CADANS
Continuous Adsorption Desorption Enhanced System

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CADANS project

Summary

In an ISPT cooperation between Friesland Campina, DSM, Cosun, A&F, ZETON and Bodec (2010-2013) the True Moving Bed concept was discussed and modelled in detail and a new unit was developed and eventually built by Zeton. This CADANS unit then was tested on site at DSM and Cosun where respectively separation of yeast components and anthocyanins was investigated using the TMB process. These screening trials confirmed the TMB potential for separation but also showed problems when running the pilot CADANS Unit.

In 2014 together with Bodec two companies participated in an extended investigation: COSUN and AVEBE. A new project then was defined to further investigate the TMB concept in the unit and elaborate on operational costs and economic feasibility. For this project the CADANS unit was transported to Bodec in Helmond and trials were performed there. AVEBE had the specific requirement of removing certain bitter components from their potato stream. Cosun focused on capturing proteins from their sugarbeet waste product.

Using the CADANS system we were able to remove the poisonous components from the feed stream with the use of smaller sized resins. To run the CADANS unit, the feed material had to be diluted and maximum resin dispersion concentration was limited. The adsorption was fast and followed the equilibrium. Comparison with the results for removal of the components from the original potato juice could not be completed because of the completely different processing route.

For the Cosun trials proteins were captured from a waste stream using DOW Chemical resins. Again equilibrium was followed for capture and because of resin sizing the concentrations and resin amounts were limited for running the CADANS system. COSUN does not have a comparable process yet to assess possible benefits from the TMB principle tested on the CADANS unit.
For Both COSUN and AVEBE the TMB principle in the CADANS unit worked and showed fast adsorption of components following the resin capture equilibrium (adsorption within 6 minutes). Desorption could not be tested in continuous mode but was established via lab-trials.

Important aspect of this investigation was also to identify processing issues and optimization possibilities for future units when scaling up.
One of the main drawbacks of the current CADANS unit was the limited resin concentration that could be used; tube sizing dictates that only low resin concentrations can be used to prevent blockage in the system and create stable running conditions. As a consequence, during desorption dilution of the eluens will occur creating a lower concentration of product in the eluate after processing.
The built-in recycles built in to mimic a counter current principle create high complexity and also limit stable operating conditions. Also non-ideal separation in the hydrocyclones immediately affects stability and decreases yield.

From these drawbacks a list of improvements was formulated which can be used as a guideline for scaling up any unit covering the TMB principle.

From an economic viewpoint operational costs could be compared only qualitatively. It is important to assess the cost levels of resin, capturing potential per kg and maintenance compared to processing time and cleaning. This will enable a basic quantitative comparison.

Index

Introduction

A novel processing concept was discussed between industrial partners COSUN, DSM, A&F Zeton and BODEC (2010-2013). Modelling of the TMB principle showed a large potential in effectively separating components from waste streams using a continuously moving system. From background modelling [1] a new unit was designed and eventually built by Zeton. This unit was called **CADANS** referring to: continuous adsorption/desorption enhanced separation of target compounds from a stream.
Both DSM and COSUN tested the unit on separation of enzymatic components from a DSM waste stream and on separation of anthocyanins from blueberry juice for COSUN [2,3]. The results from the trials were further analyzed using the existing models. Mass balances were calculated and opportunities for the TMB principle were discussed and opportunities for the use of the technique were identified [4].

Based on these preliminary findings a new project was defined in 2014 to further investigate the potential of the TMB concept on the CADANS unit.

Furthermore, with this project data could be gathered for a better economical evaluation of the TMB process and the CADANS unit. Typically one of the cases defined could be investigated in much detail to serve as a benchmark business case for further reference. Findings and operation of the CADANS unit would help to identify scale up rules and eliminate processing problems for a larger scale unit.
BODEC took the lead in the investigations on the potential of the CADANS pilot unit and directed the research towards the requested information. Both AVEBE and Cosun participated through providing raw materials, performing key analyses on samples created and providing background on materials and components.

True Moving Bed Chromatography

Chromatography is a powerful unit operation for separating and capturing components from liquid flows. Chromatography normally is performed in packed or expanded beds: the adsorption resin is always fixed in a column. Through different processing modes (a.o. simulated moving bed) a continuous system can be created. This technique is one of few that can target capture of specific components. The packed or expanded bed modus however has some drawbacks that greatly affects normal operation.

- Small fouling components present in the feed material can cause blockage problems in the packed bed system, less so for expanded beds. Extensive pre-treating the feed material includes high capex and opex.
- Both packed and expanded beds create a pressure drop; this limits the size and capacity per column and requires larger, often more expensive resins
- Resin particles are relatively large and heavy to enable the system to run smoothly and prevent resin losses (and to limit pressure buildup)
- Equal flow distribution in the system is difficult to maintain due to formation of preferent flows inside the columns (causing lower capture yield)
- Runtimes between cleaning cycles for the columns are determined by fouling and preferent flow formation; either more fouling or less efficienct use of the resin will reduce runtimes per adsorption cycle.

To improve this adsorption technique the concept of a true moving bed was modelled and discussed further [1, (2012)]. The main improvements focused on the issues for the packed and expanded columns. In the table below the strong and weak points are recapitulated.

Table: strengths and weaknesses TMB

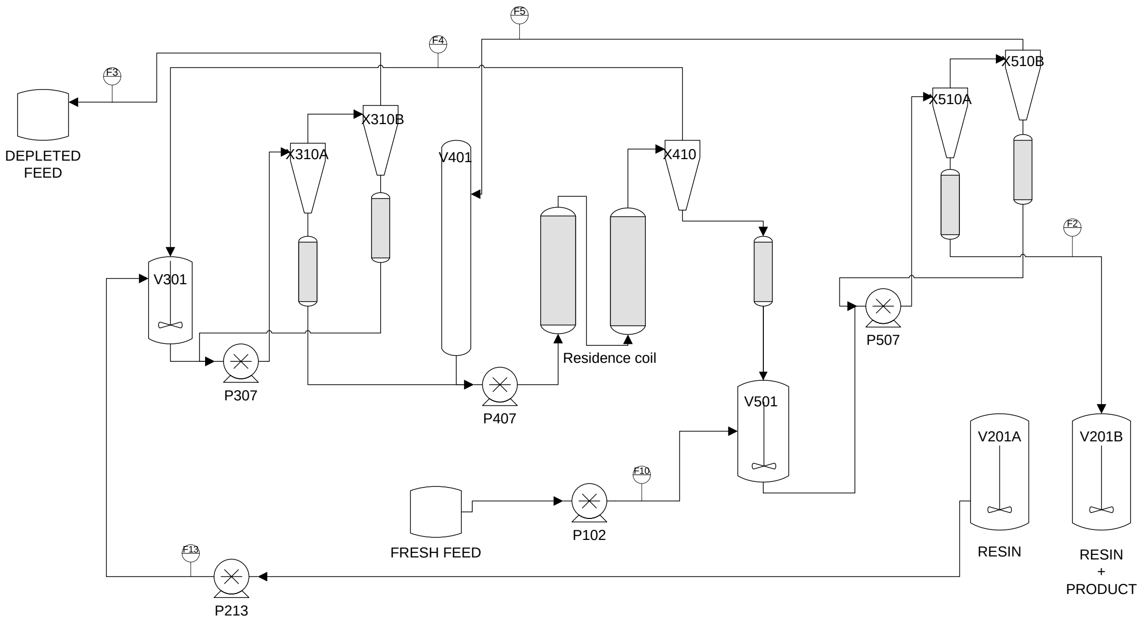
Strong points	Weak points
- Less feed clarification required before adsorption can be tested	- Resin losses and possibly attrition
- Fast process (beneficial for products with lower shelf life)	- Back mixing occurs in the operational CADANS system which will affect the purity of the streams from the unit (design point)
- Use resins with smaller particle size: increase mass transfer rates → reduce processing time	- The process is complex and relatively expensive (expectation)
- Compact process, small footprint and continuous system compared to expanded bed chromatography where a large number of tanks is required	- Dilution in the system because of the use of resin dispersion (design point)
- Scale up easier than EBA system from liquid distribution	- Continuous separation resin and liquid required

The CADANS unit

The concept for the TMB was further developed by COSUN, DSM, A&F, BODEC and ZETON and translated into a pilot unit: The CADANS Unit. Preliminary trials were performed at COSUN and DSM [2,3] and the unit then was transported to Bodec.

Figure: CADANS skid

The CADANS unit comprises two large vessels, respectively for resin dispersion and used resin dispersion, two agitated tanks and a small combiner tank for mixing feed and resin. Two double hydrocyclones and one single hydrocyclone are present for separating resin from depleted feed. All flows can be controlled independently via different pumps. However, the recycles present inside the unit design have a large effect on the flow through the system. This intrinsic counter current principle greatly complicates stable running conditions in the unit.



Key to the adsorption in the system is a 16l residence coil in which the adsorption time can be controlled through the pump-speed in that system (approximately 6 – 30 minutes).
Raw material is introduced into the CADANS system from a separate feed storage. Similarly depleted feed is collected outside the unit.

A detailed description of the processes inside is provided in [2].

Evaluating performance of the Cadans unit

In general, the separation of components is carried out by means of packed bed or expanded bed chromatography. In the TMB principle, the CADANS has combined a counter-current process where resin and liquid feed containing the target molecule will meet in two stirrer vessels (batch separation). The adsorption and desorption process will perform via chromatography on resins in a residence coil and as final step the separation process is carried out through the use of a cascade of hydrocyclones.

The CADANS pilot unit was designed based on earlier research and this system will be tested to understand its functionality and performance of chromatographic experiments for the required target molecules. Therefore, it is important to first test this pilot unit to study its capability to work efficiently and to identify all process conditions required for the chromatographic experiments. Water experiments will be performed to adjust the system to the proper configuration for the chromatographic experiments.

CADANS has implemented hydrocyclones as the resin – liquid separation step in the process. To ensure that separation is maximum, experiments with different resin concentrations will be performed and samples from overflow and underflow will be analyzed to check separation efficiency during the experiments.

Furthermore, for the trials it is essential to study binding capacity of any resin that is used. Batch experiments with the resin and the compounds will be performed at lab scale to understand the chromatography process and the adsorption equilibrium. In addition, equilibration, loading, washing, elution and sanitation must be evaluated. Within these steps, typical parameters as pH and conductivity are critical.

Having followed these important steps, CADANS will be run as a continuous multi-step system and the capture and separation of target molecule(s) will be investigated.

AVEBE and COSUN

In the EAP project two companies AVEBE and COSUN participate. Both have a different focus for the trials on the CADANS unit. Where AVEBE wants to identify the capability for removal of a bitter compound from the potato juice, COSUN focuses on capturing proteins from sugar beet pulp.

The emphasis at COSUN lies at the capture of proteins in the native state. Any economical evaluation will need to include the quality aspects of the proteins captured through use of the TMB CADANS unit. COSUN does not have a specific focus at the time of the project.

AVEBE focuses on the removal of a bitter compound. The current reference process for this removal is time consuming and uses much chemicals; the runtime for the process currently is limited due to fouling components in the raw material. In the economical evaluation the expected extended runtimes for the process must be included.

Objectives of the EAP-project

The main goal for the project is to provide evidence of CADANS as a fast, practical and suitable technology for the recovery of valuable compounds within the food industry. Overall objectives were summarized in the EAP proposal:

- Testing of different resin slurry concentrations in CADANS and performing adsorption and desorption experiments (focus for COSUN proteins and AVEBE bitter compounds)
- Evaluation of the separation efficiency of the cyclones within CADANS.
- Elaboration of starting up, operational and cleaning protocol for CADANS pilot plant.
- Assessment of the feasibility of the TMB process in the CADANS unit
- Economical evaluation on the results obtained from trials on the CADANS unit
- Assessment of the potential of the unit and scale-up requirements; Identification of bottlenecks and improvements for the TMB process
- Dissemination on the results from the investigations on the CADANS / TMB process

The above objectives were investigated for companies AVEBE and COSUN. Trials, results and discussion are described per company; the assessment of the potential of the TMB principle and scale up from the CADANS unit is based on all findings combined.`

Results AVEBE – removal of bitter compounds from a potato juice

Adsorption on CADANS-A resin

Background

For the CADANS A resin equilibrium isotherms were measured. Equilibrium was determined on labscale using beakers where resin and feed were contacted for 30-60 minutes. From the curves the Langmuir and Freundlich equations were fitted and their respective constants were determined.

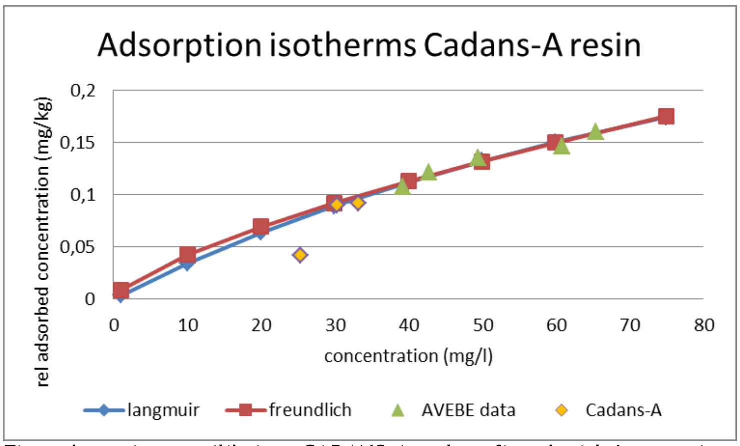


Fig. adsorption equilibrium CADANS-A - plots fitted with Langmuir and Freundlich function

The final equations describing the equilibrium on the CADANS-A resin can be represented as:

Langmuir: $Q_e = \frac{k*q0 \quad *C_e}{1+k*C_e}$ or Freundlich: $Q_e = K * C_e^{1/n}$

with: C_e in mg/l and Q_e in mg/g.

Adsorption trials - results

With the large size resin adsorption trials were performed in the CADANS unit for the AVEBE bitter components from the potato juice. In the residence coil a fixed residence time was used. Analyses of starting material and remaining compound in the potato juice showed the capture potential.

trial	adsorption time (min)	flow	liquid (mg/l)	on resin (rel)
1	4	turbulent	25,37	0,042
2	6	turbulent	33,18	0,092
3	4	turbulent	30,37	0,090

When plotted in the equilibrium isotherm, the calculated concentrations match the equilibrium state. Note that the time required to achieve the equilibrium was much less than for the lab-experiments. Form the adsorption experiments it can be confirmed that equilibrium is fast when flow is under turbulent conditions (Re > 2300, typically at residence times < 9 minutes). In the equilibrium graph above the yellow diamonds show the achieved capture at different liquid concentrations.

Adsorption on CADANS B resin

Equilibrium

Similar to the equilibrium for the CADANS-A resin, also for the smaller sized resin the capturing potential was measured. At different contact times samples were taken to measure capture potential on the resin. The first series of trials were performed using potato juice, but feed material was changed to protamylasses when trials progressed. (The protamylasses feed material was diluted 1:6 with water to lower viscosity and for being able to separate resin from depleted feed).

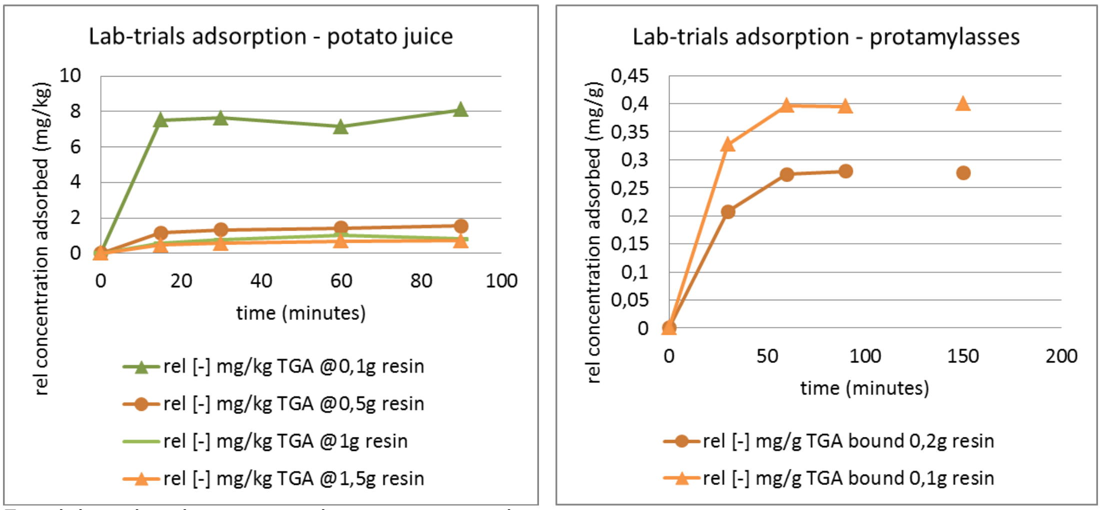


Fig. lab-scale adsorption trials potato juice solution

From the graphs it appears that the equilibrium is reached after 90 minutes. Using the data on the adsorption trials the capture equilibrium can be determined. Similar to CADANS-A resin, the equilibrium can be described using Freundlich and Langmuir isotherms. The picture below shows the calculated isotherms and superimposed the datapoints from the trials.

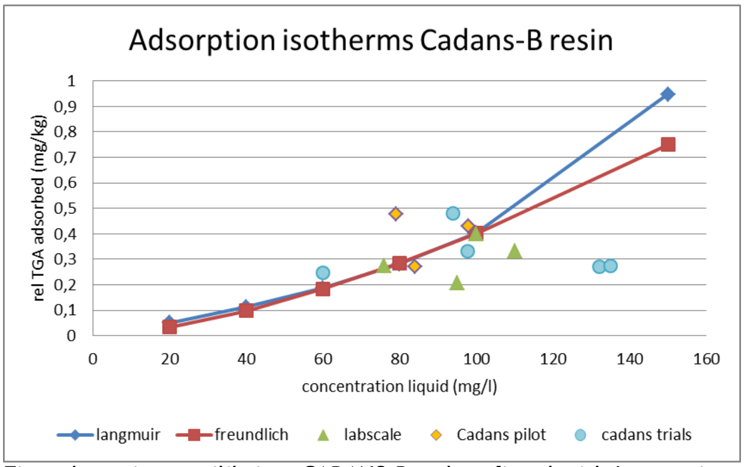


Fig. adsorption equilibrium CADANS-B – plots fitted with Langmuir and Freundlich function

Langmuir: $Q_e = \frac{k*q0*C_e}{1+k*C_e}$ or Freundlich: $Q_e = K * C_e^{1/n}$

with: C_e in mg/l and Q_e in mg/g.

Mass balances CADANS-B resin trials

After determining the adsorption equilibrium, trials were performed on the CADANS pilot unit to measure CADANS-B resin adsorption. Adsorption trials were performed at two stable flowrate conditions in the system matching 6 minutes and 11 minutes residence time. During the course of the trials some results forced repeating of trials and changing of settings due to blockage in the system or failure for resin separation.

Trial	dilution feed Product:Water	resin conc. w/w %	residence time (min)	flow	resin
1	2 : 1	1%	6	turbulent	B
2	1 : 6	5%	6	turbulent	B
3	1 : 6	5%	11	laminar	B
4	1 : 6	1%	6	turbulent	B
5	1 : 6	1%	11	laminar	B
6	1 : 6	2%	6	turbulent	B
7	1 : 6	2%	6	turbulent	B (repeat6)
8	1 : 6	1%	6	turbulent	B (repeat4)
9	1 : 6	1%	6	turbulent	A
10	1 : 6	1%	11	laminar	A

From the hydrocyclone trials the best separation was achieved using a 10% dispersion in both double and single setup. The adsorption trials were performed at maximum 5% resin dispersion due to the limited resin amount available.

During all trials three (or four) different balances were determined:

- Overall balance total mass
- Overall balance resin (wet resin taken into account)
- Overall balance bitter compound

The balance on the amount of water present could be used to improve the mass-balance accuracy. The resin always has a certain amount of moisture which differs at inlet and outlet; this could explain a possible difference in the mass balance.

Small solid particles in the protamylasses flow –comparable in size to the CADANS B resin- affected the results on separation. During analyses of the solids separated in the hydrocyclones resin could not be distinguished from these protamylasses particles. The calculation of the mass balances for resin and solids then was very difficult.

Adsorption results CADANS-B resin

From these calculations, capture efficiency and potential in the CADANS unit were determined. Analyses were performed by the AVEBE analytical department.

Table: sample analyses adsorption

trial	dilution feed Product : Water	resin %	residence time (min)	flow	Resin	relative Adsorption (mg/kg)
1	2P - W	1%	6	turbulent	B	
2	P - 6W	5%	6	turbulent	B	
3	P - 6W	5%	11	laminar	B	
4	P - 6W	1%	6	turbulent	B	0,33
5	P - 6W	1%	11	laminar	B	0,27
6	P - 6W	2%	6	turbulent	B	0,25
7	P - 6W	2%	6	turbulent	B (repeat6)	0,27
8	P - 6W	1%	6	turbulent	B (repeat4)	0,48
9	P - 6W	1%	6	turbulent	A	0,54
10	P - 6W	1%	11	laminar	A	0,44

Assumptions on ratio resin:particles were necessary for using the results and calculating adsorption efficiency in the CADANS unit.

During the trials different processing issues were encountered that affected the outcome of the balances and the separation in the system. Also large differences in bitter compound concentration were observed from the mass balance. The issues, blockage in the tubing, inhomogeneous resin distribution and unstable hydrocyclone operation were solved by cleaning the system and adjusting processing conditions i.e. lowering resin concentration, changing residence time etc.

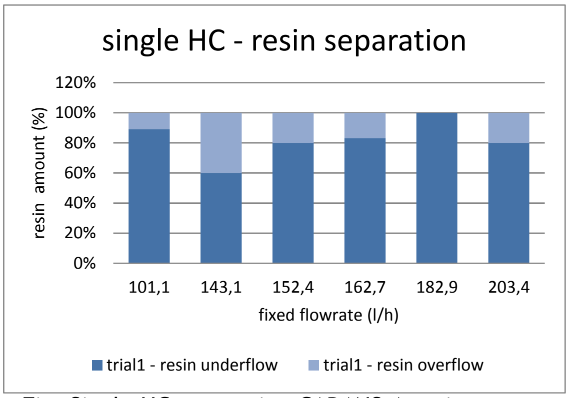
Trials 7 and 8 then were performed without processing issues and show the best results for CADANS B resin. Trials 9 and 10 were performed with CADANS-A resin as a comparison.

Separation efficiency hydrocyclones

The influence of flowrates and resin concentrations on the separation efficiency in the hydrocyclones was investigated. A single and double hydrocylone setup were decoupled from the system and trials were performed with flowrates 80-220 l/hr and resin concentrations up to 15%.
Note that restrictions from the system (and thus pressure drops) were removed and underflow and overflow outlets were to atmospheric conditions.

Separation efficiency CADANS A resin

A single hydrocyclone was tested for resin separation at different flowrates. A 10% w/w resin dispersion of CADANS –A resin (as supplied by AVEBE) was used. Results are presented in the graphs below.



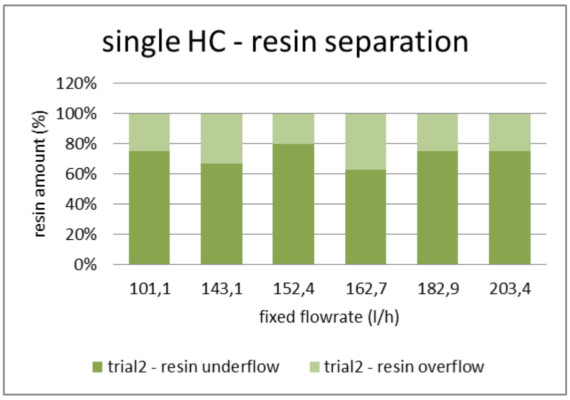


Fig. Single HC separation CADANS-A resin

On average separation efficiency of the hydrocyclone was 80% (resin collected on the HC underflow outlet).

Separation efficiency CADANS B resin

For the smaller sized CADANS B resin Hydrocyclone separation trials were performed on both a single and double HC setup (pictures in the experiments chapter). Four concentration levels (1%-5%-10% and 15%) and 3 flowrates (80, 150, 210 l/hr) were tested.

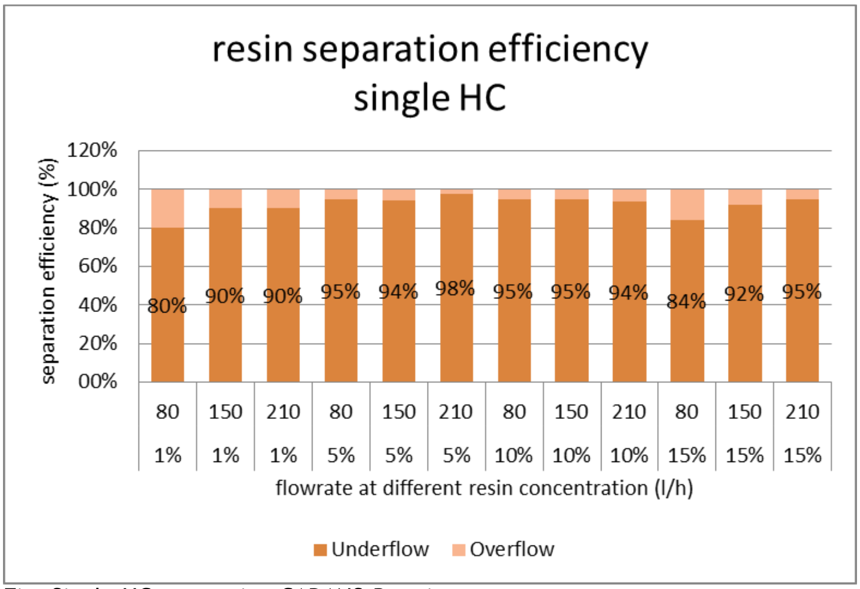


Fig. Single HC separation CADANS-B resin

In the single hydrocyclone best separation 95% was achieved at flowrates over 150 l/hr and resin concentrations of at least 5%. The separation appeared independent on higher resin concentration (comparing to 5%).

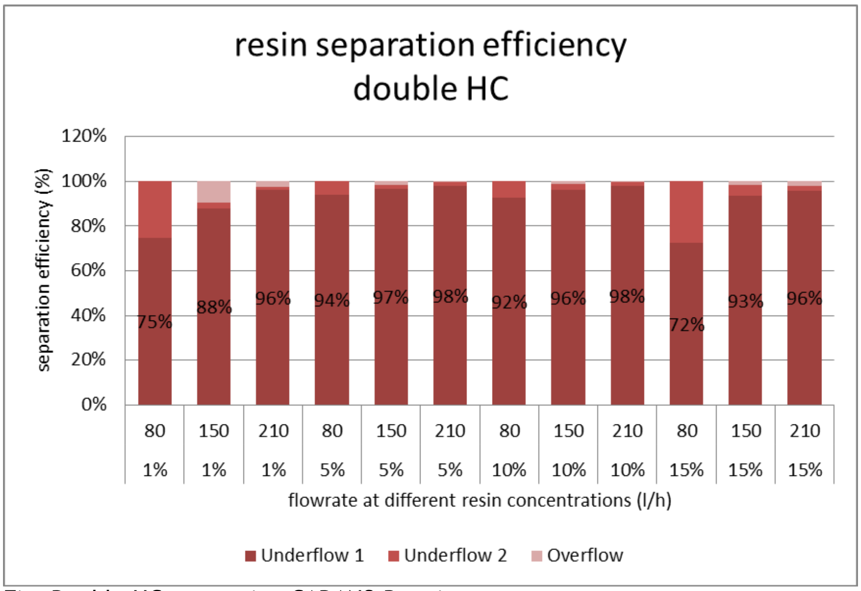
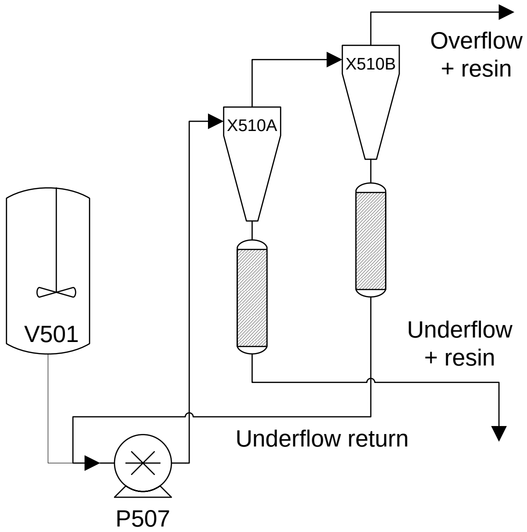


Fig. Double HC separation CADANS-B resin

Underflow 2 in the system is normally diverted back into the inlet. Separation for the double hydrocyclone setup is highest at resin concentrations 5% and -10% and flowrates 150-210 l/h. 98% of resin separation was achieved in the trials.

Desorption results CADANS-B resin

During the trials resin separation in the hydrocyclones was not ideal. Much of the small resin was not separated in the hydrocyclones and went with the overflow.



Therefore desorption experiments were performed on resin obtained from both overflow and underflow. Extra difficulty was the appearance of small solid particles in the protamylasses that look like resin particles but that do not have any adsorption capability. The overall balance for resin and particles was performed first before desorption was tested.

Adsorption on CADANS-A resin was approximately 11 % higher for equal resin amount compared to resin CADANS-B. Desorption however is much better and faster for CADANS-B resin.

Table: desorption bitter compound from CADANS-A and CADANS-B resin

Trial	resin %	residence time (min	Resin	overall TGA ads (mg)	product OUT TGA ads (mg)	product OUT TGA des (mg)	depleted feed OUT TGA ads (mg)	depleted feed OUT TGA des (mg)	overall desorption efficiency (%)
7	2%	6	B	100%	23%	39%	76%	39%	38%
8	1%	6	B	100%	46%	66%	53%	66%	66%
9	1%	6	A	100%	33%	30%	67%	8%	15%
10	1%	11	A	100%	39%	5%	61%	5%	5%

Efficiency was calculated based on the total desorbed components (both from underflow and overflow, see picture above) relative to the total adsorbed bitter component. Efficiency was NOT related to the hydrocyclone separation. Desorption was performed in lab scale beaker for 60 minutes using a 30% HAc solution.

COSUN – Removal of proteins from sugar beet-pulp

Results

Preparing protein starting solution

The beet pulp had to be pre-processed before it could be used in the trials for investigating protein capture in the TMB process. After addition of water 1:1 (w/w) the cell structure was opened using different equipment (blender, turrax, masuko and retsch mill). For optimization of the final achieved protein concentration, waiting time and cell opening time were varied. Also the influence of pH was investigated.

Three methods were used for preparation:

- **Method A:** addition water to pulp 1:1 (w/w) - blender 5 ' – hold 30' – blender 2' – hold 30'
- **Method B:** addition water to pulp 1:1 (w/w) - blender 10 ' – hold 60'
- **Method C:** blender 5 ' – hold 30' – addition water to pulp 1:1 (w/w) - blender 5' – hold 30'

Using a biureet-test the amount of proteins present can be identified through measuring the blue colour of a copper complex formed at 546nm.

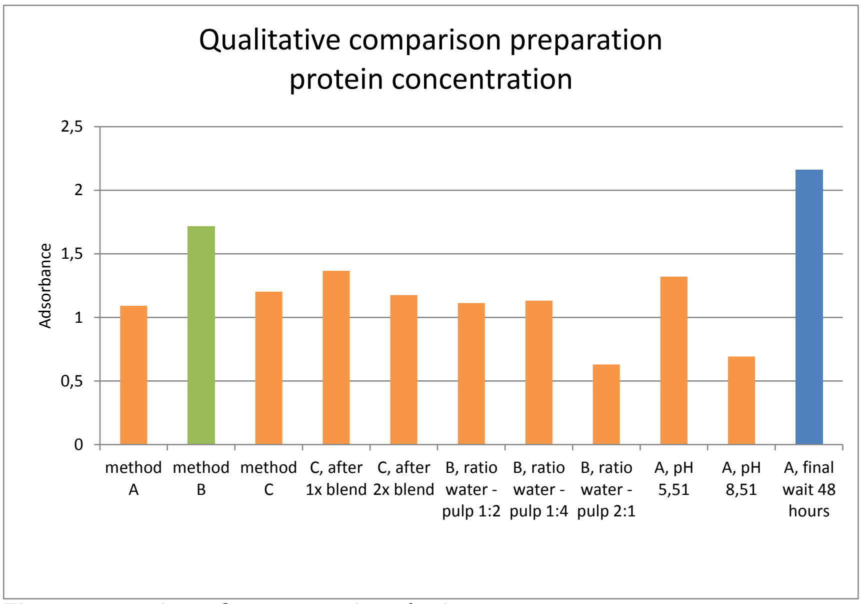


Fig. preparation of raw protein solution

The results show that highest protein concentration was achieved at long holding times and that holding time was the only significant influence affecting the amount of proteins freed from the cell matrix. The methods used for breaking open the cell structure showed no significant difference.

Concentrating protein solution

Analyses showed that the concentration obtained from beet pulp was approximately 1.2 g/kg. Based on information from COSUN a theoretical amount of maximum 16 g/kg was expected, indicating that the obtained protein concentration was very low. Concentrating in the rotavap showed an increase to 4.1 g/kg. Though acceptable in concentration, the downside of the routing was that a large quantity of protein solution had to be prepared and consecutively concentrated.

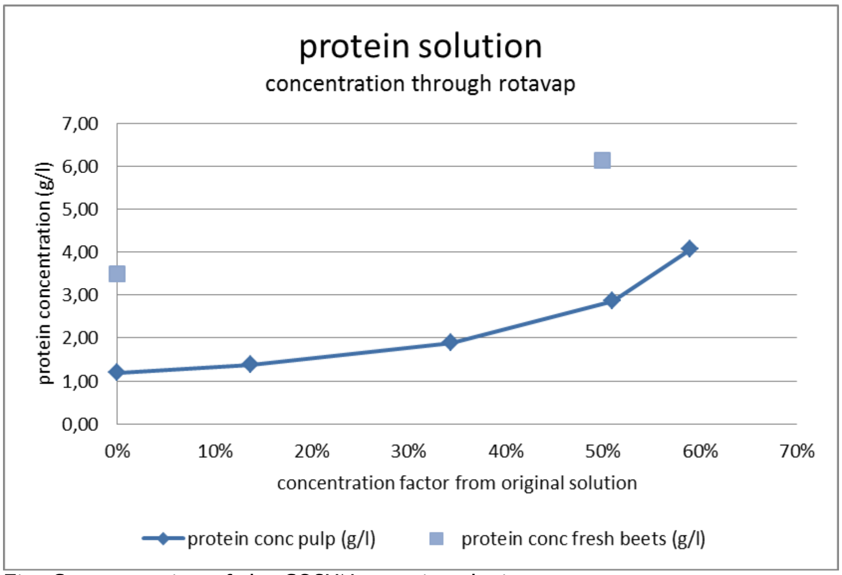


Fig. Concentration of the COSUN protein solution

An alternative route was followed in which fresh sugar beets were ground and filtered for preparing the protein starting solution. With the ease of the preparation and much higher concentrations this route was used in investigations.

Resin screening

Adsorption

Using a protein solution of 450 mg/kg Kjeldahl (Protein 6.25x: 2.81 g/l) the resins were first screened for capture of proteins. During the course of the trials also ground resin material was tested (noted with * in the graph). From a known concentration in the raw feed material analyses were performed on the residual liquid after adsorption. The residual amount of proteins was captured on the resin. From this screening it was clear that resin 1 and resin 4 were best suited for the capture of proteins from the COSUN raw material stream. Both resins respectively have a mild and strong cat-ionic function.

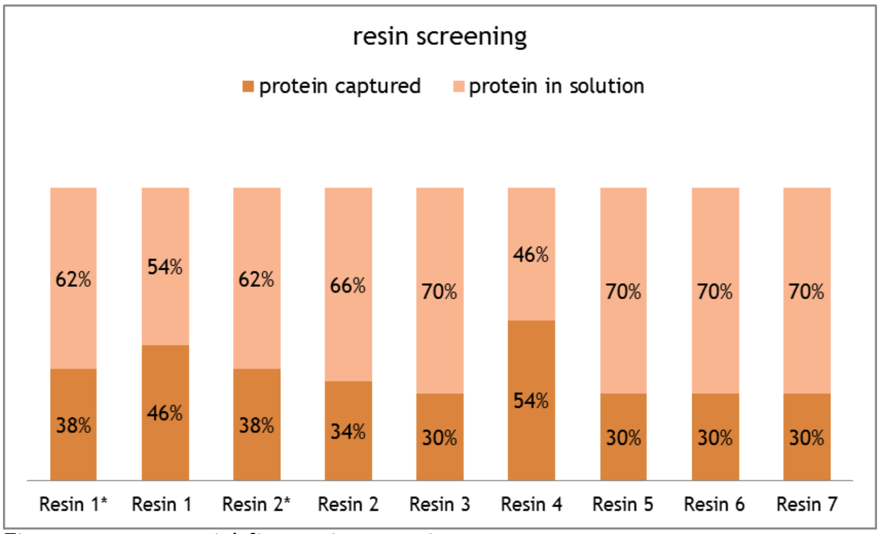


Fig. capture potential first resin screening

For these resins trials then were performed to identify minimal adsorption time. After approximately 60 minutes maximum adsorption is achieved (based on lab-scale beaker-adsorption experiments, shown in the graph below).

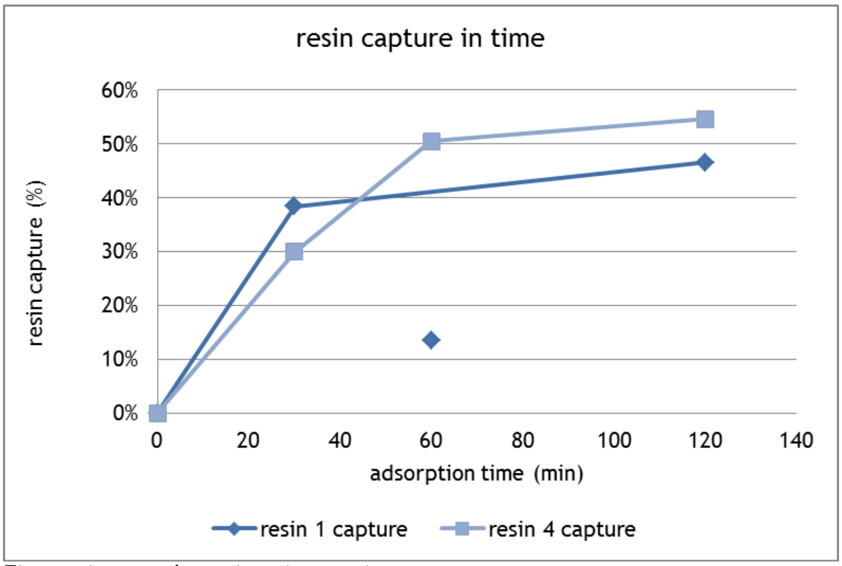
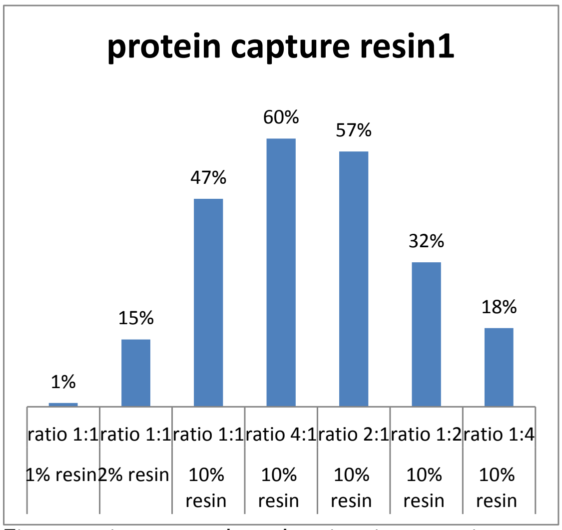


Fig. optimum adsorption time resins

Feed:resin -ratio and resin concentration influence were also investigated. Results show that higher resin concentrations and higher ratio (more feed) have highest protein capture.



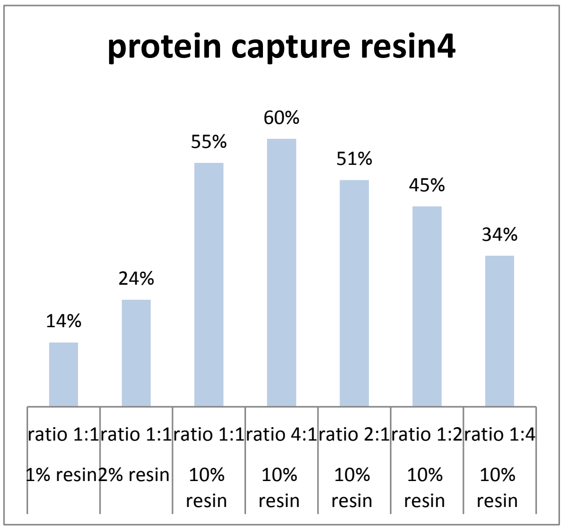


Fig. protein capture based on ingoing proteins-amount

Effectivity for capture focuses on the total amount of proteins captured per gram of resin. Where the percentage graphs appear approximately identical the results on capture efficiency per gram of resin indicate bigger differences. The results are shown in the next table for both resins 1 and 4.

Table: adsorption data and protein capture

resin	resin (%)	ratio resin:feed	resin (g)	feed (g)	protein in feed (mg)	protein in filtrate (mg)	captured protein (mg)	protein capture (%)	capture (mg/g)
1	1%	1:1	1,0	100	275,0	272,6	2	0,9%	2,4
	2%	1:1	2,0	100	275,0	233,5	42	15,1%	20,8
	10%	1:1	5,0	50	140,6	75,2	65	46,5%	13,1
	10%	4:1	16,0	40	110,0	44,0	66	60,0%	4,1
	10%	2:1	13,0	65	178,8	76,6	102	57,1%	7,9
	10%	1:2	6,5	130	357,5	241,9	116	32,3%	17,8
	10%	1:4	4,0	160	440,0	362,5	77	17,6%	19,4
4	1%	1:1	1,0	100	275,0	235,4	40	14,4%	39,5
	2%	1:1	2,0	100	275,0	209,1	66	24,0%	32,9
	10%	1:1	5,0	50	140,6	63,8	77	54,6%	15,3
	10%	4:1	16,0	40	110,0	44,0	66	60,0%	4,1
	10%	2:1	13,0	65	178,8	88,0	91	50,8%	7,0
	10%	1:2	6,5	130	357,5	197,2	160	44,8%	24,7
	10%	1:4	4,0	160	440,0	291,2	149	33,8%	37,2

As can be concluded from the table, resin 4 clearly performs better than resin 1.

Maximum 33-39 mg protein /g resin can be captured when the right conditions are met. Most effective use of the resin is at low resin concentrations and high feed concentrations: by definition then a large amount of proteins is present and an adsorption equilibrium is easy.

Desorption

Desorption experiments were also performed for all different resins. Where adsorption was on all resins, desorption was only possible on resins 1,2 and 4. The other resins were unable to lose any protein components attached to the surface. Different eluens liquids were tested.
The graph below shows that approximately 30% of the captured proteins can be removed during the elution step.

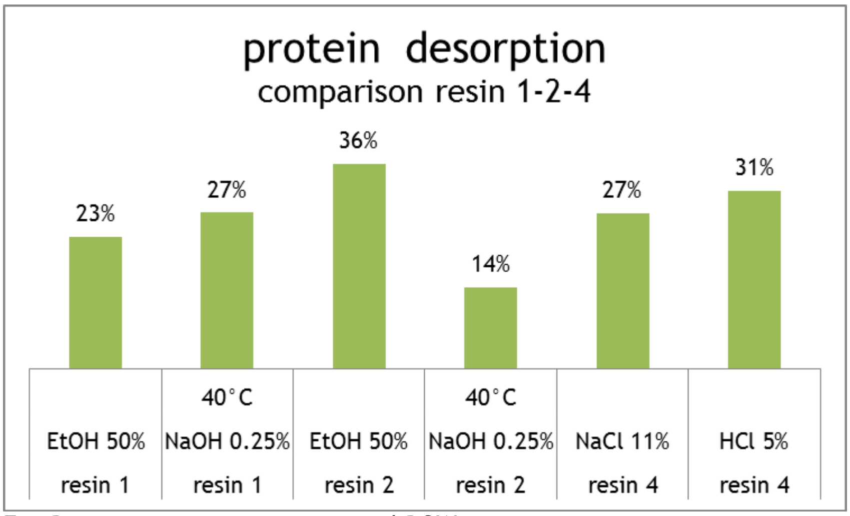


Fig. Desorption runs protein removal DOW resins

Based on these adsorption and desorption results, resin 4: Amberlite FPC 22 H was further tested in the pilot unit and the TMB principle was evaluated.

CADANS trials resin Amberlite FPC 22 H

Adsorption

Trials were performed in a feed:resin ratio of 1:4 ; limited fresh feed material was available since the beets are a seasonal product. The higher ratio was required to be able to at least run the system for a prolonged period of 25 minutes. Flowrate from the pump was 160 l/hr, fixing a residence time of 6 minutes, matching turbulent flow inside the coil.

Using the simplified setup four balances then were created over the residence coil: total mass, total resin, dry resin and proteins.

COSUN	total mass balance		protein balance		wet resin balance		dry resin balance	
	IN (kg)	OUT (kg)	IN (g)	OUT (g)	IN (g)	OUT (g)	IN (g)	OUT (g)
Feed	14,45	0	24,4		0	0	0	
Resin	55,24	0	0		575	0	263,2	
Product	0	9,84		2,46	0	180,0		70
Depleted feed	0	41,28		12,9	0	0		0
Accumulation		16		5		492,0		190
proteins on resin				4,0				
	69,69	67,12	24,4	24,4	575	672	263,24	260

From the resin it is clear that approximately 4.0 g of protein is adsorbed on the resin. Capture is 4000 mg on 575 g of resin resulting in 7.0 mg/g (on dry resin basis: 15.3 mg/g);

Note that the accumulated resin and resin in the product outlet are identical and that the captured proteins are distributed equally over all resin in the system.

Desorption

The captured resin then was washed and eluted on lab scale; three different elution times were investigated: 60-120 and 180 minutes.

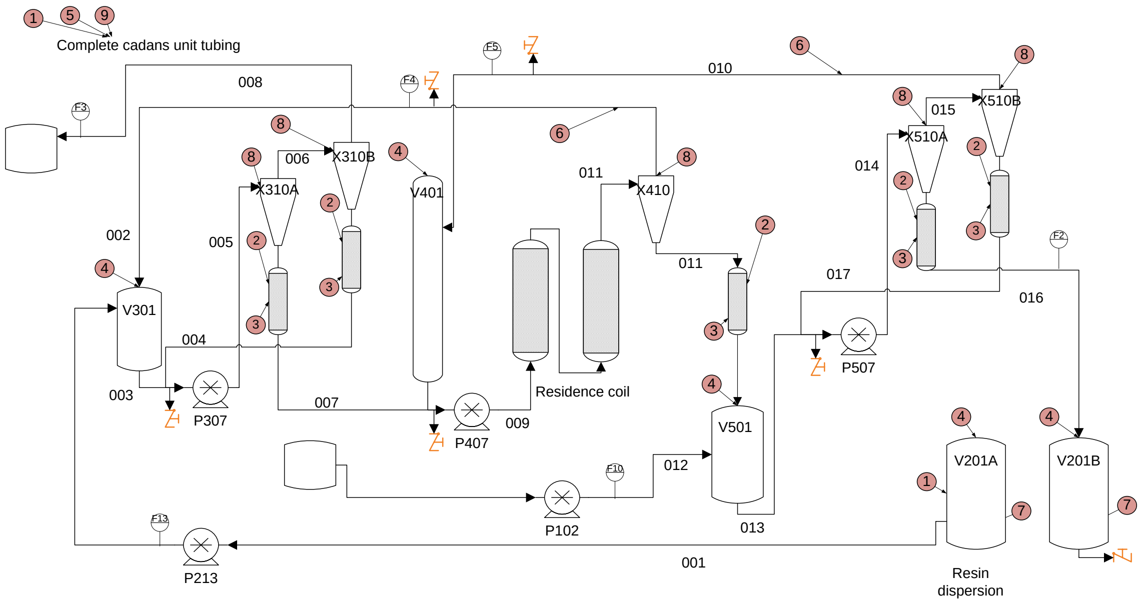
Based on the average capture potential 7 mg/g (low because of the feed:resin ratio) approximately 72% of the proteins can be removed from the resin. All samples showed identical protein concentrations, indicating that elution time longer than 60 minutes is not required.

Table: elution results Amberlite FPC 22 H resin

eluens	elution time(min)	resin IN (g)	protein conc (mg/g)	protein IN In (mg)	filtrate (g)	protein conc (mg/kg)	protein OUT (mg)	desorption efficiency (%)
NaCl 25%	60	10,002	7,0	70,00	269,716	187,50	51	72,2%
NaCl 25%	120	10,009	7,0	70,05	269,927	187,50	51	72,2%
NaCl 25%	180	10,003	7,0	70,01	270,128	187,50	51	72,3%

Scale up of the TMB system

Feasibility for the process was proven in the trials for AVEBE and COSUN. However, many problems were identified during the trials for investigating the performance of the pilot CADANS-unit. During the course of trials these issues were solved or otherwise bypassed, but when scaling up the process they require attention. This chapter foresees to sum up these bottlenecks and to comment on possible solutions which then could be implemented in a larger unit when scaling up.



Processing issues

The CADANS unit originally was developed as a multifunctional unit suitable for capture of many different components with the use of a large variety of resins. Making a unit suitable for many different specific needs also has a downside. During the trials processing issues were observed that are important to solve when scaling up.

- Blockage in the system is extensive
    1. the tubing diameter is small and resin concentrations are limited
    2. pressure coils meant for optimally configuring hydrocyclone flows in the system cause blockage when resin concentrations are higher (5 – 10%)
    3. extra restrictions in the system also implemented for separation optimization need to be fully removed to run the system

- Cleanability of the current unit is very limited;
    4. Tank openings are small which makes good cleaning of the vessels of the CADANS system not possible
    5. In the system dead volumes are present in which feed material could accumulate

6. The intrinsic recycles – built in for optimal capture from the raw material - greatly affect stability in the system. Presently only two stable operating conditions can be run in the system (also dependent on the resin size and concentration).
7. The agitation in all vessels of the CADANS unit require a minimum filling degree; since the resin mostly is present in dispersion, sedimentation will occur in the system, causing for inhomogeneous processing.

1. Separation in the CADANS system is performed through hydrocyclones. Though the specific hydrocyclones used (Krebs) have little or no abrasive impact on the resin separation in hydrocyclones always has specific limits.
   Maximum separation typically is 99% indicating that there are always resin losses. Other continuous separation systems might be interesting to use in a scaled up system and will be further explained in the next chapter.

2. In the unit hygienic design not always is followed; dead volumes and 90° angles in the tubing do not help to prevent blockage in the system when running resin dispersions.

These issues should be solved. In the development towards a new unit or scale up design care must be taken to prevent identical mistakes. A new design might include scale up rules for the current CADANS system or could include different separation techniques, optimized for smaller resin particles and continuous flow.

Towards a new TMB design, alternative separation techniques were investigated that could be used in a TMB set-up. The next paragraph combines the techniques and a qualitative assessment.

Economical evaluation adsorption processes

In the 'CADANS, Economic attractiveness' (Blom, 2011) a preliminary calculation was done to compare installation and operational costs for running the CADANS system compared to other adsorption processes. Calculations then were based on ideal behaviour of the unit and drawbacks or limitations were not taken into account. This chapter covers the different costs for installation and operation and compares these to other adsorption systems. As a basis this report is used for the comparison and further improved with results from the CADANS trials.
Note that a quantitative comparison is not possible at this stage because of the limited data available.

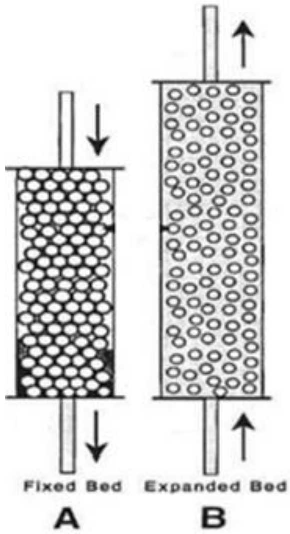
Four different systems are considered in the comparison: Two SMB (Simulated Moving bed) systems and two TMB (True Moving Bed) systems. A simulated moving bed operates with a series of columns. Each column operates one of the phases of the adsorption/desorption process, and after a fixed time each column shifts to the next phase. Thus a continuous process is created through the use of multiple batch columns. In the columns the liquid moves through a fixed resin bed. The resin is stationary in the SMB system while the liquid is the moving phase. There is no need for resin – liquid separation.

Counterpart to the SMB system is the TMB system where both resin and liquid are in the moving phase. The TMB system can be run fully continuous or semi-continuous (the latter being a preferred form when elution of valuable components gives too diluted streams. Separation of resin and liquids is required and in the CADANS unit performed by means of hydrocyclones.

SMB – fixed bed

Liquid is transported through a fixed resin bed (top down). Limited space in between the resin particles is available, creating a low velocity though the column. The components attach to the resin particles and a diluted feed stream leaves the column. Because of the limited space between the particles, this system is sensitive to fouling components which might cause blockage and pressure buildup in the SMB system.

Through using multiple columns and switching the liquid streams (elution liquid, regeneration liquid) the system can be made continuous.



SMB – expanded bed

An adjustable top flow divider is used and the feed is introduced into the column system from bottom-up. This system is less sensitive for fouling, since the space between the resin particles expands during loading (feed in) of the resins. In the expanded bed modus more feed volume is required for completely loading the resins. In the figure the two modes are shown [19].
In the expanded bed column an adjustable top plate is mounted which can be fixed according to the required function: adsorption or desorption/regeneration. In the adsorption mode the outlet is positioned high, creating the possibility for the bed to expand. For the desorption or regeneration functions the plate is moved onto the resin bed to create a packed bed and minimize use of regeneration liquid and prevent dilution of the eluted components.

TMB – fully continuous

In the fully continuous system the resin moves along with the feed through the system creating a continuous adsorption or desorption. Using clever recycles in the system enables the full use of the raw material feed and could improve capture efficiency. The system is insensitive to fouling components but requires active resin- liquid separation [4]

TMB - semi-continuous

The semi-continuous setup combines the benefits for continuous adsorption (less sensitive to fouling) with most efficient elution (undiluted eluens with product). Regeneration and elution are performed in a packed system whereas adsorption is performed in a continuous system.

In the economical comparison of these four systems CAPEX (capital expenditure - indicating the equipment) and OPEX (operational costs – power, energy, water) are discussed separately. CAPEX information is used from the previous investigations and are repeated for reference below.

CAPEX: Installation of the unit

The investment costs for most of the different setups were determined already in the previous report on the potential of the TMB technique [4]. To complete the investment cost overview the missing setup has been compared to the existing ones and calculation is adjusted accordingly.

Costs were mainly based on number of pumps, buffers and hydrocyclones. In the comparison pumps are the predominant costs for any TMB system. Columns, tanks and valves are the important cost factors for SMB systems.

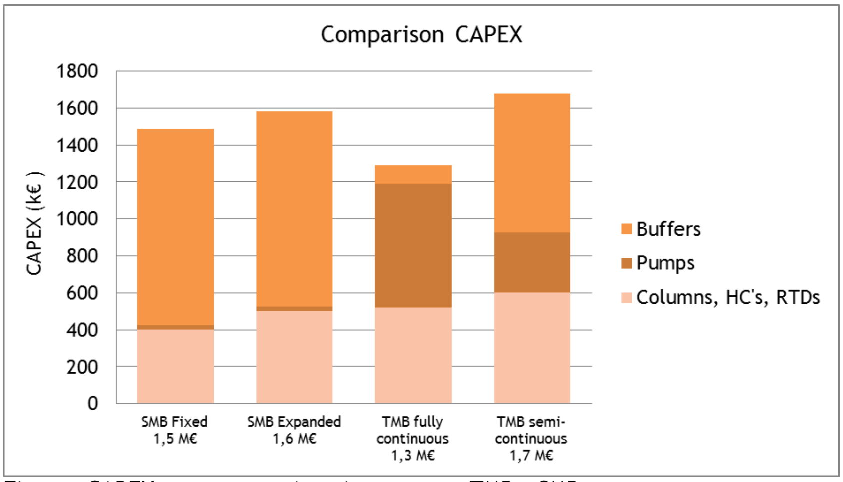


Figure: CAPEX cost comparison investment TMB – SMB systems

Costs fort the expanded SMB system increased compared to the fixed system only through column size

NOTE that the CAPEX calculations can only be used for relative comparison of the different adsorption setups. The absolute CAPEX range 1,3 M€-1,7M€ does not cover changed setups, scale up or improvements to the TMB system.

OPEX: Qualitatively discussed

Making the comparison between the different setups 5 main topics need to be addressed. The differences in setup directly affect these criteria and will give a clear –though qualitatively only- comparison:

1) Preparation of the feed
2) Suitability of the resin
3) Easy of obtaining the valuable components from the eluens
4) Processing time
5) Complexity and maintenance of the unit

Preparation of the feed

An important aspect of the feed is the clarification level. To run any adsorption process efficiently fibers and solid particles must be removed from the feed. Removal of solids and fibers also is necessary to prevent blockage and pressure buildup in the SMB systems.
In the table the TMB and SMB techniques are compared.
Assumption in the comparison is that the feed needs to be clarified by means of filtration.

Table: influence of feed preparation on OPEX – qualitatively estimated
(+) positive influence and (-) negative = more expensive process

	SMB fixed / SMB expanded	TMB fully continuous / TMB semi-continuous
Filter costs	0	0
	expectation: no large differences in filter costs; pore openings SMB system smaller	
Filter run hours	- smaller filter openings required; more likely to cause blockage and more frequent cleaning required	+ larger pores; runtime for the filter should be longer; cleaning less frequent

Not taking clarification into account will lead to more frequent cleaning of the SMB system due to fouling of the system. The TMB system is more robust at equal fouling levels.

Resin

In the adsorption processes the resin is one of the main cost contributors. Resin is expensive and over time loses some of its capturing potential. Normal resin operation should give approximately 1000 cycles in SMB systems.
Due to the setup of the SMB systems, resin particles need to be fairly large to be able to run the system. One liter of normal size resin therefore might have lower capturing potential than one liter of smaller sized resin due to its specific area.
One of the advantages for the TMB system is the use of smaller (often less expensive) resins. Binding capacity per liter also might significantly higher when the resin- component interaction is dependent on surface and capture sites.
The rate of capturing components is dependent on the availability of the resin and the openness of the resin structure: large resin particles have larger –longer pores; molecules will need to diffuse into the pores of the resin before adsorption is achieved; the process then becomes slower whereas smaller resin and small pores have faster resin-molecule interaction.
In general we can state that smaller (possibly less expensive) resin will have faster adsorption.

The table below shows the influence of resin choice on operational costs

Table: influence of resins capture potential on OPEX – qualitatively estimated
(+) positive influence and (-) negative = more expensive process

	SMB fixed + SMB expanded	TMB fully continuous /	TMB semi-continuous
Resin size; costs related to €/kg	- larger resin is required; resin is in packed bed form and needs sufficient open structure without pressure build-up	+ smaller resin to be able to move through the system; often cheaper	- larger resins for the semi-continuous mode; often more expensive
capacity capture	0 Large resin could have lower capacity than smaller sized resins. This difference is dependent on resin type and component	+ Smaller resins theoretically could capture more components (larger m2/m3). Inside the system turbulent flow can be applied, making capture onto the resin faster because of a smaller monolayer surrounding the resin particles. Alternatively with identical capture potential the TMB unit could be smaller.	0 Large resin could have lower capacity than smaller sized resins. This difference is dependent on resin type and component
Resin losses in the system	+ 0-0.5%	- 1-5% theoretical loss in HC; (experimental losses in the CADANS unit are sometimes up to 10%)	0 1-5% (theoretical loss in the HC) only during adsorption. Further processing does not have these losses.
possibility of occurring attrition	+ No attrition: resin is stationary inside the system no extra resin required	- High probability for attrition: constant movement of the resin through pumps, tubing and hydrocyclones often replenish resin amount	0 Attrition only during adsorption due to movememnt of the rein regular replenishing of the resin amount

The process

Looking at the complete process (from adsorption onward) two other factors will lead to economical differences:

- Treatment of the eluens with the captured components
- Processing time after adsorption is achieved

To extract the valuable components from the elution liquid, a concentration or post-treatment must be done. In the TMB process the component concentration is diluted; the resin concentration that can be used in the dispersion is limited for given flowrates and thus dilutes the concentration of wanted components in the eluens.
Consecutive concentrating or treating the eluate (with valuable molecules) will be more expensive. In the table this comparison is shown. Both SMB systems and the semi-continuous TMB system have a similar desorption / elution and therefore are combined.

Table: influence of complete process – concentration after desorption on OPEX
– qualitatively estimated
(+) positive influence and (-) negative = more expensive process

	SMB fixed + SMB expanded + TMB semi-continuous	TMB fully continuous
resin in dispersion for desorption	+ resin is not required to move through the system	- Resin must be in constant movement
required amount of eluens to be treated	+ eluens amount based on reisn bedvolumes	- eluens including water from the resin dispersion --> diluted eluate stream

The post-treatment of the eluate requires extra time and energy. The TMB system has the advantage that the unit is fully continuous and that adsorption and desorption / regeneration are much faster than for an SMB systems. Drawback for the TMB system is the necessary use of resin in dispersion, intrinsically diluting feed flow but also eluate when captured components are desorbed; further processing hence would require more time (the time required for washing is not included in the overview and assumed identical for all systems).

The table shows the comparison of processing time and the influence on operation costs

	SMB fixed	SMB expanded	TMB fully continuous /	TMB semi-continuous
Adsorption	- time for adsorption long; In the fixed bed columns laminar flow determines component capture	- time for adsorption long; In the fixed bed columns laminar flow determines component capture; because of the bed expansion capture might be faster from better resin - feed distribution inside the system	+ short time for adsorption; movement of resin and feed in turbulent flow ; adsorption is faster (mass transfer tanks to smaller layer for mass transfer resistance).	+ short time for adsorption; movement of resin and feed in turbulent flow ; adsorption is faster (mass transfer tanks to smaller layer for mass transfer resistance).
desorption and regeneration	- desorption and regeneration time equal to adsorption	- desorption and regeneration time equal to adsorption	+ desorption and regeneration fast ; equal to TMB adsorption	- desorption and regeneration time equal to desorption at SMB systems
Post-processing after desorption	+ relatively short time because of concentrated eluate (no water present)	+ relatively short time because of concentrated eluate (no water present)	- long time required ; diluted eluate obtained from resin dispersion must be concentrated	+ relatively short time because of concentrated eluate ; similar to SMB system

Complexity and maintenance

The final aspect for comparison is the complexity and maintenance of the unit. The counter current principle of the CADANS unit is important for fully using the feed. The recycles in the system used to achieve counter current flow make the system complex and limit the stable processing/running conditions.

For maintenance the TMB system has many pumps whereas an SMB system has multiple valves. Expectation is that the pumps require more maintenance. Fouling and blockage in the system - though no direct maintenance issue- could more likely occur in the TMB system, requiring extra cleaning.

The table indicates a possible effect on operational costs for the SMB and TMB systems

	SMB fixed	SMB expanded	TMB fully continuous /	TMB semi-continuous
Complexity (Counter current principle)	+ no counter current flow; complexity low	+ no counter current flow; complexity low	- complexity high: recycles and HC efficiency determine stable operating conditions	- complexity high: recycles and HC efficiency determine stable operating conditions adsorption
Maintenance	+ Moving parts in the SMB system are minimal; maintenance costs are low	+ Unit comparable to SMB fixed; the moving top of the column for extension of the bed is the only addition. Low maintenance	- continuous movement; multiple pumps and chances of blockage: maintenance level high compared to SMB systems	0 continuous movement; multiple pumps; pump usage only extensive during adsorption; maintenance level high; less than full TMB

Summary economics

Combining the different aspects of the SMB and TMB techniques a qualitative summary can be presented. Overall differences are minimal and greatly depend on the efficiency of resins in relation to their costs. The semi continuous TMB system is better because of the benefits in adsorption and desorption: fast adsorption under turbulent conditions; desorption in packed bed giving a concentrated eluate.

Table: summary economical comparison -qualitatively

	SMB fixed + SMB expanded	TMB fully continuous /	TMB semi-continuous
preparation feed	-	+	+
resin	-	+	-
post treatment eluate	+	-	+
processing time	-	+	0
complexity and maintenance	+	-	0

For both SMB configurations, good pretreatment of the feed is required. Capturing of the wanted components then is performed with a relatively large resin. Theoretically the resin size is linked to its capacity and larger resins might indicate low capture.
Laminar flow typically is used in the packed columns making the adsorption process somewhat slower than when turbulent flow is used.
Complexity level of the setup is minimal under the right operation for simulating moving beds. Though capture and desorption take a long time the components can be obtained in a more concentrated form because during elution dilution is not observed (or can be controlled in sweet-on and sweet-off).

Feed filtration could be more simple and smaller resins (with higher capacity) could be used when running the fully continuous TMB system. Also turbulent flow, increasing the mass-transfer rate is used. Because of the required separation resin-feed, losses (though minimal) are expected (currently hydrocyclones should have a 99% efficiency).

The true Moving Bed requires both resin and feed to be in a “moveable” state. A resin dispersion therefore must be created during both adsorption and desorption. During adsorption automatically feed is diluted by the resin dispersion, creating an equilibrium at lower feed concentration. The use of a resin dispersion also creates a diluted eluate after the components have been desorbed, making post -processing more expensive.

In the CADANS system, the dispersion is limited in resin amount from the tubing diameter size and the hydrocylones behaviour; The above issues are design issues in the current CADANS unit; for scale-up blockage inside the system must be prevented and separation must be as high as possible.

Since the TMB system has much more pumps required to transport resin dispersions, maintenance expectation is high.

Overall

The semi-continuous TMB system uses the “best of both worlds”. Possible drawback is that the used resin must be larger in size and might have less capture potential per liter.
Turbulent flow could maximize adsorption speed onto the resins, decreasing the processing time. Separation for resin and liquid needs to be performed creating a certain resin loss, which can be minimized. The packed bed operation will create a concentrated eluate, minimizing post-processing time and costs.
Downside possibly is that complexity of this system where resin can be both mobile during adsorption and fixed for elution is high.

For the economical evaluation the costs for the resin and the capture potential are of great importance; cost levels will determine the main influencing factors for economy i.e. when resin cost levels are low compared to the costs for pumps, maintenance etc. SMB will be the more economical choice.
When capture potential is much larger for the smaller sized resins and cost levels for equipment are relatively small, TMB will be the most economic choice.

Recommendations

During the course of the trials different improvements to the unit were discussed and for future reference it is important to take these into account. The improvements cover mechanical issues and operational improvements. Also from a concept viewpoint changes were discussed.

Capture of components

Often capture of proteins or other components relates to the quality as well. Besides pH and temperature equally important is the elution liquid to keep the components in their native state. The removal of bitter components has been proven as well as capture of wanted proteins. In both cases capacity of the system was limited due to minimal resin concentrations applied. Further investigations should focus on the effect of increasing resin concentration or size (identify if the resin size greatly affects capturing potential).

Since quality is important care must be taken to identify the best elution liquids to maintain the wanted components in their native, best quality state.

TMB-unit

- For scale-up it is important that the unit can be easily cleaned; Cleanability in the current CADANS system is very limited for the tanks and pumps (design issue).
- In the current CADANS system separation through hydrocyclones shows a serious loss of resin; alternative continuous techniques should be further investigated to improve the operation and separation efficiency in a TMB system

Economy

- It is important to have a precise idea on cost levels and capturing potential of the resins. Also the resin costs in relation to maintenance and processing costs must be identified.

Savings

3. The potential energy savings as predicted from the earlier trials and simulations:

   30% on pretreatment
   15-30% on processing time
   5% on resin use
   7% on installation

   cannot be verified with the data obtained from the trials.
   Also the 20% less resin use mentioned in the process cannot be quantified.

Bottleneck is the limited dataset and absence of long run trial results. For neither AVEBE nor COSUN a stable running process (SMB or other)with identical boundary conditions is available. Quantitatively identifying the energy savings therefore is not possible.

The sizing of the CADANS unit is too small to identify the TMB process benefits. The processing conditions (resin concentration, ratio feed-resin, separation efficiency) are limited and greatly affect the full potential of the TMB technique; The current size of the CADANS unit is too small for quantitative economical calculations.

Overall recommendation is to increase the amount of trials to build-up a database of trial results that can be used in assessing the effectivity of the TMB principle. Long run trials to determine resin life and efficiency should be performed as well. All of these trials to investigate the processing potential and its robustness.

Project execution

Technically
The current setup of the CADANS unit, owned by ISPT and used by the consortium in this project, has a significant number of limitations which do not allow sound conclusions about feasibility and scalability of the TMB technology. No budget was foreseen to upgrade the setup and the technical challenges were solved pragmatically during the execution of the project.

Mistakes during design and realization of the setup e.g. wrong choice in pumps / design of holding and mixing tanks / choice and location of stirrers did lead unfortunately to less usable results. By operating only parts of the setup as well as interfere pragmatically the hardware of the setup, the results as described above in this report are obtained.

The concept of a dynamic system has been shown for 2 cases for the adsorption part. Desorption via elution and regeneration was during this project not executed in the setup and mainly shown on small scale lab trials.

By using streams of the food industry provided by the 2 project partners, shelflive of the raw material and hygienic design of the setup also showed to be an issue. This needs to be taken into account for further scale-up of the setup. For the project, this was solves by dismantling parts of the setup and clean extensively by hand.

The bottlenecks in the project mentioned above and shown in earlier pargraphs of this report give good an sound input to further scale-up of the technology including also the hygienic design by applying EHEDGE guidelines.

Project organization
During the project execution no issues occurred related to project organization. Both project partners are campaign companies which gave the urge to execute and plan the execution of the project during a limited amount of months in the year. Well collaboration with both partners gave the results and analysis described above.

Difference between project execution and projectplan
The original projectplan did predict more results usable for scalability both economically and technically. Due to the less usable quality of the data obtained during execution the scalability mainly is described in a qualitative way. The project partners did agree with this approach

Difference between project budget and realization
The difference between budget and actual is mainly due to a difference in manpower to deliver results. Preparation of the feed, technical issues lead to bigger spending in manhours.
Out of pocket costs are prevented mainly due to free delivery of resins, and by more lab support of both project partners.

Knowledge dissemination
Little dissemination has been executed yet. The (preliminary) results are shown during ISPT conferences and NL-Guts update meetings.

More PR activities will be executed after final agreement by RVO.

Project details

Project number: TEEI114007
Project Title: Directe Adsorptie met Cadans uit Complexe Stromen

Project secretary: BODEC BV
Project execution & management: BODEC BV
Project partners: Cooperatie Avebe
SuikerUnie

Project Timing: Q1 2015 – Q2 2016

Contact details: Rene Houben (projectleader)
Paul Deckers (project manager)

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