Influence of the mode of raw material feeding on result of the reaction taking place in continuous production of pentaerythritol

L. KOUDELKA

Research Institute of Petrochemistry,
972 71 Nováky

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The influence of the distribution of input raw materials into the first units of a cascade of stirred reactors with overflow on continuous production of pentaerythritol was investigated. The dependence of the yield of pentaerythritol on the mode of raw material distribution was expressed by a linear model which was statistically processed into a simplified form. The influence of all independent variables occurring in this model was shown to be on the level of 95% statistical significance. The evaluated fitting of the resulting model expressed as coefficient of determinacy exceeds 95%.

Было изучено влияние способа разделения исходных материалов в первых членах каскада смешанных реакторов с перепадом при непрерывном способе производства пентаэритрита. Зависимость выхода пентаэритрита от способа разделения исходных материалов выражается линейным уравнением, которое было статистически преобразовано в более простую форму, в которой влияние всех независимых переменных было учтено на уровне 95% статистической значимости. Оцененная приятельность окончательного уравнения, выраженная в виде коэффициента детерминированности, превышает 95%.

The continuous process of pentaerythritol (*i.e.* mixture of monopentaerythritol and dipentaerythritol) production from formaldehyde and acetaldehyde in aqueous alkaline medium belongs among the modern processes which are more and more used for industrial production of pentaerythritol. The technological and engineering solution is various. The Italian company Montecatini patented [1] a flow reactor of the column type with horizontal sections and stirring in individual chambers. Owing to its flow properties, it represents a piston reactor with medium dispersion [2].

The Japanese company Koei [3] has patented a system consisting of a few cylindrical vertical and slim reactors. A two-step procedure is also known according to which the stage of aldol condensation of both aldehydes can be separated from the final Cannizzaro reaction [4, 5]. According to Czechoslovak patent [6], pentaerythritol can be continuously produced in a flow system with a few feeding openings. According to [7], the reaction system consists of a set of apparatuses equipped with external thermostatting and stirring circuit.

In this paper, we present the results concerning the influence of the mode of raw material feeding on the reaction outcome in the system consisting of a cascade of stirred reactors with overflow as well as the processing of the results in the form of simple linear models.

Experimental

Chemicals

Technical aqueous formaldehyde (Chemko, Strážske), content of formaldehyde 400 g/l, content of methanol 15 g/l. 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, content of calcium 54.6 mass % by complexometric determination.

Experimental device and working procedure

The reaction system consisted of a cascade of six reactors of 2 l volume each. They were made of stainless steel and equipped with thermostatting circuit, mechanical stirrer, thermometer, adjustable overflow, and raw material inlet. The needed quantity of technical aqueous formaldehyde was fed into the first reactor while acetaldehyde, lime milk, and diluting water were supplied to the first four reactors. The raw materials were transported with metering pumps (aqueous formaldehyde, acetaldehyde, water) and air-operated pump (lime milk). The last two steps of the cascade served for completing the reaction of the mixture, *i.e.* accomplishing the formation of pentaerythritol. The temperature was held at 40°C in the first four reactors by controlling the cooling in the thermostatting circuit and the last two reactors were thermostatted at 50°C. Equal liquid volume was maintained in all reactors so that the overall reaction time in the cascade was 40—45 min.

After starting the device and establishing the conditions which usually took 3—4 h, the samples were taken at the exit from the cascade in 1 h intervals, neutralized with concentrated formic acid and analyzed as regards the content of monopentaerythritol and dipentaerythritol. The experiment was finished after 8 h steady working and the mean value of the results obtained with individual samples was used as result of the experiment.

Analytical methods

The concentration of formaldehyde in the input technical aqueous formaldehyde and in the reaction mixture was determined colorimetrically by using the reaction with phloroglucinol and measuring the absorbance at 500 nm with a colorimeter Spekol [8].

The content of $Ca(OH)_2$ in the lime milk and in the reaction mixture was determined by reverse potentiometric titration with 0.1 M-NaOH after neutralization with excess 0.1 M-HCl.

Mono- and dipentaerythritol were determined by gas chromatography after evaporation to dry state and transformation into the corresponding silyl ethers. This analysis was carried out with a Research Chromatograph Hewlett—Packard 5756 B equipped with a column of 2 mm diameter and 2.2 m length, the packing being 38 mass % SE 30 on Chromaton N AW DMCS [8].

Results and discussion

In thirteen experiments, we investigated the influence of different quantities and distributions of the raw materials fed into the first four reactors. The following factors were evaluated:

X_1 — total quantity of applied water (including water in technical aqueous formaldehyde and lime milk),
X_2 — quantity of acetaldehyde supplied into the first reactor,
X_3 — quantity of formaldehyde supplied into the first reactor,
X_4 — quantity of calcium hydroxide supplied into the first reactor,
X_5 — quantity of acetaldehyde supplied into the second reactor,
X_6 — quantity of calcium hydroxide supplied into the second reactor,
X_7 — quantity of acetaldehyde supplied into the third reactor,
X_8 — quantity of calcium hydroxide supplied into the third reactor,
X_9 — quantity of acetaldehyde supplied into the fourth reactor,
X_{10} — quantity of calcium hydroxide supplied into the fourth reactor.

All data have been expressed in g/h·l of the reaction solution except X_1, the dimension of which is l/h·l of the reaction solution.

The yield of pentaerythritol referred to the consumed acetaldehyde was calculated from the total balance of the reaction solution and the sum of concentrations of mono- and dipentaerythritol.

The experimental conditions referred to unit volume of 1 l of the reaction solution are given in Table 1. The experimental values of the yield of pentaerythritol (comprising mono- and dipentaerythritol) are quoted in line Y_{exp}.

The coefficients of the linear model of the functional relation $Y = f(X_1, X_2, ..., X_{10})$ in the subsequent form were calculated from the data given in Table 1 by means of linear regression

$$Y_1 = b_0 + b_1X_1 + b_2X_2 + ... + b_{10}X_{10} \qquad (1)$$

where Y_1 is the yield of pentaerythritol expressed in %.

The optimum values of the coefficients are listed in the first column of Table 2 and the yields of pentaerythritol calculated for individual cases are given in line Y_1 of Table 1.

Table 1

Experimental conditions and yields of pentaerythritol referred to consumed acetaldehyde

Experiment		*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*
X_1	(l/h · l)	0.8343	0.8291	0.8285	0.8271	0.8356	0.8365	0.8306	0.8538	0.8535	0.8535	0.8535	0.8535	0.8452
X_2	(g/h · l)	7.9579	8.1610	11.9748	16.5979	11.9460	11.8321	13.7730	10.9817	12.9523	19.4627	23.8487	28.2346	14.1494
X_3	(g/h · l)	101.669	104.659	105.478	106.428	100.193	99.2366	86.8113	86.5225	86.2802	86.2802	86.2802	86.2802	93.7729
X_4	(g/h · l)	8.0544	8.4083	12.0746	17.2015	16.1850	16.0305	17.3723	29.2845	31.9353	31.9353	31.9353	31.9353	30.8349
X_5	(g/h · l)	7.9579	8.1610	10.0788	0	7.9480	7.8721	6.8865	8.2363	8.7719	8.7719	4.3860	0	9.3439
X_6	(g/h · l)	8.0544	8.4083	10.1786	0	8.0925	8.3969	7.3456	0	0	0	0	0	0
X_7	(g/h · l)	7.9579	8.1610	7.2847	9.9588	7.9480	7.8721	6.8865	5.4908	6.5104	0	0	0	6.7410
X_8	(g/h · l)	8.0544	8.4083	7.2847	9.3552	8.0925	8.3969	5.3425	2.9118	0	0	0	0	0
X_9	(g/h · l)	7.9579	8.1610	3.5924	6.6392	3.9499	3.9122	0	2.7454	0	0	0	0	0
X_{10}	(g/h · l)	8.0544	8.4083	3.5924	6.6392	0	0	0	0	0	0	0	0	0
Y_{exp}	%	73.79	72.36	75.16	69.30	76.94	80.81	82.13	85.01	70.40	66.57	67.67	67.34	67.42
Y_1	%	74.42	71.46	75.69	69.39	77.96	79.71	81.88	85.08	71.00	66.76	67.18	67.61	66.78
Y_2	%	74.22	71.58	75.62	69.33	77.91	79.66	81.85	85.04	70.96	66.72	67.14	67.56	67.73
Y_3	%	74.55	71.18	76.25	69.55	77.54	79.73	81.73	84.99	71.75	66.81	67.18	67.56	66.09
Y_4	%	73.76	71.00	75.38	71.41	77.35	79.42	81.81	85.16	71.29	69.12	67.36	65.61	66.25

Table 2

Values of regression coefficients, coefficient of determinacy, and Student test for individual compared models

1. Coefficients	Model			
	(*1*)	(*2*)	(*3*)	(*4*)
b_0	−410.6759	−372.5981	−582.0407	−412.5068
b_1	645.3373	597.8164	837.0432	640.7664
b_2	−14.9398	−14.8654	−15.0157	−13.1497
b_3	4.1041	4.0524	4.1625	3.5060
b_4	−0.1502	—	—	—
b_5	−15.0361	−14.9618	−15.1007	−12.7492
b_6	0.5040	0.6494	0.6945	—
b_7	−14.2886	−14.2136	−14.2569	−12.8170
b_8	1.2865	1.3091	2.0684	2.7904
b_9	−15.7786	−15.5518	−16.8501	−14.9721
b_{10}	−0.7400	0.6809	—	—
2. Coefficient of determinacy (%)				
B	98.93	99.02	98.08	95.59
3. Student test of statistical significance for individual coefficients				
$t(b_0)$	1.3357	1.4470	2.8925	2.5957
$t(b_1)$	1.0924	2.0380	3.6869	3.6009
$t(b_2)$	5.2671	6.3510	3.8951	3.9042
$t(b_3)$	3.9178	5.6310	3.2470	3.1471
$t(b_4)$	0.1044	—	—	—
$t(b_5)$	5.1348	6.7598	3.7839	3.7376
$t(b_6)$	0.3539	2.7943	1.6919	—
$t(b_7)$	5.0267	6.6323	3.6816	3.7209
$t(b_8)$	1.0665	1.4145	2.9827	5.5983
$t(b_9)$	3.8285	5.6987	4.0203	4.0628
$t(b_{10})$	0.6597	0.9024	—	—

The agreement of calculation with experiment is very good as evident from data Y_{exp} and Y_1. Nevertheless, it is not surprising even at a relatively wide range of several factors owing to a small number of the degrees of freedom (13 experimental points, 10 independent factors).

However, the sense and weight with which individual factors affect the yield of pentaerythritol are interesting. They are given by the sign and magnitude of the corresponding factor.

If we omit the term b_0 which is only of mathematical importance, the term X_1, *i.e.* the increase in total quantity of water is by far the most effective factor as regards the increase in yield. In accordance with this fact, the coefficients b_2, b_5, b_7, and b_9 are negative and almost equally great. Thus higher yields are achieved at lower relative quantity of acetaldehyde, *i.e.* its lower concentration.

As for formaldehyde, the tendency is according to expectation opposite, of course, it is not so marked. A higher quantity of formaldehyde and, as a matter of fact, the higher mole ratio formaldehyde : acetaldehyde contributes to the increase in yield.

The influence of lime dosage is slight. The coefficients b_4, b_6, b_8, and b_{10} are the least of all and without any distinct tendency.

The degree of adequacy of the regression model, *i.e.* the level on which the model reflects experimental material can be expressed *e.g.* by the coefficient of determinacy [9]

$$B = 1 - \frac{\sum_{n=1}^{N} (Y_{\exp(n)} - Y_{\mathrm{calc}(n)})^2}{\sum_{n=1}^{N} (Y_{\exp(n)} - \bar{Y}_{\exp})^2}$$

where N is the total number of measurements, $Y_{\exp(n)}$ and $Y_{\mathrm{calc}(n)}$ are the individual experimental or calculated values of Y and $\bar{Y}_{\exp}$ stands for the mean value of experimental data.

The coefficient of determinacy is between zero and one. It is usually expressed in percentage. In case of the perfect agreement of calculation with experiment, it is equal to 100%. In our case, the value of B obtained for model (*1*) was equal to 98.93%.

Furthermore, model (*1*) was subjected to the Student test of statistical significance of individual factors by comparing the value of the corresponding coefficient with the value of its dispersion. Provided the ratio of these two quantities exceeds the critical value of the Student distribution, we may consider the factor to be statistically proved on the chosen level of statistical probability.

For the level of 95% and model (*1*), the critical value of Student's distribution is

$$t_{\mathrm{crit}} = 4.30$$

and the values for $t(b_i)$ for the particular coefficients are in the lower part of column (*1*) in Table 2.

As seen, only the influence of factors X_2, X_5, and X_7, *i.e.* of the acetaldehyde feed to the first, second, and third reactor was statistically proved on a level of 95%. The influence of the remaining factors was not statistically proved on the chosen level.

The statistical weight of the model and increase in the level of significance of individual parameters can be achieved by the procedure described *e.g.* by *Kaplick* and *Lorenz* [9]. We gradually omit the insignificant members of the model starting with that one having the lowest value of $t(b_i)$ and evaluate the values of $t(b_i)$ and statistical significance of remaining members. Simultaneously, we bear in mind that the value of the coefficient of determinacy B must not fall too low. We proceed in this way till the influence of all remaining members of the model is proved on the chosen level of significance.

By this procedure, we eliminated the term b_4X_4 from model (*1*) and determined the values of b_i, B, and $t(b_i)$ by means of a new linear regression. The calculated values of the coefficients of model (*2*) which has the form

$$Y_2 = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_5X_5 + b_6X_6 + b_7X_7 + \\ + b_8X_8 + b_9X_9 + b_{10}X_{10} \qquad (2)$$

are listed in column (*2*) of Table 2, whereas the calculated values of yield are in line Y_2 of Table 1.

As obvious, the elimination of the term b_4X_4 did not result in impairing the fitting of the model. The critical value of the Student distribution for model (*2*) is

$$t_{\mathrm{crit}} = 3.18$$

and we can see that we succeeded in raising the number of factors with statistically proved influence for all the inputs of acetaldehyde as well as the dosage of formaldehyde. The least value of this model is $t(b_{10})$. By eliminating the term $b_{10}X_{10}$ and repeating the calculation for the model

$$Y_3 = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_5X_5 + b_6X_6 + b_7X_7 + b_8X_8 + b_9X_9 \qquad (3)$$

we obtained the values of coefficients and other data given in column (*3*) of Table 2 and the yields Y_3 presented in Table 1. The agreement of calculation with experiment was also very good ($B_3 = 98.08\%$) and with $t_{\mathrm{crit}} = 2.78$, the influence of all factors, except X_6, *i.e.* the dosage of lime into the second reactor, was proved on the level of 95% probability.

In the last step, we eliminated this term, too, and obtained the following equation

$$Y_4 = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_5X_5 + b_7X_7 + b_8X_8 + b_9X_9 \qquad (4)$$

It results from the data of column (*4*) in Table 2 that the influence of all factors has been proved on the level of 95% statistical significance for $t_{\mathrm{crit}} = 2.57$ while the coefficient of determinacy has still a very high value (95.6%).

Individual trends already observed in the first model remain unchanged. In order to improve the yield, we must rise the total quantity of water and formaldehyde and reduce the dosage of acetaldehyde, *i.e.* to work with more dilute solutions and at higher mole ratio formaldehyde : acetaldehyde. Only one term remained from the input lines of lime, *i.e.* dosage into the third reactor which, of course, has a statistically proved influence on yield, but the value of b_i is relatively low so that it represents only a small contribution to the total value of Y_4.

These results are in good agreement with literature data as well as with the results obtained by investigating this reaction in a discontinuous system [10]. The fundamental trends of individual technological factors are not affected owing to replacement of discontinuous reaction system by a cascade of reactors.

The worked-out model is very simple and gives results which are in good agreement with experimental values as evident from a comparison of the values of Y_{exp} with Y_4 (Table 1). The technological interpretation of the model is also interesting. The total quantity of water and formaldehyde, the dosage of acetaldehyde into all four reactors and the dosage of lime into the third reactor have a statistically proved influence on the yield of pentaerythritol.

However, it does not result from the above facts that the influence of dosage into other reactors may be omitted. Provided the corresponding dosage scheme for lime is kept, the dosage into the third reactor has just the greatest influence on the result of this reaction. It is due to the fact that the main region of the Cannizzaro reaction of formaldehyde with pentaerythrose following the aldol condensation of formaldehyde with acetaldehyde occurs in the third and fourth reactor and for this reason, we must provide sufficient amount of alkali for this reaction by supplying it into the third reactor.

An attempt to use model (*4*) for optimization of the yield is hazardous. The extrapolation based on empirical models could lead to nonreal technological and physical conditions and for this reason, we have to remain, in principle, in experimental region which is determined not only by pure mathematical but also secondary technological points of view that cannot be immediately seen in the model. For instance, the dosage of acetaldehyde into the second, third, and fourth reactor varies from zero to 10.0788 g/h·l, but the mole ratio of formaldehyde to total quantity of acetaldehyde varies within relatively narrow range from 4.482 to 4.703 which means that a smaller dose of acetaldehyde is compensated by its increased supply, *e.g.* into the first reactor. As for lime, the situation is similar. Thus the individual variables are not quite independent from the technological view-point. These relations must be, therefore, respected if model (*4*) is to be used.

Conclusion

The cascade of stirred reactors with overflow is usable for a reaction system designed for continuous production of pentaerythritol. The technological result is, to a great extent, dependent on distribution of the raw materials into individual members of the cascade. A simple linear model involving the influence of basic technological parameters has been developed by statistical processing of experimental material.

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