EUROPEAN ROADMAP OF PROCESS INTENSIFICATION

- TECHNOLOGY REPORT -

TECHNOLOGY: EXTRACTIVE CRYSTALLIZATION

TECHNOLOGY CODE: 2.1.2

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1. Technology

1.1 Description of technology / working principle

(Feel free to modify/extend the short technology description below)

Extractive crystallization is a hybrid process in which crystallization and extraction are combined. There are several process configurations possible. Either the solute or the solvent can be extracted from a solution.

In case the solute is extracted, the solute accumulates in the extractant until this phase becomes supersaturated and crystallization starts. In one configuration a reactive extractant is applied. Subsequently the crystals are separated from the mother liquor. In this case the crystal are the desired product.

In a second configuration absorption of a compound from a gas stream into a reactive extractant takes place, followed by crystallization of one of the compounds. In a following step the extractant is regenerated by a heat step followed by redissolution of the crystals and desorption of the originally absorbed compound.

In case the solvent is extracted, mixing of the solution with an anti-solvent takes place, the resulting decrease of the dissolving power of the solvent mixture makes the solution supersaturated until crystallization starts. Next the crystals are separated from the mother liquor. From the mother liquor the co-solvent is regenerated. This may be achieved by a temperature step followed by a phase split. The anti-solvent rich phase is recycled to the crystallization process while the solvent rich phase is recycled as process solvent. In a specific configuration the solvent is an ionic liquid and the anti-solvent is supercritical CO_2. After crystallization the ionic liquid is recovered as a solvent when the carbon dioxide vaporizes by lowering the pressure.

Furthermore, a description is given of extraction of an impurity during a recrystallization of one crystal structure of a compound into another one.

In this description conventional anti-solvent crystallization without regeneration of the solvents is not taken into account and neither is the formation of co-crystals.

1.2 Types and “versions”

(Describe the most important forms/versions of technology under consideration, including their characteristic features, differences and similarities)

Three types of extractive crystallizations can be considered:
- solute extraction with a non-miscible extractant, with the crystals as product,
- absorption of a compound from a gas stream with an extractant, followed by regeneration of the extractant, crystals are an intermediate product,
- solvent extraction with an anti-solvent with regeneration of the solvent, crystals are the product.

1.3 Potency for Process Intensification: possible benefits

(In Table 1 describe the most important documented and expected benefits offered by the technology under consideration, focusing primarily on energy; CO_2 emission and costs, providing quantitative data, wherever possible. Add other benefits, if needed).

Table 1: Documented and expected benefits resulting from technology application

Benefit	Magnitude	Remarks
lower energy use	Large	Compared to evaporation crystallization or to conventional gas desoorption

Control over CSD	Medium	Requires well-controlled mixing

1.4 Stage of development

- Crystallization with solute extraction: research process, laboratory and bench-scale, university and institutional research and development.
- Gas absorption with crystallization: both at university, research institutes and industrial process developers.
- Solvent extraction with an anti-solvent: university research.

2. Applications

2.1 Existing technology (currently used)

(Describe technology (-ies) that are conventionally used to perform the same or similar operations as the PI-technology under consideration)

Evaporation crystallization, cooling crystallization.
Gas absorption with conventional thermal extractant desorption.

2.2 Known commercial applications

(Is the technology broadly applied on commercial scale? In which process industry sectors is the technology most often applied: large volume chemicals – specialty chemicals & pharma – consumer products – ingredients based on agro feedstocks? What is the estimated number of existing applications? In Table 2 provide the most prominent examples of realized applications and provide their short characteristics)

No industrial applications known.

Table 2. Industrial-scale applications of the Technology (existing and under realization)

Sector	Company - Process/Product name/type	Short characteristic of application	Production capacity /Plant size	Year of application	Reported effects
					•

2.3 Known demonstration projects

(Are there any demonstration projects known related to the technology under consideration? In which process industry sectors are those projects carried out: large volume chemicals –

specialty chemicals & pharma – consumer products – ingredients based on agro feedstocks? In Table 3 provide the short characteristics of those projects.)

Table 3. Demonstration projects related to the technology (existing and under realization)

Sector	Who is carrying out the project	Short characteristic of application investigated, including product name/type	Aimed year of application	Reported effects
Specialty chemicals	APP	Rocket fuel	2012	• large crystals

2.4 Potential applications discussed in literature

(Provide a short review, including, wherever possible, the types/examples of products that can be manufactured with this technology)

Solute extraction: energetic compound.
Solvent extraction: bulk chemicals such as salt and superdense soda ash .
Gas absorption with crystallization: capture of acid gases.

3. What are the development and application issues?

3.1 Technology development issues

(In Table 4 list and characterize the essential development issues, both technical and non-technical, of the technology under consideration. Also, provide your opinion on how and by whom these issues should be addressed)

Table 4. Technology development issues

Issue	Description	How and by whom should be addressed?
Process development	Suitable combinations of solvent and extractant	Process developer
Process development	Separation of solution or gas stream form the extractant phase	Process developer
Scale-up		Process developer with equipment manufacturer and end-user

3.2 Challenges in developing processes based on the technology

(In Table 5 list and characterize the essential challenges, both technical and non-technical, in developing commercial processes based on the technology under consideration. Also, provide your opinion on how and by whom these challenges should be addressed)

Table 5. Challenges in developing processes based on the technology

Challenge	Description	How and by whom should the challenge be addressed?
Large investment	Existing assets are not easily replaced	End-user with process developer
Filtration/washing	Product purity versus solvent losses	Process developer
Solvent regeneration	Energy use	Process developer
Slurry handling	Encrustation / scaling poses a challenge	Process developer

4. Where can information be found?

4.1 Key publications

(Provide the list of key publications in Table 6)

Table 6. Key publications on the technology

Publication	Publication type (research paper/review/book/ report)	Remarks
Extractive crystallization of salts from concentrated aqueous solution, D. Weingaertner, S. Lynn, D. Hanson, Ind. Eng. Chem. Res. 30, 1991, 490-501	Paper	Solvent extraction
Antisolvent Crystallization as an Alternative to Evaporative Crystallization for the Production of Sodium Chloride, Tjakko G. Zijlema, Rob M. Geertman, G.J. Witkamp, G. van Rosmalen, J. de Graauw, Ind. Eng. Chem. Res., 39, 2000, 1330 -1337	Paper/Thesis	Solvent extraction
Antisolvent crystallization of anhydrous sodium carbonate at atmospherical conditions, H. Oosterhof, G.J. Witkamp 2, G. van Rosmalen, AIChE J., 47, 2004, 602 - 608	Paper/Thesis	Solvent extraction
Recovery of pure products from ionic liquids using supercritical carbon dioxide as a co-solvent in extractions or as an anti-solvent in precipitations, M. Kroon, J. van Spronsen, C. Peters, R. Sheldon and G.J. Witkamp, Green Chem., 8, 2006, 246–249	Paper/Thesis	Solvent extraction
Ion exchange extraction during continuous recrystallization of CaSO4 in the phosphoric acid production process: lanthanide extraction efficiency and CaSO4 particle shape, C. Koopman and G. J. Witkamp, Hydrometallurgy 63, 2002, 137-147	Paper/Thesis	Impurity extraction during recrystallization
Overview of the development of hydrazinium nitroformate, H. Schoeyer, W. Welland-Veltmans, J. Louwers, P. Korting, A. van der Heijden, H. Keizers, R. van der Berg, Journal of Propulsion and Power, 18, 2002, 131-137	Paper	Solute extraction
Equilibrium Solubility of CO2 in Aqueous Potassium Taurate Solutions: Part 1.	Paper/thesis	Gas absorption with crystallization

Crystallization in Carbon Dioxide Loaded Aqueous Salt Solutions of Amino Acids, P. Kumar, J. Hogendoorn, P. Feron, and G. Versteeg, Ind. Eng. Chem. Res., 42, 2003, 2832 - 2840		
Precipitation in amino acid salt CO2 absorption systems, M. Majchrowicz, J. Niederer, A. Velders, G. Versteeg	Paper	Gas absorption with crystallization

4.2 Relevant patents and patent holders

(Provide the list of relevant patents in Table 7. Under "remarks" provide, where applicable, the names/types of products targeted by the given patent.)

Table 7. Relevant patents

Patent	Patent holder	Remarks, including names/types of products targeted by the patent
EP1033357 Process for the production of crystalline energetic materials	APP	Solute extraction
EP1042226 Production of water free soda	Akzo Nobel	Solvent extraction
WO03095071 Method for the absorption of acid gases	TNO	Gas absorption with crystallization

4.3 Institutes/companies working on the technology

(Provide the list of most important research centers and companies in Table 8)

Table 8. Institutes and companies working on the technology

Institute/Company	Country	Remarks
TU Delft	Netherlands	Solvent extraction
APP bv	Netherlands	Solute extraction
TNO	Netherlands	Gas absorption with crystallization

5. Stakeholders

5.1 Suppliers and developers

(Provide the list of key suppliers/developers in Table 9)

Table 9. Supplier and developers

Institute/Company	Country	Remarks
TU Delft	Netherlands	Solvent extraction University research
TNO	Netherlands	Gas absorption with crystallization Process developer
APP	Netherlands	Solute extraction Industrial process developer

5.2 End users

(Describe the existing and potential end-users, other than those already listed in Table 2)

Solvent extraction: bulk crystals as salt, soda ash now produced by evaporative crystallization.
Solute extraction: specialty chemicals and materials.
Gas absorption with crystallization: power plants, petrochemical industry.

6. Expert's brief final judgment on the technology

(maximum 5 sentences)

Hybrid processes combining extraction with crystallization appear promising. This is especially the case for solute extraction to recover crystals for specialty chemicals (materials).

Gas absorption followed by crystallization in the extractant is a promising method to enhance the capacity of extraction or absorption processes. Required are suitable extractants and a structure to keep the stream separated from the extractant.

Solvent extraction from a solution was developed at universities during the 1990s when energy prices were low. Under current conditions with high energy prices this technology is likely to become competitive compared to conventional evaporative crystallization processes. However, scale-up requires major efforts.