Crystallization of Sodium Salt of Organic Acid as Example for Neutral Salt Recovery of Bio Acids

The optimization of a bio-acid production process downstream of fermentation is presented. Sodium salt solution of the organic acid (Na salt) solution is the product in the industrial fermentation process for the organic acid production and until today, it has not been attempted to directly crystallize/isolate the Na salt under these circumstances. Evaporation crystallization of Na salt directly from the solid-free fermentation broth without purification can be realized with high product purity. Parameters limiting the crystallization/separation process are identified and discussed. The above points are considered as a function of viscosity, crystal size, and product purity. Comparison with the existing process completes this evaluation. The impact on the process design and alternatives are illustrated. The modification of hybrid processes using crystallization also as a purification step is investigated.

**Keywords:** Bio acids, Crystallization, Fermentation process, Neutral salt recovery, Organic acid

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**1 Introduction**

Typically, downstream processing involves various steps for purification of the fermentation broth before entering the final step of crystallization to produce a dry, stable, and solid product. Especially in fermentation processes of low-molecular-weight substances like salts of amino acids it can be beneficial to use a crystallization process to purify and separate a desired component or an intermediate product directly from the fermentation broth and apply other purification processes only later. The resulting yield increases have to be evaluated against capital expenditure (CAPEX) and operational expenditure (OPEX) to define the optimal process design.

In crystallization of substances in a complex matrix like fermentation broth the interactions are in general unknown and complicated. Therefore, it is the common strategy to involve various steps for purification of the fermentation broth before entering the final step of crystallization to produce a dry, stable and solid product. This is described, e.g., for succinic acid with another strategic option of process units [1, 2].

Sometimes, intermediate precipitation steps as in the common citric acid and lactic acid downstream process are involved with the disadvantage of having two types of chemical reactions [3]. This requires precipitation chemicals and produces waste streams in an amount proportional to the final product capacity. In the review of Li et al. [4], different process units are discussed for the primary recovery, like adsorption, extraction, electrodialysis and so on.

Especially in fermentation processes of low-molecular-weight substances like salts of amino acids it can be beneficial to use a crystallization process to purify and separate a desired component or an intermediate product directly from the fermentation broth and apply only later other purification processes.

One of the targets of the European PRODIA project is to develop a generally applicable and robust crystallization process on different artificial test solutions.

Na salt solution is the salt solution produced in the industrial fermentation process for an existing organic acid production. Until today, it has never been attempted to directly crystallize/isolate the Na salt under these circumstances, although a patent announcement was published. In this study, discontinuous tests will demonstrate that the evaporation crystallization of Na salt directly from three different artificial solutions with different amount of solids without purification can be realized with high product purity. The downstream processes investigated are illustrated in Fig. 1.
GEA had already delivered the organic acid crystallization unit (no. 2) several years ago as production plant and it was not tested anymore. Our group has investigated three different upstream process units. The first one is the control with no separation at all of the biomass, application two is the use of nanofiltration to remove biomass, and option three is the use of a decanter for partial removal of the biomass.

In these experiments, parameters that limit the crystallization/separation process were identified and discussed in relation to viscosity, crystal size, and product purity. The intermediate results were used to expand the crystallization as a purification step for other fermentation downstream processes, especially other upstream process steps.

2 Experimental

A systematic multistage, bench-scale test work was conducted in which the achievable product purity and the mother liquor composition by increasing the impurity level were investigated. Fig. 2 shows the principle experimental setup for the evaporation crystallization tests.

Na salt was produced by discontinuous evaporation crystallization at 45 °C until a certain target slurry density from the feedstock was reached. After a retention time of at least 1 h for desupersaturation purposes, the obtained suspension was separated into unwashed crystals and mother liquor by means of a sieve drum centrifuge under standard conditions. The separated crystals were then washed inside the centrifuge with 10% demineralized water referred to the unwashed, wet crystal mass. Mother liquor and wash centrate were collected and evaporated in the next step in order to further crystallize the Na salt and to concentrate the soluble impurities in the remaining mother liquor. This procedure was repeated several times. In the last step a highly viscous suspension was obtained, which was separated by decantation into a sludge and solid-free mother liquor in order to get solid-free mother liquor. The use of a centrifuge is in principle possible but it may lead to fines breakthrough. Mother liquor, condensate, and crystal samples were taken at each separation step and analyzed for several chemical compounds by HPLC. Viscosity was measured by means of a Hohler falling ball viscometer.

3 Results and Discussion

3.1 Feedstock

The feedstock for the study was a fermentation broth produced by one of the PRODIAS members. The turbid solution was divided into three parts for the study, which were differently treated before entering the crystallization process. Tab. 1 presents details. The chemical composition differed mainly in
the insoluble’s concentration and represents the raw material for the three different application systems. Small deviations in the concentration of other ingredients are caused by small amounts of dilution water, which are highly water-soluble.

### 3.2 Mother Liquor Properties

It was decided to evaluate centrate samples including biomass due to the fact that the remaining or new upcoming biomass in the centrate samples did not allow the sampling of solid-free mother liquor samples for chemical analysis. However, the sedimentation behavior of the fines allows every time fully representative sampling.

In parallel, the viscosity of the mother liquor increased during that time (Fig. 5), but of course exponentially according to the experience.

In a production plant, the presence of fines suspended inside the mother liquor modifies the viscosity behavior to approach the one of a shear-thickening fluid. Another physical property, i.e., boiling point elevation, increases simultaneously with the rising potassium concentration in the mother liquor, as long as the potassium compound did not precipitate. Within the measuring inaccuracy no significant difference between all three applications was found (Fig. 6).

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**Table 1. Feedstock composition.**

| Sample name / parameter | Original broth | Decanted broth | Ultrafiltrated broth |
|------------------------|----------------|----------------|---------------------|
| Application system I   | Untreated broth | Decanter | Nano filtration / ultrafiltration |
| Hybrid system of Part 1| Crystallization | Crystallization | Crystallization |
| Dry substance at 70 °C [wt %] | 14.3 | 13.9 | 13.7 |
| Na salt based on organic acid [wt %] | 13.2 | 13.3 | 13.1 |
| Na salt based on Sodium [wt %] | 14.0 | 14.1 | 13.9 |
| Sodium [wt %] | 1.49 | 1.51 | 1.48 |
| Potassium [mg kg⁻¹] | 537 | 504 | 491 |
| Insoluble [wt %] | 0.4 | 0.2 | 0.0 |

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**Figure 3.** Decreasing Na salt concentration.
3.3 Crystal Properties

The obtained crystals are discoidal (see Fig. 7) and have a crystal size of \( d = 0.2 \text{ mm} \). At lower viscosity, the separation by centrifugation is very effective and the target of 98 % purity can easily be achieved. In the last step of these investigations (potassium concentration > 8000 ppm), the crystallization conditions became worst due to the higher viscosity of more than 100 mPa s. Consequently, the number of fines increased and the purity of the unwashed crystals decreased significantly (less 60 %). This is not a showstopper because the quality could be easily improved to the target by resuspension of the dirty product in the feed solution or pure product solution and separated again. Therefore, mother liquor viscosity is one of the important parameters limiting the crystallization/separation process beside the solubility behavior of such a matrix and heat transfer.

This new process allows increasing the process yield by at least 4 % (Tab. 2) with equal product quality. Usually, another acid is generated as a new impurity due to the acid conditions. This does not happen in similar amount at neutral pH value (novel process). Together with the mother liquor purge a certain amount of sodium salts will be removed and therefore will not stress the following cation exchange.

![Figure 4. Enrichment of sodium compounds.](image)

![Figure 5. Viscosity trend in the mother liquor.](image)
On the other side, the different tested upstream options enable an optimization of the downstream process demonstrated on the investigated system in Fig. 8. Although the ultrafiltrated broth allows easier operation, the OPEX costs in this case are permanently higher as for the other combined processes, due to the lifetime of membranes and power consumption. The impact of the CAPEX could not be treated within this study.

### 4 General Terms of Applicability of Crystallization on Other Fermentation Broths

Several fermentation processes for organic acids operate at more or less neutral pH value and the salt form of such acid is initially produced in the broth. The byproducts are often highly soluble compounds like sodium acetate and sodium formate. Additionally, the investigated sugars used as raw material are sensitive against acid conditions; decomposition and inversion reactions may occur. The third advantage of the crystallization of the intermediate product is the drain/removal for the highly soluble byproducts. These byproducts will not be forwarded to other unit operations like ion exchange and will reduce the operation costs of these operations.

The purification effect of crystallization is also important which allows the possibility of using more contaminated raw material from less efficient upstream processes. Recycling of a part of the mother liquor to previous upstream processes will also be possible, which is commonly used in other chemical reaction processes but is hard to implement in fermentation processes.

Theoretical calculations from solubility data for succinic and malic acid demonstrate in Fig. 9 the theoretical yield for the acid and salt form, which indicates the potential.

The real benefit of using crystallization as an intermediate and purification process unit has of course to be proven case by case. However, the complete downstream process balancing for CAPEX and OPEX shows how this is probable.

### 5 Conclusions

From the outcome of this study, it can be stated that it is beneficial to use the intermediate Na salt of the organic acid crystallization process to separate the final product in salt form from other salts in a fermentation broth. This leads to a total higher process yield and to a reduction of the utility costs in the next downstream process (ion exchange). In addition one can say that the tool crystallization allows a better optimization of different upstream processes and reduction of OPEX costs.

There are several reasons to investigate the application of a crystallization process as a purification step, such as higher solubility of salt byproducts, less decomposition at neutral pH value, and removal of other unwanted substances by mother liquor purge. All these results lead to the fact that this application should also be adapted to other fermentation broth solutions. Examples are malic acid and succinic acid production.

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### Abbreviations

- CAPEX capital expenditure
- OPEX operational expenditure
Figure 7. (a) Crystal purity, (b) camera images, and (c) crystal size distribution for low mother liquor viscosity (left) and high mother liquor viscosity (right).
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Figure 8. Estimated OPEX cost variation for the same production capacity for different hybrid process steps.

Figure 9. Estimated process yield by changing from acid form to salt form.
