

The potential of crystallisation as a purification step for organic chemicals can be found in the results of a study published by Matsouka in 1977. It states that over 50% of the binary organic mixtures examined (nearly 1500 were published at the time) exhibit simple eutectic behavior, while nearly 85% exhibit some form of eutectic indicating that crystallisation could produce pure products from the majority of chemical mixtures in one step¹. This article will attempt to explain the advantages of using crystallisation based separation processes. The suspension based melt crystallisation process is examined, including a state of the art solid/liquid separation process for the production of ultra pure end products.

Common practice

Separation of industrial chemical solutions is most commonly completed by distillation. However, standard distillation based separation systems are generally not economically attractive for solutions that form isomers and azeotropes. Crystallisation, in these specific cases, can often provide a better separation and a more energy efficient process. When compared with distillation, crystallisation typically requires only 25% of the energy to convert a product into solid form as it does to vapourise the same material. The normal (atmospheric) boiling temperature is much higher and can lead to degradation and loss of valuable product. Distillation and crystallisation both work by exploiting the equilibrium characteristics of specific components of the solution. These characteristics are generally illustrated using temperature/composition diagrams; vapour/liquid equilibrium (VLE) for distillation based separations and solid/liquid equilibrium (SLE) for crystallisation based separations². The differences in the equilibrium diagrams for these two separation processes are illustrated in Figure 1.

Separation theory

In Figure 1 the upper VLE curve illustrates a maximum boiling azeotrope. In VLE based systems both phases typically contain some fraction of each component. The upper line indicates the vapour composition and the lower line indicates the liquid composition connected by a horizontal tie line. An azeotrope is a non ideal form of the VLE where the vapour line meets the liquid line. At the azeotropic point ($X_{\text{azeotrope}}$) the vapour will contain both components A and B in a fixed proportion. Boiling a liquid of composition X_{liquid} will produce vapour with composition X_{vapour} . This has therefore enriched the vapour in component B but due to the azeotrope will still not be able to produce pure A by simple distillation. This example illustrates the case where crystallisation can provide a simpler separation for component A.

The SLE curve represents a simple eutectic system. The key point of true eutectic systems is the high selectivity in formation of the solid phase containing only one component. The top curve indicates the liquid concentration and the solid composition is indicated by the pure component axes and limited by the eutectic concentration. This shows that the solution forms a pure solid crystal A in the binary solution to the left of the eutectic concentration and a pure solid crystal B to the right of the eutectic concentration. Cooling a liquid of composition X_{liquid} will produce the first pure crystals around T_{eq} liquid. Since A is removed from the system as pure solid the remaining liquid (ML) composition will then follow the equilibrium curve down to T_{e} . Further cooling after reaching the eutectic temperature of T_{e} will only produce a mixed solid mass containing both A and B crystals where further separation is not possible. Eutectic behaviour can therefore lead to the formation of extremely pure product in a single step. A practical limitation in applying crystallisation based processes

Ray Ruemekorf and
Reinhard Scholz, Niro
Process Technology B.V.,
The Netherlands, discuss
the theory, practice and
benefits of crystallisation
as a purification step for
organic chemicals.

Crystal clear separation



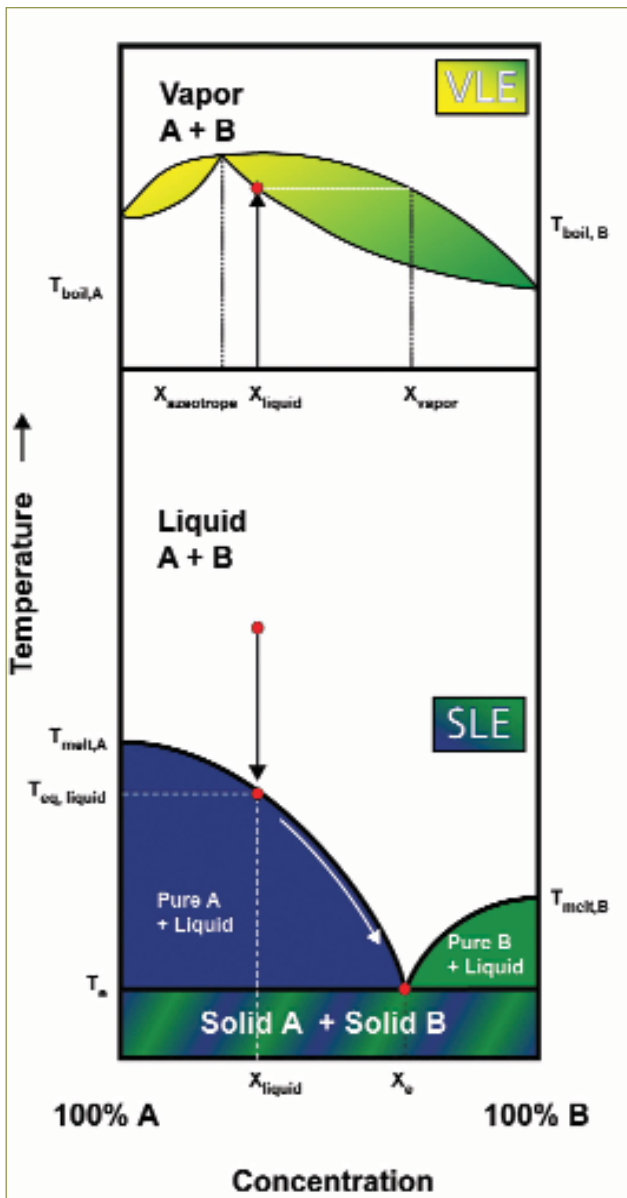


Figure 1. Differences in the equilibrium diagrams.

is the fact that very low growth rates are required to obtain pure crystals; otherwise kinetic effects can lead to the incorporation of impurities into the crystal structure even for eutectic systems. Another challenge for crystallisation based processes is the required solid/liquid separation of the solid crystal from the remaining impurity rich ML (vapour/liquid separations are generally much simpler). Whether rapid growth conditions trap ML inside the crystal structure or inefficiencies in the solid/liquid separation leave ML on the outside of the crystal either condition will significantly reduce the final product concentration. Figure 2 illustrates the effect of remaining mother liquor on the final product purity³. Even though the crystal is pure, the impurities in the remaining liquid must be completely removed from the crystal surface to ensure pure end product.

Practice

Sometimes the 'last few steps are the hardest'. This is also true in many industrial separation processes. The extra effort to reach high purity product in a fractional distillation column may not be worth it. Crystallisation may be able to provide a simpler separation step with improved product quality and efficiency. Hybrid systems (the combination of crystallisation with another separation process) can provide an effective means for the production of ultra high purity products with

much greater efficiency than either single process alone. An example would be where a distillation process could easily make an initial separation of the desired component and then the crystallisation based process can finish this to the ultra pure end product (>99.9 wt%). Another example is the adsorption based separation of paraxylene where significantly shorter adsorption columns can be used to produce a relatively pure feed (>90 wt%) that can easily be finished to pure end product by melt crystallisation.

State of the art

In the past, the problem has generally been a lack of understanding of the crystallisation based process and the technical challenges in the solid/liquid separation of the crystals from the impurities still remaining in the ML. It is easy to generate binary SLE data for an initial examination of the crystallisation process and industrial compositions can be readily tested in lab or small scale pilot equipment. Suspension based crystallisation equipment provides near ideal growth conditions and can reliably produce solid/liquid slurries that contain extremely pure crystals. Industrial equipment is readily available from a number of suppliers. This leaves the problem of solid/liquid separation for the final production of the ultra pure end product. As indicated above and illustrated in Figure 2 the impurities remaining in the ML must be completely removed from the crystal mass to ensure pure product. The wash column offers a unique opportunity to effectively remove all of the impurities in the remaining ML taking full advantage of the high selectivity of the crystallisation based process.

How does the wash column achieve such high efficiencies? This can be found within the column itself. Crystals grow by absorbing the supersaturation of the bulk liquid onto a crystal surface. Supersaturation is the condition when a certain composition of liquid is subjected to a temperature below its equilibrium temperature. For example if we place a cold steel finger at -10 °C into a container with pure water held at 0 °C the water near the surface of the steel finger will become much colder (approaching -10 °C) and form a layer of undercooled (supersaturated) water surrounding the steel surface. The water in this supersaturated layer will tend to crystallise onto the surface of the steel and energy will be released (the heat of crystallisation of water = 334 kJ/kg ice). The steel finger will therefore begin to warm up and crystallisation will continue until the steel reaches the equilibrium temperature of the water (0 °C). The heat required to warm up the steel can be calculated by using the temperature, mass and heat capacity of the steel finger. The heat released by the crystallisation of water must exactly balance this required heat and the mass of ice formed can be calculated.

The wash column operates by compressing the slurry obtained in the crystalliser (typically 25 - 35 wt% crystals) to remove most of the ML. This can be compared to a filter press operation and results in a long (typically 50 - 100 cm) and relatively 'wet' crystal bed with roughly 80% crystal mass and 20% ML (compare to a centrifuge cake of only 2 - 3 cm and 5 - 10% liquid). The crystal bed consists of individual crystals surrounded by the ML and depending on the crystal size distribution and viscosity of the ML can generally be easily washed by applying a pressure difference across the bed length. Imagine a packed bed adsorption column where the fluid to be treated is forced through the column, the adsorbent is the crystal mass and the fluid to be treated is the ML. The wash column has one significant difference in that the crystal bed is moving instead of the fluid.

Wash columns continuously push crystals through the column where they enter one end and are discharged out the other. This crystal transport can be completed by gravity,






Product Purity after Melt	Residual Liquid (30% impurities)	Effective Distribution Coefficient
99.97%		$k_{eff} = 0.001$ Wash column
99.4%		$k_{eff} = 0.02$ Centrifuge (10-20% product as wash)
98.5%		$k_{eff} = 0.05$ Centrifuge (5-10% product as wash)
97.0%		$k_{eff} = 0.1$ Centrifuge (no wash)
94.0%		$k_{eff} = 0.2$ Filter press Layer crystallizer

Figure 2. The effect of residual liquid on product purity.

reciprocating piston, screw conveyor or hydraulic flow. The available wash column designs are illustrated in Figure 3⁴. As new crystals enter one end of the column they will force old crystals out the opposite end. These exiting crystals are removed by a rotating scraper and then melted by circulating through a heat exchanger. This liquid melt is basically pure end product except for the impurities in the ML that have been trapped within the crystal mass. The wash column is uniquely able to displace these impurities within the crystal bed by washing the bed as it moves through the column. By controlling the liquid pressure difference across the column melted product (from the crystal discharge side of the column) can be effectively forced counter-currently through the crystal bed. Since the liquid velocity is relatively low the fluid flow can be assumed plug flow within the packed bed and a condition of relatively pure wash liquid can be formed that will displace the relatively impure ML. This is in contrast to the relatively ineffective cross-current wash liquid flow found in a centrifuge.

Remember the steel finger example from above? The crystals entering the column are typically much colder than the pure product melting temperature. They have just come from the crystalliser and are in equilibrium with the ML (10 - 20 °C lower than the pure melt). Therefore each crystal forms a 'steel finger' that when in contact with the pure wash liquid will cause crystallisation to occur as the space between the crystals becomes filled with the pure wash liquid. Figure 4 illustrates how this crystallisation of the wash liquid warms the crystal, displaces impurities and helps to maintain the plug flow of wash liquid. The washed portion will typically provide a higher pressure drop than the unwashed portion and provides a self stabilising effect. The zone where this occurs is called the wash front and can be seen by the sharp temperature change in the crystal bed. The wash front advances counter-currently to the crystal bed flow and will therefore displace the impurities away from the discharge end of the column. All impurities will be essentially eliminated from the crystal bed as they are forced through the column. The wash

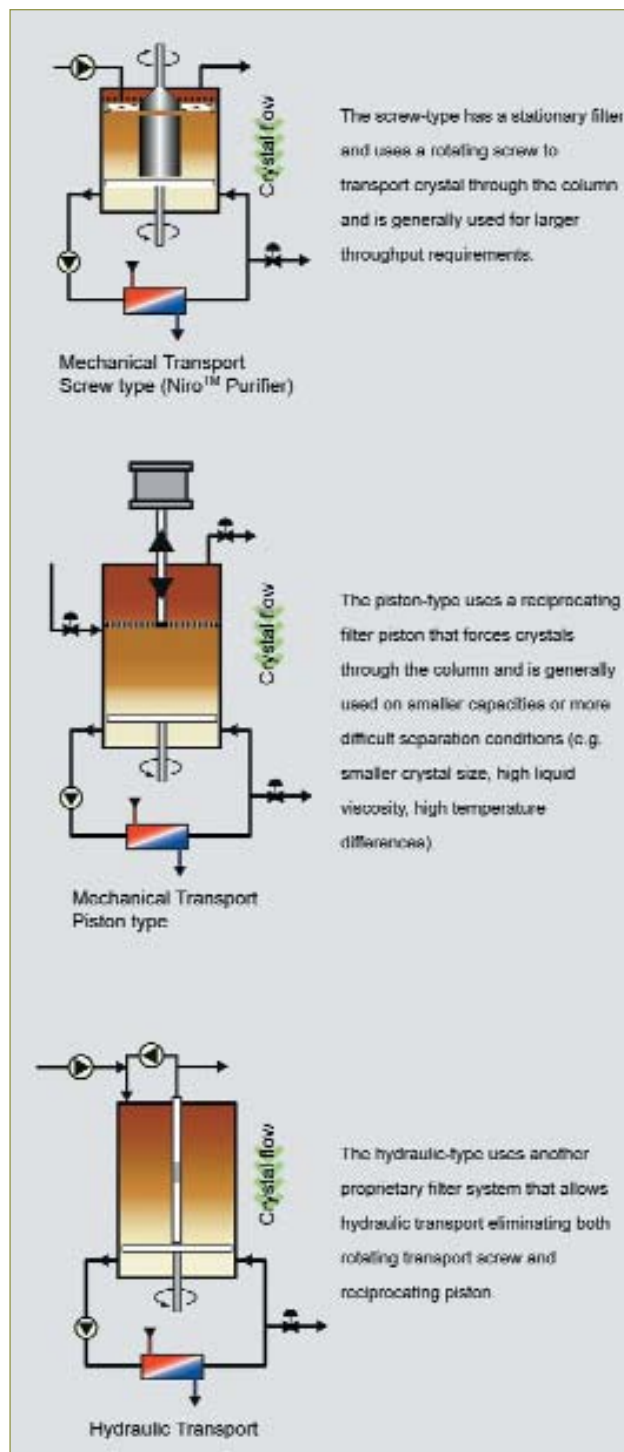


Figure 3. Available wash column designs.

liquid is allowed to crystallise and therefore leaves the column as product and will not be lost as spent wash liquid. This is in sharp contrast to the wash liquid supplied to a centrifuge that typically passes completely through the relatively short bed, creating an impure spent wash liquid and consuming a significant portion of the final product.

Industrial applications

Dichlorobenzene

The para and meta isomers are impossible to separate with simple distillation while the ortho isomer can be removed from the isomer mixture. The para-DCB isomer is industrially important for room deodorants, moth control, and other intermediates in the production of dyes and pesticides. However, its high purity requirement is found in the production of polyphenylene sulfide (PPS) an engineering plastic with

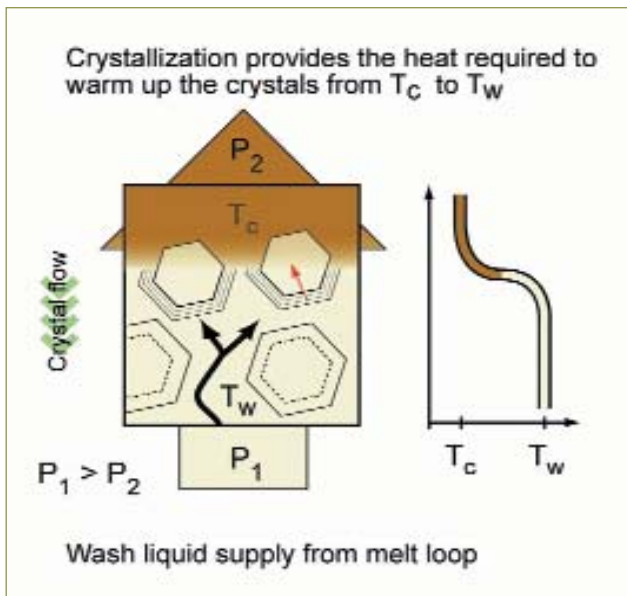


Figure 4. Crystallisation of the wash liquid warms the crystal, displaces impurities and helps to maintain the plug flow of wash liquid.

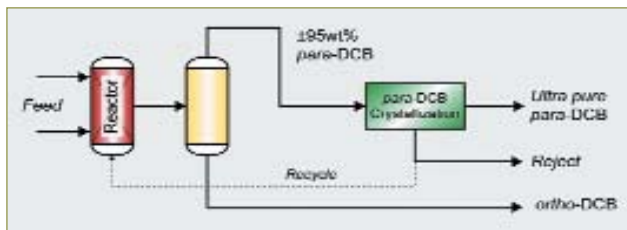


Figure 5. A typical configuration using crystallisation for the production of high purity para-DCB.

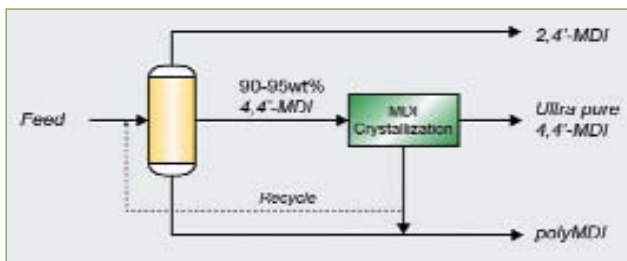


Figure 6. A configuration for the crystallisation based production of high purity 4,4'-MDI with distillation as recovery unit.

stringent purity requirements.

Distillation can separate the crude reaction product into ortho-DCB and a para-DCB enriched stream. Crystallisation can easily produce pure para-DCB with >99.95 wt% para-DCB. Figure 5 depicts a typical configuration using crystallisation for the production of high purity para-DCB.

Diisocyanates

Diisocyanates became commercially important in the 1930s with the discovery of polyurethanes. The isomer 4,4'-diphenylmethane diisocyanate (4,4'-MDI) is used in the production of various polyamide elastomers, rigid foam insulation and injection molded thermoplastics for the automotive industry. MDI is particularly heat sensitive making end purification by distillation costly and difficult. It will also form dimers and trimers upon heating which can affect the downstream processes that use the pure 4,4'-MDI isomer⁵.

Suspension based crystallisation can provide a cost

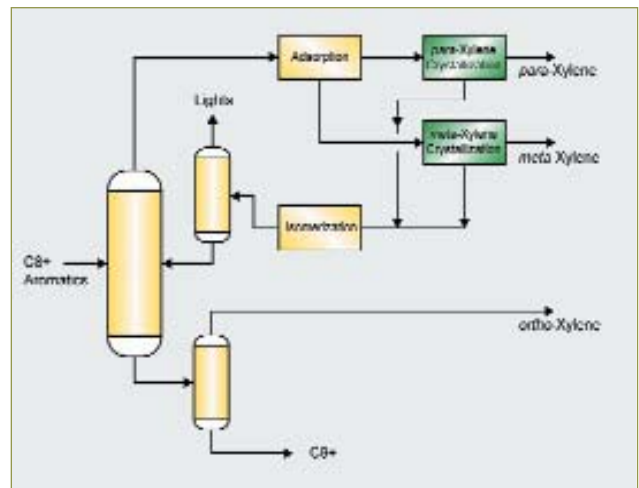


Figure 7. Configuration for the crystallization based separation of Xylene isomers.

effective solution for production of >99.9 wt% 4,4'-MDI product resulting in higher monomer yield and lower overall energy consumption. The ML reject enriched with the polymeric forms of the isomer can be recycled to the distillation where they will be dissociated back to the monomer. Figure 6 illustrates a configuration for the crystallisation based production of high purity 4,4'-MDI with distillation as the recovery unit.

Xylene

Paraxylene cannot be separated from its meta isomer by simple distillation, only the ortho isomer can be removed. The pure isomers are industrially important in the production of terephthalic acid (from PX feed), isophthalic acid (from MX feed) and phthalic acid (from OX feed). Terephthalic acid is further processed for the plastic PET and isophthalic acid is used as co-monomer in PET and to a lesser extent for the production of aramid fiber.

Suspension based crystallisation is commonly used to purify the paraxylene but the eutectic prevents crystallisation from producing metaxylene from the same feed. However, the reject from an adsorption based process (such as the PAREX process from UOP LLC) provides a stream sufficiently depleted in paraxylene that it is on the meta side of the eutectic and crystallisation can efficiently separate pure metaxylene. Figure 7 depicts a configuration using crystallisation for the production of all three isomers from a mixed xylene feed. The process combines distillation to make the initial ortho split and then adsorption splits the remainder into para rich stream and a meta rich stream that are both purified by crystallisation. The adsorption system allows the jump over the eutectic concentration for the para/meta binary solution. The rejects from both crystallisation units are then isomerised and fed back to the xylene splitter.

References

1. ULRICH, J., GLADE, H. 'Melt Crystallization: Fundamentals, Equipment and Applications', Aachen:Shaker, 2003, pp. 4.
2. WIBOWO, C., O'YOUNG, L., 'Streamlining Crystallization Process Design', CEP Jan 2004.
3. RUEMEKORF, R., SCHOLZ, R., 'The Application of Wash Column Technology for Thickening and Purification in a Two-Stage Suspension Crystallization Process' presentation for the 2002 AIChE Annual Meeting.
4. SCHOLZ, R. et al., 'Wash Columns - State Of The Art And Future Developments', proceedings of the 15th International Symposium on Industrial Crystallization, vol. 1, 2002.
5. ARKENBOUT, G., 'Melt Crystallization Technology', Technomic, 1995, pp. 315.