Crystallization reactors

Béatrice Biscans
Université de Toulouse.
CNRS -Laboratoire de Génie Chimique UMR 5503 –FRANCE
Crystallizer selection

Method of creation of supersaturation

Can be imposed:
- precipitation, extractive crystallization, salting out

Must be determined
From the temperature-solubility relationship
- high variation: cooling
- weak variation: evaporation (or vacuum cooling)

Type of crystallizer

Batch crystallizer: low production, incrustation problems
Continuous crystallizer: high production, controlled crystallization

Type of contactor

Stirred vessel: high energy cost and maintenance
Recycling slurry: efficient but risk of incrustation
Recycling liquor
Fluidized bed (classification): narrower product size distribution
easier solid-liquid separation

Beatrice.Biscans@ensiacet.fr,
Continuous crystallizers

Advantages:
Economical in operating and labour costs
Reduced space
Amount of mother liquor needed reworking is small
Elimination of impurities by flushing out
Higher reproducibility of crystal size distribution
High production rate

Drawbacks:
Encrustation of heat exchangers and pipes
Problem of continuous withdrawal
Need dense slurry for limitation of the volumes of filtration
Periodical stops – problem of steady state recovery
Difficulty for controlling secondary nucleation
Seeding: more difficult
Batch crystallizers

**Advantages**
- Interesting for 1 to 100t/week productions
- Simplicity of equipment without complicated mechanical systems
- Easy scale-up
- Minimization of encrustation on heat exchangers
- Can be cleaned thoroughly at the end of each batch
- Large crystals easy to obtain because nucleation can be controlled at the beginning of the batch cycle
- Seeding: easy
- Easy cleaning

**Drawbacks:**
- The product is not regular, lack of reproducibility
- High labour costs, high working costs
- High size
- Small production
- Cycles rather long
Cooling crystallizers

Non agitated vessels

The simplest type of cooling crystallizer is the unstirred tank: A hot feedstock solution is charged to the open vessel where it is allowed to cool, often for several days, predominantly by natural convection. Metallic rods may be suspended in the solution so that large Crystals can grow on them and reduce the amount of product that sinks to the bottom of the crystallizer. The product is removed by hand.
Cooling crystallizers

**Agitated vessels**

External circulation through an heat exchanger

The design of tank crystallizers varies from shallow pans to large cylindrical tanks.
The use of external circulation allows mixing inside the crystallizer and high rates of heat transfer between the liquor and coolant. An internal agitator may be installed in the crystallization tank if needed.
The liquor velocity in the tubes is high, therefore, small temperature differences are usually adequate for cooling purposes and encrustation on heat transfer surfaces can be reduced.

Batch or continuous
Cooling crystallizers

Agitated vessels

The large agitated crystallizer shown here has an upper conical section which slows down the upward velocity of liquor and prevents the crystalline product from being swept out with the spent liquor. An agitator located in the lower region of a draft tube circulates the crystal slurry through the growth zone of the crystallizer. If required cooling surfaces may be provided inside the crystallizer.

Internal circulation with a draft tube

Batch or continuous

Beatrice.Biscans@ensiacet.fr
Cooling crystallizers

**Agitated vessels**

It consists of two interconnected simple crystallizers, each section operating at a different temperature. Hot feed liquor enters and mixes with the circulating contents of the crystallizer, which pass downwards through the water-cooled draft tube A, under the influence of an agitator. Part of the cold magma passes under the adjustable gate B, into the second compartment of the crystallizer, where it mixes with the circulating magma in the second draft tube C, operated at a lower temperature (crystallizers in series).

Twin or double crystallizer:

Batch or continuous
Cooling crystallizers

**Trough crystallizers**

It consists of a long shallow through, about 1.2m wide, rocked on supporting rollers. The solution to be crystallized is fed in at one end and the crystals are discharged at the other end continuously. The slope of the trough towards the discharge end, is varied according to the required residence time of the liquor in the crystallizer. Heat is lost by natural convection in the atmosphere.

The Wulff-Bock crystallizer
Cooling crystallizers

Trough crystallizers

The Swenson Walker crystallizer is a trough crystallizer with internal agitation and a cooling system. An helical agitator-conveyor rotates at a slow speed inside the trough to aid the growth of the crystals by lifting them and then allowing them to fall back through the solution.

The Swenson-Walker crystallizer
Cooling crystallizers

Oslo-Krystal cooling crystallizer

A small quantity of warm concentrated feed solution enters the crystallizer vessel at point A, located directly above the inlet to the circulation pipe B. Saturated solution from the upper regions of the vessel together with the small amount of feed liquor, is circulated by pump C through the tubes of heat exchanger D, which is cooled rapidly by a forced circulation of water or brine. On cooling the solution becomes supersaturated, but not sufficiently for spontaneous nucleation to occur (metastable). The supersaturated solution flows down pipe E and emerges from the outlet F, directly into a mass of crystals growing in the vessel. The rate of the liquor is such that the crystals are maintained in a fluidized state.
Cooling crystallizers

Direct contact cooling crystallizer

Avoid the use of conventional heat exchanger and encrustation. The coolant is insoluble in the solution and its latent heat of phase change (sublimation or vaporization) is the main cause of heat removal. The low density coolant collects in the upper layers and passes to a cyclone to separate aqueous solution droplets before being recycled.

The Cerny direct coolant crystallizer (continuous)
Evaporating crystallizers

Steam heated evaporators

Most evaporation units are steam heated and a typical evaporator body used in evaporative crystallization is the short tube vertical type in which steam condenses on the outside of the tubes. A steam chest or calandria with a large central downcomer allows the magma to circulate through the tubes; during operation the tops of the tubes are just covered with liquor. To increase the rate of heat transfer, especially in dealing with viscous liquors, a forced circulation of liquor may be effected by installing an impeller in the downcomer.

Typical evaporating crystallizer with a calandria with a large central downcomer.
Forced circulation evaporators

The typical forced circulation evaporator-crystallizer is a circulating magma unit operated under reduced pressure. Magma is circulated from the conical base of the evaporator body through the vertical tubular heat exchanger and reintroduced tangentially into the evaporator below the liquor level to create a swirling action and prevent flashing.

Forced circulation evaporative crystallizer
Evaporating crystallizers

Oslo-Krystal evaporating crystallizer

The principle of the Oslo-Krystal process, already shown in cooling crystallizer, can also be applied to evaporative crystallization. Three forms of the Oslo-Krystal evaporating crystallizer are shown here. The vaporizer is directly connected with the crystallizer body to form a sealed unit.

Beatrice.Biscans@ensiacet.fr,
Vacuum crystallizers

**Draft tube agitation**

A vacuum unit capable of producing large crystals of narrow size distribution is the Swenson draft-tube-baffled (DTB) crystallizer. A slow-speed propeller agitator is located in a draft tube. The internal baffle in the crystallizer forms an annular space in which agitation effects are absent. This provides a settling zone that provides regulation of the magma density and control of the removal of excess nuclei. An integral elutriating leg may be installed underneath the crystallization zone to effect some degree of product classification.

*Swenson draft-tube-baffled (DTB) crystallizer*
**Vacuum crystallizers**

**Draft tube agitation**

The standard Messo turbulence crystallizer is another draft tube agitated unit. Two liquor flow circuits are created by concentric pipes: an outer injector tube with a circumferential slot and an inner guide tube. Circulation is effected by a variable speed agitator in the guide tube. The principle of the Oslo crystallizer is used in the growth zone; partial classification occurs in the lower regions, and fine crystals segregate in the upper regions. Feedstock is introduced into the guide tube in the lower region of the vessel and passes into the vaporizer section where flash evaporation takes place. Nucleation therefore occurs in this region and nuclei are swept into the primary circuit.

*Standard Messo turbulence crystallizer*
Vacuum crystallizers

**Fluidized bed agitation**

The Oslo-Krystal unit is a fluidized bed agitated crystallizer in which the gentle action minimizes secondary nucleation allows large crystals to grow. Two different methods of operation exist: classified suspension (circulating liquor) or mixed suspension (circulating magma).

Oslo-Krystal vacuum crystallizer showing two different methods of operation: a) classified suspension b) Mixed suspension

Beatrice.Biscans@ensiacet.fr,
Vacuum crystallizers

Multistage vacuum crystallizer

The standard Messo multistage vacuum crystallizer provides a number of cooling stages in one vessel. The horizontal cylinder is divided into several compartments by vertical baffles that permit underflow of magma from one section to another but isolate the vapor spaces. Each vapor space is kept at its operating pressure by a thermocompressor, which discharges to a barometric condenser. Hot feedstock is sucked into the first compartment which is operated at the highest pressure and temperature. Flash evaporation and cooling occur and the resulting crystal slurry passes into the successive compartments.

Standard Messo multistage vacuum crystallizer
reactive crystallizers

Swenson reaction-type DTB crystallizer

Swenson atmospheric up-pumping reaction-type DTB crystallizer

Beatrice.Biscans@ensiacet.fr