Implementation of Circular Case 4 Chemical Industry

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0. Executive summary

The Chemical circular case demonstrates the transformation of an industrial waste from the pulp and paper industry to a functional chemical used as an additive in paint and for applications within the construction sector, figure 1.

The circular case is demonstrated by a project group consisting of Domsjö Fabriker, a pulp mill that produces dissolving pulp for viscose applications. In the project Domsjö Fabriker demonstrates both the ethanol production from fibre reject and production of an improved pulp quality suitable for production of cellulose ethers; SEKAB, a chemical company that produces ethanol derivatives such as acetic aldehyde and ethyl acetate starting from ethanol. In the project SEKAB works with demonstration of ethyl chloride production; Nouryon, a chemical company with a production of a cellulose ether, Bermocoll®, using cellulose and ethyl chloride as raw materials; RISE Processum, a research institute with the overall responsibility of the circular case and contribute to the research done in the project.

The circular case start with two types of fibre rejects as a raw material for production of fermentable sugars. They are generated by an enzymatic hydrolysis process followed by a fermentation to yield ethanol using an industrially adapted yeast.

SEKAB has been working with developing the basis for chlor-alkali process and demonstration of ethyl chloride production from ethanol. The overall process is achived by transforming ethanol to ethyl chloride catalysed by a heterogenic catalyst in a continuous process. The process is novel and has been built up in an ATEX (atmosphéres explosibles) approved area. A complementary investment for this process is needed to attain dry HCl in gaseous form. This chlor-alkali process is commercially available and the technique has been investigated together with a supplier, 3V-Tech, from Italy.

In parallel, a new quality of cellulose has been developed and evaluated to fit the specification that Nouryon need to produce the substituted cellulose, Bermocoll®. Wood based cellulose suitable for cellulose ether production has been evaluated at pilot scale and demonstrated in full-scale trials at Domsjö Fabriker.

¡Error! No se encuentra el origen de la referencia. shows the overall process of the circular case. With the blue parts, being what has been developed for this case.

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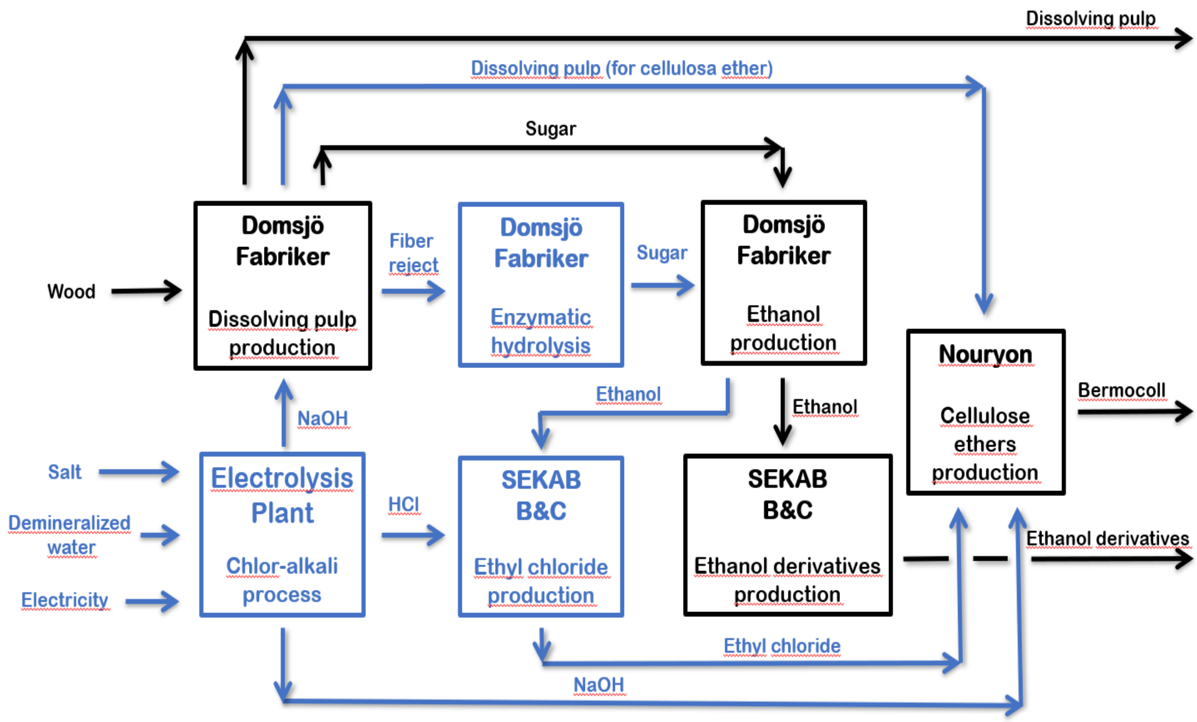

FIGURE 1 OVERALL PROCESS OF CIRCULAR CASE 4.

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Keywords

Waste fibres	Ethanol	Chlor-alkali	Ethyl chloride	Cellulose ether

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1. Demonstration of ethanol production

Fibre rejects is generally produced as a side stream in pulp mills and at Domsjö Fabriker there are two types of fibre rejects identified as suitable for ethanol production. The two types of rejected fibres, fines and knot rejects that are not digested in the cooking step, serve as raw materials in this circular case. Total amounts of the knot reject, and fibre reject sum up to about 14 500 t/a with knot reject representing about 12 000 t/a. The first step towards an ethanol production from rejects is to generate a sugar rich stream for fermentation. Therefore, a cocktail of enzymes is used to hydrolyze the two fibre rejects to produce a sugar rich stream followed by yeast fermentation. To evaluate the process as close to industrial conditions as possible, yeast from Domsjö Fabriker was used throughout all trials. The ethanol production from the fibre rejects is supposed to serve as an addition to the existing ethanol production.

The two residual streams, fibre rejects (fines reject and knot reject), were identified to have the potential to serve as raw material for enzymatic hydrolysis for production of fermentable sugars. The sugar stream could then be added to the spent sulphite liquor (SSL) and incorporated to the existing ethanol fermentation plant at Domsjö Fabriker. Today's production of ethanol is roughly 15,000 t/a which could be increased with 1000-2000 t/a if sugars generated from fibre rejects are included in the fermentation step.

Fibre reject and knot reject was used together in all trials in relation to amount at the mill site (1:5). The demonstration work was initiated in small scale to outline suitable hydrolysis and fermentation conditions for the fibre reject mixture. The results from the initial studies was then used as a basis for pilot scale demonstration. Figure 2 show the fibre rejects in the reactor.

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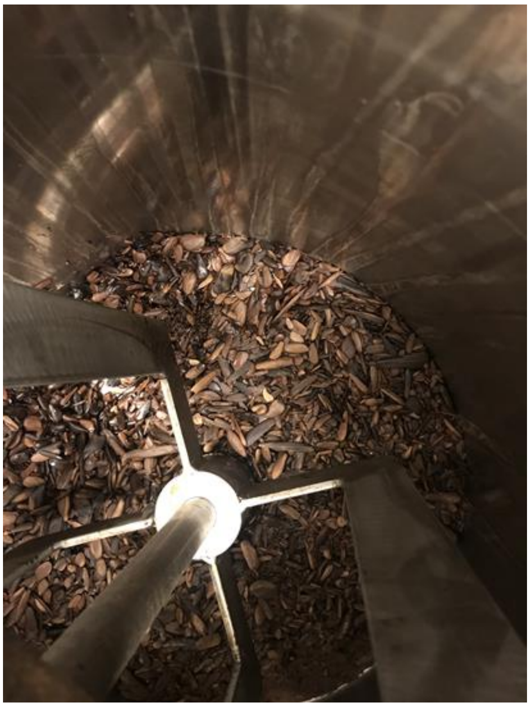

FIGURE 2. PILOT SCALE TRIAL USING FIBRE REJECTS FOR ETHANOL PRODUCTION. RESIDUAL KNOTS NOT POSSIBLE TO HYDROLYZE CAN BE SEEN IN THE REACTOR.

In the pilot scale runs 62 % of dry matter content of the fibre reject mixture was released as sugars in the hydrolysis. The remaining knots were evaluated on the energy content (23,8 MJ/kg, compare with stem wood about 19 MJ/kg) and could be delivered to project partners for further analysis or as raw material for various tests. In the next process step all of the sugars were consumed during fermentation whereof 53% were converted to ethanol. Due to usage of industrial yeast there were also byproducts formed from competing reactions consuming sugars. Mostly acetic acid and lactic acid were formed as byproducts.

The demonstration has shown that the level of inhibitors present in the hydrolysis liquid is low enough to enable fermentation. Also, the sugar concentrations reached are higher (95 g/l) than found in the SSL (45 g/l), the addition of the sugar stream from fibre rejects will increase the final sugar concentration which is an important industrial prerequisite.

The liquid phase from the hydrolysis was filtered before the fermentation trials. Filtration proved time consuming due to small sized lignin particles, so if possible it would be beneficial to the process if the filtration could be omitted. Trials of fermentation without filtration of the liquid remains to be conducted.

Figure 3. Illustrates the current and two possible paths in the production of ethanol.

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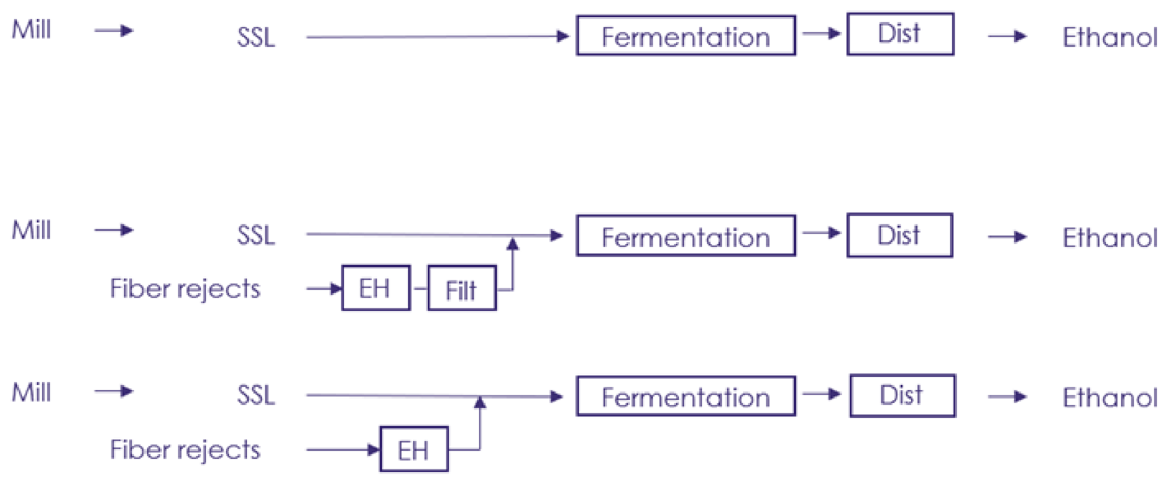

FIGURE 3. SUGGESTED USAGE OF FIBRE REJECTS TO INCREASE ETHANOL PRODUCTION. FROM THE TOP: - EXISTING ETHANOL FERMENTATION. - FIBRE SLUDGE IS ENZYMATICALLY HYDROLYSED AND FILTRATED BEFORE ADDITION TO THE SSL FOLLOWED BY FERMENTATION. - FIBRE SLUDGE IS ENZYMATICALLY HYDROLYSED AND DIRECTLY ADDED TO THE SSL FOLLOWED BY FERMENTATION.

The process of making ethanol from fibre rejects has shown high potential in converting cellulose to fermentable sugars and almost 100 % of the sugars were consumed. The ethanol yield was a bit low but a reason for part of the low yield could be explained by the inoculum used, which was of industrial standard. The inoculum was thus not free of contaminants but adapted to the fermentation environment. The relatively low yield proved that the substrate could be fermented but the process has rooms for improvement and has to be adjusted to fit an intended process.

The solid hydrolysis residue was a surprisingly interesting product that could be subjected to development of a new product.

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2. Ethyl chloride demonstration unit activities

2.1. Starting point

In the production of Bermocoll® a chemical mixture, containing ethyl chloride (EtCl) is used as one component to substitute a cellulose based core structure. The substituted cellulose derivative, Bermocoll®, is used as an additive in construction materials and paint. The general process for production of renewable EtCl will use ethanol as starting material that will react with HCl using a catalyst. To demonstrate the production of renewable EtCl to both replace the fossil alternative and secure the supply locally a demonstration unit has been built up with a complete continuous process including a catalytic reaction, purification of produced EtCl and regeneration of excess ethanol in a fully automated configuration.

The starting equipment and resources available for the demonstration unit were limited to a reactor and two separation columns controlled by an automation system (Delta V).

2.2. Planning and construction

A basic design of the process of producing ethyl chloride was made based on studies from the University of Umeå. The basic design was used to create a Process Flow Diagram (PFD), which was refined and improved, Figure 4.

The construction of the demo unit occurred simultaneously as a Piping and Instrumentation diagram (P&ID) was being developed. Some of the equipment used for the demo unit was already in place and was repurposed to speed up the construction. Other parts had to be constructed on site. The pilot plant is shown in Figure 5.

The process puts certain demands on the security and risk assessment of the unit and its surroundings. Since hydrochloric acid at high temperatures and pressure is used certain security measures has to be taken. Hydrochloric acid dissolved in water at high temperatures is incredibly corrosive and as such puts high demands on the materials in contact with it. This problem is mitigated in part by using dry HCl in its gaseous form which is not corrosive when it's dry. When the acid enters the reactor is will be dissolved and thus it puts high demands on the inner lining of the reactor and any other parts that may come in contact with it. Stainless steel is not enough to withstand the corrosion so in this process tantalum is used in the reactor and any other parts that are in risk of corrosion. Tantalum is a metal with very good acid corrosion resistance compared to other metals. This has made construction more complex since the availability of tantalum parts is quite limited. In the reaction taking place in the reactor all HCl is ideally consumed and ethanol is fed at a

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stochiometric surplus of about 2-5 % in order to ensure this. The basic formula for the reaction taking place is:

$$C_2H_6O + HCl \xleftrightarrow{Catalyst} C_2H_5Cl + H_2O$$

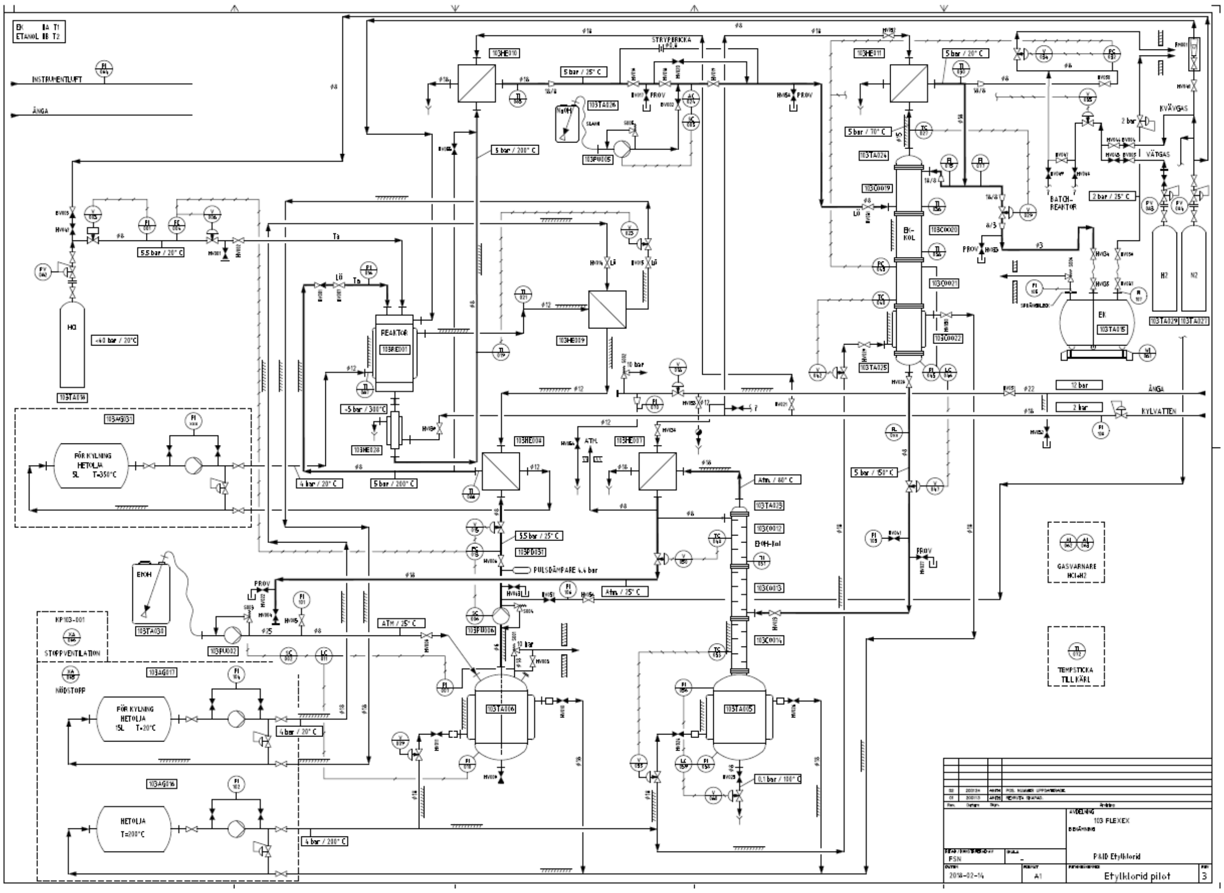

FIGURE 4. P&ID OF THE ETHYL CHLORIDE DEMONSTRATION UNIT

If there is excess ethanol the complete consumption of HCl will be more likely. If that is not enough there is a pH-meter installed after the reactor which continuously measures the pH of the stream and if the pH decreases it is an indication that unreacted HCl has exited the reactor which could cause damage to equipment if not neutralized. Thus if the pH drops, NaOH will be instantaneously pumped into the system to neutralize the acid. The measurement of the pH is handled by having a mixer installed on the pipe since without mixing there could be laminar flow of acid which could show misleading pH-measurements.

The room that contains the demo unit and all equipment in it must be ATEX-classified since there is a possibility that inflammable gases could occur in the room and considering the fact that HCl gas is present puts a lot of thought regarding risks and risk mitigation.

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Since the high temperature oil heater is not ATEX-classified it was required to be separated from the demo unit. This was accomplished by building a sealed box with ventilation to the outside.

The temperature inside the reactor is of great importance in measuring the performance of the system. The reaction-taking place is an exothermic reaction so if the temperature at the beginning and end of the reactor is measured an indication of the extent of the reaction can be received from the increase in temperature. Temperature control and measurement is paramount in maximizing the performance of the catalyst used in the reactor so a lot of testing and planning has been done to ensure good temperature control.

FIGURE 5. ETHYL CHLORIDE DEMONSTRATION UNIT.

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2.3. Test runs

The demo unit has been tested in various attempts.

The distillation columns that are to be used to separate ethyl chloride from the water/ethanol mixture as well as the column that will separate ethanol and water have both been tested by using a feed of ethyl chloride, ethanol and water and bypassing the reactor. This test verified the demo units' capabilities of separating the fractions that will be formed in the reactor.

The demo unit reactor has been tested with water as feed as to verify the units capabilities regarding heating and pressure control. When using only water the room did not have to be ATEX-classified since there were no volatile chemicals present. The first test was performed by using steam as a heating agent for the reactor and for preheating the feed with heat exchangers. The results from this test showed that the reactor could not reach and keep the desired temperature of > 300 °C. The heating had to be improved by using oil instead of steam to heat the reactor and heat exchangers. Once the demo unit had been rebuilt, a second heating test was performed. The results from that test showed that the reactor can perform reactions at > 300 °C that is what is required for the catalyst to be effective.

The complete trials using ethanol and HCl as feed will be tested after some additional test runs using water, ethanol and ethyl chloride feed. Once the pilot has been successful in production of ethyl chloride a lot of work regarding optimizing the process such as finding the optimal temperature, pressure and flows remains as well as managing good control of those parameters.

2.4. Safety considerations

The process to convert ethanol to ethyl chloride is a process that contain a number of hazardous chemicals and process parameters. Ethanol is toxic and highly flammable material together with HCl which is highly toxic and corrosive especially at the high temperatures at some parts of the process (> 300 °C). Especially the use of HCl in gaseous form puts very high demands on safety, both regarding the process equipment and for the people working on the unit. Hot HCl is incredibly corrosive if it is allowed to dissolve in water. This means that the equipment that might come in contact with the hot HCl in liquid form is built in tantalum which is capable of withstanding those conditions. There is also constant pH-measurement after the reactor to verify that no HCl is left in the stream after the reactor, residual HCl will be neutralized using NaOH added to the stream to increase the pH-value.

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A process safety assessment was held in 2018-12-18 which the purpose to identify and address various risks and implement risk mitigations. The risk assessment and risk mitigation strategies is a continuous work including personnel from Nouryon, Sekab and RISE Processum.

Also, as a risk mitigation step the demo unit should be operated with minimal amount of direct personnel interaction in the room including the unit. The entire process can be operated from a separated operating room by using an automated control software (Delta V).

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3. Chlor-alkali process

Synthesis of ethyl chloride can be performed by using ethanol and hydrochloric acid (HCl) as raw materials. Hydrochloric acid is available on the market in aqueous solution, but it has initially been found in the Paperchain project that hydrochloric acid in aqueous solution will not be an economical sustainable source of hydrochloric acid. The solution is then to use dry hydrochloric acid (gaseous), which makes the process of manufacturing ethyl chloride more economically since there is less watering entering the system and thus making the separation less demanding.

One solution to get access to dry hydrochloric acid as raw material for the ethyl chloride process is to use a chlor-alkali process as a first step. Pure salt (NaCl) and demineralized water are used as raw materials and in a first step chlorine is separated from sodium by electrolysis and in a second step sodium hydroxide is produced from sodium. In this second step pure hydrogen is also produced. The production of chlorine (Cl_2) and hydrogen (H_2) is followed by combustion to form hydrochloric acid which is dry and can be used as raw material in the manufacturing of ethyl chloride. The produced sodium hydroxide may, in turn, be used as raw material in the manufacturing of cellulose derivatives (Nouryon) and/or in the production of dissolving cellulose (Domsjö Fabriker). Within the Paperchain project, the possibility to use the sodium hydroxide locally will be of great importance for the economic potential in the circular case. In this project, it has been found that the chlor-alkali process can be "the key" to obtaining long-term profitability in the production of ethyl chloride from ethanol.

In the Paperchain project, we have begun to investigate how a suitable chlor-alkali process could be designed to match the process for production of ethyl chloride. In this work, the company 3V Tech from Italy has been identified as a potential provider of an appropriate process. This company has been hired to assist with the ability to enable SEKAB, Nouryon and Domsjö Fabriker to continue work on developing a sustainable concept for the production of ethyl chloride using residuals from pulp production. A block diagram of a possible process is illustrated in **¡Error! No se encuentra el origen de la referencia.**.

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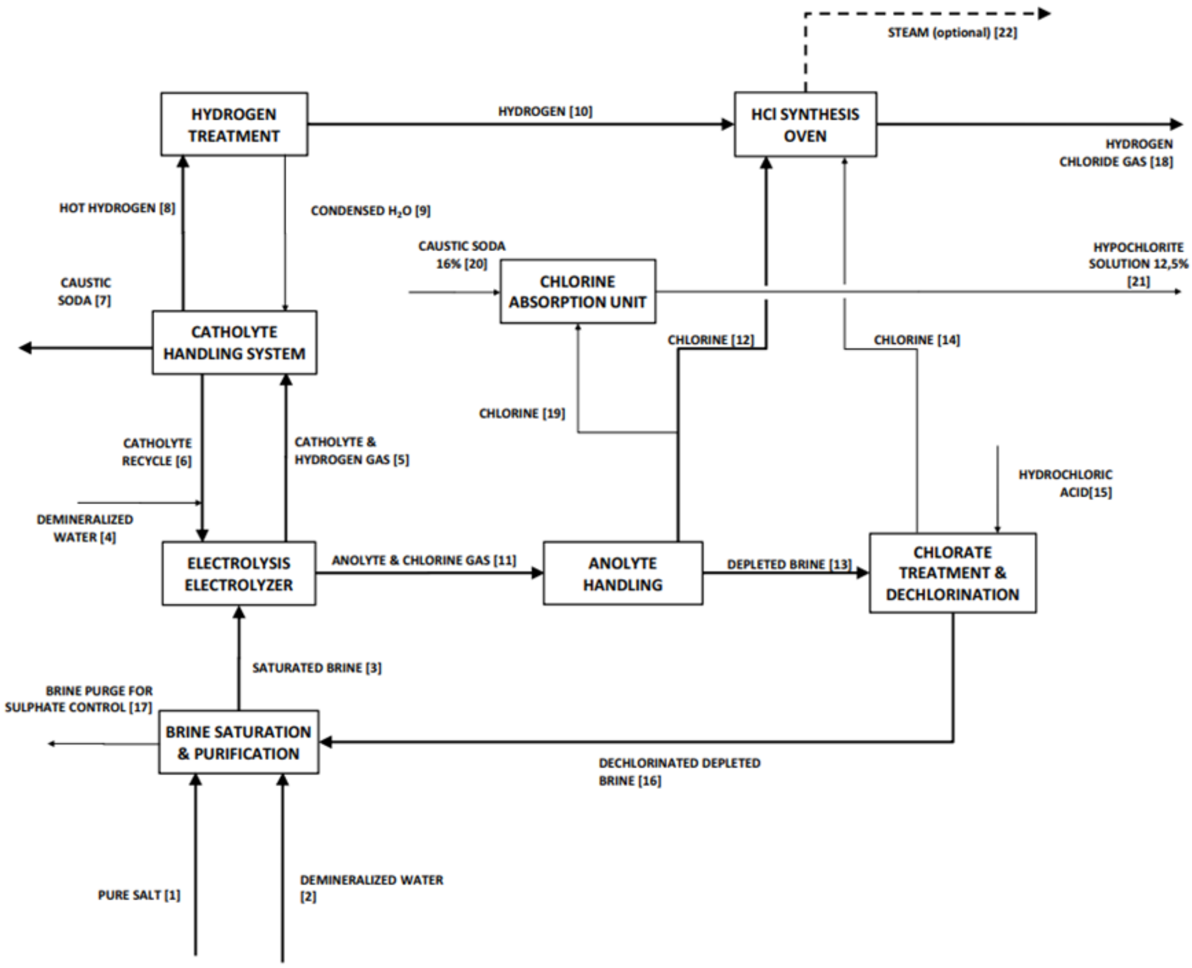

FIGURE 6 BLOCK DIAGRAM OF THE CHLOR-ALKALI PROCESS FROM 3V-TECH.

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4. Cellulose production for cellulose ether applications

Domsjö Fabriker in Sweden is a manufacturer of dissolving pulp, mainly as raw material for viscose production. Domsjö Fabriker is interested in expanding their product range towards cellulose for cellulose ether production. A new process has been evaluated in pilot scale and demonstrated in a mill trials at full scale. The trials have been successfully completed both at pilot scale with the process parameters transferred to the full-scale demonstration.

FIGURE 7. DOMSJÖ FABRIKER PRODUCT.

Domsjö Fabriker have produced 5 batches of cellulose for cellulose ether applications in full-scale. The mill is equipped with batch digesters with a capacity of about 80 t/batch. That trial was conducted in Q4 2018 and produced about 150 tons of cellulose from 400 tons of wood. Samples from this cellulose were sent to Nouryon for evaluation in their pilot plant for their Bermocoll® process. The cellulose was tested and evaluated according to Nouryon´s standard method, which comprised of the following steps, Figure 8. The cellulose was milled to a particle size of < 300 μm in a knife-cutting mill. The created powder was put in a pilot scale reactor were the synthesis was performed as according to the normal Bermocoll® recipe with grade name EBM101FQ.

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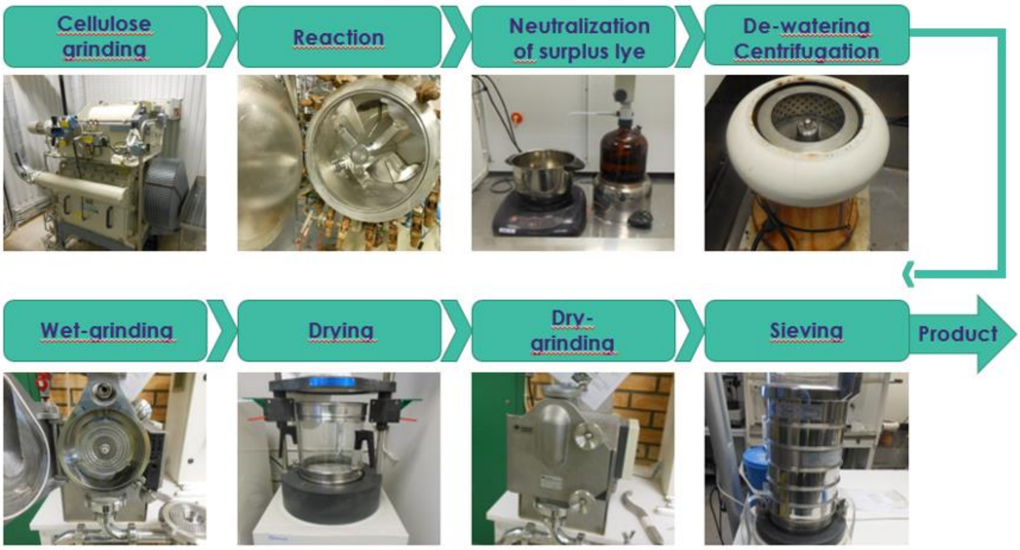

FIGURE 8. NOURYON´S PILOT SCALE EVALUATION OF WOOD BASED CELLULOSE FROM DOMSJÖ FABRIKER IN THE BERMOCOLL PROCESS. NOURYON´S PILOT SCALE EVALUATION OF WOOD BASED CELLULOSE FROM DOMSJÖ FABRIKER IN THE BERMOCOLL PROCESS.

The product was washed with sodium sulphate solution and dewatered in a centrifuge. The wet product was dried on a fluid bench dryer until the total moisture content was < 2 %. The dry material was then milled and sieved to < 200 µm particle size and analyzed according to Nouryon´s standard procedure. The results from the analysis and the specifications limits are shown in **¡Error! No se encuentra el origen de la referencia.** below.

Parameter	Pilot batch 2019022	Specification limits
Viscosity (cP)	515	500 – 800
NaCl (%)	2,9	0 – 6
Moisture (%)	1,5	0 – 4
Gel content (%)	5,5	0 – 3
Transparency (%)	82	Min 80%
S60 (%)	95	Min 85%
Parameter	Pilot batch 2019022	Specification limits

TABLE 1 ANALYSIS AND SPECIFICATION LIMITS OF BERMOCOLL®.

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5. Conclusions

The chemical circular case is split into four major parts which are combined to form the process of producing renewable cellulose ethers (Bermocoll®) from fibre reject from pulp production.

The first part is the hydrolysis and fermentation of fibre reject from Domsjö Fabriker pulp mill. The fibre rejects have successfully been enzymatically hydrolyzed into sugars and the sugars have been fermented into ethanol.

The second part is the production of ethyl chloride from ethanol and hydrochloric acid. The ethyl chloride is to be used in the Bermocoll® production. The different parts of the ethyl chloride production have been individually tested. A demo unit where they are combined is in its' final stages of construction and some parts of the process in the demo unit have been tested.

The third part is the chlor-alkali process were hydrochloric acid is to be produced for use in the ethyl chloride process. This process is well known and adaptations to ensure compatibility with the processes in this project is under investigation with the goal of increasing long-term profitability in combination with the other processes.

The fourth part is the production of Bermocoll from ethyl chloride from part two and cellulose from Domsjö Fabriker. Cellulose that were produced in full scale mill trials has been used by Nouryon to produce Bermocoll® in pilot scale. The produced Bermocoll® was not satisfactory in all aspects, there was a bit too much unreacted fibres left in the product. Improvements are necessary for producing Bermocoll® within its' specifications.

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