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PROGRESS IN CONTINUOUS FRACTIONAL CRYSTALLIZATION

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1. Introduction:

Crystallization is a far more attractive method for separation and purification of organic compounds than is often realized. When well applied, the advantages of crystallization as compared to distillation are: large separation effect, low energy consumption and low process temperature.

The large separation effect may be very advantageous, when very high purities (99-99.99 %) are aimed at or when similar compounds like isomers have to be separated.

As is well known, the boiling points of isomeric compounds generally differ so little, that separation by distillation is very difficult. Purification of mixtures of isomers by crystallization may be rather easy because of large differences between the freezing points. As an illustration the boiling- and freezing points of two isomeric systems are given in Table I.

The low energy consumption of crystallization stems from the following. The energy consumption of a counter-current separation is about proportional to the reflux ratio, As the separation effect is large in crystallization. The

TABLE I.Boiling and freezing points of two isomeric systems.

compounds	boiling point °C, 10^5 Pa	freezing point °C
ethylbenzene	136.2	- 95.0
para-xylene	138.4	+ 13.3
meta-xylene	139.1	- 47.9
ortho-xylene	144.4	- 25.2
meta-dichlorobenzene	172	- 25
para-dichlorobenzene	174	+ 53
ortho-dichlorobenzene	179	- 17

number of stages required for a distinct separation is relatively small. This relatively small number of stages demands in its turn a limited reflux ratio. The reflux ratio will usually be 2 to 10 times smaller in crystallization than in distillation. By this the energy consumption of crystallization will be considerably lower than that of distillation. Moreover the heat of transition is 2 to 4 times smaller in crystallization than in distillation.

Because of its small energy consumption continuous fractional crystallization may be very competitive in the large scale ultrapurification of organic compounds.

Though the separation effect of a single crystallization may be rather large, high purities or large yields can usually not be obtained in one step. Multistage crystallizations are required in order to arrive at the goals aimed at.

Multistage crystallizations are usually realized by repeating single crystallizations in conventional crystallizers. The process operation is cumbersome and expensive. Problems met in conventional crystallizers originate from the separation of crystals and mother-liquor and the growth of incrustations e.g. on agitators.

Metallwerk Buchs (MWB) has bypassed these difficulties by developing a multistage crystallization process based on repeating the single process, in which solid handling and phase separation are avoided¹. This process will be presented in section 3.

Another approach is to realize multistage crystallizations in one operation using one apparatus similar to multistage distillation and extraction.

A suitable countercurrent between crystals and liquid and a satisfactory rate of interfacial mass transfer, however, are difficult to establish, hampering the application of continuous fractional crystallization.

Some main developments in this field are reviewed in the sections 5, 6 and 7.

The present state of continuous fractional crystallization is discussed.

2. Possibility of separation by crystallization:

The possibilities of separation and purification by crystallization are determined by the solid-liquid phase equilibria pertinent to the system. Two well-known types of equilibrium diagrams are those belonging to the eutectic and solid solution systems.

When dealing with a eutectic system (Figure 1) it is theoretically possible to obtain a pure compound by one single crystallization. In many cases, however, crystallizations are not carried out under equilibrium conditions. Then, the separation efficiency of a single crystallization may be decreased considerably by kinetic effects, especially when the concentration of impurities is large and e.g. approaches the eutectic composition. Mother-liquor with its contained impurities will be occluded inside crystal imperfections or will be trapped in agglomerates of crystals.

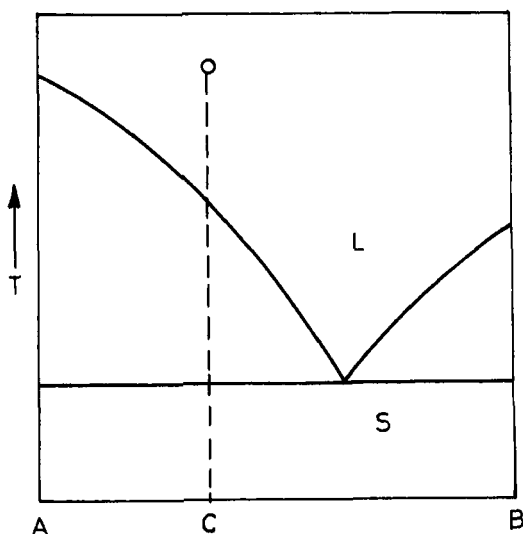


FIGURE 1.

Simple eutectic system.

When considering a solid solution system (Figure 2) it is impossible to obtain pure material in one crystallization stage.

Multistage separations are thus often required in order to arrive at the purity or the yield aimed at, not only when solid solution systems, but also when eutectic systems have to be separated.

As Figure 1 shows, the two compounds of a binary eutectic system can not be separated completely by crystallization. The mother-liquor will not be concentrated further than to the eutectic composition. This means, that the possible yield depends on the eutectic limit, when dealing with eutectic systems. The possible recovery of systems showing complete solid solution is not limited by the phase diagram. So additional means or methods are required, when a high recovery of a eutectic system is aimed at.

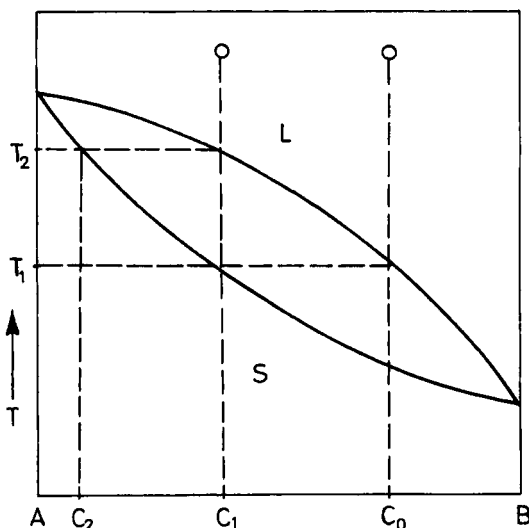


FIGURE 2.

Complete solid solution system.

Crystals can be grown from a melt or from a solution. The operation of crystallization from a melt is usually preferable, as it is less complicated than that of crystallization from a solution. Application of a solvent may be considered, however, for the following reasons:

- 1) to lower the process temperature to below the melting point, when the compound is not stable at its melting point.
- 2) to reduce viscosity, as a high viscosity hampers the growth and the settling of the crystals.
- 3) to achieve a higher yield of the pure compound from a eutectic mixture by the formation of e.g. an adduct (adductive crystallization².) A well known example concerns the recovery of para-xylene mixtures.

Adduct formation between carbontetrachloride and para-xylene may reduce the eutectic concentration of para-xylene

from 13 down to 2 wt%³. Suitable adducts are also known for the separation of para- and meta-cresol and for the separation of para- and ortho-nitrochlorobenzene.

3. Multistage separation by repeated crystallization:

Multistage separations can be obtained both by repeating the single process or by establishing a suitable counter-current contact between two phases.

A special multistage crystallization process based on repeating the single process has been developed by Metallwerk Buchs (MWB)¹. A striking feature of the MWB method is, that solids handling and phase separation are avoided.

A scheme of the MWB process is given in Figure 3. The MWB equipment comprises a crystallizer, a collecting tank, a product circulation pump, some storage tanks and a heating and cooling system.

The liquid to be crystallized is introduced at the top of the crystallizer by means of pump 4. The liquid flows down in a film and forms a solid layer on the wall of the crystallizer, as this wall is cooled to below the freezing point of the mixture. Turbulent conditions prevailing in the film promote heat and mass transfer.

The liquid collected at the bottom is fed again to the top of the crystallizer until the desired ratio between crystallized fraction and remaining liquid has been obtained.

The solid layer is melted and can be fed again into the crystallizer.

Multistage separations can be realized by repeating the process and combining crystals and mother-liquor of the several stages in a suitable way.

A flow sheet of such an operation in three stages is given in Figure 4. High purities and yields can be obtained using this process.

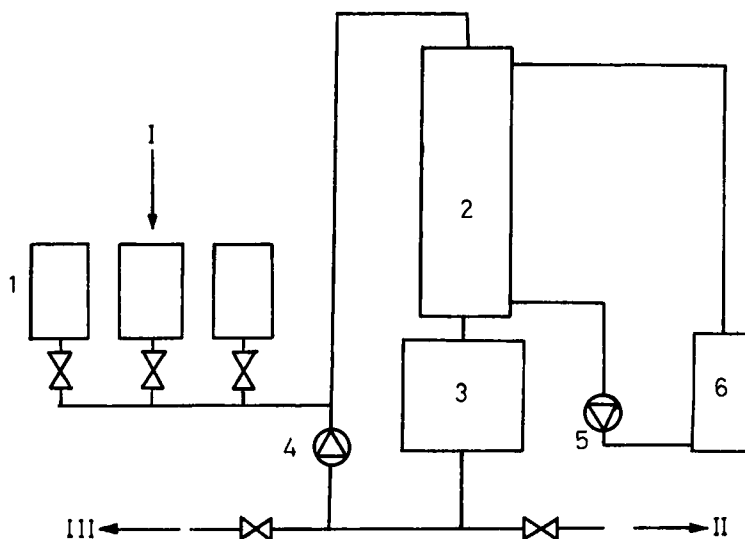


FIGURE 3.

Schematic representation of the M W B process.

- | | | | |
|---|--------------------------|-----|---------------|
| 1 | Storage tanks | I | Feed |
| 2 | Crystallizer | II | Product |
| 3 | Collecting tank | III | Mother liquor |
| 4 | Product circulation pump | | |
| 5 | Circulation pump | | |
| 6 | Cooling heating system | | |

The mechanical construction of the equipment is rather simple. The energy consumption however, is considerably higher than that of continuous fractional crystallization.

4. Principle of continuous fractional crystallization:

For the sake of convenience a short description of continuous fractional crystallization is given first.

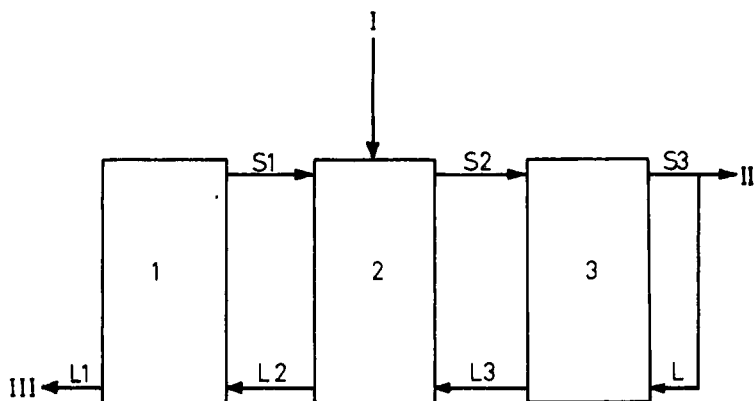


FIGURE 4.

Flow sheet of M W B process in three stages.

I	Feed	S Crystals
II	Product	L Melt
III	Waste	

Figure 5 represents a schematic flow sheet of continuous fractional crystallization from a melt.

The process of continuous fractional crystallization may be considered to be analogous to distillation.

The crystals are formed in the crystallizer (3) at one end and melted in the melter (2) at the other end of the column. In the crystallization column (1) the solid phase is transported in countercurrent to the liquid phase. The solid phase is the sum of the crystals, the entrapped and the adhering liquid. The column is preferentially held in an adiabatic condition in order to keep the flow rate of the crystals constant throughout the column.

Two mechanisms of mass transfer may be considered⁴, recrystallization and extractive washing.

Recrystallization is the mechanism by which impurities are removed from the crystals and the entrapped liquid as

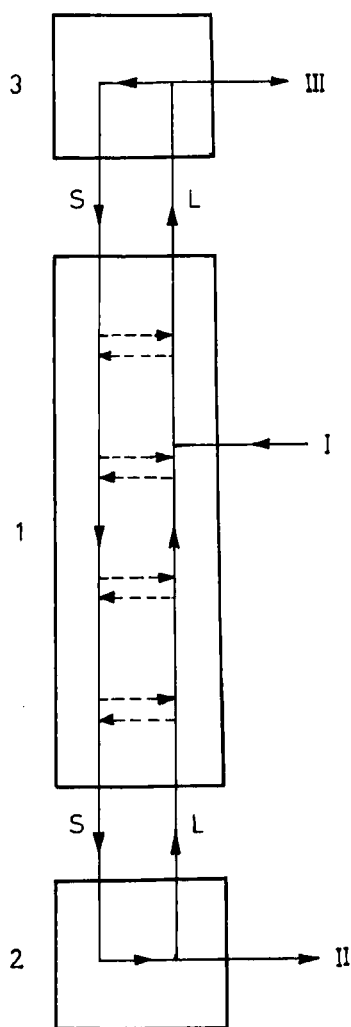


FIGURE 5.

Flow sheet of continuous fractional crystallization.

1	Crystallization column	I	Feed	S	Crystals
2	Melter	II	Product	L	Melt
3	Crystallizer	III	Waste		

the result of repeated phase changes in the liquid and the solid phase.

Extractive washing is the mechanism by which the concentration of impurities in the adhering liquid is changed by transfer into the free liquid. Both mechanisms may occur simultaneously. A mathematical description of the contribution of both mechanisms to the separation result has been given elsewhere⁵.

As in continuous distillation, product and waste may be withdrawn at both ends of the column. The feed can be introduced at a suitable point of the column. The rate of product take off is determined by the phase diagram of the related compounds, the flow rates and the mass balance in the column.

A good separation efficiency can only be obtained in a countercurrent process, when a high rate of mass transfer between the two phases can be realized.

The driving force for this interfacial mass transfer is the deviation from equilibrium at the interface. Mass transfer through the interface will occur in such a way, that the equilibrium deviation decreases.

The transport by diffusion of material to and from the interface often limits the rate of interfacial mass transfer. Therefore the separation efficiency can be increased by speeding-up the rate of diffusion. Stirring is e.g. a well known method for promoting diffusion in a liquid or a vapour.

When crystals and a liquid are transported counter-currently in a column like a liquid and a vapour in a distillation column, the contribution of recrystallization is small because of the extremely low rate of diffusion in a solid. Extractive washing is the dominating mechanism of mass transfer in such a column.

Consequently the separative power is limited, which makes these columns less suitable for the separation of compounds forming solid solutions as well as for the attainment

of extra high purities. Washing columns are the only counter-current crystallization columns used in large scale productions thus far.

Well known examples are those applied in the "Phillips process and the Brodie Purifier" (see section 5).

In the column for continuous fractional crystallization developed by TNO the interfacial mass transfer is promoted by exerting a mechanical action on the crystals resulting in a high separation efficiency per unit of length (see section 7).

5. Phillips process and Brodie Purifier:

Many attempts to realize countercurrent crystallization are described in literature. Several excellent reviews are available on the subject^{6,7,8,9}.

In this article the principle of 4 main developments are discussed: the Phillips process, the Brodie Purifier, the Schildknecht column and the TNO process.

The "Phillips" process^{10,11} and the Brodie Purifier^{11,13} are based on:

- slow crystallization to grow crystals as pure as possible, with suitable dimensions,
- countercurrent washing of the crystals with a reflux flow obtained from molten crystals.

The "Phillips" equipment (Figure 6) consists of a long scraped cooling system, where the crystals are formed and a washing column with a piston, a wall filter and a heater.

The crystals are forced down the column by the piston, impure liquid is removed through the filter, and washing liquid, formed by melting crystals at the bottom of the column, is transported upward countercurrently to the crystal flow.

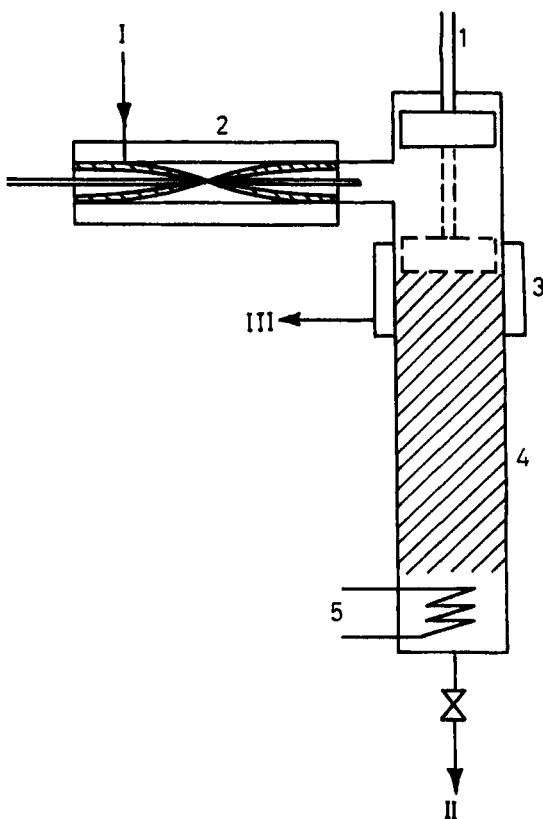


FIGURE 6.

Phillips process.

- | | | | |
|---|------------------------------|-----|---------------|
| 1 | Reciprocating piston | I | Feed |
| 2 | Scraped surface crystallizer | II | Product |
| 3 | Wall filter | III | Mother liquor |
| 4 | Washing column | | |
| 5 | Melter | | |

Pulsed washing columns have also been used.

The process is applied on a large scale for the purification of para-xylene and the freeze concentration of beer.

The features of the "Brodie Purifier" (Figure 7) are a long, horizontal freezing section consisting of a series of cooling scraper crystallizers, a feed which continuously enters the crystallizer section somewhere in the middle and a long vertical purification section.

A temperature gradient is forced upon the crystallizer sections and a countercurrent between the melt- and the crystal flow is established. The purpose of this set-up is to

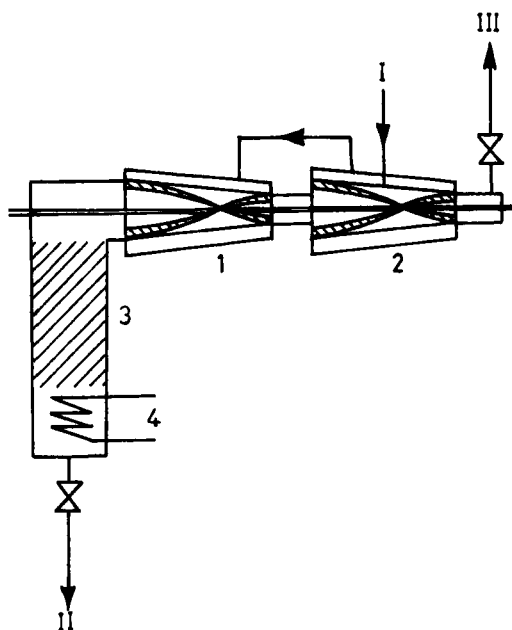


FIGURE 7.

Brodie Purifier.

- 1 Refining section
- 2 Recovery section
- 3 Washing column
- 4 Melter

- I Feed
- II Product
- III Waste

grow crystals from as pure a melt as possible, rather than all from the least pure reject waste.

The crystallizer is very long to decrease the growth rate. The residence time may be up to 24 h.

Technical applications of the Brodie Purifier are known for the separation of para- and ortho-dichlorobenzene and the purification of naphthalene.

Extractive washing is the dominant mechanism of mass transfer in these crystallization columns. The contribution of recrystallization to the separation effect is small. The number of crystallization stages obtainable is therefore rather limited. This makes these processes not very suitable for the separation of compounds forming solid solutions or for the attainment of extra high purities and yields, especially when kinetic effects decrease the separation efficiency of the single process.

6. Schildknecht column:

Schildknecht has developed a column for continuous fractional crystallization applicable on a lab. scale (Figure 8)¹⁴. This type of column has been investigated and further improved a.o. by Betts and Girling^{7,15} and by Powers, Albertins and Henry^{15,17}.

Crystal growth, countercurrent flow of solid and liquid and melting of the crystals all take place in one vertical column.

The column is annular in cross-section. A forced transport of the crystals is realized by means of a rotating helix. The rotating spiral conveys the crystals between the two concentric tubes in the desired direction, in countercurrent to the liquid phase.

Acceptable results have been reported in lab. scale columns based on this principle. The process appears to be applicable to both solid solution systems and eutectic mix-

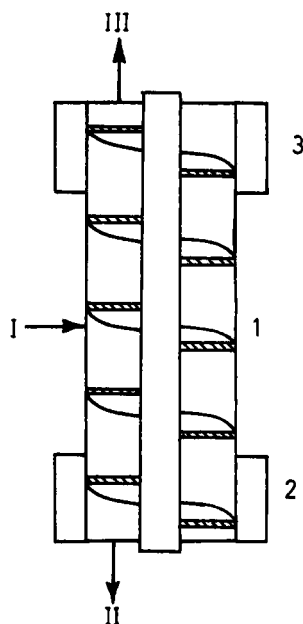


FIGURE 8.

Schildknecht column.

1	Purification section	I	Feed
2	Melting section	II	Product
3	Freezing section	III	Waste

tures. Most reported results concern the purification of benzene. Though the separation effect of the column is limited in a number of cases, high throughputs have been obtained (51/h using a 50 mm column).

The Schildknecht column has a number of disadvantages.

The construction of the column is rather complicated and the dimensions appear to be very critical. As the column size is increased, the helical coil becomes more difficult to fabricate and operate with the necessary small clearance between the helix and the walls. The helical coil may be re-

placed by an Archimedean screw, in which the helix is attached to a central shaft and rotates with it, but this screw, too, must have appropriate, closely defined geometric proportions.

The operation of the column is insufficiently reliable. The control of crystal growth, crystal flow and product- and waste streams is difficult. Pilot columns of up to 200 mm diameter have been operated successfully.

Attempts to further scaling-up the column to dimensions of technical interest have been unsuccessful thus far.

In order to overcome these difficulties of continuous fractional crystallization, TNO has developed a new crystallization column. The striking feature of the TNO column is the promotion of the interfacial mass transfer by exerting a mechanical action on the crystals resulting in a high separation efficiency per unit of length.

Principle of TNO process.

In the TNO crystallization column the separative action is not only obtained by washing but also by an even dominating process of continuous repeated crystallization^{18,19,20}. A flow sheet of the process is given in Figure 9.

It appeared, that the interfacial mass transfer between the crystals and the liquid phase in a countercurrent column can be promoted by exerting a mechanical action on the crystals.

This mechanical action may result in damaging, breaking, cleaving, splitting and/or grinding of the crystals. By this a suspension of partly damaged crystals with very different particle sizes is obtained. Such a suspension is not stable. The small or damaged particles will melt, whereas the larger and more perfect crystals grow, at least when the system is held in an adiabatic condition. In this way impurities may transfer from the solid to the liquid phase.

At the same time a great number of dislocations is introduced in the crystals increasing the mobility of the impurities in the solid phase. The composition and the

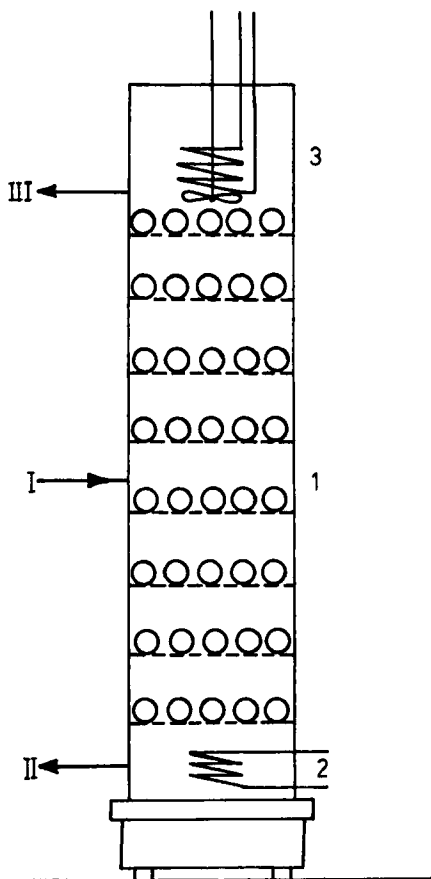


FIGURE 9.

TNO process.

- 1 Crystallization column
- 2 Melter
- 3 Ultrasonic crystallizer

- I Feed
- II Product
- III Waste

temperature of the liquid phase meeting the crystals counter-currently will deviate from the equilibrium values of the solid phase enhancing the melting or dissolving of the small and damaged crystals being not stable and thus increasing supersaturation.

By the countercurrent transport of crystals and liquid phase the (re) crystallization occurs from another (more pure) melt or mother liquor than surrounding these crystals originally. In this way concentration differences can be realized in a column in a way analogous to distillation and extraction.

Vibration of the column containing proper combinations of balls and sieve plates appears to be a simple method for providing a suitable mechanical action on the crystals enhancing recrystallization. Besides for this mechanical action, the combination of balls and perforated plates provides for a good countercurrent transport of crystals and liquid.

At the same time an intensive stirring is obtained at the crystal interfaces promoting diffusion in the liquid phase by decreasing boundary layers e.g. in the pores of the crystals.

The possible rate of transport of the crystals through the column is determined by the sedimentation properties of the crystals; the separative power of the column per unit of length by the result of mechanical action and rate of recrystallization. The higher the rate of recrystallization is, the smaller the residence time of the crystals can be.

The production rate of the column is limited either by the transport rate or the residence time of the crystals depending on the properties of the system and the difficulty of the separation.

8. Calculation of the separation efficiency:

When testing a crystallization column it is desirable to express the separation efficiency in numerical terms e.g.

in relation to the column properties and product flow. The theoretical plate concept can be used for this purpose, as in distillation^{5,18}.

The number of theoretical plates can be calculated according to the following method.

When dealing with a binary system, forming solid solutions, the relation between the concentrations in the two phases leaving the n^{th} plate in the production side of the column may be presented by (Figure 10)

$$K = \frac{x_n}{y_n} \left(\frac{1 - y_n}{1 - x_n} \right) \quad (1)$$

where K is the equilibrium constant

x_n is the mole fraction of the impurity in the crystal phase leaving the n^{th} plate and entering the $(n + 1)^{\text{th}}$ plate.

y_n is the mole fraction of the impurity in the liquid phase leaving the n^{th} plate and entering the $(n - 1)^{\text{th}}$ plate.

The mass balance in a cross section of the production side of the column may be given by:

$$Sx_n - Ly_{n+1} = Px_p \quad (2)$$

where S is the flow rate of the crystal phase

L is the flow rate of the liquid phase in the production side of the column.

P is the rate of product flow.

x_p is the mole fraction of the impurity in the product flow.

When dealing with the waste side of the column, the equilibrium condition may be written as

$$K = \frac{x_m}{y_m} \left(\frac{1 - y_m}{1 - x_m} \right) \quad (3)$$

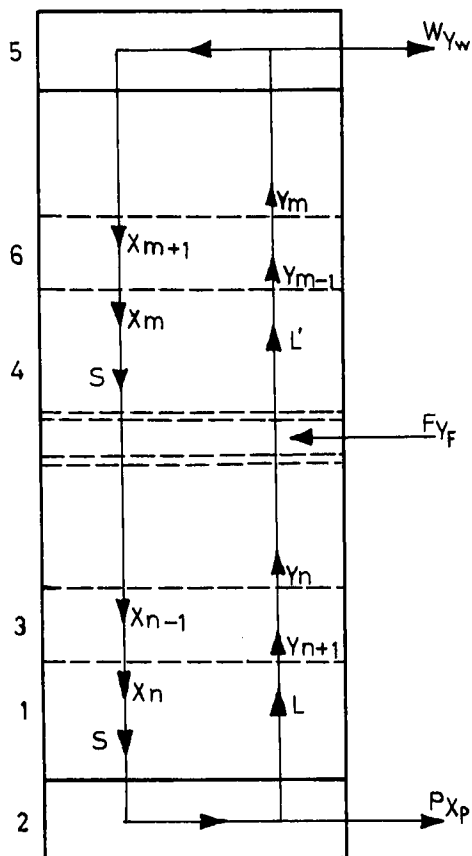


FIGURE 10.

Flow sheet for the calculation of the number of theoretical plates.

- 1 Refining section
- 2 Melter
- 3 The n^{th} plate

- 4 Recovery section
- 5 Crystallizer
- 6 The m^{th} plate

where x_m is the mole fraction of impurity in the crystal phase leaving the m^{th} plate and entering the $(m - 1)^{\text{th}}$ plate.

y_m is the mole fraction of impurity in the liquid

phase leaving the m^{th} plate and entering the $(m + 1)^{\text{th}}$ plate.

In this case the mass balance may be represented by

$$L y_m^1 - S x_{m+1} = W y_W \quad (4)$$

where L^1 is the flow of the liquid phase in the waste side of the column .

W is the rate of waste flow and

y_W is the mole fraction of impurity in the waste flow.

It is assumed, that S , L , L^1 and K are constant throughout the column.

The number of theoretical plates corresponding with the separation result can be calculated from the equations 1,2,3 and 4. This calculation can be easily carried out with a pocket calculator.

The number of theoretical plates can also be determined graphically using the McCabe Thiele method.

As an illustration, the number of theoretical plates required for a distinct separation has been calculated. The ratio between the rates of product- and crystal flow was varied. It was assumed that the equilibrium constant amounts to 0.4.

The results are summarized in Table 2.

Table 2 shows, that quite a number of crystallization stages may be required in separations of solid solution systems, when high purities are aimed at.

When the separative action of a crystallization column is based on repeated crystallization, it must be possible to realize such a number of crystallization stages in one operation.

It may be noticed, that the applicability of the theoretical plate concept in continuous fractional crystallization

Table 2.

Calculated number of theoretical plates, required
for a distinct separation assuming $K = 0.4$.

concentration of impurity mole fraction feed	product	ratio between rates of product- and crystal flow	number of theoretical plates
0.1	0.01	0.0	2.7
0.1	0.01	0.1	2.9
0.1	0.01	0.2	3.3
0.1	0.01	0.4	4.9
0.2	0.001	0.0	6.0
0.2	0.001	0.1	6.8
0.2	0.001	0.2	7.9
0.2	0.001	0.4	13.8
0.3	0.0001	0.0	9.2
0.3	0.0001	0.1	10.4
0.3	0.0001	0.2	12.2
0.3	0.0001	0.4	24.0

is limited to solid solution systems. It is not useful to express the efficiency of a column as a number of theoretical plates when dealing with a eutectic system.

According to the solid-liquid equilibrium line of a eutectic system the possible separation can always be obtained in one theoretical stage. Then the separative action of a column always corresponds with less than one theoretical stage.

When kinetic effects can be taken into account, an effective single stage separation effect could be defined for eutectic systems. Then it could be possible to express the plate efficiency for eutectic systems in numerical terms, too.

9. Separation of systems forming solid solutions:

It is well known, that the removal of thiophene from benzene usually occurs by chemical means, the physical means like distillation and crystallization being inadequate thus far.

Tackling the separation of this "solid solution" system by crystallization was considered as a challenge to prove the efficient separating power of the column developed.

The value for the equilibrium constant of the benzene - thiophene system has been obtained by normal freezing experiments and by temperature - heat content curves²¹. The efficiency of the normal freezing process was increased using a special stirring device²². The value obtained for the equilibrium constant was 0.40. This means, that after a single step crystallization the crystals will contain at least 40 % of the original impurity content, which is a very poor result.

The column conditions applied were: diameter 80 mm, opening of plates 0.6 x 0.6 mm, number of metal balls -30, diameter of balls - 12 mm, amplitude of vibration -0.3 mm, frequency -50 c/s, rate of crystal flow - 0.6 kg/h, total reflux.

The concentration of the thiophene and a number of column conditions have been varied.

The samples were analyzed by GLC using carbowax as stationary phase.

The concentrations at top and bottom of the column have been related with the number of theoretical plates according to the procedure described in section 8. If it is assumed, that the action of the crystallizer equals to one theoretical plate, the action of the column equals to the number of theoretical plates obtained minus 1.

The data obtained are summarized in the Tables 3, 4, 5, 6 and 7^{18,19}. The data of Table 3 indicate the dependence

TABLE 3.

Dependence of separation result on thiophene concentration.

length of column mm	number of sieve discs	concentration thiophene (%)	number of theoretical plates	number of theoretical plates minus 1	plate effi- ciency (theoreti- cal plates per plate) %
700	6	2.01	3.9	2.9	50
700	6	2.27	4.1	3.1	50
1200	11	20.9	6.4	5.4	50
1200	11	23.6	7.2	6.2	60
1200	11	23.7	8.4	7.4	70
1200	11	3.80	5.0	4.0	40
1200	11	3.27	5.3	4.3	40
1200	11	3.90	5.9	4.9	40
1400	13	0.63	6.4	5.4	40
1400	13	0.69	5.7	4.7	40
1400	13	0.94	6.8	5.8	40

TABLE 4.

Dependence of separation result on distance between sieve plates.

length of column mm	number of sieve plates	distance between sieve plates	concentration thiophene (%) top bottom	number of theoretical plates minus 1	plate effi- ciency (theoreti- cal plates per plate) %
1400	13	100	0.69 0.004	4.7	40
1400	13	100	0.94 0.002	5.8	40
1400	7	200	0.61 0.018	2.9	40
1400	7	200	0.65 0.020	2.9	40
1400	7	200	0.64 0.034	2.3	30
1400	7	200	0.72 0.032	2.5	40
1400	13	100	0.64 0.007	3.9	30
1400	13	100	0.47 0.009	3.4	30

TABLE 5.

The dependence of separation result on crystal flow.

length of column	number of sieve plates	distance between sieve plates mm	rate of crystal flow kg/h	concentration thiophene % top bottom	number of theoretical plates minus 1	plate efficiency (theoretical plates per plate) %
1200	11	100	0.6	3.27 0.028	4.3	40
1200	11	100	0.6	2.43 0.044	3.5	30
1400	13	100	0.6	0.80 0.003	5.1	40
1400	13	100	1.2	0.67 0.023	2.8	20
1400	13	100	1.8	0.54 0.061	1.5	10
1400	13	100	2.4	0.52 0.062	1.4	10
1400	7	200	0.6	0.63 0.019	2.9	40
1400	7	200	1.2	0.54 0.057	1.3	20
1400	7	200	0.6	0.68 0.033	2.4	30
1400	7	200	1.2	0.55 0.055	1.3	20
1400	13	100	0.6	0.47 0.008	3.5	30
1400	13	100	1.2	0.50 0.035	1.9	15

TABLE 6.

Relation between separation efficiency per sieve
plate and a number of column conditions.

column condition	variation	plate efficiency (theoretical plates per plate)
column length	700 - 1400 mm	not dependent
concentration	25 - 0.002 %	slightly dependent ($< 2x$)
distance between sieve plates	100 - 200 mm	not dependent
crystal flow	$0.033 - 0.1 \text{ kg/m}^2 \text{ s}$	inversely proportional

TABLE 7.

Dependence of separation result on vibration.

frequency vibrations / sec.	amplitude mm	layers of balls	plate efficiency (theoretical plates per disc) %	
			0.033 kg/m ² s	0.066 kg/m ² s
50	0.25 - 0.35	1	40-50	20
25	0.5	1	37	24
25	0.8	1	44	33
25	1.0	1	43	36
25	1.0	2	51	39

of the separation result on the thiophene concentration and the column length Table 4 shows the dependence of the separation results on the distance between the sieve plates and Table 5 the dependence on the crystal flow. Table 6 gives a summary of the tables 3, 4 and 5. Table 7 gives the dependence of the separation results on vibration.

It follows from table 3, that a satisfactory separation efficiency per sieve plate can be obtained.

Various concentrations of thiophene have been tested and all gave about the same efficiency per sieve plate. Thus, the separation obtained with the column, expressed in number of theoretical plates, shows little dependence on the concentration.

Table 3 shows, that very high as well as very low concentrations of impurity may be removed, proving that this crystallization column may be suitable for the preparation of very pure compounds.

During this series of experiments not only the concentration has been varied, but also the length of the column, the distance between the sieve plates and the rate of crystal flow in order to investigate the dependence of the separation efficiency of the crystallization column on these conditions.

It follows from the results obtained, as is indicated in Table 3, that the separation efficiency per sieve plate does not depend on the column length when the length is varied between 700 and 1400 mm. This means, that the separation action of the crystallization column may be considered to be proportional to the length of the column.

The separative action of the column decreases when the distance between the sieve plates is enlarged from 100 to 200 mm. In this region the separation action of the column appears to be inversely proportional to the distance between the sieve plates. The separation efficiency per sieve plate, however, remains the same.

The separation efficiency of a sieve plate decreases when the rate of crystal flow increases. In the experimental conditions applied, the sieve plate efficiency was about inversely proportional to the crystal flow.

In a number of experiments a small amount of dye-stuff was added to the test mixture. In all cases a sharp boundary between coloured and colourless substance was seen at the first sieve plate just below the crystallizer. No evidence was obtained from the colour observations, that the decrease of separation efficiency may be caused by an increase of longitudinal dispersion.

When supposing, that at higher rates of crystal flow the residence time of the crystals is the limiting factor of the process, it may be expected, that the separation efficiency does not depend on the distance between the sieve plates.

This is not the case, however, as may be seen in Table 5. Both at crystal flow rates of 0.6 kg/h and 1.2 kg/h the separation efficiency of the column is inversely proportional to the distance between the sieve plates. This means, that the decrease of the separation efficiency at increasing crystal flow rates can not be explained by a too short residence time of the crystals.

From this it may be assumed, that the "grinding" efficiency is the primary limiting factor, when the crystal flow rate is increased.

To see whether this assumption may be valid, the amplitude of vibration was increased in a series of experiments. As follows from Table 7., the separation efficiency was improved considerably then for the higher rate of crystal flow.

In a limited number of experiments product and waste have been withdrawn.

From the results of analysis it appeared that the experimental relation between purity and product flow corresponds with the theoretical one calculated from the phase diagram.

From the decrease of column contents between the start and steady state of the column it could be deduced that about 30 vol % of the column contents are crystals. As has been shown, 5 theoretical plates per meter have been obtained, when the rate of crystal flow amounts to 0.6 kg/h. From this it follows that the residence time of the crystals per crystallization stage amounts to 30 min.

The minimal residence time is difficult to estimate. It will be investigated whether the residence time per crystallization stage can be decreased further, e.g. by increasing the "grinding" efficiency. As will be obvious, the residence time required will always be system dependent.

It may be concluded from these experiments with the model system benzene-thiophene, that multistage separations can be realized in the TNO column for continuous fractional crystallization.

10. Survey of experimental results:

After the encouraging results obtained with the benzene-thiophene system, many other systems, including products of technical interest like a number of aromatic hydrocarbons, have been separated using columns with a length varying from 500 up to 1500 mm and with a diameter of 80 mm.

The mixtures have been crystallized from a melt as well as from a solution. Concentration gradients of more than 50 wt % per meter have been established. Multistage separations can be obtained in such a column.

Plate numbers equal to 5 per meter have been realized corresponding with a plate efficiency (number of theoretical plates per sieve plate) of about 50 %.

The removal of very low amounts of impurity is possible, proving that this crystallization column is also useful for the preparation of very pure compounds.

As an example benzene has been purified to a very high degree.

Only 2 ppm have been left from the impurities detectable by the gaschromatographic method applied, whereas the starting material contained 700 ppm.

Such a very low impurity content as attained is seldom found in the high cost samples of pure benzene, which are offered for scientific purposes.

Process temperatures from minus 80°C up to plus 100°C have been applied. The rate of product flow has been varied (depending on the properties of the mixture provided) from 0.03 up to $0.3\text{ kg/m}^2\text{s}$.

The conditions of operation are not critical. The column, once set at the proper conditions demanded by the systems to be separated, needs hardly any attention. Full automation of the process and unattended operation of the column is achieved.

The results of separation and purification hardly depend on the conditions of crystal formation in the cooling scraper crystallizer.

The column can be combined with any type of crystallizer.

As will be clear, good settling properties of the crystals facilitate the operation of the column. The crystal flow can be speeded up by a simple pulse action obtainable by a discontinuous removal of product at the bottom of the column.

11. Scaling-up:

It was learnt from industrial sponsors, that the commercial feasibility of the process seems rather good.

The simple construction of the column and the easy and reliable operation of the process are some promising features according to the sponsors.

Moreover, high speed mechanical equipment for the separation of crystals and mother liquor like centrifuges is not required, when crystallizing from a melt.

From this it was concluded, that scaling-up the laboratory column to dimensions of technical interest is worthwhile.

A plan for the scaling-up based on a cooperation between a manufacturing company, some producers of chemicals and TNO was set up.

The manufacturing company, Apparaten- en Ketelfabriek AKF at Goes, the Netherlands, made a design for a technical column with a diameter of 500 mm. The main difference between the designs of the technical and the lab. column concerns the method of vibrating. The lab. column is vibrated itself in order to move the metal balls. In the technical column the sieve plates are mounted on a common rod connected to an excentric. By vibrating the central rod the metal balls are agitated.

A series of tests with respect to the mechanical operation of such a column using prototypes containing 1 and 5 sieve plates with a diameter of 500 mm has been carried out. No essential difficulties have been encountered.

On the base of this experience AKF has constructed a pilot plant column with a length of 3 m, a diameter of 500 mm and containing 19 sieve plates. Mechanical tests showed very satisfactory results. Stresses in and accelerations of the vibrating parts remain within acceptable limits, which will guarantee continuous operation for years. Noise level during operation turned out to be surprisingly low.

A 5-sieve tray model having the same design and construction principles as the pilot plant column has been tested to determine the process parameters for the pilot plant and to study scaling-up effects on the process. Mixtures containing para-xylene or benzene as main component have been investigated. It was established, that a stable crystal bed could be achieved. The results with the para-xylene based

(eutectic) system were fully comparable with those of laboratory experiments using an 80 mm glass column. With the benzene based (solid solution) system the results were slightly lower than those of earlier experiments. This effect seems to be due to dimensional details and these will be improved. The experiments have shown, that operation is rather easy.

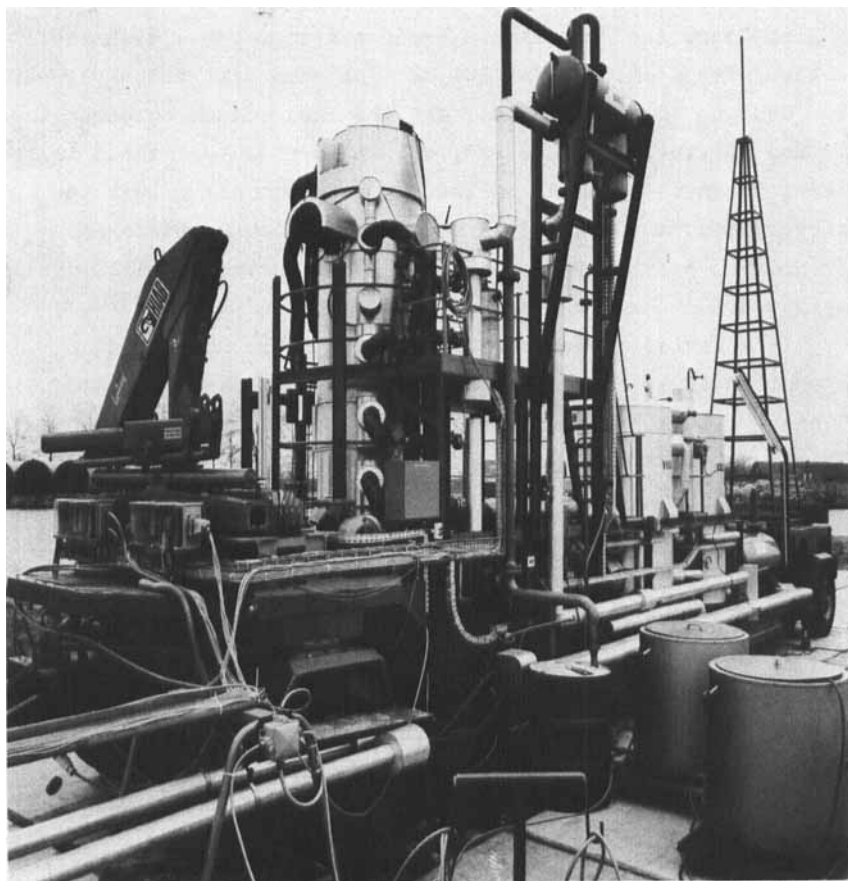


FIGURE 11.

General view of pilot installation.

To obtain results for a 300 tons per year unit, a pilot plant has been constructed, using the 19 sieve 500 mm dia. column which had already been tested mechanically. This pilot plant has been built as a skid-mounted transportable unit. Figure 11 gives a general view of this pilot unit. At the moment production tests are carried out at AKF. The first compound to be purified is naphthalene.

Since the capacity of a 19 sieve tray 500 mm column is estimated at about 300 tons per year, its most promising fields of application seem to be those of pure and ultrapure chemicals, photo-chemicals and pharmaceuticals. For the evaluation of the possibilities for bulk chemicals, scaling-up to columns with larger diameters is essential. Using the information obtained while testing the 500 mm column, a 5-sieve tray model with a diameter of 2000 mm has been designed. One sieve is now under construction and will be exposed to vibration tests. If the test results are positive, the 5-sieve tray model will be tested mechanically, after which production tests will be carried out, using the existing facilities on the mobile unit.

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