

Bis(3-methyl-1-propene) ether and 3-(3-methyl-1-propene)-3-methyl-1,2-epoxypropane ether synthesis during the epoxidation of 1-butene-3-ol with hydrogen peroxide over the TS-2 catalyst

Agnieszka Wróblewska, Grzegorz Wójtowicz

West Pomeranian University of Technology, Szczecin, Institute of Organic Chemical Technology, ul. Pułaskiego 10, 70-322 Szczecin, Poland, e-mail: Agnieszka.Wroblewska@zut.edu.pl

The influence of technological parameters on the transformation of 1-butene-3-ol (1B3O) to bis(3-methyl-1-propene) ether (2x1B3O ether) and 3-(3-methyl-1-propene)-3-methyl-1,2-epoxypropane ether (1B3Ox1,2EB3O ether) over the TS-2 catalyst was presented. The reaction was performed in a glass reactor at atmospheric pressure and in methanol medium (protic solvent). The optimum conditions of 2x1B3O ether and 1B3Ox1,2EB3O ether obtaining were established by the mathematical method of experiments design (rotatable-uniform design) and after the analyses of the layer drawings.

Keywords: bis(3-methyl-1-propene) ether, 3-(3-methyl-1-propene)-3-methyl-1,2-epoxypropane ether, TS-2, hydrogen peroxide, epoxidation in liquid phase.

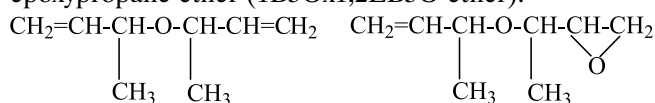
INTRODUCTION

One of the main challenges in contemporary chemical technology is the development of new alternative technologies – cleaner, safer and more environmentally friendly. An interesting alternative in oxidation processes is hydrogen peroxide, which gives water as the by-product. It is currently produced on a large scale and it is relatively cheap. The use of titanium-silicalite catalysts in combination with hydrogen peroxide enables many processes to be conducted under mild conditions (low temperatures, atmospheric or autogenic pressure). The group of titanium-silicalite catalysts includes: TS-1, TS-2, Ti-Beta, Ti-MCM-41, Ti-MCM-48, Ti-MWW, and Ti-SBA-15.

One of the best known titanium silicalite catalysts is TS-2. The TS-2 catalyst crystallises in the tetragonal system and has a linear arrangement of channels (one-dimensional structure of MEL type). The channel openings are restricted by ten edges, making a window of the size 0.53 x 0.54 nm. The content of titanium (up to five Ti⁴⁺ ions) in a single elementary unit is in this catalyst greater than that of TS-1. The template used in the synthesis of this catalyst is tetrabutylammonium hydroxide (TBAOH)¹⁻³. Our preliminary investigations the process of 1-butene-3-ol epoxidation at atmospheric pressure made over TS-1, TS-2 and Ti-Beta catalyst showed that the best in this

process are TS-1 and TS-2 catalysts – Table 1⁴⁻⁶. Over these two catalysts the selectivity of transformation to epoxide was 100 mol%, over TS-2 only the conversion of 1-butene-3-ol and selectivity of transformation to organic compounds in relation to hydrogen peroxide were lower than for TS-1 (for about 19 mol% and 16 mol%, respectively). Moreover, the total conversion of hydrogen peroxide was almost the same for TS-1 and TS-2 catalyst. Definitively, we decide to take the TS-2 catalyst for optimization because the repeatability of its syntheses – was better than for the TS-1 catalyst.

As the main product of 1-butene-3-ol (1B3O) epoxidation with 30 wt% hydrogen over titanium silicalite TS-2 catalyst 1,2-epoxybutane-3-ol (1,2EB3O) is obtained. This compound is used in the synthesis of many drugs, especially against an HIV virus. On the other hand, the process of 1B3O epoxidation can be performed in the direction of two ethers: bis(3-methyl-1-propene) ether (2x1B3O ether) and 3-(3-methyl-1-propene)-3-methyl-1,2-epoxypropane ether (1B3Ox1,2EB3O ether).



The first of the ethers is obtained from two molecules of organic reagent (1B3O), the second one from the

Table 1. The best conditions established during the preliminary investigations the process of 1B3O epoxidation and values of main functions describing the process⁴⁻⁶

Parameters and main functions of the process	TS-1 ⁴	TS-2 ⁵	Ti-Beta ⁶
Temperature (°C)	20	20	20
Molar ratio 1B3O/H ₂ O ₂	1	1	1
Methanol content (wt %)	80	80	40
TS-2 content (wt %)	3	5	3
Reaction time (h)	3	5	5
S _{epoxide/1B3O} (mol %)	100	100	69
S _{1,2,3-butanetriol/1B3O} (mol %)	0	0	31
C _{1B3O} (mol %)	82	63	85
C _{H₂O₂} (mol %)	97	96	98
S _{org.comp./H₂O₂} (mol %)	84	68	86

*C_{1B3O} – conversion of 1B3O, C_{H₂O₂} – conversion of H₂O₂, S_{org.comp./H₂O₂} – selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed

molecule of 1B3O and the molecule of the product of 1B3O epoxidation – 1,2EB3O or eventually by the epoxidation of 2x1B3O ether. These ethers have a lot of applications and, for example, can be used as additives for the obtained polyester and alkyd resins and also as thickeners for polyurethanes and polyacrylates⁷⁻¹⁰.

The aim of this work was the optimization of 1B3O epoxidation process in the direction of 2x1B3O ether and 1B3Ox1,2EB3O ether as the main products. The influence of the technological parameters (temperature, the molar ratio of 1-butene-3-ol/H₂O₂, the concentration of methanol in reaction mixture, the concentration of TS-2 in reaction mixture and the reaction time) on the selectivity of bis(3-methyl-1-propene) ether and 3-(3-methyl-1-propene)-3-methyl-1,2-epoxypropane ether in relation to 1B3O consumed was described in this paper. The optimum conditions of 2x1B3O ether and 1B3Ox1,2EB3O

ether obtaining were established by the mathematical method of experiments design (rotatable-uniform design) and after analyses of the layer drawings made for each ether individually.

EXPERIMENTAL

In the process the following raw materials were used: 1-butene-3-ol (1B3O) (98%, Fluka), hydrogen peroxide (30 wt%, POCh Gliwice) and methanol (analytical grade, POCh, Gliwice).

The TS-2 catalyst was obtained by the method described by Reddy et al.² The catalyst was characterised using the following methods of instrumental analysis: XRD (X-ray diffraction spectroscopy), XRF (X-ray fluorescence spectroscopy), IR (infrared spectroscopy), UV-VIS (ultra-violet-visible spectroscopy) and SEM (scanning electron microscopy). XRD pattern of the obtained TS-2 catalyst

Table 2. Levels of the examined factors

Level	Coded factor	Temperature (°C)	Molar ratio 1B3O/H ₂ O ₂	Methanol content (wt. %)	TS-2 content (wt. %)	Reaction time (min)
	X _i	x ₁	x ₂	x ₃	x ₄	x ₅
Basic	0	35	2.4	47	4.250	225.0
Higher	1	47	3.9	69	6.125	322.5
Lower	-1	22	1.6	26	2.375	127.5
Star higher	2	60	5.0	90	8.000	420.0
Star lower	-2	10	0.5	5	0.500	30.0

x₁, x₂, x₃, x₄, x₅ – independent factors

Table 3. Design matrix and experimental results

No.	X ₁	X ₂	X ₃	X ₄	X ₅	Z ₁	Z ₂
						(mol %)	
1	-1	-1	-1	-1	-1	0	0
2	1	-1	1	-1	-1	17	0
3	1	-1	-1	-1	1	2	0
4	1	-1	-1	1	-1	5	2
5	1	1	-1	-1	-1	0	0
6	-1	1	1	-1	-1	48	0
7	-1	1	-1	-1	1	0	0
8	-1	1	-1	1	-1	69	0
9	1	-1	1	1	1	29	0
10	-1	-1	-1	1	1	16	4
11	-1	-1	1	1	-1	33	0
12	-1	-1	1	-1	1	11	0
13	-1	1	1	1	1	46	0
14	1	1	-1	1	1	66	0
15	1	1	1	1	-1	29	0
16	1	1	1	-1	1	21	0
17	-2	0	0	0	0	21	0
18	2	0	0	0	0	52	0
19	0	-2	0	0	0	15	0
20	0	2	0	0	0	71	0
21	0	0	-2	0	0	11	3
22	0	0	2	0	0	15	0
23	0	0	0	-2	0	0	0
24	0	0	0	2	0	52	0
25	0	0	0	0	-2	46	0
26	0	0	0	0	2	46	0
27	0	0	0	0	0	50	0
28	0	0	0	0	0	51	0
29	0	0	0	0	0	51	0
30	0	0	0	0	0	54	0
31	0	0	0	0	0	58	0
32	0	0	0	0	0	51	0

confirmed the crystalline structure (MEL) of the catalyst and was the same as in literature^{11–13}. The content of titanium determined by XRF recalculated on TiO₂ was 0.40 wt%. The IR spectrum of the catalyst shows an absorption band at 960 cm⁻¹, whereas the UV-VIS spectrum shows a band at 220nm, which confirmed the incorporation of titanium into the crystalline structure of the catalyst. The morphology of the TS-2 catalyst was evaluated on the basis of SEM micrographs showing uniform crystals of about 2µm in length and 0.3 µm in width.

The process was carried out in the glass vials with the capacity of 12 cm³, equipped with a rubber septum and a capillary. The vials were located in a shaker holder and immersed in the water bath. The products were identified by GC-MASS analyses, performed on a Hewlett Packard 6890 apparatus equipped with a mass detector HP 5973 and using a capillary column HP 5MS (30 m x 250 µm x 0.25 µm). The products were quantitatively analysed by gas chromatography using a Focus apparatus with the flame-ionisation detector (FID) and a capillary column Quadrex (30 x 250 mm x 0.25 mm). The parameters of chromatographic separation were as follows: helium pressure 50 kPa, sensitivity 10, sample chamber temperature 150°C, detector temperature 250°C. The thermostat temperature was programmed in the following way: isothermally 40°C for 3 min, followed by an increase at the rate 10°C/min to 250°C, isothermally 250°C for 5 min, cooling to 60°C.

The unreacted hydrogen peroxide was determined iodometrically¹⁴. After performing the mass balance for each of the synthesis, the main functions characterizing the process such as the selectivity of transformation to 2x1B3O ether in relation to 1B3O consumed and the selectivity of transformation to 1B3Ox1,2EB3O in relation to 1B3O consumed were determined. These selectivities were calculated according to the following equation:

$$S_{\text{ether}/1\text{B3O}} = \frac{\text{amount of ether obtained}}{\text{amount of 1B3O consumed}} \times 100 \text{ [mol \%]}$$

An experimental design and the calculations were performed by applying a computer software Cadex:Esdet 2.2, furthermore layer drawings were plotted with the help of software Surfer 5.0 (all work at MS Windows XP Professional).

RESULTS AND DISCUSSION

The optimization of the technological parameters was performed according to the rotatable-uniform design^{15–18}. The plan was realized for five input variables $x_1 - x_5$, where: x_1 – temperature 10 – 60°C, x_2 – the 1B3O/ H₂O₂ molar ratio 0.5 – 5.0, x_3 – methanol concentration 5 – 90 wt.%, x_4 – TS-2 concentration 0.5 – 8.0 wt.% and x_5 – reaction time 30 – 420min. The real values of input variables $x_1 - x_5$ were recalculated into the normalized values. A universal experimental design with the values of normalized input variables in the dimensionless range [-2, 2] was achieved as a result of the normalization operation. The real and normalized input variables at the levels resulting from the experimental design are shown in Table 2. The response functions characterizing the process were: z_1 – the selectivity of transformation to 2x1B3O ether in relation to 1B3O consumed, z_2 – the selectivity

of transformation to 1B3Ox1,2EB3O ether in relation to 1B3O consumed. The design matrix of the experimental design and the experimentally determined values of the response functions $z_1 - z_2$ are shown in Table 3.

The influence of normalized independent factors ($X_1 \div X_5$) of the process on the values of the response functions were presented in the form of a polynomial of second order. The coefficients of the regression function for the normalized input variables (technological parameters) were determined by the least-squares method with the application of matrix calculations (Table 4). After the determination of function approximating the experimental results, a verification of an adequacy of this function was performed based on the Fisher-Snedecor test by a comparison with the critical value of $F(\alpha)$ taken from tables¹⁹. The relative errors of the approximation and the correlation coefficient R for the respective functions were calculated. In Table 3 the values of: S^2_{repeat} – variance of inaccuracy, f_{repeat} – freedom degrees number of variance of inaccuracy, S^2_{adeq} – variance of adequacy, f_{adeq} – freedom degrees number of variance of adequacy, R – coefficient of multiple correlation, Δz_{max} – the maximum error of approximation, are also provided. All the calculations were carried out for the significance level $\alpha=0.05$. The highest values of the response functions and corresponding to them the values of the technological parameters were summarized in Table 5.

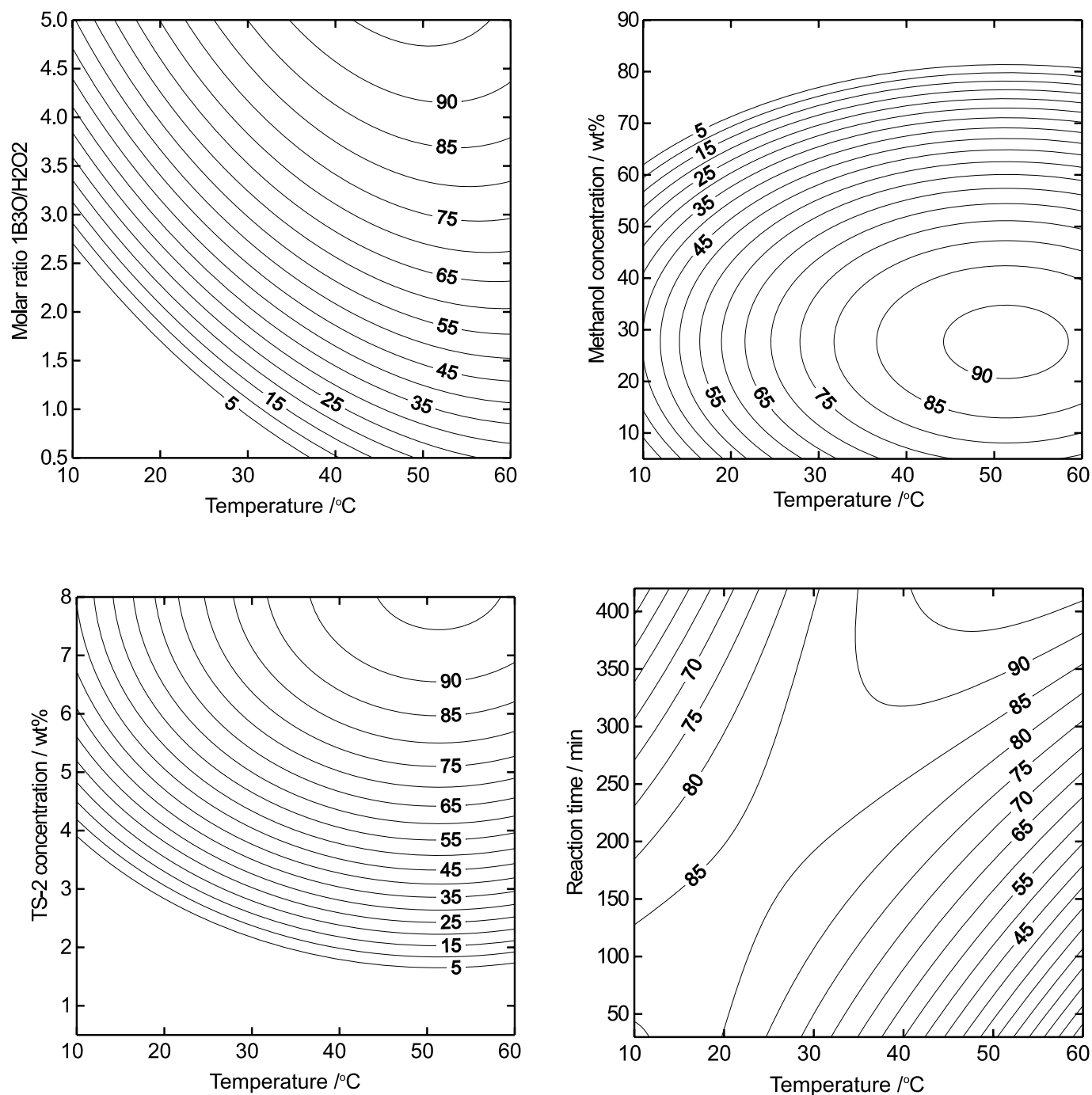
In order to definitely determine which values of the parameters are the optimum parameters for z_1 and z_2 functions, the analysis of each function should be performed. For this purpose the courses of function variations during the changes of two technological parameters

Table 4. Coefficients of the regression equation and results of statistic analysis

Coefficients	Z_1	Z_2
b_{00}	53.09	0.00
b_{01}	0.33	-0.08
b_{02}	11.50	-0.25
b_{03}	3.50	-0.50
b_{04}	12.50	0.25
b_{05}	-0.42	0.08
b_{11}	-4.72	0.00
b_{12}	-2.63	0.13
b_{13}	-1.86	0.13
b_{14}	-0.88	-0.13
b_{15}	9.00	-0.38
b_{22}	-2.97	0.00
b_{23}	-3.63	0.38
b_{24}	5.38	-0.38
b_{25}	-1.00	-0.13
b_{33}	-10.47	0.38
b_{34}	-7.13	-0.38
b_{35}	-1.75	-0.13
b_{44}	-7.22	0.00
b_{45}	3.25	0.13
b_{55}	-2.22	0.00
S^2_{repeat}	9.10	0
F_{repeat}	5	5
S^2_{adeq}	81.75	0.24
f_{adeq}	10	10
R	0.97	0.95
Δz_{max}	16.11	0.5

Table 5. Parameters determining maximum values of the response functions

	Unit	Functions	
		$S_{2 \times 1B3O \text{ ether}/1B3O}$	$S_{1B3O \times 1,2EB3O/1B3O}$
Values of the functions	mol %	100	11
Temperature	°C	46	18
Molar ratio 1B3O/H ₂ O ₂	–	4.6	0.6
Methanol concentration	wt. %	33	14
TS-2 concentration	wt. %	7.3	7.9
Reaction time	min	412	405

**Figure 1.** Layer drawings for the selectivity of transformation to bis(3-methyl-1-propene) ether in relation to 1B3O consumed

were plotted, maintaining the other ones' constant. The constant parameters determined the maximum of a given function.

The influence of the changes of the two selected technological parameters of the process on the selectivity of transformation to 2x1B3O ether in relation to 1B3O consumed (z_1) at the optimum values of the remaining

independent variables (factors) allowed to obtain the maximum of the function, was shown in Figure 1. Figure 1 shows that high temperatures (45 – 58°C) and also high molar ratios 1B3O/H₂O₂ (4.6 – 5.0) support the formation of 2x1B3O ether. At low temperature this ether can not be obtained. It is also clearly visible that high concentrations of solvent (methanol) are not beneficial for ob-

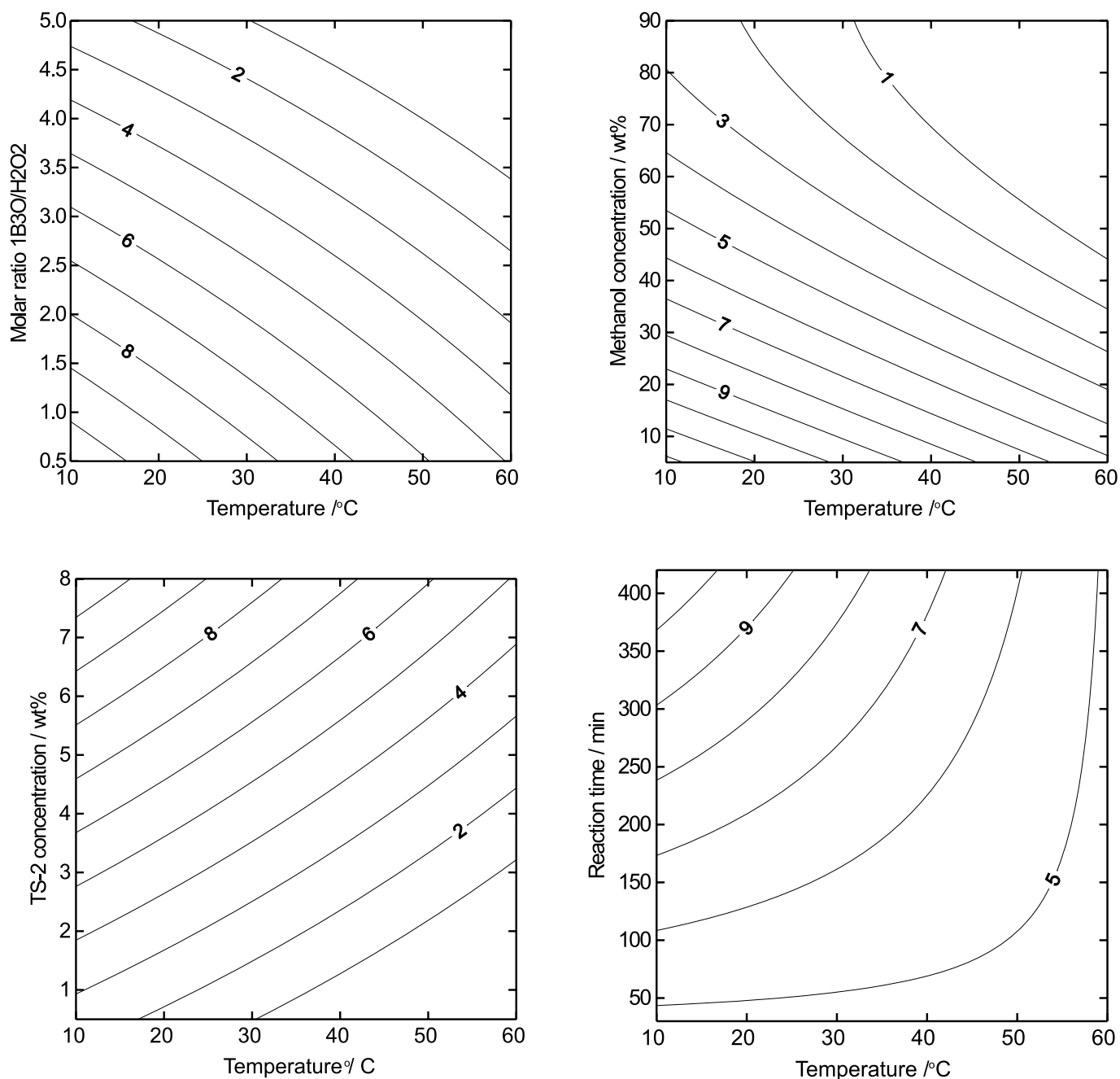


Figure 2. Layer drawings for the selectivity of transformation to 3-(3-methyl-1-propene)-3-methyl-1,2-epoxypropane ether in relation to 1B3O consumed

taining this ether (the concentrations of methanol 20 – 38 wt.% are the best). The concentrations of the catalyst in the reaction mixture have to be high (7.5 – 8.0 wt%) and a long reaction time (350 – 420 min) should be used to obtain this ether with high selectivity (about 100 mol%).

The influence of the changes of two selected technological parameters of the process on the selectivity of the transformation to 1B3Ox1,2EB3O ether in relation to 1B3O consumed (z_2) at the optimum values of the remaining independent variables (factors) allowed to obtain the maximum of the function, was shown in Figure 2. Figure 2 shows that very low temperatures (10 – 25°C) and also very low molar ratios 1B3O/H₂O₂ (0.5 – 1.5) are the most beneficial for the 1B3Ox1,2EB3O ether obtaining. Similarly to the first ether, also in the case of 1B3Ox1,2EB3O ether low methanol concentrations (2 – 22 wt.%), high TS-2 concentrations (6.5 – 8.0) and the long reaction time (310 – 420 min) are very beneficial.

The maximal selectivity of this ether is very small (11 mol%) in comparison with the selectivity of 2x1B3O ether (100 mol%). This phenomenon is probably connected with the structure of these compounds (spacious obstacle). Moreover, 1B3Ox1,2EB3O ether can be only obtained in reaction epoxidation of 2x1B3O ether or in etherification reaction from 1B3O and 1,2-epoxybutane-3-ol but these reactions are secondary reactions.

CONCLUSIONS

The presented results show that the most beneficial technological parameters for the selectivity of transformation to 2x1B3O ether in relation to 1B3O consumed are: temperature 45 – 58°C, molar ratio 1B3O/H₂O₂ = 4.6 – 5.0, methanol concentration 20 – 38 wt.%, catalyst concentration 7.5 – 8.0 wt.% and reaction time 350 – 420 min. However, for the selectivity of transformation to 1B3Ox1,2EB3O ether in relation to 1B3O consumed the

most beneficial are the following technological parameters: temperature 10 – 25°C, molar ratio $1\text{B}_3\text{O}/\text{H}_2\text{O}_2 = 0.5 - 1.5$, methanol concentration 5 – 22% wag., catalyst TS-2 concentration 6.5 – 8.0 wt.% and reaction time 310 – 420 min. The conversion at the presented parameters amounts to about 20% mol for the first function, but in the case of the second function reaches to 50 – 70% mol.

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