PURIFICATION BY SOLID LAYER MELT CRYSTALLIZATION

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Abstract

The application of solid layer crystallization techniques in industry is arousing ever more interest. One reason is the increasing demand for ultrapure products, and another is the energy-saving potential of this separation technology.

This article examines solid layer melt crystallization as concerns its purification efficiency. The crystallization process was carried out in two different modes, whereby the process parameters were varied and post-crystallization treatments were additionally applied. The experimental results were used as the basis for a mathematical fit of a semi-empirical expression which predicts the purification efficiency. It was used for a design of different multistage plants, which operate with different crystallization strategies. One result is that a comparable product quality is attainable with a simple process technique in combination with post-crystallization treatments, instead of a more complicated and therefore more expensive process technique.

Keywords: caprolactam, dynamic mode, melt crystallization, plant design, static mode

Introduction

Melt crystallization is well known in industry. It is applied, for example, to separate organic mixtures, especially thermosensitive substances or organic mixtures which are difficult to separate by distillation (e.g. isomers). Due to the high selective separation performance of melt crystallization, ultrapure qualities can be achieved.

Solid layer melt crystallization, a quite frequently used technology, can be carried out in different modes [1, 2]. Post-crystallization purification treatments can additionally be applied to improve the separation results [3, 4]. The achievable purity of the product is influenced by a number of parameters. Industry is interested in establishing the magnitude of each such parameter as concerns its influence on the purity of the product. With this knowledge, a better design of crystallization plants should be possible.

Experimental

In solid layer melt crystallization, the technical equipment always has a cooled surface in contact with the feed melt, which should be separated. The compound

with the lower melting point will crystallize on the cooled surface. The crystallizing compound forms a solid layer on the surface (Fig. 1).

In general, the success of the separation will be quantified by the distribution coefficient k_{diff}, defined as the ratio of the impurity concentration of the formed solid layer c_{cr} and the initial feed concentration c_{Feed} of the melt ($\approx$feed):

$$k_{diff} = \frac{c_{cf}}{c_{Feed}} \qquad (1)$$

According to this definition, no separation at all occurs when $k_{diff}=1$. In this case, the amount of impurity in the resulting crystal layer c_{cr} is identical to the impurity concentration of the feed c_{Feed}. In contrast, a 100% pure crystal layer, i.e. $c_{cr}=0$ wt.%, will be obtained when $k_{diff}=0$.

Solid layer melt crystallization was used here to separate caprolactam from its impurity cyclohexanone. The experimental work focused on an examination of the crystallization technique in the static and the dynamic mode. Static mode means here that the melt remains stagnant in front of the cooled surface. The dynamic mode was carried out so that the melt flowed as a falling film over the cooled surface. Lab-scale equipment was used for the experiments, with a melt volume of 5 l. The equipment allowed crystallization in both the static mode and the dynamic mode [5].
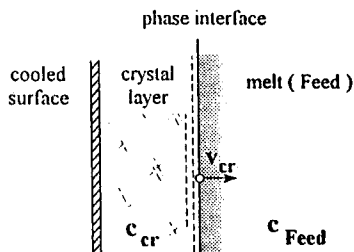

Fig. 1 General situation of the solid layer melt crystallization

The key parameter which distinguishes the static and dynamic modes is the mass transfer coefficient k. In the dynamic mode, the mass transfer coefficient is almost ten times higher than in the static mode. Further investigated parameters of the crystallization process were the initial melt concentration c_{Feed} and the crystal growth rate v_{cr}, i.e. the velocity of solid layer interface growth in the direction perpendicular to the cooled surface into the melt (Fig. 1). Finally, the post-crystallization purification treatments were examined. Sweating and diffusion washing experiments relating to the purification effect on the crystal layer were monitored.

Results

All parameter variations led to improvements in the purification process. For a comparison of all the results, the presentation in Fig. 2 was chosen. In this Figure,

the highest value of k_{diff} was set to 100% as reference value for all the other k_{diff} results. The highest value of k_{diff} represents the worst separation (Eq. (1)).

This was observed in the static mode in which a "high" crystal growth rate v_{cr} of $2.0 \cdot 10^{-6}$ m s^{-1} was used. A "low" crystal growth rate ($v_{cr} = 1.0 \cdot 10^{-6}$ m s^{-1}) leads to a better separation, i.e. to a lower impurity concentration of the crystal layer. As an
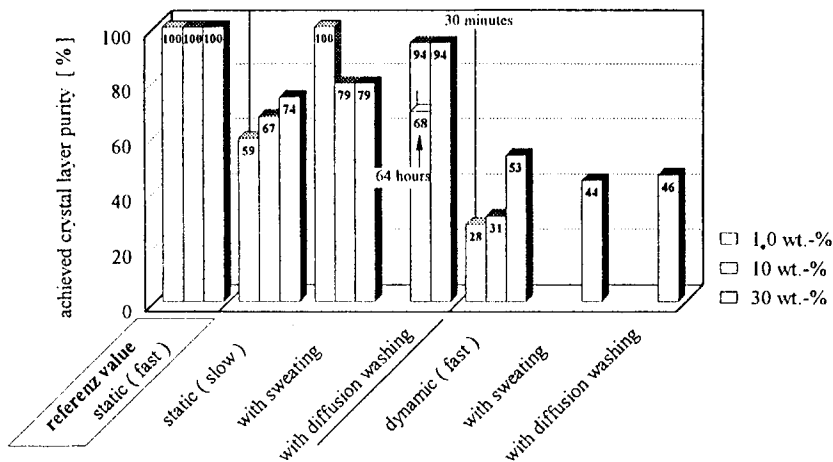

Fig. 2 Purification results of caprolactam/cyclohexanone by different kind of crystallization strategies
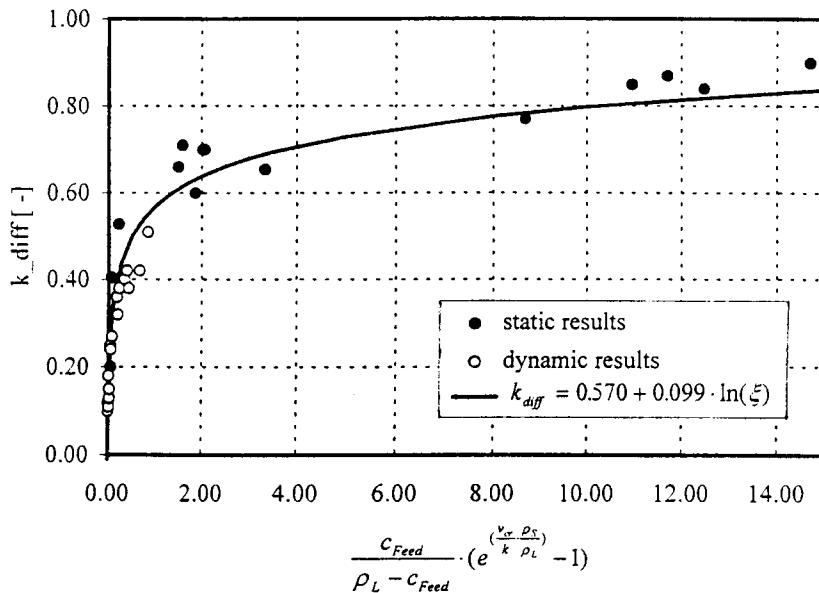

Fig. 3 Uniform presentation of the static and dynamic crystallization results of caprolactam/cyclohexanone

example, for a feed concentration of 1.0 wt.%, a reduction of the crystal layer impurity concentration down to 59% of the initial value was achieved. Similar improvements could be established for other feed concentrations, in the dynamic mode as well as in combination with post-crystallization treatments [6].

The practical transfer of the results is possible if the results can be described by an uniform mathematical expression, i.e. an expression with which the distribution coefficient can be predicted. Wintermantel [7] has suggested an uniform presentation which includes all significant parameters in terms of the distribution coefficient:

$$k_{diff} = f(k, c_{Feed}, v_{cr}) => k_{diff} = f\left(\frac{c_{Feed}}{\rho_L - c_{Feed}}\left(e^{(v_{cr}/k \cdot \rho_s/\rho_L)} - 1\right)\right) \qquad (2)$$

By means of Eq. (2), results of application of the static and the dynamic mode can be plotted together in one diagram, as may be seen in Fig. 3.

The results measured for the examined organic mixture of caprolactam with the impurity cyclohexanone can be fitted by a curve of the following form:

$$k_{diff} = \alpha + \beta \ln(\xi) \qquad (3)$$

Here

$$k_{diff} = 0.570 + 0.099\ln(\xi)$$

(standard errors: in $\alpha = 8.5152\%$, in $\beta = 0.6088\%$)

with

$$\xi = \frac{c_{Feed}}{\rho_L - c_{Feed}}\left(e^{(v_{cr}/k \cdot \rho_s/\rho_L)} - 1\right)$$

Discussion

An industrial plant generally consists of several stages [8]. In order to determine the number of stages, the desired product purity and yield have to be fixed. The stages can be distinguished as purification stages (PS) and stripping stages (SS). A schematic illustration of a multistage crystallization plant is to be seen in Fig. 4. In each stage, the initial feed features, i.e. the mass of feed m_{Feed} or the feed concentration c_{Feed}, and the process conditions, i.e. k_{diff} or the crystal growth rate v_{cr}, vary. Equation (3) allows a prediction of the separation efficiency of each stage by fitting the different process conditions. If such a mathematical tool is available, it is possible to design and optimize an industrial crystallization plant.

An optimization should lead to a minimum in the number of stages. As a rule of thumb, it may be stated that, the lower the number of stages, the lower the investment and running costs. The key value of such an optimization is the freezing ratio r_f of each stage. The freezing ratio is the ratio of the crystallized mass m_{pp} and the mass of liquid feed m_{Feed} per stage:

$$r_f = \frac{m_{pp(stage)}}{m_{Feed}} \qquad (4)$$

r_f itself depends on the achievable distribution coefficient and the initial feed concentration. It is limited by the eutectic point of the given binary mixture:

$$r_{f.max} = \frac{c_{eut} - c_{Feed}}{c_{eut} - c_{Feed} k_{diff}} \qquad (5)$$

The optimization of a multistage crystallization plant is the optimization of r_f for each stage, considering the changing stage conditions and the r_f limit according to Eq. (5) [9]. This optimization runs iteratively. The first run starts with fixed values of r_f. A mass balance for each considered stage will be carried out whereby the results for one stage are the initial values for the next stage and so on. In the next run, r_f for the first stage will first be increased. The final product purity achieved and the yield are compared with the values for the previous run. If the results are better, r_f will be increased; if they are worse, r_f will be decreased. A new run starts and r_f for each stage will be varied until no significant improvement of the product can be observed.
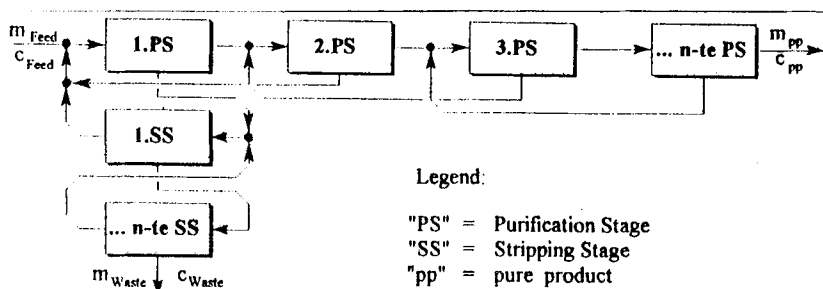

Fig. 4 General multistage cristallization chart

For each of the different crystallization strategies (the results are shown in Fig. 2), a plant is designed and optimized. The design is based on Eq. (3) and the experimental data of the purification achieved by sweating and diffusion washing. The desired product purity c_{pp} should involve an impurity concentration of less than 1.0 wt.%, with a yield m_{pp} of more than 66% of the feed mass m_{Feed}. The task was to find the minimum number of stages required to reach this fixed aim. The maximum number of stages considered was three purification stages combined with two stripping stages. The results of the optimization are listed in Table 1.

One result of the process optimization is that, purely by crystallization in the static mode, the desired production aim is not attainable with 5 or fewer stages. It is possible, however, in the static mode in combination with post-crystallization treatments such as sweating or diffusion washing.

A purification in the dynamic mode leads to much better results. The desired product quality and quantity can be achieved. With two stages fewer than in the

Table 1 Evaluation of the given separation task

Crystallization strategy	Required stages	Impurity	Yield	Assessment
Static	3PS+2SS	1.0 wt.%	<66%(!)	aim not reached !
With sweating	3PS+2SS	1.0 wt.%	68%	OK
With diffusion washing	2PS+1SS	1.0 wt.%	73%	OK
Dynamic	2PS+1SS	1.0 wt.%	72%	OK
With sweating	2PS+1SS	1.0 wt.%	75%	OK
With diffusion washing	2PS	1.0 wt.%	74%	OK

static mode. With dynamic crystallization combined with diffusion washing, a further stripping stage can be saved.

If the technical costs are taken into account, the static mode processes are cheaper than the dynamic ones. The static mode requires much simpler technical components than the dynamic mode. A further finding of the comparison is that the static mode combined with diffusion washing can be an economic alternative to a dynamic process. A comparable product purity and yield can be achieved in the two process variants.

On the other hand, the advantage of the dynamic process is the smaller size of the equipment required, due to the shorter overall retention time. The running costs are also lower with dynamic equipment, if only the phase transition energies are considered. The smaller the numbers of stages, the smaller the resulting phase changes, too.

Conclusion

A semi-empirical equation which predicts the purification achievable by crystallization was derived from the results of crystallization experiments carried out under a wide variety of process conditions. The equation was used to design several multistage crystallization plants, which operate with different crystallization strategies. A comparison of the number of stages required to attain a desired product purity reveals the advantages or disadvantages of the different crystallization strategies. Such a comparison facilitates the search for the most economic process strategy for industrial application.

Symbols

c	in general: amount of impurity, concentration/wt.% $- g_{impurity}/g_{melt}$
c_{cr}	impurity concentration of solid crystal layer/wt.%
c_{eut}	eutectic concentration/wt.%
c_{Feed}	impurity concentration of melt (feed)/wt.%
c_{pp}	impurity concentration of pure product/wt.%
c_{waste}	impurity concentration of waste/wt.%
k_{diff}	distribution coefficient $- c_{Feed}/c_{cr}$

v_{cr} crystal growth rate/m s^{-1}
r_f freezing ratio $- m_{pp}/m_{Feed}$
m_{pp} mass of pure product/g
m_{Feed} mass of feed/g
m_{waste} mass of waste/g
k mass transfer coefficient/m s^{-1}
ρ_L density of melt (liquid)/kg m^{-3}
ρ_S density of crystal layer (solid)/kg m^{-3}

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References

1 Y. Özoguz, Zur Schichtkristallisation als Schmelzkristallisationsverfahren, PhD-Thesis, Universität Bremen 1991, VDI-Verlag, Düsseldorf 1992.
2 J. Ulrich and B. Kallies, Developments in crystallization processes from the melt, in current topics in crystal growth research, India, 1994, p. 1.
3 M. Matsuoka, M. Hishi, A. Sumitani and K. Ohori, Phenomena of Sweating and Application to Purification of Organic Crystals, in World Congress III of Chem. Eng., Tokyo 1986, p. 980.
4 M. Neumann and J. Ulrich, Purification by diffusion washing-a Model, in J. Ulrich (Ed.), BIWIC 1994, Verlag Mainz, Aachen 1994, p. 14.
5 M. Neumann and J. Ulrich, Progressive Freezing Process-Static/Dynamic-a Comparison, in Z. H. Rojkowski (Ed.), 12th Symposium on Industrial Crystallization, Warschau, Vol.1, 1993, p. 61.
6 M. Neumann, Vergleich statischer und dynamischer Schichtkristallisation und das Reinigungspotential der Diffusionswäsche, PhD-Thesis, Universität Bremen 1995.
7 K. Wintermantel, Die effektive Trennwirkung beim Ausfrieren von Kristallschichten aus Schmelzen und Lösungen-eine einheitliche Darstellung, Chem.-Ing.-Tech., 6 (1986) 498.
8 G. Matz, Fraktionierte Kristallisation, Chem.-Ing.-Tech., 7 (1980) 562.
9 G. Wellinghoff and K. Wintermantel, Schmelzkristallisation-theoretische Voraussetzungen und technische Grenzen, Chem.-Ing.-Tech., 9 (1991) 881.