Influence of basic technological factors on discontinuous production of pentaerythritol

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The influence of input factors (mole ratios formaldehyde : acetaldehyde, alkali : acetaldehyde and initial concentration of aldehydes) on fundamental technological characteristics of discontinuous production of pentaerythritol from formaldehyde and acetaldehyde in aqueous alkaline medium was investigated. The obtained relations were processed and transformed into complete quadratic functions which were used for determining the optimum technological conditions from the view-point of individual characteristics as well as their simultaneous evaluation.

Было изучено влияние исходных условий (молярное отношение формальдегид : ацетальдегид, основания : ацетальдегид, начальная концентрация альдегидов) на основные технологические характеристики дисконтинуальной продукции пентаэритрита из формальдегида и ацетальдегида в щелочном водном растворе. Полученные зависимости были преобразованы в виде полных квадратичных функций, и с их использованием были рассчитаны оптимальные технологические условия как с учетом отдельных характеристик, так и с учетом их одновременной оценки.

The basic and in industry generally used method of pentaerythritol production consists in the reaction of formaldehyde with acetaldehyde in aqueous alkaline solution while sodium or calcium hydroxide is most frequently used as alkali. Though four moles of formaldehyde and one equivalent of alkali are consumed for one mole of acetaldehyde according to the summary equation

$$4HCHO + CH_3CHO + NaOH = C(CH_2OH)_4 + HCOONa \qquad (A)$$

the real technological conditions are different. In order to obtain high yields of pentaerythritol with respect to consumed aldehydes and to eliminate undesirable side reactions, a higher formaldehyde : acetaldehyde ratio must be used. In addition, though in far less extent, an excess of alkali is added with respect to stoichiometrical requirement for the same reason. The technological conditions are different for batch reactor and continuous reactor because of which the technological and economical result of production is also different in these two cases.

The mechanism and kinetics of the reactions taking place in the production of pentaerythritol are very complicated [1]. Up to the present, these reactions are not quantitatively cleared up in spite of a great number of attempts in this sense [2—6]. Therefore, we measured the influence of basic technological factors on different aspects of pentaerythritol production in the form of statistically planned experiments by using the scheme proposed by *Box* and *Wilson* [7, 8]. Thus we could express the restults obtained for the individual investigated dependent variables in the form of complete quadratic function of the selected factors, which should be a good starting point for seeking the optimum technological conditions of the reaction from different standpoints.

Analysis of the problem

Though many papers [9—19] are concerned with quantitative description of the influence of basic technological factors on the course and results of the reactions giving rise to pentaerythritol, the data and conclusions are frequently inexact and contradictory. Besides the temperature which should generally vary in the temperature range 30—50°C according to recipes, the initial concentrations of both aldehydes and alkali expressed mostly in terms of the mole ratios formaldehyde : acetaldehyde, alkali : acetaldehyde, and overall concentration of aldehydes belong evidently among the fundamental factors. In this respect, some authors allege the mole ratios formaldehyde : acetaldehyde 4—10, alkali : acetaldehyde for calcium hydroxide 0.6—0.75 and for sodium hydroxide 1.1—1.5 and overall concentration of aldehydes 3—20 mass % as the optimum values [9]. It is obvious that these broad limits are due to differences in optimality criteria of the process and kinds of the process guiding.

We attempted to perform a more complex analysis of the influence of these main factors on all characteristics of the process which should be important from the technological point of view. We used the method of central planned experiment with three factors [7, 8]. This method requires the basic factorial scheduling 2^3 and other six measurements as well as a measurement in the centre of scheme, altogether 15 measurements. All experiments of this series took place at 40°C. Calcium hydroxide was used as alkali. We chose the mole ratio formaldehyde : acetaldehyde (X_1), mole ratio calcium hydroxide : acetaldehyde (X_2), and overall concentration of aldehydes (X_3) (in mass %) as independent variables.

The values of X_i in the transformed coordinates, their real values and the corresponding initial concentrations of components are listed in Table 1.

This experimental scheme enables us to express the variation of the investigated dependent variable Y in terms of a complete polynomial of the second order

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 \qquad (1)$$

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Table 1

Initial conditions of measurements

Experiment	Level			Conditions		Aldehydes mass %	Initial composition of reaction mixture		
	X'_1	X'_2	X'_3	$HCHO/CH_3CHO$ mol/mol	$Ca(OH)_2/CH_3CHO$ mol/mol		HCHO mol l^{-1}	CH_3CHO mol l^{-1}	$Ca(OH)_2$ mol l^{-1}
1	−1	−1	−1	4.6	0.6	8.5	2.215	0.481	0.289
2	+1	−1	−1	18.4	0.6	8.5	2.687	0.146	0.088
3	−1	+1	−1	4.6	1.8	8.5	2.294	0.499	0.898
4	+1	+1	−1	18.4	1.8	8.5	2.714	0.147	0.265
5	−1	−1	+1	4.6	0.6	13.5	3.610	0.785	0.471
6	+1	−1	+1	18.4	0.6	13.5	4.322	0.235	0.141
7	−1	+1	+1	4.6	1.8	13.5	3.625	0.824	1.483
8	+1	+1	+1	18.4	1.8	13.5	4.376	0.238	0.428
9	−1.215	0	0	3.12	1.2	11.0	2.686	0.861	1.033
10	+1.215	0	0	19.88	1.2	11.0	3.538	0.178	0.214
11	0	−1.215	0	11.5	0.47	11.0	3.356	0.292	0.137
12	0	+1.215	0	11.5	1.93	11.0	3.431	0.298	0.576
13	0	0	−1.215	11.5	1.2	7.96	2.424	0.211	0.253
14	0	0	+1.215	11.5	1.2	14.04	4.387	0.382	0.458
15	0	0	0	11.5	1.2	11.0	3.389	0.295	0.354

The fundamental characteristics of the process comprise:

Y_1 — yield of monopentaerythritol referred to consumed formaldehyde,
Y_2 — yield of monopentaerythritol referred to consumed acetaldehyde,
Y_3 — total conversion of formaldehyde,
Y_4 — yield of monopentaerythritol with respect to consumed aldehydes,
Y_5 — amount of the formed calcium formate (mol/mol CH_3CHO),
Y_6 — increase in the amount of methanol expressing the undesirable Cannizzaro reaction of formaldehyde (mol/mol CH_3CHO).

Experimental

Chemicals

Technical aqueous formaldehyde (Chemko, Strážske), content of formaldehyde 400 g/l, content of methanol 1.5 mass %.

Acetaldehyde (import from the USSR), content of acetaldehyde over 99.5 mass %.

Calcium hydroxide (Lachema, Brno), content of $Ca(OH)_2$ 96.3 mass % by titration and content of calcium found complexometrically 54.63 mass %, traces of silicon, magnesium, and copper found spectroscopically.

Working procedure

The reaction took place in a three-litre flask equipped with a stirrer, thermometer, and outlet for sampling. The reaction temperature was held constant at 40°C by external cooling or in the later reaction stage by heating with a water bath.

The calculated amount of diluting water and technical aqueous formaldehyde with known content of formaldehyde was added into the 10% lime milk prepared and analyzed beforehand. The suspension was quickly heated and thermostatted to 35—37°C and the necessary quantity of about 50% aqueous solution of acetaldehyde which had been analyzed beforehand was added. While the suspension was intensively stirred (500 min^{-1}), the temperature rose in the course of 1 min to 40°C where it was held by thermostatting till the end of reaction.

The samples were taken at particular time intervals and subjected to complete analysis after neutralization with formic acid.

Analytical methods

Formaldehyde was determined colorimetrically by using the reaction with phloroglucinol and measuring the absorbance at 500 nm with a colorimeter Spekol [20].

Monopentaerythritol was determined by gas chromatography after transformation into the corresponding silyl ether. The analyses were carried out with a Research Chromatograph 5756 B Hewlett—Packard. The column length was 2.20 m. It was packed with 38 mass % of SE 30 on Chromaton N AW DMCS [20] and its diameter was equal to 2 mm.

The content of $Ca(OH)_2$ was determined by potentiometric reverse titration with 0.1 M-NaOH after neutralization with excess 0.1 M-HCl.

Results

The values of the dependent variables Y_1—Y_6 obtained in the scope of the experimental scheme presented in Table 1 are given in Table 2. Each set was separately processed by linear regression and thus the values of the coefficients in eqn (*1*) were obtained for real, not transformed values of the independent variables. They are listed in Table 3.

The calculation of the coefficients and graphical representation of the functions $Y_i = f(X_1, X_2, X_3)$ were carried out with a computer Tesla 200 by means of the programs developed in Computation Centre of the Institute of Chemical Technology in Prague and ÚSIP in Prievidza.

By means of the coefficients listed in Table 3, we may easily deduce the expressions for the partial derivatives with respect to X_i from eqns (*1*). Then we may put them equal to zero and solve the three equations thus obtained to determine the coordinates of the stationary point. By back insertion, the value of the function in the stationary point can be ascertained. The character of the stationary point (maximum, minimum, saddle point) may be cleared up either by pure mathematical procedure or simpler by the use of the set of graphs provided for each technological characteristic by the above-mentioned computing program.

The results of such evaluation are summarized in Table 4.

Discussion

A great deal of important technological knowledge results from a more detailed analysis of the obtained relations.

The yield of monopentaerythritol referred to consumed formaldehyde is very little dependent on total concentration of aldehydes in the reaction mixture, but it is significantly dependent on their mole ratio and on the ratio $Ca(OH)_2$: acetaldehyde. The yield in the investigated experimental region increases with decreasing values of X_1 and X_2 from the minimum value of about 26% and exhibits the highest level (77.6%) at the lower limit of these parameters ($X_1 = 3.12$, $X_2 = 0.47$).

The yield of monopentaerythritol referred to consumed acetaldehyde manifests different character. Its dependence on the ratio $Ca(OH)_2$: acetaldehyde is not very distinct though it shows a decreasing tendency. The influence of the mole ratio and concentration of both aldehydes exhibits a saddle form with the saddle point at the concentration of aldehydes of about 11%, their mole ratio equal to 15 approximately, the value of Y_2 being 92.5%. The optimum technological yield (100%) may be put into the point $X_1 = 18.4$, $X_2 = 1.8$, $X_3 = 8.5$ (the experimental value of Y_2 in this point is 98.5%). It results from the course of contour lines $Y_2 = f(X_1, X_3)$ at a constant value of X_2 that, in order to attain the yield *e.g.* of 95%, we can compensate a decrease in mole ratio formaldehyde : acetaldehyde by rising the overall concentration of aldehydes, which is a very welcome functional course from the view-point of vapour consumption in further processing of the solution.

In accordance with expectation, the overall conversion of formaldehyde is maximum at low X_1 and high X_2. Its dependence on overall concentration of

Table 2

Values of the investigated characteristics

Experiment	Y_1	Y_2	Y_3	Y_4	Y_5	Y_6
	%	%	%	%	mol/mol CH_3CHO	mol/mol CH_3CHO
1	73.9	85.0	100.0	75.9	0.460	0.200
2	72.2	86.6	26.1	74.7	0.640	0.610
3	49.6	57.0	100.0	50.9	0.470	0.185
4	32.0	98.5	66.8	37.0	1.591	0.922
5	68.3	78.5	100.0	70.1	0.519	0.041
6	69.3	90.1	28.3	72.7	0.556	0.0
7	45.6	52.5	100.0	46.9	0.400	0.216
8	28.7	90.6	68.6	33.2	0.950	0.982
9	50.2	39.0	99.7	47.4	0.332	0.112
10	51.1	95.3	37.5	56.3	1.102	1.291
11	55.5	91.0	57.0	60.2	0.475	0.0
12	32.3	92.0	99.0	37.2	1.115	0.505
13	33.1	91.0	95.6	37.9	1.000	0.491
14	36.1	94.5	91.0	41.2	1.257	0.592
15	36.8	90.0	85.1	41.7	0.850	0.542

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Table 3

Values of the coefficients in eqn (*1*) for individual characteristics of the process

Coefficient	Characteristics					
	Y_1	Y_2	Y_3	Y_4	Y_5	Y_6
b_0	149.846	127.967	187.454	150.327	0.033	−0.308
b_1	− 5.334	6.092	− 1.410	− 4.185	0.136	−0.002
b_2	−63.179	−35.381	27.534	−64.086	1.381	0.634
b_3	− 5.128	−10.803	−18.223	− 5.787	−0.180	0.033
b_{12}	− 1.021	2.005	2.446	− 0.876	0.044	0.034
b_{13}	0.025	0.048	0.029	0.029	−0.005	−0.003
b_{23}	0.100	− 0.783	− 0.033	0.000	−0.057	0.072
b_{11}	0.254	− 0.300	− 0.245	0.205	−0.004	0.002
b_{22}	20.866	6.165	−14.667	21.175	−0.396	−0.626
b_{33}	0.195	0.491	0.812	0.229	0.013	−0.005

Table 4

Coordinates of stationary points and the pertinent values of the function

Function	Coordinates			Y_{stat}	Character of stationary point
	X_1	X_2	X_3		
Y_1	13.57	1.82	11.81	25.94	minimum
Y_2	14.98	1.16	11.19	92.48	saddle point
Y_3	4.12	1.27	11.17	100.22	maximum
Y_4	13.19	1.79	11.80	31.35	minimum
Y_5	17.50	1.69	14.05	1.123	saddle point
Y_6	−0.55	1.18	11.95	0.263.	saddle point

aldehydes exhibits a maximum in the region of 11 mass % and fairly uniformly decreases with increasing as well as decreasing value of X_3.

From the technical and economical standpoint, the yield of monopentaerythritol referred to consumed aldehydes is a very important criterion. It is almost insensitive to their overall concentration, which is again very welcome from the view-point of vapour consumption, but it considerably reacts to mole ratio of aldehydes and alkali content in the mixture. The yield increases with decreasing both factors from the minimum value of 31.35% at the mole ratio 13 and high content of lime up to the maximum value $Y_4 = 77.5\%$ in the investigated region at $X_1 = 3.12$ and $X_2 = 0.47$ (technological calculation gives the value $Y_4 = 75.7\%$).

The quantity of the formed calcium formate is a secondary and less important characteristic of the process. The formate is a product of the last step of the main reaction (Cannizzaro reaction of formaldehyde with pentaerythrose) as well as of the side reaction of formaldehyde giving rise to formate ion and methanol. It is, therefore, logical to estimate the origination of formate in connection with the formation of methanol which characterizes this undesirable side reaction of formaldehyde.

If the mole ratio formaldehyde : acetaldehyde increases the formation of formate rises to the mole ratio 15—19, which is practically at the limit of the experimental region. An increase in lime content has equal influence. If the concentration of aldehydes increases, the formation of formate passes through a minimum which shifts with increasing ratio of aldehydes from 9.5 to 15 mass % of aldehydes and is on the level of 1.20—1.25 mole of formate per one mole of acetaldehyde.

In accordance with expectation, the formation of methanol significantly increases with mole ratio of aldehydes. Its dependence on lime content goes through a maximum which occurs at low mole ratios of aldehydes in the region characterized by the ratio $Ca(OH)_2$: acetaldehyde equal to 0.8 approximately and shifts up to the value of 1.6 at high mole ratios. An increase in concentration of aldehydes

suppresses the formation of methanol and the undesirable Cannizzaro reaction of formaldehyde itself as well.

An assignment of the technological conditions for which all main characteristics would be optimum is not feasible because there are sometimes opposite tendencies. For instance, the high yield of monopentaerythritol referred to consumed acetaldehyde appears in quite a different region than the yield referred to both aldehydes consumed. Notwithstanding, we may assign a region where all individual characteristics are high though not all of them are optimum. It is approximately encompassed by the mole ratio formaldehyde : acetaldehyde equal to 8—10, mole ratio $Ca(OH)_2$: acetaldehyde equal to 0.5—0.6, and concentration of aldehydes equal to 11—14 mass %. Under these conditions, we may achieve the value of Y_1 of about 70%, Y_2 of about 95%, and the total conversion of formaldehyde Y_3 on the level of 80% while the yield with respect to consumed aldehydes is 70—75% and the Cannizzaro side reaction is rather suppressed.

If one of the characteristics appears to be more significant in special cases according to real technological requirements, we may easily determine the necessary technological conditions by means of the deduced equations and simultaneously calculate the values of other characteristics for particular values of X_i. For instance, we could reach a high, almost 100% yield with respect to acetaldehyde, of course, to the detriment of utilization of formaldehyde.

Conclusion

The relationships between major characteristics of discontinuous production of pentaerythritol and main technological conditions expressed in the form of complete quadratic equations may be used not only for calculating the optimum coordinates for individual characteristics, but also for assigning the region which is optimum from various technological view-points. By using a convenient selection of experimental region, we succeeded to cover the whole range of conditions which are interesting from the technological standpoint.

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