TNO Hydraulic Wash Column (TNO-HWC®)
A versatile Solid-Liquid separator for High Purity Products
Melt crystallization and HWC technology

Drivers for melt crystallization - HWC:
  • Reducing costs and energy consumption in industry
  • Make high purity products

High potential applications:
  • Ultra purification of chemicals (organic bulk and fine chemicals, phosphoric acid, NaOH, aluminium, ….)
  • Solvent switch: efficient transfer of solids between solvents
  • Pure water and salts (Eutectic Freeze Crystallization)
Pure crystals are usually formed when an impure feed is cooled below its freezing point, while the impurities are concentrated in the mother liquor.
The counter current washing process

- **Bottoms zone**: crystal bed moves down and the pure wash liquid moves up.
- **Wash Front**: recrystallization of the pure wash liquid on cold crystals in the bed (see example water).

**Diagram:**
- Ice crystals in salt water (-8 °C)
- Ice crystals in pure water (0 °C)
- S-L separation
- Position filter
- Wash front
- Counter current washing
Principle of the TNO Hydraulic Wash Column

A 15 cm TNO HWC® with para-xylene.

Schematic diagram of the TNO wash column.
Purification of phenol
comparison hydraulic wash column vs. centrifuge

- Feed contains 90% phenol and 10% impurities

\[
\text{Removal (\%)} = \left( 1 - \frac{[\text{Imp}]_{\text{product}}}{[\text{Imp}]_{\text{mother\ liquor}}} \right) \times 100
\]

**Conclusions**

- Eutectic impurities: A, B, C and D
- Solid solution forming impurities: E and F
- Separation efficiency: wash column > centrifuge especially for eutectic impurities
Purification of organic bulk chemicals

<table>
<thead>
<tr>
<th>compound</th>
<th>[impurity] mother liquor</th>
<th>[impurity] product</th>
<th>distribution coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>acrylic acid</td>
<td>4.8 wt %</td>
<td>0.04 wt %</td>
<td>0.008</td>
</tr>
<tr>
<td>p-dichlorobenzene</td>
<td>5.98 wt %</td>
<td>0.025 wt %</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>0.02 wt % solid solutions in product</td>
<td></td>
<td></td>
</tr>
<tr>
<td>maleic anhydride</td>
<td>4.03 wt %</td>
<td>0.03 wt %</td>
<td>0.007</td>
</tr>
<tr>
<td></td>
<td>co-crystallized fumaric acid in product</td>
<td></td>
<td></td>
</tr>
<tr>
<td>naphthalene</td>
<td>5.64 wt %</td>
<td>0.475 wt %</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>10.0 wt %</td>
<td>0.02 wt %</td>
<td>0.002</td>
</tr>
</tbody>
</table>

first system: 0.44 wt % solid solutions
second system: eutectic impurities

distribution coefficient = [impurity, product]/[impurity, mother liquor]
Solvent switch in a HWC

Solvent switch is an efficient transfer of crystals/solids from one solvent into another solvent

Drivers
- Add value by increased product purity
- Diminish wash liquid consumption
- Reduce costs for solvent recovery

Examples of potential applications
- Separation of polymers in emulsion polymerization
- Transfer of crystals in multi-stage processes
- Continuous regeneration of IX-particles
- Isolation of heterogeneous catalysts from a reactor
Solvent switch in HWC

Feed slurry (solids in solvent A)

slurry feed pump

filter

counter-current washing process

unwashed crystal bed

washed crystal bed

Filtrate (solvent A with Small amount of B)

Wash liquid

Solvent B

Product slurry Solids in solvent B

Wash liquid

Solvent B

product = suspension
Photographs HWC in stallation for solvent switch
Differences between solvent switch and melt crystallization

- No recrystallization at the wash front
- Wash front always at the position of the filters
- HWC product is typically a suspension instead of a melt
- Difference in layout of bottom section (e.g. no melter)

A 15 cm HWC during solvent switch of Carnalite (KMgCl$_3$.6 H$_2$O)
Scale-up strategy of a Hydraulic Wash Column

Case-study Para Xylene

- diameter column = 1.13 m = 1 m²
- effective height column ≈ 1-2 m
- 200 filter tubes (with d = 2.5 cm)
- capacity ≥ 15 tonnes/m².hr

- d column = 8 cm
  1 filter tube
  capacity = 0-20 l/hr

- d column = 15 cm
  6 filter tubes
  capacity = 0-100 l/hr
HWC-55: design aspects

Dimensions Skid and Wash Column

- Skid: 2 * 3 * 8 m, turn key
- Wash column:
  1.5 * 0.55 m (height * diameter)
  50 filter tubes

Certifications

- Explosion proof: ATEX zone 2,
- Group IIA, T3
- CE-certified (PED)

Design parameters

- Capacity: 1.5-5 ton purified product/hour
- Maximum operating pressure: 10 bar
- T-range: -15 to 80°C
- Different operating options possible
HWC-55 : pilot plant

Sold
HWC-55 : in operation
HWC-55: Overview test results

- Easy start up (on day 2) and stable operation
- Illustrative process conditions:
  - feed and wash pressures: ± 3 en ± 1.5 bar
  - bed en wash front heights: 30 cm and 10 cm
  - $\Delta T$ wash front: 7-8°C
- High production capacity: up to 5 ton pure product per hour = 20 ton per hour per m$^2$ wash column !!
- High product purity: 99.94 wt% (> specs) for 85 wt% mother liquor. I.e. distribution coefficient = ± 0.004.

CONCLUSION:
- Performance of HWC-55 was at least similar to that in smaller scale units (HWC-8/HWC-15)
- Customer satisfied, scale-up strategy proven and first HWC implemented at industrial scale
Intellectual property position of HWC

Patents

1. The granting of the patent on the Scraper-less Design proceeds well (a.o. granted in USA and Indonesia, final stage for China)

2. TNO got a royalty-free non-exclusive license on 4 patents filed by BASF on (Hydraulic) Wash column Technology. TNO has a right to sub-license, but 4 chemicals are excluded.

3. TNO has recently filed 2 new patent applications on the Hydraulic Wash Column, based on the solutions implemented in the HWC-55

4. Two improvements could strengthen patent position further. One is related to equipment and the second relates to the Process/Operation
Research & Commercialization of the HWC

1. TNO and Fine Chemicals company will soon reach a License Agreement for a high purity product, including (pilot) production unit (HWC-30).

2. The TNO-HWC is selected by a Bulk Chemicals company for replacement of a purification step currently done by distillation. After industrial pilot plant (HWC-8) up scaling to full scale installation (2 HWC-55 or 1 HWC-80) is foreseen.

3. A big chemical company signed an order for the feasibility study of a solvent switch on lab scale with HWC-6. Test installation is under construction, experiments start in December 2009.

4. Agreement on technical contents of lab scale feasibility study for a solvent switch for a pharmaceutical. Project can start as soon as customer finished internal research on preparation of the particles.
TNO’s business model for the HWC

• TNO is and remains responsible for R&D activities from the desk and lab studies up to the pilots and demonstrations at industrial scale

• TNO can freely license its know-how and IP to industrial customers. Exclusive licenses are possible.

• For each industrial implementation project TNO and the customer can select the best partner for engineering and construction of the Wash Column(s). TNO has several candidate partners. We even don’t exclude our “competitors” as ad-hoc project partner.

• In future, this could evolve in a strategic, exclusive co-operation with one Technology Supplier
Conclusion

• Technical feasibility for use of TNO Hydraulic Wash Column in suspension-based melt crystallization and solvent switch proven for various systems

• Impurity concentration in product is 100 – 1000* lower than in mother liquor.

• TNO Hydraulic Wash Column offers:
  • relatively low investment and operating costs
  • robust operation due to absence rotating components
  • a straight forward scale-up potential, proven up to 55 cm
  • a good turn down ratio
  • control strategies for automatic operation