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SYNTHESIS OF IMINODIACETIC ACID IN A CASCADE REACTOR

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The present paper deals with the modernization of the manufacturing of iminodiacetic acid, enhancing the conversion and the reactor-intensity, as well as with the elaboration of a procedure permitting continuous production.
During the investigation of the industrial synthesis of iminodiacetic acid our important recognition is that glycine, produced together with the desired iminodiacetic acid, can be converted with monochloroacetic acid to iminodiacetic acid after removal of the excess of ammonia from the reaction mixture. For utilization of glycine, an industrial procedure has been elaborated. According to this, production of iminodiacetic acid is carried out in a quadrate cascade reactor, so that the reaction mixture leaving the second reactor element is freed from ammonia, concentrated, and then reacted with an equivalent of monochloroacetic acid calculated on the basis of the glycine-content. In this way, iminodiacetic acid is obtained in the laboratory-scale experimental reactor with a 91 % yield, based on monochloroacetic acid.
Calculations for the optimization of the reactor-cascade are also presented. These clearly prove that the required new investment is reimbursed upon manufacturing on an industrial scale.

Keywords: iminodiacetic acid, reactor-cascade, optimization.

Introduction

The industrial production of iminodiacetic acid can be realized in two ways. One is the reaction which proceeds between monochloroacetic acid, ammonia and calcium hydroxide in water solution, which ensures 60-65 % of the product, but leaves ca. 20-27 % of glycine in the system, thus decreasing the effective conversion of monochloroacetic acid [1]. The second route is the reaction of glycine with monochloroacetic acid. According to our investigations, for reactor-technological reasons the latter reaction could be the more convenient choice for production of iminodiacetic acid. Namely, in this system the effective conversion of monochloroacetic acid is higher.

As the whole process, following the reaction between monochloroacetic acid, ammonia and calcium hydroxide in water, ammonia should be removed from the system, and then glycine should be reacted with monochloroacetic acid, to be introduced into the system, to produce a further amount of iminodiacetic acid. During this latter reaction no damage of the formerly produced iminodiacetic acid occurs.

The present paper deals with the modernization of the manufacturing of iminodiacetic acid, enhancing the conversion and the reactor-intensity, as well as with the elaboration of a procedure permitting continuous production.

Experimental

Materials

Monochloroacetic acid, ammonia solution and $Ca(OH)_2$ were purchased from Aldrich (Germany) and were used as received.

Instruments

The concentration of IMDA of the solutions was determined with a BECKMAN Acta M IV. spectrophotometer.
The Cl^- ion concentration of the solution was determined with an OP-Cl-7113-D type chloride-ion selective electrode (Radelkis, Budapest, Hungary).

The intensity of the spot of glycine and iminodiacetic acid on the TLC plates was determined at 510 nm with a CS-20 type videodenzitometer (Shimadzu, Japan)

Thin Layer Chromatography (TLC)

The quantitative determination of glycine (R_f=0.56) and iminodiacetic acid (R_f=0.85) was performed on FIXION-50x8-type cation-exchange thin-layer plates using citrate buffer (pH=3.28) as the mobil phase and and phenylalanine (R_f=0.14) as the internal standard. The spots were visualized with ninhydrin.

Results and Discussions

Investigation of the formation of iminodiacetic acid in a laboratory cascade reactor

The reaction was carried out in a quadrate cascade reactor built up from elements of equal volume. A schematic line diagram of the reactor is depicted in Figure 1.

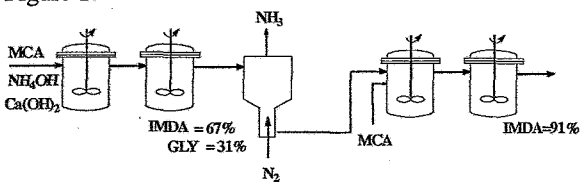

Fig. 1 Laboratory cascade reactor

Iminodiacetic acid (IMDA) and (GLY) glycine is produced in the first two elements of the reactor cascade in the reaction of monochloroacetic acid (MCA) ammonia and calcium hydroxide in water solution. As the increase of the concentration is favoured, this reaction is carried out in a relatively concentrated solution, containing 2 mole/dm^3 of the calcium salt of monochloroacetic acid and 8 mole/dm^3 of ammonia. Such a large concentration of ammonia was selected to avoid the formation of glycolic acid.

Concerning the reaction rates and the rate constants in this system, the following cascade model can be concluded for the first two elements of the reactor-cascade [1-5]:

$$\frac{c_{MCA}}{c_{0,MCA}} = \prod_{i=1}^{2} \frac{1}{1+Da_I} = \left(\frac{1}{1+k_B t_{i1}}\right)^2 \qquad (1)$$

$$\frac{c_{IMDA}}{c_{0,MCA}} = \frac{k_{2B}}{k_B}\left(1-\prod_{i=1}^{2}\frac{1}{1+Da_1}\right) = \frac{k_{2B}}{k_B}\left[1-\left(\frac{1}{1+k_B t_{i1}}\right)^2\right] \qquad (2)$$

where t_{i1} in equations (1) and (2) means the average residence time of the reactants in the first and the second elements of the cascade. c_{MCA} and c_{IMDA} represent the concentration of MCA and IMDA, and the 0 subscript means the initial concentration of the materials. With this mathematical model one can calculate that the conversion of monochloroacetic acid is almost complete at t_{i1} = 190 min average resi+dence time at 60 °C.

In the reaction mixture leaving the second element of the cascade the conversion of monochloroacetic acid into iminodiacetic acid is 67 % and into glycine is 31 %. When the glycine-content of the mixture is utilized by the discussed subsequent conversion, the effective conversion of monochloroacetic acid into iminodiacetic acid can be enhanced.

This mixture, possessing a high ammonia concentration, is led to a desorber kept at 105 °C, and freed from ammonia to ensure a 10-15 % increase in the concentration. As previous experimental data have shown, the conversion into iminodiacetic acid can be raised by increasing the concentration of glycine (and at the same time, each of the proportion of formation of glycolic acid and the reaction time is decreasing), an amount of concentrated aqueous solution of the calcium salt of monochloroacetic acid equal with the glycine-content is added to the mixture, which has been previously freed from ammonia.

The resulting system consisting of monochloroacetic acid, calcium hydroxide, glycine and water is allowed to react in the second two elements of the reactor cascade, and the changes in concentration can be described by the following cascade model [2-5]:

$$\frac{c_{MCA}}{c_{0,MCA}} = \left(\frac{1}{1+k_I \quad t_{i2}}\right)^2 \qquad (3)$$

$$\frac{c_{GLY}}{c_{0,GLY}} = \left(\frac{1}{1+k_{2I}\cdot c_{GLY}\cdot t_{i2}}\right)^2 \qquad (4)$$

where t_{i2} means the average residence time of the reactants in the third and fourth elements of the reactor cascade and c_{GLY} is the concentration of glycine. In these experiments the conversion of the residual glycine is 82 %, and the overall yield of iminodiacetic acid is 91 %, based on monochloroacetic acid. From this mixture the crystalline hydrochloric acid salt of iminodiacetic acid is isolated in 86 % yield, which is better by 26-30 % than that of the currently employed industrial process. This value of conversion may be further enhanced by optimization of certain technological parameters, including the flow-rate, administration of the reactants, the reaction time and concentration, as well as by improving the technique of the isolation of the product.

Optimization of the Reactor Cascade

Realization of a continuous reaction on an industrial scale calls for the knowledge of relations, with the aid of which the desired product can be manufactured with the lowest possible investment and production expenses.

For economic reasons, a technological system constructed from standardized elements is much more preferable than that built up from individually produced components. A cascade reactor can be built from LAMPART autoclaves.

Concerning the economical aspects, for the determination of the optimum cascade number we must know the volume-price relation [6].

Supposing that the price of the autoclave units P [Hungarian Forint, HUF], is in an exponential relation with their volume V [dm^3].

$$P = b_0 V^b \tag{5}$$

The exponent b and the b_0 constant can be determined by linearization of equation (5) to obtain:

$$\ln P = \ln b_0 + b \ln V \tag{6}$$

For the LAMPART reactors the volume-price relation is shown in Figure 2.

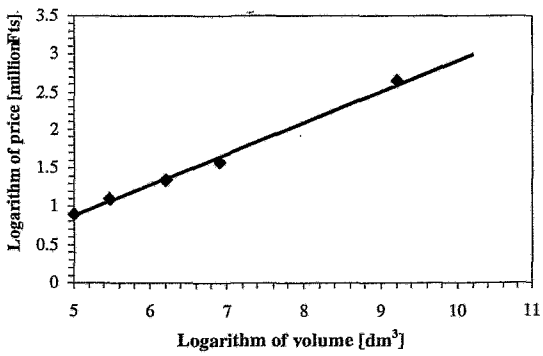

Fig.2 Volume – price relation of LAMPART reactors

According to the data of Figure 2, b_0 = 10.7451 and b = 0.427, and the corrected correlation coefficient r* = 0.99 for the linearized equation, which proves that equation (5) is correct.

The price of a cascade reactor built from **n** number of elements is

$$P = b_0 V^b n \tag{7}$$

According to the cascade model, the value of the desired conversion in a first-order reaction is

$$x = 1 - \left(\frac{1}{1 + k \cdot t_i} \right)^n \tag{8}$$

The average residence time is the ratio of the volume of the reactor and the volumetric flow of the reactant:

$$t_i = \frac{V_i}{B} \tag{9}$$

By substituting the average residence time (8) into equation (9), and by expressing the volume, it comes that

$$V_i = \frac{\left[(1-x)^{-\frac{1}{n}} - 1 \right] \cdot B}{k} \tag{10}$$

and substituting equation (10) into equation (7) we obtain:

$$P = b_0 \left[\left((1-x)^{-\frac{1}{n}} - 1 \right) \cdot W \cdot k^{-1} \right]^b n \tag{11}$$

and by transposing equation (11) we get the relation:

$$\left(\frac{P}{b_o} \right)^{\frac{1}{b}} \frac{k}{B} = \left[(1-x)^{-\frac{1}{n}} - 1 \right] \cdot n^{\frac{1}{b}} \tag{12}$$

By denoting the left side of the equation (which contains only constants) with Q, it comes:

$$Q(n) = \left[(1-x)^{-\frac{1}{n}} - 1 \right] n^{\frac{1}{b}} \tag{13}$$

The extreme value of the Q(n) expense-function can be calculated with a non-linear optimization method [7-8].

In Figure 3 the optimum cascade-number versus conversion correlations for cascade systems built up from LAMPART autoclaves are summarized.

By analysing the curve, the optimum cascade number with which the reaction proceeds with the desired extent of conversion (independently of the rate constant of the reaction), and with the lowest investment costs can be determined. In the knowledge of the cascade number and the rate of the reaction, the average residence time can be determined according to equation (8). The volume of the built-in reactors is determined by the desired daily production, in accordance with the ratio of conversion and the average residence time.

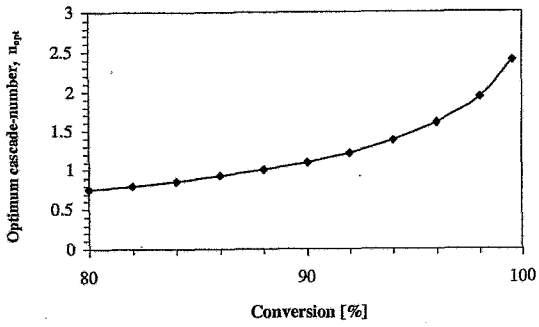

Fig.3 Optimum cascade number versus conversion of LAMPART reactors

In most cases the desired extent of conversion does not require an integer number of reactors as the optimum. In such cases the most economic number of the operational units should be calculated by rounding up or down, depending on the price of the product and the investment expenses.

Concerning the investigated present reaction system, it was an essential starting condition that the overall conversion of monochloroacetic acid must be nearly complete, i.e., at least 98 %. The reaction was conducted at 60 °C, which was considered as an optimum parameter. The diagram shows that an $n_{opt} = 2$ optimum cascade number belongs to such an extent of conversion, and according to equation (7, 11) the costs of investment of building the cascade reactor system can be simply calculated:

$$P = b_0 V_{opt}^b n_{opt} = \cdot$$
$$= b_0 \left[\left((1-x)^{\frac{1}{n_{opt}}} - 1 \right) W k^{-1} \right]^b n_{opt} \qquad (14)$$

Conclusion

For utilization of glycine, and industrial procedure was elaborated. According to this, production of iminodiacetic acid was carried out in a quadrate cascade reactor, so that the reaction mixture leaving the second reactor element was freed from ammonia, concentrated, and then reacted with an equivalent of monochloroacetic acid calculated on the basis of the glycine-content. This way, iminodiacetic acid was obtained in the laboratory-scale experimental reactor with a 91 % yield, based on monochloroacetic acid. Calculations for the optimization of the reactor-cascade was also presented. These clearly prove that the required new investment were reimbursed upon manufacturing on an industrial scale.

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SYMBOLS

c	concentration, mol/dm^3
b	constant
Da_I	first Damköhler number
k	rate constant, min^{-1}
n	number of cascade
t	time, min
t_i	average residence time, min
T	temperature, K
P	price of LAMPART reactor, HUF
Q	expense-function
x	conversion
W	volumetric flow, dm^3 min^{-1}

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