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Industrial Purification of Caprolactam by Means of Crystallization from Aqueous Solution

A course of investigations and the adopted method of caprolactam crystallization process on industrial scale have been discussed. The product characteristics as well as economic indices of the process were mentioned. The presented method gives new possibilities in technology of the product purification.

Die Forschung und Entwicklung eines industriellen Kristallisationsverfahrens von Caprolactam werden beschrieben. Charakteristik des erzeugten Produktes sowie ökonomische Richtsätze des Prozesses werden genannt. Das Verfahren bietet neue Möglichkeiten in der technischen Reinigung dieses Produktes.

1. Introduction

ε-caprolactam ($C_6H_{11}ON$) is one of the basic raw materials used in manufacturing high quality synthetic fibres and various plastics. The quality of products made of caprolactam is strictly dependent on its purity grade. Thus the requirements regarding this parameter are very rigorous and continuously increasing.

The most evident example of changes realised lately in the evaluation of caprolactam quality is the increase of requirements concerning so called manganese number (MN) being the one of major and commonly used factors of caprolactam purity.

If in the early sixties, the product having MN circa $(3-5)\ 10^2$ s was deemed as being of good quality whereas nowadays a monomer which is to be processed into a textile raw polymer should have MN of at least $1 \cdot 10^4$ s. It is not a rarity to find a product with MN of more than $2 \cdot 10^4$ second (for 3% solution of caprolactam).

The methods of caprolactam purification employed in practice are connected with the process of its production and the nature of impurities which are present in crude product. The majority of methods described in patents involve organic solvent (benzene, toluene, trichloroethylene) extraction of crude lactam of ε-aminocaproic acid with the following multistage purification using chemical and physical methods. Multistage distillation and in recent times also crystallization from solutions in various solvents or from melts are used as finishing treatment of caprolactam owing to which the highest quality may be obtained (ULLMANN's).

The process and plant presented below were accomplished in an industrial scale in 1975 on the basis of our own research and design works (SYNOWIEC et al.; PRL-Patent).

2. Laboratory studies

The main purpose of this stage of work were: choice of proper solvent, collection of physicochemical data characterising considered system and determination of crystallization process parameters.

As a caprolactam solvent water, cyclohexane, ethyl acetate and tetrachloroethylene have been considered. The initial comparison itself of the caprolactam solubility in said solvents (ULLMANN's . . .) and taking into account their basic properties allow to conclude that water is far more advantageous than the other liquids: it solves high amounts of caprolactam and besides it is commonly available, cheap, nontoxic and nonflammable. Also its purifying action expressed as the ratio of analysed constituent content in solid crystals and mother liquor is very satisfying (see Tab. 1).

Table 1

Grade of the caprolactam purification by means of crystallization from solutions of various solvents

Quality index	solvent		
	water	cyclohexane	tetra chloroethane
division factor	40	31	26
manganese number	13—15	2—3	8—11
volatile bases content	0.26	0.67	0.32

Table 2

Supercooling temperature and limiting supersaturation for intensively mixed caprolactam-water solutions

Concentration, kg/kg	0.86	0.88	0.90
supercooling temperature, K	12.8	11.2	8.3
limiting supersaturation, kg/kg	0.055	0.044	0.035

Table 3

Dependence of boiling temperature of caprolactam-water solution on pressure (concentration 0.90 kg/kg, measurement precision $\pm 5\%$)

Pressure, Pa	$1.3 \cdot 10^3$	$2.7 \cdot 10^3$	$5.3 \cdot 10^3$	$8 \cdot 10^3$	$1.3 \cdot 10^4$
boiling temp., K	295	309	324	337	345

In order to complete the physico-chemical data for caprolactam-water system supercooling temperatures and limiting supersaturation for the intensively mixed solutions (Tab. 2) as well as dependence of boiling temperature on pressure (Tab. 3) and sedimentation velocity have been determined experimentally.

The sedimentation velocity for the crystal size fraction of 0.2 to 1.02 mm ranged from $(1.9 \text{ to } 3.3) \cdot 10^{-3}$ m/s.

A series of caprolactam crystallization tests in the crystallizer equipped with a stirrer and a cooling jacket type MSMPR of 2 dm^3 volume and made of glass in order to facilitate the visual supervision of the process, has led to the following conclusions:

— Crystallization time and crystalline product size depend on the amount of solid phase in the crystallizer. Thus in the same cooling conditions, introducing 30 mass per cent of solid phase into the crystallizer allowed to shorten the process duration 3.5 times without causing any essential changes of product quality.

— For the formation of product having mean particle size of 0.5 mm, the crystals residence time (in a crystallizer) of circa $5.4 \cdot 10^3$ s is sufficient.

— With the increase of solid phase content in a suspension a mechanical stirrer efficiency is deteriorating. When a crystal phase amount exceeds 45% weight a suspension colour and consistency is honey-like and agitating is reduced to the zone in the close vicinity of a stirrer.

— Purification efficiency can be substantially improved if crystals are rinsed with cold condensate after separating them from mother liquor.

3. Designing assumptions

The general guide lines for the future plant design were based on the analysis of collected literature data and the results of laboratory investigations compared with the manufacturer's requirements concerning the production capacity of the plant, product quality and the parameters of available energetical factors (limited amounts of steam, surplus of industrial water of 15 °C). From the three suggested variants of the problem solution the two-stage vacuum-isohydric cooling crystallization process has been chosen. As the decisive criteria the results of economic calculations were used regarding reliability in practice, possibilities of home machine-building industry and investment inputs. The concept of the chosen solution is presented on the attached diagram (Fig. 1) as a concentration versus temperature plot.

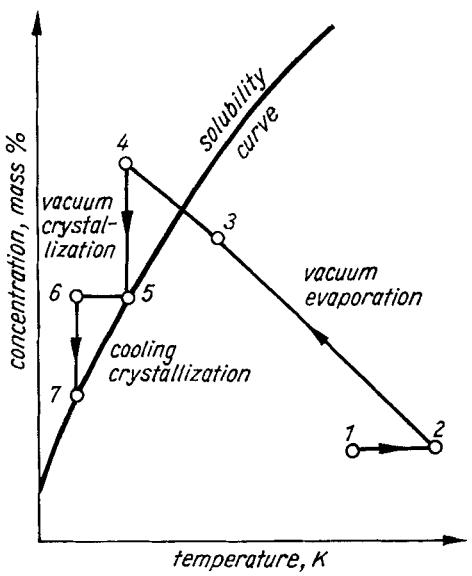

Fig. 1. Idealized diagram of caprolactam crystallization process

The feed solution being a mixture of crude caprolactam and mother liquor returns whose parameters are described in point No 1 is supplied into the crystallization plant. Owing to its varying temperature and generally negative heat balance the solution is heated up to the temperature determined in point No 2. Then it is cooled adiabatically i.e. by evaporating the part of solvent under the reduced pressure and afterwards minimally concentrated (point 3), reaching thus the point close to the saturation. In the next operation the solution is directed into a vacuum crystallizer where owing to the evaporation of further amount of water the solution becomes concentrated and cooled to the state determined by the parameters of point No. 4. As a result, an

equivalent amount of crystal phase is produced (point No. 5). The final stage of the process involves isohydric cooling crystallization which proceeds at constant water content under atmospheric pressure (point No. 6). During this stage, a further crystal growth occurs and the suspension reaches the state designated by point No. 7.

The suggested solution provides high working flexibility and makes possible the full control of the process run at each of its stages.

The following assumptions were accepted to the design of the plant:

— to reduce the risk of scale transfer as well as to increase working flexibility of the plant, the process should be put into practice in several production lines the capacity of each ought to amount to $30 \cdot 10^6$ kg of caprolactam per year,
— the average particle size of the product should be 0.5 mm,
— 3/5 of the total crystalline mass is educed in vacuum crystallizer and the rest i.e. 2/5 — in isohydric cooling crystallizer,
— residence time of crystals in each crystallizer is $5.4 \cdot 10^3$ s.

High viscosity of crystal suspension and a large amount of educed crystal phase (Ist stage — ca 33 mass.%, IInd stage — ca 51 mass.%) were the basic criteria for the constructional designing of each crystallizer. It was decided to use the crystallizer with suspension circulated by means of a propeller pump for the vacuum crystallization, and the drum crystallizer with water-cooled jacket and a spiral agitator — for the isohydric crystallization.

The main dimensions of the individual apparatuses were calculated by means of the algorithm presented in details on the 7th Symposium (SYNOWIEC 1979a, b).

For calculating the evaporator and vacuum crystallizer the developed relationship was most useful in determining the unitary load of vaporization surface:

$$q = 3.56 \cdot 10^4 \cdot P^{0.132} \cdot \Delta T^{1.375} \cdot H^{-1} \text{ kg/m}^2 \text{ s}$$

where

P — pressure in crystallizer, Pa
$\Delta T = T - T_0$ the grade of overheating of solution, K
T — bulk of solution temperature,
T_0 — boiling temperature of solution at "P" pressure,
H — evaporation enthalpy, J/kg.

The equation aproximates with the exactness to $\pm 20\%$ experimental data gathered in several industrial plants. It is applicable to $P \lessapprox 10^5$ Pa and $\Delta T \lessapprox 5$ K.

4. The industrial plant

The final development of the discussed process is presented in a flow diagram (Fig. 2) and two photographs (Fig. 3a, b).

In a feed tank [1] there are temporarily stored: water solution of caprolactam from the synthesis, mother liquor, solutions obtained by distillating waste fractions and solutions from washing crystals in a centrifuge. The parameters of this mixture range as follows: concentration from 80 to 86 mass.% and temperature from 72° to 78 °C.

The centrifugal pump [2] pumps the solution through the heat exchanger [3] to vacuum evaporator [4] working under the pressure of ca $5.3 \cdot 10^3$ Pa. Then the solution flows down gravitationally to the circulation pipe of the vacuum crystallizer [5] working under the pressure of $2.7 \cdot 10^3$ Pa. The propeller circulating pump [6] forces a big amount of crystalline suspension to circulate through the crystallizer and

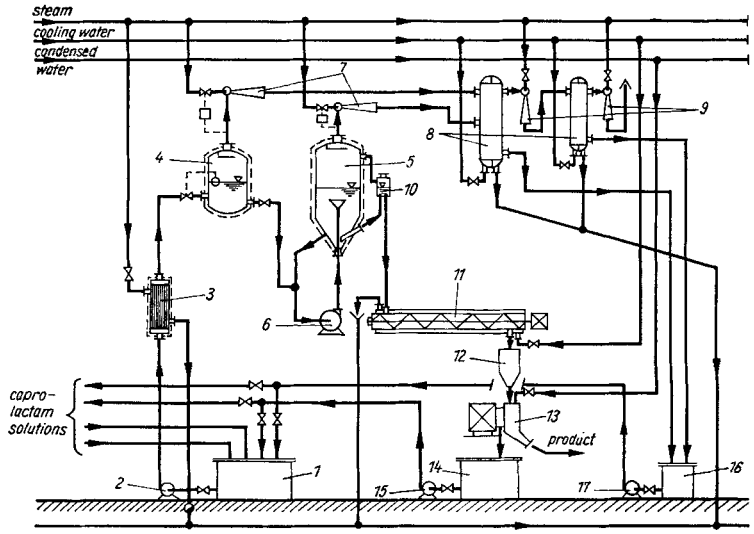

Fig. 2. Flow sheet of caprolactam crystallization plant (condensed read condensate)

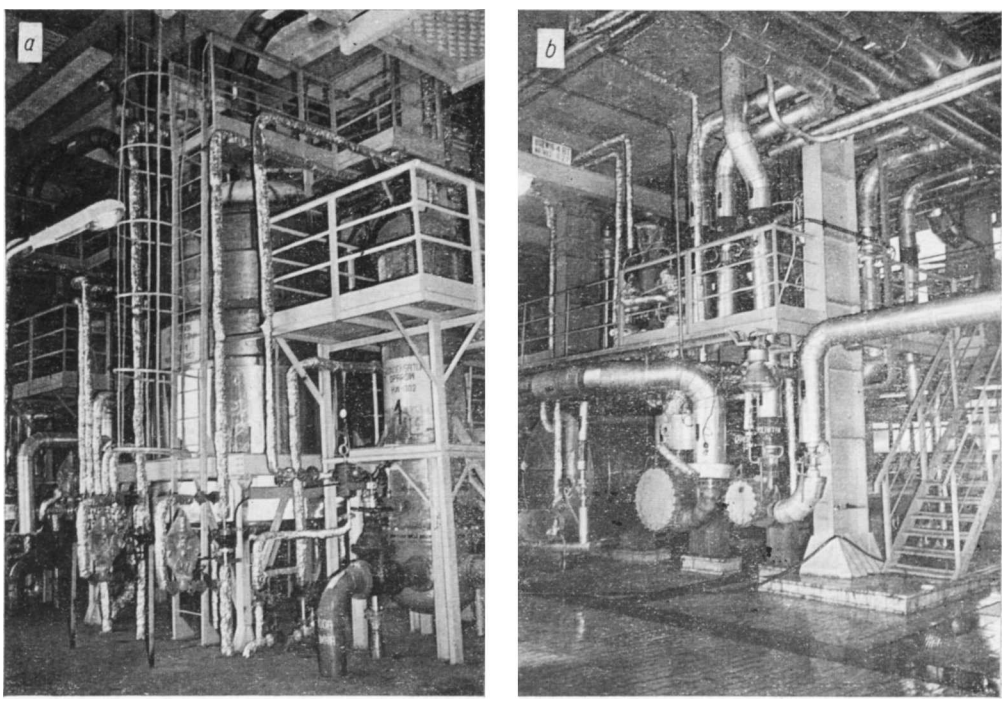

Fig. 3. a – Fragment of vacuum crystallizer, b – Fragment of cooling drum crystallizer

this enables the crystals to be suspended and the solution supersaturation to be maintained at required level. The vacuum in the evaporator and crystallizer is generated by the condensation-vacuum system consisting of three-stage ejector set [7, 8, 9].

The crystalline suspension produced in vacuum crystallizer flows down through an overflow [10] into a surface cooled drum crystallizer [11]. Thanks to a further cooling and a high content of solid phase there are favourable conditions for the crystal growth and a complete supersaturation rebuilding. The spiral agitator mounted in the crystallizer counteracts to some extent too rapid formation of deposits on the heat exchange surface and causes the uniform transfer of the suspension to the buffer tank [12] situated on the opposite end and connected directly to the centrifuge [13].

The crystals, after rinsing in the centrifuge with cold condensate are directed to the further processing and despatch whereas the mother liquor flows down to a collecting tank [14]. From the collecting tank it is returned by centrifugal pump [15] partly to the crystallization process (tank 1) and partly to the chemical purification installation.

The division of the crystallization line into two stages enables to run the process with a high volume capacity at sufficient possibility of its control and assures high working reliability especially at the transfer and removal of very dense suspension containing over 50% weight of solid phase.

In the proposed vacuum crystallizer the solid phase is produced at a comparatively high rate (140—180 kg/m^3 · h) and at considerable supersaturation of the solution what makes that not all the grains are adequately shaped and the crystallizer effluent is still supersaturated. The disadvantages of this stage are eliminated by a horizontal water cooled drum crystallizer. More moderate conditions prevailing in this crystallizer permit the "rippening" of crystals making them grow bigger, better shaped and cleaner.

Owing to the over 30% evaporation of water introduced with the feed solution the mass of educed caprolactam of increases considerably and at the same time the mass of mother liquor decreases. It has essential importance for the latter's utilization.

5. Operating data

Basing an experiences gained in a period of several years' plant work it can be claimed that the plant has been designed adequately and its operation and control do not cause any difficulties.

The product quality is high:

- manganese number (3% solution) (10—18) 10^3 s
- volatile bases content (as NH_3) 5—9 ppm
- colouration of 5% solution (in APHA scale) 5
- extinction (optical density) at 290 nm max. 0.6
- moisture content max. 0.15%
- granulometric composition:

size (mm)	mass per cent after		
	vacuum crystallizer	cooling drum crystallizer	centrifuge
1.02	0.4	0.5	0.5
−1.02 +0.6	31.3	37.0	31.7
−0.6 +0.3	42.5	43.4	36.5
−0.3 +0.2	19.6	16.3	26.6
0.2	6.2	2.8	4.7

The data of energy consumption per 1 t of crystalline caprolactam:

- power 50 kWh
- steam 0.62 t
- cooling water (288 K) 100 m^3

The process does not pollute air or waste-waters and gives no burdensome for utilisation wastes. The presented method of caprolactam purification by crystallization may be easily introduced almost into all known production processes of this compound and especially into those where the extraction of lactam at final stage is made means of water.

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