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CATALYSTS FOR PROPENE OXIDATION  
TO ACRYLIC ACID

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*Catalysts used in industry represent, in many cases, multicomponent compounds and/or their mixtures therefore. The catalytic properties depend not only on a suitable selection of elements but also on the way of preparation. To optimize this chemical process, a great many different parameters have to be taken into account. It is very useful to utilize the methods of mathematical statistics for effective research. This paper shows the use of the Plackett-Burman statistical block in exploring the significant variable parameters of preparing multicomponent oxide catalysts for the oxidation of propene and acrolein.*

### Introduction

At present the catalytic oxidation of propene with atmospheric oxygen in the gaseous phase represents a most prospective method of the preparation of acrylic acid and its esters. The process is performed in two stages. In the first reactor, acrolein and/or a mixture of acrolein and acrylic acid is obtained. The optimum temperature of oxidation is 570 to 600 K, and the gas phase of volume composition 5 - 8 % propene, 20 - 40 % water vapour in air is treated. In the second reactor, acrolein is oxidized at 510 - 540 K to acrylic acid. In both cases, multicomponent oxide catalysts are employed of which the first is based on

molybdenum and bismuth and the second on molybdenum and vanadium. It is economically advantageous to realize the process without isolating the intermediate products after the first oxidation. By condensing the products of the second reactor, a dilute solution (about 30 %) of acrylic acid is obtained from which the acid is separated by combined extraction and distillation. The esterification is carried out in the presence of strong acid catalysts most often *p*-methylbenzenesulfonic acid and cation exchange resins. Methyl, ethyl, *n*-butyl, and 2-ethylhexyl acrylates are produced industrially in ton amounts.

With respect to the complete dependence of the whole ester production on the oxidation catalysts, great attention has been paid to their development and research. Excellent activity and selectivity cannot be attained for these polycomponent catalysts only by finding the optimum molar ratios of individual metals, but it is also necessary to choose the corresponding conditions of preparation which ensure the formation of active crystallographic modifications and texture properties. Further it is necessary to realize that before transferring newly developed catalyst from laboratory to industrial scale, the different conditions in the two arrangements must usually be verified in a pilot plant, especially the problems of product quality, safety of operation, formation of pollutants, and the like. The economic point of view, on the other hand, requires a rational preparation of the catalyst with respect to energy and raw material consumption. Consequently it is necessary, even on a laboratory scale, to investigate the effect of some variable parameters of the catalyst preparation, to determine their significance and the way in which they may influence the overall catalyst quality. The solution of this problem in the classical way, i.e., by changing one variable while the others remain constant, would require much experimental time and effort. The Plackett-Burman statistical method<sup>1</sup> is a method allowing investigation of great many variable parameters of the preparation in a relatively small number of experiments and at the same time selection of the quantities which have the greatest effect.

### The Plackett-Burman Statistical Block

The Plackett-Burman statistical method makes it possible to study  $N$  variables in  $(N + 1)$  experiments. The authors set several patterns for various numbers of variables. The construction of the entire statistical block is simple. The first row of the basic cyclic pattern is given against the number of variables  $N$ .

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$N = 7$	+	+	+	-	+	-	-																
$N = 11$	+	+	-	+	+	+	-	-	-	+	-												
$N = 15$	+	+	+	+	-	+	-	+	+	-	-	+	-	-	-								
$N = 19$	+	+	-	-	+	+	+	+	-	+	-	+	-	-	-	+	+	-					
$N = 23$	+	+	+	+	+	-	+	-	+	+	-	-	+	+	-	-	+	-	+	-	-	-	-

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The basic row is selected and written as first for the respective value of  $N$ . The remainder of the whole block is made up by shifting this line cyclically by one place to the left ( $N + 1$ ) times and adding the last line with sign (-). This results in a statistical block of  $N$  columns and ( $N + 1$ ) rows.

As an example, Table I for fifteen variables and Table II for eleven variables are presented, which were utilized in this work. The tables comprise ( $N + 1$ ) experiments, i.e., ( $N + 1$ ) prepared catalysts which investigate  $N$  variables showing the effect on their properties. Each of the variables is included in the block in its limiting values which we consider in preparation, (+) denoting the maximum value and (-) the minimum value. Each variable appears  $[(N + 1)/2]$  times in the block at its minimum value and  $[(N + 1)/2]$  times at its maximum value. The effect of each variable is given by the difference of average results at the maximum and minimum values

$$E_i = \frac{\sum R(+)}{(N+1)/2} - \frac{\sum R(-)}{(N+1)/2} \quad (1)$$

where  $E_i$  is the effect of variable,  
 $R$  is the result of the experiment

Table I Plackett-Burman statistical block for  $N = 15$

Catalyst designation	Variables														
	A	B	C	D	E	F	(G)	H	I	J	K	L	M	(N)	(O)
1	+	+	+	+	-	+	-	+	+	-	-	+	-	-	-
2	+	+	+	-	+	-	+	+	-	-	+	-	-	-	+
3	+	+	-	+	-	+	+	-	-	+	-	-	-	+	+
4	+	-	+	-	+	+	-	-	+	-	-	-	+	+	+
5	-	+	-	+	+	-	-	+	-	-	-	+	+	+	+
6	+	-	+	+	-	-	+	-	-	-	+	+	+	+	-
7	-	+	+	-	-	+	-	-	-	+	+	+	+	-	+
8	+	+	-	-	+	-	-	-	+	+	+	+	-	+	-
9	+	-	-	+	-	-	-	+	+	+	+	-	+	-	+
10	-	-	+	-	-	-	+	+	+	+	-	+	-	+	+
11	-	+	-	-	-	+	+	+	+	-	+	-	+	+	-
12	+	-	-	-	+	+	+	+	-	+	-	+	+	-	-
13	-	-	-	+	+	+	+	-	+	-	+	+	-	-	+
14	-	-	+	+	+	+	-	+	-	+	+	-	-	+	-
15	-	+	+	+	+	-	+	-	+	+	-	-	+	-	-
16	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Table II Plackett-Burman statistical block for  $N = 11$ 

Catalyst designation	Variables										
	A	B	C	D	E	F	G	H	I	(J)	(K)
1	+	+	-	+	+	+	-	-	-	+	-
2	+	-	+	+	+	-	-	-	+	-	+
3	-	+	+	+	-	-	-	+	-	+	+
4	+	+	+	-	-	-	+	-	+	+	-
5	+	+	-	-	-	+	-	+	+	-	+
6	+	-	-	-	+	-	+	+	-	+	+
7	-	-	-	+	-	+	+	-	+	+	+
8	-	-	+	-	+	+	-	+	+	+	-
9	-	+	-	+	+	-	+	+	+	-	-
10	+	-	+	+	-	+	+	+	-	-	-
11	-	+	+	-	+	+	+	-	-	-	+
12	-	-	-	-	-	-	-	-	-	-	-

If, e.g., quantity  $A$  is in its maximum values, variable  $B$  occurs in  $(N + 1)/4$  cases in the maximum and in  $(N + 1)/4$  cases in the minimum value. In calculating  $E_A$ , the effect of variable  $B$  is cancelled, which holds also for the other variables. So it is possible to calculate, in a simple way, the effects of single variables at simultaneous changes of the other process variables.

The variables denoted in Tables I and II by letters in parentheses are the so-called "false", "dummy" or also "empty" variables and serve for estimating the experimental deviation. Their effect is calculated in the same way as for actual variables. From the found values of effects of "empty" variables  $E_d$  it is possible to calculate the variance of effect  $V$

$$V = \frac{E_d^2}{N_d} \quad (2)$$

where  $N_d$  is number of "empty" variables. Equation (2) shows that the variance is equal to the average of squares of effects of "empty" variables.

The effect of single variables on the resultant catalyst properties is determined by the  $t$ -test.

$$t = \frac{|E_j|}{V^{1/2}} \quad (3)$$

The values of relative significance of variables can be obtained from the critical values of the Student  $t$ -distribution<sup>2</sup>. The level of significance is obtained from the graph of dependence of  $t_{\nu, \alpha}$  on  $\alpha$ . The number of degrees of freedom  $\nu$  is

calculated from the relation

$$v = N_d - 1 \quad (4)$$

The relation between  $\alpha$  and relative significance  $RV$  reads as follows

$$RV = (1 - \alpha) 100 \quad (\%) \quad (5)$$

The value for  $\alpha = 0.35$  and for  $RV = 65 \%$  was chosen in this work as the critical limiting value.

### Catalyst for Propene Oxidation

An oxide catalyst of general formula  $Mo_{12}Bi_1Co_3Ni_1Fe_1K_{0.08}O_x$  was prepared from aqueous solutions of hexaammonium heptamolybdate, potassium hydroxide, cobalt (II), nickel(II), ferrum (III), and bismuth (III) nitrates, tartaric acid and ammonium hydroxide<sup>3,4</sup>. The resulting solution of pH 7.5 to 8 was, on continuous stirring thickened to a thin paste which was dried, calcinated (exothermic decomposition of ammonium nitrate) and, in the end, annealed. The annealing regime was chosen on the basis of the DTA results and after analysing the literature data on molybdates of the metals chosen.

Table III Name and magnitude of variable parameters of catalyst preparation for propene oxidation

Designation	Variable name	Variable (-)	Value (+)
<i>A</i>	amount of tartaric acid, g	16	32
<i>B</i>	volume of initial solution, cm <sup>3</sup>	250	500
<i>C</i>	temperature of solution thickening, K	343	373
<i>D</i>	drying time, h	4	12
<i>E</i>	temperature of first calcination - 4 hours, K	433	453
<i>F</i>	time of second calcination at 493 K, h	0	4
<i>G</i>	empty variable		
<i>H</i>	time of 1 <sup>st</sup> annealing at 553 K, h	0	4
<i>I</i>	time of 2 <sup>nd</sup> annealing at 603 K, h	0	4
<i>J</i>	time of 3 <sup>rd</sup> annealing at 653 K, h	0	4
<i>K</i>	time of 4 <sup>th</sup> annealing at 693 K, h	6	24
<i>L</i>	time of 5 <sup>th</sup> annealing at 723 K, h	0	6
<i>M</i>	drying temperature, K	393	413
<i>N</i>	empty variable		
<i>O</i>	empty variable		

To study the effect of conditions of preparation on the catalyst properties altogether twelve variables were chosen which are given in Table III along with three "empty" variables. The maximum and minimum values were assigned to them on the basis of experimental experience. According to Table I, the procedures of preparation of the individual catalyst were then elaborated and are given in Table IV.

The catalysts prepared were tested in a flow apparatus with integral reactor<sup>5</sup> at the following set of conditions: catalyst amount - 2 g, catalyst grain size 0.4 to 0.6 mm, reaction gas mixture flow rate - 5 dm<sup>3</sup> STP h<sup>-1</sup>, reaction mixture composition (volume %) - 5 % C<sub>3</sub>H<sub>6</sub>, 12 % O<sub>2</sub>, 20 % H<sub>2</sub>O, 63 % N<sub>2</sub>, reaction temperature - 593 K.

The propene conversion  $X_p$  was found chromatographically and calculated from the relation

$$X_p = \frac{C_p^o - C_p}{C_p^o} 100 \quad (\%) \quad (6)$$

here  $C_p^o$  is the initial propene concentration, mol %  
 $C_p$  is the stationary concentration, mol %

Table IV Conditions of preparation of catalysts for propene oxidation

Catalyst	Variable											
	A g	B cm <sup>3</sup>	C K	D h	E K	F H	H h	I h	J h	K h	L h	M K
1	32	500	373	12	433	4	4	4	0	6	6	393
2	32	500	373	4	453	0	4	0	0	24	0	393
3	32	500	343	12	433	4	0	0	4	6	0	393
4	32	250	373	4	453	4	0	4	0	6	0	413
5	16	500	343	12	453	0	4	0	0	6	6	413
6	32	250	373	12	433	0	0	0	0	24	6	413
7	16	500	373	4	433	4	0	0	4	24	6	413
8	32	500	343	4	453	0	0	4	4	24	6	393
9	32	250	343	12	433	0	4	4	4	24	0	413
10	16	250	373	4	433	0	4	4	4	6	6	393
11	16	500	343	4	433	4	4	4	0	24	0	413
12	32	250	343	4	453	4	4	0	4	6	6	413
13	16	250	343	12	453	4	0	4	0	24	6	393
14	16	250	373	12	453	4	4	0	4	24	0	393
15	16	500	373	12	453	0	0	4	4	6	0	413
16	16	250	373	4	433	0	0	0	0	6	0	393

The amount of acrolein was determined polarographically according to Moshier<sup>6</sup>, that of acrylic acid by the titration with 0.01 M NaOH using phenolphthalein as indicator, and that of carbon dioxide by gas chromatography. The yields of individual products were calculated from the relation

$$Y_i = \frac{C_i}{v_i C_p^o} 100 \quad (\%) \quad (7)$$

where  $C_i$  is the stationary concentration of acrolein, acrylic acid and/or carbon dioxide (where  $v_i = 1$  for acrolein and acrylic acid and  $v_i = 3$  for  $\text{CO}_2$ ).

The specific surface of the catalysts was determined by the method of thermal desorption of nitrogen.

The results of the catalyst testing are given in Table V. All the catalyst give high yields of useful products, i.e., of acrolein and acrylic acid, however, they differ in their activity and magnitude of specific surface. Therefore, the propene conversion and magnitude of specific surface were chosen on the basis of experiment and, in terms of these quantities, the effects of single variables and their significance were calculated. The result is given in Table VI. The sign

Table V Results of testing catalysts for propene oxidation

Catalyst	$\text{C}_3\text{H}_6$ conversion %	$\text{C}_3\text{H}_4\text{O}$ yield %	$\text{C}_3\text{H}_4\text{O}_2$ yield %	$\text{CO}_2$ yield %	Specific surface $\text{m}^2\text{g}^{-1}$
1	74.5	69.6	2.2	1.5	5.28
2	35.5	35.5	0	0	1.37
3	91	85.1	5	1	8.83
4	89	84	3.9	1	7.95
5	64.1	61.5	1.4	1	5.53
6	68.7	66.3	1.5	1	4.22
7	60	58.9	0.5	0	4.68
8	73.7	69.6	2.6	1	5.25
9	94	87.4	5.5	1	11.23
10	49.2	47.3	1.1	1	3.68
11	69.4	65.4	2.2	1	5.74
12	73	69.1	2.7	1	5.17
13	70.1	68.4	1.1	1	4.04
14	74.2	71.2	2.2	1	6.3
15	72	68	2.8	1	6.09
16	75	71	2.7	1	6.96

of effect of the given variable determines how its chosen value influences the result of the experiment, i.e., the propene conversion and the specific surface. If the sign is positive, then the maximum value increases the result of the experiment, if the sign is negative, then a better result is obtained at the minimum value of the variable. It follows from Table VI that the temperature of thickening of solution and time of drying have the greatest effect on the catalyst activity. A greater catalyst activity can be attained at the thickening temperature of 343 K and drying time of 12 hours. Another factor significantly influencing the catalyst properties is the amount of tartaric acid whose effect is positive. The significant variables in the thermal treatment of catalyst mass involve time of calcination at 493 K which increase the catalyst activity, and the time of first annealing at 553 K and fifth annealing at 723 K which decrease the catalyst activity. The volume of initial solution which influences the thickening time also has a partial effect. The other variables have no perceptible effect on the catalyst activity. The annealing time at 723 K (negative), temperature of solution thickening (negative), drying time at 393 K (positive) and annealing time at 653 K (positive) have the greatest effect on the magnitude of the catalyst specific surface.

Table VI Evaluation of Plackett-Burman statistical block for  $N = 15$

Variable	Effect on activity			Effect on yield			Effect on specific surface		
	<i>E</i>	<i>t</i>	<i>RV</i> %	<i>E</i>	<i>t</i>	<i>RV</i> %	<i>E</i>	<i>t</i>	<i>RV</i> %
<i>A</i>	8.18	1.34	70	8.23	1.4	70	0.78	0.75	
<i>B</i>	- 6.63	1.09	65	- 6.7	1.14	65	- 0.85	0.81	
<i>C</i>	-10.90	1.79	80	- 10.83	1.84	80	- 1.65	1.54	75
<i>D</i>	10.50	1.73	80	10.23	1.74	80	1.34	1.28	70
<i>E</i>	- 3.78	0.56		- 3.40	0.58		- 1.12	1.07	
<i>F</i>	8.63	1.42	70	8.30	1.41	70	0.46	0.44	
<i>G</i>	- 9.45			- 9.23			- 1.76		
<i>H</i>	- 8.20	1.35	70	- 8.50	1.44	70	- 0.47	0.45	
<i>I</i>	6.30	1.04		6.00	1.02		0.78	0.74	
<i>J</i>	5.10	0.84		5.35	0.91		1.22	1.16	
<i>K</i>	- 5.28	0.87		- 4.83	0.82		- 0.84	0.80	
<i>L</i>	- 8.35	1.37	70	- 8.33	1.42	70	- 2.07	1.98	85
<i>M</i>	5.88	0.97		5.68	0.96		1.12	1.07	
<i>N</i>	3.15			3.18			0.34		
<i>O</i>	- 3.45			- 2.95			0.28		



## Catalyst for Acrolein Oxidation

The effect of preparation conditions on the properties of a polycomponent oxide catalyst of general formula  $\text{Mo}_{12}\text{V}_3\text{Cu}_2\text{Fe}_{0.5}\text{O}_x$  was studied. The catalyst preparation started from aqueous solutions of hexaammonium heptamolybdate, ammonium vanadate (V), ferric and cupric nitrates and tartaric acid. The resulting solution whose pH was adjusted by means of ammonia hydroxide to the value of 7.5 to 8<sup>7,8</sup> was thickened to a paste. This was dried, calcined, and annealed. Nine variables were chosen for the investigation appearing in the catalyst preparation which are given in Table VII along with their maximum and minimum values and two "empty" variables. According to Table II, the procedures of preparing the single catalyst specimens were elaborated as shown in Table VIII.

The catalyst specific surface was determined by the method of thermal desorption of  $\text{N}_2$  and testing was carried out in a flow apparatus with an integral reactor<sup>9</sup> under the constant conditions: reaction temperature 503 K, catalyst amount was 1 g, catalyst grain size 0.4 to 0.6 mm, reaction gas mixture flow rate  $5 \text{ dm}^3 \text{ STP h}^{-1}$ , reaction mixture composition (volume %) 4 %  $\text{C}_3\text{H}_4\text{O}$ , 7 %  $\text{O}_2$ , 17 %  $\text{H}_2\text{O}$ , 72 %  $\text{N}_2$ .

The acrolein oxidation to acrylic acid took place with high selectivity. In the whole range of measurement, the yield of by-products, i.e., carbon dioxide and acetic acid, did not exceed, in total, 3 relative %. The yield of acrylic acid was chosen as efficiency criterion, i.e., the result of the experiment, defined by the relation

$$Y_{KA} = \frac{C_{KA}}{C_A^0} 100 \quad (\%) \quad (8)$$

Where  $C_A^0$  is the initial acrolein concentration, mol %

$C_{KA}$  is the stationary acrylic acid concentration, mol %.

The results of this series of measurements are given in Table IX.

The relative significance of individual variable parameters of the catalyst preparation on its specific surface and on the acrylic acid yield was calculated by the Plackett-Burman procedure, and the result is given in Table X. On using the statistical calculation, the following order of effect of variable factors of preparation on the yield of acrylic acid was found: amount of tartaric acid, temperature of solution thickening, annealing time at 573 K, and calcination temperature. The acrylic acid yield increases with decreasing amount of tartaric acid, with increasing temperature of thickening the initial solution, by omitting the annealing at 573 K and by choosing a lower calcination temperature. With respect to the high selectivity of oxidation on the chosen catalyst, the measured values of the acrylic acid yields may be considered comparable to the values of acrolein conversion and consequently identical conclusions may be drawn about

Table VII Name and magnitude of variable parameters of catalyst preparation for acrolein oxidation

Designation	Variable name	Variable	Value
<i>A</i>	volume of initial solution, cm <sup>3</sup>	200	300
<i>B</i>	amount of tartaric acid, g	8	16
<i>C</i>	temperature of solution thickening, K	343	373
<i>D</i>	drying temperature, K	403	423
<i>E</i>	drying time, h	3	14
<i>F</i>	calcination temperature, K	433	463
<i>G</i>	time of calcination, h	3	6
<i>H</i>	time of annealing at 573 K, h	0	6
<i>I</i>	time of annealing at 623 K, h	6	12
<i>J</i>	empty variable		
<i>K</i>	empty variable		

Table VIII Conditions of preparation of catalysts for acrolein oxidation

Catalyst	Variable								
	<i>A</i> cm <sup>3</sup>	<i>B</i> g	<i>C</i> K	<i>D</i> K	<i>E</i> h	<i>F</i> K	<i>G</i> h	<i>H</i> h	<i>I</i> h
1	300	16	343	423	14	463	3	0	6
2	300	8	373	423	14	433	3	0	12
3	200	16	373	423	3	433	3	6	6
4	300	16	373	403	3	433	6	0	12
5	300	16	343	403	3	463	3	6	12
6	300	8	343	403	14	433	6	6	6
7	200	8	343	423	3	463	6	0	12
8	200	8	373	403	14	463	3	6	12
9	200	16	343	423	14	433	6	6	12
10	300	8	373	423	3	463	6	6	6
11	200	16	373	403	14	463	6	0	6
12	200	0	343	403	3	433	0	0	6

the effect of the parameters of preparation on the catalyst activity.

The amount of tartaric acid (negative), annealing time at 623 K (positive), temperature of solution thickening (negative), annealing time at 573 K (positive), and volume of initial solution (negative) have the greatest effect on the magnitude of specific surface.

Table IX Results of testing catalysts for acrolein oxidation

Catalyst No.	C <sub>3</sub> H <sub>4</sub> O <sub>2</sub> yield %	Specific surface m <sup>2</sup> g <sup>-1</sup>	Catalyst No.	C <sub>3</sub> H <sub>4</sub> O <sub>2</sub> yield %	Specific surface m <sup>2</sup> g <sup>-1</sup>
1	5	4.4	7	25.5	8.3
2	24	6.1	8	39	8.3
3	16	5.5	9	4	6.7
4	8	5.6	10	37.5	5.7
5	13.5	6.5	11	3	4
6	15	7.4	12	16.5	7.2

Table X Evaluation of Plackett-Burman statistical block for  $N = 11$ 

Quantity	C <sub>3</sub> H <sub>4</sub> O <sub>2</sub> yield			Specific surface		
	Effect $E_i$	$t_i$	Rel. significance %	Effect $E_i$	$t_i$	Rel. significance %
<i>A</i>	- 0.16	0.08		- 0.72	1.8	65
<i>B</i>	-18.00	9.33	93	- 1.74	4.35	85
<i>C</i>	8.17	4.23	84.5	- 0.90	2.25	73
<i>D</i>	2.84	1.47		- 0.38	0.95	
<i>E</i>	- 4.50	2.33		- 0.30	0.75	
<i>F</i>	- 6.66	3.45	65	- 0.18	0.45	
<i>G</i>	- 3.50	1.81		- 0.06	0.15	
<i>H</i>	- 7.16	3.71	67	0.76	1.90	67
<i>I</i>	3.50	1.81		1.20	3.00	80
( <i>J</i> )	1.66	0.86		0.56	1.40	
( <i>K</i> )	- 2.16	1.12		0	0	

## Conclusion

The utilization of tartaric acid in combination with ammonium hydroxide ensures the perfect homogeneity of catalysts and reproducibility of their preparation. As is apparent from the results of the investigation performed, this procedure proved very advantageous for controlling the catalyst activity over a wide range of conditions on keeping the high selectivity of both oxidations. The combination of tartaric acid, ammonium hydroxide along with nitric acid can also be employed in regenerating the catalysts used<sup>10,11</sup> or when isolating the

metals from them<sup>12-14</sup>.

## References

1. Plackett R. L., Burman J. P.: *Biometrika* **33**, 305 (1946).
2. Dandy S., Warden S.: *Statistics for Research*, J. Wiley, New York 1983.
3. Czech 185 016 (1980).
4. Czech 242 277 (1988).
5. Švachula J., Tichý J., Machek J.: *Chem. Prům.* **35**, 354 (1985).
6. Moshier R. W.: *Ind. Eng. Chem., Anal.* **15**, 107 (1943).
7. Czech Patent 188 418 (1981).
8. Czech Patent 244 033 (1988).
9. Tichý J., Kůstka J., Venci J.: *Collect. Czech. Chem. Commun.* **39**, 1797 (1974).
10. Czech Patent 243 445 (1988).
11. Czech Patent 246 777 (1988).
12. Czech Patent 260 553 (1990).
13. Czech Patent 260 554 (1990).
14. Czech Patent 260 562 (1990).