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Optimization of the Epoxidation of Rapeseed Oil with Peracetic Acid

Eugeniusz Milchert,* Anna Smagowicz, and Grzegorz Lewandowski

Institute of Organic Chemical Technology, West Pomeranian University of Technology, Szczecin, Pułaskiego10, PL 70-322 Szczecin

Abstract:

The epoxidation of rapeseed oil (RO) with peracetic acid generated *in situ* by the reaction of 30 wt % hydrogen peroxide and acetic acid has been studied. The optimization studies were performed by the application of statistical experimental design methodology with the utilization of a rotatable uniform design. Four parameters for the RO epoxidation process were studied: temperature, molar ratio of hydrogen peroxide to rapeseed oil, molar ratio of acetic acid to rapeseed oil, and reaction time. The output of the process was described by five response functions: iodine number, epoxy number, conversion, yield, and the selectivity. The highest levels of all response functions, with the exception of the selectivity, were predicted for the same parameter values: temperature 65 °C, molar ratio of hydrogen peroxide to RO 11.1:1 mol/mol, molar ratio of acetic acid to RO 1.89:1 mol/mol, and the reaction time 6 h. In a confirmatory experiment, these conditions provided the epoxidized rapeseed oil with the yield of 59.3 mol %, and 83.7 mol % conversion of oil. The epoxy number of the product amounted to 0.1862 mol/100 g, whereas the iodine number was 0.0513 mol/100 g. The highest values of selectivity were predicted to require the use of different conditions: 51.5 °C, 9.7 equiv of H_2O_2, 0.63 equiv of AA, 6 h. These conditions gave the product with 99.2% selectivity. Epoxidized rapeseed oil is of high commercial importance as a plasticizer and stabilizer for plastics, ingredient of lubricants, polyol in manufacture of polyurethanes, and an intermediate for the synthesis of surfactants.

1. Introduction

Considerable amounts of epoxidized vegetable oils are currently utilized in the production of surfactants, emollients, and oleochemicals for polymers as the plasticizers and stabilizer agents. They are also used as the ingredients of lubricants, and polyols in polyurethane manufacture.

The most important epoxidized vegetable oil is soybean oil, and its worldwide production in 1999 amounted to about 200,000 mg.[1,2] Although, numerous data exist in the technical literature concerning the methods of the epoxidation of soybean oil[3−5] and rapeseed oil,[6] the data concerning the tropical oils such as palm or karanja oil have been published in a few references.

The epoxidized oils or the products of their transesterification with low-molecular weight alcohols are used as the plasticizers, particularly for the production of polyvinyl chloride. Moreover, they perform a function of polyvinyl chloride stabilizers.[1,2,7−9] The epoxidized oils improve the elasticity of plastics hence their importance in the manufacture of packing materials such as wrapping foils.[10] Due to the high reactivity of the oxirane ring, they are used as renewable raw materials for the manufacture of such intermediates as: alcohols, glycols, alkoxyalcohols, hydroxyesters, *N*-hydroxyalkylamides, mercaptoalcohols, hydroxynitriles, alkanolamines, and complex carbonyl compounds.[1,2,7] Many of these compounds have been used as oleochemicals in polymer production. Epoxidized vegetable oils are used for both the formation of thermosetting composites[11] and the coatings obtained by UV initiated cross-linking.[11,12] Epoxidized soybean oil functionalized with diamine is an excellent antioxidant, antifriction agent and bearing grease that reduce abrasive wear. Because of its amphiphilic character this oil is added to the base grease oils to improve their application properties.[13]

The objective of these studies was to determine the influence of the technological parameters on the course of the epoxidation process of rapeseed oil.

2. Epoxidation of Vegetable Oils

The epoxidation of vegetable oils can be carried out with carboxylic peracids in an acidic environment with organic hydroperoxides or with hydrogen peroxide in the presence of metals of variable valence.[8]

2.1. Epoxidation with Peracids. A widely used commercial method of the epoxidation of vegetable oils relies on the application of previously prepared carboxylic peracids or generated *in situ* carboxylic peracids.[8] This method is also used to introduce the epoxy groups to replace the ethylene-type

* Corresponding author. Telephone: +48 914494855. Fax: +48 914494365. E-mail: Eugeniusz.Milchert@zut.edu.pl.

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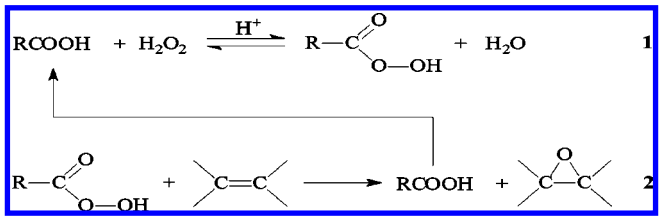

Figure 1. **The main reactions of epoxidation of the rapeseed oil with peracids generated *in situ*.**

double bonds in the different kinds of more complex compounds, including those of natural origin, occurring as the intermediates for the organic synthesis.[14]

During the epoxidation using *in situ* generated peracids, two reactions proceed simultaneously, a reversible reaction of the formation of peracid from hydrogen peroxide and acid (1), and the epoxidation of the unsaturated compound (2) (Figure 1).[15,16]

The acid formed in the reaction 2 in Figure 1 reacts again with the hydrogen peroxide to form a peracid. The rate-limiting stage of the process is the formation of peracid. The course of reaction 1 is accelerated by strong mineral acids, most often by sulphuric acid.[3,7] The selection of the process parameters, so that the epoxidation will proceed faster than the formation of peracid, is an important issue. Otherwise, generated peracid may decompose ineffectively under the reaction conditions, and the yield of epoxidation recalculated on the consumed hydrogen peroxide will be small.[15,16] The reaction environment contains water, mineral (catalyst), and organic acids, which may cause the decomposition of the epoxy groups due to the hydrolysis or acylation (Figure 2).[4,5,15] This decreases the yield of epoxidized oil.

Various methods can be used to limit the course of these reactions. For this purpose the sulphuric acid is replaced by the cation exchangers, e.g., sulfonated styrene−divinylbenzene copolymer.[8]

The epoxidation method with *in situ* generated peracetic acid has the greatest technological importance. This method is the cheapest; moreover, the separation of aqueous solution of acetic acid from the epoxidized oil can be easily performed. On an industrial scale this method is used for the epoxidation of soybean oil.[15,17]

The epoxidation of previously generated peracids also has technical importance.[15,18,19] The peracetic acid of various degrees of purity can be used for a wide range of applications. This peracid is obtained in the reaction of acetic acid and hydrogen peroxide in the presence of sulphuric acid. The disadvantage of this method is a difficulty in the preparation of relatively pure (free from acetic acid) and concentrated peracid.[15] The peracids with the enhanced purity exhibit a higher reactivity, but they always contain smaller or larger amounts of water, a mineral acid (most of it H_2SO_4), and carboxylic acid.

The advantages of the epoxidation with organic peracids are the low costs of synthesis of peracids themselves, particularly peracetic acid, and the fact that the epoxidation with peracids is an irreversible reaction (if the acid does not contain admixtures). The drawback of this method is the strongly exothermic character of the reaction and the necessity of operations with concentrated solutions of peracids. As a consequence, this may cause an explosion. The above problems imply the necessity for strict control of temperature and the epoxidation time.[8] The other peracids such as formic, propionic, butyric, benzoic, monophthalic, chloroacetic, perfluoroacetic are used in addition to the peracetic acid.[8,20]

3. Experimental Section

3.1. Materials. Rapeseed oil (RO), manufactured by the Fat Industry Co., Warsaw, was used in the studies. The molar mass of oil calculated on the basis of percentage content of carboxylic acids was 882 g/mol. The following raw materials were used in the syntheses: glacial acetic acid (AA) (99.5 wt % from POCh Gliwice), hydrogen peroxide (30 wt % aqueous solution from POCh Gliwice), sulphuric acid(VI) (98 wt % from Chempur).

3.2. Testing Equipment. The epoxidation of rapeseed oil was carried out in a four-neck flask, equipped with a thermometer, dropping funnel, stirrer and a reflux condenser. The flask was placed in a thermostatic water bath, whose temperature was controlled within ±0.5 °C.

3.3. Epoxidation Procedure. The epoxidation of RO was carried out with the use of the organic peracid, generated *in situ* by the reaction of 30 wt % solution of hydrogen peroxide and appropriate carboxylic acid. The following technological parameters were varied during the epoxidation of rapeseed oil: temperature, molar ratios of reagents, stirring speed, and the reaction time. The amounts of starting materials were changed, depending on the molar ratio of H_2O_2/AA/RO. For the reaction on the basic level the reactor was charged with RO (140.2 g), acetic acid (10.5 g) and concentrated sulphuric acid(VI) (3.9 g) as a catalyst. The 61.5 cm^3 of 30 wt % hydrogen peroxide was added to this solution with the speed enabling to maintain a constant reaction temperature.

In some of the experiments the reaction flask was cooled with water. Depending on the amounts of reagents and applied process parameters, the introduction of hydrogen peroxide lasted for 10−40 min. After separation of the reaction mixture the resulting organic layer was neutralized with a 20 wt % solution of sodium hydroxide and washed with distilled water (5 × 450 cm^3 of water per 0.16 mol RO). The washed organic layer was dried with anhydrous magnesium sulphate(VI). After performing the mass balance, the iodine and epoxy number was determined. On the basis of these numbers it was calculated the conversion of RO, the yield and the selectivity of transformation to epoxidized oil. The conversion of hydrogen peroxide was calculated after determination of its concentration in the water layer in accordance with standard iodometric method.

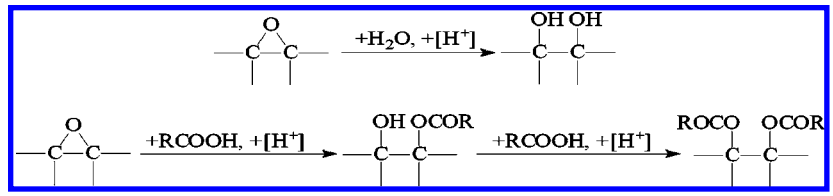

Figure 2. **Side reactions of the epoxidation process.**

Table 1. **Content of fatty acids in the rapeseed (RO) oil used**

A^a:B^b	fatty acid	formula	concentration of carboxylic acid in the RO %
14:0	myristic	$CH_3(CH_2)_{12}COOH$	0.1
16:0	palmitic	$CH_3(CH_2)_{14}COOH$	4.5
16:1	oleopalmitic (9 *cis*)	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$	0.4
18:0	stearic	$CH_3(CH_2)_{16}COOH$	2.1
18:1	oleic (9 *cis*)	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	64.5
18:2	linolic (9 *cis*, 12 *cis*)	$CH_3(CH_2)_3(CH_2CH{=}CH)_2(CH_2)_7COOH$	18.3
18:3	linolenic (9 *cis*, 12 *cis*, 15 *cis*)	$CH_3(CH_2CH{=}CH)_3(CH_2)_7COOH$	6.8
20:0	arachidic	$CH_3(CH_2)_{18}COOH$	0.8
20:1	gadoleic (9 *cis*)	$CH_3(CH_2)_9CH{=}CH(CH_2)_7COOH$	1.3
22:0	behenic	$CH_3(CH_2)_{20}COOH$	0.4
22:1	erucic (13 *cis*)	$CH_3(CH_2)_7CH{=}CH(CH_2)_{11}COOH$	0.8

Theoretical maximum oxirane oxygen[c], **OO = 5.02 [%/100 g RO]**

[a] Number of carbon atoms. [b] Number of unsaturated bonds. [c] Calculated as $OO = [IN_{be}/(100 + (IN_{be}/A_O))]100A_O$, where $IN_{be} = 0.314$ mol/100 g RO, $A_O = 16$ g/mol is the molecular mass of oxygen.

3.4. Analytical Methods. The iodine number (IN) was calculated in accordance with the required standards,[21] according to the following equation:

$$IN = \frac{0.1269(V_1 - V_2)c_{Na_2S_2O_3}}{m_1} \cdot 100 \cdot \frac{1}{2A_I}$$

where

V_1 is the volume of sodium thiosulphate(VI) solution used to titrate blank sample [cm^3],

V_2 is the volume of sodium thiosulphate(VI) solution used to titrate right sample [cm^3],

$c_{Na_2S_2O_3}$ is the concentration of sodium thiosulphate(VI) solution [mol/dm^3],

m_1 is the mass of the sample [g],

0.1269 is the mass of iodine corresponding to 1 cm^3 of sodium thiosulphate(VI) solution at concentration $c = 1$ mol/dm^3[g],

A_I is the molecular mass of iodine [g/mol] equal to 126.9 g/mol.

The epoxy number (EN) was calculated in accordance with the required standards,[22] according to the following equation:

$$EN = \frac{(V_4 - V_3)c_{HClO_4}100}{1000m_2}$$

where

V_3 is the volume of chloric acid(VII) solution used to titrate blank sample [cm^3],

V_4 is the volume of chloric acid(VII) solution used to titrate right sample [cm^3],

c_{HClO_4} is the concentration of chloric acid(VII) solution [mol/dm^3],

m_2 is the mass of sample [g].

Chemical Composition of Oil. In Table 1 are presented the relative content of fatty acids in the used rapeseed oil. The determination was performed in accordance with the international standards.[23]

3.5. Magnitudes Characterizing Process. As the magnitudes characterizing process of epoxidation were also used:

Conversion of Rapeseed Oil.

$$C = \frac{IN_{be} - IN_{ae}}{IN_{be}} \cdot 100\%$$

where

C is the conversion of rapeseed oil, calculated from the iodine number,

IN_{be} is the iodine number of rapeseed oil before epoxidation, 0.314 mol/100 g RO,

IN_{ae} is the iodine number of rapeseed oil after epoxidation [mol/100 g].

Yield.

$$Y = \frac{EN}{EN_{max}} \cdot 100\%$$

where

Y is the field of epoxidized rapeseed oil, calculated from the epoxy number,

EN is the epoxy number of rapeseed oil after epoxidation [mol/100 g],

EN_{max} is the maximum value of the epoxy number of rapeseed oil, calculated from the number of unsaturated bonds before the epoxidation, $EN_{max} = IN_{be} = 0.314$ mol/100 g.

Selectivity.

$$S = \frac{EN}{IN_{be} - IN_{ae}} \cdot 100\%$$

where

S is the selectivity of the epoxidation process.

4. Results and Discussion

In the first stage of studies the course of the epoxidation was compared in the presence of performic acid and peracetic

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Table 2. **Independent factors (parameters) and the ranges of their changes at the individual levels**

	level coded factors	temperature (°C)	H_2O_2/RO molar ratio (mol/mol)	AA/RO molar ratio (mol/mol)	reaction time (h)
level	x_i	X_1	X_2	X_3	X_4
star lower	−2	35.0	4.7	0.630	2.0
lower	−1	42.5	6.3	0.945	3.0
basic	0	50.0	7.9	1.260	4.0
higher	1	57.5	9.5	1.575	5.0
star higher	2	65.0	11.1	1.890	6.0

acid. The peracetic acid was selected for further studies because it allowed to achieve the high values of epoxy numbers and in the presence of this acid the process proceeded in a safety way.

On the basis of the preliminary studies[24] the ranges of changes of the particular parameters of process were established.

Optimization of the epoxidation process of rapeseed oil. The optimization of the technological parameters was performed based on the mathematical method of experimental design. The rotatable uniform design was used. This design is a more informative in a comparison with the orthogonal design with regard to the permanent variance of inaccuracy of measurements, which undergoes variations in the case of orthogonal design. The influence of input variables X_1-X_4, in the form of real values on the response functions: IN, EN, C, Y, S in the epoxidation process of rapeseed oil was presented in the form of general regression equations, having the form of the second-order polynomial:

$$\hat{Y} = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i<j}^{k} b_{ij} X_i X_j + \sum_{i=1}^{k} b_{ii} X_i^2$$

where

$\hat{Y}$ is the dependent variable, which is one of the response functions (IN, EN, *C*, *Y*, *S*);

b_0, b_i, b_{ij}, b_{ii} are coefficients of the approximation function (regression equation) ($i, j = 1, ..., k$);

X_i, X_j are process parameters as independent factors in the real form ($i, j = 1, ..., k$);

k is the number of factors in the experimental design ($k = 4$).

The experimental design and the calculations of the values of functions describing the process were performed by computer applying the program Cadex:Esdet 2.2[25,26] The real and coded values of input variables (parameters) at the levels resulting from the experimental design are presented in Table 2.

The matrix of experimental design (in real values) and experimentally determined values of the response functions: iodine number (IN) of epoxidized rapeseed oil, epoxy number (EN) of epoxidized rapeseed oil, rapeseed oil conversion (*C*), yield of epoxidized rapeseed oil (*Y*), the selectivity of transformation to epoxidized rapeseed oil (*S*) are shown in Table 3.

Calculated coefficients of the regression equation and the results of statistic analysis are presented in Table 4. The statistical parameters of models inserted in Table 4 were generated on the basis of the following equations:

Variance of Inaccurancy (S^2).

Table 3. **Design matrix and obtained experimental results**

lp.	X_1 temp. (°C)	X_2 H_2O_2/RO	X_3 AA/RO	X_4 time (h)	IN (mol/100 g RO)	EN (mol/100 g RO)	*C* (mol %)	*Y* (mol %)	*S* (mol %)
1	42.5	6.3	0.945	3.0	0.1606	0.1002	48.85	31.92	65.34
2	57.5	6.3	0.945	3.0	0.1611	0.1301	48.69	41.42	85.06
3	42.5	9.5	0.945	3.0	0.1647	0.1237	47.56	39.38	82.80
4	57.5	9.5	0.945	3.0	0.1509	0.1621	51.96	51.64	99.38
5	42.5	6.3	1.575	3.0	0.1845	0.1119	41.23	35.63	86.42
6	57.5	6.3	1.575	3.0	0.1738	0.1401	44.64	44.61	99.92
7	42.5	9.5	1.575	3.0	0.1781	0.1355	43.27	43.14	99.71
8	57.5	9.5	1.575	3.0	0.1429	0.1711	54.50	54.50	99.99
9	42.5	6.3	0.945	5.0	0.1946	0.1092	38.04	34.79	91.46
10	57.5	6.3	0.945	5.0	0.1785	0.1351	43.15	43.03	99.72
11	42.5	9.5	0.945	5.0	0.1832	0.1305	41.67	41.57	99.77
12	57.5	9.5	0.945	5.0	0.1570	0.1569	50.01	49.97	99.91
13	42.5	6.3	1.575	5.0	0.1760	0.1341	43.96	42.69	97.12
14	57.5	6.3	1.575	5.0	0.1624	0.1513	48.27	48.17	99.79
15	42.5	9.5	1.575	5.0	0.1553	0.1495	50.55	47.61	94.17
16	57.5	9.5	1.575	5.0	0.1241	0.1832	60.48	58.35	96.48
17	35	7.9	1.260	4.0	0.1825	0.1099	41.87	34.99	83.58
18	65	7.9	1.260	4.0	0.1525	0.1566	51.42	49.89	97.02
19	50	4.7	1.260	4.0	0.1851	0.1165	41.06	37.10	90.35
20	50	11.1	1.260	4.0	0.1458	0.1675	53.55	53.34	99.60
21	50	7.9	0.630	4.0	0.1865	0.1167	40.61	37.17	91.53
22	50	7.9	1.890	4.0	0.1567	0.1481	50.11	47.15	94.10
23	50	7.9	1.260	2.0	0.1677	0.1281	46.60	40.80	87.55
24	50	7.9	1.260	6.0	0.1569	0.1569	50.03	49.97	99.89
25	50	7.9	1.260	4.0	0.1637	0.1461	47.86	46.53	97.21
26	50	7.9	1.260	4.0	0.1679	0.1458	46.54	46.44	99.79
27	50	7.9	1.260	4.0	0.1695	0.1434	46.02	45.66	99.21
28	50	7.9	1.260	4.0	0.1672	0.1435	46.76	45.71	97.75
29	50	7.9	1.260	4.0	0.1677	0.1462	46.59	46.57	99.95
30	50	7.9	1.260	4.0	0.1639	0.1428	47.79	45.49	95.20
31	50	7.9	1.260	4.0	0.1640	0.1410	47.78	44.89	93.95

$$S^2 = \frac{1}{f_1} \cdot \sum_{\nu=1}^{n_0} [Y^{(\nu)} - \bar{Y}^{(0)}]^2$$

where

S^2 is the variance of inaccuracy;

$Y^{(\nu)}$ is the experimental value of the response function in the ith experiment in the design centre ($\nu = 1, ..., n_0$);

$\bar{Y}^{(0)}$ is the average experimental value of the response function in the design centre ($\nu = 1,. .., n_0$);

$$\bar{Y}^{(0)} = \frac{1}{n_0} \sum_{\nu=1}^{n_0} Y^{(\nu)}$$

f_1 is the number of degrees of freedom of repeatability variance: $f_1 = n_0 - 1$;

n_0 is the number of experiments in the design centre.

Variance of the Adequacy (S_a^2).

$$S_a^2 = \frac{1}{f_2} \cdot \left\{ n_0[\bar{Y}^{(0)} - \hat{Y}^{(0)}]^2 + \sum_{u=1}^{N-n} [Y^{(u)} - \hat{Y}^{(u)}]^2 \right\}$$

where

S_a^2 is the variance of the adequacy;

$\bar{Y}^{(0)}$ is the average experimental value of the response function in the design centre ($\nu = 1, ..., n_0$);

$$\bar{Y}^{(0)} = \frac{1}{n_0} \sum_{\nu=1}^{n_0} Y^{(\nu)}$$

where

$\hat{Y}^{(0)}$ is the value of the response function in the design centre calculated by means of the regression equation;

$Y^{(u)}$ is the experimental value of the response function in the uth experiment ($u = 1, ..., N$ is n_0);

$\hat{Y}^{(u)}$ is the value of the response function in the uth experiment calculated by means of the regression equation ($u = 1, ..., N - n_0$);

f_2 is the number of degrees of freedom of variance of the adequacy: $f_2 = N - N_b - 1$;

N is the total number of experiments in the experimental design: $N = 20$;

N_b is the number of coefficients in the regression equation ($N_b = 15$).

Coefficient of Multidimensional Correlation ($R(\alpha)$).

$$R = \left[\frac{\sum_{u=1}^{n} (\hat{Y}^{(u)} - \bar{Y})^2}{\sum_{u=1}^{n} (Y^{(u)} - \bar{Y})^2} \right]^{\frac{1}{2}} \quad (1)$$

where

$\hat{Y}^{(u)}$ is the value of the response function in the uth experiment calculated by means of the regression equation ($i = 1, ..., n$);

$Y^{(u)}$ is the experimental value of the response function in the uth experiment ($u = 1, ..., n$);

$\bar{Y}$ is the average experimental value of the response function in the experimental design;

$$\bar{Y} = \frac{1}{n} \sum_{u=1}^{n} Y^{(u)}$$

(u)= system of the design of experiments;

α is the assumed level of significance, $\alpha = 0.05$ *R.*

The studies of the epoxidation of rapeseed oil with peracetic acid generated *in situ* allowed to determine the optimal values of functions describing the process and corresponding to them parameters. The optimization of the regression functions was performed numerically applying the Gauss−Seidel and Box

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

	iodine number	epoxy number	conversion	yield	selectivity
coefficient	Y_1	Y_2	Y_3	Y_4	Y_5
$\mathbf{b_0}$	−0.22063214000000	−0.194592150000	172.792009000000	−60.9924017000	−391.5121910000
$\mathbf{b_1}$	0.00321812996000	0.005907531420	−1.113216520000	1.9132354500	6.6660254600
$\mathbf{b_2}$	0.03045305520000	0.004708542600	−9.812775530000	1.1245535700	23.4612630000
$\mathbf{b_3}$	0.16995642000000	0.064345356200	−53.626257800000	20.0799674000	146.8411870000
$\mathbf{b_4}$	0.07006752230000	0.014107328900	−22.432936400000	4.4516279200	53.1436719000
$\mathbf{b_{11}}$	0.00000373015873	− 0.000043042328	−0.000621428571	−0.0139640212	−0.0305407407
$\mathbf{b_{12}}$	−0.00033854166700	0.000171875000	0.110572917000	0.0550000000	−0.1293750000
$\mathbf{b_{13}}$	−0.00092592592600	− 0.000132275132	0.296031746000	− 0.0486772487	−0.6862433860
$\mathbf{b_{14}}$	−0.00022500000000	−0.000241666667	0.073416666700	−0.0770000000	−0.3058333330
$\mathbf{b_{22}}$	−0.00016217912900	−0.000164504278	0.050798688600	−0.0353422619	−0.2145182290
$\mathbf{b_{23}}$	− 0.00706845238000	0.000124007936	2.260664680000	0.1364087300	−4.1145833300
$\mathbf{b_{24}}$	− 0.00191406250000	− 0.000742187500	0.601953125000	− 0.2445312500	−1.6757812500
$\mathbf{b_{33}}$	0.01093294460000	− 0.026919939100	− 3.589875100000	− 8.6215791400	− 10.9767364000
$\mathbf{b_{34}}$	− 0.02757936510000	0.008531746030	8.692460320000	2.7658730200	− 11.2619048000
$\mathbf{b_{44}}$	− 0.00116517857000	− 0.000171130952	0.382544643000	− 0.0492261905	− 0.8629166670
$R(\alpha)$	0.9778	0.9932	0.9728	0.9933	0.9644
S^2	0.000004905	0.00000381	0.5589	0.4032	5.361
S^2_a	0.00001726	0.000008717	2.156	0.8704	5.957
F	3.5193	2.2881	3.8569	2.1586	1.1112
$F(\alpha)$	3.9717	3.9717	3.9717	3.9717	3.9717

$R(\alpha)$ is coefficient of multidimensional correlation, S^2 is variance of inaccuracy for freedom degree number of variance of inaccuracy $f_1 = 6$, S^2_a is variance of adequacy for freedom degree number of variance of adequacy $f_2 = 15$, F is Fisher−Snedecor test value, $F(\alpha)$ is the critical value of the Fisher−Snedecor test.

Table 5. **Optimal parameters of the response functions (IN, EN, *C*, *Y*, *S*) and the results of confirmatory experiments**

parameter	IN (mol/100 g RO)	EN (mol/100 g RO)	*C* (mol %)	*Y* (mol %)	*S* (mol %)
temperature (°C)	65	65	65	65	51.5
molar ratio H_2O_2/RO (mol/mol)	11.1	11.1	11.1	11.1	9.7
molar ratio AA/RO (mol/mol)	1.890	1.890	1.890	1.890	0.630
reaction time (h)	6	6	6	6	6
optimal values of the response function (predicted)	0.0268 ± 0.0134^a	0.2069 ± 0.0118	91.0 ± 4.5	66.2 ± 3.8	$107.5 \pm 14{,}0$
values of the response function (experimental)	0.0513	0.1862	83.7	59.3	99.2

[a] Minimal value for IN function.

methods with the use of the computer program Cadex:Esdet 2.2.[25,27] Both methods resulted in the same optimum values of the independent variables for a given function. The maximum values of each of the response functions calculated on the basis of the regression function, and the corresponding optimum parameters as well as the results of confirmatory experiments are shown in Table 5. For the same values of the technological parameters: temperature 65 °C, the H_2O_2/RO molar ratio 11.1 mol/mol, the AA/RO molar ratio 1.89 mol/mol, and reaction time 6 h, the functions IN, EN, *C*, *Y* achieve the optimal values. The selectivity of epoxidation at these parameters amounts 50.3 mol % and is not an optimal value. The parameters allowed to achieve the maximum selectivity of transformation are presented in Table 5. However, significant decreases in the values of functions IN, EN, *C*, and *Y* take place at these parameters.

A graphical presentation of the influence of the individual technological parameters on the functions describing the epoxidation process of rapeseed oil is shown in Figures 3−7. The charts present the influence of one independent variable on the levels resulting from the experimental design, while the remaining independent variables (parameters) were established at the optimal levels.

The influence of process parameters $X_1 \div X_4$ (temperature, the H_2O_2/RO molar ratio, the AA/RO molar ratio, reaction time) on the value of iodine number is presented in Figure 3. The values of the parameter under study were established on the characteristic levels resulting from the experimental design (coded factor - Table 2). This chart indicates a significant influence of all studied parameters. An increase of value of each parameter in the range from $-\alpha$ to $+\alpha$ causes a decrease of iodine number in a comparative manner. The largest influence has the AA/RO molar ratio, whereas the influence of the H_2O_2/RO molar ratio, reaction time, and temperature is slightly smaller. In the upper ranges of changes of studied parameters $+\alpha$, the iodine number assumes the lowest and constant value for each parameter.

The influence of studied parameters on the values of epoxy number is shown in Figure 4. The following parameters: temperature, the H_2O_2/RO molar ratio, the AA/RO molar ratio, and the reaction time were also established on the characteristic

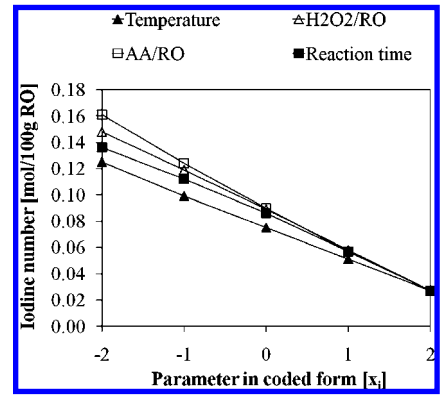

Figure 3. **Influence of the parameters (in coded form) on the values of iodine number.**

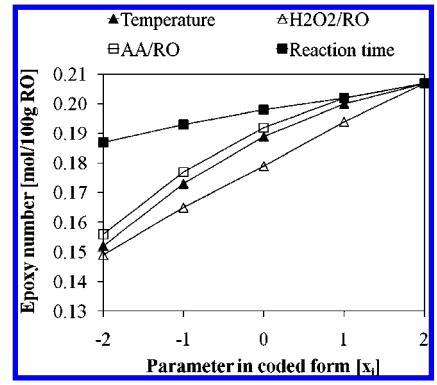

Figure 4. **Influence of the parameters (in coded form) on the values of epoxy number.**

levels resulting from the experimental design. A significant influence of all studied parameters is also observed in this case. The reaction time has the smallest influence on the value of epoxy number. The remaining parameters influence in a comparative degree. The influence of the molar ratio of hydrogen peroxide to rapeseed oil (H_2O_2/RO) is slightly larger than the influence of the molar ratio of acetic acid to rapeseed oil (AA/RO) and temperature. The influence of parameters on the values of epoxy number is the largest on a level $\alpha = -2$.

The influence of considered parameters on the conversion of rapeseed oil in the characteristic points of experimental design (coded factor - Table 2) is shown in Figure 5. Each of the parameters has a different influence on the degree of RO conversion. The influence of process temperature is the smallest. A slightly larger influence is the reaction time and the H_2O_2/RO molar ratio, whereas the influence of the AA/RO molar ratio is even larger.

The influence of parameters on the yield of epoxidized rapeseed oil is presented in Figure 6. The values of parameters were established on the levels resulting from the experimental

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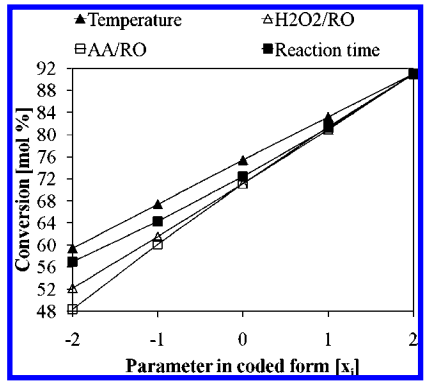

Figure 5. **Influence of the parameters (in coded form) on the conversion of rapeseed oil.**

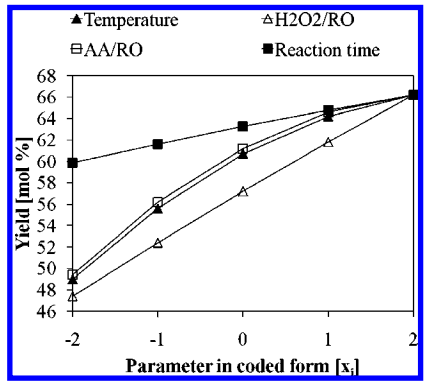

Figure 6. **Influence of the parameters (in coded form) on the rapeseed oil yield.**

design (coded factor - Table 2). The largest influence on the yield of epoxidized rapeseed oil has the molar ratio of hydrogen peroxide to oil, whereas the smallest influence has the reaction time. The temperature and the molar ratio of acetic acid to oil influence in an identical manner.

The influence of parameters with characteristic values and resulting from the experimental design on the selectivity of transformation to epoxidized rapeseed oil was presented in Figure 7. All the parameters are significant in the course of changes of the selectivities of transformation to epoxidized rapeseed oil. A decrease in the selectivity along with an increase in the AA/RO molar ratio is most characteristic in this case, particularly after exceeding of the value of AA/RO = 1.260: 1. In that situation takes place the increase of the reaction rate of formed epoxy group with acetic acid and water. Glycols and hydroxyacetooxy derivatives of rapeseed oil are formed as a results of this reaction. The smallest changes of the selectivity occur in the case of the temperature higher than 57.5 °C. The H_2O_2/RO molar ratio higher than 7.9:1, practically do not influence on the change of selectivity. The largest and mutually contradictory changes take place in the case of AA/RO molar ratio and the reaction time. In the studied ranges of changes of parameters, the epoxidation proceeded the most selective in the bottom range of changes of AA/RO molar ratio and in the upper range of changes of the reaction time.

For the technological parameters determining the maximum values of function IN, EN, *C*, *Y* (Table 5) a value of the selectivity functions amounts only $S = 50.3$ mol %. The maximum value of the selectivity function ($S = 100$ mol %) occurs after the application of the following parameters:

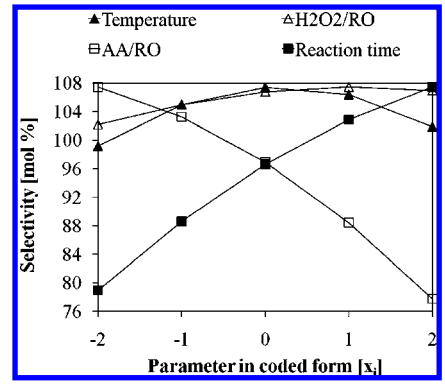

Figure 7. **Influence of the parameters (in coded form) on the selectivity of transformation to epoxidized rapeseed oil.**

temperature 51.5 °C, the H_2O_2/RO molar ratio 9.7 mol/mol, the AA/RO molar ratio 0.630 mol/mol, and reaction time 6 h. However, at these parameters the values of functions IN, EN, C, Y achieve a significantly lesser values than the optimal: IN = 0.1975 mol/100 g RO, EN = 0.1307 mol/100 g RO, $C = 36.6$ mol %, $Y = 41.4$ mol %.

For the parameters allowing to obtain the selectivity at a level of about $S = 80$ mol %, the values of the remaining functions: IN, EN, *C*, *Y* were calculated from the regression equation changing successively one parameters: temperature, the AA/RO molar ratio, the H_2O_2/RO molar ratio. It was found that the smallest deviations of values for the functions IN, EN, *C* and *Y* from their optimal values occur after the applications of the following parameters: temperature 65 °C, the H_2O_2/RO molar ratio 11.1 mol/mol, the AA/RO molar ratio 1.200 mol/mol, and reaction time 6 h. Thus, the function values amount: IN = 0.0961 mol/100 g RO, EN = 0.1896 mol/100 g RO, $C = 69.1$ mol %, $Y = 60.4$ mol %. The selectivity equal to 80 mol % is also achieved at the molar ratio of H_2O_2/RO = 6.0 and at the remaining parameters determined as the optimal for the functions: IN, EN, *C*, *Y* (Table 5) or at temperature 35 °C and the remaining parameters also maintained at the optimum level. However, for the last two cases the differences between the values of functions IN, EN, *C*, *Y* and the optimal value are larger.

In all experiments the hydrogen peroxide conversion was high and amounted to 98−100 mol %. The remaining amount of H_2O_2 is then decomposed to water and oxygen.

5. Conclusions

The studies of the epoxidation of rapeseed oil with peracetic acid predicted that the same values of temperature (65 °C), molar ratio of hydrogen peroxide to oil (11.1:1 mol/mol), molar ratio of acetic acid to oil (1.89:1 mol/mol), and reaction time (6 h), would give the best values of four of the response functions describing the process: IN, EN, *C*, *Y*. Under these conditions the iodine number (IN) was 0.0513 mol/100 g RO, the epoxy number (EN) was 0.1862 mol/100 g RO, the conversion of oil (*C*) was 83.7 mol %, and the yield of epoxidized oil (*Y*) was 59.3 mol %. While these results are poorer than predicted by the response surface model, they are better than any obtained at the 31 design points and thus represent a significant improvement to the process. The highest

selectivity in the transformation to epoxidized oil (S = 99.2 mol %, vs a prediction of 107.5 mol %) was achieved at temperature 51.5 °C, at the H_2O_2/RO molar ratio 9.7:1 mol/mol, at the AA/RO molar ratio 0.63:1 mol/mol, after the time of 6 h.

Epoxidized rapeseed oil is obtained with the selectivity of 80 mol % after the application of the following parameters: temperature 65 °C, the molar ratio of hydrogen peroxide to oil 11.1: 1 mol/mol, the molar ratio of acetic acid to oil 1.200: 1 mol/mol, the reaction time 6 h.

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