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BENEFITS OF ENERGY INTEGRATION IN A FREEZING PROCESS

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This thesis discusses the energy requirements of the freeze towing and dissolution of a cellulose-based material (e.g. disposed clothing) in a chemical textile recycling process. The energy required for heating and/or cooling in each phase of the process were calculated, acknowledging the variation of the chemical properties of the process stream between phases. Then a model was proposed for circulating excess heat within the system (energy integration) to minimize the external power required. In addition, it was assessed how lowering the water concentration of the process stream could reduce the energy requirements of the process.

The treated phases included the preliminary heating of the process stream, preparation of a ZnO-NaOH solution and freezing as well as melting of the process stream in a freezing tunnel (including liquid nitrogen preparation). The heating was assumed to be completed with hot water or saturated steam and the cooling with cold water or liquefied nitrogen. These phases only cover a part of the entire textile recycling process; the pretreatment of cellulose (e.g. tearing and bleaching) or further processing after the dissolution phase were not discussed in this study.

It was found that heat circulation effectively removes the need for saturated steam in all process phases except the preliminary heating, which occurred at temperatures of over 130 C. Heated cooling water from the nitrogen compressor can, at least, fully melt the frozen pulp and partly preheat the fresh water going to the ZnO-NaOH preparation tank. The most significant questions concerning the energy efficiency of the whole process are linked to the liquid nitrogen, as the power requirements of its production are potentially over ten times as large than the requirements of all the other process stages combined. In addition, several compressors may be needed to produce liquid nitrogen at sufficient efficiency, which would further increase the costs.

Reducing the water content of pulp would have a great effect on the total need of liquid nitrogen but further study is required to assess where and how much of the water can be reduced. Other still unanswered questions are how fully the cooling potential of evaporated but still very cold nitrogen can be realized inside the freezing tunnel and what the maximum achievable efficiency of the liquefaction process is.

KEYWORDS:

Energy integration, textile recycling, energy efficiency

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ENERGIAINTEGRAATION HYÖDYT JÄÄHDYTYSPROSESSISSA

Tämä opinnäytetyö käsittelee selluloosapohjaisen materiaalin jäädytysavusteisen liuotuksen energian tarvetta kemiallisessa tekstiilinkierrätysprosessissa. Käytännössä lämmitykseen ja/tai viilennykseen tarvittu energian määrä laskettiin kussakin prosessin vaiheessa huomioiden prosessivirran kemiallisen koostumuksen muuttuminen vaiheiden välillä. Työssä ehdotettiin tapaa kierrättää ylijäämälämpöä prosessien välillä ulkoisen energiantarpeen minimoimiseksi (energiaintegraatio). Lisäksi laskettiin, kuinka paljon prosessivirran vesikonsentraation alentamisella voisi vähentää kokonaisenergiantarvetta.

Käsitellyt vaiheet olivat prosessivirran esilämmitys, ZnO-NaOH-liuoksen valmistaminen ja selluloosamassan kulkeminen jäädytystunnelin läpi. Lämmityksen oletettiin tapahtuvan joko kuumalla vedellä tai kyllästetyllä höyryllä ja jäädytyksen kylmällä vedellä tai nestetypellä (jäädytystunnelissa). Nämä vaiheet ovat vain osa koko tekstiilinkierrätysprosessia: selluloosan esikäsittely (esimerkiksi revintä ja valkaisu) sekä liuotuksen jälkeiset vaiheet eivät kuuluneet tähän tutkimukseen.

Energiaintegraation huomattiin poistavan kylläisen höyryn tarpeen kaikista muista prosessin vaiheista paitsi esilämmityksestä, joka tapahtui yli 130 asteen lämpötilassa. Typpikompressorin jäähdytyksen sivutuotteena syntyvä kuuma vesi pystyy sulattamaan jäädytetyn selluloosamassan täysin ja lisäksi osin lämmittämään ZnO-NaOH-preparaatiotankkiin sisään menevän veden. Tärkeimmät kysymykset prosessin energiatehokkuuden kannalta liittyvät nestetypen tuotantoon, jossa tehontarve on mahdollisesti yli kymmenen kertaa suurempi kuin kaikkien muiden prosessivaiheiden yhteensä. Lisäksi useita kompressoreja saatetaan tarvita nestetypen riittävän tehokkaaseen tuotantoon, mikä ennestään lisää kuluja.

Selluloosamassan vesikonsentraation alentaminen vähentäisi erittäin merkittävästi nestetypen tarvetta, mutta lisätutkimuksia tarvitaan osoittamaan, kuinka paljon ja missä prosessin vaiheissa veden määrää voi laskea. Muita kysymyksiä, joihin tässä työssä ei saatu vastausta, ovat muun muassa, onko jäädytystunnelissa kaasuuntuneella, mutta edelleen hyvin kylmällä typellä edelleen jäähdytyspotentiaalia, ja mikä on sen suurin mahdollinen nesteytysprosessin tehokkuus.

CONTENTS

ATTACHMENTS

VTT Technical Research Centre of Finland provided the author with Excel files, PI diagrams and a word document which included technical data related to the machinery and processes treated in this work. The information contained is confidential and these attachments were not included in the publication.

FIGURES

TABLES

1 INTRODUCTION

Global-scale cotton cultivation requires massive amounts of water and energy. The environmental burdens of the cotton industry also include chemical pollution due to pesticide use, dyeing and other processes. At present there is a pressing need for a systematic and scalable industry for the recycling of cellulose-based products (see e.g. Haule et al. 2016).

Cellulose is an abundant renewable organic material with the potential to be repeatedly recycled into new fiber. Textile recycling methods can significantly lower the energy and water requirements of textile production by using textile waste as a material for new fabric. Recycling can reduce the need for cultivating new cotton and promote the use of textile waste as material for new products (Zamani 2014, 8–28).

However, the extraction of cellulose from e.g. cotton-based clothing and its chemical treatments carry their own environmental burdens, and not all methods can be considered a significant improvement to cultivating new cotton (Zamani 2014, 8–28). The end product of the process described in this thesis, cellulose carbamate, is a promising material (still at pilot facility level) which can be prepared from many cellulose-based products, such as used clothes. It resembles viscose, another synthetic cellulose-based material with a longer history, yet its production is safer for humans and causes less environmental toxicity (Teng et al. 2018).

2 FOUNDATIONS

This thesis discusses the energy requirements of the **carbamation and dissolution** of cellulose in a chemical textile recycling process. It also presents ways to reduce the total heat and electrical energy requirements of these processes via **energy integration**. The aim was to give an estimate of the power required by the separate process phases and quantify the potential for reducing this power with heat circulation and reduction of water in the process stream. It should be noted that the phases described in this thesis only cover a part of the whole recycling process: pretreatment of the cellulose before carbamation (e.g. tearing and bleaching) or further processing after the dissolution phase (needed to prepare ready cellulose carbamate fiber) are not discussed in this study.

Chapter 2 has numerous figures visualizing the inputs and outputs of the treated processes. In these figures the process streams are always depicted with thick, black arrows. The utility streams are depicted with red and blue arrows; when heating, the input stream is red and the output stream is blue, while when cooling the input stream is blue. Other streams (ZnO, NaOH, N and fresh water) are marked with thin black arrows. The streams that have energy integration potential are surrounded with a blue ellipse and will be discussed further in chapter 4. These notations are demonstrated in Figure 1. In these figures, numbers obtained from the given VTT data are in plain text, while numbers calculated by the author are in *italics*.
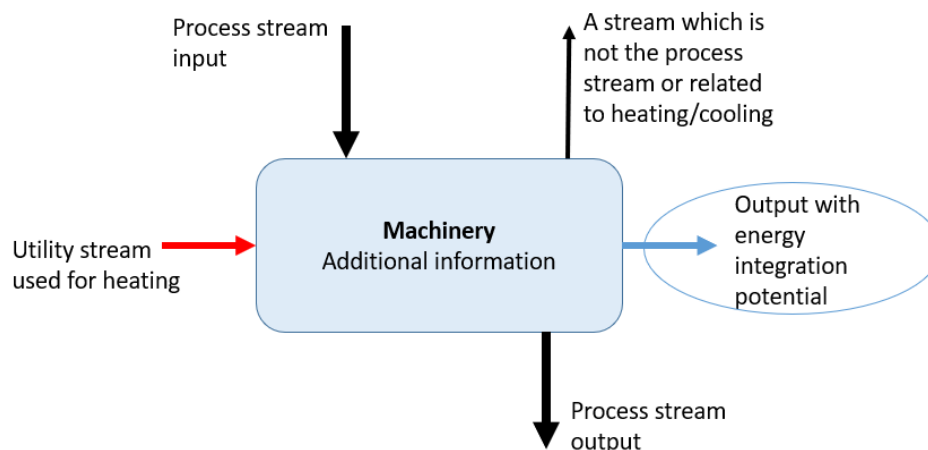
Figure 1 A description of the notation used in the figures of the study.

The approach temperatures of heat exchangers were agreed with P. Kangas of VTT to be between 5-10 °C, depending on the process. The process stream input and output

temperatures and mass flows are the same as in the given VTT data. Cooling waters were agreed to be of temperature 10 °C. The only exception is the cooling water of heat exchanger EA-201 the input temperature of which is assumed in this work to be 5 °C. In this case the original PI diagram states that the process stream is cooled from 80 °C to 5 °C using the cooling water of temperature 4 °C. This would require an approach temperature of "1" for the heat exchanger, which was considered in this work to be too effective. In addition, the process stream output was agreed to be 10 °C in this work, instead of the original 5 °C temperature, due to the approach temperature limit.
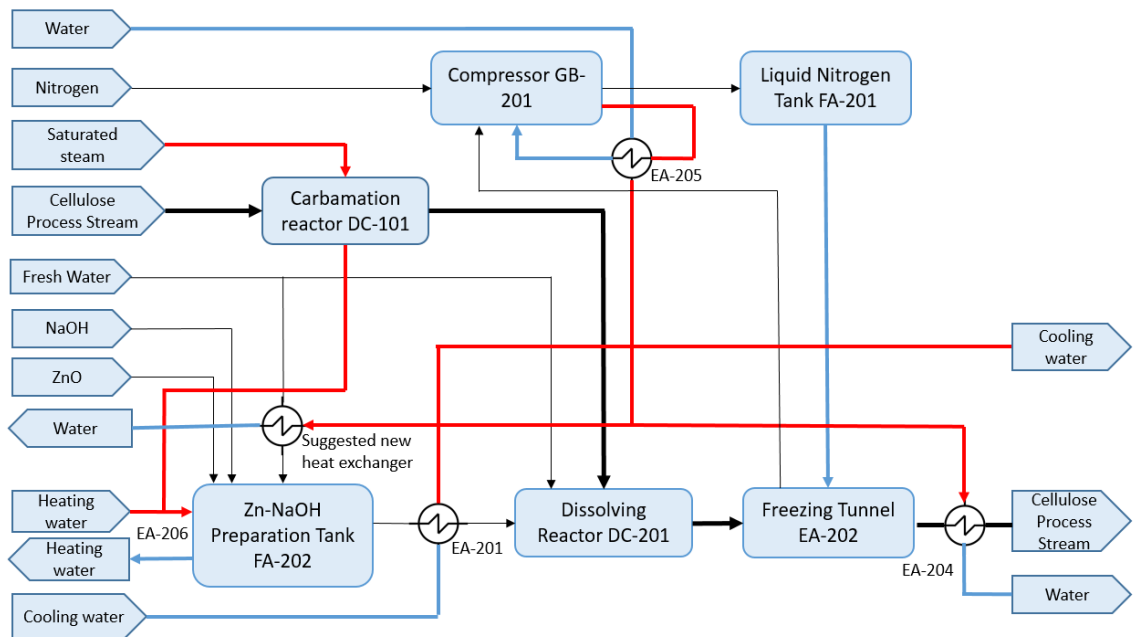
Figure 2 A flow chart of the process phases included in this report, including a part of the suggested energy integration solution (new heat exchanger and recycled nitrogen), described in chapter 4. The thick black arrows represent the process stream while blue and red arrows the cooling and heating utility streams, respectively. Thin black arrows are used for all other streams (ZnO, NaOH, N, fresh water).

2.1 Process Overview

This chapter gives a brief overview of the processes and main machinery included in this thesis. The included processes and the respective material flows are depicted in Figure

2 above. Firstly, the **process stream** (which in this phase is mostly pretreated cellulose pulp mixed with urea) is heated up to 133 °C in the **carbamation reactor** (DC-101) and mixed to produce cellulose carbamate. The carbamate is then mixed (and dissolved) in the **dissolving reactor** (DC-201) at 5 to 10 °C with a sodium zincate solution which is separately prepared in the **preparation tank** (FA-202) by combining and heating a mixture of sodium hydroxide (NaOH) and zinc oxide (ZnO). Finally, the pulp is cooled to -20 °C in the **freezing tunnel** (EA-202) to enhance the dissolution, and molten back to +4 °C. Cold water is generally used for cooling, except in the freezing tunnel where liquid nitrogen (at -196 °C) is required. Saturated steam and hot water is used for heating.

The heating and cooling of the process stream is produced with **heat exchangers,** which are devices used to transfer heat between materials. Shell and tube heat exchangers, for example, consist of a large shell which has a tube bundle inside; the heat is transferred between the fluids through the metal via conduction. The operation of one variation of such a heat exchanger, a straight-tube heat exchanger, is depicted in Picture 3. Another form of a shell and tube heat exchanger is the U-tube heat exchanger, in which the tube bundle is formed in a U-shape.
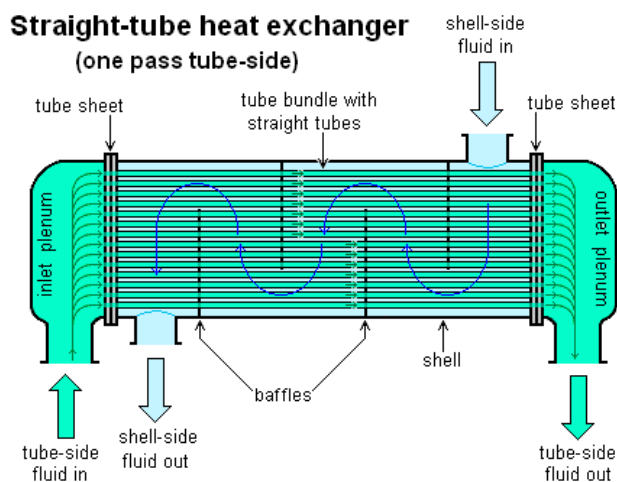
Figure 3 One variation of a shell and tube heat exchanger, the straight-tube model (H Padleckas created this image in March-April 2006 for use in article on shell-and-tube heat exchanger in Wikimedia. H Padleckas 17:42, 28 May 2006, UTC).

3 THE ENERGY BALANCES OF THE RELEVANT PROCESSES

In this chapter the energy balances of the relevant processes are calculated, along with (specific) heat capacities of the process stream at each phase. As a reminder, the numbers that are written in *italics* in the figures are calculated by the author, while all other numbers (in the figures) were provided by VTT. The calculated numbers are mostly required amounts of saturated steam, hot water or cold water used in heat exchangers to change the temperature of the process stream.

3.1 The Carbamation Reactor DC-101
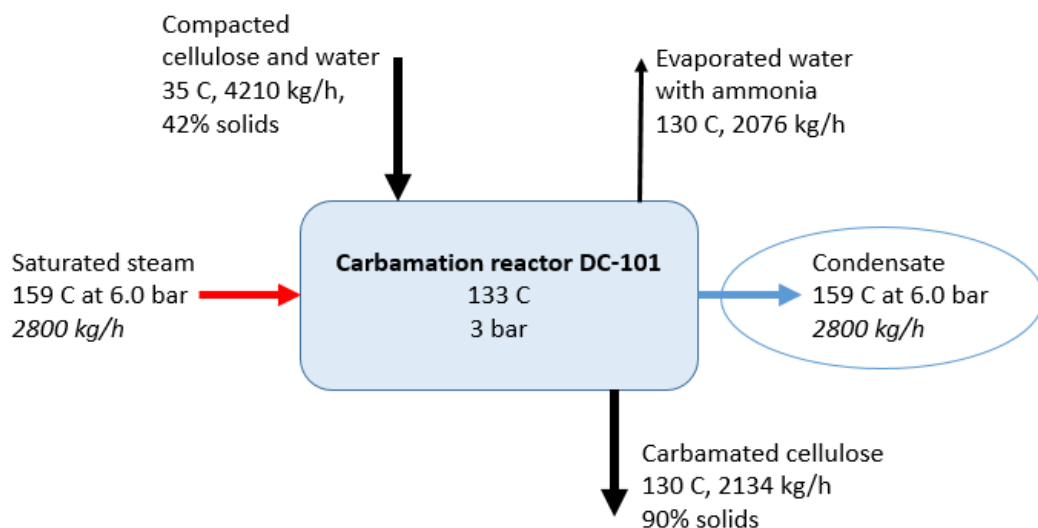
Figure 4 The inputs and outputs of the carbamation reactor DC-101.

In the carbamation reactor the pulp, consisting mainly of compacted cellulose, water and urea, is heated to its boiling point at a temperature of 133 °C and a pressure of 3 bar. Excess water is evaporated from the pulp, which increases its solids content from 42 % to 90 %. The evaporated mass flow, 2076 kg/h, consists mainly of water steam and ammonia but is for simplicity treated as pure water in the energy calculations.

The latent heat of water at this temperature is 2163.22 kJ/kg (Mills 1999, 931–933). The specific heat capacity of the process stream input was estimated as a weighted mean:

$c_p = w_1 c_{p1} + w_2 c_{p2} = 0.42*1.4 \text{ kJ/(kgC)} + 0.58*4.2 \text{ kJ/(kgC)} = \textbf{3.0 kJ/(kgC)}$,

where c_{p1} and c_{p2} are the specific heat capacities of cellulose and water, respectively. Using these numbers, the power needed to heat and vaporize the water within the pulp is

$P = m_1 c_p(T_f - T_i) + m_2 L = 4210 \text{ kg/h} * 3.0 \text{ kJ/(kgC)} * (133C - 35C) + 2076 \text{ kg/h} * 2163.22$ kJ/kg $= 5.7286 * 10^6$ kJ/h $= \textbf{5.8} * \textbf{10}^6 \textbf{ kJ/h = 1600 kW}$,

Where L = 2163.22 kJ/kg is the latent heat of water at 133 °C and m_1 = 4210 kg/h and m_2 = 2076 kg/h are the mass flows of the compacted cellulose input and the evaporated water, respectively.

The saturated steam (159 °C, 6 bar) of the utility stream has a latent heat of 2085.03 kJ/kg, so we get for its mass flow (knowing that the required power is 5.8 kJ/h):

$m = P/L = (5.8 * 10^6 \text{ kJ/h})/(2085.03 \text{ kJ/kg}) = \textbf{2782 kg/h = 2800 kg/h.}$

This corresponds to the mass flow, 2812 kg/h, in the carbamation process PI diagram.

To produce the saturated steam, let us assume (based on VTT data) that water is heated from +10 °C to +159 °C (at 6.0 bars) and vaporized. The efficiency of the steam preparation process is unknown, but the theoretical power minimum is

$P = m c_p T + m L = 2800*(4.25*149 + 2085.03) = 7611184 \text{ kJ/h} = 2114 \text{ kW} = \textbf{2100 kW.}$

This means about 2100 kW – 1600 kW = 500 kW more power is required to produce the saturated steam than is (ideally) required to heat the process stream. This is partly because the initial temperature of the utility stream is lower and the end temperature higher than that of the process stream.

3.1.1 Uncertainties and Notes

The analysis does not consider possible endothermic or exothermic reactions within the carbamation reactor. It is also uncertain whether the true specific heat capacity of the pulp cellulose mass is close enough to 1.4 kJ/(kgC), or if the total c_p can be approximated with a simple weighted mean. Finally, since the evaporated mass flow probably contains significant amounts of ammonia (with a lower specific heat capacity and latent heat), the "pure water" assumption might lead to exaggerated needs for evaporation energy.

3.2 The ZnO-NaOH Preparation Tank FA-202
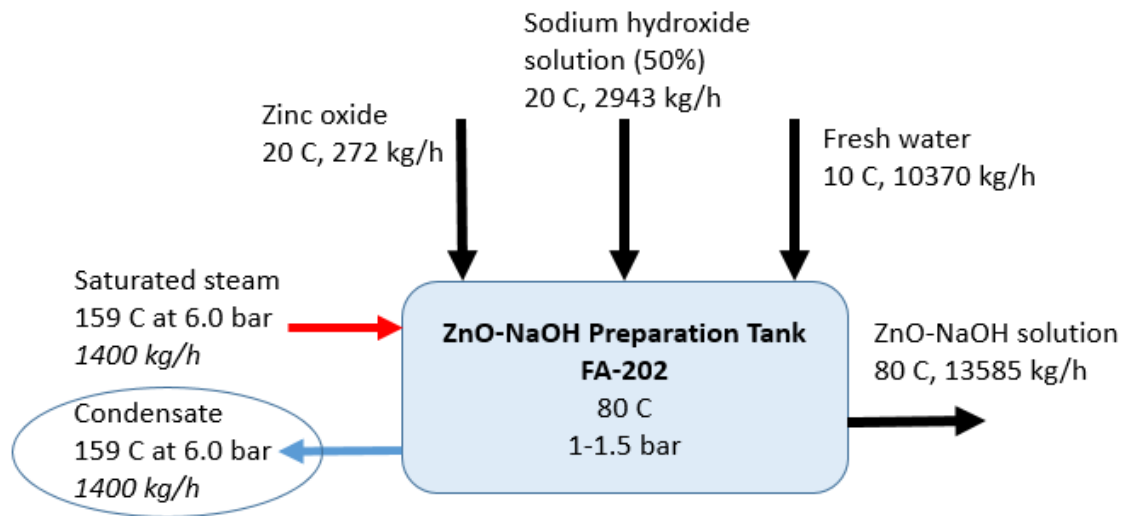
Figure 5 The inputs and outputs of the ZnO-NaOH Preparation Tank FA-202.

3.2.1 Heat Generated by Sodium Zincate Formation

In the ZnO-NaOH preparation tank, sodium hydroxide, water and zinc oxide react at 80 °C to form sodium zincate (note that the cellulose pulp itself does not take part in this phase). The reaction is

ZnO + H2O(l) + 2NaOH(l) = 2Na(+a) + Zn(OH)4(-2a).
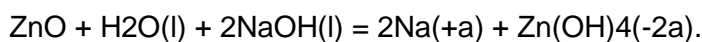
This is an exothermic process which produces 152 kJ of energy per mole of zinc oxide (Kangas, P. Email 11.10.2016). Let us calculate how much heat this releases to the process stream. The molar mass of zinc oxide is

M(ZnO) = M(Zn) + M(O) = 65.38 g/mol + 16.00 g/mol = 0.0814 kg/mol,

Where M(Zn) and M(O) are the molar masses on zinc and oxygen, respectively. This means that the amount

n = m/M = (272 kg/h)/(0.0814 kg/mol) = 3340 mol/h of ZnO

enters the preparation tank (the mass flow m was provided by VTT). The heat produced by the reaction is then:

P = 152 kJ/mol * 3340 mol/h = 507 900 kJ/h = **141 kW** (heat produced when sodium zincate is formed at 80 °C)**.**

That is, the exothermic nature of zodium zincate formation lowers the required amount of external heating power by 141 kW.

3.2.2 Specific heats of NaOH and ZnO

The following approximation was made for the specific heat of the ZnO-NaOH solution, since no ready data for sodium zincate solutions were found.

First, we find the specific heat for only the water and NaOH. The water and NaOH streams form a 2943 kg/h + 10370 kg/h = 13313 kg/h solution with 1471.5 kg/h of NaOH and 11841.5 kg/h of H_2O. The molar mass of NaOH is 0.039997 kg/mol, hence the solution contains

n = m/M = (1471.5 kg/h)/(0.039997 kg/mol) = 36790 mol/h of NaOH.

Therefore, the molality is (36790 mol/h)/(13313 kg/h) = 2.763 mol/kg. The specific heat capacity of the NaOH solution is then approximately 3.8 kJ/(kgC) between the temperatures of 50 °C and 80 °C (Schrödle et al. 2008).

The ZnO has a small lowering effect on the specific heat capacity of the ZnO-NaOH solution. The specific heat capacity of ZnO can be calculated with the equation

$c_p = 53.999 + 7.851*10^{-4} * T – 5.868*10^5 * T^{-2} – 127.50 \, T^{-1/2} + 1.9376*10^{-6} * T^2$,

where T is the temperature in kelvins (250…1800 K) (Madelung et al. 1999). The unit given by the equation is J/(molK), which is converted to kJ/(kgC) using the ZnO molar mass of M(ZnO) = 0.0814 kg/mol.

Using the above equation for c_p, the specific heat of ZnO at 25 °C is 0.504 kJ/(kgC) and at 80 °C it is 0.583 kJ/(kgC). The mean value during heating is approximately 0.54 kJ/(kgC), and the relative amount of ZnO in the solution is 2 wt-%. As a weighted mean, we then get the total specific heat capacity of

c_p = 0.98 * 3.8 kJ/(kgC) + 0.02 * 0.54 kJ/(kgC) = **3.7 kJ/(kgC)** (for the mixed NaOH-ZnO solution).

In short, in this chapter we have calculated the amount of pure NaOH streaming in the process (36790 mol/h) and its molality in the H_2O-NaOH mixture (2.763 mol/kg) as well as acknowledged the (minuscule) effect of ZnO to get the specific heat capacity of the NaOH-ZnO solution (3,7 kJ/(kgC)).

3.2.3 Heating Power and Mass Flow

Now the total power needed for heating the solution in the preparation tank can be calculated:

P = P(fresh water heated from 10 °C to 20 °C) + P(ZnO-NaOH solution heated from 20 °C to 80 °C) – P(heat generated by sodium zincate reaction)

= 10370 kg/h * 4.2 (kJ/(kgC)) * (20 °C - 10 °C) + 13585 kg/h * 3.7 kJ/(kgC) * (80 °C – 20 °C) – 507 900 kJ = 2.9435 $*10^6$ kJ/h = 2.9 * 10^6 kJ/h = **810 kW.**

From this, we get the mass flow of the saturated steam:

m = P/L = (2.9 * 10^6 kJ/h)/(2085.03 kJ/kg) = 1390 kg/h = **1400 kg/h.**

The dissolving PI diagram states a mass flow of 1634 kg/h, which is slightly higher. However, the process described in the PI diagram uses fresh water of temperature 4 °C. If the previous calculations used 4 °C water and estimated the specific heat capacity of the mixed solution to be 3.8 kJ/(kg°C) instead of 3.7 kJ/(kg°C), the utility stream mass flow would round up to 1600 kg/h. Producing this steam mass flow from +10 °C water requires a minimum heating power of

1400*4.2*149 + 1400*2085.03 = 3795162 kJ/h = 1054 kW = **1.0 * 10^3 kW**.

In short, we calculated the power needed for heating the solution in preparation tank FA-202 (810 kW) and the mass flow of required saturated steam (1400 kg/h) to find the minimum heating power required to produce this steam flow (1,0 * 10^3 kW).

3.2.4 Notes

This treatment assumes that the specific heat capacity of a solution can be estimated as a weighted mean of the specific heat capacities of its constituents. This is generally

considered acceptable with liquid mixtures (Teja 1983) and was accepted as a reasonable estimate by VTT (Kangas, P. Email 11.10.2016).

3.3 Heat Exchanger EA-201
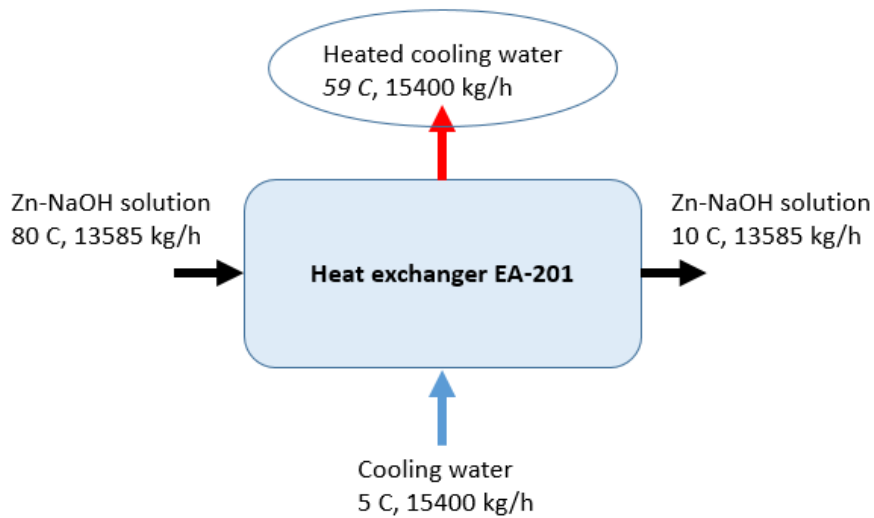
Figure 6 The inputs and outputs of the heat exchanger EA-201.

The heat exchanger EA-201 cools down the sodium zincate solution so that it can be mixed with the cellulose pulp in the dissolving reactor (after carbamation but before the freezing tunnel). The output temperature of the cooling water can be calculated using the equation

$$M_H c_{pH}(T_{iH}-T_{oH}) = m_C c_{pC}(T_{oC}-T_{iC}) \rightarrow T_{oC} = T_{iC} + [m_H c_{pH}(T_{iH}-T_{oH})]/(m_C c_{pC})$$

$$= 5 + (13585*3.7*70)/(15400*4.2) = 59.4 \ °C = 59 \ °C,$$

where the previously estimated specific heat capacity 3.7 kJ/(kgC) was used for the Zn-NaOH solution (and units were left out of the intermediate steps to simplify the equation).

3.4 The Dissolving Reactor DC-201

The dissolving phase does not involve any changes in temperature. The carbamated cellulose pulp and the ZnO-NaOH solution are just mixed together, after which the mixture continues towards the freezing tunnel. However, this phase requires a slight alteration to the PI diagrams provided by VTT. In these diagrams the reactions in the dissolving reactor occur at 5 °C, with both the fresh water and ZnO-NaOH solution inputs at the same 5 °C temperature. In this work both inputs are at the temperature of 10 °C, due to limitations of heat exchanger approach temperatures and cool water temperatures (which were both provided by VTT for this study but differ from the assumptions made when constructing the PI diagrams). It is uncertain whether a 10 °C temperature will negatively affect the process. If the original 5 °C temperature is essential, colder water and more capable heat exchangers may be required.

3.5 The Freezing Tunnel EA-202
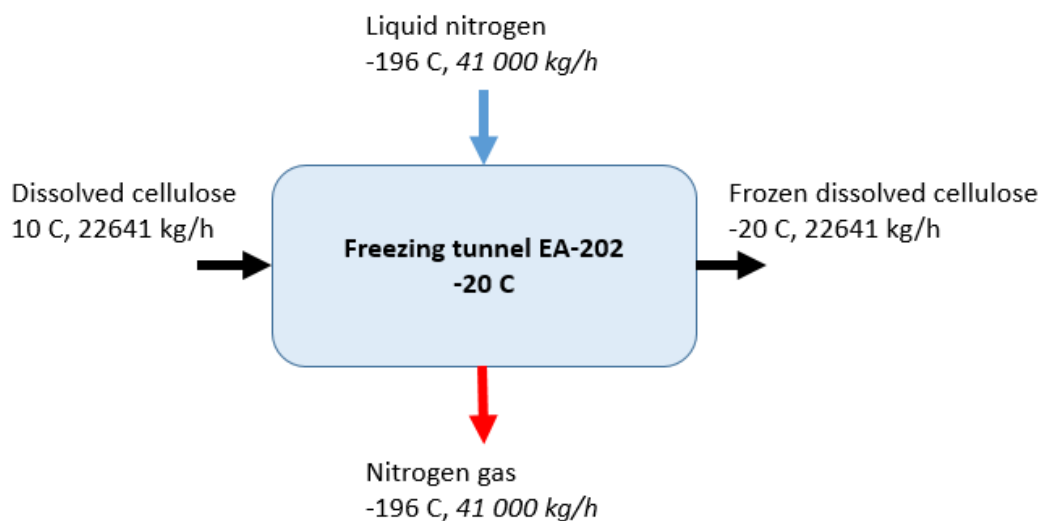
Figure 7 The inputs and outputs of the freezing tunnel EA-202.

As part of the carbamation process, the dissolved cellulose is frozen and cooled down to -20 °C in the freezing tunnel EA-202.

3.5.1 Specific Heat Capacities

Here the process stream input is a solution of ZnO (272 kg/h), NaOH (1471.5 kg/h), H_2O (18976.5 kg/h) and cellulose (1921 kg/h) with a total mass flow of m_{tot} = 22641 kg/h. These numbers are calculated assuming all the NaOH and ZnO from the preparation tank FA-202 are still in the solution and that the carbamated cellulose flow is 90 % of cellulose and 10 % of water (because of the drying at the carbamation reactor DC-101).

To calculate the specific heat capacity of the process stream input entering the freezing tunnel, the H_2O and NaOH are considered a separate solution (mass flow 20448 kg/h) whose c_p is estimated using data by Schrödle et al. (2008). Remembering that there are 36790 mol/h of NaOH (see chapter 3.2.2), we get a molality of (36790 mol/h)/(20448 kg/h) = 1.799 mol/kg for the NaOH-H_2O solution, which approximately corresponds to the specific heat capacity c_p = **3.8 kJ/(kg°C).** This could not be directly retrieved from the data of Schrödle et al. (2008) since their lowest considered temperature is at +50 °C but will serve as an extrapolated approximation.

As in Chapter 3.2.2., the specific heat capacity of ZnO is acquired using the equation

$c_{p, ZnO}$ = 53.999 + 7.851*10^{-4} * T – 5.868*10^5 * T^{-2} – 127.50 $T^{-1/2}$ + 1.9376*10^{-6} * T^2.

At +10 °C, c_p = 0.49 kJ/(kgC) and at -20 °C, c_p = 0.46 kJ/(kgC). The value **c_p = 0.48 kJ/(kg°C)** will be used in calculations (although ZnO has almost no effect within the limits of calculation accuracy and could also be ignored).

The total specific heat capacity of the process stream input (between temperatures +10 °C and -2.6 °C) is calculated as the weighted mean of the NaOH-H_2O solution (with specific heat capacity c_1 and mass flow m_1), ZnO (c_2, m_2) and cellulose (c_3, m_3):

$c_{p, tot}$ = (c_1m_1 + c_2m_2 + c_3m_3)/m_{tot} = (3.8*20448 + 0.48*272 + 1.4*1921)/22641 = 3.556 kJ/(kg°C) = **3.6 kJ/(kg°C)** (specific heat capacity of process stream between +10 °C and -2.6 °C)**.**

Between approximately -2.6 °C and -20 °C the process stream is frozen. The freezing temperature of -2.6 °C is an estimation obtained from the PI diagrams, which state that the eventual melting of the stream is in the VTT PI diagrams executed in two heat exchangers: EA-203 and EA-204, respectively. (Due to lack of space, in Figure 1 only

EA-204 is shown.) First, the stream is heated to -2.6 °C and molten, and then from -2.6 °C to 5 °C.

Due to lack of data on the specific heat capacity of pure NaOH, the same value as for cellulose, 1.4 kJ/(kg°C), was used here. This will not have a significant impact on the accuracy of the energy calculations since the concentration of NaOH is small and most of the applied energy is needed to freeze the ice (the enthalpy of fusion for water is L = -333.55 kJ/kg). The c_p for ice in this temperature range is approximately 2.0 kJ/(kg°C), and so the weighted mean of specific heat capacities of ice, cellulose, NaOH and ZnO is

c_p = (18976*2.0 (ice) + 1921*1.4 (cellulose) + 1471.5*1.4 (NaOH) + 272*0.48 (ZnO))/22641= 1.891 kJ/(kg°C) = **1.9 kJ/(kg°C)** (estimated specific heat capacity of the frozen process stream)**.**

3.5.2 The Amount of Liquid Nitrogen Required

We are now ready to calculate how much heat is transferred when the process stream is cooled from +10 °C to -20 °C. Firstly, the heat required for the phase change from liquid to solid is the mass flow of water times its enthalpy of fusion:

18976.5 kg/h * 333.55 kJ/kg = 6329611 kJ/h = **1758 kW** (power needed to freeze the water).

The power needed for the temperature change from +10 °C to -20 °C, excluding the freezing, is

P = P(cooling from +10 °C to -2.6 °C) + P(cooling from -2.6 °C to -20 °C) = 22641*3.6*12.6 + 22641*1.9*17.4 = 1775507 kJ/h = **493.2 kW = 5.0 * 10^2 kW** (heat exchanged when cooling the process stream, freezing not included)**.**

Therefore, the total heat exchanged is

P_{tot} = 6329611 kJ/h + 1775507 kJ/h = 8105118 kJ/h = 8.1 * 10^6 kJ/h = 2251.4 kW **= 2300 kW** (the sum of the powers needed for cooling and freezing the process stream with a total mass flow of 22641 kg/h).

The cooling is achieved by addition of liquid nitrogen under a pressure of 1 bar and temperature of -196 °C. The latent heat of nitrogen in these conditions is L = 199 kJ/kg. If all the heat from the process stream is assumed to only vaporize nitrogen (that is, not to raise its temperature), the required mass flow is

$m_N = P_{tot}/L = (8105118 \text{ kJ/h})/(199 \text{ kJ/kg}) = 40729 \text{ kg/h} = $ **41 000 kg/h** $ = 11 \text{ kg/s}$.

It should be noted that if 41 000 kg/h of gaseous nitrogen streams to the compressor input at 15 °C and 1.0 bar. Its volume flow rate is approximately 9.9 m^3/s which could cause problems with small pipe sizes (in addition to the other problems, considered further in the following chapters, caused by such a large required amount).

If in addition to being vaporized the nitrogen temperature increases, the needed total power can be expressed as

$P_{tot} = m_N c_{p,N}(T_f - T_i) + m_N L = m_N[c_{p,N}(T_f - T_i) + L] \rightarrow m_N = P_{tot}/[c_{p,N}*(T_f - T_i) + L]$,

where m_n is the mass flow of nitrogen, $c_{p,N}$ the mean specific heat capacity of nitrogen and T_f and T_i are the final and initial temperatures of the nitrogen, respectively. In the temperature range from -192 °C to -30 °C, the mean specific heat of nitrogen is approximately 1.05 kJ/(kgC) (Mills 1999, 931–933). If the nitrogen could be vaporized and heated to -30 C, increasing its temperature by 166 °C, the required mass flow would be

$m_N = P_{tot}/[c_{p,N}*(T_f - T_i) + L] = (8105118)/(1.05 * 166 + 199) = 21 712 \text{ kg/h} = $ **22 000 kg/h** (liquid nitrogen required when gas temperature rises from -196 °C to -30 °C)**.**

This result would correspond with the mass flow of the PI diagram and previous estimations by VTT. It is improbable that the heating can be this efficient. However, it is noteworthy that by introducing heating of the nitrogen gas to the process, the mass flow can theoretically be almost halved. If the nitrogen gas temperature rises to -50 °C instead, which could be a more reasonable goal, only **23 000 kg/h** of liquid nitrogen is required.

3.6 The Liquid Nitrogen Compressor

The power required by the compressor system was estimated based on simple thermodynamic laws and perhaps unrealistic assumptions. Estimating realistic power

levels and most efficient liquefaction methods are beyond the scope of this work, though possible efficiencies of different alternatives are shortly considered in Chapter 3.6.3. For example, pressure, mass flow, cycle type, and type of compression (isentropic, isothermal, etc.) affect the liquefaction process.

3.6.1 The System Assumptions of an Ideal Compressor

To calculate an ideal minimum for nitrogen liquefaction power requirements, it was assumed (based on an email conversation with P. Kangas of VTT on 11 October 2016) that the compressor system consists of an electric motor with the efficiency of 95 % which gives power to a compressor with the efficiency of 80 %. That is, the compressor works to the nitrogen with 0.80*0.95*100% = 76 % of the total electric power P_{tot} used. The unexploitable 5% from the motor escapes as heat to the atmosphere, while the compressor's unexploitable 95 % - 87 % = 19 %, caused by friction inside the machinery, cannot escape and is transferred to the nitrogen.

The heat Q_{LN} (=0.76*P_{tot}) generated by liquid nitrogen generation and the compressor operation is

$$Q_{LN} = m_N c_{p,N}(T_i - T_f) + m_N L + P_{friction},$$

where m_N is the mass flow, $c_{p,N}$ the specific heat capacity, T_i the initial temperature, T_f the final temperature, L the latent heat and $P_{friction}$ = 0.19*P_{tot} the heat generated by the compressor. It is noteworthy that $P_{friction}$ causes a 19 % efficiency loss twice, first as friction and then as extra heat in the nitrogen gas:

$$Q_{LN} = 0.76*P_{tot} = m_N c_{p,N}(T_i - T_f) + m_N L + 0.19*P_{tot} \rightarrow 0.57*P_{tot} = m_N c_{p,N}(T_i - T_f) + m_N L.$$

This means **the actual efficiency of the system is considered in this work to be 57 %.** In contrast, previous data provided by VTT had apparently assumed that the friction heat generated by the compressor escapes to the environment as well as that 80 % is the efficiency of the whole compressor system (including possible electric motors). It should again be emphasized, however, that even the 57 % efficiency is unattainable in an actual liquefaction process, where the efficiencies of generally used methods can be between 7 – 14 % (as was discovered after most of the work for this thesis was already completed), and actually attainable efficiencies need to be addressed in further studies.

3.6.2 Compressor Cooling Waters (41000 kg/h Nitrogen Flow)

Heated cooling water
80 C, 120 000 kg/h

Nitrogen gas
15 C, 41 000 kg/h
1 bar

Compressor(s) GB-201

Liquid nitrogen
-196 C, 41 000 kg/h

Cooling water
20 C, 120 000 kg/h
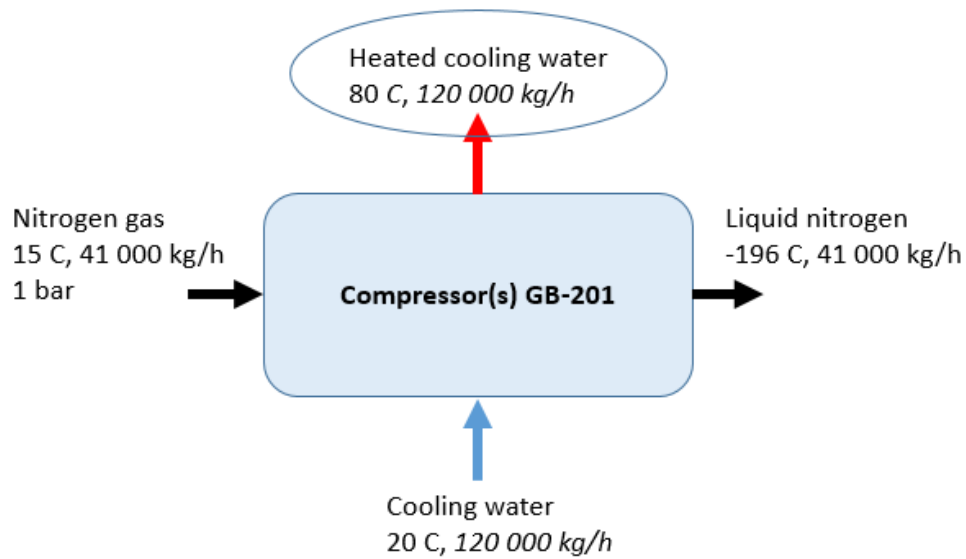
Figure 8 Inputs and outputs of the compressor(s) GB-201.

The nitrogen flow of 41 000 kg/h corresponds to the situation in which the gaseous nitrogen does not participate in the cooling of the cellulose process stream. The compressor system is treated as a lossless heat exchanger so the heat Q_{LN} is fully transmitted to the compressor cooling agent. For a nitrogen temperature decrease of $T_f - T_i = 211$ C, we get a total power of

$P_{tot} = [m_N c_{p,N}(T_f - T_i) + m_n L]/0.57 = (41000*1.05*211 + 41000*199)/0.57 = 3.025 * 10^7$ kJ/h = 8403 kW = **8400 kW.**

Table 1 Ideal-Work Requirements for Liquefaction of Gases Beginning at 194 K and Atmospheric Pressure (Walker, G., 285).

Table 6.2. Ideal-Work Requirements for Liquefaction of Gases Beginning at 294 K and Atmospheric Pressure[a]

Gas	Normal boiling point (K)	Ideal work of liquefaction (kJ/kg)
Helium, He[4]	4.2	6650
Hydrogen, H_2	20.3	11,594
Neon, Ne	27.1	1291
Nitrogen, N_2	77.3	742
Air	78.7	710
Carbon monoxide, CO	81.6	742
Fluorine, F_2	85.3	479
Argon, A	87.2	465
Oxygen, O_2	90.2	613
Methane, CH_4	111.6	1044
Carbon tetrafluoride, CF_4	145	171
Ethane, C_2H_6	184.5	330
Ammonia, NH_3	239.1	232

[a] After Barron (1966).

Interestingly, this corresponds to the "ideal work of liquefaction" in Table 1: 742*41000 = 3.04 * 10^7 kJ = 8450 kW. Based on this, and the discussion in the following chapter, the power calculated (and used in the rest of this work) is a realistically unattainable minimum power.
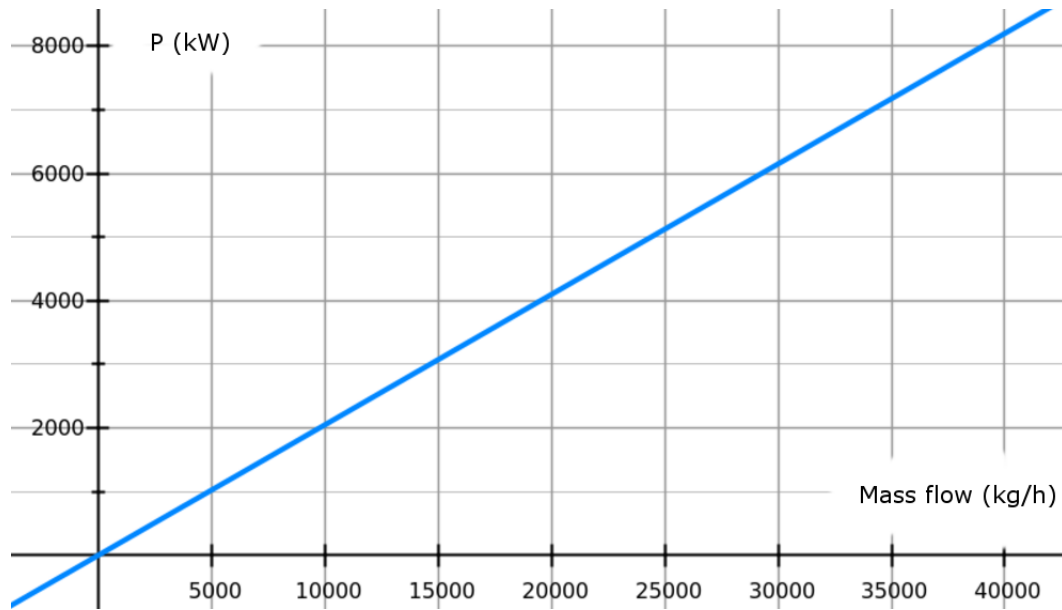
Figure 9 Total electric energy (in kW) needed to produce liquid nitrogen as function of mass flow (kg/h). Efficiency 57 % (corresponds to ideal liquefaction). Graph made with https://graphsketch.com/ .

The largeness of this value, when compared to previous estimations of VTT, is due to the assumptions that only the latent heat of liquid nitrogen is used in cooling, which raised the required mass flows. In addition, the compressor efficiency was estimated to be 57 %. If the cooling agent is heated from +20 °C to +80 °C (VTT data), the required mass flow for this power is

$m = P_{tot}/(c_p*(T_f - T_i)) = 30250087/(4.18*60) =$ **120614 kg/h = 120 000 kg/h.**

This is a mass flow of 34 kg/s.
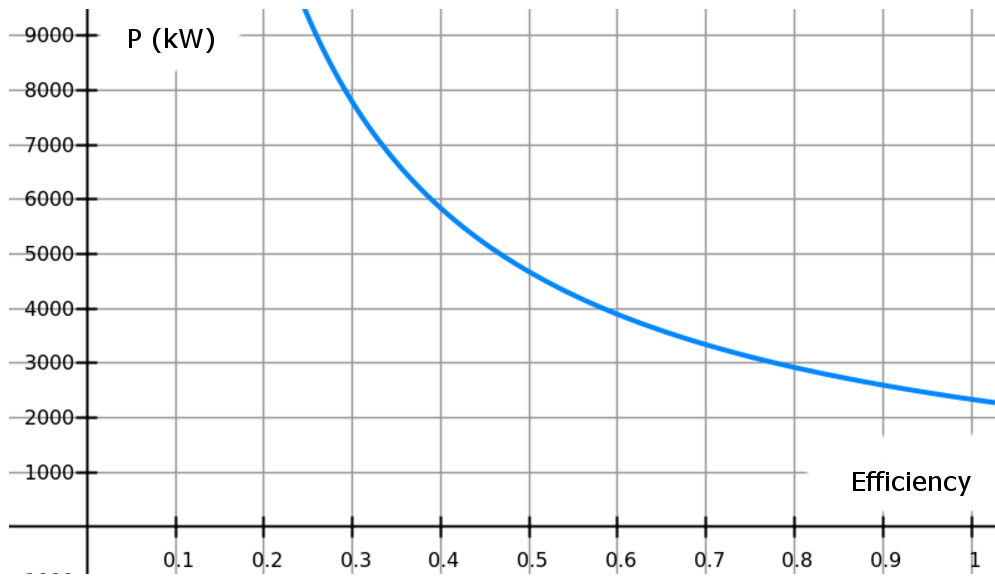
Figure 10 Total electric power needed (in kW) to produce 20 000 kg/h of liquid nitrogen as function of efficiency (from 0 to 1). Graph made with https://graphsketch.com/ .
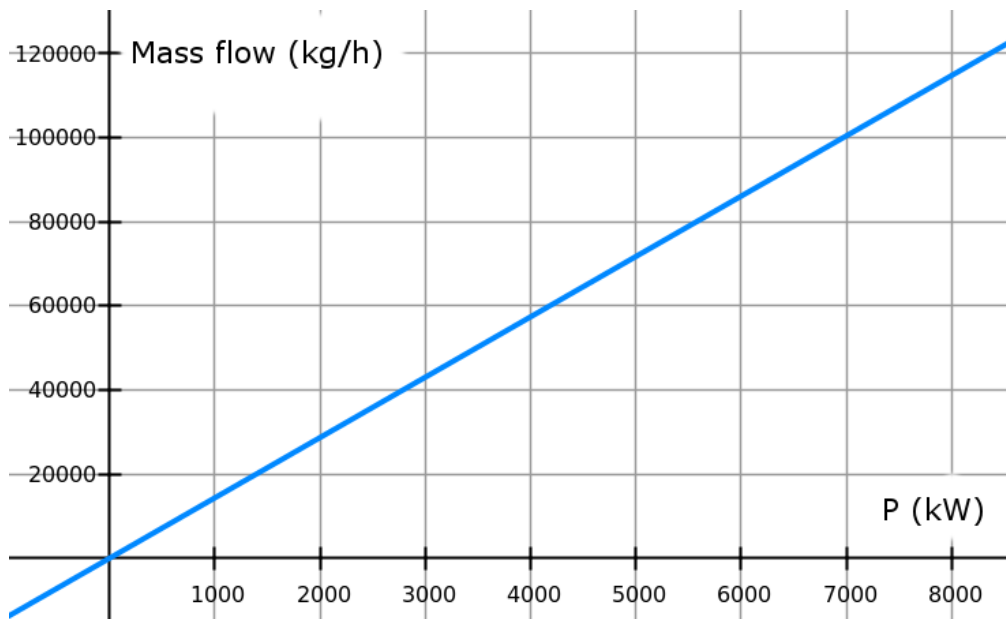
Figure 11 Mass flow of cooling agent (kg/h) as function of total electric power (kW). Graph made with https://graphsketch.com/ .

3.6.3 Discussion about Compression Efficiency

The values of the previous chapter were used to design energy integration solutions in this work. However, some online references gave even still significantly larger estimations for needed power. Two possible methods of gas liquefaction, the Linde-Hampson cycle and the Claude cycle, are available in the SmoWeb online tool for calculating nitrogen liquefaction powers (SmoWeb Liquefaction Cycles). For both cycles, a ready example for nitrogen liquefaction is available (that fills all the boxes with suggested values). The main differences between the cycles is that the Linde-Hampson cycle is simple, but ineffective and requires large pressures (preferably 100 bar or more), while the Claude cycle is more complicated but efficient and works with lower pressures (beginning from under 10 bars).

The ready example setups give nitrogen liquefaction energies of 6130 kJ/kg and 2937 kJ/kg for the Linde-Hampson and Claude cycles, respectively. For a nitrogen mass flow of **41 000 kg/h**, these give a power requirement range of **33.4 MW - 69,8 MW**, which would correspond to an efficiency range of 7 % - 14 % in the calculations of the previous chapter (as opposed to the 57 % efficiency used). In these cases, assuming a linear connection, the amount of required cooling water would be **480 000 kg/h – 1.0 * 10^6 kg/h.**

In the context of energy integration these are highly troubling numbers because the conclusion is that only a tiny fraction of the total energy required can be circulated around the system. The compression process would produce massive amounts of heat in a relatively useless flow of 70 °C water. We will see in the following chapters that even the 8.4 MW compressor power (calculated in Chapter 3.6.1) will leave a large amount of surplus water in 60 °C.

3.7 Heat Exchanger EA-205
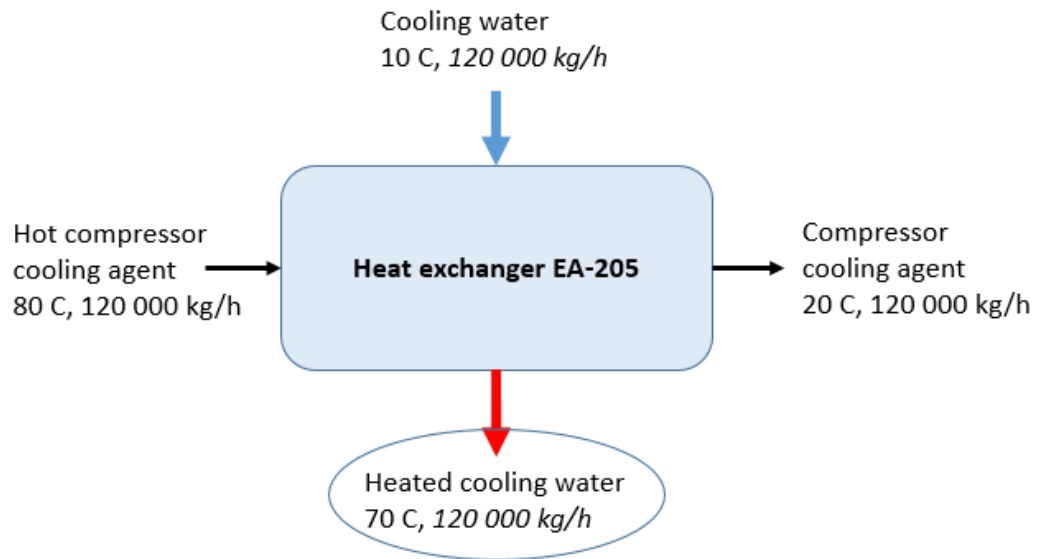
Figure 12 The inputs and outputs of the heat exchanger EA-205.

This is a shell and tube heat exchanger which cools the cooling agent of the compressor from +80 °C to +20 °C, enabling its recirculation. With an approach temperature of 10 °C, the cooling water temperature changes from 10 °C to 70 °C. In the idealized nitrogen compression case the mass flow of the cooling water is

m_c = ($m_{HC_{pH}}$ * 60)/(c_{pC} * 60) = (120614 * 4.18 * 60)/(4.2 * 60) = 120 040 kg/h ≈ **120 000 kg/h.**

3.8 Heat Exchangers EA-203 and EA-204

The (shell and tube) heat exchangers EA-203 and EA-204 heat the frozen cellulose solution from -20 °C to +5 °C. Their combined exchanged heat can be evaluated as the total heat exchanged in the freezing tunnel minus the heat of heating from +5 °C to +10 °C:

P(EA-203 and EA-204) = P(freezing tunnel total heat) – P(heating the pulp from +5 °C to +10 °C) = 8105118 kJ/h – 22641 kJ/h * 3.6 kJ/(kg°C) * 5 C = 7697580 kJ/h = 2138.2 kW ≈ **2100 kW.**

Here using two significant digits in rounding the results is misleading. If only the heat to raise the temperature from +5 °C to +10 °C is calculated, we get 22641 kJ/h * 3.6 kJ/(kg°C) * 5 °C = 407 538 kJ/h = 113.2 kW ≈ 110 kW.

These heat exchangers are some of the primary targets of energy integration in this work since they require the most heat and are compatible in terms of approach temperatures with all the other condensates and heated cooling waters.

4 ENERGY INTEGRATION ALTERNATIVES

4.1 Overview

Sources of heat:

1) Condensate of the carbamation reactor DC-101: 2800 kg/h of 159 °C water.
2) Condensate of the heat exchanger EA-206 (at the Zn-NaOH preparation tank FA-202): 1400 kg/h of 159 °C water.
3) Heated cooling water from heat exchanger EA-201 (between the Zn-NaOH preparation tank FA-202 and the dissolving reactor DC-201): 15400 kg/h of 59 °C water.
4) Heated cooling water from heat exchanger EA-205 (which cools the compressor cooling water): 70 °C, mass flow depends on the required amount of liquid nitrogen and the liquefaction efficiency but is at least 120 000 kg/h.

Possible targets (with suggested heat sources after the colon):

1) Heat exchangers EA-203 and EA-204 (melting the process stream after the freezing tunnel): source 4.
2) Fresh water pipe to the Zn-NaOH preparation tank, and the tank itself (EA-206): sources 1, 2 and 4.
3) Preheated water for saturated steam production (mainly to the carbamation reactor DC-101): sources 3 and 4.
4) Other heat-requiring process phases that are not treated in this work (before the carbamation reactor DC-101 or after the heat exchangers EA-203 and EA-204): source 4.

Nitrogen gas at -196 °C also carries considerable cooling potential. For example, we set the energy required to change its temperature to be of equal size as its latent heat,

$$[m*c_p*(T_f - T_i)]/mL = 1, \text{ then } T_f - T_i = 199/1.05 = 190 \text{ °C},$$

where L = 199 kJ/kg is the latent heat of nitrogen and c_p = 1.05 kJ/(kg°C) is its specific heat. This means that raising the temperature of an arbitrary amount of nitrogen gas by 190 °C requires as much heat as boiling the said amount. However, since the nitrogen expands rapidly when vaporized and has poor thermal conductivity, effectively using its

gas phase as a coolant may prove difficult. That is why one potential solution is to direct the cold nitrogen gas back to the compressor for reliquefaction without losing significant amounts of heat during the way. However, the possibly impure nitrogen would perhaps have to be pretreated or filtered before reliquefaction, which would also require energy (according to Kangas, P. Email 7.10.2016).

4.2 Suggested Ways to Circulate Heat
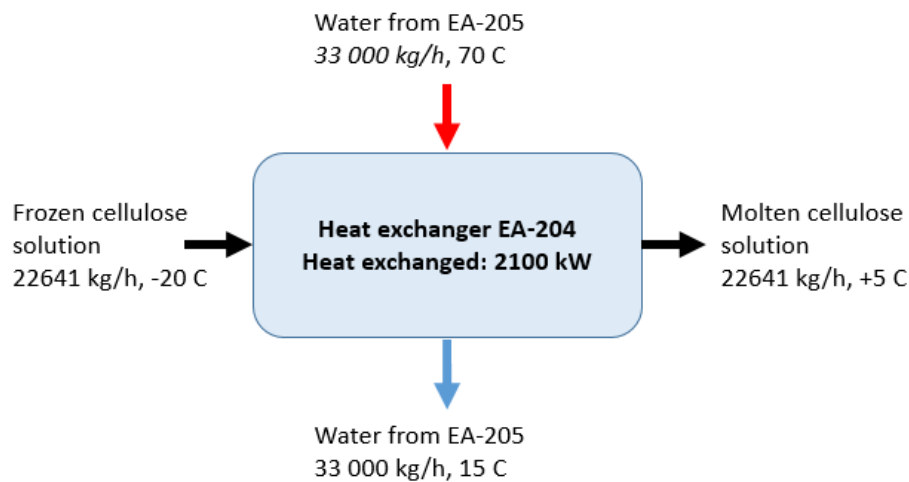
Figure 13 Stream 1 from heat exchanger EA-205 melts the cellulose solution with a mass flow of 33 000 kg/h (see below).

The most energy intensive stream of the whole carbamation process is the heated cooling water output from heat exchanger EA-205 (see chapter 3.7), with mass flow of at least 120 000 kg/h and temperature of 70 °C. The stream could be divided into at least two parts. Let us call them stream 1 and stream 2. To melt the frozen pulp (with mass flow 22641 kg/h) after the freezing tunnel and achieve the temperature change from -20 °C to 5 °C, P = 7697580 kJ/h = 2100 kW of heat power is needed (as calculated in Chapter 3.8.). Assuming the heat exchanger EA-204 has an approach temperature of 10 °C, stream 1 undergoes a temperature change from +70 °C to +15 °C degrees. The required mass flow is then

m = Q/(cT) = 7697580/(4.2*55) = 33323 kg/h **= 33 000 kg/h,**

where T is the temperature difference between the stream 1 input and output. This would remove the need for another heat exchanger (EA-203) and use of saturated steam altogether.

The rest of the water, stream 2, could continue to preheat the fresh water heading towards the ZnO-NaOH preparation tank. In this case a new heat exchanger would be installed near the tank and the heating would take place in two phases. In addition to stream 2, additional heating will be required and could be provided partly by the output condensate of the carbamation reactor DC-101. As was calculated before in Chapter 3.2.3, **810 kW** is needed to heat the ZnO-NaOH solution from 10 °C to 80 °C. Combining the condensate from DC-101 with 1400 kg/h of water from an external source at 159 C constitutes a mass flow of 2800 + 1400 = 4200 kg/h and a temperature of 159 C at 6 bar. If this flow was cooled down to 90 C (assuming again a 10 °C approach temperature), it would release 4.28*4200*69 = 1240344 kJ/h = 344 kW = **340 kW** of heat power. This would raise the temperature of the water by (1240344 kJ)/(10370 kg/h * 4.2) = 28.48 °C = **28 C**. The needed heat power from stream 2 would then be 3048780 kJ/h – 1240344 kJ/h = 1808436 kJ/h = 502.34 kW = **500 kW**. This would raise the water temperature by 1808436/(10370*4.2) = 41.52 C **= 42 °C.** That is, stream 2 will raise the water temperature from 10 °C to 52 °C and the condensate mixture raises it after that from 52 °C to 80 °C. We can now calculate the flow for stream 2:

m_2 = $(m_1*c_{p1}*T_1)/(c_{p2}*T_2)$ = (10370*4.2*42)/(4.2*10) = 43554 kg/h = **44 000 kg/h.**

Fresh water
10 C, 10370 kg/h

Stream 2 from heat
exchanger EA-205.
60 C, 44 000 kg/h

**Heat exchanger added to the
fresh water pipe before the
Zn-NaOH preparation tank.**

Stream 2 from heat
exchanger EA-205.
70 C, 44 000 kg/h

Fresh water
52 C, 10370 kg/h

Heating water and
DC-101 condensate
159 C, 4200 kg/h

**Zn-NaOH Preparation Tank
FA-202
80 C**
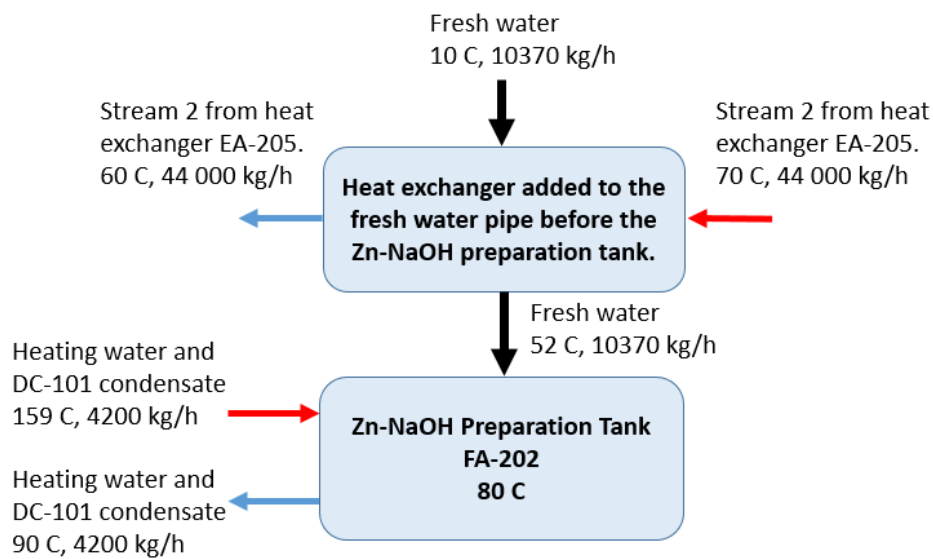
Heating water and
DC-101 condensate
90 C, 4200 kg/h

Figure 14 Using "stream 2" from heat exchanger EA-205 and the condensate from the carbamation reactor DC-101 combined with 1400 kg/h of additional (liquid) water to provide necessary heat for sodium zincate formation.

The conclusion is that heating processes at the Zn-NaOH preparation tank will need no saturated steam at heat exchanger EA-206. The external heating consists of 1400 kg/h of 159 C liquid water instead of saturated steam with same mass flow and temperature. Therefore, the saved amount of energy is the latent heat of this water:

mL = 1400 * 2085.03 = 2919042 kJ/h = 810 kW.

4.3 Unused Streams

- Even after streams 1 and 2 are used, there is still a "stream 3" from EA-205 at 70 C and with a minimum flow of 43 000 kg/h.
- The heated cooling water from EA-201 with flow 15400 kg/h and temperature of 59 C.
- The heating water output of the Zn-NaOH preparation tank with flow 4200 kg/h and temperature of 90 C.

Small savings would come from using some of these waters for preheating the water for saturated steam production. For example, at the carbamation reactor 2800 kg/h of 159 °C steam was produced from 10 °C water, requiring 2100 kW of energy. Using preheated

water at 70 °C would save 2800*4.2*60 = 705600 kJ/h = 196 kW = **200 kW**, which is almost 10 %.

The most effective way to reduce the amount of surplus warm streams would be to reduce the amount of liquid nitrogen required at the freezing tunnel, either by more effective heat transfer or reduced water content in the dissolved cellulose. The latter possibility will be discussed in the next chapter.

5 WATER CONCENTRATIONS AND REQUIRED FREEZING POWER

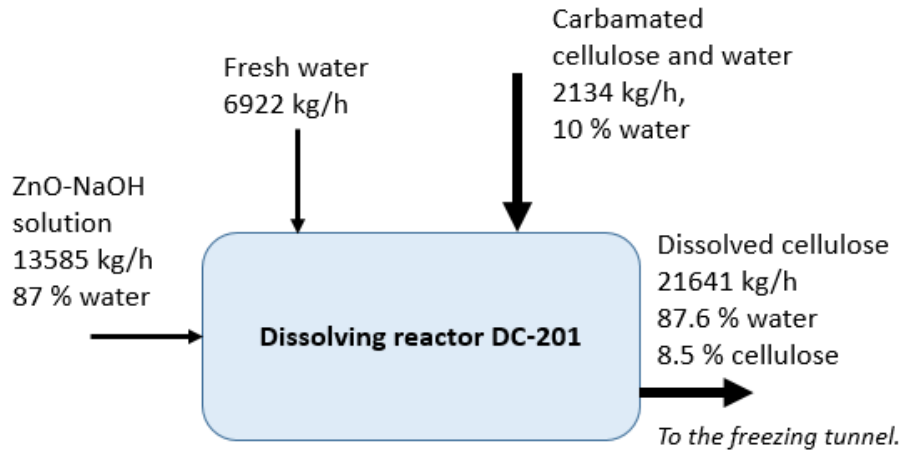## 5.1 Further Increasing the Solids Content of the Pulp

Figure 15 The original inputs and outputs of the dissolving reactor DC-201, focusing on water content (VTT).

Increasing the solids content of the dissolved cellulose before it enters the freezing tunnel could greatly lower the energy requirements of the following cooling and melting stages, and specifically the required mass flow of liquid nitrogen. The dissolving reactor DC-201 is the last step before the freezing phase. Here the main process stream is mixed with additional water and the ZnO-NaOH solution which was made in preparation tank FA-202. The term "solids content" refers to the cellulose mass flow in the process stream. In this work the effects on cooling/melting energy and liquid nitrogen mass flows will be considered with solids contents of 15 wt-%, 22 wt-% and 30 wt-% (the original solids content being 8.5 wt-%). These percentages were suggested by VTT.

Increasing the solids concentration is completed in this work by decreasing water mass flows while keeping the cellulose, NaOH and ZnO mass flows constant at 1921 kg/h, 1494 kg/h and 272 kg/h, respectively. More study is needed to verify at which stages the volume of water could be reduced, and how different water concentrations would affect, for example, the dissolution process at the dissolving reactor DC-201 or the preparation of the sodium zincate solution. If DC-201 requires the current concentration of water, an

additional drying phase before the freezing tunnel might still be more energy-efficient than freezing all the water.
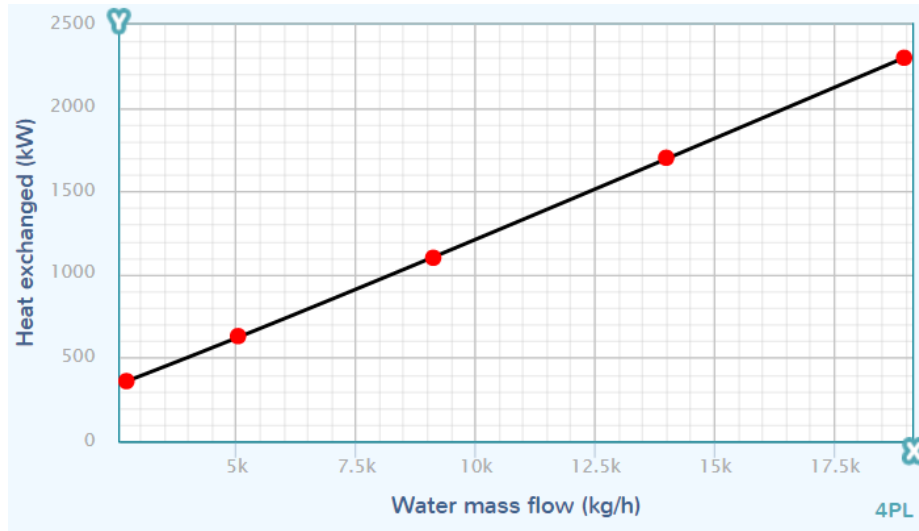
5.2 Effects of Water Mass Flow on Energy Requirements

Figure 16 Heat exchanged when the dissolved cellulose is cooled (+10 °C → -20 °C) as a function of water mass flow. Graph created with https://www.mycurvefit.com/ .

Figure 13 presents the heat exchanged when the pulp is cooled from +10 °C to -20 °C, as a function of water mass flow. In these calculations, for simplicity, the specific heat capacity of NaOH is approximated to be the same as that of cellulose (1.4 kJ/(kgC)) in all phases. The calculations and relevant data are shown below. The curve resembles a straight line even at very low water mass flows, i.e. even if the relative amount of other ingredients is larger. In conclusion, the heat exchange depends linearly on the mass flow of water in all cases relevant to the process, and other ingredients in the pulp do not noticeably affect the required energy. The need for liquid nitrogen then also depends linearly on the mass flow of water, as is seen in Figure 14.
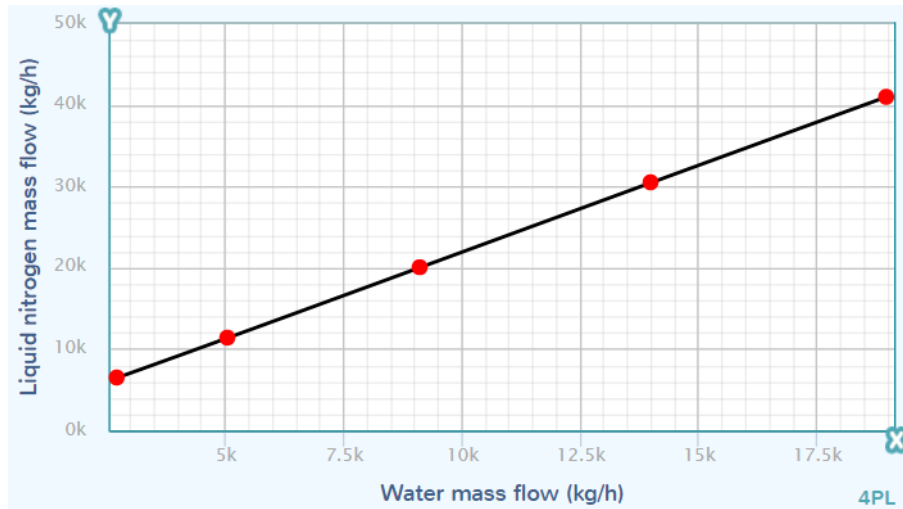
Figure 17 The liquid nitrogen mass flow as function of the water mass flow, when the dissolved cellulose process stream is cooled from +10 °C to -20 °C (and gaseous nitrogen does not contribute to the cooling). Graph made with https://www.mycurvefit.com/ .

5.2.1 Solids Content of 15 %

The total flow m_{tot} can be calculated from the equation

$0.15m_{tot} = m(cellulose) \rightarrow m_{tot} = 1921/0.15 =$ **12807 kg/h.**

The mass flow of water is

$m(H_2O) = m_{tot} - m(cellulose) - m(ZnO) - m(NaOH) = 12807 - 1921 - 272 - 1494 =$ **9120 kg/h.**

Since the original water mass flow is 18954 kg/h, this is already a 52 % decrease in water usage, or an absolute water decrease of 9834 kg/h. The specific heat capacity before freezing is approximately

(9120*4.2 + 272*0.48 + 1494*1.4 + 1921*1.4)/12807 = **3.4 kJ/(kg°C),**

while the heat generated by the water enthalpy of formation is 9120*333.55 = 3041976 kJ/h = **845 kW.**

The specific heat capacity after freezing is approximately

(9120*2.0 (ice) + 272*0.48 (ZnO) + 1494*1.4 (NaOH) + 1921*1.4 (cellulose))/12807 = **1.8 kJ/(kg°C).**

Using these values, we get the total heat transferred (while assuming the melting point is at -2.6 °C):

12807*3.4*(10 – (-2.6)) + 3041976 + 12807*1.8*(-20 – (-2.6)) = 3991743 kJ/h = 1108.8 kW = **1100 kW.**

Finally, we can calculate the corresponding mass flow of the required liquid nitrogen (considering only its latent heat 199 kJ/kg):

3991743/199 = 20059 kg/h = $2,0 * 10^4$ **kg/h.**

Using the equation and temperature difference (+15 °C → -196 °C) from the "Compressor Cooling Waters" chapter, we obtain the total electric energy needed to operate the compressor system

$P_{tot} = [m_N c_{p,N}(T_f – T_i) + m_n L]/0.57$ = (20059*1.05*211 + 20059*199)/0.57 = 14799700 kJ/h = 4111 kW = **4100 kW.**

In comparison with the original system, the power requirements are halved.

5.2.2 Solids Contents of 22 % and 30 %

As before, we calculate the total mass flows, water flows, specific heat capacities (before and after freezing) as well as the heat generated by the enthalpy of formation. These figures are then used to get the total heat exchanged. The results are as follows:

22 %: total flow 8731 kg/h, water flow 5044 kg/h, specific heat capacity before freezing 3.0 kJ/(kgC), after freezing 1.7 kJ/(kgC), heat generated by the enthalpy of formation 1682426 kJ/h = 470 kW, total heat exchanged 2270720 kJ/h = **630 kW,** corresponding mass flow of liquid nitrogen **11400 kg/h.**

30 %: total flow 6403 kg/h, water flow 2716 kg/h, specific heat capacity before freezing 2.5 kJ/(kgC), after freezing 1.6 kJ/(kgC), heat generated by the enthalpy of formation 905921 kJ/h = 250 kW, total heat exchanged 1285900 kJ/h = **360 kW,** corresponding mass flow of liquid nitrogen **6500 kg/h.**

It should be noted that the pulp streams with 22% and 30% solids may have too little water for the dissolution to properly work. The maximum levels of solids have to be empirically tested.

6 RESULTS AND CONCLUSION

6.1 Calculated Results

From Table 2 we obtain the following total power requirements and saving potentials. By summing the numbers in the "External power required" row we obtain the total external power required for all considered processes to be at the minimum **13600 kW.** However, the efficiency of the nitrogen liquefaction process is likely much lower than estimated in calculating this number and the actual power required could range from **30 MW to even 70 MW** (see Chapter 3.6.3). In addition, the efficiencies of producing steam to the carbamation reactor DC-101, and hot water to the Zn-NaOH preparation Preparation Tank FA-202 are assumed to be 100 %, though the effect of this is considerably smaller than that of the liquefaction.

The total saving potential (not including effects of lowering water content in the dissolved cellulose), as calculated from Table 2, is **3110 kW**.

Table 2 Heat exchange process data results.

	DC-101	FA-202	EA-201	EA-202	GB-201	EA-205	EA-203 EA-204
Heat transferred (kW)	1600	810	980	2300	8400	8400	2100
Specific heat of process stream (kJ/(kgC))	3.0	3.7	3.7	3.6/1.9 (liquid/frozen)	1.05	4.18	1.9/3.6 (frozen/liquid)
Utility stream output mass flow (kg/h)	2800 (H20)	1400 (H20)	15400 (H20)	41000 (gas N)	120000 (H20)	120000 (H2O)	33000 (H2O)
Utility stream output temperature (C)	159 (condensate)	159 (condensate)	59	-196 (gas N)	80 (H2O)	70 (H2O)	15 (H2O)
Utility stream input temperature (C)	159 (steam)	159 (steam)	5	-196 (LN2)	20	10 (H2O)	70 (H2O)
External power required (kW)	2100	1.0*10^3	-	(included in GB-201)	8400	-	2100
Potential power saving (kW)	200 (steam preheating)	810 (EA-205 and DC-101)	-	Depends on solids content	Depends on efficiency	-	2100

However, the water and nitrogen requirements are linearly related which means that halving the amount of water (corresponding to a solids content of 15 %) would halve the required amounts of liquid nitrogen. In addition, heating the vaporized nitrogen in the

freezing tunnel up to -50 °C from its initial -196 °C state could itself almost halve the required amounts of nitrogen for a second time. The required nitrogen amounts could optimistically be reduced to one fourth of what it would be if the potential of -196 °C gaseous nitrogen was all lost and the original water concentrations were conserved. Ideally this would lead to nitrogen requirements of about 11500 kg/h, which even with the 7-14% efficiency of Linde-Hampson or Claude cycles would enable liquefaction power requirements of 10 – 15 MW.

6.2 Conclusion

Heat circulation effectively removes the need for saturated steam in all processes except the carbamation reactor. Heated cooling water from the compressor can fully melt the frozen pulp and, in addition, preheat the fresh water going to the Zn-NaOH Preparation tank. Perhaps there are processes before the carbamation tank or after the melting phase which could still benefit from the vast reservoir of heated cooling water at 70 °C, but these stages of the process were out of the scope of this work.

The most significant questions concerning the energy efficiency of the whole process are linked to the liquid nitrogen, as the power requirements of its production are potentially over ten times as large than the requirements of all the other process stages combined. In addition to the total electric power, there would be more costs if several compressors are needed to produce enough liquid nitrogen. Reducing the water content of pulp would have a great effect on the total need of liquid nitrogen but the next challenge is to determine where and how much of the water can be reduced. Other still unanswered questions are how fully the cooling potential can be realised inside the freezing tunnel and what the maximum achievable efficiency of the liquefaction process is.

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