

Influence of the Technological Parameters on the Selectivity of the Transformation to Glycidol in Relation to Allyl Alcohol Consumed (z_1)

The influence of two independent factors (parameters) on the course of changes of the selectivity of the transformation to glycidol in relation to AA consumed, at the values of the remaining parameters allowing to reach the function maximum (Table 4) is shown in Fig. 1. Two-dimensional sections of the response surface for analyzed functions were plotted using the computer program Surfer 5.01. It results from Fig. 1*a* that a high selectivity of the transformation to glycidol in relation to AA consumed can be achieved not only at temperature 89 °C and at the mole ratio

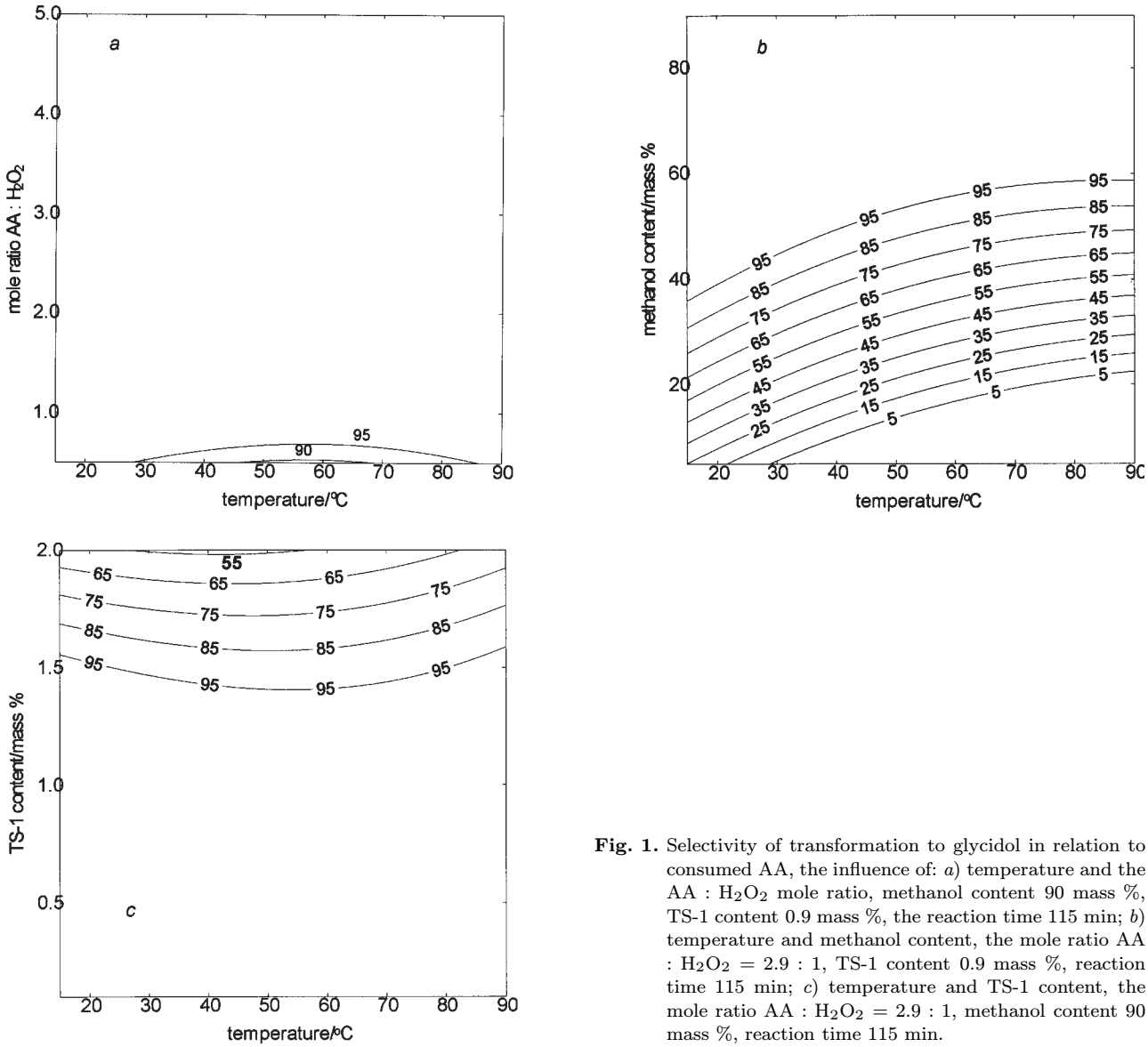

Fig. 1. Selectivity of transformation to glycidol in relation to consumed AA, the influence of: *a*) temperature and the AA : H_2O_2 mole ratio, methanol content 90 mass %, TS-1 content 0.9 mass %, the reaction time 115 min; *b*) temperature and methanol content, the mole ratio AA : H_2O_2 = 2.9 : 1, TS-1 content 0.9 mass %, reaction time 115 min; *c*) temperature and TS-1 content, the mole ratio AA : H_2O_2 = 2.9 : 1, methanol content 90 mass %, reaction time 115 min.

of reagents 2.9 : 1. Thus the function z_1 takes the highest values almost over the entire range of examined interval of temperatures and the mole ratios AA : H_2O_2. This concerns both the temperature 20 °C as well as the mole ratios of AA : H_2O_2 = 1 : 1. It results from Fig. 1*b* that the epoxidation of AA to glycidol is not necessary to be carried out at temperature 89 °C. Glycidol can be obtained with the maximum selectivity of the transformation in relation to AA consumed at lower temperatures. The temperature 20 °C and methanol content 40 mass % is sufficient to achieve $S_{\mathrm{glc/AA}}$ = 95 mole %. An increase in process temperature requires to increase the methanol content in order to maintain the maximum selectivity of the transformation to glycidol. The required methanol content amounts to 50 mass % at temperature 40 °C, whereas about 60 mass % at 65—90 °C. Fig. 1*c* demonstrates that the function $S_{\mathrm{glc/AA}}$ takes the value of 95 mole % at the catalyst content below 1.5 mass % over the examined temperature range. In connection with this it is purposeful to establish the catalyst content at the level below 1.5 mass % and to carry out the process at ambient temperature. The reaction time necessary to achieve a high selectivity of the transformation to glycidol over a wide range of temperatures amounts to 70 min. Too long time results in a decrease of the selectivity due to the hydration of glycidol to glycerol. Moreover, the solvolysis of the epoxide ring in glycidol may proceed in a small degree. In the earlier studies [13, 14] 3-allyloxypropane-1,2-diol and 2-allyloxypropane-1,3-diol were identified in the reaction mixture.

The investigations of influence of the technological parameters on the selectivity of the transformation to glycidol (z_1) reveal that the highest value of this function can be achieved under the conditions: temperature 20 °C, the mole ratio AA : H_2O_2 = 1 : 1, methanol

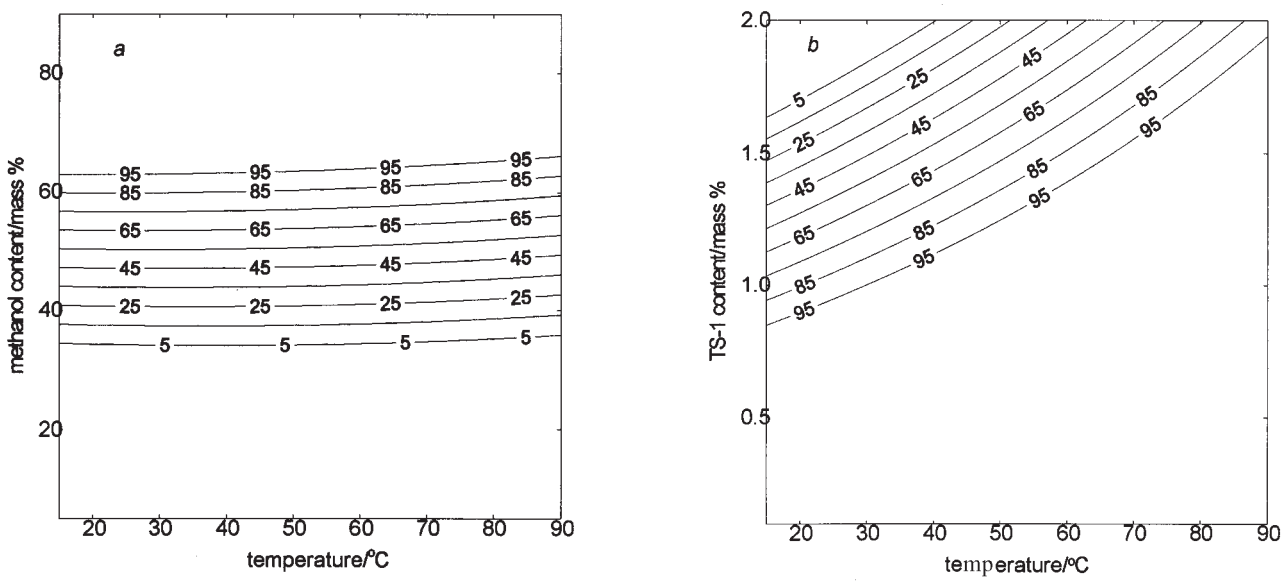

Fig. 2. Selectivity of transformation to glycidol in relation to consumed H_2O_2, the influence of: *a*) temperature and methanol content, the mole ratio AA : H_2O_2 = 2.6 : 1, TS-1 content 0.1 mass %, reaction time 120 min; *b*) temperature and TS-1 content, the mole ratio AA : H_2O_2 = 2.6 : 1, methanol content 90 mass %, reaction time 120 min.

content 70 mass %, TS-1 content 0.1 mass %, reaction time 70 min. These are the conditions similar to those determined in the preliminary studies [13, 14]. These conditions minimize the consumption of raw materials, allow to work at lower energy consumption in comparison with the conditions determined by the mathematical method ($S_{\mathrm{glc/AA}}$, Table 4).

Influence of the Technological Parameters on the Selectivity of the Transformation to Glycidol in Relation to H_2O_2 Consumed (z_2)

An analysis of the regression function z_2 reveals that the highest selectivity of the transformation to glycidol in relation to consumed H_2O_2 (100 mole %) is achieved at the following parameters: temperature 90 °C, the mole ratio AA : H_2O_2= 2.6 : 1, methanol content 90 mass %, the TS-1 catalyst content 0.1 mass %, reaction time 120 min. From the interaction of two parameters on the selectivity of the transformation to glycidol in relation to H_2O_2 consumed can be seen significantly more areas in which the function reaches the maximum values (Fig. 2). The influence of methanol content and temperature (Fig. 2*a*) reveals that after exceeding the methanol content 61 mass % in the examined temperature range the function $S_{\mathrm{glc/H_2O_2}}$ reaches the highest values of 95 mole %. From this dependence it also results that the epoxidation process of AA to glycidol proceeds with a high selectivity in relation to consumed H_2O_2 at low temperatures (20 °C) and at a high content of methanol (90 mass %). It can be seen from Fig. 2*b* that at temperatures 90 °C and 20 °C the function z_2 takes the maximum value if the catalyst content does not exceed 0.8 mass %. Lowering of temperature extends the range of changes of the reaction time allowing to achieve the highest selectivity of the transformation to glycidol in relation to H_2O_2 consumed. In the investigated range of changes of the mole ratio and temperature the selectivity of the transformation to glycidol in relation to H_2O_2 consumed amounts to 100 mole %. An analysis of Figs. 2*a* and *b* reveals that high selectivities of the transformation to glycidol in relation to H_2O_2 can be achieved using the following technological parameters: temperature 20 °C, the mole ratio AA : H_2O_2 = 1 : 1, methanol content 90 mass %, TS-1 content 0.1 mass %, reaction time 15—120 min.

An analysis of the influence of the technological parameters on the value of the functions z_1 and z_2 shows that such parameters as the mole ratio AA : H_2O_2 = 1 : 1, methanol content 90 mass %, and time 120 min are the most advantageous and identical for these functions. They are also close to the parameters determining the maxima of these functions. These maxima were determined numerically based on the regression equations (Table 4). These parameters should be recognized as optimal for the functions z_1 and z_2. Temperatures within the range 20—60 °C and the catalyst content in the range 0.1—1.0 mass % determine the high values of the functions z_1, z_2. The mentioned functions achieve the maximum values at temperature 90 °C. However, these functions also achieve the high values at lower temperatures (20 °C). Due to the reaction rate it is purposeful to elevate the temperature above 20 °C. Taking into consideration the achievement of high selectivity of the transformation in relation to H_2O_2 consumed, lowering of temperature below 90 °C is purposeful. The choice of the most advantageous content of the catalyst is out of question and results from the need of achievement of a high yield

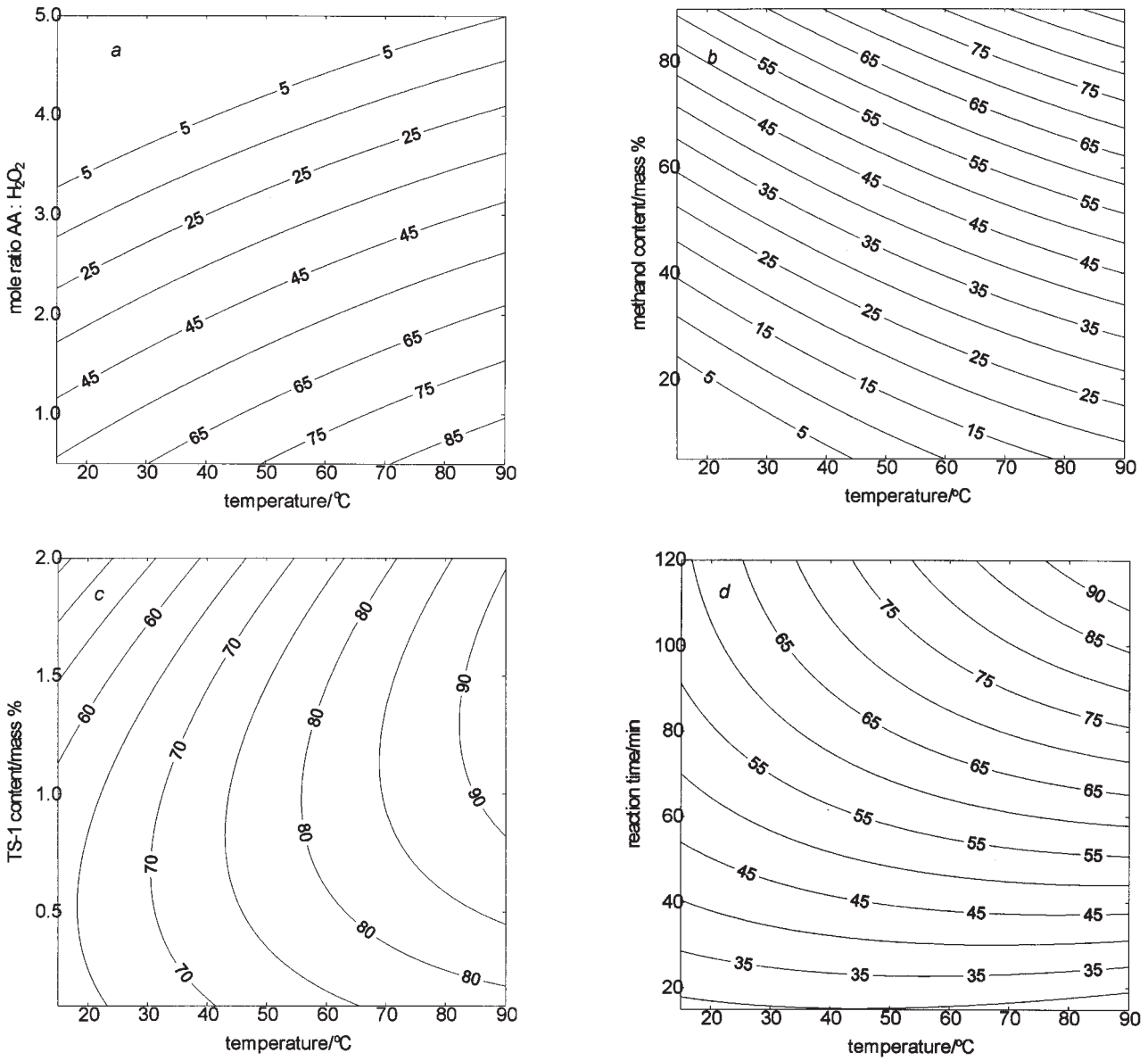

Fig. 3. The degree of AA conversion as a function of: *a*) temperature and the AA : H_2O_2 mole ratio, methanol content 90 mass %, TS-1 content 1.4 mass %, reaction time 120 min; *b*) temperature and methanol content, the mole ratio AA : H_2O_2 = 0.5 : 1, TS-1 content 1.4 mass %, reaction time 120 min; *c*) temperature and TS-1 content, the mole ratio AA : H_2O_2 = 0.5 : 1, methanol content 90 mass %, reaction time 120 min; *d*) temperature and reaction time, the mole ratio of AA : H_2O_2 = 0.5 : 1, methanol content 90 mass %, TS-1 content 1.4 mass %.

and the selectivity of the transformation in relation to AA. The usefulness of established parameters was verified in a series of additional syntheses. The following results were obtained in these syntheses: $S_{\mathrm{glc/AA}}$ = 61 mole %, $S_{\mathrm{glc/H_2O_2}}$= 58 mole %.

Influence of the Technological Parameters on the Degree of Conversion of Allyl Alcohol (z_3) and Hydrogen Peroxide (z_4)

The maximum values of the degree of conversion of AA (C_{AA}) and H_2O_2 ($C_{\mathrm{H_2O_2}}$) are presented in Table 4. The influence of changes of two parameters on the degree of AA conversion maintaining other parameters corresponding to the function maximum is shown in Fig. 3. An analysis of the plots reveals that the greater the temperature, methanol and catalyst contents and the lower the mole ratio AA : H_2O_2, the higher is the degree of AA conversion. The maximum value of the z_3 (C_{AA}) function is 95 mole %. Lowering the temperature to 60 °C and establishing the mole ratio AA : H_2O_2 = 1 : 1 causes a decrease of the degree of AA conversion to 70 mole %. Carrying the process at temperature 60 °C at the methanol content about 80 mass % the degree of AA conversion about 80 mole % can be achieved. There is no need to maintain the catalyst content of 1.4 mass % (Table 4). The application of the catalyst content 1 mass % allows to obtain

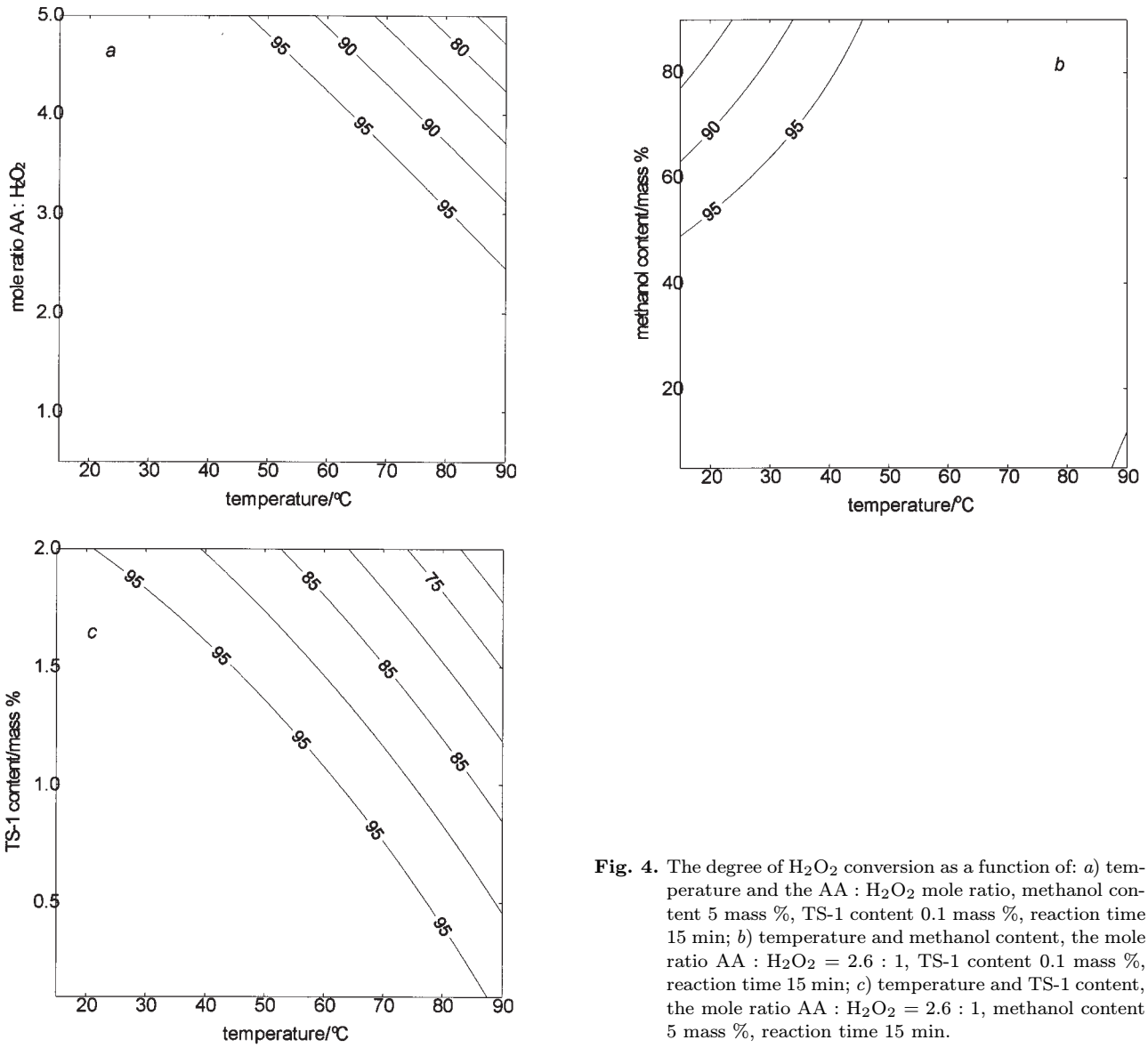

Fig. 4. The degree of H_2O_2 conversion as a function of: *a*) temperature and the AA : H_2O_2 mole ratio, methanol content 5 mass %, TS-1 content 0.1 mass %, reaction time 15 min; *b*) temperature and methanol content, the mole ratio AA : H_2O_2 = 2.6 : 1, TS-1 content 0.1 mass %, reaction time 15 min; *c*) temperature and TS-1 content, the mole ratio AA : H_2O_2 = 2.6 : 1, methanol content 5 mass %, reaction time 15 min.

the same degree of the AA conversion. An analysis of changes of the degree of AA conversion as a function of the technological parameters (Fig. 3) reveals that the parameters recognized as optimal in the investigated process also allow to achieve a high degree of AA conversion. These parameters result from an analysis of the functions z_1, z_2 and they are: temperature 60 °C, the mole ratio AA : H_2O_2 = 1 : 1, methanol content 90 mass %, TS-1 content 1 mass %, reaction time 120 min. Under these conditions the degree of AA conversion amounts to 80—85 mole %. This is consistent with the degree of AA conversion experimentally determined 90.5 mole % after taking into account the approximation errors.

The influence of changes of two technological parameters on the hydrogen peroxide conversion, maintaining other parameters allowing to achieve the function maximum (Table 4) is shown in Fig. 4. It can be seen that over a wide range of changes of parameters, the function achieves the maximum values. The z_4 function has the maximum value at the mole ratio AA : H_2O_2 = 1 : 1 over the entire range of the investigated temperatures. The behaviour of this function is similar at the methanol content 90 mass %, catalyst content 1 mass %, after the reaction time 120 min when the temperature does not exceed 60 °C. The application of the optimum parameters from the point of view of the selectivity of transformation to glycidol in the process allows to achieve the degree of H_2O_2 conversion in the range 97—100 mole %. Experimentally obtained value of the degree of H_2O_2 conversion under the mentioned conditions amounts to 95 mole %.

CONCLUSION

The mathematical calculations of the maxima of

functions describing the process and an analysis of the course of the consecutive functions z_1, z_2 in the system of two variable parameters, maintaining other parameters corresponding to the function maximum allowed to establish the optimum technological parameters of AA epoxidation. These investigations reveal that the optimum parameters are as follows: temperature 60 ℃, the mole ratio AA : $H_2O_2 = 1 : 1$, methanol content 90 mass %, the TS-1 catalyst content 1 mass %, reaction time 120 min. These parameters allow to obtain glycidol with the high selectivity of the transformation to glycidol in relation to AA and hydrogen peroxide. Under these parameters the degree of conversion of AA is satisfactory (60 mole %). The elaborated parameters differ in a slight degree from those obtained in the preliminary investigations [13, 14] (temperature 20 ℃, the mole ratio AA : $H_2O_2 = 1 : 1$, methanol content 80 mass %, the TS-1 catalyst content 1 mass %, time 60 min). The obtained results were confirmed in a series of additional experiments ($S_{\mathrm{glc/AA}} = 61$ mole %, $S_{\mathrm{glc/H_2O_2}} = 58$ mole %).

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