

DESIGN OF DOWNSTREAM PROCESSING OF NON-GASEOUS PRODUCTS FROM FINNOFLAG PROCESS

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Index

1. INTRODUCTION	3
1.1 DOWNSTREAM-PROCESSING	3
1.2 LAB TESTS	4
1.3 UPSCALING OF THE DOWNSTREAMING PROCESS TO PILOT SCALE	9
1.4 CONCLUSIONS AND OUTLOOK	11
2. REFERENCES	12

Figures

Figure 1: Separation of the two phases (2,3-BDO and water) after adding K_2CO_3 to the mixture. (2,3-BDO phase is colored with methyl red)

Figure 2: Flow sheet of the downstream processing for 2,3-BDO recovery from Pilot A Biorefinery process. 5

Figure 3: Pre-cleaning of the fermentation broth (left) by adding precipitation agent to the centrifuged solution (center). "Cleaned" sample (right).

Figure 4: Salting out of 2,3-BDO from pre-cleaned fermentation broth. Water free K_2CO_3 (left), Formation of two layers in separatory funnel after K_2CO_3 addition, Contaminated 2,3-BDO phase with precipitated organic material.

Figure 5: Salt recovery using a rotary evaporator. Minor 2,3-BDO leftovers in the aqueous salt solution (left). Recovered salt after flash distillation (right).

Figure 6: Flow sheet of downstream process in pilot scale using a spray dryer for salt recovery.

Figure 7: Exemplary layout of a pilot scale downstreaming plant using a spray dryer for salt recovery.

Figure 8: Flow sheet of downstream process in pilot scale using alternating vessels for salt recovery.

Figure 9 Exemplary layout of a pilot scale downstreaming plant using alternating vessels for salt recovery.

1. Introduction

This report deals with the design of a downstream process for the non-gaseous products from Finnoflag process (Pilot A). The objective was to create a method to extract a valuable product, in this case 2,3-butanediol (2,3-BDO), from the fermentation broth that leaves the pilot plant.

2,3-Butanediol is a valuable chemical that is used as antifreeze agent and as a platform chemical for the production of pesticides, pharmaceuticals, odorous substances, humectant or softening agents. Furthermore it can be used to produce the solvent/fuel additive Methyl ketone and the bulk-chemical 1,3-Butadien (1,3-BD). 1,3-BD is being produced from fossil raw materials only at present with a production of approx. 8 Mio. Mg/a. It is an important preliminary stage for artificial rubber and other plastics.

Deriving from its large bandwidth of possible uses 2,3-BDO can be seen as a new bio-based platform chemical, produced from different types of waste materials. [1]

With its high boiling point of approx. 180°C and with low concentrations of maybe 40 g/l it is economical not useful to separate the 2,3-BDO by distillation. This would be too energy consuming. So different methods for the downstreaming had to be developed.

1.1 Downstream-processing

The downstreaming process mostly includes multiple steps. With each of the steps to purity of the product shall be risen.

The first step here is the removal of microorganisms and other particular matter from the fermentation broth. It needs to be taken into account if the product is produced intra- or extracellular. In case of intracellular production a previous cell breakup is necessary.

There are different methods for the removal of particular matter:

- Filtration
- Centrifugation
- Membrane processes

The next step is the separation of the product from the liquid phase of the fermentation broth. The substance properties of the product are of high importance for this step. For example the aggregate state, the density, the dew- and boiling point and the concentration of the product play an important role.

The following methods can be used for the separation and enrichment of the product:

- Extraction
- Distillation
- Salting out
- Filtration
- Membrane processes
- Chromatographic methods

A repeated operation of a single method and/or the follow up of different processes can lead to an enhancement of the product purity. Anyhow it has to be taken into account that there may be a loss of product after every single step as well.

1.2 Lab tests

One of the first tests in the lab have been done with a Dow-Filmtec TW-20-24 membrane to separate 2,3-butanediol with a concentration of 10 g/l from an aqueous solution. As this approach did not work out at all, tests have been ended. There are some better results for the membrane separation of 1,3-propanediol in the literature but no explicit results for 2,3-BDO. [1] [2]

One reason for the bad results could be the aging of the membrane by 2,3-BDO. This needs to be further examined.

As a result from literature research the method of salting out the 2,3-BDO from aqueous solution by water free potassium carbonate (K_2CO_3) has been found. [3]

An initial test with a mixture of 40 g/l 2,3-BDO in water showed a very good separation of the two phases (see Figure 1). The mass amount of salt was in the range of 50-100% of the fermentation broth. This leads to the necessity of an additional recovery process for the salt.



Figure 1: Separation of the two phases (2,3-BDO and water) after adding K_2CO_3 to the mixture. (2,3-BDO phase is colored with methyl red)

The promising results from this pre-test led to a downstreaming process containing several steps:

- Centrifugation/Filtration (pre-cleaning of the broth)
- Salting out with K_2CO_3 (extraction of the product)
- Flash distillation / Spray drying (recovery of the salt for recycling)

In order to gain information about the downstreaming quality of the real fermentation broth (which was not available at this time) an artificial broth has been created. This broth contained:

- Water
- Growth medium
- Shredded straw
- A mixture of *Bacillus subtilis*, *Bacillus amyloliquefaciens*, *Bacillus lichenformis*
- Approx. 10 g/l 2,3-BDO

The 2,3-BDO concentrations have been measured with a Shimadzu HPLC (LC-20AD Chromatograph, MultoHigh Bio 300-C4 5 μ column and RF-20 A fluorescence detector).

Small scale centrifugation (up to 50 ml) have been performed using a Heraeus Multifuge 1S-R at 10350 rpm. Medium scale (up to 1 l) has been performed using a Sorval RC BIOS centrifuge at 7000 rpm. Both program runtimes have been 20 minutes.

To recover the salt a rotary evaporator Heidolph Laborota 4010-digital has been used. The temperature of the water bath was 100°C with a pressure of 30 mbar in the piston.

From the pre-test the downstream process as shown in Figure 2 has been developed.

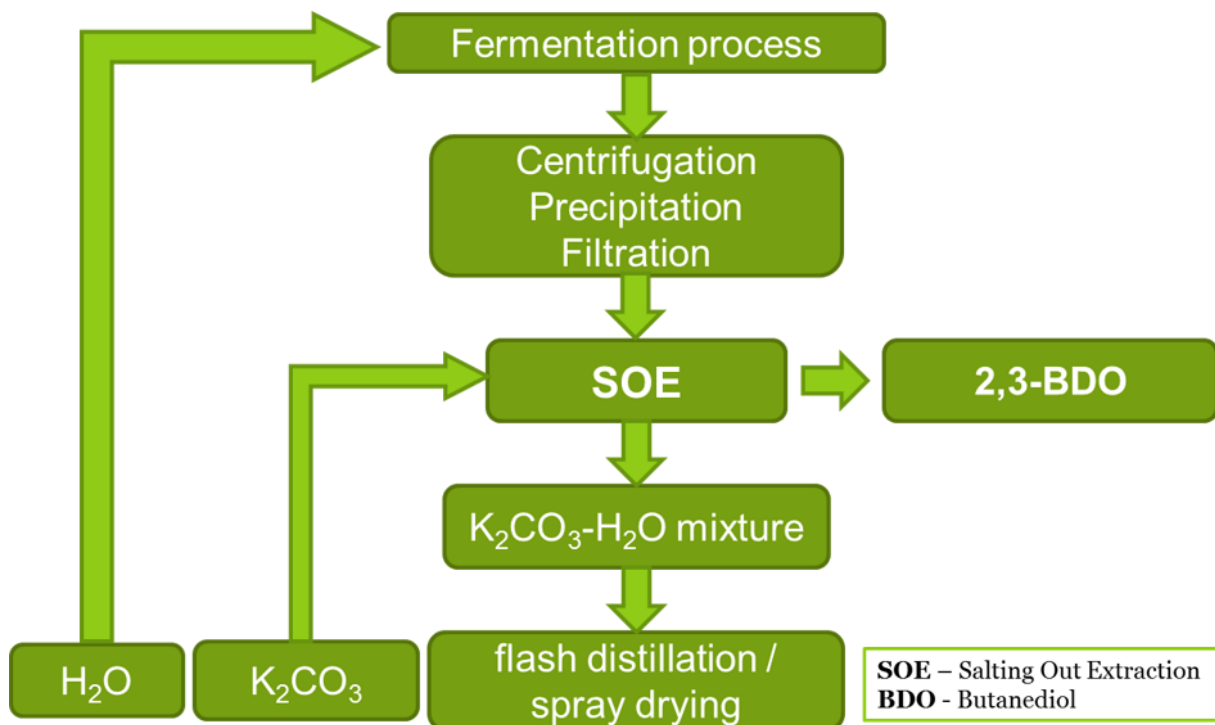


Figure 2: Flow sheet of the downstream processing for 2,3-BDO recovery from Pilot A Biorefinery process.

As a first step the fermentation broth is being centrifuged. As there are still a lot of dissolved substances in the supernatant additional cleaning is necessary. For this purpose a Iron-III-chloride solution has been added as a precipitation agent, followed by another centrifugation/filtration step to remove the precipitated material. This cleaning step is shown

in Figure 3. As can be seen in the figure, the solution is still coloured. Additional test should be performed regarding the best suitable precipitation agent.



Figure 3: Pre-cleaning of the fermentation broth (left) by adding precipitation agent to the centrifuged solution (center). "Cleared" sample (right).

Also the main step, the salting out with water free K_2CO_3 , shows that there has to be additional effort to investigate the pre-cleaning of the solution. As there still proteins, amino acids, sugars and so on dissolved in the broth, they start to precipitate when the salt is added. This leads to a top layer consisting of the 2,3-BDO contaminated with the precipitated organic material (see Figure 4 for details). The recovery rates of 2,3-BDO have been up to 85% when using a 2,3-BDO/water mixture and up to ~60% when using a matrix as mentioned in Chapter 1.2 or a mix with material from the hydrolysis from Pilot A.



Figure 4: Salting out of 2,3-BDO from pre-cleaned fermentation broth. Water free K_2CO_3 (left), Formation of two layers in separatory funnel after K_2CO_3 addition, Contaminated 2,3-BDO phase with precipitated organic material.

After this step the main part of the downstreaming is finished. Now the fine cleaning of the 2,3-BDO would start. As there is only a very small amount of water left in the product a distillation would now be suitable for fine cleaning. The exact steps should be examined further in order to end up with the necessary product quality (e.g. by distillation, rectification, liquid-liquid extraction, etc.).

As the added salt can be removed from the leftover aqueous solution this would make the process more economic. The salt was removed in the lab test by flash distillation in a rotary evaporator. Afterwards the wet salt has been dried in a heating and could then be reused (see Figure 5). The recovery rates of the salt has been up to ~90%. So it has to be added additional salt for every new extraction but the amount can be kept quite low.

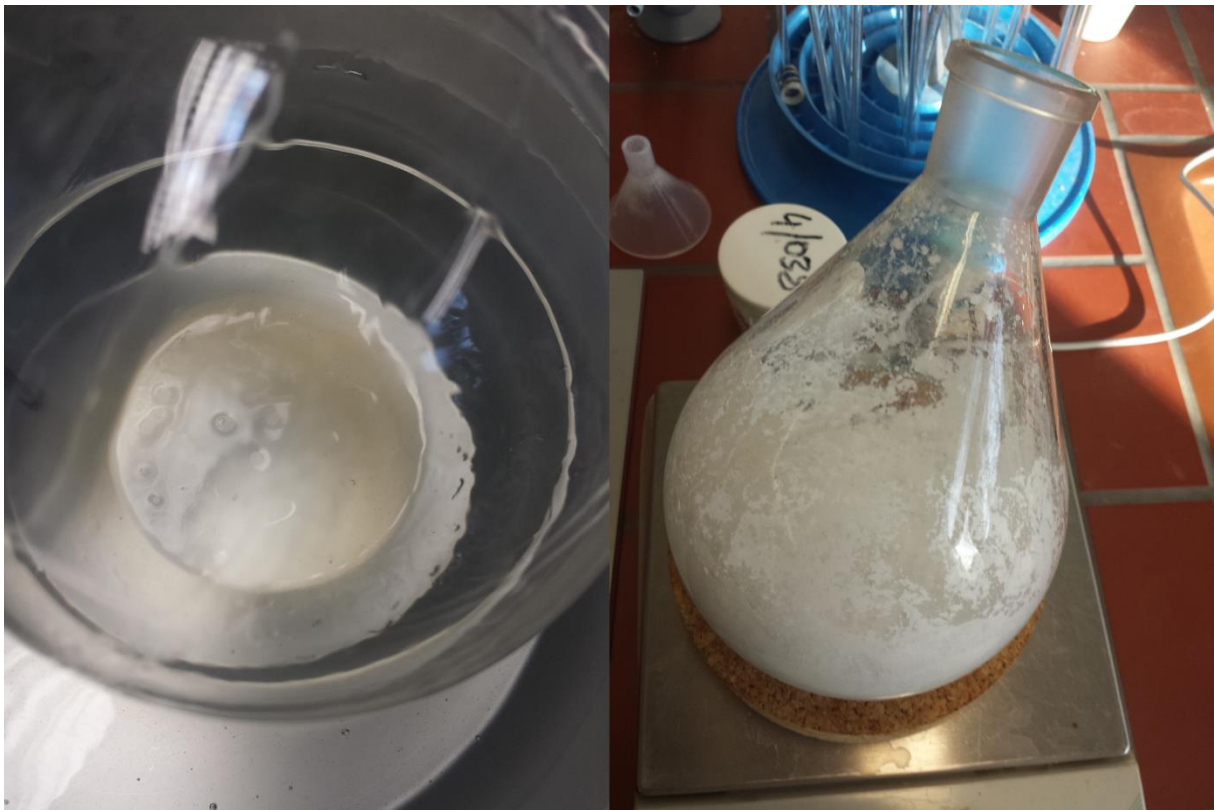


Figure 5: Salt recovery using a rotary evaporator. Minor 2,3-BDO leftovers in the aqueous salt solution (left). Recovered salt after flash distillation (right).

Additional optimization of the single as well as the overall process is necessary. This should be done hand in hand with the Finish partners with original material from the pilot plant Biorefinery process.

1.3 Upscaling of the downstreaming process to pilot scale

To gain more information about full scale implementation first design for a pilot scale downstream process are ongoing. This chapter shows basic design data for a container sized (40-feet) plant using the methods described earlier in this report. This pilot plant will be fully connectable with Pilot A in order to investigate the whole production chain.

Figure 6 shows the process design using two stirred vessels for precipitation and the salting out process. A centrifuge can be used after both of these steps. To recover the salt a spray dryer is being utilized.

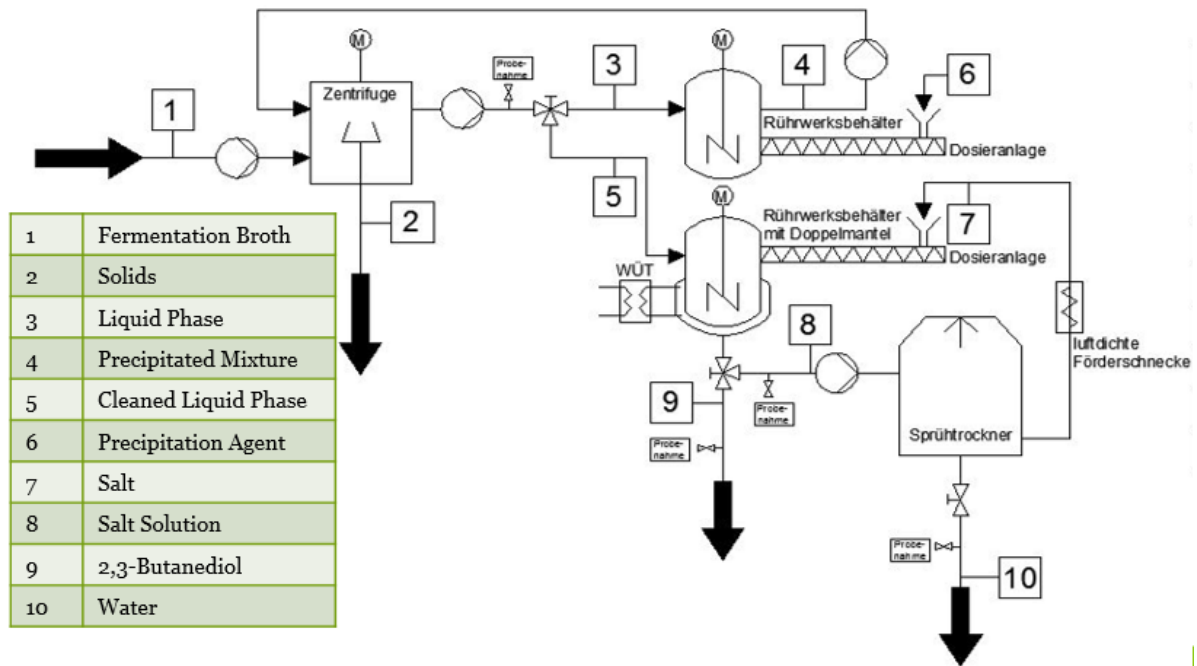


Figure 6: Flow sheet of downstream process in pilot scale using a spray dryer for salt recovery.

The resulting container layout could look like in Figure 7.

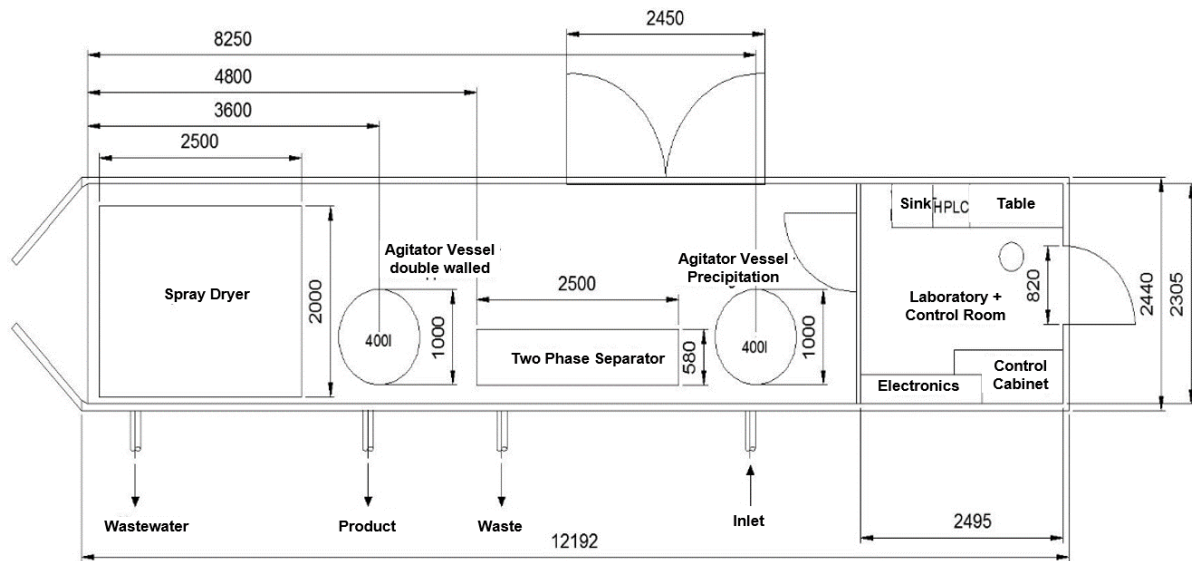


Figure 7: Exemplary layout of a pilot scale downstreaming plant using a spray dryer for salt recovery.

Another approach would be to use two alternating vessels, in which the salting out process takes place. The leftover salt solution would then be pumped into the next vessel where water and salt are being separated. New pre-cleaned broth would go into the vessel that now contains the salt (see Figure 8).

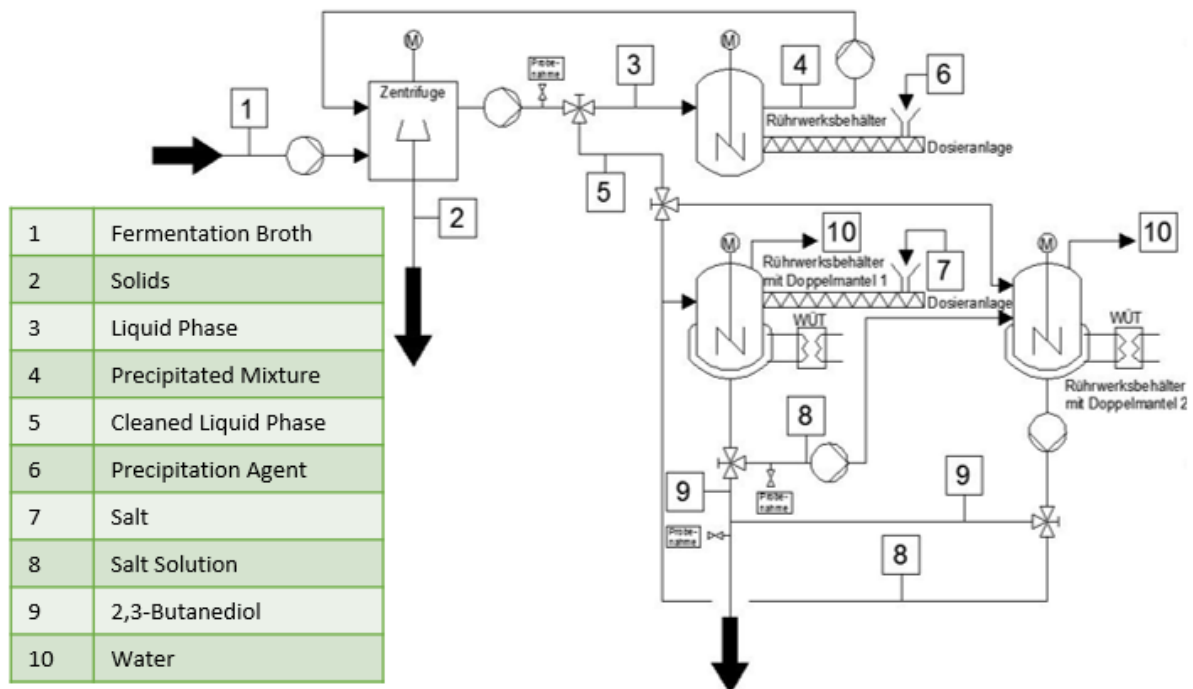


Figure 8: Flow sheet of downstream process in pilot scale using alternating vessels for salt recovery.

The resulting plant layout could look like in Figure 9.

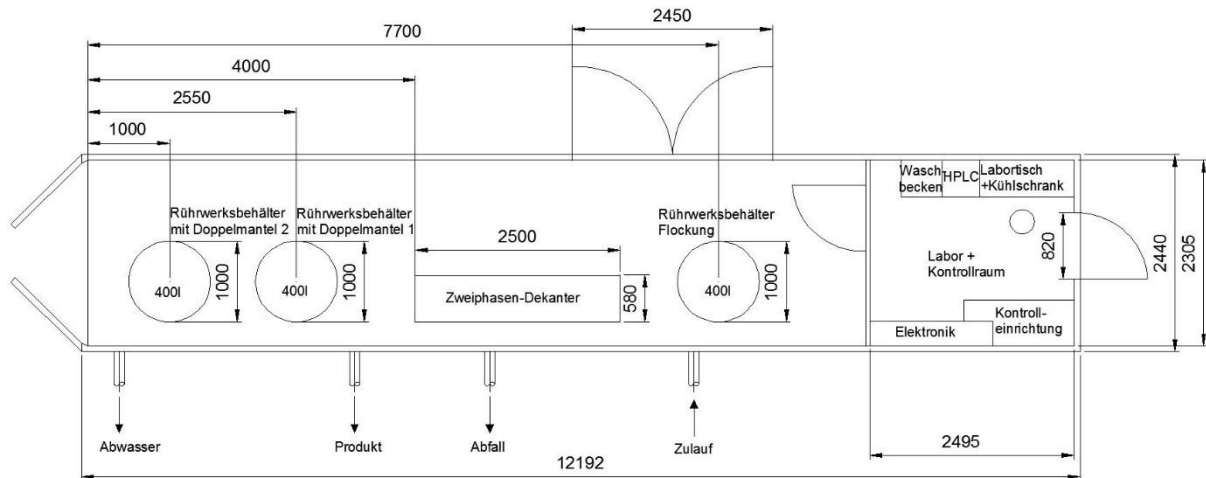


Figure 9 Exemplary layout of a pilot scale downstreaming plant using alternating vessels for salt recovery.

1.4 Conclusions and Outlook

The design of a downstream process for the recovery of 2,3-Butanediol from the Biorefinery process in Pilot A, using different waste materials as a substrate for the microbiological production, has led to some promising results.

The method of salting out the 2,3-BDO worked well in the lab. The overall process and the salting out as well need to be optimized in order to reach better recovery rates.

Preliminary designs for a pilot scale downstream system have been done and will be further developed following the results of the optimization process.

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