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MEMBRANE BASED PRODUCTION OF LACTIC ACID AND AMINO ACIDS – GREEN BIOREFINERY UPPER AUSTRIA

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Abstract
Within the project "Green Biorefinery (GBR) Upper Austria" a demonstration plant for the separation of resources from grass silage was built up and operated near the biogas plant in Utzenaich (Upper Austria). The aim of the project, which includes as partners the "OÖ Bioraffinerie GesmbH", Joanneum Research and BiorefSys, is to produce lactic acid and various amino acids from pressed silage juice.
The procedure of upgrading includes ultrafiltration, nanofiltration, reverse osmosis, electrodialysis and a five-stage ion exchanger process. By sequential treatment with these processes a clarified lactic acid and an amino acid stream are performed. Up to 150 L per hours of sedimented juice are handled in the plant, where the processes are still in the optimisation phase. The lactic acid stream, which is free from impurities, is concentrated to 35g/L in five hours, other organic acids, i.e. acetic acid and small amounts of butyric acid, formed during the silaging process, are still contained in the product stream. A series of ion exchangers is used to separate the second recovery stream (the amino acid enriched phase). With 180L exchanger feed, the separation of 18g/L asparatic acid, 14g/L leucine and 13g/L alanine into various fractions is possible.

Introduction
The concept behind green biorefinery, which is presented in this paper, is the use of green biomass for manufacturing upgraded products. Grass and silage are processed as an important resource with high market potential [1], not only for the farming industry as raw material, but also as technical raw material in food industry, the chemical industry, in cosmetics and the pharma industry. The products amino acids and lactic acid, which are produced in the pilot plant can be utilised in many different ways. Depending on the purity the amino acids can be used in dietary supplements for animals or humans. Another application field of the products of the GBR is the pet food industry. The factory farming of the animals increases the importance of the limiting growth factors, like methionine and lysine. These limiting amino acids have to be added to the standard feed in corresponding amounts. The production of amino acids powders, which can be used in the cosmetic industry, presents another line of products; the powders are used in the making of creams.
Lactic acid finds its most important usage as acidification additive in the food processing industry. Other applications are the production of a cleaning agent based on lactic acid, or a neutralisation solution, which can be used in the farming industry to increase the stability of corn. Secondly, the production of ethyl-lactate, a solvent for organic components, can be achieved with lactic acid as raw material.
The standard route of production of amino acids and lactic acid is the fermentative way with high down stream efforts to recover the resources. In the green biorefinery the fermentation of lactic acids and the hydrolisation of the proteins are done simultaneously during the silaging process. The purification of the juice is accomplished by membrane technology. Electrodialysis is used for the recovery of lactic acid. In former studies the opportunity of an electrodialysis method to obtain the lactic acid as an alternative to commercial chromatographic methods was investigated [2]. In the "Green Biorefinery" ion exchangers are

used for the separation of the amino acids to split the mixture into enriched phases.
One of the corner posts of the GBR is the raw material silage. Firstly, it is very important to the farmers to have an alternative usage for their grass and silage; secondly the production of silage is a well known process. Apart from the usage of the juice, there are a lot of alternative applications of silage press cake. The cake can be fed to a biogas plant as energy source or used for the production of insulating materials or fleeces [7]. Another possibility is the production of pellets, which are used in pellet heating systems. The waste streams of the GBR-plant are also potentially useful. The recycle in the plant itself is used for example as water alternative in the press phase or in the biogas plant to dilute the feed stream.
The aim of this project is to show the potential of grass and silage in industrial applications and to advance and optimise a process for the production of amino acids and lactic acid. This paper presents a short overview of the production and presents first results.

Materials and methods

Silage juice

For the experiments juice from silage was used. Different raw materials, namely grass or clover enriched grass, cause variable properties, especially the amounts of resources are differing. Table 1 shows a short summary of raw material properties, which relate to sedimented juice.

Table 1: Property of silage juice (sedimented juice)

Property	Value	Unit
Dry Matter	10-12	%
Lactic acid	28-37	g/L
Sum of other organic acids*	10-15	g/L
Sum of amino acids	22-28	g/L
Sugars	11	g/L
pH	4-4,5	
conductivity	20-25	mS/cm

*Sum other organic acids: acetic acid, butyric acid, formic acid, propionic acid, valeric acid,

A good silage quality can be identified by the amounts of acetic acid and butyric acid in the raw material [3], the lower these values, the more suitable is the silage for the process. According to [4] the percentage of lactic acid to acetic acid should be 10 to 1 and the butyric acid ratio should be even lower.

Analytics

The amounts of organic acids and amino acids are the most interesting factors for these experiments.

For the detection of organic acids a HPCL (Dionex Ultimate 3000) with a pre column, Micro Guard Cartridge (Cation-H Refill Cartridge) was used. The main column was an Aminex HPX-87H from Bio-Rad Co., using a 5 mM H_2SO_4 – solution as mobile phase at 60°C. An UV detection and an RI detection system were used.
The amino acid detector was a BioChrom 30 (BIOCHROM). The detection was done with a hydrolysate program with lithium salt. Using this apparatus 18 amino acids and ammonium can be detected.
The dry matter content of the juices was determined by drying the sample in a drying balance. For better results the measurement was repeated three times and the average value was calculated.

Experimental set up

Preparation of the membrane feed

After the pressing, the juice is allowed to sediment for 24 hours to remove sand and slurry from the liquid. The feed for the membrane plants was taken from the top of the tank, a fabrication without fibres and other interfering materials is ensured. There are no further preliminary steps like pH-changes or pre-filtrations. For all experiments the preparation steps have been the same.

Membrane processes

The process used in the green biorefinery-plant to recover amino acids and lactic acid from silage is carried out with membrane filtrations, state of the art plants, and an ion exchanger process. In figure 1, a schematic flow sheet of the process is shown.

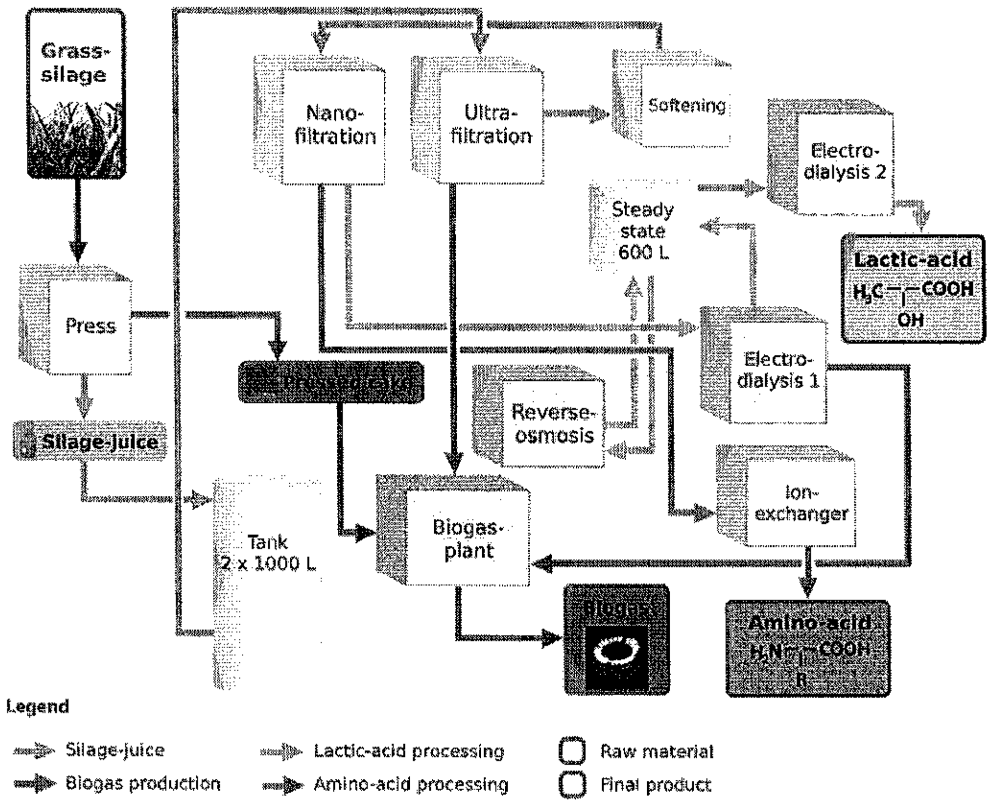

Figure 1: Process flow diagram (Source: Fabrik der Zukunft GmbH, Federal Ministry of Transport, Innovation and Technology, translated by the author)

The first step is an ultrafiltration unit with ceramic membranes, in which interfering macromolecules and proteins are separated from the product stream. This clarified permeate-stream is further processed in a softening plant, to ensure a good pre-treatment for the nanofiltration units. These nanofiltration plants are considered as the most important separation step in the whole process. The filtration step is not a purification step by itself, it is used to produce a retentate and a permeate, enriched with different products. The permeate of these filtration units is a lactic acid enriched stream, the amino acids stay in the retentate, which presents the second produced enriched stream. The high retentions of the amino acids have also been observed by other authors [6]. For the increase of the separation a two stage nanofiltration process is used. The retentate of the first plant obtains the feed of the second unit; a diafiltration mode enables the increase of the productivity of the nanofiltration plants. After the separation the stream enriched in lactic acid is fed into an electrodialysis plant. The desalination step reduces the amount of inorganic salts in the stream. The concentrate stream, with its high amount of impurities, is discarded. Within the diafiltration mode the diluted lactic acid stream hast to be concentrated in a reverse osmosis plant to increase the concentration of the product before it is fed in the diluate cycle of the second electrodialysis plant. This step is the last in the lactic acid loop as the product recovery takes place in this plant. The achieved results are comparable to the literature [4]. The concentrate stream, which is enriched with lactic acid, or lactate respectively, can be further processed in a drying unit to get an even higher concentrated solution.

Ion exchanger unti

The second product stream, the amino acid stream, is purified in a series of ion exchangers. In five columns different acid fractions are recovered. For the production of the amino acids these silage ingredients have to be enriched in the membrane filtration steps. For the recovery the retentate stream of the nanofiltration is used and stored in a tank. The refreshed columns can be rinsed with 300-400 L retentate, dependent on the content of amino acids. The amounts of amino acids in the fractions are mostly a function of the mixture of the ion exchanger feed and thus of the silage itself. After the column charging the fractions are eluted one by one using an ammonia solution. Before the next charging step the resin has to be regenerated again, and after that, a new batch process can be started.

Results

The results for the lactic acid stream and the amino acid enriched stream are presented separately.

Lactic acid stream

The clarification of the mixed product stream in an ultrafiltration plant is no concentrating process for lactic acid and amino acids. It is well known that there is no selectivity for small molecules in an ultrafiltration plant because of its high cut off, 1000 Dalton. The use of this plant is mainly to prepare a particle free stream for the nanofiltration step. The losses of lactic acid during purification are illustrated in figure 2. The highest amount of losses occurs in the ultrafiltration unit. This stream can be recycled in the press phase to wet the silage before pressing.

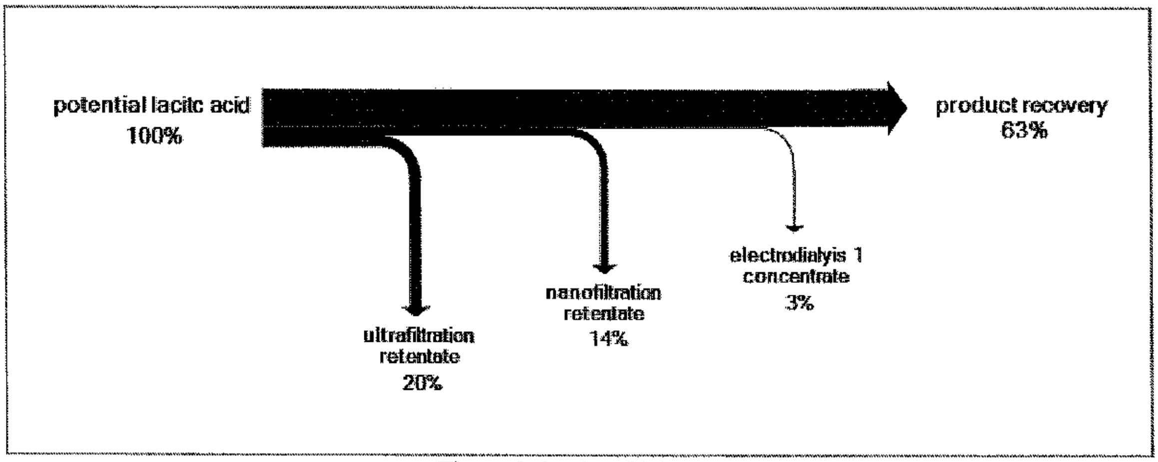

Figure 2: lactic acid flows

The retention of lactic acid in the nanofiltration steps reaches about 30%, mostly depending on the flux [9]. Despite the high retention, a significant amount of product is found in the permeate-stream. By using a second nanofiltration the loss can be reduced to 18%, calculated

relative to the potential inlet stream. The retention can be reduced down to 15% for organic acids, without a significant influence to the retention of the amino acids. As shown in figure 2 there are still 63% of the original lactic acid able to be recovered through the process. The figure does not include the main product step, "the electrodialysis 2", because in this step the product recovery depends on the mixture of the feed. The process is able to catch 80% or more of the available lactic acid, but with increasing recovery the transport of the other organic acids also increases. Most of the time the second electrodialysis is run in a semi continuous manner. This process is started after reaching a high conductivity in the diluate phase and stopped after transporting most of the ingredients into the concentrate tank. The production rate, which reaches up to 0,5kg/h, depends on the conductivity of the diluate and the run time. The most important influence remains the mixture of the silage juice. The relations of the organic acid amounts do not change during the membrane processes. There are no selective methods to separate the butyric acid or the acetic acid, although this acid shows higher transporting rates in an electrodialysis plant. It was found that there is a reduction of this acid in the product stream during the first electrodialysis, expressed in higher transport rates relative to the diluate concentrations.
The value of the used current density for the product recovery depends on the conductivity and the amount of charged ions respectively. With higher concentrations in the reverse osmosis plant the value of the limiting current density is increasing. The higher this value the more current can be applied for the transportation and accordingly the treatment capacity is needed to transport the impurities in the first step and the product in the second step is increased. With typical concentrations, a current density of 120 A/m^2 in the second plant was achieved.

Table 2: Sumary membrane plants operating data

Nanofiltrations		
Permeate flow	200	L/h
Mode	Diafiltration	
Retention		
Lactic Acid	30-35	%
Amino Acids	89-92	%
Electrodialysis		
Current density	80-100	A/m^2
Transport rate*	0,5-0,8	kg/h

*depends mostly on the diluate mixture and concentration, [5]

Amino acid stream

The amino acid enriched stream is transported through the membrane plants without big losses in the nanofiltration steps, see figure 3. Most of the acids stay in the retentate of the nanofiltrations, the retention varies from 89 to 95 %, depending on the mode of operation. Examining the specific acids, glycine and alanine show the highest losses of all acids, the retention of these acids is below 25%, see also [8]. These small acids pass the membranes without any steric barriers. With aspartic acid and leucine the highest retention ratios are observed.

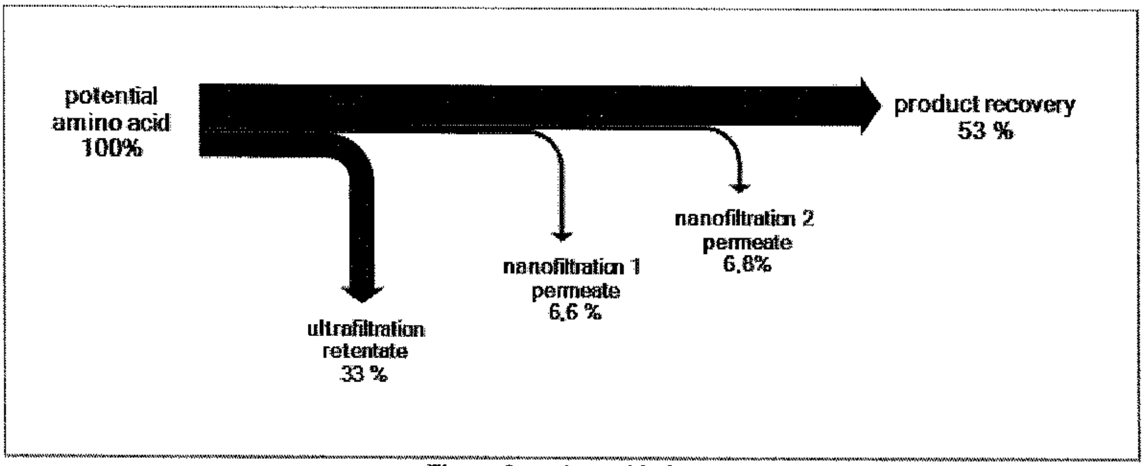

Figure 3: amino acids flows

At the beginning of the experiments there was a loss in the capacity of the resin. This results from dyestuffs, which block some exchange places in the resin. After the first runs equilibrium is reached and no loss in capacity is recorded.
The charging of the columns is done at a temperature of about 60°C. The ingredients of the stream have big influence on the amount of resin needed to recover the products. If the amount of impurities is high, the loss of bed material to purify the feed stream increases rapidly. The reduction of resin, which is available to the proper fractionation, is acceptable, to guarantee clear products in good quality at the end. The charging of the columns takes place one by one, the impurities are caught in the first and the second columns. After the charging of the first columns with calcium, magnesium and potassium the proper product recovery is started. The amount of charging depends on the amount of potential product in the feed stream of the ion exchanger street. On average 4 L per litre resin can be rinsed through the exchanger. The eluted portions are enriched by different amino acids fractions, which include fractions enriched up to 18 g/L aspartic acid or 14 g/L leucine and a fraction mostly enriched with 13 g/L alanine.
First tests show that the amount of rejected lactic acid in the nanofiltration retentate is no problem in the ion exchanger street. The option to recycle the lactic acid, which rinses through the ion exchanger will be tested soon.

Conclusion

The process, developed in a laboratory and built up in a pilot size plant in Utzenaich shows the possibility of recovering two different products from silage juice. The process is still implemented and tested out, now the optimization and adaption phase has been started.
First results show the importance of good silage as raw material in the production. The composition of lactic acid and other organic acids can not be influenced during the purification steps. Almost the same composition of the acids like in the silage juice is found in the end product of the lactic acid stream, the electrodialysis 2 concentrate.
The amount of water added in the nanofiltration plants is still in discussion and in a testing phase, the absolute transport of lactic acid is high when using a diafiltration mode, but the amount of energy needed for the pumps increases rapidly with higher diafiltration rates. Further tests will lead to the best process mode, for example a concentration step at the beginning and a diafiltration step in the second nanofiltration unit.
The recovery of lactic acid and lactate is accomplished by electrodialysis. First tests show that the specific energy amount of these plants is low, because the acid has good transport properties through the membranes. The best way to implement the second electrodialysis plant seems to be a semi continuous process; the optimised operation of this plant can be

obtained with highly concentrated diluate streams. For completely continuous production the capacity of the reverse osmosis plant has to be adapted.
The recovery of a mixture of amino acids with a series of ion exchangers has been shown successfully. The separation of the amino acid fractions works very well, although the cut-offs in the fractions may bee changed in the future. This enables a fabrication of optimised raw materials for varying lines of products.

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