TS03.032016-H

Organic Chemical Purification

Comparision of Layer and Suspension Crystallization Processes

Purification Process

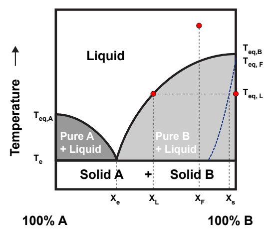
Melt crystallization can provide an economic and efficient alternative purification step in cases where standard distillation becomes difficult:

- Close boiling isomers
- Azeotropic systems
- Heat sensitive products
- Products that tend to polymerize
- Explosive substances

Eutectic systems form a pure solid phase when cooled below their equilibrium temperature. The remaining liquid will become depleted in the crystallized product and therefore enriched in the impurity. This is caused by the fact that the impurity molecules are generally not incorporated into the highly ordered crystal lattice as long as the growth is slow and impurities are not trapped in a rapidly growing crystal mass.

Solid-solution forming systems do not form a pure solid when cooled. The impurity is included in the lattice and these systems require multiple crystallizations similar to vapor-liquid separation used in distillation. Melt crystallization systems typically remove heat to provide the driving force required for crystallization. Many organic solutions can be easily represented by simple binary systems, where phase diagrams are used to describe the solid-liquid equilibrium relationship of the solutions.

The figure below provides an illustration of a typical eutectic binary phase diagram. The crude feed product forms solid B upon cooling. The remaining liquid becomes enriched in A and moves down the equilibrium curve until it reaches the eutectic point (Xe, Te). The eutectic point represents the theoretical limit for melt crystallization processes since a pure crystal mass is no longer possible. Crystal growth can also be inhibited as the impurity concentration increases. Pure crystals will only be obtained under slow, near equilibrium growth conditions. Rapid growth rates result in the liquid phase impurities being entrapped in the crystals mass.



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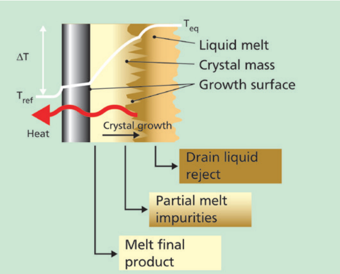
Industrial Melt Crystallization

There are basically two forms of cooling melt crystallization processes available. The layer-based process is typically batch operated, removes heat and grows the crystal mass from a fixed surface and is further characterized by the flow conditions of the liquid melt. The suspension-based process is typically a continuous process, grows crystals suspended in the bulk melt and is further characterized by the type of heat removal used.

The Layer Process

The dynamic process is typically carried out with the melt flowing through a series of parallel tubes and the refrigerant flowing on the outside of the tubing. The tubes can be flooded with product or operated with falling films. The static system grows crystals on a series of plates suspended in a vessel filled with the stagnant liquid melt. The refrigerant flows inside the plates. Both systems start with a batch of melt and continue the cooling process until a certain mass of product (typically 50-75% of the starting mass) has crystallized onto the heat exchange surface. The refrigerant temperature must be steadily decreased to maintain crystal growth since the equilibrium concentration decreases during the operation and the increasing layer thickness inhibits heat flow through the wall. The crystal growth is basically linear, away from the heat transfer surface and is limited to the actual surface area of the heat transfer equipment.

Once the required crystal mass has been formed the remaining liquid is drained from the crystallizer and stored in the reject collecting tank. The crystal mass is then very carefully heated. This partial heating process, known as sweating, allows part of the impurities that are trapped in the crystal mass to be expelled and drained where it is stored in another intermediate tank. Once the sweating process has been completed the remaining crystal mass is completely melted and drained into a third holding vessel. Depending on the purity this may be discharged as final product. The process is then repeated with fresh feed or combinations of the various intermediate products.



Simplified schematic layer process

Layer

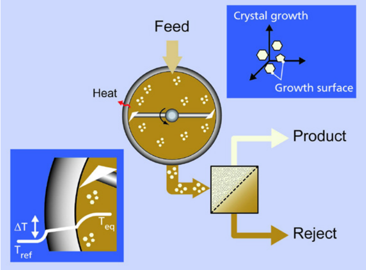
- Batch
- Crystal fixed to surface
- Relatively simple components
- Simple scale up
- Complex dynamic
- Rapid growth requires sweating and multiple crystallization steps
- Simple gravity separation
- Low efficiency leads to high utility and capital costs
- Broad application base in small to

The Suspension Process

Suspension-based crystallization systems with indirect cooling remove heat through a scraped heat exchange surface. Direct cooling systems use evaporation of a solvent or secondary refrigerant in the melted liquid to remove heat from the melt. The indirect cooling systems are more common with melt crystallization systems and will be used here to further describe the suspension-based process.

The refrigerant flows on the outside of the heat exchanger surface. The inside surface is swept by metal or plastic scraping knives. This prevents build-up of a crystal layer and improves the efficiency of the unit. The melt is thereby cooled and mixed with the rest of the suspension. The crystals suspended in this under-cooled melt will thus grow and release heat directly into the surrounding melt. The crystallizer is typically operated with 30-40% of the vessel volume containing solid crystals (with nearly 100 billion crystals per ton). The growth surface is the total crystal surface area, approximately 20,000 m² per ton of product. This massive surface area allows for the near ideal growth rates characteristic of suspension based processes. Slow growth rates allow pure crystal formation even in relatively impure melt.

Pure product can be obtained by separating the crystals after just one crystallization step. Part of the crystal suspension is transferred to a solid-liquid separator such as a filter, centrifuge or wash column. After the crystals have been separated and washed to remove any mother liquor adhering to the crystal mass they are melted and discharged as pure product. The mother liquor is also discharged from the system and both purified product and residue are continuously replaced by fresh feed.



Simplified schematic of suspension based crystallization process

Suspension

- Continuous
- Crystal free flowing in suspension
- More complex components
- Scale-up requires specific know how
- Simple steady state control
- Slow growth produces pure crystals in a single crystallization step
- Complex separation required
- High efficiency reduces utility and capital costs

On-site demonstration of this technology is possible in various configurations using GEA pilot plants. For more information regarding this technology and your specific configuration requirements, please contact us or get in touch with your local GEA contact on gea.com via the Application Chemical, Specialty & Fine Chemicals.

GEA Netherlands

GEA Niro PT B.V.

De Beverspijken 7-b
5221 EE 's-Hertogenbosch, Netherlands

Tel +31 73 6390390
Fax +31 73 6312349

info.niropt.nl@gea.com
gea.com