

HCl based disintegration of lignocellulose to cellulose nanocrystals

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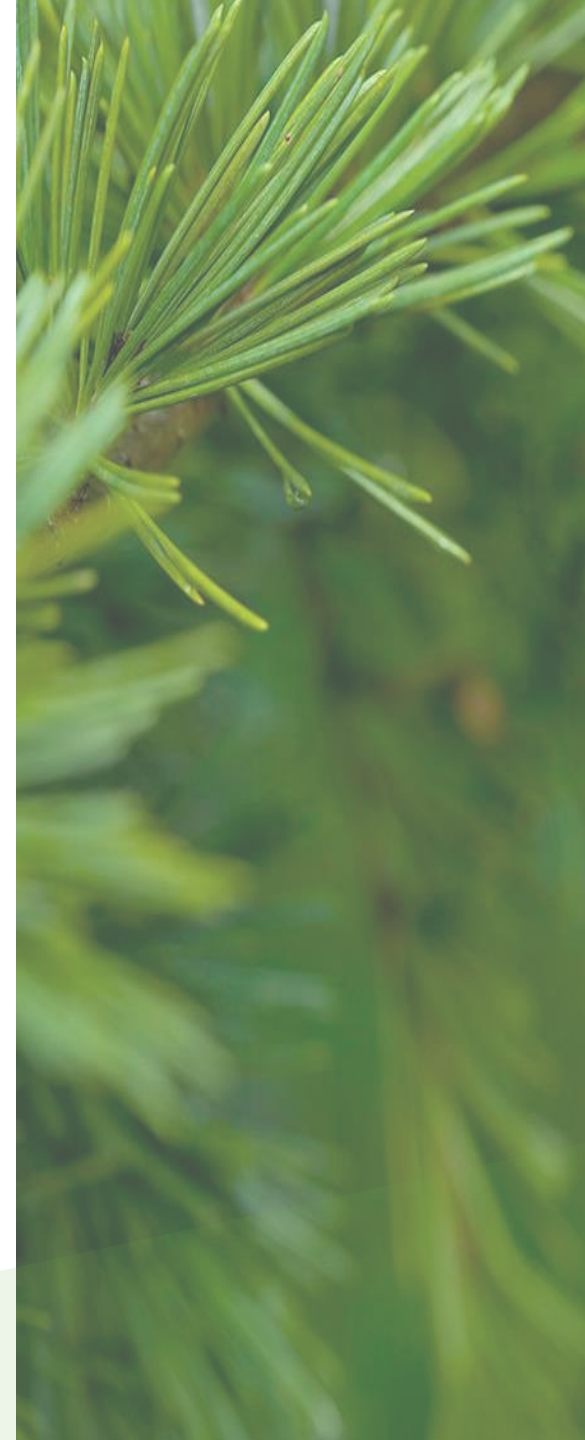
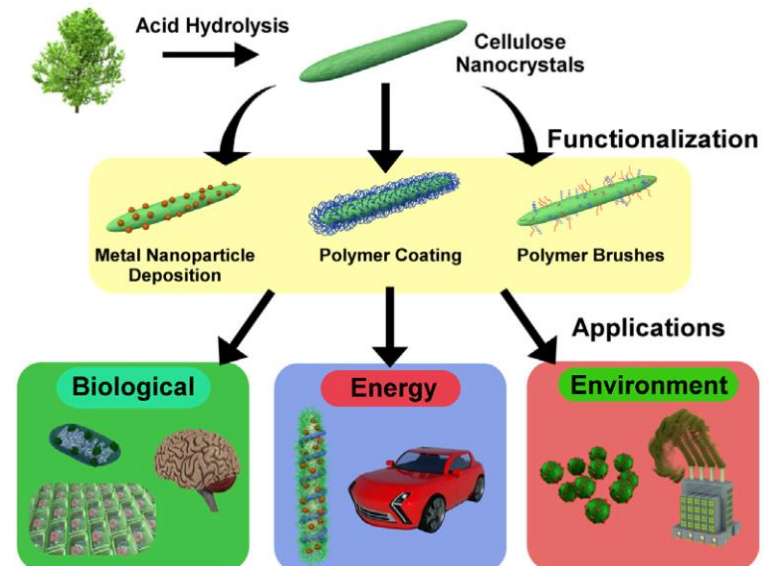


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Introduction

- A promising new technique for producing Cellulose Nano Crystals (CNC) from lignocellulosic material has been developed at Aalto University. The technique utilizes gaseous HCl under moderate pressure. The treatment hydrolyzes accessible cellulose structures producing a novel type of cellulose nanocrystal material
- The current study is a first attempt at describing the technique in the form of an industrial process. Central questions include flows in and out (mass-balance), equipment options, product characteristics as well as identified risks and problems.
- The current study is based on the article "From vapour to gas: optimising cellulose degradation with gaseous HCl" by Timo Pääkkönen et al in React. Chem. Eng., 2018, 3, 312–318¹.
- This study highlights the research findings that are central to developing an industrial embodiment. The study further contains an outline of a process, a mass balance of that process, discussion regarding equipment options and a final discussion on the current level of understanding regarding feasibility of the process.
- The end product from hydrolytic cellulose degradation is cellulose nanocrystals. Such crystals are foreseen to have a large number of uses, varying from serving as drug release platforms, being part of new types of batteries to functioning as adsorption media for pollutants in environmental protection².
- The novel CNC production method appears promising as it utilizes a gaseous reagent, this is expected to reduce chemical consumption both directly and by making it easier to recycle the residual. As the HCl used is actually not consumed by reactions, but works as a catalyst, the chemical consumption is expected to be very modest.



Prior art knowledge

- Cellulose is the major structural ingredient in plant fibres. Its degradation is important for two reasons:
 - for obtaining sugars for fermentation^{1,2} or commodity chemical production via HMF, CMF, and levulinic platforms^{3–5}
 - for extracting nano-sized components, i.e., nanocellulose, from native fibers
- Cellulose hydrolysis is usually a heterogeneous system consisting of solid fibres and an aqueous liquid with a catalyst. Considering acid-catalysed hydrolysis, increased acid concentration is required to degrade cellulose efficiently. Due to the high concentrations, full acid recovery is nearly impossible and it is laborious to purify the desired product from the reaction mixture. This is especially the case when aiming for the production of CNC.
- The typically used acid in liquid phase processes is H_2SO_4 , a basic, fairly low cost industrial chemical

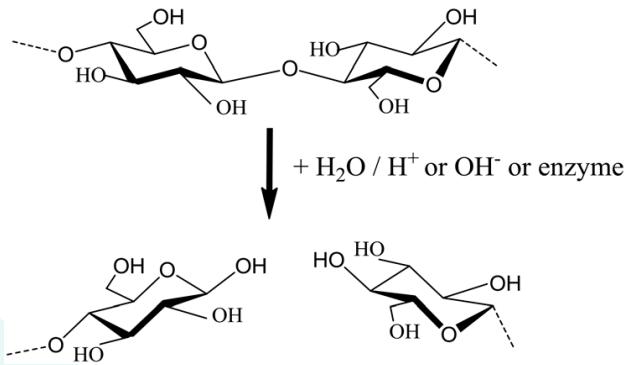


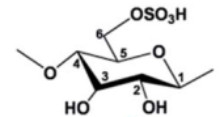
Fig 1. Hydrolysis of cellulose, catalyzed by acid, base, or enzymes.

Advantages of H_2SO_4 based hydrolysis of cellulose in CNC production:

- OSO_3^- groups are introduced on the surface on of CNC`s
- Dispersion of CNC`s is effortless due to the OSO_3^- groups

Challenges of H_2SO_4 hydrolysis of cellulose:

- Low yield
- High water consumption
- Acid (in the fiber mixture) is hard to recycle
- Purification of the product is hard



Methods that reduce the chemical consumption in CNC production would clearly solve some of the inherent problems.

Research and experimental data

- The research into the process has been conducted at Aalto University, starting at “gram scale” using HCl vapor, thereafter on “tens of grams” scale in a purpose built pressurized reactor system. The reactor system is presented on the right. The system was built by SciTech-Service.
- The central new finding achieved by use of the new equipment is the impact of HCl pressure on the reaction kinetics. This lays the foundation for an industrial process.

Materials tested

- In the experimental work, industrial HCl gas was used for pressurizing the system.
- Filter paper (=cotton cellulose fibers) were used as the cellulose source. Unreported experiments have confirmed that wood based cellulose (dissolving pulp from wood) behaves analogously.

Basic outline of experiments

- The cellulose samples were placed in the reactor. Air was expelled by increasing system pressure with HCl gas, pressure was released through the “flush” line, this was repeated 5 times where after the system was brought to desired HCl gas pressure.
- The experiments are described in detail in accompanying literature. A point to notice is that the pressure indicated in the article is gauge pressure (= pressure above normal air pressure), not absolute pressure.

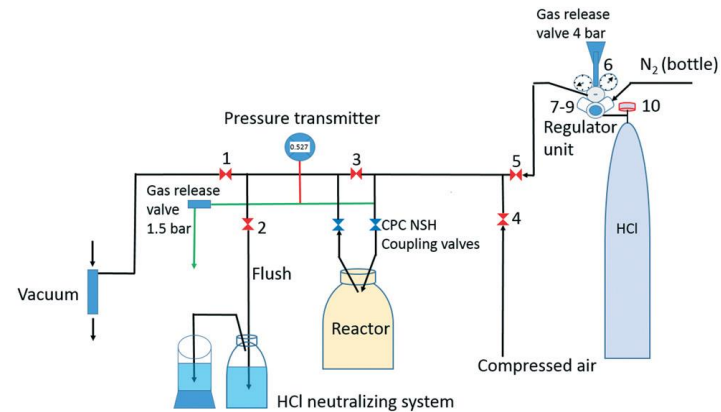


Fig 2. Schematic illustration of the laboratory system. Valves: (1) vacuum valve, (2) flush line valve, (3) bypass valve, (4) compressed air valve, (5) HCl gas valve.

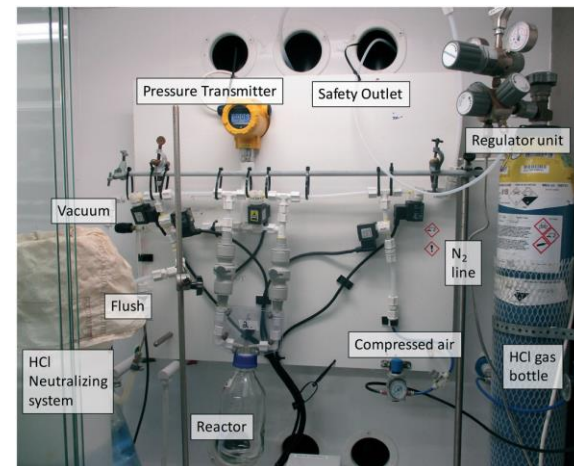


Fig 3. Snapshot of the actual reactor system used.

Research and experimental data

Reaction kinetics

- The pressure used impacts the speed of hydrolysis. The hydrolysis levels of at the (apparent) leveling off degree of polymerization (LODP) threshold. Figure 4 to the right shows the extent of de-polymerization vs. time. The pressure indicated in the legend denotes pressure over atmospheric pressure (gauge pressure), therefore the absolute pressure is 101 kPa higher than the pressure indicated. Based on the figure 80-100 kPa gauge pressure and 1 h reaction time takes the depolymerization close to the LODP.

Process yield

- The yield of the process is very high as indicated by the bottom right figure. Considering the ~1h, 80-100 kPa (p_g) assumption, a yield of 96-98% on incoming cellulose is seen. The final yield depends on the purity of the material introduced. In the research it has been seen that hemicellulose is rapidly hydrolyzed and thereby contributes to yield loss. It is therefore foreseen that dissolving wood pulp (almost purely cellulose) is the preferred raw-material in commercial CNC production.
- In theory, more hemicellulose containing paper pulp could be considered, but it opens up the question of how to separate the hydrolyzed hemicellulose. Water washing is unfeasible as the point of the process is the gas phase operation.

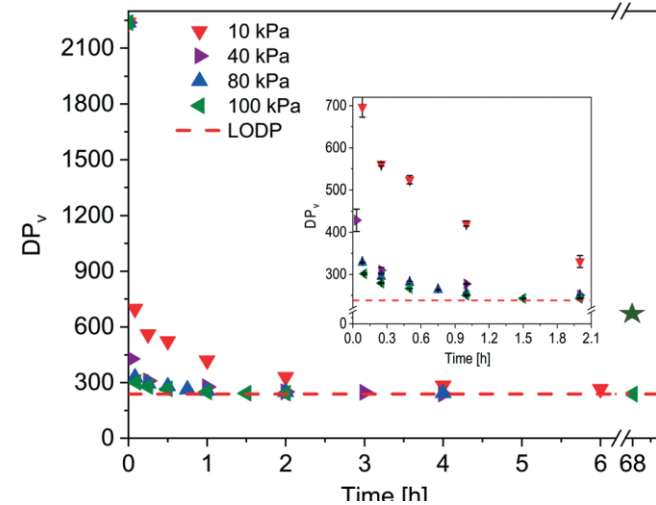


Fig 4. Reduction of the degree of polymerization (DPV) as a function of reaction time with different pressures. The dashed line represents the LODP. Dry matter content of all samples was 95% excluding sample which was dried in the oven overnight (green star, 100 kPa).

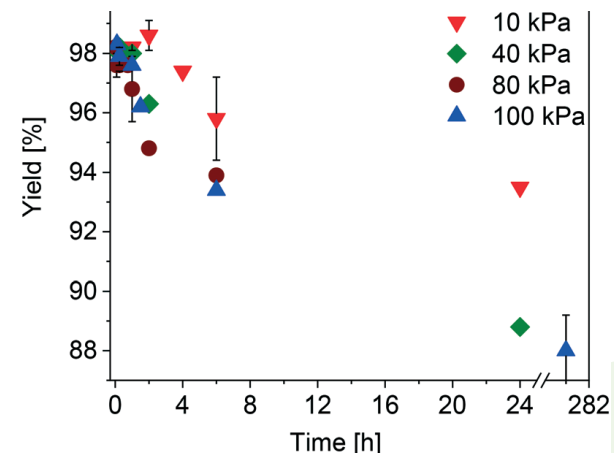


Fig 5. Yields of HCl gas degraded filter paper samples. After HCl hydrolysis (gas), all samples were washed with Milli-Q water, dried overnight at RT, and homogenized prior to the yield analysis and DPV determination.

Research and experimental data

Adsorption of HCl

- From a production cost point of view, the adsorption of HCl to the material is central. It will influence both the amount of gas needed in the reactor to reach a given reactor pressure, as well as affecting losses in the process. The top right figure shows the measured amount of HCl that adsorbs at varying pressures (p_g).

Effect of moisture

- The moisture content of the pulp significantly impacts hydrolysis speed and the extent of hydrolysis that can be reached². (LODP is lower when samples are wet). This is seen in the bottom right figure.
- Side reactions lead to formation of humin at very long reaction time or when sample is very wet. Such extreme conditions are to be avoided in the industrial version of the process.
- The final challenge in producing commercial CNC is the need to disperse the nanocrystals. Due to the high surface to weight ratio of the particles, they exhibit a very high agglomeration tendency. The research group has shown that the particles can be dispersed using either formic acid or CMC. The dispergation furthermore requires ultrasound sonication. In the present work the CMC route is chosen as the preferred concept even though the dispergation yield is only ~60%. Formic acid has close to 100% yield, but brings other complication. In the concept the dispergation is considered to be part of the end use, it is not described in detail in this report.

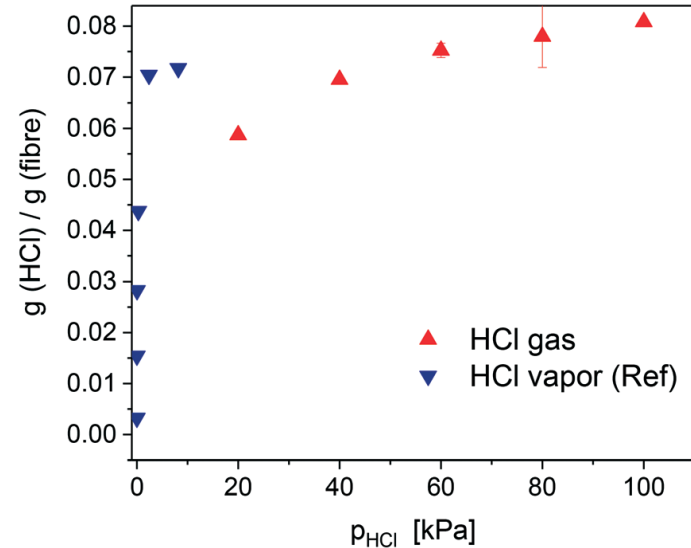


Fig 6. Adsorption of HCl on fibres. HCl adsorption was analysed by weighting the papers before and immediately after the hydrolysis. Whatman 1 filter paper was hydrolysed with the HCl device at adjusted pressure (default 1 h reaction time).

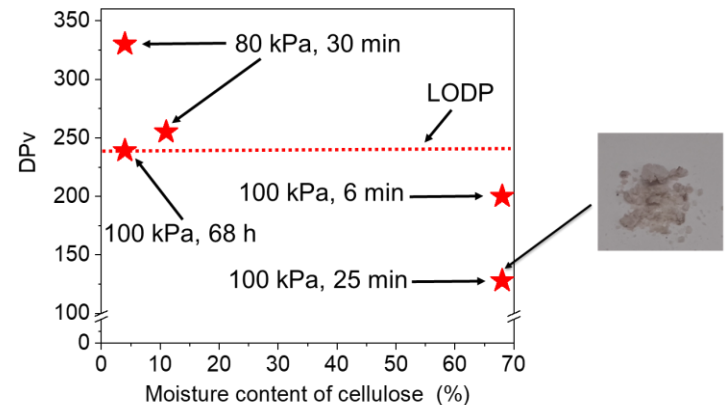
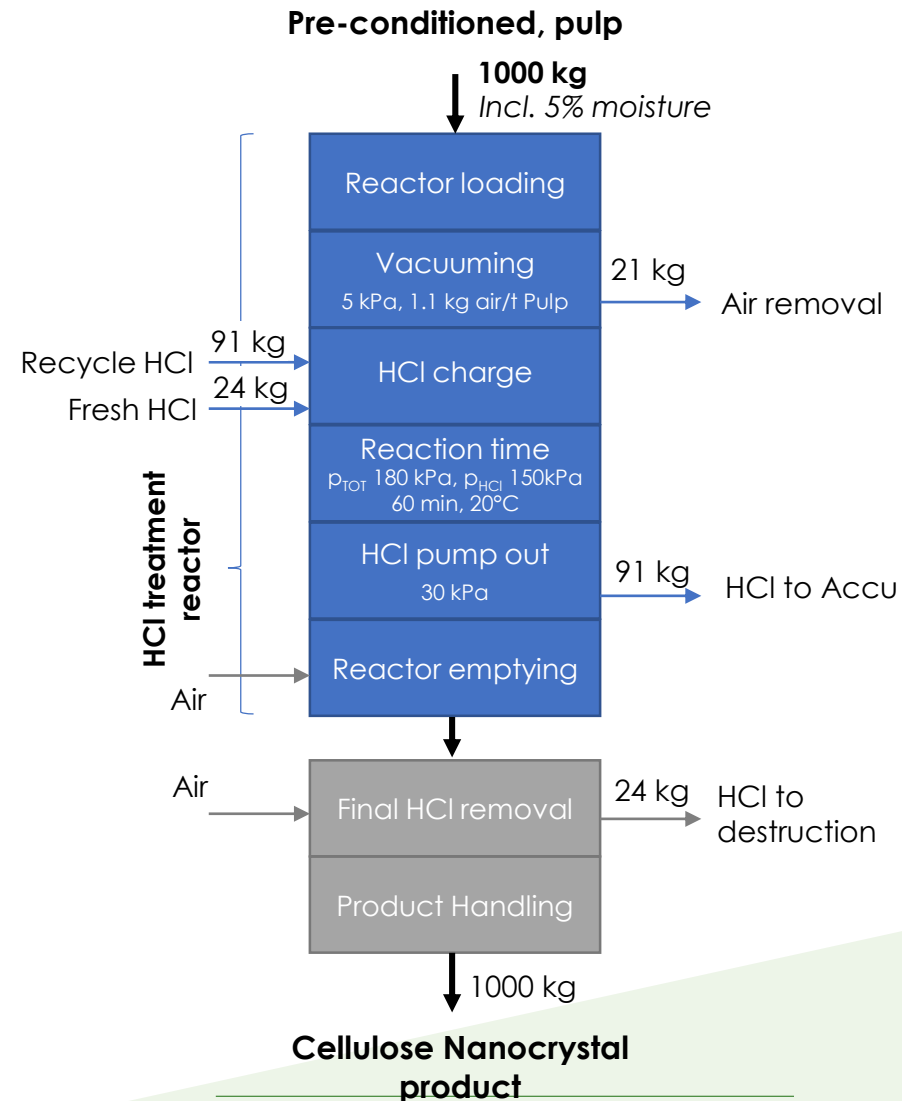


Fig 7. Effect of moisture content on level of depolymerization reached at varying HCl overpressure and treatment times

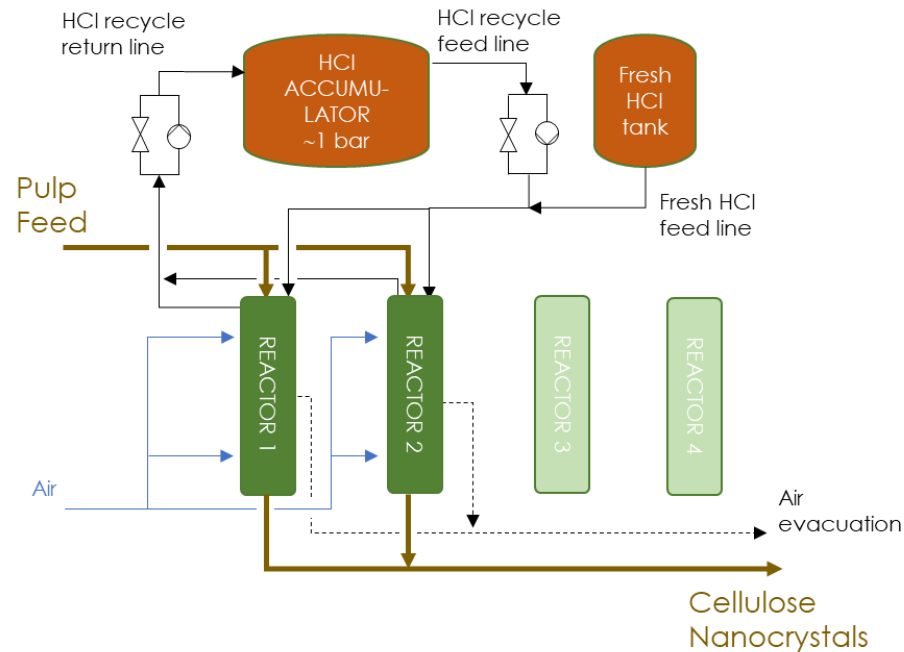
Process concept overview

- The adjacent scheme gives an overview of the process concept outline
- The HCl treatment is carried out as a batch process in four or more parallel batch reactors that are operated sequentially. All steps of the process cycle are operated at ambient temperature.
- The pulp feed is assumed to be conditioned to 5% moisture content. *The mass balance shown only applies to pulp at 5% moisture.* HCl is highly soluble in water and any changes in the pulp feed moisture content greatly affect the HCl balance.
- The total HCl charge applied is 115 kg/t pulp. 91 kg of the total HCl charge can be recycled resulting in net consumption of 24 kg HCl/t pulp.
- A small part of the cellulose, and most of the hemicellulose impurity in the pulp feed degrades during the treatment. The reaction products are assumed to be conveyed with the pulp, i.e. negligible yield loss over the process is assumed (there is no washing of the pulp; the products are non-volatile).
- The HCl part that cannot be recycled is stripped out of the pulp with air and sent to destruction, i.e. neutralization with NaOH.
- The foreseen equipment setup and the balance calculation details are presented on the following pages.



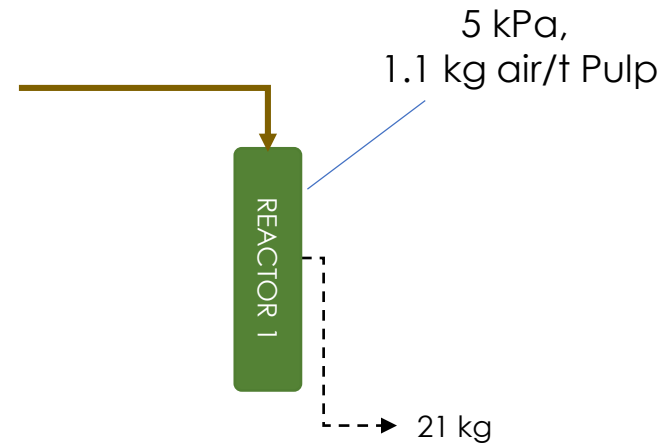
Equipment setup

- The equipment setup considered for the process is shown in the scheme below.
- The HCl treatment is carried in reactor closets. The pulp is placed into the reactors as a sheet stack with individual sheets sufficiently apart to allow easy gas flow between the sheets.
- The reactors are connected to a recycle HCl storage tank called “HCl accumulator”. The recycle HCl charge into the reactors is taken from the accumulator and after completing the HCl treatment, the spent HCl is returned to the accumulator. The HCl accumulator is operated at approx. 1 bar.
- The recycle HCl becomes contaminated by air due to the small amount of air left inside the reactors after the vacuum step. The equilibrium composition of the recycle gas is 94% HCl and 6% air (equilibrium calculation is introduced in more detail on p. 14-15).
- Fresh HCl is charged through the same gas feed line as recycle HCl.



Reactor loading and vacuum

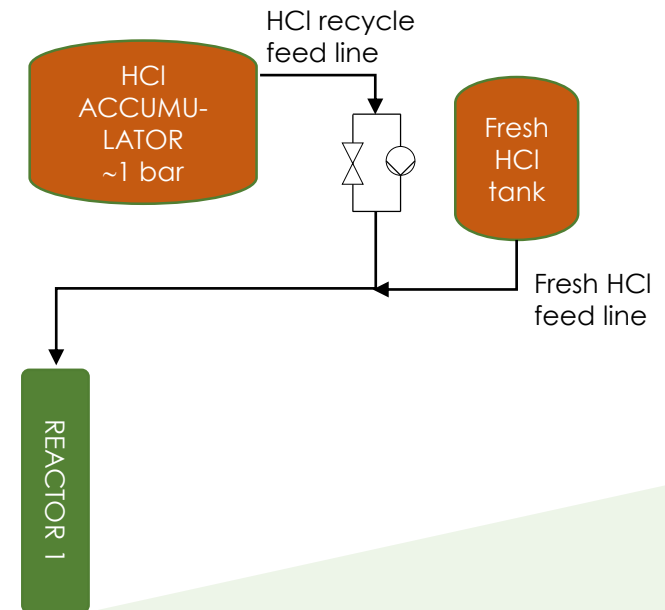
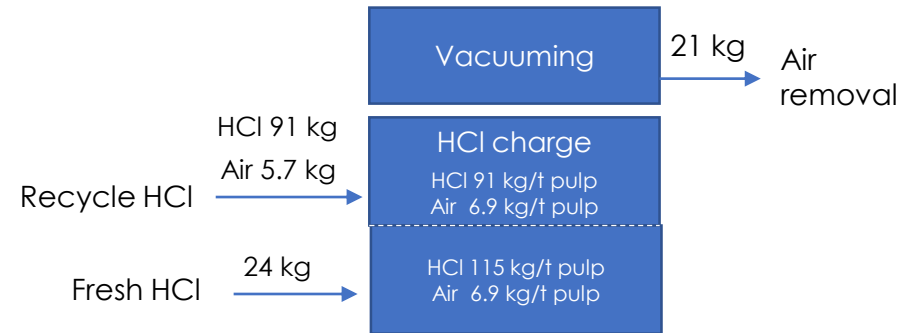
- The feed pulp is pre-conditioned to 5% moisture. The pulp is placed into the reactor as a sheet stack with individual sheets sufficiently apart to allow easy gas movement between the sheets.
- The pulp-to-free-gas-volume ratio in the reactor setup is assumed to be such that one ton of pulp takes 20 m^3 of reactor volume. With the solid fiber wall material having a density of 1.5 t/m^3 , the free gas volume in the reactor becomes $19.3 \text{ m}^3/\text{t}$.
- Air is evacuated from the reactor to reach absolute 5 kPa pressure (-95 kPa). The amount of air removed is 21 kg/t pulp ($17.4 \text{ Nm}^3/\text{t}$ pulp), and the amount of air remaining in the reactor is 1.1 kg/t pulp.



HCl charge

HCl charge execution

- The recycle HCl is first charged into the reactor.
- The HCl recycle charge is achieved by opening a connecting line between the accumulator and the reactor. The recycle HCl will first flow freely into the reactor (driven by pressure difference). When gas flow slows down, the feed line pulp is turned on to complete the recycle HCl feed.
- Recycle HCl feed is continued until the reactor total pressure is 141 kPa. At this point 91 kg HCl and 5.7 t Air/t pulp has been fed. The HCl immediately starts to adsorb onto the pulp and majority of the HCl is assumed to be adsorbed, when the recycle HCl feed is completed. HCl adsorption is assumed to follow the curve given in Figure 8. The 141 kPa pressure target represents the equilibrium state pressure (adsorption is completed).
- After completing the recycle HCl feed, fresh HCl gas is fed until 180 kPa total pressure is reached. This corresponds to 24 kg/ t pulp fresh HCl charge. Again, part of the HCl fed becomes adsorbed and the 180 kPa total pressure represents the equilibrium state pressure (adsorption is completed).



HCl treatment, pressure relief and discharge

HCl treatment

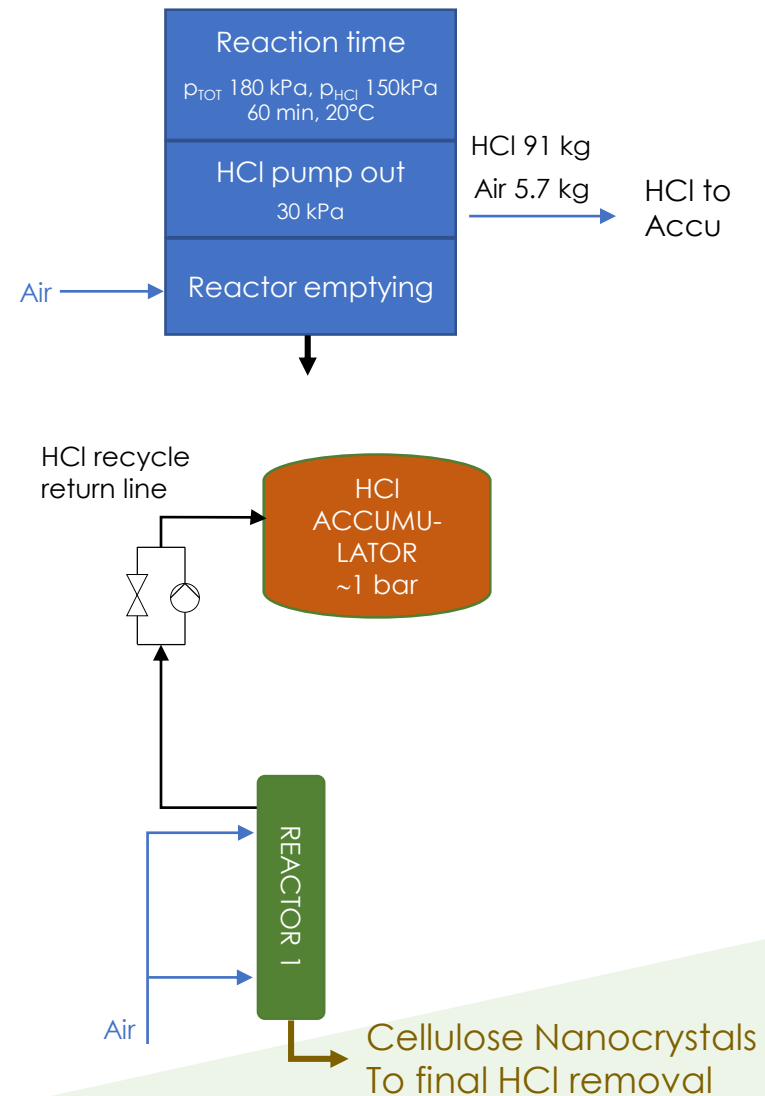
- The treatment time at 150 kPa HCl pressure (180 kPa total pressure) is 60 min. Based on the DP development data given in Figure 4, the 60 min treatment time is assumed to be sufficient to reach LODP or close to LODP level.

HCl pump out

- After completing the reaction time the HCl (and air impurity) is returned back to the HCl accumulator. The gas flow is first spontaneous and is continued with a pump after the spontaneous flow starts to slow down.
- The reactor gas emptying is continued until 30 kPa absolute pressure is reached. It is assumed that HCl desorption from the fibers takes place as the reactor gas volume is emptied. It is assumed that, when the 30 kPa pressure is reached, the gas phase composition is the same as when HCl pump out was started and the correlation between the adsorbed HCl and gas phase HCl corresponds to that in Figure 8.
- The gas return to HCl accumulator is 91 kg HCl and 5.7 kg Air / t pulp, which is equal to the recycle gas feed (two steps earlier).

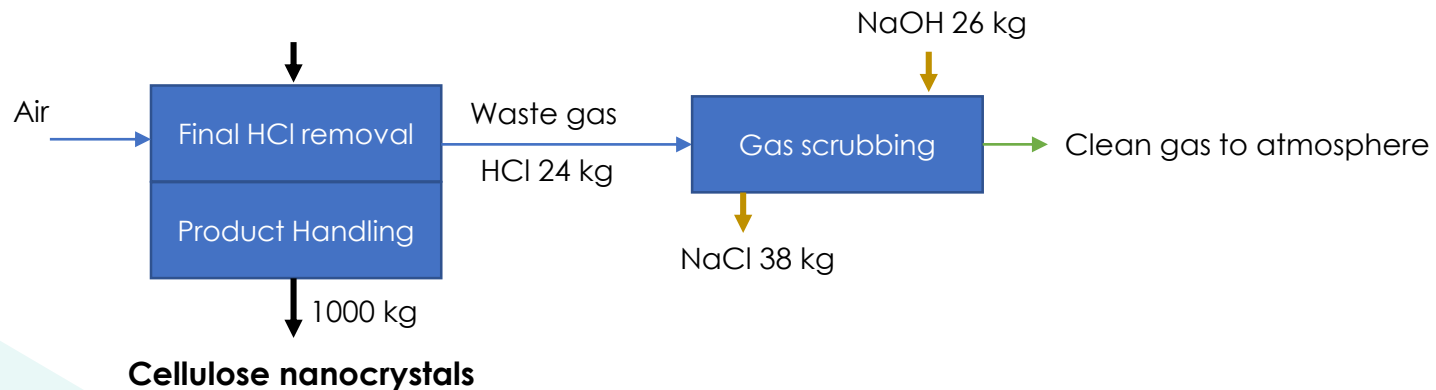
Reactor emptying

- The reactor is brought back to ambient pressure by allowing air to enter the reactor through the air feed lines.
- Then the reactor is opened and the treated pulp sheets are taken to final HCl removal.



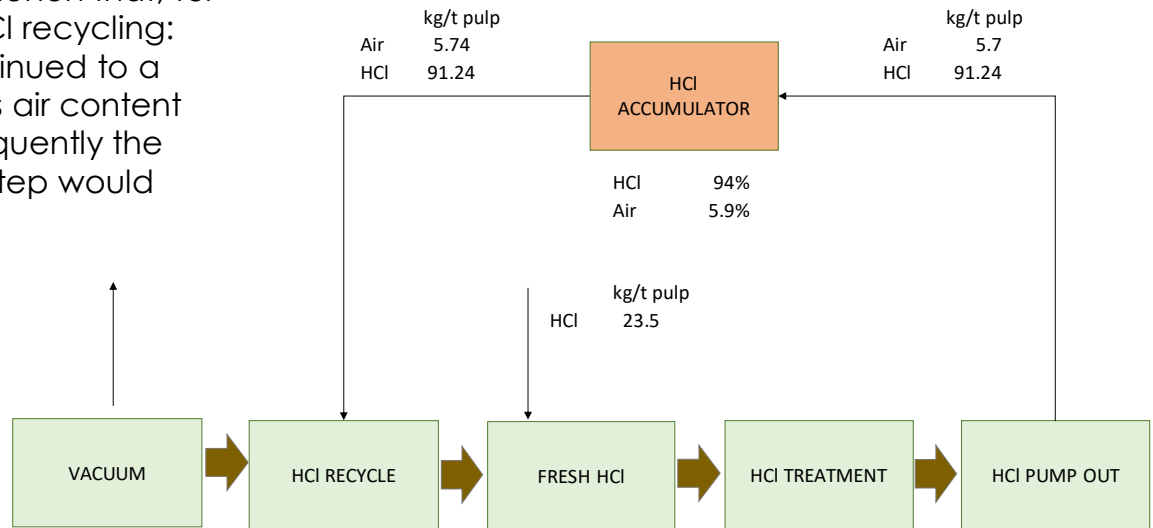
Final HCl removal and disposal

- After being discharged from the HCl treatment reactor the cellulose nanocrystal product contains a notable HCl residue. The HCl residue is stripped from the product with air and the waste gas is sent to scrubbing.
- The carbohydrate degradation products generated in the HCl treatment step are assumed to be non-volatile and HCl is assumed to be the only component transferred from the cellulose product in to the waste gas.
- Product handling may include crushing the sheet form pulp to smaller pieces for easy transport. The decisions regarding pulp handling must be made together with the end customer. The end customer will also use carboxy methylcellulose (CMC) and sonication to disperse the cellulose nanocrystals (CNC) in a form suitable for their use.
- The HCl in the waste gas is scrubbed with NaOH in a dedicated scrubber, and the cleaned gas is released to atmosphere. The scrubber gives a NaCl solution as a product. The waste gas handling consumes 26 kg /t pulp NaOH and produces 38 kg /t pulp NaCl.



Calculation of the HCl and air balance (1/2)

- The HCl and Air balance calculation of the process concept is shown in the scheme below.
- The vacuum step leaves 1.15 kg Air per t pulp inside the reactor before starting recycle HCl feed. The same amount of air (1.15 kg/t pulp) remains inside the reactor after completing HCl pump out.
- From the process design point of view, air contamination of the recycle HCl is a key phenomenon that, for instance, restricts more efficient HCl recycling: if the HCl pump out would be continued to a lower pressure, the recycle HCl gas air content would increase rapidly and consequently the HCl pressure in the HCl treatment step would decrease.
- A lower pressure after the vacuum step would allow a higher HCl recycling efficiency, but the feasibility of targeting < 5 kPa (abs) in industrial scale needs to be checked before using in the design.



Pressures

Component	Unit	VACUUM	HCl RECYCLE	FRESH HCl	HCl TREATMENT	HCl PUMP OUT	
Air	kPa	5	30	30	17%	5	17%
HCl	kPa	0	111	150	83%	25	83%
Total	kPa	5	141	180		30	

Component mass balance

Component	Unit	VACUUM	HCl RECYCLE	FRESH HCl	HCl TREATMENT	HCl PUMP OUT
Air	kg/t pulp	1.15	6.9	6.9		1.15
HCl adsorbed	kg/t pulp	0	59.0	71.3		16.2
HCl gas	kg/t pulp	0	32.2	43.4		7.2
HCl total	kg/t pulp	0	91.2	114.7		23.5

Calculation of the HCl and air balance (2/2)

The HCl and air balance shown on the previous page is constructed on the following basis:

- HCl and air are the only components in the system.
- Reactor empty volume is 19.3 m³/t pulp.
- The air evacuation step reaches 5 kPa (abs) pressure; the total pressure target for the HCl treatment step is 180 kPa.
- The HCl inside the reactor comprises two portions:
 1. One part of the HCl becomes adsorbed onto the fibers and dissolved in the fiber moisture -> "adsorbed HCl"
 2. The second part of HCl occupies the reactor gas -> "gaseous HCl"
- The relationship between adsorbed HCl and gaseous HCl follows the experimental relationship given in Figure 8 (below).
- HCl adsorption and desorption are practically instantaneous.
- HCl only catalyses the hydrolysis reactions, i.e. it is not consumed.

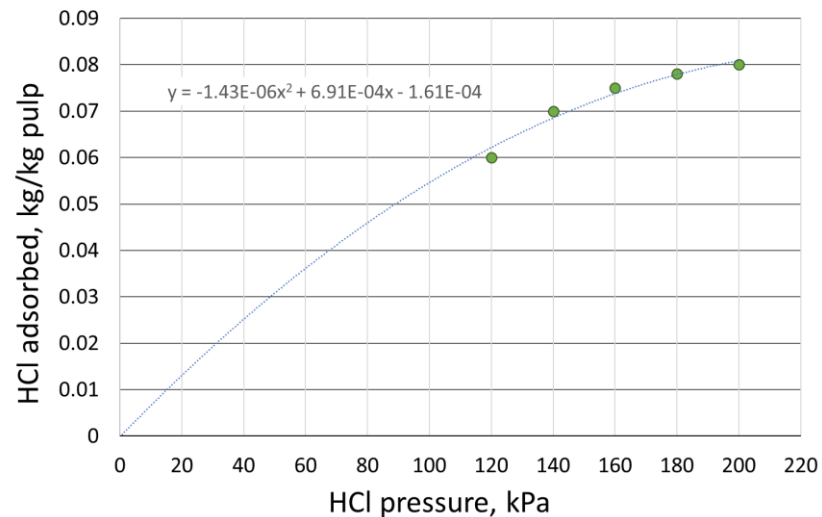


Fig 8. Extrapolation of HCl adsorption on fibres. The HCl gas adsorption data from Fig 6. is used to obtain a correlation curve for HCl gas pressures over the range 0 ... 200 kPa.

Equipment options

- A batch process is foreseen. Sheet form dissolving pulp is used.
- A series of chambers, similar to ovens, with a large front door, slightly wider than the pulp sheets are to be used. Pulp sheets are typically 85-92 cm x 67-73 cm, therefore the chambers should be approximately 1 m x 0.8 m internal size, with an e.g. 2 m high space for shelves holding the sheets.
- Pulp sheets are loaded on trays made of stainless steel wire that are stacked on “shelves” (holders that support the edges of the trays). The shelves have wheels and are loaded into the chambers from the front doors. The sheet loading onto the trays can be automated using the same type of sheet handling used in pulp mills for stacking the sheets into bales.
- Assuming standard pulp sheets of 1000 g/m² and 0.9 x 0.7 m sheets gives 630 g/sheet. With 1.6 cm between the trays the loading in the reactor will become 62.5 sheets/m reactor height. This corresponds to 20 m³ of reactor volume / t of pulp. High reactor loading will be crucial for minimizing the amount of HCl gas needed.
- The gas handling system consists of standard industry machinery. The layout of the gas system is as described in the process section. Material issues need to be discussed in the detailed design phase but for dry HCl gas ordinary stainless steel can be used.
- Waste gas is scrubbed using NaOH. The gas scrubbing equipment should be designed according to industry standards.

Risk analysis

The following risks and possible mitigations have been identified:

Risk	Severity	Suggested mitigation
The product is new and unknown in the market	Showstopper, no market = no process	Comparison of the end product to known NCC products. Market research
Price of product is unclear	Significant	The question of outputs is connected to the market risk
Disintegration of the hydrolyzed NCC	Significant	The NCC properties will depend on how well the crystals can be separated from each other. The assumed route is CMC aided disintegration, the needed product properties must be studied together with potential end use customers.
Gas accessibility/hydrolysis uniformity in large scale reactor	Low/Moderate	Lower than expected accessibility will impact the absolute amount of gas needed and the needed processing time
Feasibility of HCl recycle (suitable equipment for compression of HCl gas)	Low/Moderate	As HCl gas is produced industrially, equipment is expected to be readily available
Practically achievable level of vacuum in equipment evacuation	Low/Moderate	The level of evacuation will affect the accumulation of inert air in the process and thereby determine the potential for HCl recycle.
Energy (electricity) consumption of the process. (HCl re-cycle will require compressors running on electricity)	Low/Moderate	The overall concept can be optimized based on relative cost of electricity and HCl
Corrosiveness of HCl	Low	There are other applications of gaseous HCl in industry, the central issue is to keep the system as dry as possible. World production of HCl is ~20Mt/a ³
Side reactions (formation of humins) take place at excessive process time or conditions	Low	The process conditions are easily controlled, thus reducing risk for over processing

Conclusions and recommendations

- An industrial process has successfully been outlined based on the research performed at Aalto University into gas phased cellulose nanocrystals (CNC) production from cellulosic material. Based on the conceptual work performed it seems feasible to build a production process around the research findings.
- Benefits of the identified process:
 - Gas phase reactions reduce the need of acid compared to current liquid phase (H_2SO_4) processes
 - The reactions take place at room temperature and at low to moderate pressure, this lowers the cost of process equipment
 - A concept of gas recovery has been designed that reduces the consumption of fresh HCl
 - The product is a dry sheet formed CNC that is easy and cheap to transport to customers
- Certain gaps in knowledge have been identified. The most pressing are:
 - The market and market price for CNC needs to be determined. Laboratory samples are marketed for 1.75-20 USD/ODg⁵, this however hardly reflects a real market price
 - The steps needed at the customer end for disintegration of the CNC need to be further studied
 - The technology used for compression of HCl gas would be helpful to discuss with machinery manufacturers, this would ensure that the process parameters used are realistic
- The basic operating costs identified in the current production concept are approximated as follows:

(All numbers / t of dry undispersered CNC)

 - Dissolving grade wood pulp: 1033 USD (930 USD/Adt, 1.1 Adt / t CNC)
 - Fresh HCl gas: 150 USD (20-25 kg/t CNC, 6-9 USD/kg)
 - NaOH for HCl destruction – 16 USD, (26 kg/t, 0.6 USD/kg)
 - Electricity – unknown, estimated at 5 USD

In all, the direct production costs are <2000 USD/t. Considering the fact that carboxymethyl cellulose (CMC) aided dispergation of the crystals gives a 60% yield, the cost of <3500 USD / t of dispersed CNC.
- It is recommended that financing is sought for detailed planning of pilot production of CNC using the HCl gas method.

Literature cited

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