Falling Film Crystallization

This is how the melt crystallization process from a falling film works:

Phase 1:
A crystalline layer is grown from a falling film of melt on
the inside of a tube which is cooled externally
by a cocurrent falling film of a heat transfer fluid.

Phase 1a: The melt is drained off.

Phase 2: The tube wall is heated to induce partial melting
(sweating); the melted material is drained off.

Phase 3: The remaining crystal layer is melted off and
collected as (intermediate) product.

Figure 6:
Phases of operation of the Falling Film Crystallization.

Figure 7 is a simplified flow diagram. At
the beginning of the first phase, the
collecting tank is filled with feed liquor.
Both product pump and heat transfer
liquid pump are started, and a layer of
frozen product begins to form in the
crystallizer. Consequently, the liquid
level in the collecting tank falls. When it
reaches a preset value, freezing is
stopped and the collecting vessel is
drained through the residue line to the
battery limit or, in multistage operation,
to a storage vessel. In the sweating
phase which follows, warm heat trans-
fer liquid is circulated. Sweat liquor is
collected until a preset level is reached
in the collecting vessel. It is then pumped
back to the respective storage vessel.
During the third phase, the remaining solid layer is melted into the collecting vessel and then transferred to the product line or, in multistage operation, used in the subsequent purification step.

Product purity is influenced by the amount of melt adhering to the solid layer at the end of phase two.

Any degree of purity can be obtained by using the intermediate product as feedstock and repeating the procedure.

In a similar way, the residue drained off in the first phase may be further depleted by additional melt/freezing processes to give enhanced yield.

Figure 8 illustrates a three-stage process. In industrial application, the number of stages varies between one and seven.

Note: Staging does not require multiple crystallizers. The steps are run in sequence in a single crystallizer.
Figure 10 shows the key piece of equipment in the process. Basically it consists of a system of vertical tubes. However, there is a special feature; neither the shell side nor the inside of the tubes is filled with liquid. Falling films are used instead. The product runs down inside the tubes, whereas the liquid used for cooling and heating is distributed to wet the external tube surfaces. During freezing (phase 1), cold heat transfer liquid is used to chill the tubes. Partial melting (phase 2) is induced by raising the temperature of the heat transfer liquid, and the final melting (phase 3) is achieved by applying higher temperatures. The distribution system (Figure 13) is designed to equalize flow through the tubes. Optimum performance is achieved through accurate control of the heating and cooling profiles.

Figure 11: Process phases in the crystallizer elements.

Figure 12: Temperature-time profile of the Falling Film Crystallization.
Figure 14:
Installation of a crystallizer in an existing plant.

Figure 15:
Large capacity plant (150,000 tons/year).
The plant consists of six crystallizers, two of them are shown in the model.
designs and builds purification and separation plants using Fractional Crystallization for chemicals such as:

- Acenaphthene
- Acrylic acid
- Benzoic acid
- BHT
- Bisphenol A
- Caprolactam
- DMT
- HMD
- Hydrazine
- MDI
- Monochloro acetic acid
- Naphthalene
- p-Chlorotoluene
- p-Dichlorobenzene
- p-Nitrochlorobenzene
- p-Xylene
- TDI
- Xylenols

SULZER CHEMTech Ltd
Fractional Crystallization
Industriestrasse 8
P.O. Box
CH-9470 Buchs
Phone: 081 - 756 03 11
Telefax: 081 - 756 40 12
PRODUCT INFORMATION

\[ \text{CH}_2 = \text{CH} - \text{C} = \text{O} \]

Acrylic Acid
GENERAL

Acrylic acid is a versatile monomer for providing performance properties to a wide variety of polymers. Polyacrylic acid or copolymers find applications in superabsorbents, detergents, dispersants, flocculants and thickeners. The production of superabsorbents, demanding high purity and used primarily in disposable diapers, has grown rapidly in recent years and will continue to grow in the future.

Catalytic propylene oxidation is the major route for production of acrylic acid. The choice of catalyst and reaction parameters is important for maximising yield and purity of the acrylic acid.

Purification of acrylic acid is required if used to produce acrylic fibres with high absorptive capacity, textiles or acrylic plastics. Today's purity requirements are often at 99.9+ % and specifications on individual impurities like aldehydes, acetic acid, undesired stabilisers, etc. are in the ppm range. The traditional purification techniques, well described in the literature, rely on a combination of distillation with chemical treatment.

Scaling and blockages in distillation columns caused by polymerization at elevated temperatures and lack of inhibitors in the vapor phase cause regular shut downs and necessitate manual cleaning.

In the past, yield was not important since the residue from distillation was blended with the crude acid used for esterification. However, the growing demand for high purity acrylic acid is now producing a surplus of impure acid due to the limited yield of distillation. With its Fractional Crystallization Process, Sulzer Chemtech offers a solution to reduce this surplus.

SULZER CHEMTECH'S PROCESS

A purification process using fractional crystallization has been developed and is in use industrially since the end of the 1980's. Patents have been filed for this technology world-wide. In this process crude acid is fed to a falling film crystallization unit. After two crystallization steps the required purity is reached. Additional recovery stages enable very high yields.

<table>
<thead>
<tr>
<th>PHYSICAL PROPERTIES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific heat: 2.1 kJ/kg K</td>
</tr>
<tr>
<td>Heat of fusion: 154 kJ/kg</td>
</tr>
<tr>
<td>Melting point: 13.5 °C</td>
</tr>
<tr>
<td>Boiling point: 141 °C (1013 mbar)</td>
</tr>
<tr>
<td>Molecular weight: 72.06 g/mol</td>
</tr>
<tr>
<td>Density (liquid): 1040 kg/m³ (30 °C)</td>
</tr>
<tr>
<td>Density (solid): 1060 kg/m³ (10 °C)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PRODUCT SPECIFICATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purity: &gt; 99.9 % Acrylic Acid</td>
</tr>
<tr>
<td>Impurities:</td>
</tr>
<tr>
<td>Water &lt; 100 ppm</td>
</tr>
<tr>
<td>Acetic Acid &lt; 350 ppm</td>
</tr>
<tr>
<td>Aldehydes &lt; 1 ppm</td>
</tr>
<tr>
<td>Dimer &lt; 10 ppm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PRODUCT FEATURES</th>
</tr>
</thead>
<tbody>
<tr>
<td>• yields of up to and over 99 %</td>
</tr>
<tr>
<td>• aldehydes and ketones separation down to ppm / ppb level</td>
</tr>
<tr>
<td>• good acid separation</td>
</tr>
<tr>
<td>• no polymer formation in the plant</td>
</tr>
<tr>
<td>• high purities of 99.9+ %</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PROCESS FEATURES</th>
</tr>
</thead>
<tbody>
<tr>
<td>• 100 % availability</td>
</tr>
<tr>
<td>• no emissions</td>
</tr>
<tr>
<td>• no solvent used</td>
</tr>
<tr>
<td>• no slurry handling, no filtration</td>
</tr>
<tr>
<td>• low maintenance costs</td>
</tr>
<tr>
<td>• no unscheduled shut downs</td>
</tr>
<tr>
<td>• easy shut down and restart without time loss and off-spec product</td>
</tr>
<tr>
<td>• operational flexibility to reach desired purities</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SERVICES FROM SULZER CHEMTECH</th>
</tr>
</thead>
<tbody>
<tr>
<td>• studies</td>
</tr>
<tr>
<td>• pilot testing</td>
</tr>
<tr>
<td>• test production in a mobile unit</td>
</tr>
<tr>
<td>• engineering</td>
</tr>
<tr>
<td>• equipment supply</td>
</tr>
<tr>
<td>• modular plants</td>
</tr>
<tr>
<td>• consulting</td>
</tr>
</tbody>
</table>
RANGE OF FREEZING POINTS DEPENDING ON WATER CONTENT

FLOW DIAGRAM

1) Extraction with an organic solvent
2) Water removal
3) Solvent removal and recovery
4) Light ends cut
5) Water / solvent separator

Source: Ulmone Vol A1 and Salzer Chemtech
PRODUCTS PURIFIED BY FRACTIONAL CRYSTALLIZATION

Excerpt from the product list

Feedstocks for agricultural chemicals and dyestuff industries
- para-Dichlorobenzene
- para-Nitrochlorobenzene
- para-Nitrotoluene
- para-Chlorotoluene
- Dichloronitrobenzene

Feedstocks for the plastics industries
- Acrylic acid
- Bisphenol A as melt or adduct
- Methacrylic acid
- TDI 100
- MDI
- Caprolactam
- HMD
- DMT
- Diaminocyclohexane
- Trioxane

Coal tar chemicals
- Naphthalene
- Xylenols
- para-Cresol
- Anthracene
- Acenaphthene

Others
- Paraxylene
- Benzoic acid, pharmaceutical grade
- Hydrazine, propellant for satellite thrusters
- Monochloroacetic acid
- BHT, food grade

For more information on this or other products call our representative in your area or our office in Buchs.
PRODUCT INFORMATION

Bisphenol A

Fractional Crystallization
DESCRIPTION

Bisphenol A produced by reaction of Phenol and Acetone in presence of acid catalysts or ion exchangers has to undergo a dedicated purification should it be used for the production of polycarbonates. High vacuum distillation and adduct crystallization with phenol followed by phenol stripping are methods well described in the literature. Degradation at high temperature, colour instability, handling of large quantities of phenol, etc. are often referred to in context to these purification methods.

Purification by melt crystallization has been developed in the early 90ies and applied for patent world-wide.

The reaction product is separated from phenol and light boilers in vacuum evaporation equipment. The bottom product, Bisphenol A melt containing isomers, small amount of phenol and high boilers is directly fed into a falling film crystallization unit and separated into a solid BPA and a liquid containing isomers and impurities. The solid BPA is molten and recrystallized 1 or 2 times. The so purified BPA is of very high purity and can be solidified on a flaker to a colour stable polycarbonate grade product. The liquid fraction of the first crystallization is crystallized in separate steps to recover valuable BPA. The final liquid, highly concentrated with isomers, phenol, etc. can be recycled to the reaction plant. In the scope of this purification method, Sulzer Chemtech designs and supplies the falling film crystallization section. Details to this crystallization process are compiled in the brochure "Fractional Crystallization".

PHYSICAL PROPERTIES

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific heat</td>
<td></td>
</tr>
<tr>
<td>liquid</td>
<td>2.49 kJ/kg K (177 °C)</td>
</tr>
<tr>
<td>solid</td>
<td>1.32 kJ/kg K</td>
</tr>
<tr>
<td>Heat of fusion</td>
<td>147 kJ/kg</td>
</tr>
<tr>
<td>Melting point</td>
<td>156.8 °C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>360 °C (1013 mbar)</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>228.3 g/mol</td>
</tr>
<tr>
<td>Density liquid</td>
<td>1060 kg/m³</td>
</tr>
<tr>
<td>Density solid</td>
<td>1195 kg/m³ (25 °C)</td>
</tr>
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SPECIFICATION

<table>
<thead>
<tr>
<th>Purity</th>
<th>&gt; 99.9 % BPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impurities</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>&lt; 50 ppm</td>
</tr>
<tr>
<td>Isomers</td>
<td>&lt; 100 ppm</td>
</tr>
<tr>
<td>Others</td>
<td>&lt; 100 ppm</td>
</tr>
<tr>
<td>Colour</td>
<td>colour stable flakes</td>
</tr>
<tr>
<td>General</td>
<td>fulfills requirements for polycarbonate grade BPA</td>
</tr>
</tbody>
</table>

FEATURES

- Colour stable product
- No use of solvent
- Closed equipment, no off gas, no waste water
- Flexibility to adjust purity to market demands
- Pumps are the only rotating equipment, maintenance therefore is kept to a minimum.

SERVICES OF SULZER CHEMTECH

- Studies
- Pilot testing
- Test production in a mobile unit
- Engineering
- Equipment supply
- Modular built plants
- Consulting
Fractional Crystallization

**PHASE DIAGRAM**

![Phase Diagram](image)

- **Temperature (°C)**
- **Bisphenol A (%)**

**Liquid + Adduct**

**Liquid + Bisphenol A**

**FLOW DIAGRAM**

Large capacity plant consisting of six crystallizers

![Flow Diagram](image)

- Reaction
- Stripping
- **Fractional Crystallization**
- Solidification
PRODUCTS PURIFIED BY FRACTIONAL CRYSTALLIZATION

Excerpt from the product list

Up stream products for agriculture chemicals and dye stuff industries
para-Dichlorobenzene
para-Nitrochlorobenzene
para-Nitrotoluene
para-Chlorotoluene
Dichloronitrobenzene

Up stream products for the plastics industries
Acrylic Acid
Bisphenol A as melt or adduct
Methacrylic acid
TDI 100
MDI
Caprolactam
HMD
DMT
Diaminocyclohexane
Trioxane

Down stream products of coal tar
Naphthalene
Xylenols
para-Cresol
Anthracene
Acenaphthene

Others
para-Xylene
Benzoic acid, pharmaceutical grade
Hydrazine, propellant for satellite rockets
Monochloroacetic acid
BHT, food grade

For more information on this or other products call our representative in your area or our office in Buchs.

Handed over by:

Sulzer Chemtech Ltd
Industriestrasse 8
P.O. Box
9471 Buchs / Switzerland
Telephone 081/756 03 11
Telefax 081/756 40 12
PRODUCT INFORMATION

Paraxylene

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]
GENERAL
Approximately 10 Mio. metric tons of paraxylene are produced annually worldwide with an average increase of 4 to 5 % per year. Paraxylene is an important base chemical for the production of TPA (terephthalic acid) and DMT (dimethylterephthalate). These products are used for the production of fibres and films with an increasing percentage going into PET (polyethyleneterephthalate) bottle manufacturing.
Increasing pressure on the chemical industry to minimize waste, this is to say maximize yields on the downstream product have resulted in a demand for higher purities on the base chemical. Today's paraxylene is being produced and sold at a purity of 99.5 to 99.7 %, but the market starts to demand 99.9 %.
The traditional aromatics plant produces isomer mixtures with para content between 19 and 22 %. Two different technologies are used to bring this up to required purity.
- Approximately 40 % of the present capacity is purified by suspension crystallization using various technologies. Here the purities can be pushed to the new requirements without a change of technology.
- A major part of today's production is purified by UOP's molecular sieve technology. These plants are built to produce paraxylene at approximately 99.2 to 99.7 %. Increased purities are possible but with a loss in capacity.

SULZER CHEMTECH'S PROCESS
With its fractional crystallization process, Sulzer Chemtech offers a solution to overcome this capacity loss.
Paraxylene can very efficiently be purified by fractional crystallization. The process can be employed in two ways:
- Debotlenecking of existing plants where feed of approximately 99 % is brought up to 99.9 %. The residue is fed back into the existing installation. An increase on capacity of 10 or more % can be expected.
- Final purification for Mobil's new selective toluene disproportionation technology (MSTDP), which produces from the outset a para content of 80 to 90 %. This type of feed is taken directly into a fractional crystallization plant producing the required purity of 99.9 % with maximum yield.
- Energy system is based on direct evaporation of a refrigerant (NH₃, Propane, Propylene) with the use of a heatpump for max. energy efficiency.

PHYSICAL PROPERTIES

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td>Specific heat (liquid)</td>
<td>1.7 kJ/kg K (25 °C)</td>
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<td>Heat of fusion</td>
<td>161 kJ/kg</td>
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<tr>
<td>Melting point</td>
<td>132.26 °C</td>
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<tr>
<td>Boiling point</td>
<td>138.4 °C (1013 mbar)</td>
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<tr>
<td>Molecular weight</td>
<td>106.16 g/mol</td>
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<tr>
<td>Density (liquid)</td>
<td>861 kg/m³ (20 °C)</td>
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PRODUCT SPECIFICATION

<table>
<thead>
<tr>
<th>Name</th>
<th>Purity</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purity</td>
<td>&gt; 99.9</td>
<td>% paraxylene</td>
</tr>
<tr>
<td>Impurities</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>&lt; 60</td>
<td>ppm</td>
</tr>
<tr>
<td>Ethyl benzene</td>
<td>&lt; 40</td>
<td>ppm</td>
</tr>
<tr>
<td>Isopropyl benzene</td>
<td>&lt; 1</td>
<td>ppm</td>
</tr>
<tr>
<td>Methylenylen</td>
<td>&lt; 700</td>
<td>ppm</td>
</tr>
<tr>
<td>Orthoxylen</td>
<td>&lt; 200</td>
<td>ppm</td>
</tr>
</tbody>
</table>

Typical Figures

PRODUCT FEATURES
- High purity product 99.9 % and higher
- Maximum yield
- Purity and yield are adjustable to requirements and over all process scheme

PROCESS FEATURES
- 100 % availability
- No emissions
- No solvent used
- No slurry handling, no filtration
- Low maintenance costs
- No unscheduled shut downs
- Easy shut down and restart without time loss and off-spec product
- Operational flexibility to reach desired purities

SERVICES FROM SULZER CHEMTECH
- Studies
- Pilot testing
- Test production in a mobile unit
- Engineering
- Equipment supply
- Modular plants
- Consulting
Refrigeration
As mentioned, the crystallizers are components of a refrigeration cycle. For crystallization one crystallizer operates as evaporator. Liquid refrigerant is pumped from the receiver to this crystallizer where it is distributed inside the crystallizer tubes. The temperature level within the crystallizer can be controlled by a valve that controls the evaporation pressure. The low-pressure vapour flows then via the receiver to the compressor. The gas is compressed to a point where the vapour can be condensed in the other crystallizer, which is operating in the heating mode to sweat or melt the crystals. The condensed refrigerant flows from the crystallizer via a float valve, back into the receiver. The refrigeration cycle is thus completed.

In order to switch cooling/heating mode at the end of the crystallization or melting, the feeding of liquid refrigerant and vapour to the crystallizers is stopped. Remaining refrigerant is drained away into the collecting tank. The process is then continued by heating the crystallizer that contains the crystal layer and by cooling the other crystallizer to start with a new crystallization stage.

The compressor for the plant operates in an defined pressure range. When the pressure exceeds a high or low set point vapour can be condensed by cooling water or evaporated by steam respectively, for this the refrigeration plant is equipped with auxiliary condenser and evaporator.

Low Energy and Investment Costs
The heat pump concept improves p-Xylene crystallization significantly:

1. Energy costs are reduced due to the use of condensation enthalpy for crystal melting. And evaporation energy is higher due to direct cooling inside of the crystallizer tubes.
2. A minimum of equipment is required since process energy is directly used within the crystallizer. Refrigeration unit is only equipped with relatively small heat exchangers to eliminate excess energy and to facilitate start-up.

Pilot Testing and Scale-up
The design of SULZER heat pump crystallization plants is based on intensive pilot testing. For such tests SULZER uses crystallizers with standardized tubes of equal geometry, hydrodynamics and heat transfer characteristics to secure the optimal performance of the crystallization process. The industrial crystallizers simply contain a multiple of such tubes to attain the capacity, so that the separation efficiency established during the testing is retained. In this way uncertainties usually involved in scale-up are totally eliminated.
CRISTALLIZATION WITH HEAT PUMP TECHNOLOGY

GENERAL INTRODUCTION
The Heat Pump Crystallization System of SULZER CHEMTECH is a new development to purify p-Xylene from an isomer mixture. The system is based on the well-known and proven falling film crystallization process and combines extensive know-how on fractional crystallization and refrigeration. The Heat Pump Crystallization features:

- high flexibility for a wide range of feed composition and any desired purity
  (up to 99.95 %)
- low investment cost
- low energy cost
- low maintenance cost
- high yield
- fully automatic microprocessor control
- ease of restart and shut-down of production
- no slurry handling

PROCESS AND EQUIPMENT DESCRIPTION

Basics
The SULZER process involves repetitive crystallization of an isomer mixture. It is based on the principle of forming a crystal layer on a cooled heat transfer surface. The solid is the purified p-Xylene while impurities are concentrated in the remaining melt. After the crystal layer is grown a heating phase follows to sweat the crystal layer and to separate adhering or trapped mother liquor. Finally the crystals are melted off the tubes.

Heat Pump Crystallizers
The key equipment of the process are the heat pump crystallizers. Depending on the plant capacity two or more crystallizers of equal size are used per plant. These crystallizers are components of a heat pump refrigeration cycle. The crystallizer is designed to allow switching between cooling with liquid refrigerant and heating with refrigerant vapour. Whilst one crystallizer operates in the crystallization mode as an evaporator, the other one operates in the sweating or melting mode and is used as condenser.

The heat pump crystallizer basically consists of a system of vertical tubes used as heat transfer surface. The isomer mixture enters at the top of the tubes. Distributors put the liquid in a falling film flow on the outside surface of the tubes. The refrigerant for cooling is distributed at the top through an internal tube to wet the inside of the crystallizer tubes.
Fractional Crystallization

PHASE DIAGRAM

FLOW DIAGRAM

Case 1:
mixed Xylenes $\rightarrow$ 19-24% px $\rightarrow$ Prepurification Section $\rightarrow$ Fractional Crystallization

Case 2:
$\rightarrow$ Separation Columns $\rightarrow$ 19-23% px $\rightarrow$ Prepurification Section $\rightarrow$ 99-99.5% px $\rightarrow$ Fractional Crystallization $\rightarrow$ 99.7-99.9%+ px

Case 3:
Toluene $\rightarrow$ Toluene Disproportioning $\rightarrow$ Separation Columns $\rightarrow$ 80-90% px $\rightarrow$ Fractional Crystallization $\rightarrow$ 99.7-99.9%+ px

Benzene
PRODUCTS PURIFIED BY FRACTIONAL CRYSTALLIZATION

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- para-Nitrotoluene
- para-Chlorotoluene
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- Bisphenol A as melt or adduct
- Methacrylic acid
- TDI 100
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- Caprolactam
- HMD
- DMT
- Diaminocyclohexane
- Trioxane

Coal tar chemicals
- Naphthalene
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- Hydrazine, propellant for satellite thrusters
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Handed over by:

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