Introduction Melt Crystallization

Background info technology

Information for Dennis Dever
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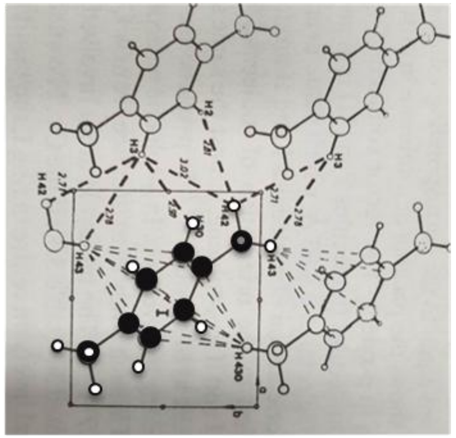
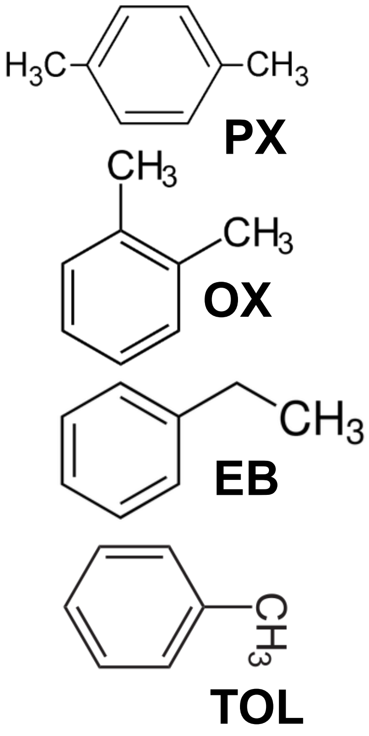
For public use

Contents of the presentation

Suspension Melt/Freeze Crystallization

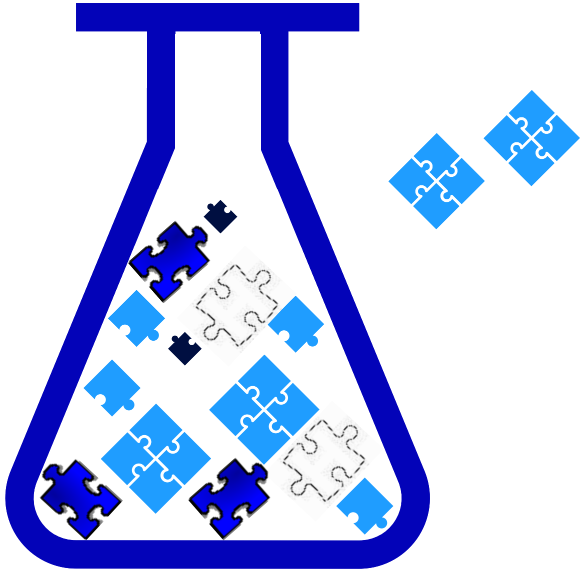
- Crystallization is highly selective. Molecules with different size and/or shape will not fit in the crystal lattice. Almost no kinetic incorporation of impurities at slow growth rates typical for suspension crystallization. Typically, the crystals will be pure, and the impurities are concentrated in the remaining liquid (Mother Liquor)
- A high purity can be reached when the pure crystals can be separated efficiently from the impure Mother Liquor from which the crystals were grown





Drivers for melt and freeze crystallization

- Lower costs
- Higher purity
- Reduce energy consumption
- Batch to continuous
- Electrification of Process Industry
- Sustainable Processes & Products
- ……..



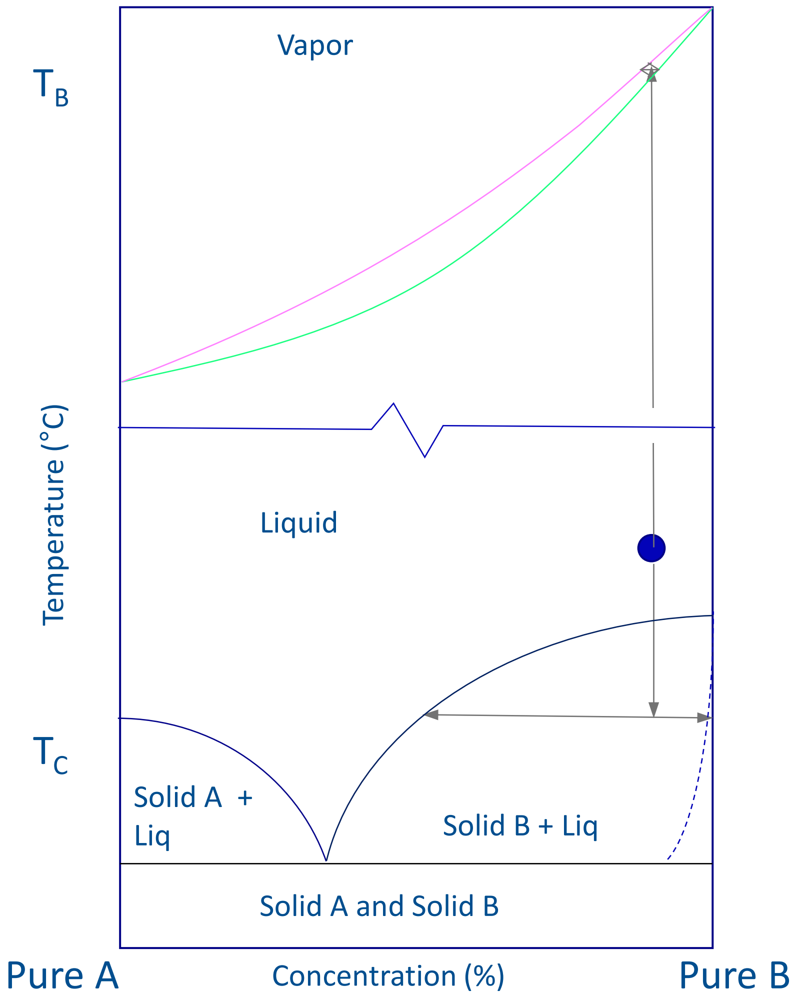
Sustainable products: some characteristics and trends

- Reduce Carbon Footprint by the lowest possible material and energy consumption
- Are suited/prepared for Renewable Energy and the transition Electrification of the Process Industry
- Transition to the Circular Economy: bio-based chemicals/products preferably bio-degradable and/or recyclable; recycling of (fossil-based) plastics (back to monomer-grade), recycling of solvents, ….
- Examples of new products/applications requiring higher purity

- ❑ *Battery grade salts and electrolytes for Li-batteries in EV*
- ❑ *Food concentrates to reduce transport/drying costs and enabling new formulations*
- ❑ *Solvents for chemical analyses of high purity products (e.g. acetonitrile for HPLC)*
- ❑ *High purity monomers to get new/extra functionality in polymers (flexibility, colour, high speed spinning, permeability, …)*
- ❑ *Electronic grade phosphoric acid as etchant for semiconductor production (to ppb level concentrations of ions/metals)*

Melt crystallization versus distillation

- Illustrative SLV binary equilibrium diagram
- Distillation operates at (much) higher T than crystallization
- Separation efficiency per stage of crystallization is much higher than for distillation
- Heat of crystallization for organic chemicals is usually 4 times lower than the heat of evaporation
- (Large) energy saving potential for melt crystallization compared to distillation (typically 25-95%): see next slide
- The eutectic limits purification/yield in melt crystallization. Azeotropes do the same in distillation
- Melt crystallization can make pure B but also pure A depending on composition of the Feed not on the melting temperature
- Crystallization and distillation are not (always) enemies. In many processes a combination of distillation and crystallization is the optimal technical – economic solution



Melt crystallization: much less energy than distillation

Product	Energy consumption (GJ/ton)		E-Saving (GJ/ton)	E-Saving (%)
	Conventional	+ Crystallization		
Benzene	1,47	1,07	0,40	27
Styrene	2,51	1,70	0,81	32
Caprolactam	0,95	0,37	0,57	60
Phenol	3,70	1,35	2,35	63
DMT	4,82	0,18	4,64	96

Reasons

- Crystallization very selective: no-limited reflux needed for high purity
- Heat of crystallization is 1/3 of heat of vaporization for organic chemicals
- Operating T crystallization << Operating T distillation

GEA Scope of supply

Crystallization from concept to industrial innovation

First concept

Lab testing,
Initial process design,
Capital cost estimate

Application development

Pilot testing,
Validation process design

ATEX

Industrial realization

Scale up,
Engineering,
Construction,
Commissioning and operator training

After sales

Process optimization, Service and
Spare parts

Melt Crystallization

General application in chemical industry

Drivers

- Lower costs
- Ultra-high purity (up to 99.999wt%)
- Energy reduction
- Electrification of industrial processes
- Reduce, reuse and recycle (e.g. solvents)
- ……

Typical application areas

- Separation components with close boiling points
- Isomer/enantiomer separation
- Azeotropes, no need for solvents
- Temperature sensitive products (polymerize, degrade, hazard)
- Monomer purification
- New properties/products by increasing the purity
- Upgrade raw materials
- ……..

Typical property range

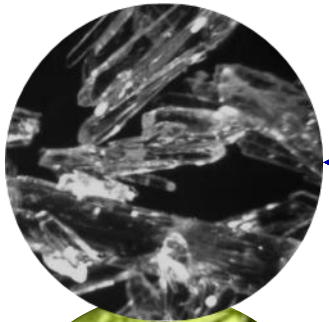
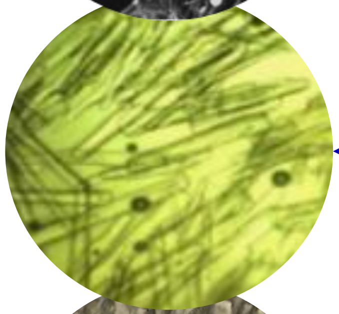
- Pure melting temperature -50 to +150°C
- Viscosity < 50 mPa-s

Typical application areas

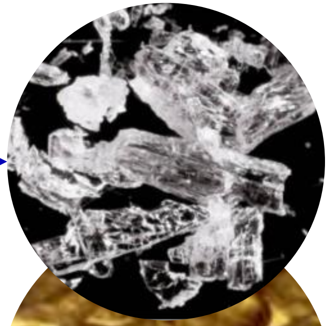
- *Aromatics*
  - Halogenated aromats *(pDCB, pDIB, pCT)*
  - Nitro aromatics *(pNT, pCNT, pNCB)*
  - Xylenes and aromatics *(pX, mX, Durene, bio-PX)*
  - Phenol compounds *(pTBP, oPP)*
- *Aliphatic and carboxylic acids*
  - Fossil-based (MCA, Acetic acid, Acrylic acid)
  - Bio-based acids *(L-Lactide,fatty acids, levulinic acid, glycolic acid*
- *Miscellaneous (high purity)*
  - Solvents – HPLC-grade acetonitrile, battery grade electrolytes (*EC, VC)* electronic grade – *H3PO4,* green solvent *(ethyl lactate)*
- *Freeze concentration*
  - Process and waste-water streams

Organic chemicals tested and/or installed by GEA

Suspension-based melt crystallization – wash column technology

Product	Formula	CAS No.	Mol. Wt.	Tboil (°C)	Tmelt (°C)
p-phenylenediamine (pPDA)	$C_6H_8N_2$	106-50-3	108.2	267.0	141.4
p-diiodobenzene	$C_6H_4I_2$	624-38-4	329.9	285.1	129.5
benzoic acid	$C_7H_6O_2$	65-85-0	122.1	249.0	122.4
p-tert butylphenol	$C_{10}H_{14}O$	98-54-4	150.2	233.9	98.9
L-Lactide	$C_6H_8O_4$	4511-42-6	144.1	264.7	98.7
p-Nitrochlorobenzene	$C_6H_4NO_2Cl$	100-00-5	157.6	242.0	82.5
naphthalene	$C_{10}H_8$	91-20-3	128.2	298.2	80.3
Durene (tetramethylbenzene)	$C_{10}H_{14}$	95-93-2	134.2	196.8	79.2
Stearic acid	$C_{18}H_{36}O_2$	57-11-4	284.5	361.1	69.5
Caprolactam	$C_6H_{11}NO$	105-60-2	113.6	268.0	69.2
isosorbide	$C_6H_{10}O_4$	652-67-5	146.1	372.1	62.5
Mono chloroacetic acid (MCA)	$C_2H_3ClO_2$	79-11-8	94.5	189.0	61.2
m-phenylenediamine (mPDA)	$C_6H_8N_2$	108-45-2	108.2	286.9	60.9
Stearin	$C_{57}H_{110}O_6$	555-43-1	891.5	813.0	60.0
o-Phenylphenol (OPP)	$C_{12}H_{10}O$	90-43-7	170.2	282.0	57.5
p-dichlorobenzene	$C_6H_4Cl_2$	106-46-7	147.0	173.0	53.1
Maleic anhydride	$C_4H_2O_3$	108-31-6	98.1	200.0	52.0
2-Coumaranone	$C_8H_6O_2$	553-86-6	134.1	248.8	49.5
3,4 dichloronitrobenzene	$C_6H_3Cl_2NO_2$	99-54-7	192.0	255.6	42.9
MDI - 4,4'	$C_{15}H_{10}N_2O_2$	101-68-8	250.3	392.0	40.4
Ethylene carbonate	$C_3H_4O_3$	96-49-1	88.1	248.0	36.4
dicyclopentadiene	$C_{10}H_{12}$	77-73-6	132.2	167.9	32.0
Phosphoric Acid (hemi-hydrate)	H_3PO_4-½H_2O	7664-38-2	107.0	180.0	29.3
Vinylene carbonate	$C_3H_2O_3$	872-36-6	86.1	178.0	22.0
ToluenediIsocyanate (2,4 TDI)	$C_9H_6N_2O_2$	584-84-9	174.2	120.0	21.8
Acetic acid	$C_2H_4O_2$	64-19-7	60.1	244.2	16.7
Methacrylic acid	$C_4H_6O_2$	79-41-4	86.1	163.0	14.4
Acrylic acid	$C_3H_4O_2$	79-10-7	72.1	139.0	13.5
N-vinyl-2-pyrrolidone (NVP)	C_6H_9NO	88-12-0	111.1	92.0	13.5
p-Xylene	C_8H_{10}	106-42-3	106.2	138.5	13.3
p-Chlorotoluene	C_7H_7Cl	106-43-4	126.6	162.0	7.6
γ-picoline	C_6H_7N	108-89-4	93.1	144.9	3.7
Hydrogen Peroxide	H_2O_2	7722-84-1	34.0	108.0	-0.4
Ethyl lactate (S)	$C_5H_{10}O_3$	687-47-8	118.1	154.0	-2.7
3,5 dimethylpyridine	C_7H_9N	591-22-0	107.2	172.0	-6.5
Acetonitrile	C_2H_3N	75-05-8	41.1	81.5	-44.5
m-Xylene	C_8H_{10}	108-38-3	106.2	138.5	-47.9

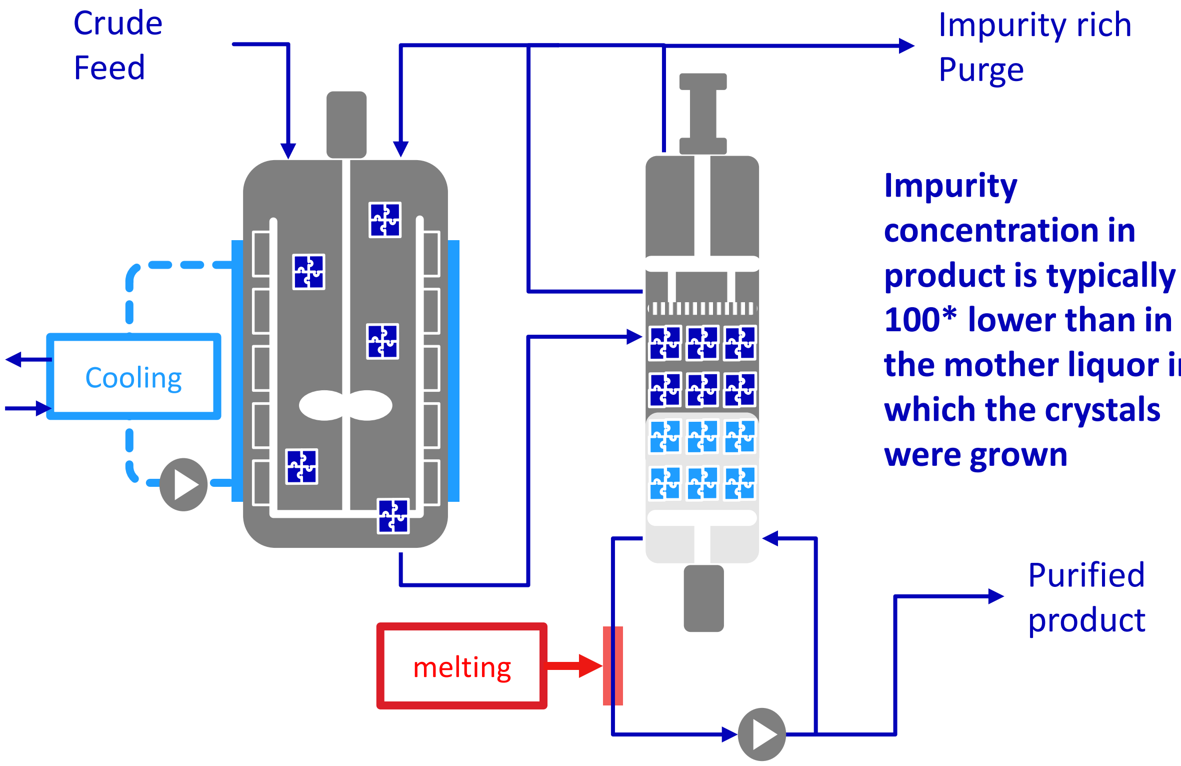




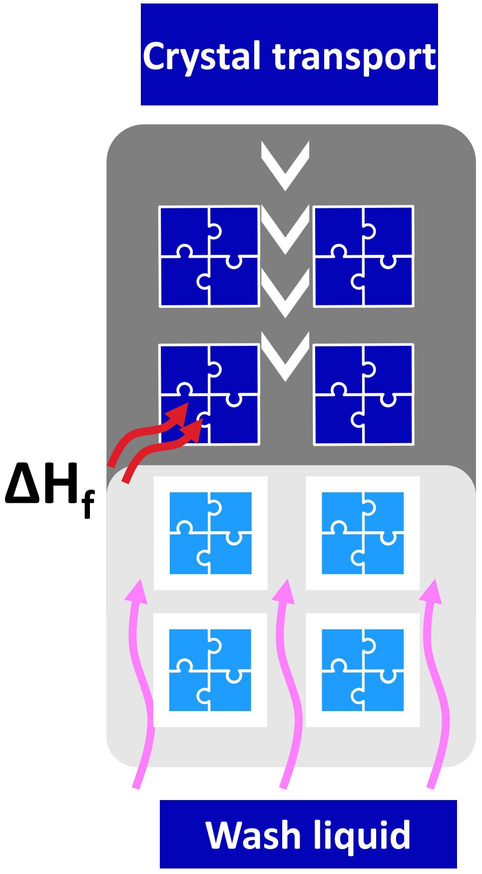
- Reference list with 37 products in the table excluding confidential products.
- Target list with more than 450 potential products to be purified by suspension melt crystallization – wash column technology
- Reference and target lists grow every year
- Wide temperature range (-47.9 up to +141.4°C). T-range limited by equipment/MoC, not by the technology
- For unknown products/ applications development will typically start with lab scale batch crystallization test to gain information on phase diagram, crystal size & shape, filtration and purification potential

Single stage Melt/Freeze Crystallization

Process scheme, similarities and differences



Impurity concentration in product is typically ≥ 100* lower than in the mother liquor in which the crystals were grown



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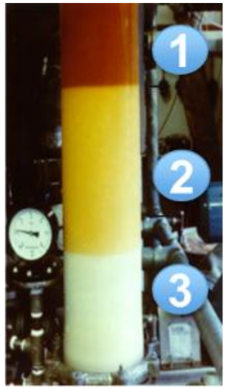
- In Freeze crystallization, the concentrated Mother Liquor is the PRODUCT and the ice crystals the REJECT. Ice is at the top of the wash column
- In melt crystallization, the pure crystals are the PRODUCT and Mother Liquor the REJECT. Crystals are at the bottom of a wash column
- For high purity products, ΔT between Feed suspension and Product in single stage is max. 10-20°C

Purification of monomers/monomer intermediates with melt crystallization - Wash Column technology

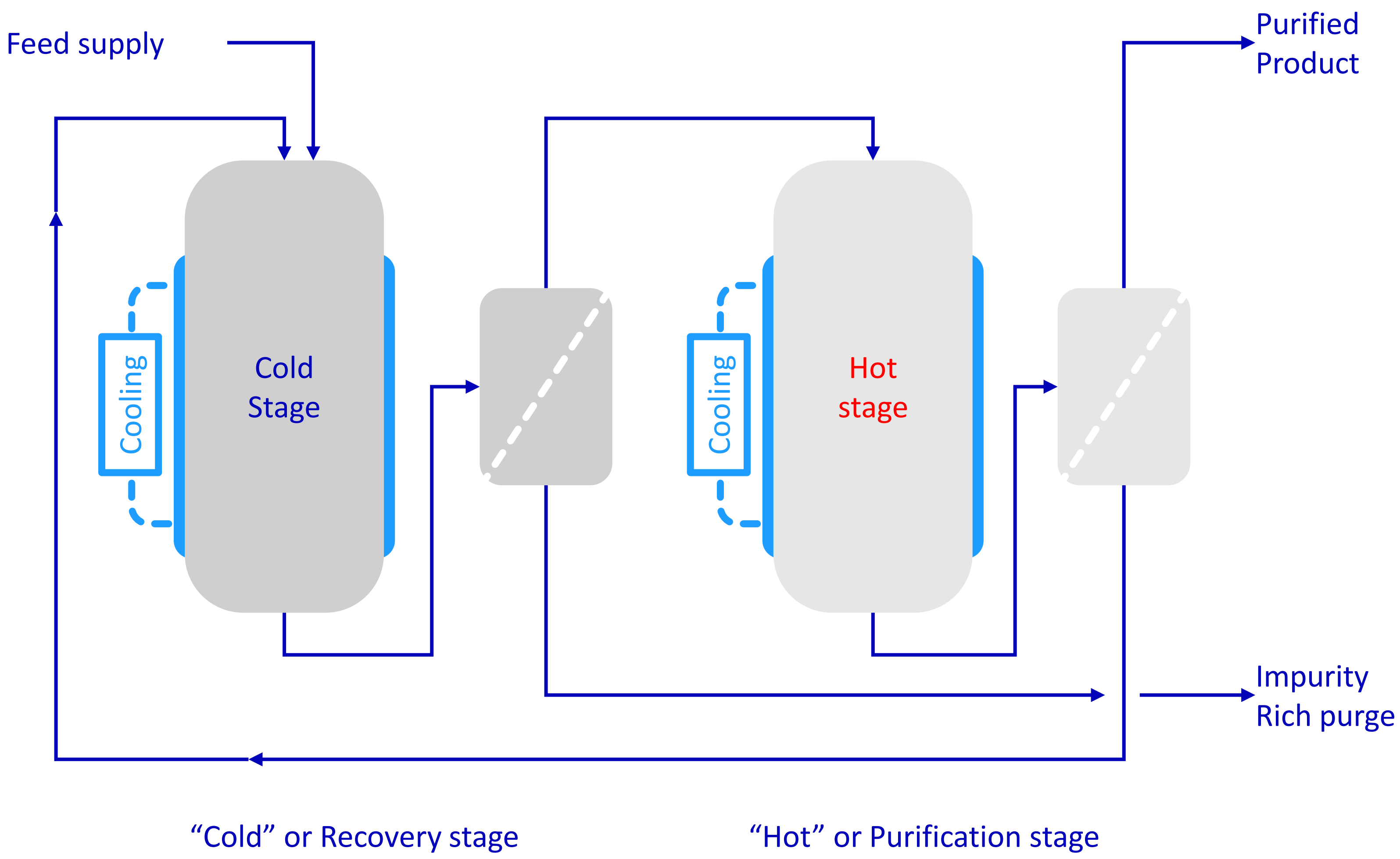
Compound	[Impurity] Mother Liquor	[Impurity] Product	Distribution coefficient
Para-xylene	10.8 wt%	0.07 wt%	0.006
Acrylic acid	4.8 wt%	0.04 wt%	0.008
Caprolactam (colour/A_{290})	158 / 2.58	<1 / 0.024	<0.0063 / 0.0093
Maleic Anhydride	4.03 wt%	0.03 wt%	0.007
Phenol	2.63 wt%	0.069 wt%	0.026

- Impurities with deviating size and/or shape don't fit in the very regular crystal lattice.
- Selectivity of crystallization is very high also for colour removal
- Usually, purities of ≥ 99.9+ wt% can be achieved



Two stage suspension-based

Melt crystallization with maximum recovery



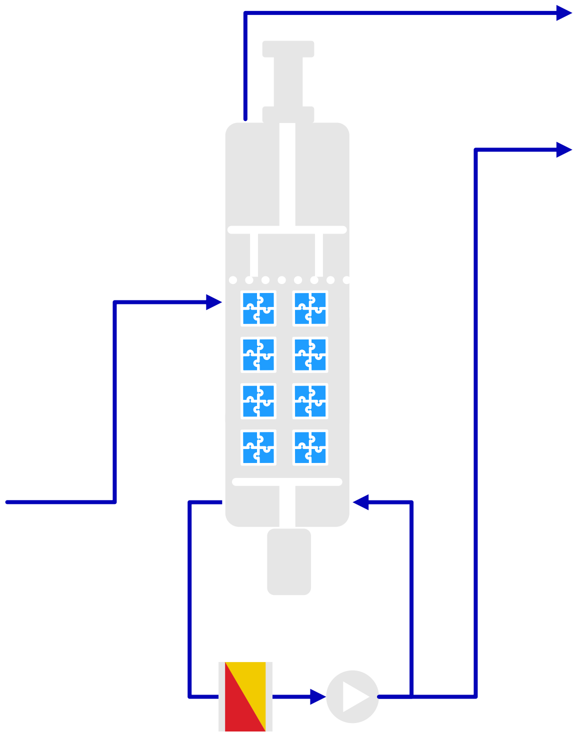
Two stage melt crystallization

- Maximum recovery from relatively pure feed stock
- Purge composition near eutectic
- Configuration with standard components
- Separate purification step from recovery step for maximum purity

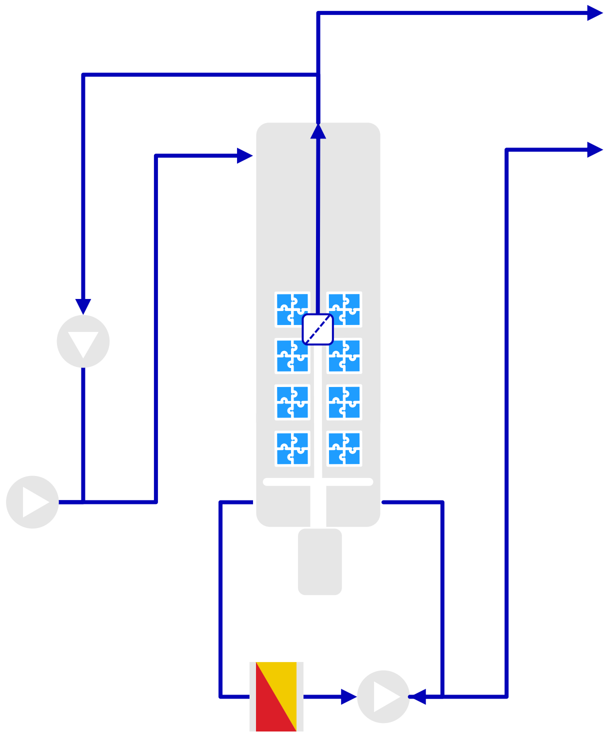
Wash columns

Commercially available systems

Piston Wash Column (pW)



Hydraulic Wash Column (hW)



Piston wash column (pW)

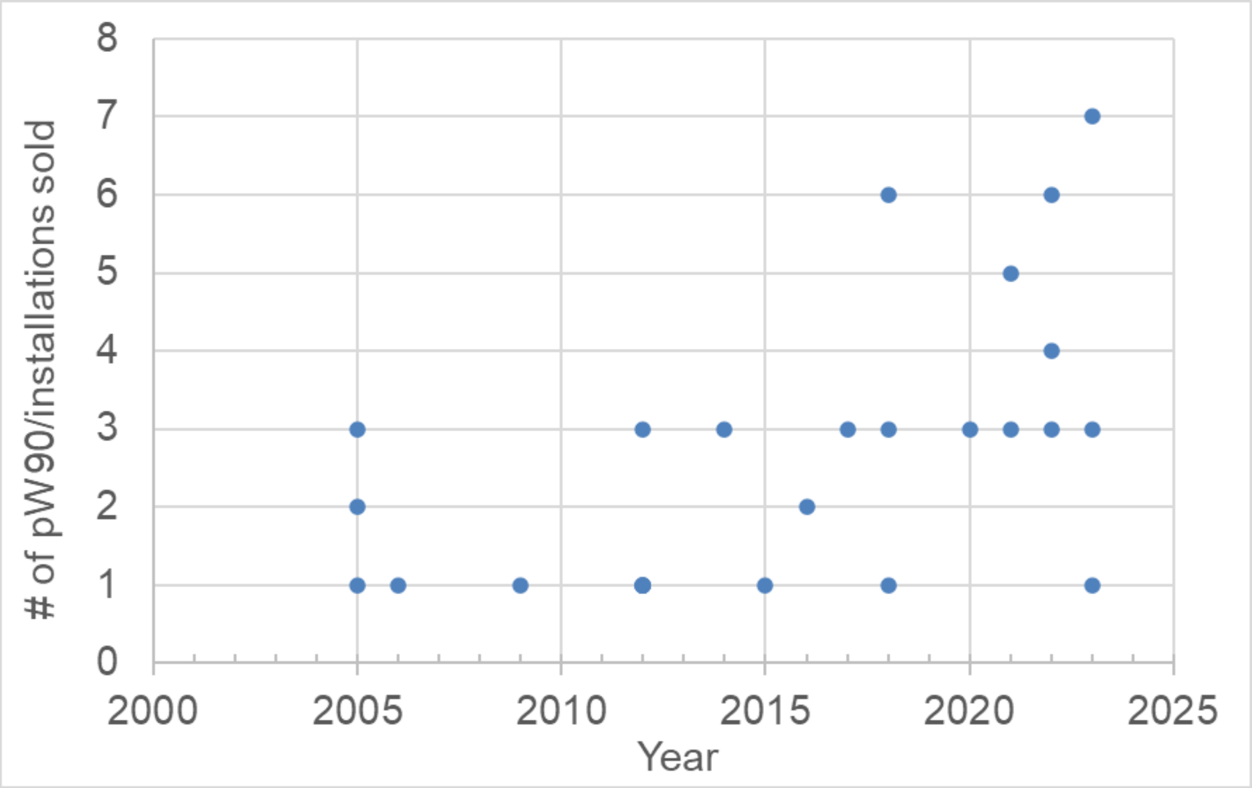
- Crystal transport via fixed stroke linear actuator
- Mechanical compression
- Installed units – pW6, pW20, pW30, pW60 & pW90
- Capacity range 5-2000 kg/h/pW

Hydraulic wash column (hW)

- Crystal transport via fluid flow
- No mechanical compression
- Installed units – hW6 , hW15, hW60, hW90
- Capacity range 10 – 25000 kg/h/hW

References GEA Wash Columns Chemicals

- Active in chemical industry since 1987, with more than 30 installations/ 100 wash columns installed worldwide in chemical industry



- First installations had screw-type Wash Columns, most installations with Piston Wash Columns, a few with Hydraulic Wash Columns (expect to increase in bulk applications)
- Diameter installed Wash Columns from 6 up to 90 cm with intermediate standard sizes

Products in reference list

- Chloroprene
- Para-xylene
- Waste water
- Para-Di Chloro Benzene
- Ethylene Carbonate
- Para Tertiary Butyl Phenol
- Phosphoric Acid
- Benzoic Acid
- Acetonitrile
- Mono Chloro Acetic Acid
- Acrylic Acid
- Para Nitro Chloro Benzene
- L-Lactide
- Confidential applications

- Operating range: -55°C to +130°C

References for some (precursors) for monomers

Melt Crystallization – Wash Column Technology

Principle and advantages

- An impure feed is **cooled** to form **crystals**. Most **impurities** do not fit in crystals lattice and **remain in the Mother Liquor**. **Wash Columns** can **separate** the **pure crystals** almost completely from the **impure Mother Liquor**.
- Suspension Melt Crystallization – Wash Column technology provides **high purity** products (99.9+ wt%) against a **lower energy consumption** and **smaller footprint** than competing technologies.

We offer

- A **one-stop shop** for the whole trajectory of conceptual idea, lab and pilot tests, supply of industrial installations and after-sales

We have

- **50 years experience** in the **ultra-purification** of **chemicals**, have a list with **450 target products**, tested **more than 40 organic chemicals** on **pilot** scale and installed **more than 30 installations** worldwide in the **chemical industry**
- **Proven technology with industrial references for the monomers and precursors for polymers, plastics and resins (including color removal).**

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