Melt Crystallization

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Introduction

Melt crystallization, sometimes referred to as 'fractional crystallization,' is a collective term for physical separation processes aimed at purification of organic compounds from a multi-component mixture by crystallization without addition of a solvent. The driving force for crystallization is created by cooling, evaporating or pressuring the melt.

The main advantage of this separation technique is the superior selectivity of the crystallization process caused by restricted mobility in the crystal lattice and strong molecular bonds. The energy consumption can be low because the heat of fusion of most organic compounds is two to four times smaller than their heat of evaporation and the operating conditions are generally mild. Finally, the absence of hazardous solvents is important from an environmental point of view. Disadvantages are the inherent slowness of crystal growth leading to voluminous equipment and the need for intensive slurry handling in certain process designs.

Balancing the merits and drawbacks, melt crystallization is usually applied for ultrapurification (> 99.99%), separation of isomers and purification of thermally unstable components. Some examples of industrial applications are acrylic acid, bisphenol A, caprolactam, cresol, dichlorobenzene, fatty acids, naphthalene, paraffin and xylene.

In this chapter, the designs of conventional and emerging melt crystallization processes are described and evaluated. Also the related field of freeze-concentration of aqueous solutions is briefly touched upon. Extensive coverage of all types of equipment on different scales is beyond the scope of this article. There is a focus on large-scale applications with a bias on state-of-the-art equipment provided by equipment manufacturers rather than the proprietary processes of end-users. More elaborate overviews of the principles and applications of melt crystallization are given in the Further Reading.

Theory

The technical feasibility and economic viability of separation and purification of an organic mixture by melt crystallization entirely depend on its solid–liquid phase equilibrium (SLE). A survey of SLE data in 1986 demonstrated that more than 70% of organic substances have melting points between 0°C and 200°C, indicating that no special thermal media are needed to achieve separation (**Figure 1**).

The classification of about 1500 binary systems in the International Critical Tables (**Figure 2**) has revealed that more than 50% form simple eutectic mixtures and 25% form an intermolecular solid compound which forms simple eutectics with the two constituent components. This type also includes the formation of more than two solid compounds. The formation of a pure solid phase in one crystallization step is feasible for roughly 85% of the systems. The formation of solid-solutions is limited to only 10%, for which complete separation in a single crystallization step is fundamentally impossible.

Even for eutectic systems, however, the product from industrial crystallizers is not 100% pure. This is caused by the adherence of mother liquor to the crystal surface and by the inclusion/entrapment of mother liquor inside the crystals. Further purification is required and this can be achieved by washing and by sweating.

- Washing is done by contacting the crystals with a fresh solvent or, preferably, with pure melted product. This operation removes adhering impurities and is widely used in commercial plants.
- Sweating can be induced by exposing the impure solid phase to slightly elevated temperatures. This operation removes locally dispersed included impurities. Upon a temperature increase, the fraction of liquid inside the crystals increases according to the lever-rule whereby the more impure sections
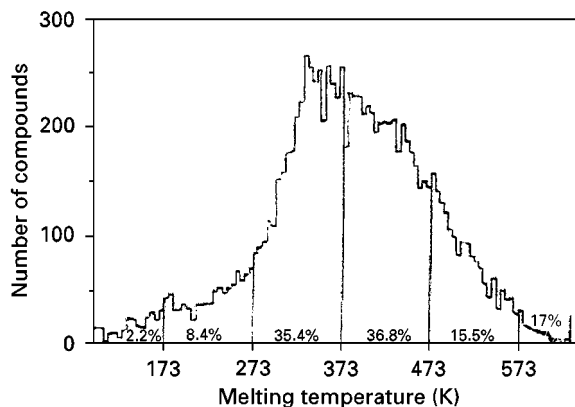

Figure 1 Distribution of atmospheric melting points of organic components (after Matsuoka and Fukushima, 1986).
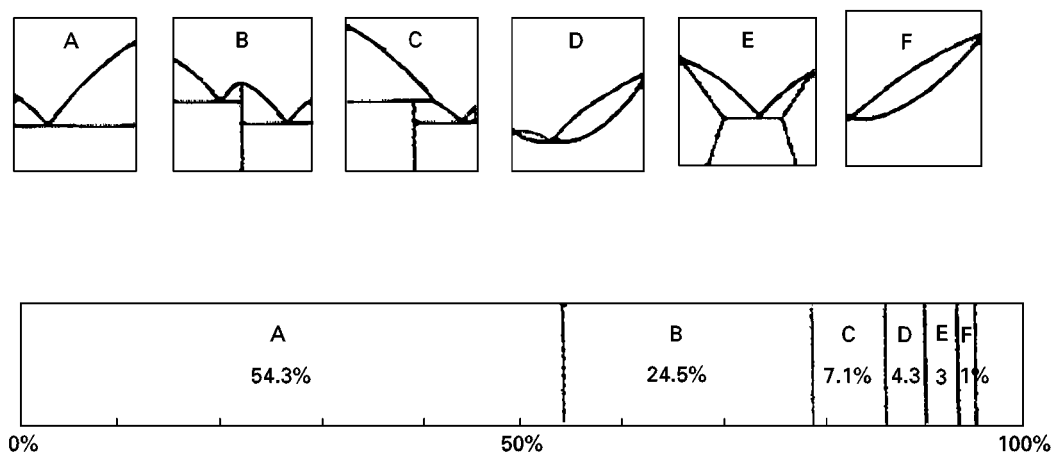
Figure 2 Distribution of binary phase diagrams of organic mixtures (after Matsuoka and Fukushima, 1986).

melt preferentially due to a lower melting point. The impure liquor comes out of the crystalline body through cracks and pores. Sweating can also be applied to solid solution systems and plays an important role as a purification mechanism in layer and suspension growth processes.

Process and Equipment Design

Indirect cooling is the most widely applied technique to produce crystals from a melt. In this context the term 'indirect' refers to the mechanism of heat transfer from the melt to the cooling medium, which takes place via the wall of a heat exchanger. Crystal growth may either take place as a layer on a cooled surface or freely suspended in the mother liquor. The principles of both techniques and their large-scale applications are discussed below. See **Table 1** for an overview and an evaluation of both techniques.

Layer Growth

In this technique the crystals grow as a layer fixed and perpendicular to a cooled wall. The heat of crystallization is removed through the crystal layer and the wall. At low growth rates (typically $< 10^{-7}$ m s^{-1}) and proper mixing of the mother liquor, a stable crystal morphology can be maintained, which results in a good selectivity of the crystallization step. In industrial practice, however, very high growth rates $(10^{-6}–10^{-5}$ m s$^{-1})$ must be applied leading to roughening of the crystal surface (cellular and dendritic growth) and consequently to entrapment of impure liquor in the layer. High growth rates are required to achieve a reasonable productivity since the growth area is limited to the heat-exchange area $(\leq 100$ m^2 m$^{-3})$.

Industrial layer growth equipment is normally operated batch-wise, whereby static and dynamic processes can be distinguished. In *static equipment*, crystal growth occurs from a stagnant melt. Commercial equipment is manufactured by BEFS Technologies (France) and Sulzer Chemtech (Switzerland). Their similar designs feature a closed rectangular vessel equipped with a high heat-exchange area in the form of finned tubes or structured plates (**Figure 3**). One full operating cycle takes about one day and comprises five steps: (1) filling of the vessel, (2) crystallization by programmed cooling, (3) sweating by gradual heating, (4) draining of residual mother liquor and (5) melting and draining of the product layer. Equipment sizes range from 0.1 to 35 m^3. Typical growth rates are in the order of 10^{-6} m s^{-1} but the overall separation efficiency of a full operating cycle is relatively good (up to 99.9 wt% product purity).

In *dynamic processes*, there is forced mixing of the mother liquor during the crystallization step. The mixing is usually achieved by circulating the liquor as a falling film or as a fully developed flow over vertical heat-exchanger tubes. Other designs whereby mixing was achieved by stirring, pulsation or bubbling-through an inert gas, were not successfully commercialized. Sulzer Chemtech provides the dynamic falling film system whereby both the melt as well as the coolant are circulated as falling films over the tube wall (**Figure 4**).

The turbulent flow regime of the mother liquor enhances heat and mass transfer, which enables higher growth rates of typically $10^{-6}–10^{-5}$ m s^{-1}. Similar to the static process, one full operating cycle comprises five stages but is completed in 1.5 h. Tubes are about 0.1 m in diameter and 12-m long while up to 1250 tubes are fitted in one shell.

Table 1 Comparison of layer and suspension growth processes (values represent order of magnitude; operation/maintenance relative to distillation)

Parameter	Layer growth	Suspension growth
Crystal surface area	Up to 100 m^2 m^{-3}	Up to 10 000 m^2 m^{-3}
Growth rate	10^{-6}–10^{-5} m s^{-1}	10^{-8}–10^{-7} m s^{-1}
Mixing intensity	Poor (static)/good (dynamic)	Good
Separation efficiency	Good (static)/moderate (dynamic)	Excellent
Product purity in one stage	$\leq 99.9\%$	$\geq 99.95\%$
Mode of operation	Repetitive batch	Once through, continuous
Heat transfer coefficient	~ 200 W m^{-2} K^{-1}	~ 1250 W m^{-2} K^{-1}
Energy efficiency	Good (static)/moderate (dynamic)	Good
Slurry handling	No	Yes
Solid–liquid separation	No	Yes
Design	Simple	Complex
Operational attention	Normal	Above average
Maintenance intensity	Normal	Above average
Scale-up	Mutiplication of units	Engineering
Economy of scale	Not good	Good
World-scale plant capacity	~ 150 kT year^{-1}	~ 350 kT year^{-1}
Feed concentration	Preferably $> 90\%$	Preferably $< 99\%$
Viscosity	< 10 cP	< 50 cP
Purification of solid solutions	Suitable	Less suitable
Freeze concentration	Less suitable	Suitable

The overall separation efficiency of one dynamic operating cycle is moderate relative to a static process but the short cycle time makes the dynamic process well suited to sequential countercurrent staging. Staging requires intermediate storage tanks but makes it possible to produce ultrapure products at good recovery. The stages are actually operating cycles which can be executed in the same crystallizer (**Figure 5**).

One of the drawbacks of the dynamic process until now has been its poor energy efficiency resulting from the need to repeatedly crystallize and melt a product to attain the desired purity. This problem was
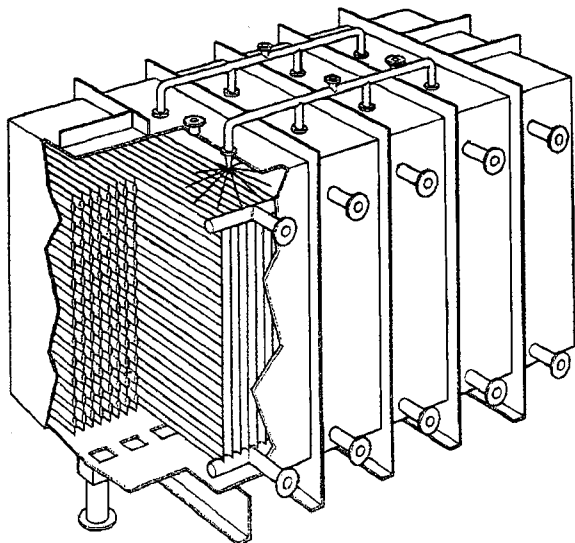
Figure 3 Static crystallizer. (Courtesy of Sulzer Chemtech.)
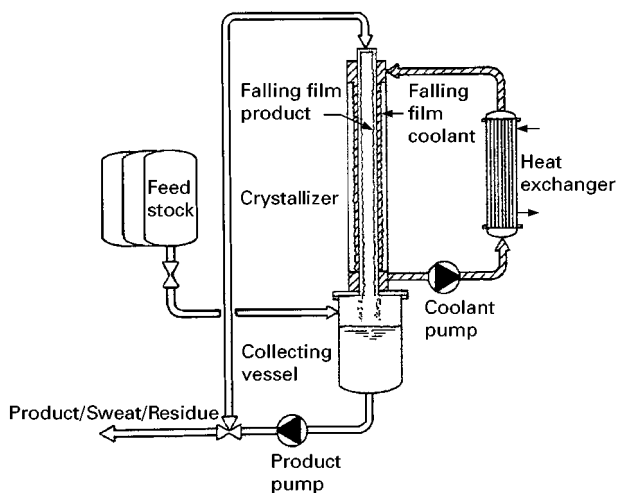
Figure 4 Dynamic falling film crystallizer. (Courtesy of Sulzer Chemtech.)
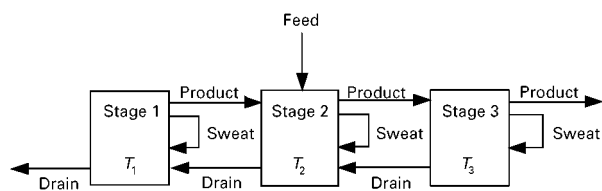
Figure 5 Multistage operation of layer growth processes (temperatures $T_1 < T_2 < T_3$).

addressed by the introduction of heat integration in 1996. The principle is based on a heat pump where a crystallizer alternatively acts as a condensor or as an evaporator for the cooling agent (**Figure 6**).

Continuous processes, whereby the layer growth occurs on a rotary drum or an endless belt, have been designed but are not applied commercially for purification of organics for various reasons (low selectivity, mechanical complexity, economy of scale).

Static and dynamic layer growth equipment are applied commercially to a wide range of products (e.g. acrylic acid, p-xylene, naphthalene, bisphenol A and paraffin). A relatively high feed purity is required, particularly for the dynamic processes, since this promotes the adhesion of the crystal layer to the cooled surface.

Suspension Growth

In this technique, the crystals form and grow freely suspended in the mother liquor. The heat of crystallization is absorbed by the supercooled liquor. High
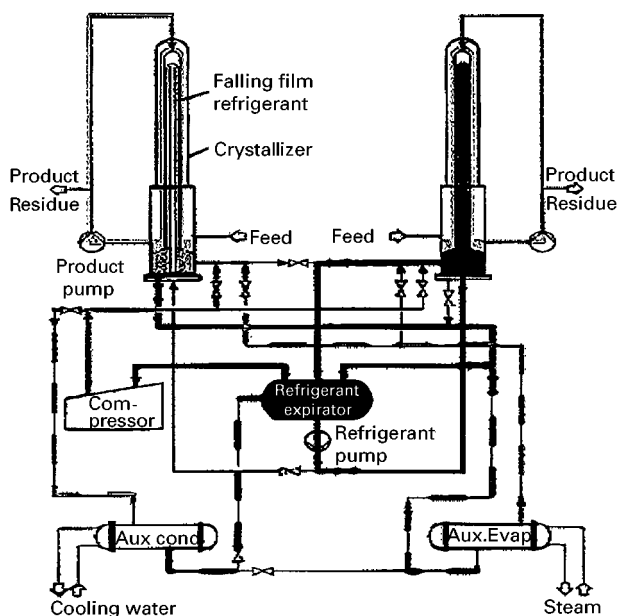

Figure 6 Heat integration of dynamic falling film crystallizers. (Courtesy of Sulzer Chemtech.)

specific productivity can be achieved at low growth rates because the crystal surface area is very large (up to 10 000 m^2 m^{-3}). Typical growth rates in industrial units are only 10^{-8}–10^{-7} m s^{-1} which contributes to an excellent selectivity of the crystallization process.

Suspension growth processes generally comprise separate sections for crystallization and solid–liquid separation. The effectiveness of the final solid–liquid separation has a major impact on the overall separation efficiency. The design of the crystallization section should be focused therefore on producing crystals with a good filterability which means essentially growing large crystals with a narrow size distribution. The fundamentals of modelling particulate processes are also applicable to suspension growth from the melt.

Crystallization section   Single-stage crystallization is often unfavourable because the nucleation and growth of all crystals occurs at the lowest operating temperature, which is determined by the yield, from an impurity-rich mother liquor. The simplicity of this design often does not outweigh the potential disadvantages:

- poor filterability of crystals due to high nucleation : growth ratio;
- reduced selectivity due to inclusion or incorporation of impurities;
- moderate energy efficiency;
- difficult solid–liquid separation.

Cascades of crystallizers, operated either cocurrent or countercurrent, are found in most processes. In *cocurrent cascades* crystals and mother liquor are transported in parallel from stage to stage at decreasing temperature. The GMF-CDC (**Figure 7**) is an example of a cocurrent cascade, where the crystal slurry flows freely from one compartment to the next via openings in the cooling elements. Along the flow direction, the impurities are concentrated in the mother liquor but the nucleation rate and the crystal growth rate decrease. As a result, the filterability of the crystals improves throughout the cascade while a good selectivity is maintained. The product crystals suspended in the impure mother liquor are withdrawn from the cold end of the cascade, which is a major drawback for solid–liquid separation.

In *countercurrent cascades* crystals and mother liquor are transported in opposite directions. TSK (Japan) and Niro-PT (Netherlands) provide similar countercurrent cascades, although the design of the individual stages differs considerably (**Figure 8**; see also Figure 17). The feed is usually supplied to the hot end of the cascade making sure that here too a large
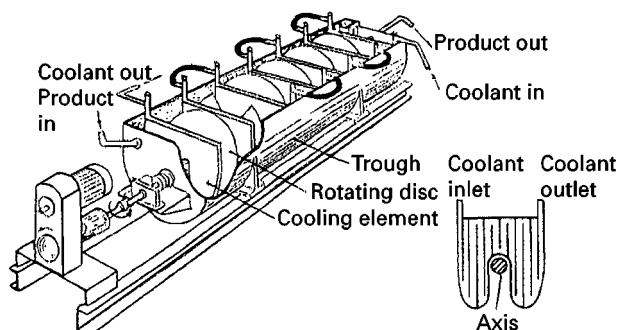
Figure 7 Cocurrent cascade of crystallizers. (Courtesy of GMF-Gouda.)

part of the crystal production occurs at high temperature from a relatively pure mother liquor. Purification of the crystals by Ostwald ripening (growth of large crystals by dissolution of fines driven by a reduction of surface energy) can play a role but it is doubtful whether there is a contribution from sweating. Product withdrawal occurs from the hot end, which simplifies solid–liquid separation.

A comparison of cocurrent and countercurrent crystallizers is shown in **Table 2**.

Solid–liquid separation section Product recovery is more and more executed in wash columns, which combine an effective solid–liquid separation with a pure melt wash and a single recrystallization step. The principle of wash columns is illustrated by **Figure 9**. A crystal slurry is pumped into the column, where the mother liquor escapes via a filter leaving behind the crystals as a packed bed. This bed is transported upwards by means of a rotating screw. At the top, the crystals are scraped off, suspended in wash liquid (recycled pure melt) and melted in an external melter. The wash-liquid circuit is kept pressurized, which causes the wash liquid to flow downward (reflux). The wash liquid does not leave the column but recrystallizes on the cold crystal bed, thereby producing the so-called 'wash front'. This front marks steep gradients in concentration, temperature and porosity.
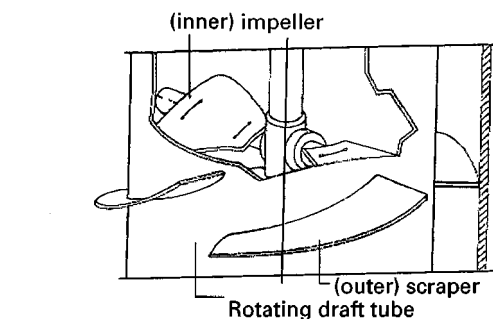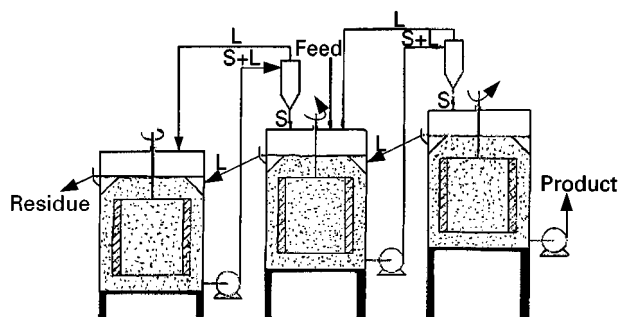

Figure 8 Countercurrent cascade of crystallizers. (Courtesy of Tsukishima Kikai Co. (TSK).)

The crystal bed can be transported under gravity, by hydraulic pressure or via a mechanical aid (screw/piston). The direction of transport is normally downwards for organic crystals and upwards for ice.

If the temperature of the feed slurry is low (single-stage or cocurrent cascade crystallization), more wash liquid will recrystallize causing a large drop in porosity over the wash front. At a given transport force exerted on the crystal bed, the throughput reduces with decreasing porosity due to an increased back-pressure from the wash liquid. Alternatively at constant throughput, the compressive stresses exerted on the crystals increase considerably which may result in deformation of some organic crystals, which are mechanically weak. Ideally, the temperature increase over a wash column should be 2–5°C.

Mass and heat transfer in the wash columns are governed by axial dispersion of the liquid phase while

Table 2 Comparison of crystallization sections consisting of a single-stage, a cocurrent cascade or a countercurrent cascade

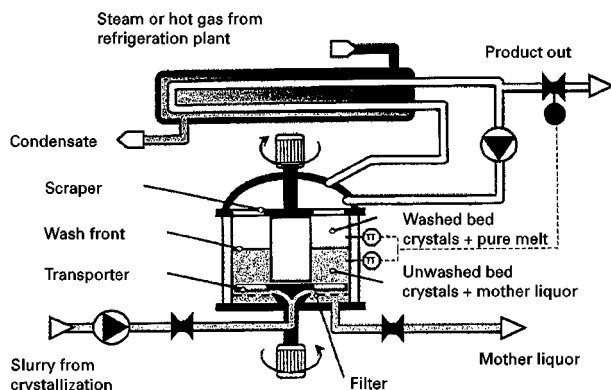| Parameter	Single	Cocurrent	Countercurrent
Operating temperature	Constant low	Decreasing	Increasing
Product withdrawal	Cold	Cold end	Hot end
Product crystal filterability	Moderate	Good	Good
Product liquor	Impure	Impure	Relatively pure
Internal slurry handling	None	Limited	Intensive
Equipment and process design	Simple	More complex	Complex

Figure 9 Principle of wash column. (Courtesy of Niro-PT.)

Figure 10 Classification of wash columns based on the crystal transport mechanism (after Jansens and Van Rosmalen, 1994).

heat-transfer limitation in the solid phase may be neglected. In the more densely packed hydraulic and mechanical wash columns, purification occurs almost exclusively by displacement washing. In the loosely packed gravity wash columns, further purification by sweating occurs because of the longer residence time.

Gravity and mechanical wash columns have been commercialized by TSK and Niro-PT, respectively. TNO (Netherlands) has developed a hydraulic wash column equipped with separate filter tubes. See **Figure 10** and **Table 3** for a more detailed comparison.

Suspension growth equipment is applied commercially to purify various organic products (e.g. *p*-xylene, naphthalene and *p*-dichlorobenzene) but also for concentration of aqueous solutions (freeze concentration, see below). There are virtually no restrictions on feed purity, while a product purity ≥ 99.99% is feasible.

Column crystallizers Column crystallizers are designs where a single-stage crystallizer and a gravity-wash column have been integrated in one shell (similar to distillation columns). The back-mixing column, for example, has been successfully commercialized by Nippon Steel Chemical Co. (Japan) for the purification of naphthalene. The pro-
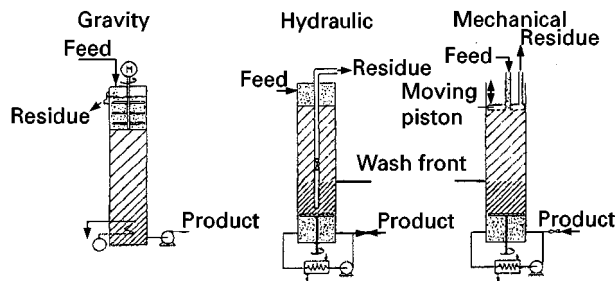
duction rate is limited by the capacity of the wash columns ($\leq 1500 \text{ kg m}^{-2} \text{ h}^{-1}$). A new development by Matsuoka is the inclined column crystallizer. The inclination promotes settling and reduced axial dispersion (**Figure 11**).

Alternative Process Designs

Evaporative Melt Crystallization

Direct cooling is the driving force for evaporative crystallization. The heat of crystallization is withdrawn by evaporation of a portion of the mother liquor, which is induced by a reduction of the operating pressure. The vapour phase is condensed in an overhead condensor and refluxed to the crystallizer. Crystal formation and growth take place freely suspended in the bulk of the mother liquor. The main advantage of direct over indirect cooling is that the heat of crystallization is transferred to the cooling medium via a clean condensing duty rather than via a (scraped) heat exchanger. Hence the heat transfer is more effective while the design and scale-up of equipment can be simplified.

In conventional evaporative crystallization processes, low boiling solvents (propane and carbon dioxide) are used to crystallize heavier organic components but the addition of solvents is not desirable for various reasons (equipment size, safety and the

Table 3 Comparison of wash columns

| Parameter	Gravity	Hydraulic	Mechanical
Height : diameter ratio	4–6	1	1
Minimum crystal size	500 μm	150 μm	150 μm
Residence time: whole column	1 h	10–15 min	10–15 min
Residence time: wash section	30 min	3–5 min	3–5 min
Purification mechanism	Washing and sweating	Washing	Washing
Maximum temperature rise	10–15°C	5–10°C	5–10°C
Compressive stress	Negligible	Considerable	Considerable
Capacity	500–1500 kg m^{-2} h^{-1}	5000–10 000 kg m^{-2} h^{-1}	5000–10 000 kg m^{-2} h^{-1}
Scale-up	Proven to 2 m	Under study	Proven to 1.2 m
Equipment design	Simple	More complex	Complex
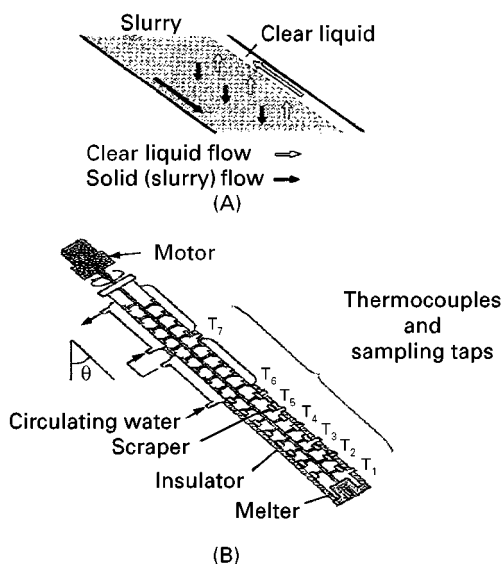
Figure 11 Inclined column crystallizer. (A) Schematic presentation of flows. (B) Experimental facility. (Reproduced with permission from Matsuoka M, Takiyama H and Soutome O (1997) Separation characteristics of an inclined column crystallizer. *Transactions of the Institution of Chemical Engineers* 75(A): 206–212.)

environment, product purity). The potential of applying direct cooling to melt crystallization, however, was not recognized until recently.

In 1993 TSK proposed a purification processes based on evaporative melt crystallization for caprolactam, acrylic acid and bisphenol A. **Figure 12** illustrates the set-up of a continuous process featuring a single-crystallization stage and a wash column (purifier).

In recent years, a batch-wise evaporative melt-crystallization process with caprolactam–water as a model system has been developed and optimized. **Figure 13**
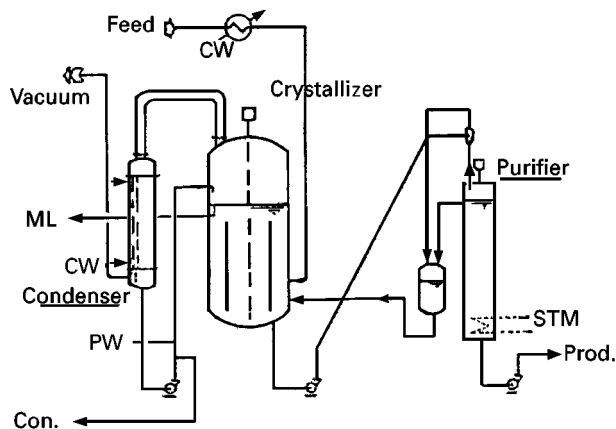

Figure 12 Continuous evaporative crystallization. ML, mother liquor; Con., condensate; Prod., product; STM, steam; CW, cooling water. (Courtesy of Tsukishima Kikai Co. (TSK).)

shows the pressure temperature–fraction temperature (PT–XT) phase diagrams where the three-phase equilibrium curve (S_cLV) stretches from the triple point of caprolactam (T_c) to the quadruple point of the binary system (T_q). Lowest operating cost can obviously be achieved near 5 wt% water, where the operating pressure is maximum and the temperature fairly high. Deep vacuum would be required for water concentrations below 1 wt% and above 20 wt%. Operating at a high temperature generates cost savings for the condensor (low area, no chilled cooling water).

Figure 14 shows the PT-trajectory for the batch-wise crystallization of caprolactam from a melt containing 4 wt% of water. Starting from point A, the pressure in the crystallizer is reduced until the vapour–liquid equilibrium is reached at point B and the melt starts to boil. Upon a further reduction of pressure, the evaporation of mainly water causes the melt to cool down but the composition of the melt does not change since the vapour is condensed and refluxed. At point C the solid–liquid–vapour equilibrium is reached and caprolactam starts to solidify. From C to D the crystal content steadily increases to 20 wt%, while the water concentration in mother liquor increases to 5 wt%.

Scale-up to 50–100 m³ crystallizers appears to be feasible, which is world scale for suspension crystallization equipment. Until now, there are few commercial installations with limited capacity. TSK has installed two units for caprolactam with a capacity of 2500 tons per year.

Pressure Crystallization

In this technique, crystallization is induced by compression rather than by cooling. The solid phase of most (organic) materials has a higher density than the liquid phase and consequently the melting point rises with increasing pressure. Benzene, for example, has an atmospheric melting point of 5.5°C but solidifies at room temperature when the pressure is about 2 MPa. Not only the melting points but also solid–liquid phase equilibria shift upward upon a pressure increase, which is illustrated for a mixture of cresols in **Figure 15**.

An additional advantage of pressure crystallization is found in the transmission of pressure being much faster than the transfer of heat in both liquid and solid phases. This means that a uniform pressure can be established quickly throughout the system. Therefore local variations in supercooling of the mother liquor can easily be avoided.

The separation of cresol isomers by conventional (atmospheric) cooling crystallization is rather difficult due to a high viscosity of the melt. Kobe Steel
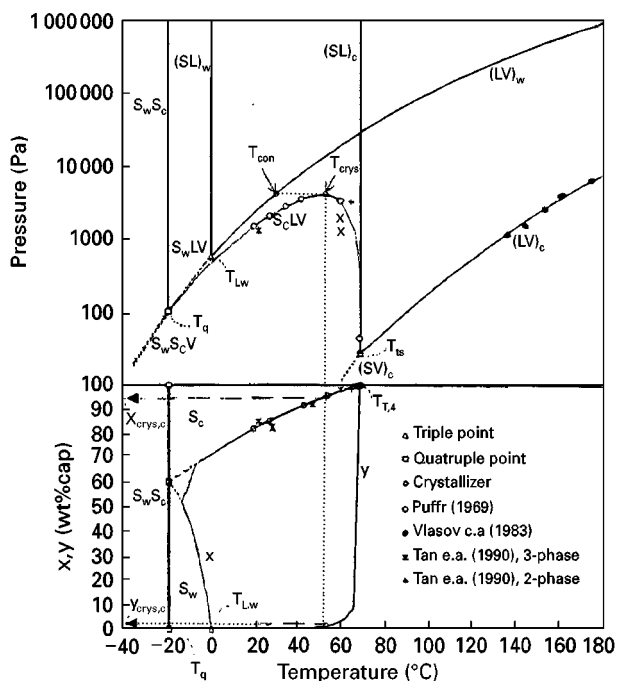
Figure 13 Pressure–temperature–composition diagram of ε-caprolactam–water. $T_{t,i}$ = triple point component i; T_q = quadruple point; T_{crys} = crystallizer temperature; T_{con} = condenser temperature; S_i, L_i, V_i = solid, liquid, vapour phase component i; $(LV)_i$, $(SL)_i$, $(SV)_i$ liquid–vapour, solid–liquid, solid–vapour equilibrium curves pure component i; x, y = liquid, vapour concentration (wt%) at three-phase equilibrium; S_iLV = three-phase equilibrium line with solid phase of component i. (Reproduced with permission from Diepen PJ (1998) *Cooling Crystallization of Organic Compounds*. PhD thesis, Technical University Delft.)

Figure 14 Part of pressure–temperature diagram of ε-caprolactam–water. (Reproduced with permission from: Diepen PJ (1998) *Cooling Crystallization of Organic Compounds*. PhD thesis, Technical University Delft.)

(Japan) developed in the 1970s a pressure-crystallization process, which was applied for the separation of *p*-cresol from its isomers on a commercial scale. A given amount of slurry from a chiller is fed to a cylindrical pressure vessel, compressed to crystallize and drained to remove residual impure melt (**Figure 16**). During the subsequent depressuring, purification by sweating can occur. Finally, a cylindrical block of purified crystals is taken out as the product. The operating temperature is 62.5°C at 200 MPa (versus 12.5°C at atmospheric pressure) which effectively reduces the viscosity of the mother liquor. Under these conditions, the selectivity and the rate of crystal growth rate are enhanced while solid–liquid separation is facilitated. Purification by sweating during depressuring is analogous to (thermal) sweating at elevated temperatures.

The features of pressure crystallization can be summarized as follows:

● batch-wise operation;
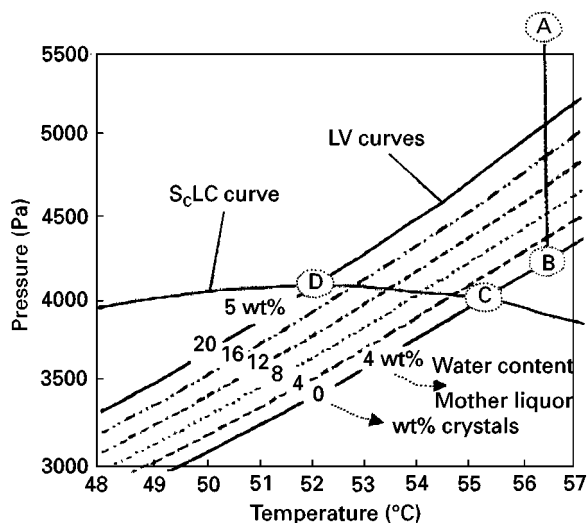● product purity up to 99.5%, feasible in one operating cycle from 70 to 80% in feed;

● high yield, limited only by the solid–liquid equilibrium of a given system;
● short cycle times, only a few minutes per cycle, due to rapid penetration of pressure;
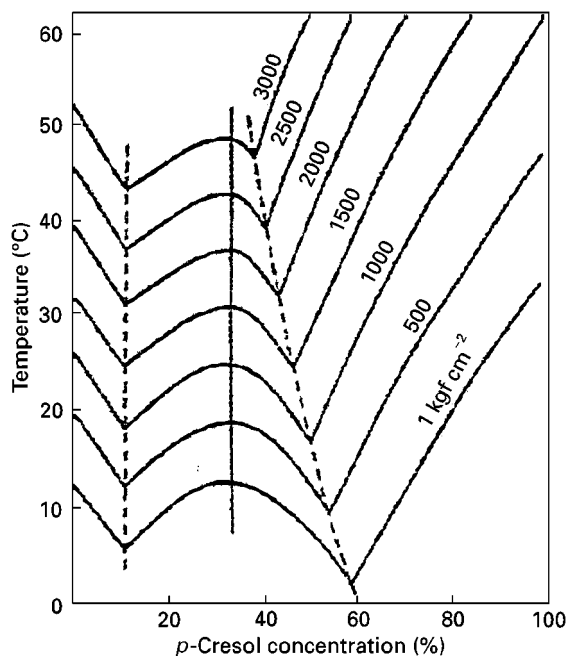● low energy consumption – only mechanical energy used for compression;

Figure 15 Phase diagram of mixture of *p*-cresol and *m*-cresol. (Reproduced with permission from Yasuda M, Sato Y and Suematsu H (1991) *p*-Cresol with high pressure crystallization. *Kagaku Kogaku* 55(4): 290–291.)

Figure 16 Operating cycle of pressure crystallization process. (Reproduced with permission from Yasuda M, Sato Y and Suematsu H (1991) *p*-Cresol with high pressure crystallization. *Kagaku Kogaku* 55(4): 290–291.)
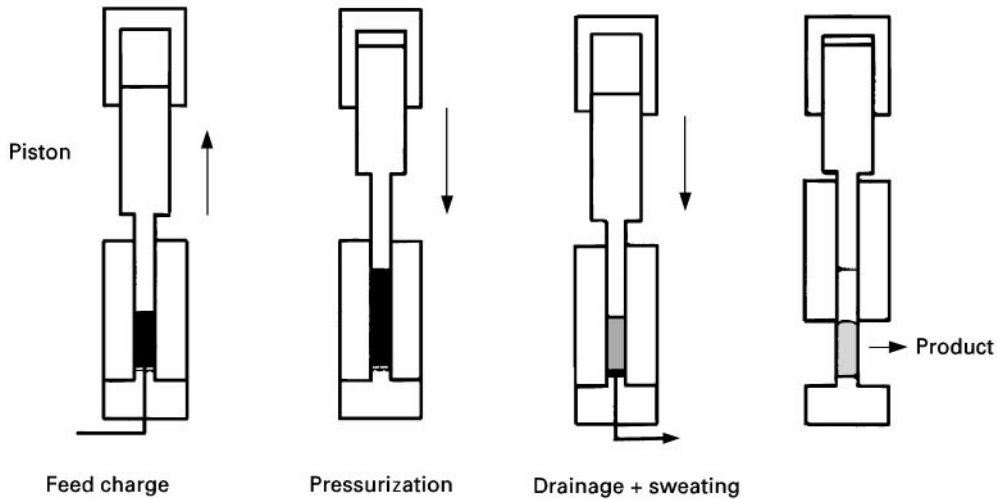
- simple process design – crystallization, separation and sweating are carried out in a single vessel;
- complex mechanical design – materials selection and construction of mechanical parts are critical factors for success.

The scale-up of pressure-crystallization equipment is not easy due to mechanical complexity, and it becomes increasingly difficult at larger vessel diameters to remove residual melt from the centre of the cake by compression. The production capacity of a single plant is in the order of 500 tons per year.

Freeze Crystallization

Freeze concentration is a separation technology aimed at concentration of aqueous solutions by means of cooling crystallization. This technology is closely related to melt crystallization based on sus-

pension growth in terms of process synthesis and equipment design.

Commercial processes feature a countercurrent cascade of crystallizers while the final solid–liquid separation takes place in mechanical wash columns (**Figure 17**). Indirect cooling is usually preferred over direct cooling to prevent contamination of the concentrate and to contain the volatile components. Large spherical ice crystals can be grown relatively easily through Ostwald ripening. The individual stages of the cascade therefore feature separate sections for nucleation and growth. Crystallization (nucleation) takes place on the surface of the external scraped surface heat exchangers. Ripening (growth) occurs in large stirred vessels.

Nearly identical process flow schemes and equipment designs can also be found in some melt-crystallization processes, e.g. to separate *p*-xylene from its isomers.
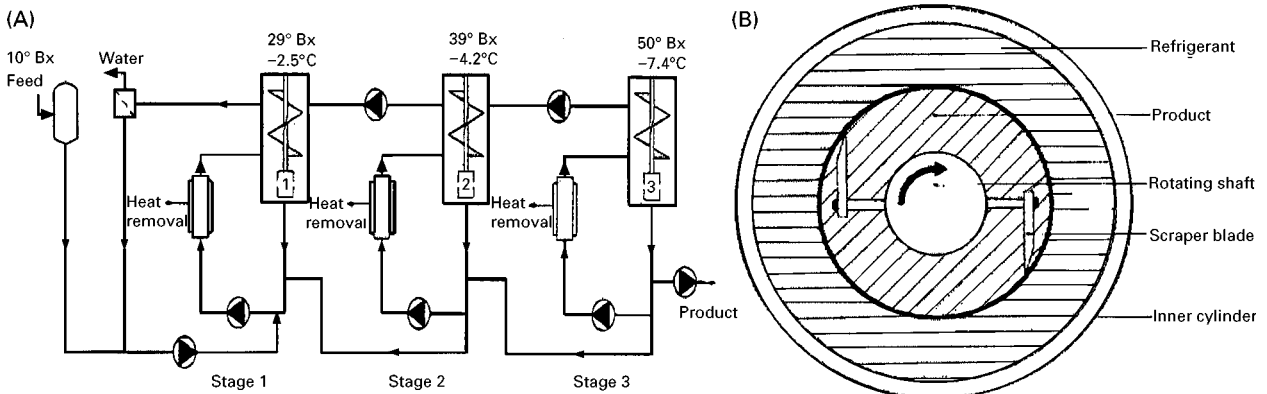

Figure 17 A three-stage countercurrent freeze concentration process. (Courtesy of Niro-PT.) (A) Simplified process flow scheme. (B) Cross-section of a scraped surface heat exchanger. °Bx is a measure for concentration of water phase (based on the breaking index).

Traditionally, most applications are found in the food industry for the concentration of fruit juice, wine, beer and coffee extract. In this field, the advantages of freeze concentration over competing technologies (membranes and evaporation) are the superb preservation of aromas and colour while decay reactions are slowed down by the low operating temperature.

Recently, world-scale installations have come on-stream where wastewater from chemical plants is concentrated. The produced melt water can be re-used as process water while the residual concentrate is incinerated. Here the advantages of freeze concentration are the low energy costs and the capability to concentrate beyond the eutectic point, where salts start to precipitate.

Drawbacks of freeze crystallization are the relatively high investment cost and the above-average maintenance intensity (there are many pieces of rotating equipment).

Conclusion and Future Outlook

Melt crystallization is the third most applied physical separation technology after distillation and extraction. Conventional processes are based on layer or suspension growth by indirect cooling.

- *Layer growth* may be considered as proven and mature technology, whereby the absence of slurry handling is a major advantage. Fully automated semi-continuous units can be delivered as turnkey projects. The need for repeated recrystallization steps to achieve a high product purity, however, increases both investment and operating cost. The desire to develop economically attractive continuously operated equipment seems to be in conflict with the basic characteristic of layer growth on a cooled surface.
- *Suspension growth* is also proven but not yet mature technology. The superior selectivity and high specific productivity of crystal growth in a suspension create a huge potential, which can be further exploited by simplification of equipment design and minimization of slurry handling.
- *Evaporative melt crystallization* is a relatively young technology which combines the merits of suspension growth with a minimum of slurry handling. For certain applications, such as caprolactam, this technique is expected to take off in coming years.
- *Pressure crystallization* is an alternative technology, which is well suited to purify components with a very low melting point at ambient temperature but elevated pressure. Outside this niche use, pressure crystallization probably cannot compete with indirect/direct cooling crystallization due to high equipment cost.

See Colour Plate 36.

Further Reading

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Polymorphism

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Introduction

When the molecules of a chemical substance are able to crystallize in more than one three-dimensional structure arrangement, the substance is said to display polymorphism. This phenomenon was discovered in the early nineteenth century but only since the middle of the twentieth century have its wider implications been appreciated by scientists investigating the crystallization, properties and interconversion of solid phases. These implications stem from the fact that different polymorphs of a given substance may