Conversion of cellulose and disaccharides to hydroxy carboxylic acids with high temperature alkali treatment

Lappeenranta–Lahti University of Technology LUT

Master Thesis

2022

Joonas Laine

Examiner(s): Professor Tuomo Sainio

D.Sc. (Tech) Jari Heinonen

ABSTRACT

Lappeenranta–Lahti University of Technology LUT

LUT School of Engineering Science

Chemical Technology

Joonas Laine

Conversion of cellulose and disaccharides to hydroxy carboxylic acids with high temperature alkali treatment

Master's thesis

2022

64 pages, 39 figures, 13 tables and 6 appendices

Examiner(s): Professor Tuomo Sainio

D.Sc. (Tech) Jari Heinonen

Keywords: Alkaline degradation, Cellulose, Lactose, Cellobiose, Peeling reaction, Alkaline hydrolysis, GISA, Carboxylic acids.

Cellulose alkali degradation is a viable method to produce organic acids from waste cellulosic raw material. These organic acids, where the most abundant is GISA, have many applications as adhesives, coatings and in polymer production. In this study, microcrystalline cellulose and toilet paper in different forms were subjected to alkali degradation under nitrogen atmosphere to study the effects of reaction temperature, time and alkali concentration on the degradation. The reaction mechanism was discussed based on the knowledge in the literature.

Microcrystalline cellulose was degraded to organic carboxylic acid with 66% mass yield at 200 ℃ temperature. In the same temperature, toilet paper was degraded to organic carboxylic acid with 50 % mass yield.

For efficient cellulose degradation the use high enough temperature >160℃ is required as the crystalline region becomes unstable. The effect of NaOH concentration on the peeling off reaction is neglectable but the rate of alkali hydrolysis (scission) increases when alkali concentration is increased.

Also, degradation of disaccharides lactose and cellobiose in presence of alkali were studied. Lactose degradation seems to obey the proposed peeling off mechanism where the glucose unit is directly converted to a hydroxy acid while the galactose unit first forms a free monosaccharide that is then converted to mainly lactic acid. Cellobiose was fully degraded at temperatures < 100℃ with 70% yield.

TIIVISTELMÄ

Lappeenrannan–Lahden teknillinen yliopisto LUT

LUT Teknis-luonnontieteellinen

Kemiantekniikka

Joonas Laine

Selluloosan sekä disakkaridien konversio hydroksi karboksyylihapoiksi korkean lämpötilan sekä alkalin avulla.

Diplomityö

2022

64 sivua, 39 kuvaa, 13 taulukkoa ja 6 liitettä

Tarkastaja(t): Professori Tuomo Sainio

TkT Jari Heinonen

Avainsanat: Emäksinen hajoaminen, Selluloosa, Laktoosi, sellobioosi, Peeling-reaktio, Alkaali hydrolyysi, GISA, karboksyylihapot.

Selluloosan emäksinen hajoaminen on potentiaalinen tapa tuottaa orgaanisia happoja jäteselluloosasta. Näitä happoja, joista suurin osa on GISA:aa voidaan käyttää eri käyttökohteissa kuten sidosaineena, päällysteenä sekä polymeereissä. Tässä työssä mikrokiteinen selluloosan sekä vessapaperi altistettiin alkaalille typpi ilmakehässä ja tutkittiin lämpötilan, ajan sekä alkaalikonsentraation vaikutusta hajoamiseen. Lisäksi reaktiomekaniikka esitettiin kirjallisuuden pohjalta.

Mikrokiteinen selluloosa saatiin hajotettua antaen 66% massasaannon 200℃ lämpötilassa. Samoissa olosuhteissa kyettiin myös hajottamaan vessapaperia orgaanisiksi karboksyylihapoiksi 50% saannolla.

Selluloosan tehokkaaseen hajoamiseen tarvitaan riittäväni korkea lämpötila >160°C, jotta sen kristallirakenne muuttuu epästabiiliksi. NaOH-konsentraation vaikutus peeling-off-reaktioon on mitätön mutta sillä on suoraan verrannollinen vaikutusta alkaali hydrolyysiin (scission).

Laktoosin sekä sellobioosin alkaalihajoamista tutkittiin myös. Laktoosin hajoaminen seuraa esitettyä peeling off mekanismiä missä glukoosi muuntuu hapoksi jättäen samalla galaktoosin liuokseen, joka lopuksi muuttuu maitohapoksi. Sellobiosi saatiin täysin hajotettua alle 100°C lämpötiloissa antaen 70% saannon.

ACKNOWLEDGEMENTS

I would like to extend my sincere thanks to Tuomo Sainio and Jari Heinonen for their knowledge, constructive criticism, and valuable advice that were much needed during writing of this thesis.

I gratefully acknowledge the assistance of Markku Rahikainen, Mikko Huhtanen and Liisa Puro in the laboratory.

Lastly, I’m extremely grateful to my family and Aliina for their support and patience that cannot be underestimated.

Table of contents

ABBREVIATIONS

GISA	Glucoisosaccharinic acid
XISA	Xyloisosaccharinic acid
2-HBA	2-hydroxybutanoic acid
2,5-DHPA	2,5-dihydroxypentanoic acid
NaOH	Sodium hydroxide
L/S	Liquid to solid
mcellulose	microcrystalline cellulose

1. Introduction

1.1. Background

The evident depletion of fossil fuels in near future, growing concern of the climate change and honouring of the Paris agreement has driven the research towards the use of renewable resources. The importance of effective exploitation of renewable resources are evident in order to pursuit circular economy. Cellulosic biomass is the most abundant raw material on earth and is being used many ways by the industry. Pulp and paper industries, sawmills and agriculture produce cellulosic side streams, like sawdust, crop residue and cellulosic rejection water. These side streams, among other cellulosic side streams could be utilized in production of carboxylic acids by the means of alkali degradation in high temperature. Cellulose degradation in alkali is well studied subject considering the popularity of Kraft pulping and it is known to undergo peeling reaction, thus producing aforementioned acids. These carboxylic acids are used in polymer production, coatings, adhesives and in many other applications (Badea and Radu, 2018). This way the cellulosic side streams could be utilized to produce high value-added products.

1.2. Objective and research questions

Aim of this thesis was to study the degradation of cellulose, parameters affecting the degradation and reaction mechanisms to produce hydroxy carboxylic acids. Additionally, hydrolysis of lactose and cellobiose was also conducted. Glucoisosaccharinic being the main degradation of cellulosic alkali treatment under nitrogen atmosphere thus the stability of GISA under 200°C in nitrogen atmosphere was studied.

In this work the cellulose degradation under alkaline is discussed and compared to the kraft process to lay the foundation. Then the reaction mechanism and parameters affecting the alkali degradation is discussed. Additionally, lactose peeling mechanism and cellobiose alkali system is discussed.

The research questions are: 1. What are the reaction mechanisms leading to hydroxy acids under nitrogen atmosphere? 2. How reaction conditions (temperature, alkali concentration) affect the reaction rates and yield of hydroxy acids? 3. Can disaccharides (lactose, cellobiose) and milder operating conditions be used to study the formation of hydroxy acids from carbohydrates?

2. Cellulose and cellulose degradation in alkali

Carbohydrates in wood constitutes of Cellulose and hemicellulose. Cellulose is linear polysaccharide comprising of glucose (β-D-Glucopyranose) units which are connected together via β-1,4 glycosidic bond to form hundreds to thousands glucose units long chains. In native wood, cellulose has a degree of polymerization of 10 000. This tough, fibrous and water-insoluble biomaterial has an important role in keeping the structure of plants. It has a tendency to form intra and intermolecular hydrogen bonds and aggregates to microfibrils. This means that cellulose is relatively inert in chemical treatment and there are only few solutions that dissolves it. (Stenius, 2000)

Hemicellulose is the other major carbohydrate polymer in wood and is described as a heteropolysaccharide. It has much more undefined structure than cellulose. Where cellulose building blocks were only glucose units, hemicellulose comprises of variety of building blocks. These are D-glucose, D-mannose and D-galactose which are hexoses. Moreover, units belonging to the pentose family are D-xylose, L-arabinose and D-arabinose. There are also some deoxyhexoses like L-rhamnose or 6-deoxy-L-mannose and small amounts of some uronic acids. The chemical and thermal stability of hemicellulose is lower than that of cellulose which is notable in kraft process, this is presumed to be due to the lack of crystallinity and lower degree of polymerization around 100-200. (Stenius, 2000)

The chemical composition of these carbohydrates as well as lignin differs between different species (hardwood vs softwood). In addition, they also differ inside the tree itself (stemwood, roots etc). Generalization can be made that the composition falls somewhere between 35-50% cellulose, 20-35% hemicellulose and 10-25% lignin (Isikgor and Becer, 2015). (Stenius, 2000)

2.1 Kraft process

Kraft process is used to treat wood chips to produce “free” carbohydrate fibers by means of delignification. It is a full chemical pulping method using sodium hydroxide (NaOH) and sulphide (Na_2S) at elevated temperature, usually 160-180°C. Pulping time averages between

0,5-3 hours depending on the degree of delignification target. Hydroxide ion and hydrosulphide anions speed up the reaction making the lignin fragments into smaller fragments. This acceleration means that the biomass must reside in the alkali and high temperature environment lesser time thus resulting in less carbohydrate degradation and producing stronger pulp than with other methods can be produced, namely soda. Hence the name kraft pulping.(Chakar and Ragauskas, 2004)

Kraft pulping can be divided into three different phases. Initial phase, bulk phase, and residual phase. The initial phase starts below 150°C and leads to dissolution of 15-20% lignin and 20-25% of the carbohydrates present where mainly hemicellulose dissolute approximately 40%. The delignification rate follows first order kinetics in respect of lignin concentration provided that enough alkali is available. (Chakar and Ragauskas, 2004; Stenius, 2000)

The bulk phase begins after the 150°C and is the phase where majority of the lignin (approximately 60%) is removed. The bulk phase includes the heating from 150 to 170°C. The residual phase happens at 170°C and degrades approximately 10-15% of the original lignin present. This last phase is slow and is dependent on temperature and OH^- ion concentration, moreover the selectivity in this phase for lignin is poor and the cooking should be stopped. If continued the carbohydrates start to degrade which results in low quality pulp in terms of pulp strength. The residual lignin is usually in between 4-5% and should be removed by other means, namely bleaching. (Chakar and Ragauskas, 2004; Stenius, 2000)

Overall, approximately 90% lignin, 60% of the hemicelluloses and 15% of the cellulose is removed during the kraft process. This means that the black liquor composition is 40-45% aliphatic carboxylic acids 35-45% lignin and 10-15% other organics. Attempts have been made to both recover some of the carboxylic acids from the black liquor (Reyes et al., 2020) as well as reducing the carbohydrate reactions with the use of additives that stabilises polysaccharide. In kraft pulping the peeling of reaction can be think of unwanted phenomena when in our case it is wanted. (Alén, 2011)

2.1. Reaction pathways

2.1.1. Reducing end sugar

Before the reaction mechanism for carbohydrate reactions and disaccharide can be understood it is important that concept of reducing end sugar is explained. Reducing sugars can work as a reducing agent due to the fact that they have either aldehyde group or a free ketone group. In case of ketone group, they are able to tautomerize to aldose. In general, all the monosaccharides such as glucose, galactose and fructose are reducing sugars having reducing end. (Eugene, 2020; W.pratt and Cornely, 2017)

Disaccharides consist of two monosaccharides connected and can be either reducing or non-reducing sugars. In case of disaccharide the tautomerization is not possible because of the connection between the two monosaccharides. Some of the reducing disaccharides are maltose and important in this work lactose and cellobiose. (Eugene, 2020; W.pratt and Cornely, 2017)

2.1.2. Peeling reaction

The fundamental idea of kraft pulping is to degrade lignin enough to free up the carbohydrate but at the same time trying to preserve the carbohydrate. This is not fully possible as described above in kraft pulping initial phase as some of the carbohydrates namely hemicellulose but also some cellulose degrades to carboxylic acid. The carbohydrates degrade to carboxylic acids in a way that is in literature known as peeling reaction.

There are four distinct phenomena involved in the reaction of carbohydrate with alkali. First the peeling reaction also called as primary peeling. Second is stopping reaction. Third and fourth are alkaline hydrolysis and secondary peeling respectively.

To start the primary peeling reaction there must be a reducing end group in the polysaccharide chain. The first phase is the keto-enol tautomerization (i) of reducing end group to enediol (2) intermediate. Then the enediol deprotonation (ii) is followed by anion isomerisation (iii) to produce intermediate (4) that now has methoxyl group in the right

position for ß-alkoxy elimination (vii). This elimination produces diketodeoxyglycitol product (6) and also the rest of the polymer chain which now has a new reducing end that can undergo the same steps.

Diketodeoxyglycitol (6) keto-enol tautomerism (v) produces 4-deoxy-d-glycero-2,3-hexodiulose (8) which then forms glucoisosaccharinic acid (10) via benzylic acid rearrangement (vi). (Knill and Kennedy, 2003)

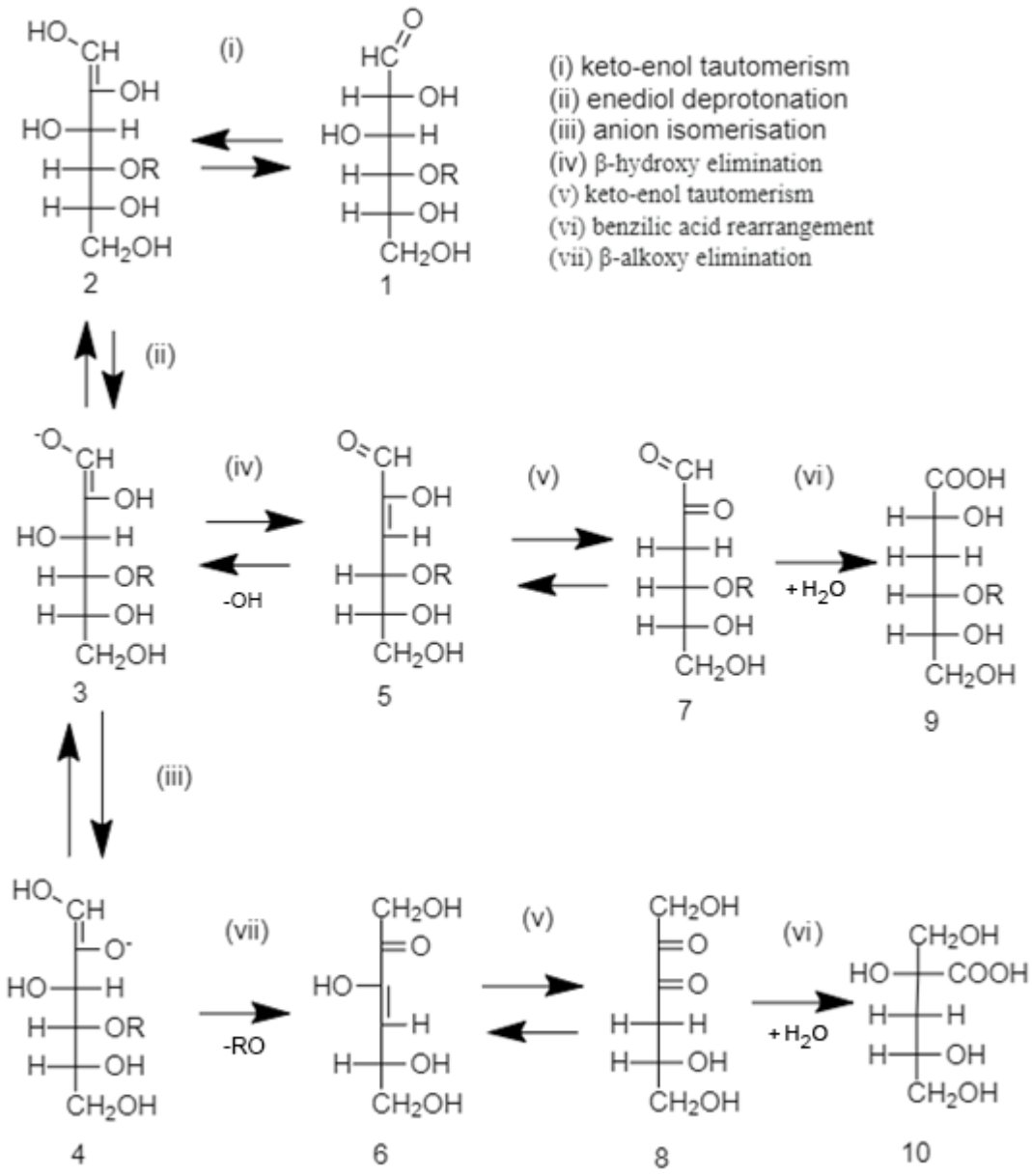

Figure 1 stopping reaction and peeling reaction (Chen et al., 2017; Knill and Kennedy, 2003)

2.1.3. Stopping reaction

The peeling-off reaction could one monomer at the time destroy the whole polymer chain if there were not a stopping reaction. There are two distinct stopping phenomena, Chemical

stopping reaction and physical stopping. The main route of chemical stopping reaction is by ß-hydroxy elimination (iv). In ß-hydroxy elimination (iv) the enediol anion (3) converts to intermediate (5) which then keto-enol tautomerize (v) and benzylic acid rearranges (vii) to produce D-glucometasaccharinic acids (9). This alkali stable metasaccharinic acid stops the peeling of the whole chain as it is linked to the rest of the polymer chain. I.e in the figure 1 R represents the rest of the polymer (cellulose) chain. Also other possible end groups are also known from the literature (Johansson and Samuelson, 1974). (Stenius, 2000)

The physical stopping happens when the reducing end sugar reaches the crystalline structure of the cellulose and thus alkali is unable to access it (Van Loon and Glaus, 1997). The physical stopping reaction is not abrupt as there is distinct gradual transition from amorphous region to crystalline region, rather than a distinct interface (Loon and Glaus, 1998).

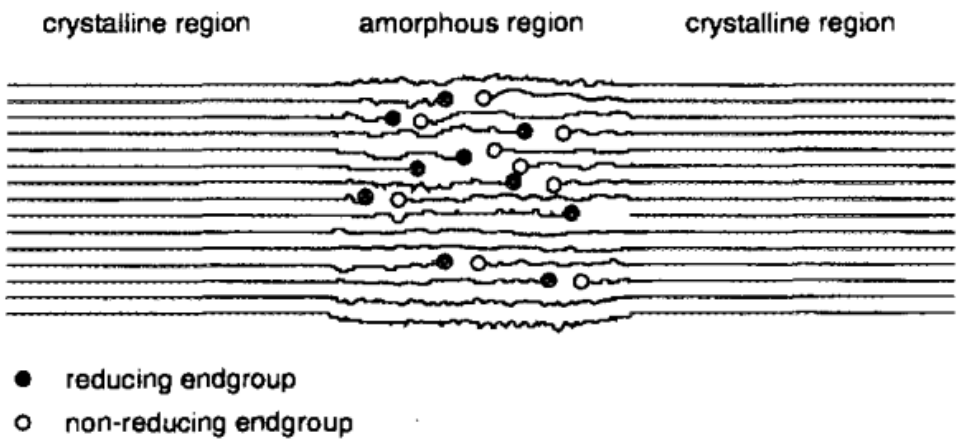

Figure 2 Amorphous and crystalline region of cellulose (Loon and Glaus, 1997)

2.1.4. Alkaline hydrolysis (random scission)

Alkaline hydrolysis of glycosidic bonds in cellulose occur in high temperatures. Some authors state that its neglectable under 120°C (Lai and Ontto, 1979). Others state that it is not detectable under 140°C (Mozdyniewicz et al., 2013). Usually it happens in 160-170°C. In this slow reaction the glycosidic bonds are randomly cleaved. This results in huge weight loss and decrease in DP. In other words, alkaline hydrolysis cleaves the polymer chain in random part to make two shorter chains. These chains can then go through the peeling reaction but this time it is called secondary peeling. Some acids produced this way are formic acid and acetic acid for example. Alkaline hydrolysis favours the cleavage at the centre of cellulose chain (Adibi Larijani, 2020). (Stenius, 2000)

Alkaline hydrolysis mechanism has been studied by Kaylor et al., (1995). They used cellulose based model compound that is conformationally rigid but does not have reducing end to avoid possible peeling reaction. The authors proposed mechanisms for both cleavages from the side of glycosyl-oxygen and oxygen-aglyclone. Proposed mechanism is shown in figure 3 and 4 respectively. (Adibi Larijani, 2020)

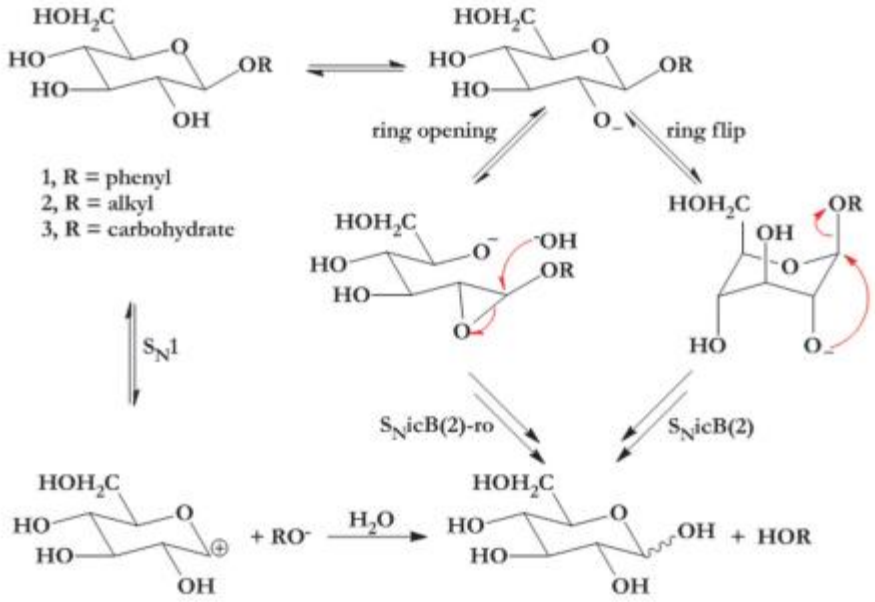

Figure 3 Glycosyl-oxygen mechanism (Adibi Larijani, 2020)

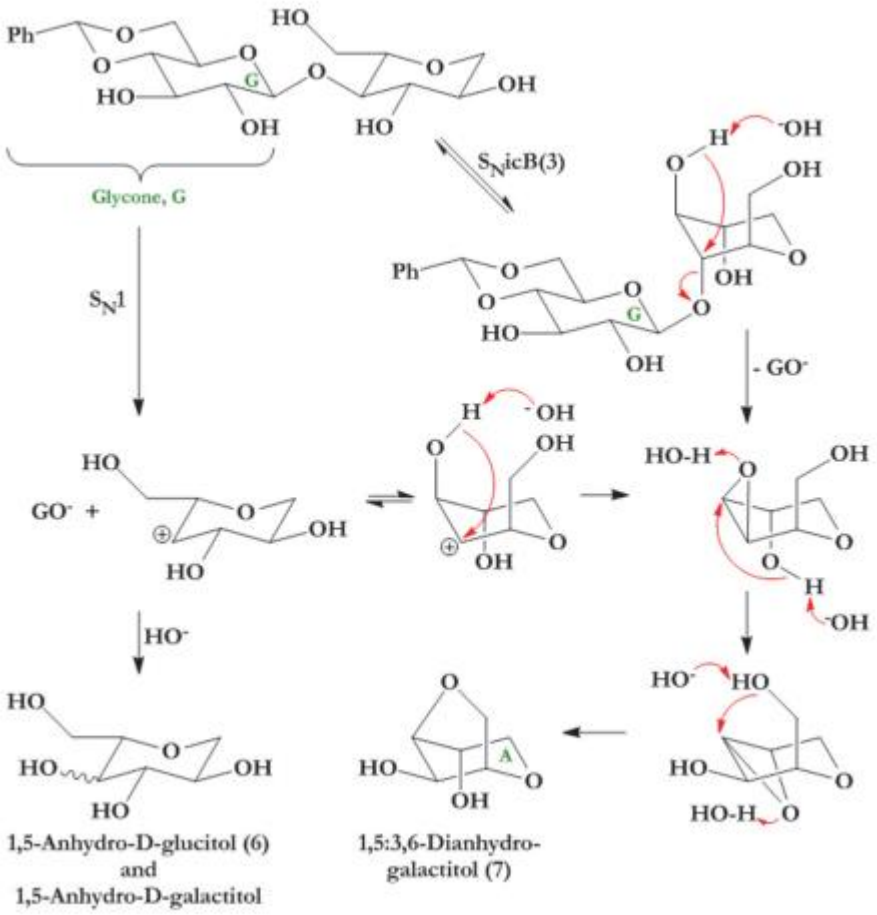

Figure 4 Mechanism for oxygen-aglycone (Adibi Larijani, 2020)

2.1.5. Other reactions

The formation of other known acids found in black liquor happens via fragmentation and rearrangement of the cleaved cellulose unit. These are smaller acids such as formic-, lactic- and 2,5-dihydroxypentanoic acids. Their pathways are shown in figure 5.

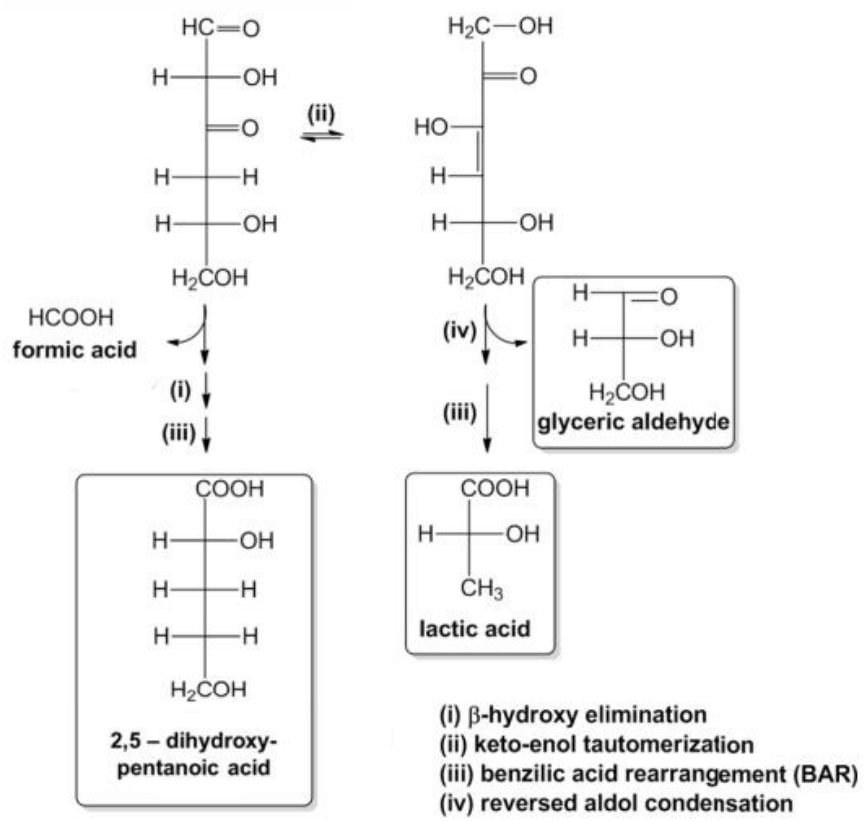

Figure 5 Formation of main hydroxy acids (Paananen, 2016)

Depending on the reaction temperature, time, atmosphere, base ionic composition, and cellulosic material many different acids with specific reaction mechanism can be formed. For example in the study conducted by Niemelä and Sjöström (1986), they produced 65 degradation products from cotton in 170-190°C and 1 to 3 M NaOH. Also, the formation of 3,4-dideoxypentonic acid from maltose (Lindstrom and Samuelson, 1977) and the formation of anhydroisosaccharinic acid from cellulose (Petersson and Samuelson, 1976) among other papers depicts the complex nature of cellulosic degradation in alkali environment.

Good generalization was done by Glaus and Van Loon (2004) on the degradation of cellulose in alkali. The process is shown in figure 6. "Lobry de Bruyn-Alberda van Ekenstein transformation is a base-catalysed enolization of and aldose or ketose to the enediol, followed by isomerization" (Berg, 1993). This is in some detail explained in the peeling of reaction (figure 1) but for more information reader is referred to Speck, (1958).

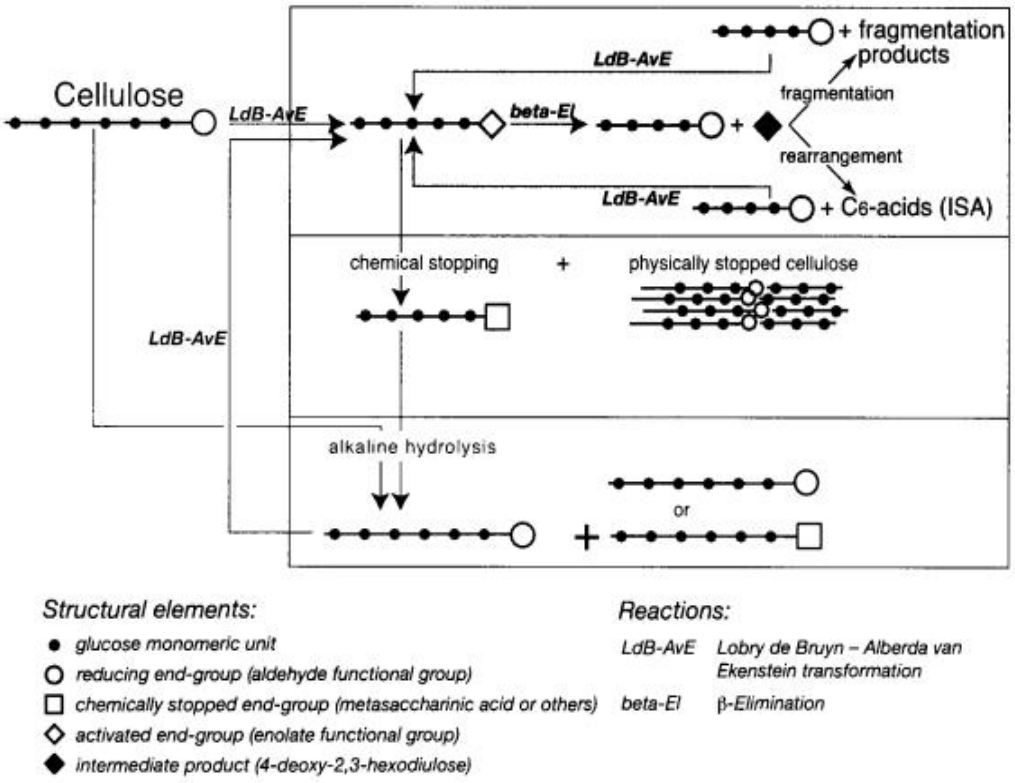

Figure 6 Simplified process for cellulose alkali degradation (Glaus and Van Loon, 2004)

The cellulose chain undergoes LdB-AvE transformation and produces activated end-group with enolate functional group (compound (2) in figure 1). Then through b-elimination produces intermediate product which can produce either GISA (figure 1) or other smaller carboxylic acids through fragmentation (figure 5). The left-over chains can then be peeled once again as stated before. The chemical stopping reaction produces alkali stable metasaccharinic acid and alkali hydrolysis cleavages the chain to produce shorter chain with either stable or reducing end. This Figure (6) is not accurate representation but a rather good simplified overview on the reactions and more importantly their connection to each other in the bigger picture. (Glaus and Van Loon, 2004)

3. Observed carboxylic acids

The hydroxy carboxylic acid of main interest in this work are glycolic acid, lactic acid, formic acid, acetic acid, 2,5-dihydroxypentanoic acid (2,5-DHPA), glucoisosaccharinic acid with both alpha and beta form (GISA), 2-hydroxybutyric acid (2-HBA) and xyloisosaccharinic acid (XISA). These acids are known to be major degradation products in pine kraft black liquor (Paananen, 2016). There are also many other acids found as shown by review done by Knill and Kennedy (2003) where they compiled the main degradation products from different carbohydrate materials like sawdust/wood, cellulose, cellobiose and glucose from different articles published between years 1957-1999. From this gathered data the authors stated that the major difference due to the different reaction conditions was the relative concentrations of the degradation products, implying that by changing for example ionic nature of the base or other reaction parameter no new degradation products would form.

In this study all of the observe carboxylic acids were found in all of the experiments except XISA and 2-HBA which are known main degradation products from hemicellulose or more precisely from arabinoxylan (Paananen, 2016). XISA was not found in any of the experiments done in this study and 2-HBA was only quantitively analysed in the experiments done with toilet paper and qualitatively in the experiments done with cellobiose.

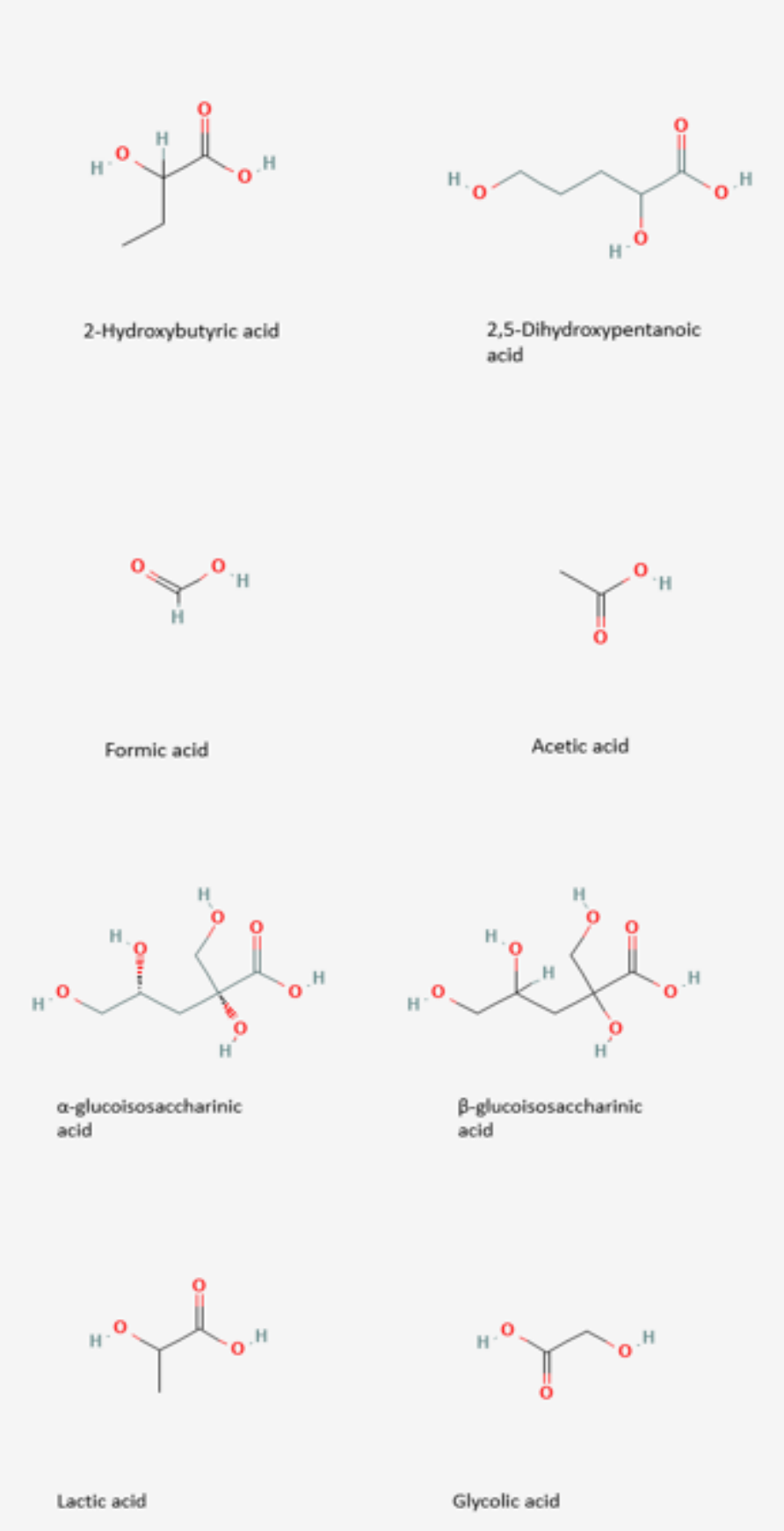

Figure 7 Molecular structures of the main acids of interest

4. Parameters affecting cellulose degradation

4.1. Effect of temperature

Effect of temperature on the **peeling reaction** was studied by Haas et al., (1967) in temperatures between 65°C and 132°C and in 1,25M NaOH with hydrocellulose. The rate constants were determined to peeling-off reaction (k_1), chemical stopping reaction (k_2) and for physical stopping (k_{cr}). Plotted Arrhenius equation gave activation energy for the peeling-off reaction 101 kJ/mol and for the overall stopping reaction (k_2+k_{cr}) 97 kJ/mol. This small difference in activation energy explains why in lower temperatures the degree of degradation is smaller than at higher temperatures. (Loon and Glaus, 1997; Shaw, 2013)

Effect of temperature on the **alkaline hydrolysis** was studied by Lai and Sarkanen, (1967) in temperatures ranging from 146 to 185°C in 1,25 M NaOH. From this data the alkaline hydrolysis constant in (k_{obs}) 25°C was extrapolated resulting in 5,25 x 10^{-11} h^{-1}. This calculated rate was shown to be over 8 order magnitude higher than that of **peeling reaction** showing why in low temperatures alkaline hydrolysis is neglectable compared to peeling. Moreover, the calculated constant was about 7 order magnitude lower than in 146°C which was 4 x 10^{-3} h^{-1}. This shows the sensitivity of alkaline hydrolysis to the temperature. (Loon and Glaus, 1997; Shaw, 2013)

Niemelä and Sjöström, (1986a) studied the degradation of cotton linters at the temperatures slightly above of that where cellulose crystalline structure is known to degraded 170-190°C. They utilized 1 M and 3 M NaOH solutions. Reaction times where 4h,3h and 2h for 170,180 and 190°C respectively. Carboxylic acid yield increased from 67% to 79% when temperature was raised from 170°C to 190°C in 3 M NaOH solution. The main degradation products where GISA, formic and lactic acid from the 65 products that were identified.

More interestingly the continuum of this research was done by Niemelä, (1990) with 3 M NaOH solution but this time in temperatures 260°C and 280°C. Total acid yield was over 95% in the experiment with 280°C. They found that this time only minor amounts of GISA were detected and instead anhydro isosaccharinic acid were found more readily. The authors

stated that this was due to that the dicarbonyl intermediate (figure 1 (8)) dehydration occurs more readily than direct benzylic acid rearrangement or that the GISA is degraded to more stable compounds in such high temperature, the latter we will discuss later in chapter 6. Main degradation product was lactic acid.

4.2. Effect of base concentration

Kinetic constants for the peeling-off reaction (k_1) and chemical stopping reaction (k_2) were studied by Lai and Sarkanen, (1969) in different hydroxyl concentrations at temperature 100°C. Study was done with amylose which has no microfibrillar structure such as cellulose and thus no physical stopping occurs. Study showed that constant (k_1) increased when the OH^- concentration was increased to 0,3 mol/l, after that it remained constant at 290 h^{-1}. The stopping constant (k_2) increased until 1,5mol/l OH concentration on after that remained constant at 140 h^{-1}. (Loon and Glaus, 1997)

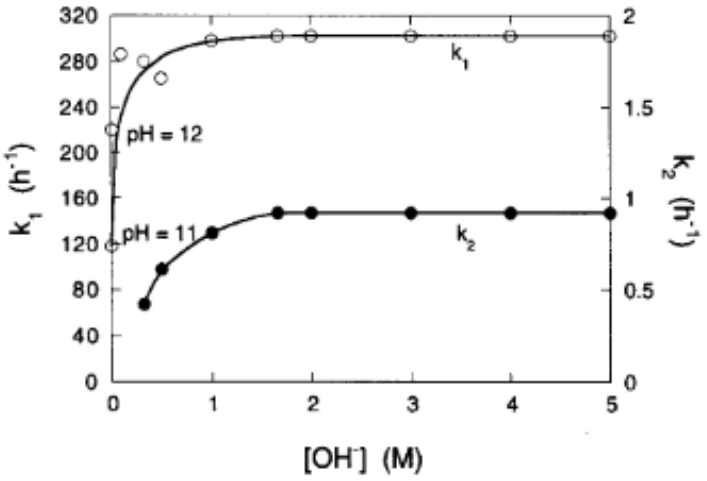

Figure 8 Rate constants dependency on the OH- concentration on amylose at 100°C (Loon and Glaus, 1997)

The effect of base concentration to alkaline hydrolysis constant (k_{obs}) was found to be linear between OH^- concentrations of 0 mol/l to 2 mol/l. Reaching value of 20 x 102 h^{-1} in 2 mol/l and in 185°C. (Loon and Glaus, 1997)

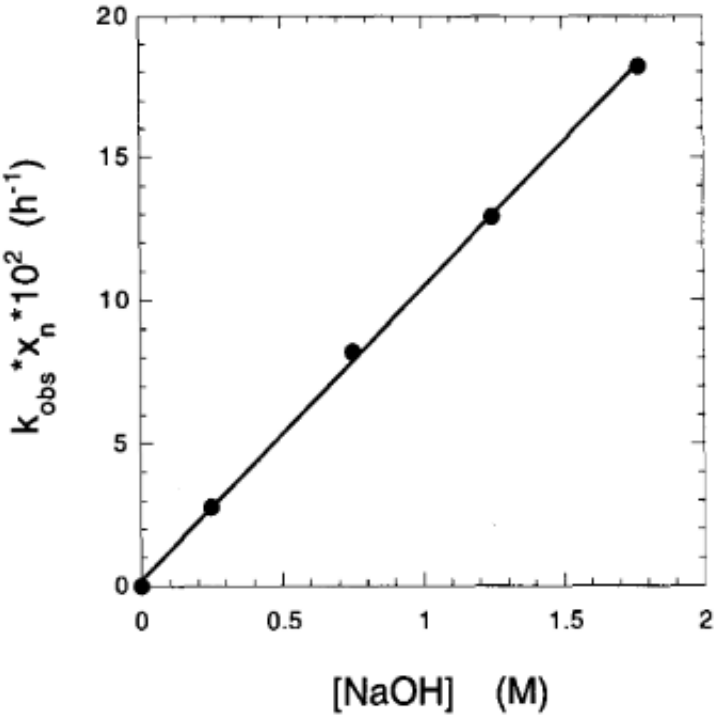

Figure 9 Dependency of hydrolysis kinetic on the OH- concentration at 185°C (Loon and Glaus, 1997)

The use of $Ca(OH)_2$ more precisely Ca^{2+} has been shown to catalyses the benzylic acid rearrangement leading to the formation of GISA but at the same time it has been shown to catalysed also the chemical stopping reaction more readily. Overall effect of Ca^{2+} is lower degradation and relatively more GISA than other side products. Compared experiments done with NaOH and $Ca(OH)_2$ showed that only 32% of total degradation products were GISA when NaOH was used as a solvent compared to $Ca(OH)_2$ where 63% of total degradation products were GISA. NaOH has also been shown to induce additional fragmentation and producing smaller organic acids. Moreover, its usage as a solvent has shown to produce three times more β-GISA than α-GISA. (Loon and Glaus, 1997; Shaw, 2013; Machell and Richards, 1960)

4.3. Nature of cellulose

The nature of cellulosic material that is being used for the production of organic acids does matter. It comes down to two aspects of the material which are degree of polymerization

(DP) and accessibility. Degree of polymerization means the number of monomeric units linked together. Accessibility basically means the amorphousness of the cellulosic material.

Loon et al., (1999) conducted a study on degradation on different types of cellulosic material differing mainly on the DP. Cellulosic materials such as microcrystalline cellulose (Aldrich), tissue paper (Tela), cotton, and paper were degraded at low temperature (25°C) and under nitrogen atmosphere. They proposed that maximum degradation of cellulosic material can be calculated using equation (1)

$$(celdeg)max = \lim_{t=\infty}(celdeg) = K/DP \qquad (1)$$

Where $K=k_1/k_t$ (availability)

DP=degree of polymerization

The k_1 is the propagation peeling reaction and k_t is the overall stopping reaction (k_2+k_{cr} in chapter 4.1). By calculating the kinetic parameters, they plotted maximum cellulosic degradation versus DP and got figure 10. As the degradation of cellulosic material also depends on the availability (K) it is not possible to describe it by a single curve. Dashed and solid lines represent the lowest and highest calculated availability in their study. The lower number means lower availability and higher number higher accessibility. K=12 and K=38 for cotton and microcrystalline cellulose respectively. The K value is constant for specific cellulosic material. This study shows that in low temperatures the nature of cellulosic material affects the amount of cellulose that is possible to convert to acids. (Loon et al., 1999)

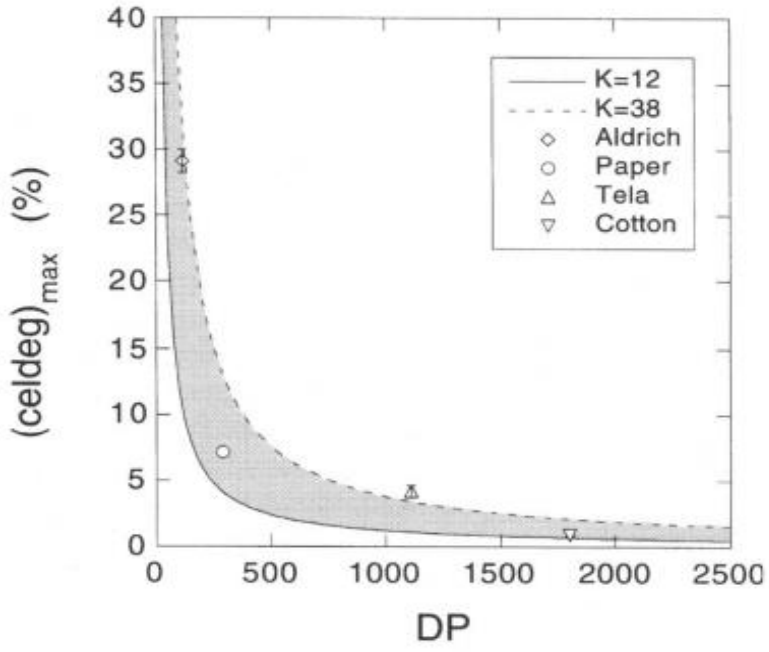

Figure 10 Maximum degradation of cellulose versus DP (Loon et al., 1999)

4.3.1. Mercerization

Mercerization is an old method for cellulose fiber modification. It is widely used in cotton textiles to enhance the affinity towards dyes and other chemical finishes. Mercerization also gives fibers increased tensile strength, mechanical properties and luster depending on the various methods available. Mercerization changes natural cellulose I to cellulose II and usual concentration of NaOH used in the process is 20-30%. (Dinand et al., 2002; Faruk and Ain, 2013)

Mercerization does not always happen when cellulose in introduced on NaOH solution. NaOH forms a series of hydrates when interacting with water. Different hydrates exist in different temperatures and in different NaOH concentrations. In short when NaOH concentration is increased the amount of water molecules forming the hydrate is decreased. This results in smaller diameter and enables the penetration of cellulosic fiber structure and thus swelling occurs. In case of dilute NaOH solutions the opposite occurs. (Budtova and Navard, 2016)

According to Dinand et al., (2002) mercerization starts when the concentration of NaOH is increased to 8% for acid purified cellulose in room temperature. This is in line with our

experiments where microcrystalline cellulose was introduced to both 5% and 10% NaOH solution and was found to swell in the latter. As the mercerization depends both on the temperature and NaOH concentration what happens in the heating period of cellulosic materials in 5% NaOH is unknown. Study conducted by Duchemin, (2015) showed that mercerization of high DP cellulose was achieved in -17°C and in 1 wt.% (0,25N). This would suggest that swelling in lower NaOH concentration would require lower and not higher temperature.

Lai and Ontto, (1979) studied the degradation of hydrocellulose in different NaOH concentrations (0,05-18,6N) and in moderate temperature 120°C where according to them alkaline hydrolysis could be neglected. Test time was 1 hour. Dependency on cellulose degradation on alkali concentration is shown in figure 11.

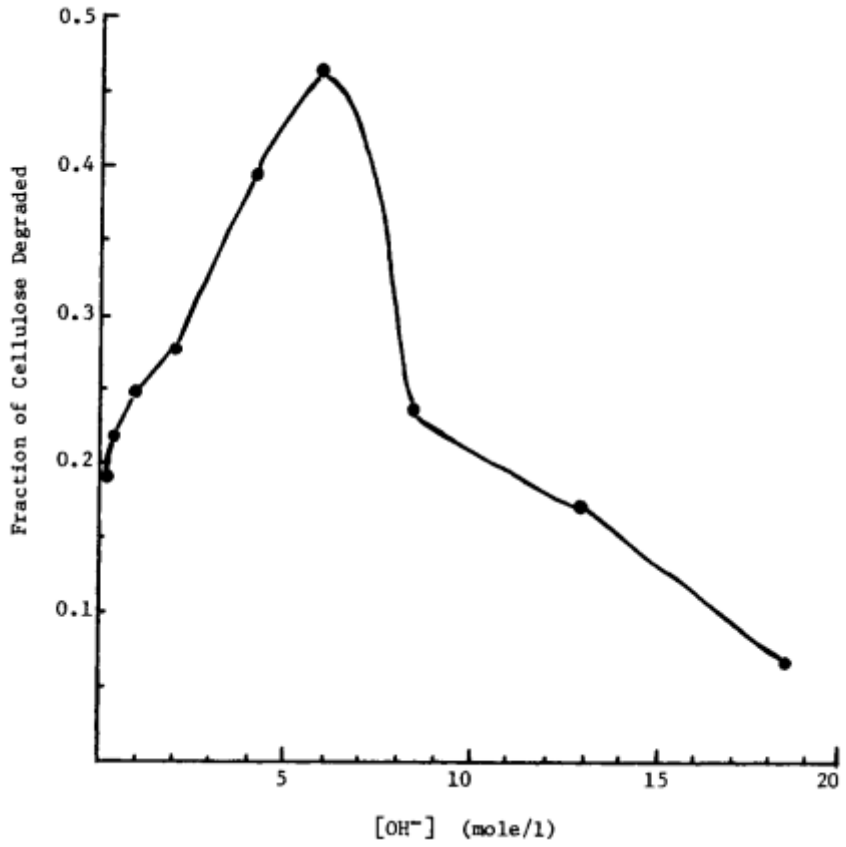

Figure 11 Hydrocellulose degradation in different OH- concentrations (Lai and Ontto, 1979)

The extent of degradation is rapidly increased between 4-6N NaOH concentration and is controlled by the relative accessibility of cellulose to the alkali. At lower NaOH concentrations the low degradation of cellulose is most likely due to lower rate of reaction as was discussed in chapter 4.2. More interestingly after 6N NaOH concentration the cellulose fraction degraded rapidly decreased. Lai and Ontto, (1979) proposed that this could be explained by submicroscopic changes in the cellulose and relative rate of peeling and stopping reactions.

Changes in cellulose nature they studied by reheating the previous samples again in 1,15N NaOH and found that between 0,05-2N NaOH concentration there were no significant differences at the cellulose degradation but between 2-6N the degradation decreased. In other words, the residues that were previously degraded in 2N or higher concentration showed stability towards further degradation. Their study also showed that increase in alkalinity increased the rate of stopping reactions.

Atalla, (1986) studied the effect of cellulose physical structure on the alkaline reaction rates. He conducted studies on both fibrous cotton hydrocellulose and with amorphous hydrocellulose in 1N NaOH, oxygen free-atmosphere and in temperatures 60 and 80°C. The fibrous cotton was predominantly crystalline and showed no significant changes in physical structure during degradation. Moreover, fibrous cotton stabilized more dominantly via physical stopping when in contrast the amorphous hydrocellulose demonstrated more chemical stopping pathway. Author also showed that some alkaline hydrolysis occurs even in low temperature 80°C in amorphous region of cellulose.

4.4. Effect of atmosphere and pressure on degradation

It is known that oxygen atmosphere inhibits the production of GISA. The main reason for this is that under aerobic conditions the dicarbonyl intermediate moiety (figure 1, (8)) that is produced by peeling reaction is very oxygen labile and results in water soluble fragmentation products rather than GISA. Oxygen can induce reactions such as autoxidation which can then lead to formation of peroxides or radicals (Adibi Larijani, 2020). Oxygen also inhibits the overall cellulosic degradation by producing alkali stable aldonic acid end groups. (Shaw, 2013)

In this work nitrogen atmosphere was used and thus the effect of nitrogen pressure rather than oxygen is important. The effect on kinetics of cellulose degradation under different nitrogen pressures has not been done as most of the kinetical studies reported here are from the studies relating to storage of radioactive waste material. In most of the studies nitrogen or oxygen free atmosphere is more important for the actual degradation of cellulose than the applied pressure in each case and thus it is mostly not mentioned in the studies. In the radioactive waste storage units the oxygen is removed by formation of rust and thus anaerobic conditions are formed (Shaw, 2013).

Adibi Larijani, (2020) studied the alkali degradation cellobiose in low temperatures (20,35,50°C) and in both nitrogen and oxygen atmosphere over 24 hours. Different pressures used in nitrogen atmosphere were 1, 5 and 10 bar. The degradation experiments showed that by raising the pressure from 1 to 10 bar the total degraded cellobiose slightly decreased from 78% to 65% in 20°C and from 84% to 83% in 35°C. On the contrary the experiment in higher temperature (50°C) showed increase in the total cellobiose degradation from 83% in 1 bar to 92% in 10 bar. In addition, the relative amounts of produced lactic acid and GISA were almost unchanged between the different pressures. Biggest difference was observed in 50°C where relative GISA content were 54% in 1 bar and 59% in 10 bar. At the same time relative lactic acid content were 30.5 % and 34% respectively.

Even though in this work the effect of applied pressure on the degradation of cellulose were not studied the study done by Adibi Larijani (2020) with cellobiose showed that pressure has only minor effect on the degradation rate, and it is more important that oxygen free atmosphere exists. So, it is plausible that the same is assumption can be applied to other cellulosic materials.

5. Degradation of disaccharides under alkaline conditions

5.1. Lactose and galactose under alkaline conditions

Lactose (4-O-ß-D-galactopyranosyl-D-glucopyranose) is a heterogeneous disaccharide comprising of galactose and glucose monosaccharides linked together via ß -1,4-glycosidic

bond. Lactose is a reducing disaccharide and to be more precise the reducing end is located in glucose moiety as there is free hemiacetal linkage between carbons 1 and 5. Lactose reaction in strong alkaline is important reaction considering the results obtained from the lactose experiments in this study. (Berg, 1993)

Lactose degradation route to acid and galactose moiety in alkali consist of epimerization of lactose to lactulose, degradation of lactulose's fructose moiety to produce acid. This leads to free galactose acid in the solution that can epimerize to tagatose and the tagatose produces trioses which then produce for example lactic acid. This reaction pathway is shown in figure 12. (Berg, 1993)

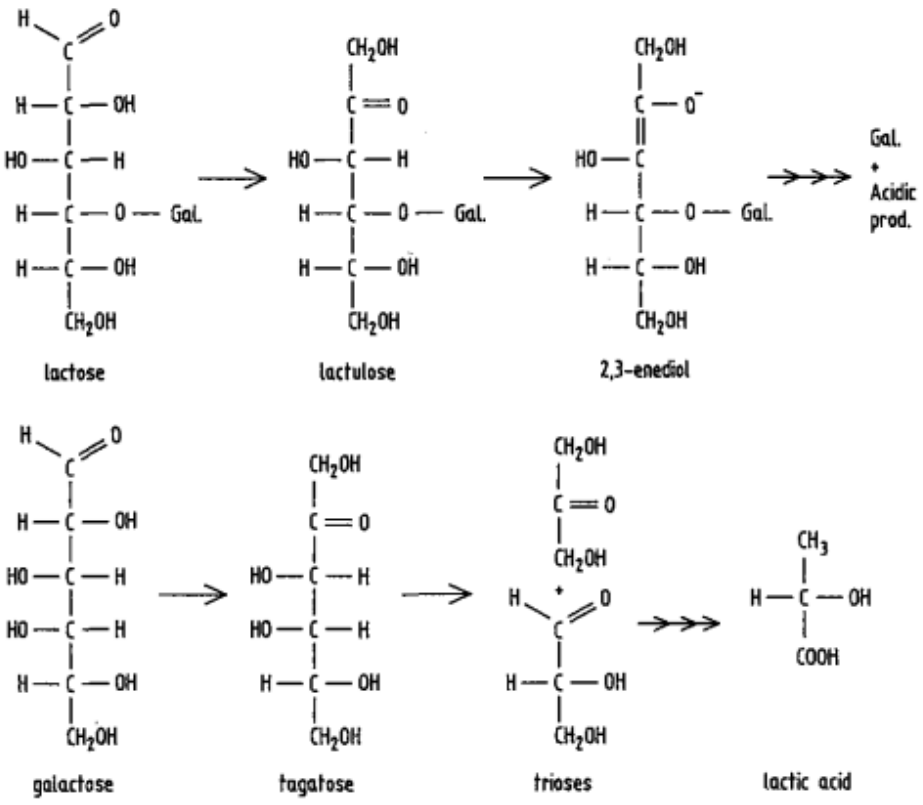

Figure 12 Lactose alkali degradation (Richards and Chandrasekhara, 1960)

Mention must be made that lactose can also produce compounds via reaction called Maillard reaction. Maillard reaction happens in high temperature when lactose reducing end reacts with amino group of protein. This is known reaction in food production. Most notable

compounds produced this way is HMF and formic acid. This reaction pathway is not possible in our case due to the absence of amino group. (Berg, 1993)

5.2. Cellobiose under alkaline conditions

Cellobiose is a disaccharide that consist of two glucose molecules linked together via β-(1,4') glycosidic bond just like in cellulose. Cellobiose can be think of like building block for cellulose. Glucose pairs forms cellobiose, cellobioses linked together forms oligosaccharide or cellulose in the end, depending on the number of monomers linked together. Cellobiose is reducing disaccharide just like lactose is. Cellobiose structure compared to cellulose is represented in figure 13. (Ouellette and Rawn, 2018, p. 907)

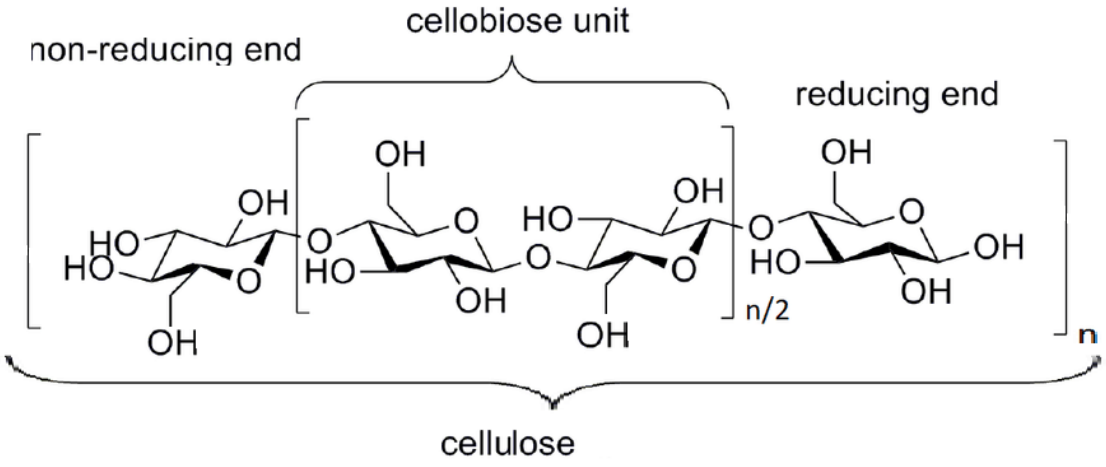

Figure 13 Cellobiose, adapted from (Montet, 2021)

Cellobiose behaviour in alkali environment is a complex process where isomerization between main disaccharides cellobiose, cellobiulose and glucosylmannose occur at the same time degradation of these disaccharides occur to either acid products or monosaccharides. Monosaccharides can also isomerase to three main hexoses which are glucose, fructose and to a lesser extend mannose. These monosaccharides can then degrade further to form for example organic acids among other products via different pathways such as retro-aldol

condensation, β-hydroxy/carbonyl elimination, benzylic acid rearrangement, α-dicarbonyl cleavage. (Bonn et al., 1985; Khondakar et al., 2021; MacLaurin and Green, 1969; Mohd Shafie et al., 2014)

5.2.1. Cellobiose transformation and degradation

Mohd Shafie et al., (2014) studied the decomposition of cellobiose at high temperature water 200-275 °C to find the primary decomposition pathways. He found that most of cellobiose 63-81% is isomerized to cellobiulose whereas isomerization to glucosylmannose and hydrolysis to produce two glucose moieties contributed only 8-12% and 6-27% respectively depending on the temperature. Finally minor degradation pathway to glucosyl-erythrose was also found, contributing less than 5% of total cellobiose decomposition.

The authors reasoned that it is plausible that isomerization is catalyzed by hydroxyl ions (OH^-) which is produced when the temperature of water is high and at the same time produced hydronium ions (H_3O^+) have high affinity towards water molecules and would not interfere. On the other hand, authors stated that hydroxyl ions are insufficient to catalyze all of the cellobiose which means some of the cellobiose is also catalyzed by hydronium ions. In summary decomposition of cellobiose in hot water have alkali/acidic nature to it. Moreover at the beginning of the decomposition some organic acids are produced which affect the decomposition (Khondakar et al., 2021). (Mohd Shafie et al., 2014)

Khondakar et al., (2021) studied the degradation of cellobiulose in high temperature water 200-250 °C and proposed novel pathways for its decomposition. The summary of the pathways is shown in figure 14 and it should not be confused with cellobiulose in alkali even thou they share some similarities as mentioned before. Figure 14 is good summary on the complex di/monosaccharide system. The abbreviations at the end are ISM=isomerization, DHD=dehydration, RAC=retroaldol condensation, BAR=benzilic acid rearrangement, ADC= α-dicarbonyl cleavage, BHE= β-hydroxy/carbonyl elimination which most of are already discussed about in this work.

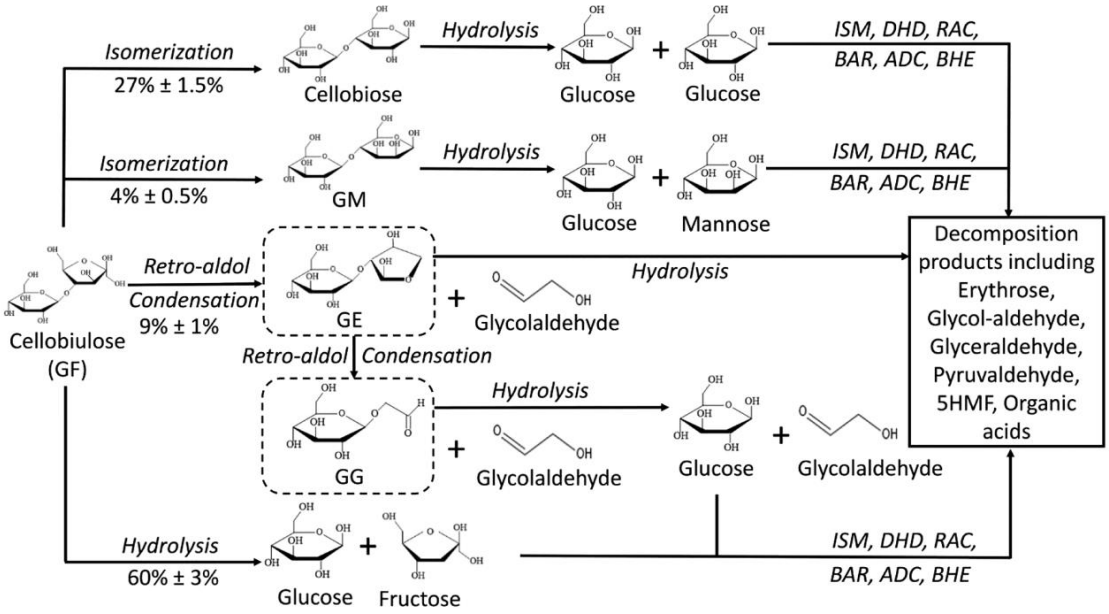

Figure 14 Cellobiulose pathways in hot water 200°C (Khondakar et al., 2021)

Cellobiulose hydrolysis to produce glucose fructose monosaccharides is primary pathway contributing 60% of the total decomposition and the isomerization to two other major disaccharides cellobiose and glucosylmannose (GM) contribute only 27 % and 4 % respectively. When compared to previous study Mohd Shafie et al., (2014) where cellobiose were decomposed in similar conditions up to 61% of cellobiose isomerized to cellobiulose rather than hyrdolyzed to glucose glucose moieties (8%). Khondakar et al., reasoned that transformation of glucose-glucose$_{\text{open-chain}}$ to glucose-fructose$_{\text{open-chain}}$ is much easier and leads to higher selectivity to cellobiose to isomerized to cellobiulose. The main end products were glycer/pyruv aldehydes having 7,6% and 20,7% selectivity respectively. Traces of 5HMF (<1,5%) was found and particularly organic acids such as formic, lactic and metasaccharinic acid having 5%, 11%, 7,5% selectivity.

MacLaurin and Green, (1969) degraded cellobiose, cellobiulose and glucosylmannose in 1 M NaOH solution and at 22°C. They found that by introducing any of these three disaccharides in NaOH solution two of the other disaccharides appeared as did three monosaccharides: glucose, fructose, and mannose. The authors calculated the rate constants and proposed reaction scheme for the system. Figure 15 shows two different triangles for the system, one for the disaccharides and one for the monosaccharides.

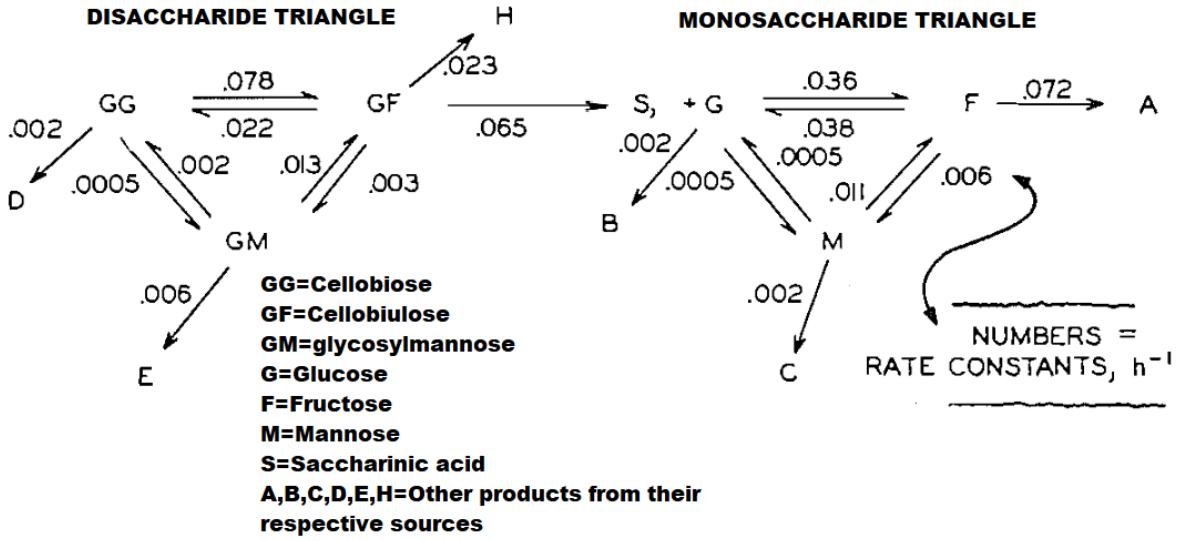

Figure 15 Reaction scheme in 1M NaOH and 22°C adapted from (MacLaurin and Green, 1969)

The same way as in hot water treatment, cellobiose in alkali seems to degrade via cellobiulose intermediate. The peeled of fructose moiety from cellobiulose produces "free" glucose monosaccharide which can in alkali isomerize to either fructose or mannose which then eventually degraded to end products, carboxylic acids. MacLaurin and Green stated that when excess alkali is available there is no equilibrium as the degradation by peeling or directly proceeds indefinitely. Moreover, they stated that 80% of starting cellobiose proceed through cellobiulose to the peeling reaction. Also, reaction rates seem to unfavor the formation of glucosylmannose on the disaccharide triangle and analogically the same can be seen on the monosaccharide triangle to mannose.

Cellobiose degradation under anaerobic atmosphere produces similar carboxylic acids as alkali degradation of cellulose. Adibi Larijani, (2020) identified 12 degradation products from cellobiose where most abundant were lactic acid, GISA, 2,5-DHPA. Also, glucose was found more readily than fructose and mannose. Moreover Macleod and Schroeder, (1982) degraded cellobiose in dilute NaOH 0,099M and in temperatures 25°C and 45°C. The authors detected eight acid products where lactic acid and GISA comprised approximately 63-65% of total observed products.

6. Stability of GISA

The stability of GISA has been studied as it is known to form a threat to the integrity of nuclear waste storage by forming complexes with americium and plutonium and release these radionuclides into the environment (Galadima, 2018). Either chemical or microbial degradation is likely to give products that have reduced complexing power (Greenfield et al., 1994a)

Greenfield et al., (1994b) studied the degradation of GISA by bubbling GISA and $Ca(OH_2)$ solution with O_2 and N_2 at room temperature and 80°C. Samples were taken after 10 months. Room temperature experiment showed no additional peaks in HPLC analysis for nitrogen bubbled samples and slight additional peaks for oxygenated. Experiment conducted at 80°C clearly showed additional peaks for oxygenated samples but only minor peaks for those in nitrogen atmosphere. Observed peaks in the oxygenated degradation were formic acid, lactic acid, and acetic acid. Oxygen seems not only to have inhibiting factor on the formation of GISA from cellulosic material but also accelerating effect on the degradation of GISA to smaller acids. The study also showed that in anaerobic conditions and slightly elevated temperature, minor amount of GISA is fragmented.

Greenfield's study is in line with study done by Niemelä, (1990). According to Niemelä GISA at 280°C could degrade to more stable acids and would thus also explain high lactic acid yields in his study. Moreover Pulidindi, (2014) agitated GISA with microwaves in presence of NaOH for 5 minutes. Degradation products were lactic acid, formic acid and ethylene glycol.

It would seem that GISA is not fully stable at elevated temperatures and also some other types of agitation can fragment it. This knowledge is important when considering the conditions for acid production from cellulose based raw materials.

7. Materials and methods

7.1. Equipment

Experiments were carried in PARR autoclave (shown in figure 16) which was connected to PARR 4842 control module where mixing speed and desired temperature could be monitored and adjusted. Autoclave itself had pressure and temperature sensors, nitrogen line, sampling line, mixer, heat exchanger for cooling and heater. For the heater there was two options I or II. Setting I was used in in all of the experiments to ensure same temperature derivative for the system.

Figure 16 Autoclave used in the experiments

7.2. Analyses

Acid analyses were done using HPLC-DAD, Agilent Technologies 1260 infinity with Phenomenex Synergi™ 4 µm Fusion-RP 80 Å column. Luna® Omega 5 µm Polar C18 100Å is also tested and suitable for analysis. Used eluent was 0,1% phosphoric acid (H_3PO_4) + 50mM Monosodium phosphate (NaH_2PO_4) with addition to methanol as a co-eluent. Used flowrate was 0,5 ml/min and used temperature 30°C.

Sugar analyses were done using HPLC-RID, Agilent Technologies 1260 infinity II. Phenomenex Rezex™ RPM-Monosaccharide Pb+ column was used to analyse sugars in lactose test. For this column the samples were neutralized. Used flowrate was 0,8 ml/min and analysis temperature 80°C. Rest of the sugars were analysed using Agilent technologies HI-PLEX Na (Octo) column with the same temperature and flow rate as above mentioned. Samples for this column were only diluted to water. Eluent for both columns were purified water. NaOH concentration at the end of experiment were determined using Mettler Toledo T50 titrator with 0,1M HCL.

Samples for acid analysis were first acidified under 1 pH using hydrochloric acid (HCL) and Finex CS16GC H+ resin with polystyrene-8%DVB matrix. Volumetric capacity and dry capacity of the used resin were 1,93eq/l and 5,10 meq/g respectively. Succinic acid was used as internal standard to observe the volume change by the precipitation. Later stages of the reaction some unknown products had the same retention time as succinic acid. Hence the volume change correction at the beginning of the reaction was applied to also account the samples that were taken at the later stages of the reaction as it was observed by eye that the precipitation amount decreased towards the end of the reaction. Precipitation only occurred this visibly on the microcrystalline and toilet paper experiments. The mono/disaccharide experiments showed no visible precipitation.

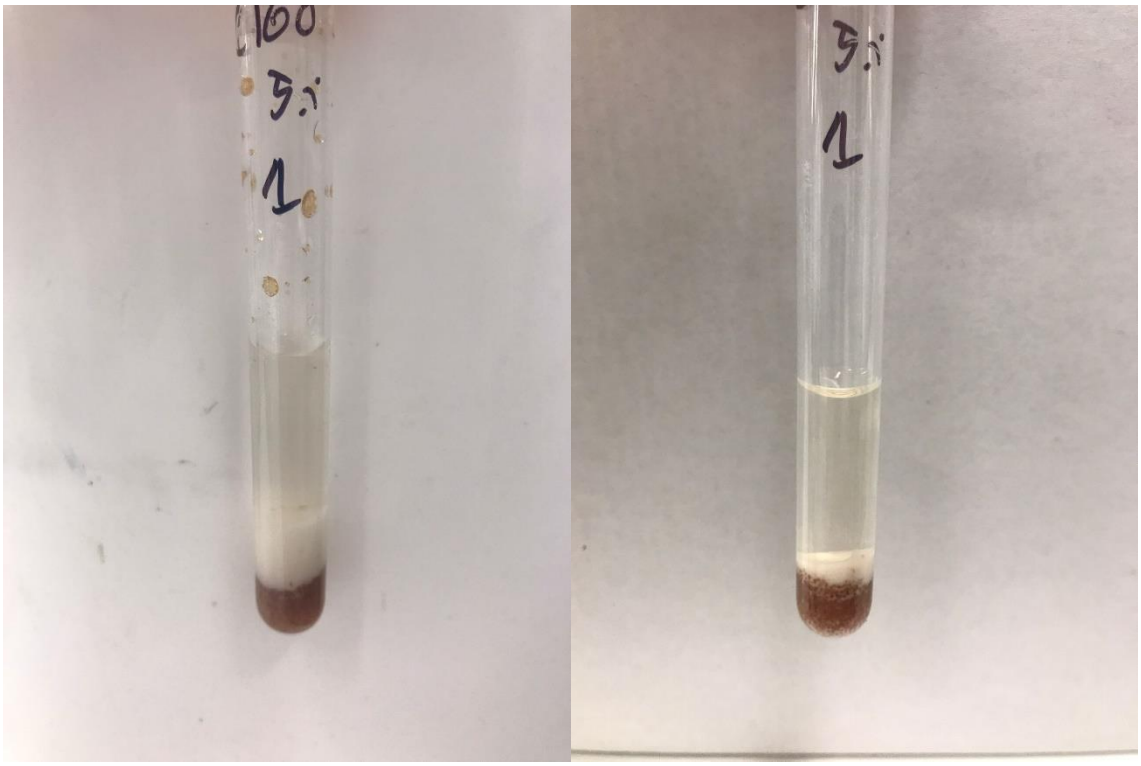

Figure 17 example of the precipitation. Cellulose sample on the left and same sample centrifuged on the right. Resin at the bottom

7.3. Chemicals

The sodium hydroxide (NaOH) solution was done by diluting sodium hydroxide pellets (98,8%, VWR) to purified water. D(+)-Lactose Monohydrate (≥ 98%) from Honeywell Fluka™ was used in lactose experiments. Sigma-Aldrich D-(+)-Galactose (≥ 98%) was used in experiment done with galactose. Cellulose tests were done with microcrystalline cellulose (100%, Alfa Aesar). Cellobiose test were done with D-(+)-cellobiose (≥ 98%) from Sigma-Aldrich and for the toilet paper Serla yellow toilet made from recycled fibers was used (appendix VI).

7.4. Experiments

In this work, the experimental results are reported and discussed in separate sections based on the raw materials. Conversion of disaccharides (lactose, cellobiose) to hydroxy acids and degradation of monosaccharide galactose are discussed first, followed by experiments with microcrystalline cellulose and finally with toilet paper

Experiments were done to study the concentration of organic acids at the beginning of the reaction. The autoclave was filled with desired amount of NaOH solution and solids. After the autoclave was assembled nitrogen atmosphere was added by opening the nitrogen valve and rising the pressure to ~10 bar and then emptying the vessel. This was done five times to purge air, and lastly the nitrogen pressure was left at ~10 bar. Mixer was set to ~470 RPM in lactose experiments and ~670 RPM in cellulose, cellobiose and toilet paper experiments.

The experiment time varied depending on the reaction temperature. Heating time varied between 15 minutes (80°C) to 57 minutes (200°C) depending on the desired temperature. Timer was started at the same time reactor heating was started.

In lactose experiment the samples were taken every three minutes until desired temperature was achieved. Then the experiments were carried for two more hours, and two more samples were taken, first after one hour after the desired temperature was achieved and second after two hours. In galactose and cellulose experiments samples were taken at the beginning the same way as in lactose experiments but after desired temperature was reached, then four sample were taken every 30 minutes.

Table I Lactose experiments

Lactose	Temperature [°C]	L/S ratio	c(NaOH) wt%	Reaction time [h,min]
1	80	9	10	2h 15min
2	100	9	10	2h 18min
3	120	9	10	2h 24min
4	140	9	10	2h 33min
5	160	9	10	2h 39min
6	180	9	10	2h 48min
7	200	9	10	2h 57min

Table II Galactose experiments

Galactose	Temperature [°C]	L/S ratio	c(NaOH) wt%	Reaction time [h,min]
1	120	9	10	2h 27min

First pair of cellobiose experiment were done with 5% and 10% NaOH and at 100°C. The second pair of experiments were done with 5% NaOH concentration and at lower temperatures 80°C and 60°C as the degradation in 100°C and 10% NaOH concentration were quite fast. Also, the L/S ratio was increased to 18 by keeping the same amount of NaOH 270g but inserting only 15g of cellobiose. Samples for cellobiose experiment were taken once every 3 minutes until desired reaction temperature was reached then once every 15 minutes until 2 hours was passed.

Table III Cellobiose experiments

Cellobiose	Temperature [°C]	L/S ratio	c(NaOH) wt%	Reaction time [h,min]
1	100	18	10	2h 21min
2	100	18	5	2h 21min
3	80	18	5	2h 18min
4	60	18	5	2h 12min

Plenty of microcrystalline cellulose tests were conducted to 1. observe the effect of how different NaOH concentrations (10%, 5% and 2,5%) degrade cellulose in different temperatures and 2. how cellulose degrades in differing temperatures 100°C to 200°C. Some of the cellulose experiments were done differently as was observed that it would be more efficient to take the first sample at 18 minute mark that was right before the reaction seemed to start and almost zero point for acid yield was obtained. As we removed sampling from the start of the experiment, we increased them at the end of the experiment and took one sample every 15 minutes after desired temperature were reached.

*Table IV Cellulose tests with same NaOH concentration. *Experiments in 180°C were done thrice with extended time.*

Microcrystalline cellulose	Temperature [°C]	L/S ratio	c(NaOH) wt%	Reaction time [h,min]
1	100	9	10	2h 18min
2	140	9	10	2h 30min
3	160	9	10	2h 43min
4	180	9	10	2h 48min,5h,7h*
5	200	9	10	3h

Table V Cellulose tests with dilute NaOH

Microcrystalline cellulose in dilute NaOH	Temperature [°C]	L/S ratio	c(NaOH) wt%	Reaction time [h,min]
1	100	9	5	2h 21min
2	160	9	5	2h43min
3	200	9	5	3h
4	100	9	2,5	2h 21min
5	200	9	2,5	3h

Last group of experiments were done with toilet paper in different forms (shredded, milled and slurried). Idea was to mimic rejection water from fiber mills and see how “real” raw materials would behave in reactor. Sampling for these experiments were quite difficult as blocking of the reactor tubes occurred but nevertheless these experiments were tried to conduct like those of microcrystalline cellulose.

Table VI Toilet paper experiments

Toilet paper	Temperature [°C]	L/S ratio	c(NaOH) wt%	Reaction time [h,min]
1.Shredded	200	18	10	3h
2.Shredded	200	18	10	3h
3.Milled	200	18	10	2h58min

4.Slurry	160	25	10	6h
5.Slurry	200	25	10	4h

8. Results

8.1. Lactose and galactose experiments

Lactose experiments were the first ones that was conducted. Experiment with lactose gave good opportunity to refine the use of autoclave, sampling technique, sample acidifying and HPLC-analysis for both carboxylic acids and sugars. All the lactose experiments were done with same parameters: L/S, [NaOH] except the temperature and to some extend reaction time (See table 1). 30g of lactose was weighed to decanter glass and 270g of 10% NaOH was added. First the lactose absorbed the liquid and produced slurry like mixture but after a short period of stirring with glass rod the lactose started to dissolute and light yellow watery like fluid was then poured into the reactor vessel. Total mass-yield for the different lactose experiments is shown in figure 18

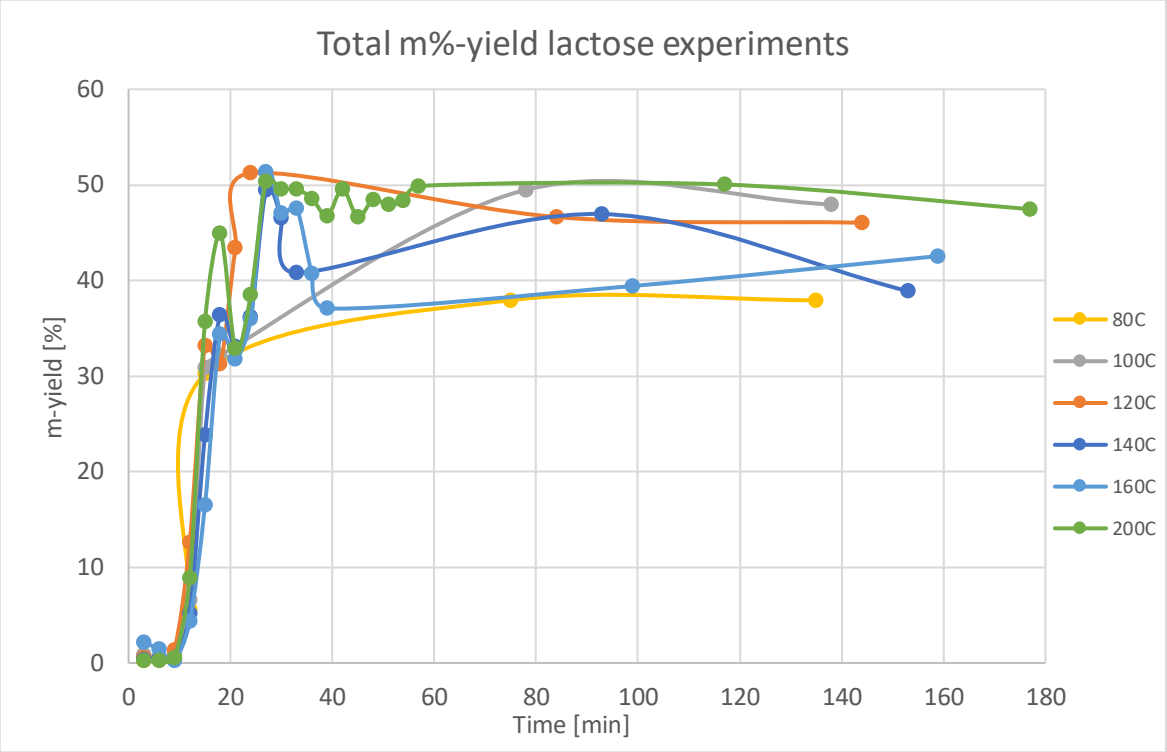

Figure 18 Formation of carboxylic acids from lactose during high-temperature alkali cooking. "m%-yield" means the mass fraction of raw material that is converted to carboxylic acids that are visible in HPLC analysis. See table I for details.

Total acid yield from 30g of lactose was between 37% and 47% for 80°C and 200°C respectively. Main degradation products were GISA 67% and lactic acid 24% of the total detected degradation products in 80°C and similarly in 200°C GISA and lactic acid amount observed were 66% and 22% respectively. In other words, total degradation was higher in higher temperatures, but the composition of the main acids remained quite similar. Different experiments took a bit different time due to the time it took to heat the reaction solution to desired temperature.

HPLC-Analytic of the produced acids were quite challenging for lactose as unknown intermediates formed during the heating period at roughly 15-25 minutes into the experiment when temperature of the reactor vessel was between 80-116°C. This analytical problem caused the total acid yield curve to dip down. Dip of the curves is shown in figure 19 which is same as figure 18 but time-axis is limited to 30 minutes. It should be noted that experiments done in 80°C and 100°C sampling was delayed to 1h because both reached the

reaction temperature desired for them. This means that no “dip” was observed on these experiments because no samples were taken at the time of these intermediates being in the solution.

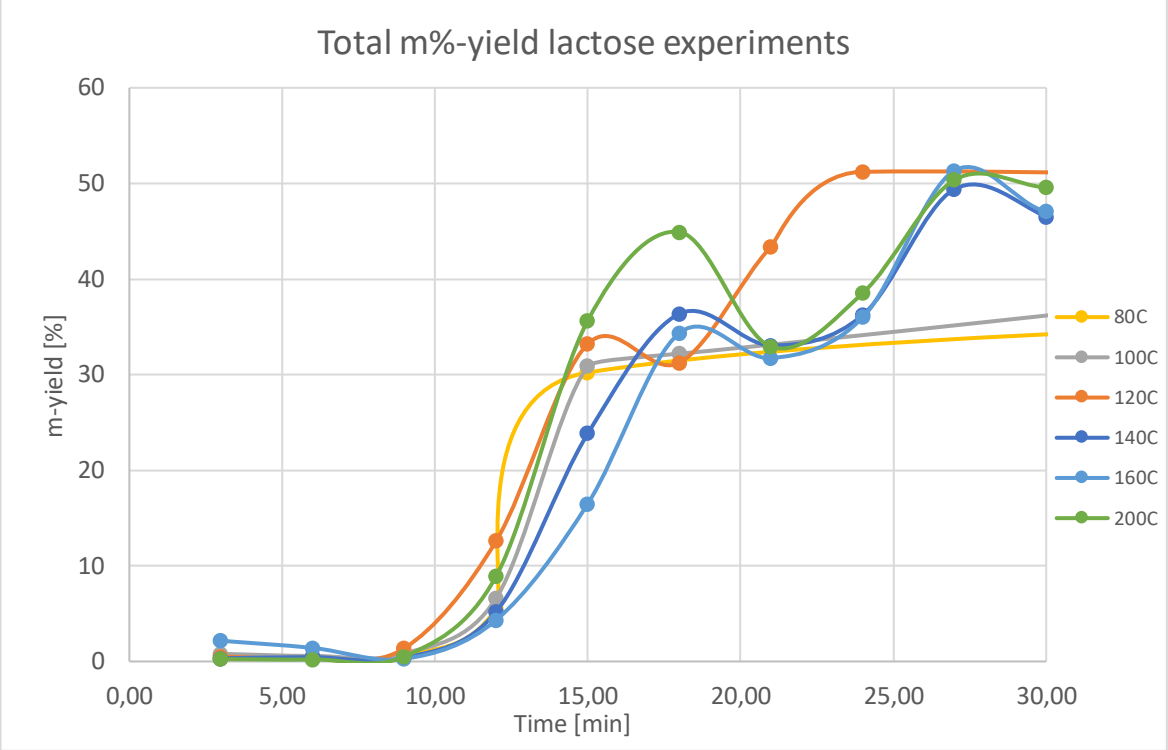

Figure 19 Total acid yield x-axis zoomed to 30 minutes to highlight the m-yield “dip”

The disturbing intermediates had similar retention times as the main degradation product GISA had. No intermediates were observed prior to 15 minutes or then at the later parts of the experiments. HPLC-diagram is shown in figure 20 and it clearly shows two additional peaks one right and one left of GISA peak.

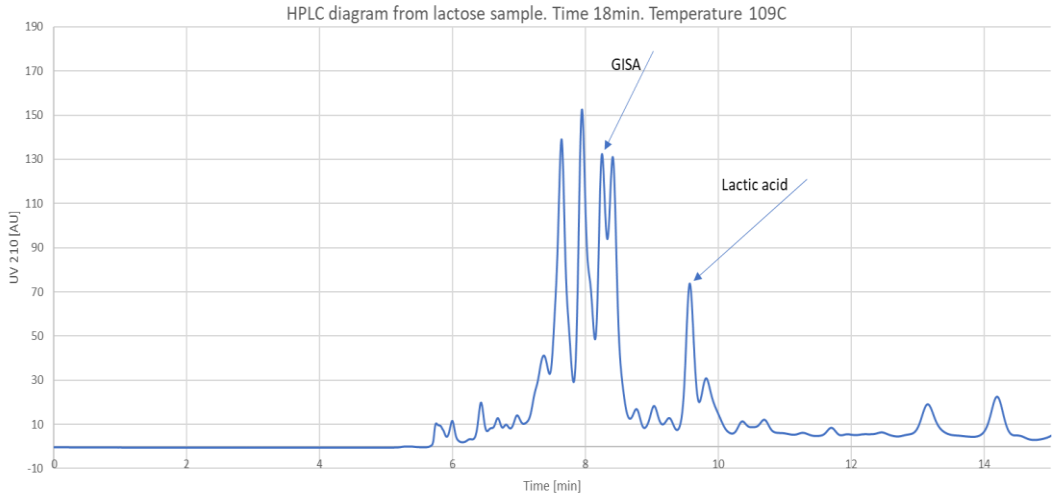

Figure 20 example HPLC diagram from lactose experiment 3 sample which was taken at 18 minutes into the experiment at temperature 109°C (See table I for more details).

The lactose experiments gave the possibility to analyse produced sugars. The analysis shows that full degradation of lactose took approximately 27 minutes and it produced "free" galactose into the solution. No peaks at glucose retention time were observed indicating that no "free" glucose molecules are produced from lactose degradation. The galactose amount in the solution increases momentarily accounting 20 w-% of total lactose mass at 15 minutes and the decreases. GISA analysis problem is also observable in the figure 21 where after 18 minutes the GISA amount seems to drop and then again in increase. Lactose degradation seems to obey the proposed mechanism discussed in chapter 5. Relative mass of found sugars and main degradation acids is shown in figure 21.

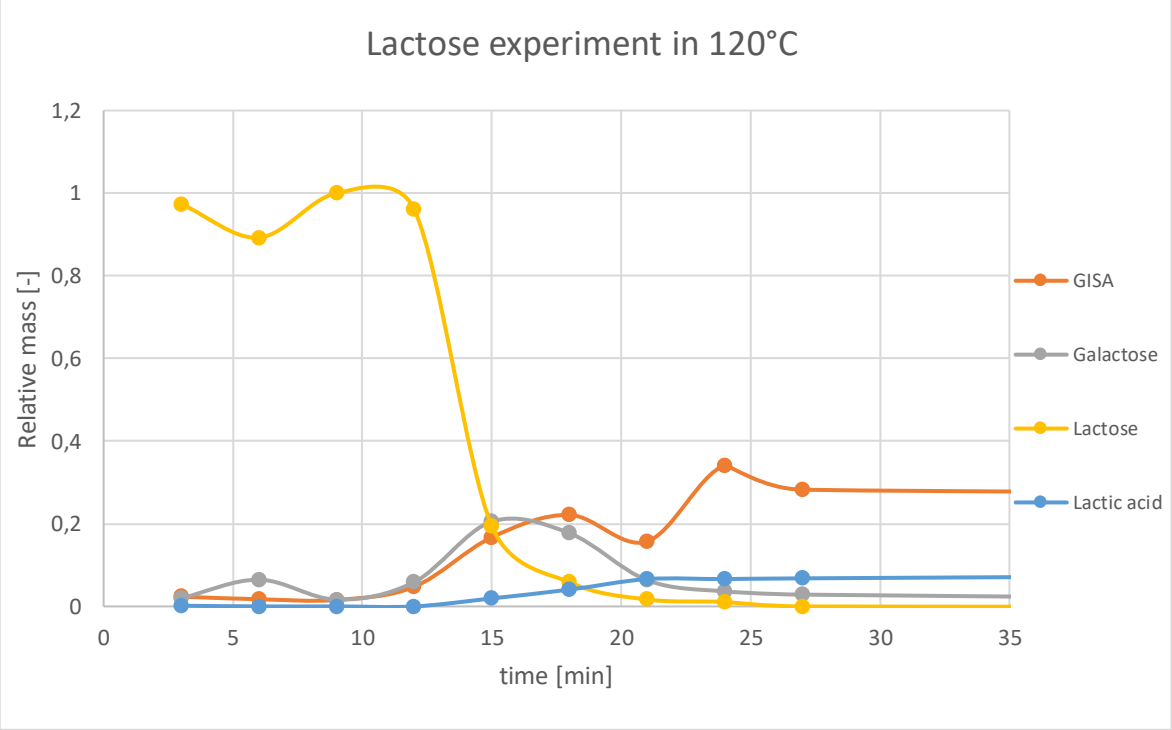

Figure 21 Lactose degradation to monosaccharides and main acids. See table I for more information.

Last part of lactose experiments was to study the galactose alkali degradation. The galactose's main degradation product has been found to be lactic acid. Total acid yield from 30g of galactose was 21% and composed mainly of Lactic acid (>85%). Simple monosaccharide galactose degraded very rapidly in 12 minutes when temperature was only 63°C. The sudden increase in GISA amount after 15 minute is similar analysis problem most likely as was observed in lactose case. This is also supported by the fact that GISA amount after 18 minute decreases, which is unlikely as it has been shown to be quite stable in nitrogen atmosphere and the temperature mild temperature 120°C. The small GISA amount (<5%) at the end of the reaction was most likely due to impurities from the galactose. The Y-axis is scaled according to the initial galactose amount that was put into the reactor. The starting values of galactose is lower because galactose is known to isomerase to D-Talose and D-Tagatose (Khuwijitjaru et al., 2018).

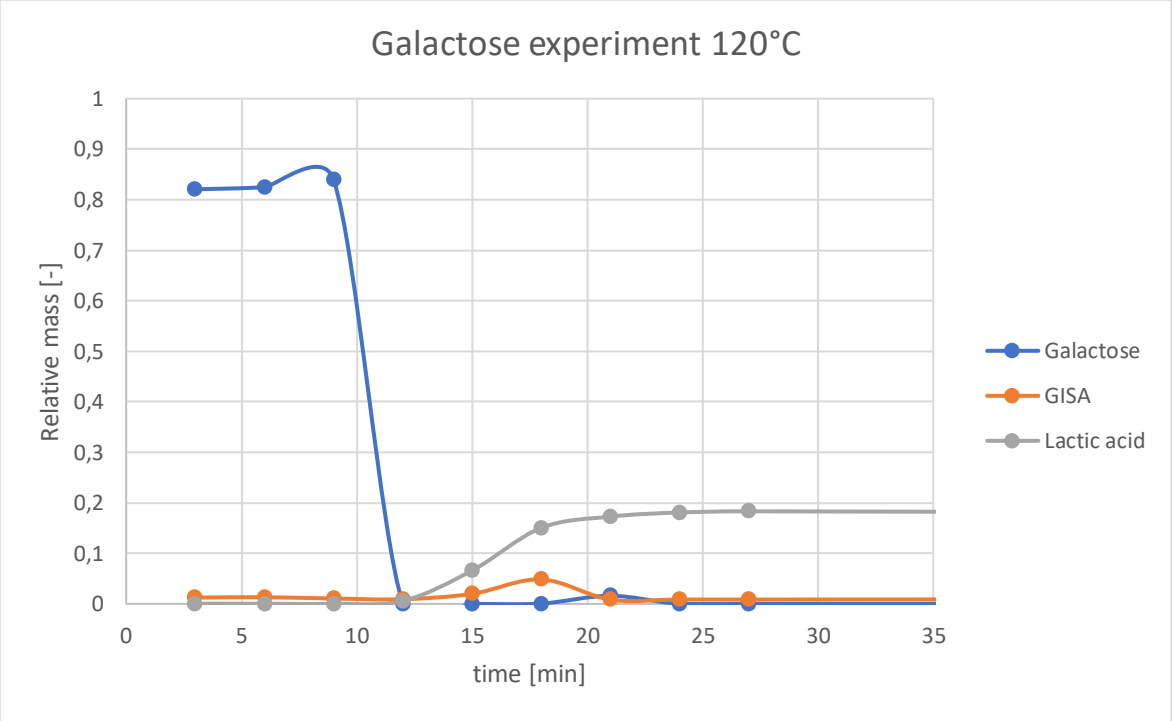

Figure 22 Galactose alkali degradation to GISA and Lactic acid. See table II for more information.

In summary the use of lactose for cheap alternative for modelling the cellulose degradation was not successful due to the intermediates formed during the reaction. The experiments however gave good opportunity to refine the techniques used further in this study.

8.2. Cellobiose

Before we can discuss the cellobiose results we need to understand how the analysis of sugars were done. The analysis was done with HI-PLEX Na (Octo) column which did not separate fully the two main disaccharides cellobiose and cellobiulose that are present in the alkali solution. The example HPLC diagram is shown in figure 23. It is evident that the shoulder on the left side of cellobiose peak is cellobiulose and thus in the following kinetic diagrams cellobiose amount is equal to sum of cellobiose and cellobiulose (cb+cbiu).

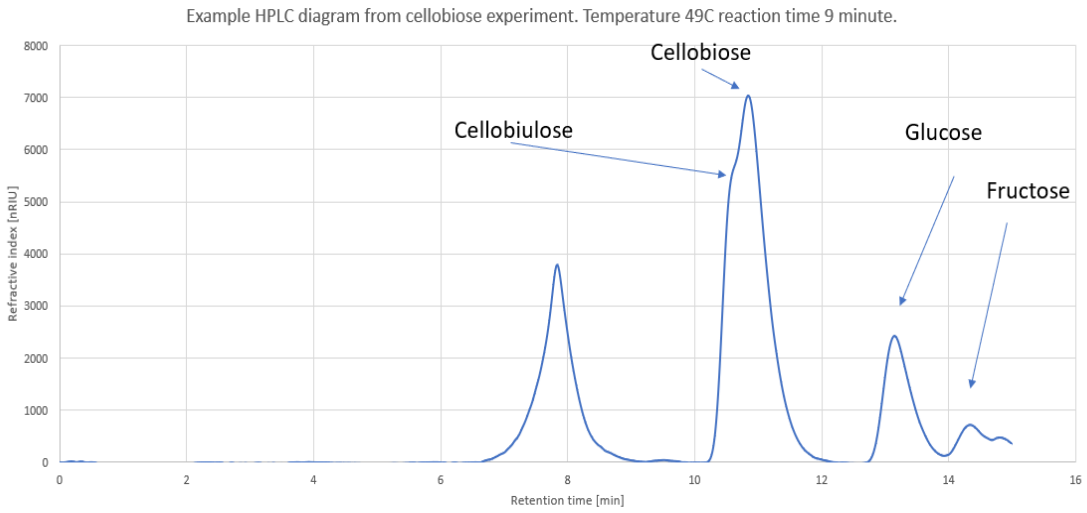

Figure 23 Example HPLC diagram from cellobiose test 1, sugar analysis side. Sample in the figure is taken at 9 minutes into the experiment at temperature 49°C. See table III for details.

Cellobiose test were done to study the kinetics of alkali degradation as it has similar bond between the glucose units as cellulose. From the lactose experiments it was found that high temperatures were quite unnecessary for simple disaccharide and the chosen temperatures for cellobiose was much lower to better observe kinetics and the L/S ratio was increased to 18 by halving the amount of cellobiose added to reactor (15g). The first pair of experiments were done in 100°C and in two different NaOH concentrations 5% and 10%. Cellobiose behaved similarly to lactose when NaOH was introduced. The experiment results are shown in figure 24 and figure 25.

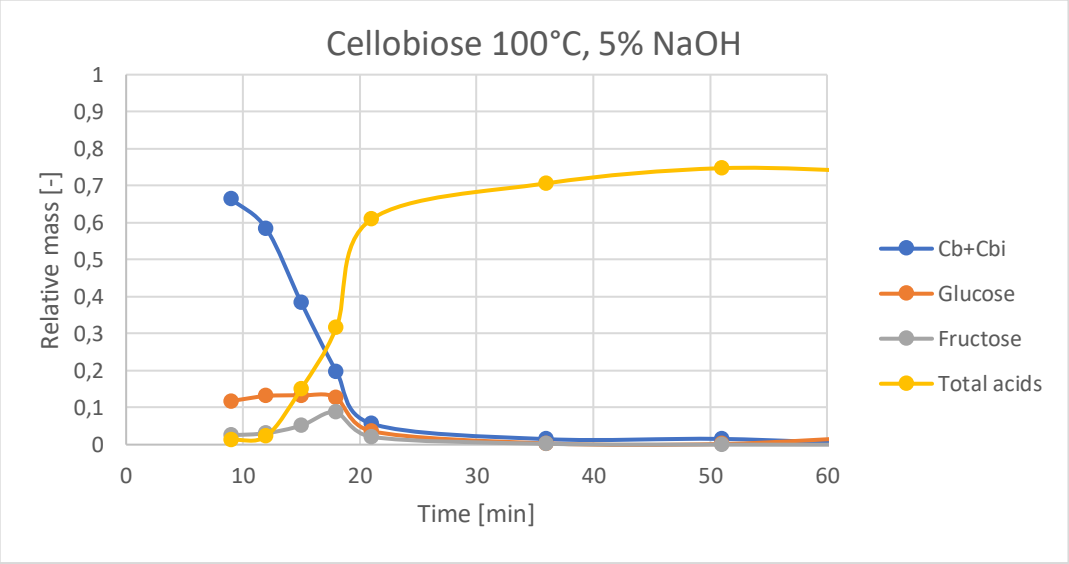

Figure 24 Cellobiose experiment in 100°C and 5% NaOH. See table III for details

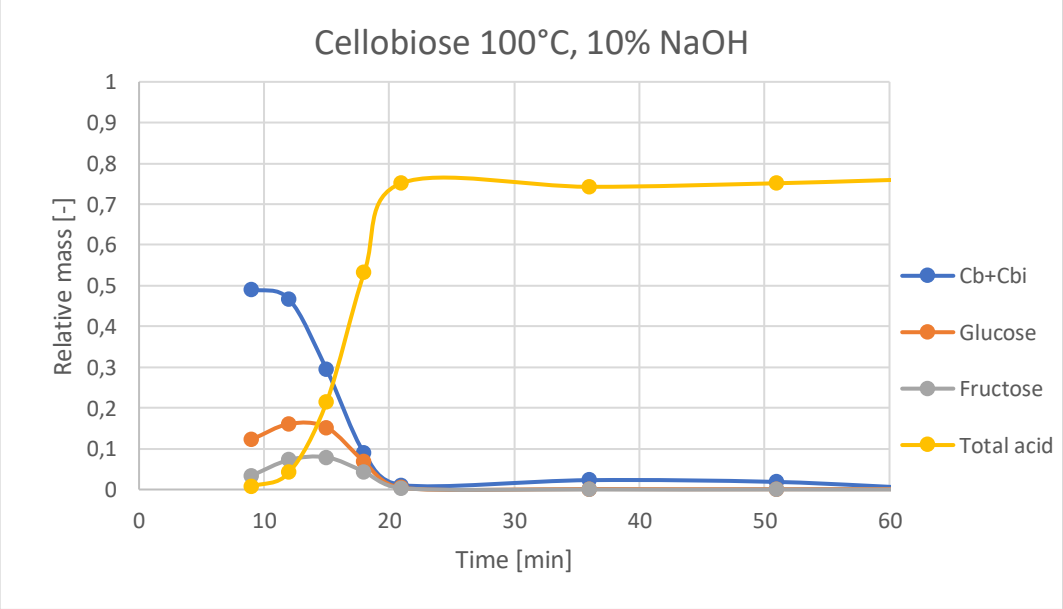

Figure 25 Cellobiose experiment in 100°C and 10% NaOH. See table III for details

The y-axis was scaled to match the initial cellobiose concentration at the beginning of reaction. In the first experiment at the 9 minute, 34% of cellobiose is converted to glucose (12%) and only 1% to acid and 1% to fructose. However, in 10% NaOH the at the same 9-minute mark already 51% of initial cellobiose is converted to glucose (12%) with an increased amount of fructose (3%) and similar amount of acids (1%). Total acid yield was roughly 75% for both of the experiments but the one with increased NaOH concentration seemed to achieve the yield in 21 minutes when in the dilute one it took 50 minutes. The

composition of acids in both experiments is shown in table VII. The composition of acids between the test were almost identical.

Table VII Acid composition of cellobiose experiments See table III for details

Experiment	Cellobiose 1 acid composition [%]	Cellobiose 2 acid composition [%]	Cellobiose 3 acid composition [%]	Cellobiose 4 acid composition [%]
GISA	58	61	55	55
Lactic acid	26	28	27	29
Formic acid	7	5	7	6
2,5-DHPA	4	4	5	4
Acetic acid	4	1	5	5
Glycolic acid	1	1	1	1

The second pair of cellobiose test were done with 5% NaOH solution and in lower temperature 80°C and 60°C to better observe the reaction rate, other parameters were kept same. The test results are shown in figure 26 and 27. Reaction rate clearly decreases when the temperature is decreased and the full degradation of cellobiose in 60°C takes approximately 72 minutes when in above 80°C it takes 21 minutes. Also the total acid yield is approximately 69% and 72% in the experiments done in 60°C and 80°C respectively. Acid composition for these experiments were almost identical.

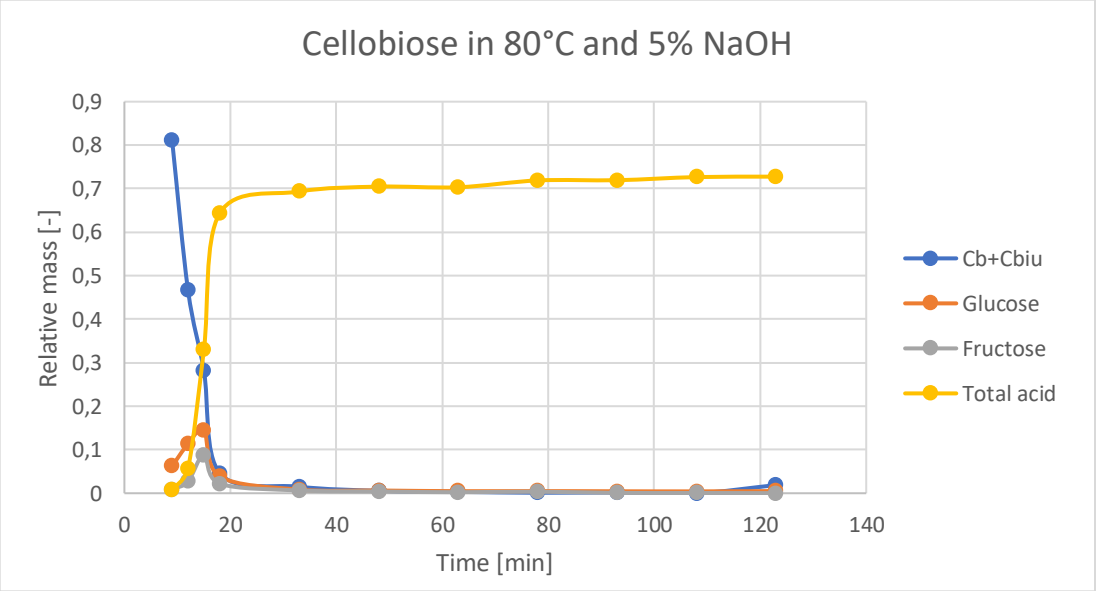

Figure 26 Cellobiose test 3 See table III for details

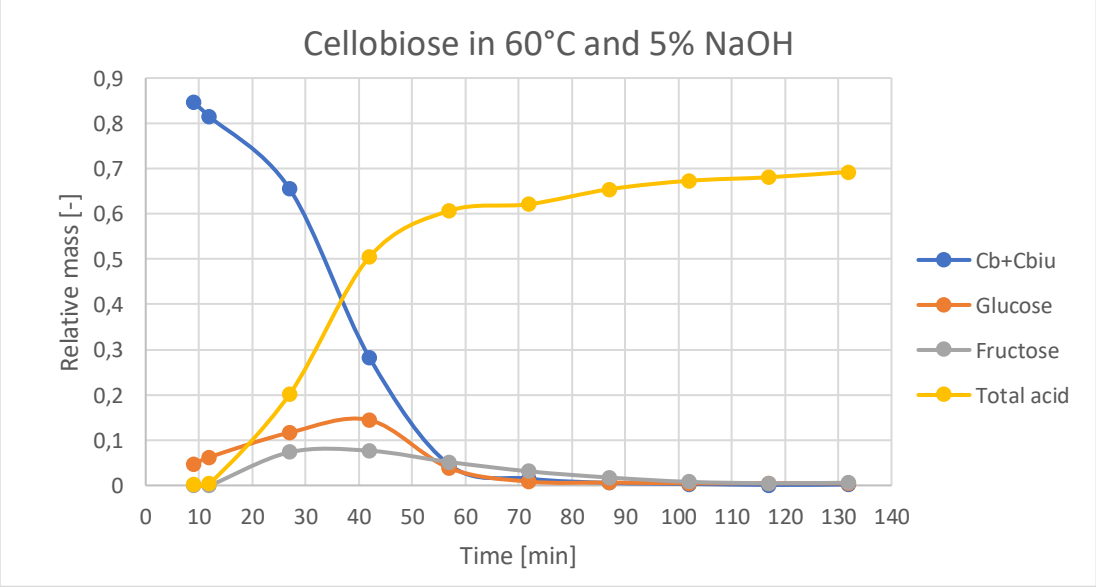

Figure 27 Cellobiose test 4 See table III for details

8.3. Microcrystalline cellulose

Microcrystalline cellulose alkali degradation was a major part of this study. With it, both the effect of temperature and effect of NaOH concentration on the degradation was studied. First the effect of temperature was studied in seven different experiments with differing temperature 100-200°C. L/S ratio was 9 meaning 270g of 10w% NaOH was mixed with 30g of microcrystalline cellulose. Microcrystalline cellulose swelled immediately when it contacted the 10% NaOH resulting in slurry like mixture.

Experiments 1, 2 and 5 samples were taken every 3 minutes until desired temperature was reached then every 30 minutes until end of the experiments. The rest were done bit differently as it was observed that cellulose starts to degrade after 18 minutes so first sample was taken then. Then every five minutes until desired temperature was reached and then every 15 minutes until end of the experiments.

Experiments in 180°C were done three times with different timing of sampling. First experiment in 180°C was done as mentioned before. The second (2) was done similarly but at the end it was continued until 5 hours and two more samples was taken. In the third (3) experiment only three samples were taken after 5, 6 and 7 hours.

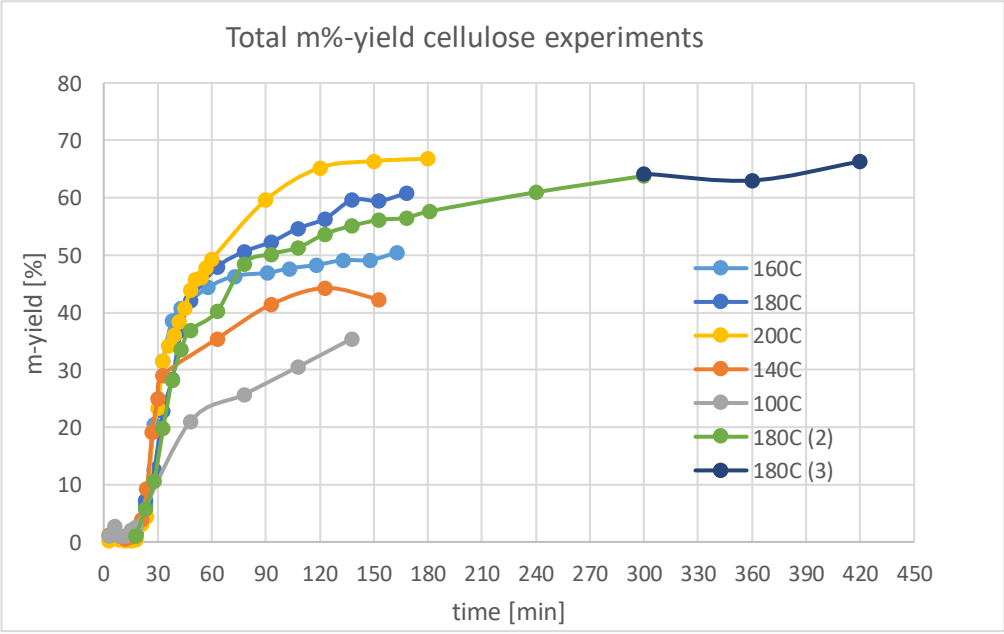

Figure 28 Total acid yield in cellulose experiments with 10w% NaOH concentration. See table IV for more information.

Total acid yield of cellulose experiments is shown in figure 28. Highest acid yields (66%) were obtained at 200°C in 3h and at 180°C in 7h. The lowest yield was for the 100°C experiment with 35% yield. It is evident that higher temperature allows further degradation of cellulose and thus better acid yield. Moreover, cellulose was fully degraded in these two highest yield experiments meaning that there were no visible cellulose solids in the reactor vessel after the experiment. Solids were however found in all the other experiments in differing amounts. So, it can be concluded that cellulose was fully degraded in 200°C and approximately 20 g of acids were produced from 30g of cellulose. It must be mentioned that for cellulose experiments no sugar analysis was conducted meaning that there could be soluble oligosaccharides, but this is however unlikely given the drastic temperature and/or long reaction time.

The experiments done at 180°C showed that by increasing the experiment time to 7h we can reach the same total yield as at 200°C in 3h. This highlights the alkaline hydrolysis phenomena as it is described to be slower than peeling and thus becomes rate limiting step when all the accessible amorphous cellulose is degraded.

Solid residues after experiments were washed until pH 7 and then dried in vacuum oven. Weighed residue solids were plotted against the targeted experiment temperature and resulted in figure 29. In figure 29 washed and dried solid residue is shown, the white colour indicates that it is unreacted cellulose.

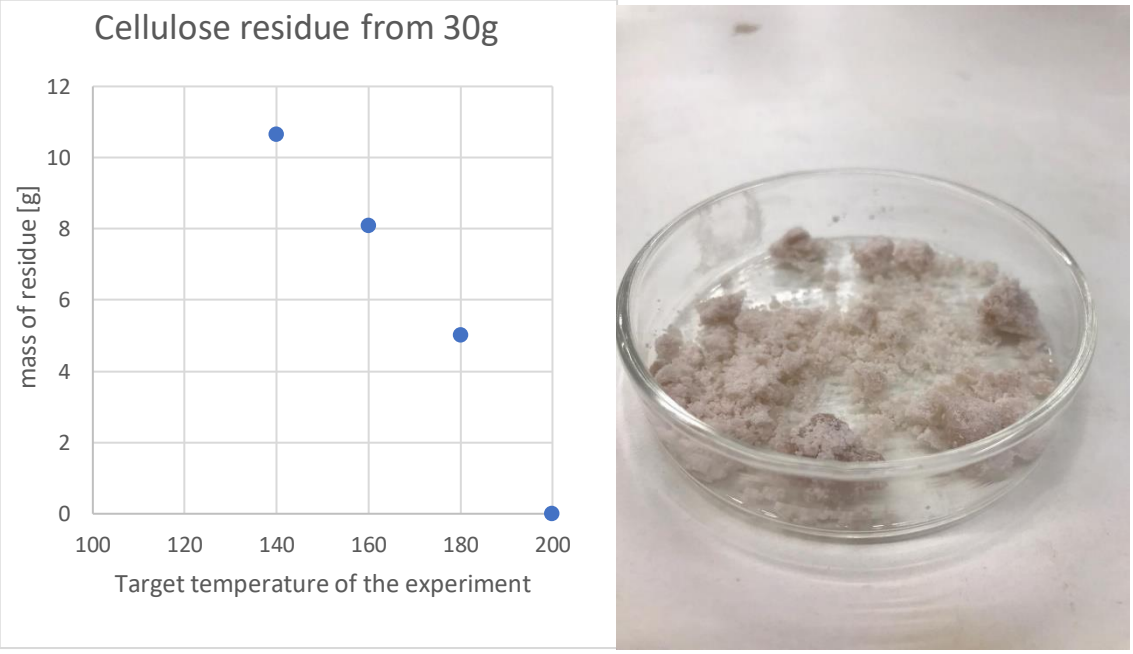

Figure 29 (left) cellulose residue amount versus reaction temperature. (Right) washed and dried cellulose residue from the experiment done in 160°C

Table VIII Acid composition at the end of experiments. See table IV for details and experiment conditions.

Reaction temperature [°C]	GISA [%]	Formic acid [%]	Lactic acid [%]	2,5-DHPA [%]	Glycolic acid [%]	Acetic acid [%]	**Total m-% yield [%]**	**End alkali concentration [mol/l]**
200	63	14	12	9	2	1	**67**	**1,45**
180 (7h)	67	11	9	10	1	1	**66**	**1,48**
180 (5h)	67	13	9	9	2	1	**64**	**1,66**
180	71	10	8	9	1	0	**60**	**1,77**
160	74	10	6	9	1	0	**50**	**1,79**
140	75	11	5	7	1	0	**42**	**1,81**
100	83	7	3	6	0	1	**35**	**1,96**

Acid composition of cellulose experiments in 10w% NaOH is shown in table VIII. GISA's relative amount decreases by 20 percentage points while at the same time the total yield is

doubled when the temperature is increased from 100°C to 200°C. This is most likely due to other acids being produced more readily like lactic acid and formic acid. From the acid production point of view there could be potential to produce higher concentration GISA in lower temperature rather than lower concentration GISA in higher temperature. This depends on the application of the acids however and the total acid yield should also be taken into consideration. These experiments were done in 10w% NaOH which equals to 2,77 mol/l. Full degradation of 30g of microcrystalline cellulose required approximately 12,3g of NaOH.

8.4. Dilute NaOH experiments

More microcrystalline cellulose experiments were done in 5w% and in 2.5w% NaOH to study the effect of OH^- concentration on the degradation. Microcrystalline cellulose in dilute NaOH behaved differently than in 10w% as there was no mercerization phenomenon visible. The figure 30 shows the effect of dilute NaOH to cellulose.

Figure 30 Microcrystalline cellulose in 5w% and in 10w% NaOH concentration with L/S 9

The 5w% NaOH mixture behaved like there were no interaction between the phases it could be described as solid like particles in water whereby shaking the tube the microcrystalline cellulose mixed but given time, they settled at the bottom. On the other hand, in the 10w% NaOH solution mercerization is visible as the mixture became more slurry and viscose and there was no distinct interphase between the phases. This finding is in line with the study done by (Dinand et al., 2002). Additionally, this phenomenon affects slightly on the temperature ramp up in the experiments as the slurry like mixture does not heat as steadily as the other.

The experiments were done in 3 different temperatures 100°C, 160°C and in 200°C. 2,5w% Experiment was only done in 100°C and in 200°C. The total acid yield of experiment conducted in 100°C is shown in figure 31 and it shows that there is not much, only 5 percent point between the experiments on the total acid yield, but the total acid yield is quite low which is understandable in for such a low temperature experiment.

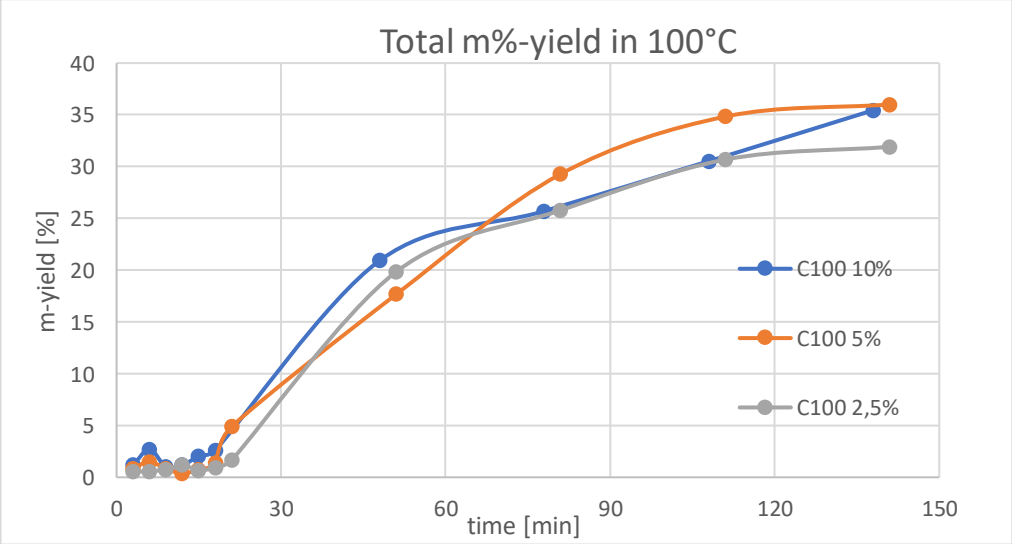

Figure 31 total acid yield in 3 different NaOH concentration at 100°C. See table V for details

Table IX Acid end composition of 100°C experiments. See table V for details and experiment conditions

Experiment in 100°C	GISA [%]	Formic acid [%]	Lactic acid [%]	2,5-DHPA [%]	Glycolic acid [%]	Acetic acid [%]	**Total acid yield [%]**	**Consumed alkali [mol]**
10 %	83	7	3	6	0	1	**35**	**0,80**
5 %	76	10	5	8	0	1	**36**	**0,62**
2,50 %	63	15	8	12	1	0	**32**	**0,60**

The end composition of acids is shown in table IX. GISA formation seems to favour higher NaOH concentration and on the other hand lower alkali concentration seems to favour the formation of formic acid, lactic acid and 2,5-DHPA. Consumed alkali is calculated by subtracting end concentration from the initial NaOH concentration and multiplying by liquid volume. Initial NaOH concentrations are 2,77 mol/l, 1,385 mol/l and 0,69 mol/l for 10w%, 5w% and 2,5% respectively.

Two experiments were done in 160°C with 5w% and 10w%. The total acid yield was increased to approximately 50% compared to the experiments done in 100°C. This happens most likely due to some alkaline hydrolysis occurring and creating more reducing ends from the alkali inaccessible crystalline region. The alkali concentration between 5w% to 10w% does not seems to have an effect in neither the total degradation of cellulose in 160°C or in the acid end composition.

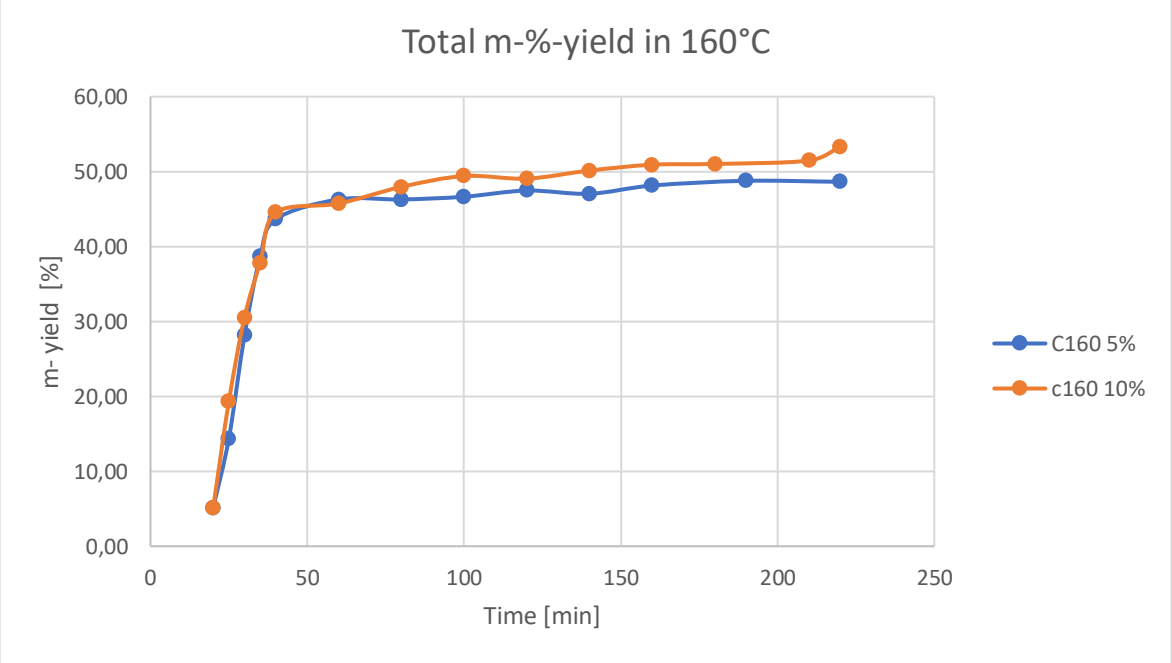

Figure 32 Total acid yield in experiment done at 160°C. See table V for more information

Table X Acid end composition of the experiment at 160°C. See table V for details and experiment conditions

Experiment in 160°C	GISA [%]	Formic acid [%]	Lactic acid [%]	2,5-DHPA [%]	Glycolic acid [%]	Acetic acid [%]	**Total acid yield [%]**	**Consumed alkali [mol]**
10 %	74	10	6	9	0	1	**50**	**0,97**
5 %	71	11	7	9	1	0	**49**	**0,82**

The last experiment with different NaOH concentration was done in 200°C. Solid residue was found from all the experiments except from the one that was done in 10w% NaOH. The total acid yield is shown in figure 33 and shows that the 5w% experiment is a bit slower compared to the 10w% experiment. Now that the temperature is quite high the alkaline hydrolysis is the rate limiting step and it is known that alkali concentration affects kinetics of it.

The 5% experiment would have probably reached the similar acid yield as the 10w% if given enough time as there was still unreacted cellulose after the experiment and the titration of showed that there was still alkali available. The 2,5w% experiment however showed that it

is possible that all alkali is consumed by the process. The end solution of this experiment was not titrated, but the pH of the solution showed 6,89 meaning that it had turned to acidic.

The acid composition of the experiments indicated similarly as in the experiments at 100°C that the lower NaOH concentration favours the formation of formic acid and 2,5-DHPA rather than GISA.

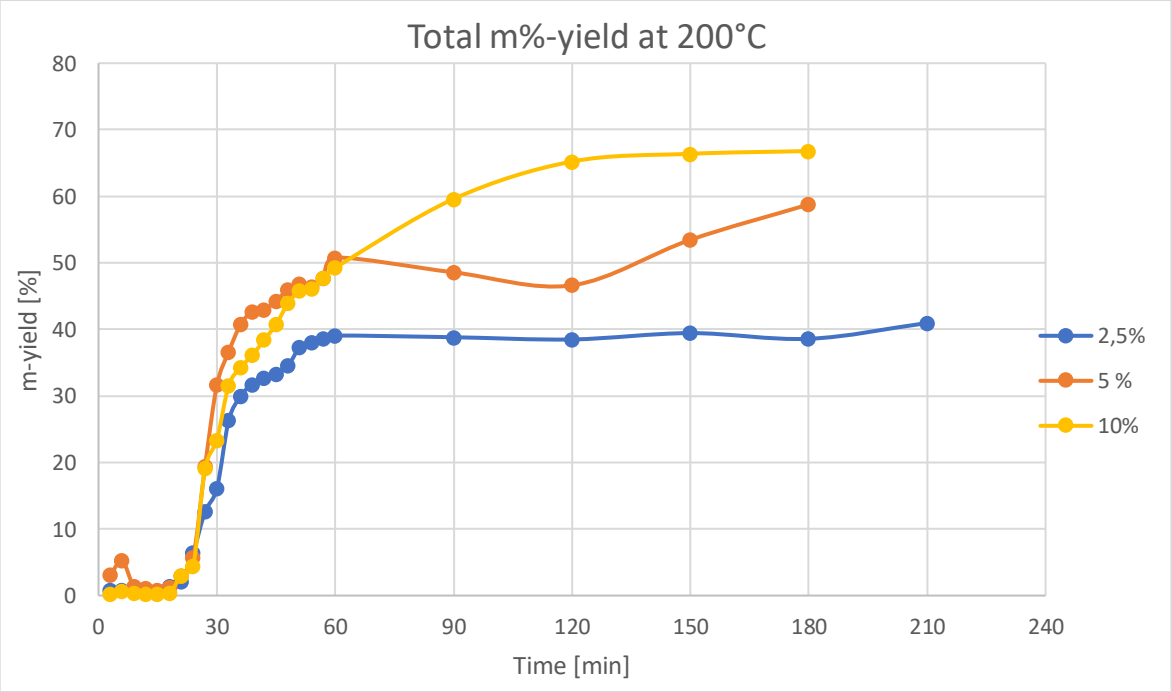

Figure 33 Total acid yield in experiments done at 200°C. See table V for more information

Table XI Acid end composition of the experiments done at 200°C. See table V for details and experiment conditions

Experiment in 200°C	GISA [%]	Formic acid [%]	Lactic acid [%]	2,5-DHPA [%]	Acetic acid [%]	Glycolic acid [%]	**total acid yield [%]**	**Consumed alkali [mol]**
10 %	63	14	12	9	2	1	**67**	**1,32**
5 %	67	16	12	11	1	3	**59**	**1,04**
2,50 %	50	22	10	14	1	4	**41**	**pH= 6.89**

8.5. Stability of GISA

Stability of GISA was studied with the autoclave used in this study. GISA batch was prepared from GISA calcium salt form by dissolving it in HCL. After that the brownish solution was treated with CS16GC H+ resin to produce 50ml of pure GISA solution with concentration approximately 20g/l.

All the produced GISA was then poured into the reactor vessel and 10% NaOH was added so that the pH of the whole solution was approximately 13,3. Right after the NaOH was added 0-sample was taken which was then acidified back with same methods as other samples in this study. Then the reactor vessel was closed, nitrogen atmosphere applied, and experiment started. Reactor was heated to 200°C and two samples were taken after 6h and 7h, these samples were then compared against the 0-sample. GISA 0-sample and 6h sample is compared in figure 34.

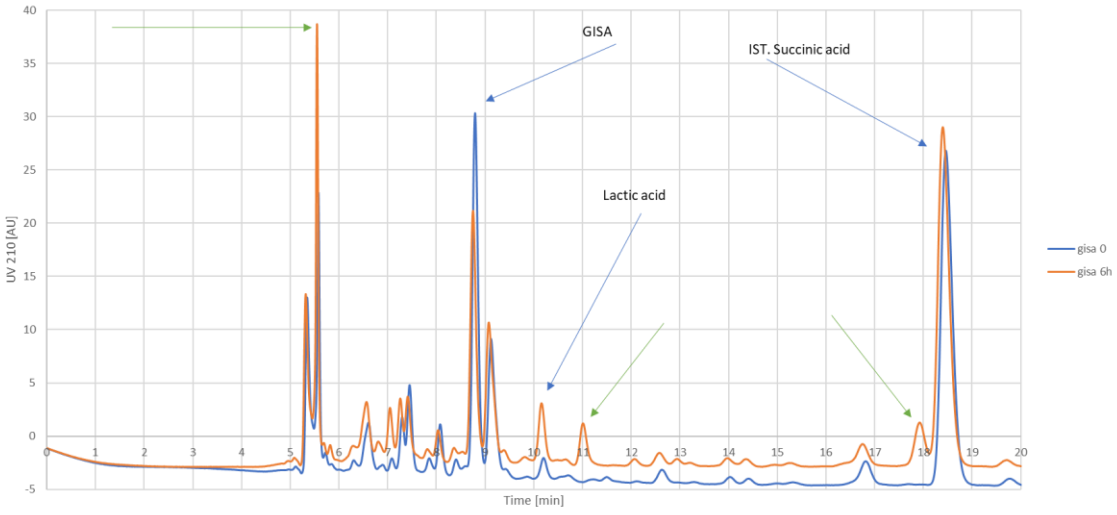

Figure 34 GISA HPLC-diagram. 0 sample is right after introduction of NaOH. 6h sample is after 6h into the experiment at 200°C.

It is shown that GISA is not stable at 200°C under nitrogen atmosphere and degrades to lactic acid and to other unknown products. Largest unknown peaks were: one near the internal standard at retention time 18 min, one close to acetic acid with retention time 11 minutes and the highest peak between 5 to 6 minutes with height approximately 38 AU.

Some effort was done to identify the peak at the beginning but in vain. Ethylene glycol was compared against the 6h GISA sample as it was found to be product from microwaving GISA as was shown by Pulidindi, (2014). But it was found to have retention time of approximately 7 minutes. Oxalic acid was also possible degradation product but comparing it to the 6h sample (figure 35) proved that the unknown peak was not oxalic acid.

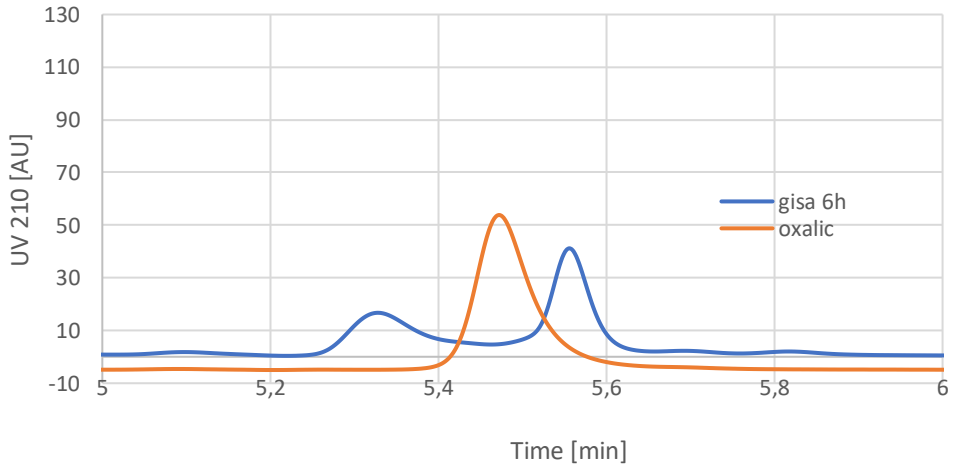

Figure 35 HPLC diagram of pure oxalic acid and gisa 6h sample to show that the unknown product formed from GISA degradation is not oxalic acid.

8.6. Toilet paper experiments

Two different experiment procedures were done with toilet paper. In the first one, toilet paper was shredded, milled and NaOH solution was added. In the second one paper slurry was produced and it was converted to basic with solid NaOH pellets prior experiments. Toilet paper experiments were quite difficult to conduct, and the sampling pipe was clogged multiple times during the experiments.

With the first procedure three experiments were done. Two with shredded toilet paper and one with milled toilet paper. The L/S ratio was increased to 18 by decreasing the amount of toilet paper to 15g from the normal 30g. This was done because the with L/S ratio 9 there was no possibility to take samples at the beginning of the reaction because the toilet paper absorbed all the liquid.

For the preparation of the shredded toilet paper experiments the toilet paper was first shredded to pieces approximately 3 by 3 cm. and inserted to the reactor vessel and after that NaOH was added. For the milled experiment the toilet paper was introduced to planetary mill and milled to dust like material. Figure 36 shows the preparation of the raw materials for these experiments.

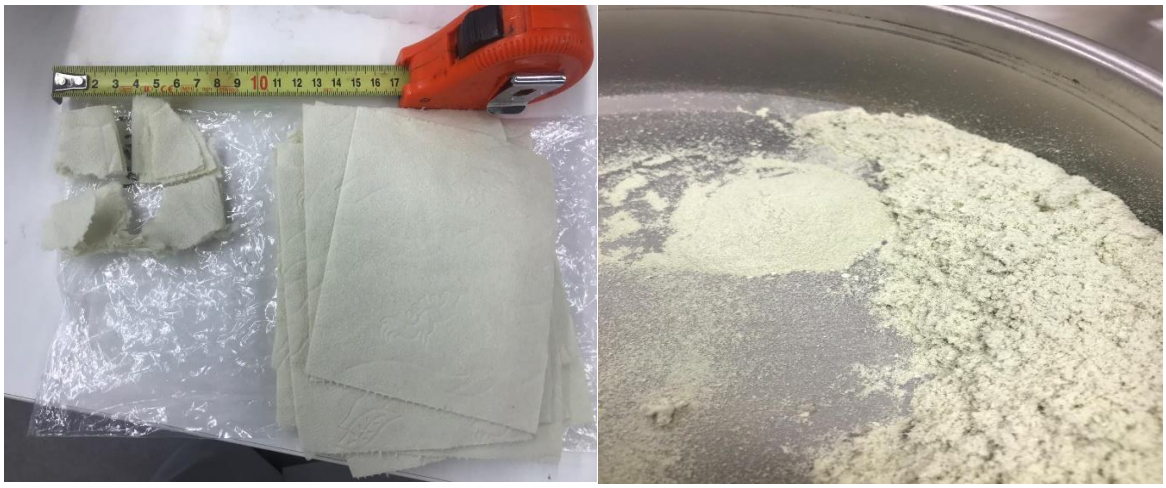

Figure 36 Preparation of toilet paper, Left one for the shredded experiments and right one for the milled experiment

All the first procedure experiments were done in 200°C with reaction time approximately. 3h and with 10 wt% NaOH. For the shredded experiments, samples were taken when possible and for the shredded paper 1 experiment 4 samples were taken. For the second one, 1 sample was taken at the end of the reaction due to clogged pipes. Milled experiment on the other hand was conducted like previous experiments because it showed no clogging.

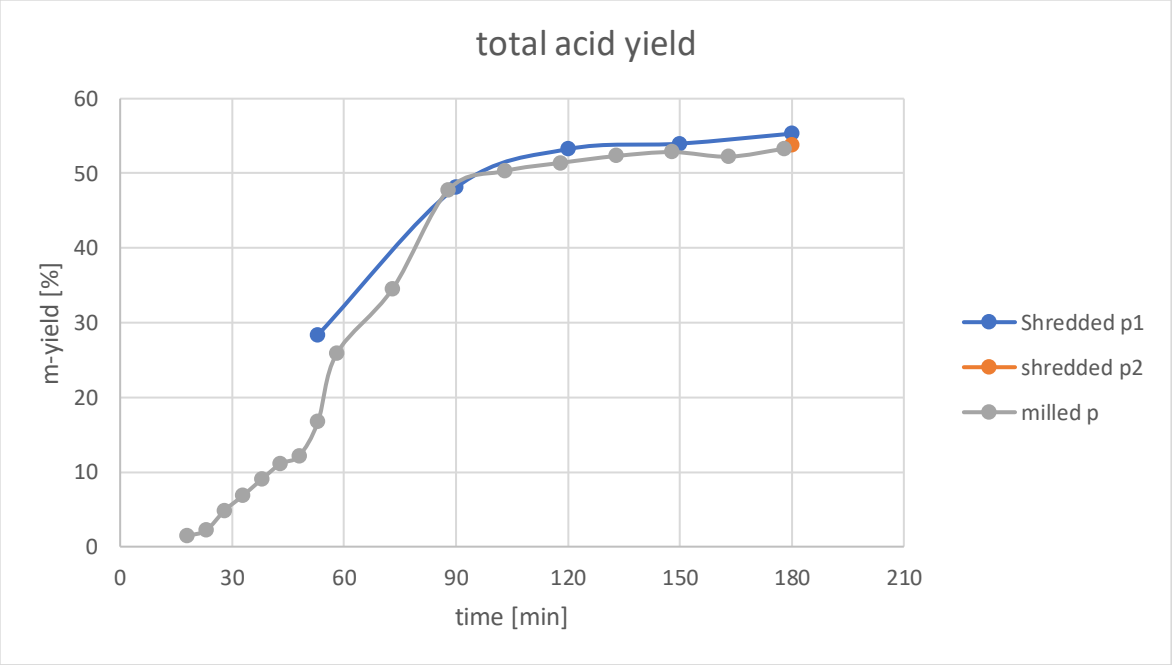

Figure 37 Total acid yield from the first set of toilet paper experiments. See table VI for more information.

The total acid yield reached approximately 55% which is slightly less than similar experiment with microcrystalline cellulose which reached total acid yield of 66%. This is slightly lower yield could be due to some amount of hemicellulose in the toilet paper. This could also explain why small amount of 2-HBA was found in these experiments as it is known to mainly produce from hemicellulose. On the other hand, if hemicellulose residues were in fact present in toilet paper, this would also mean that XISA is produced, however no XISA was detected.

Acid composition (Table XII) of the first procedure toilet paper experiments showed almost no difference between the experiments. Milled paper had slightly increased GISA yield compared to shredded ones. Milling is known to reduce the DP of the cellulosic material (Mattonai et al., 2018) and its possibility to produce afore mentioned difference is unclear. Moreover, the total acid yield (figure 37) and thus total degradation behaved similarly this is most likely due to the experiment temperature. 200°C is over the hydrolysis temperature and thus the crystalline region becomes unstable and accessible for the alkali which means that the DP has little to no effect on the degradation. No accurate measurements for the cellulosic materials were conducted such as crystallinity or degree of polymerization.

Table XII Acid composition of toilet paper experiments shredded and milled. See table VI for details and process parameters.

Experiments in 200°C	GISA [%]	Formic acid [%]	Lactic acid [%]	2,5-DHPA [%]	Acetic acid [%]	Glycolic acid [%]	**total acid yield [%]**	**Consumed alkali**
Shredded p1	53	13	19	12	2	2	**55**	**0,74**
Shredded p2	52	14	19	12	2	2	**54**	**0,78**
Milled p	56	13	17	11	2	1	**53**	**0,74**

8.7. Slurry experiments

Last experiments done were slurry experiments in 160°C and in 200°C with 10wt% NaOH. 1L of purified water was added to blender with 40g of toilet paper to produce slurry with L/S ratio of 25. Approximately 300g of this slurry was weighed for both experiments. Slurry was converted to alkali via NaOH pellets which were added while the slurry was embedded in ice path with mixer to reduce the amount of unwanted peeling reaction due to heat release when pellets dissociate. Sampling for the experiments were started after 1h and after that every 15 minutes until end of the experiment which were 4h and 6h for 200°C and 160°C experiments respectively.

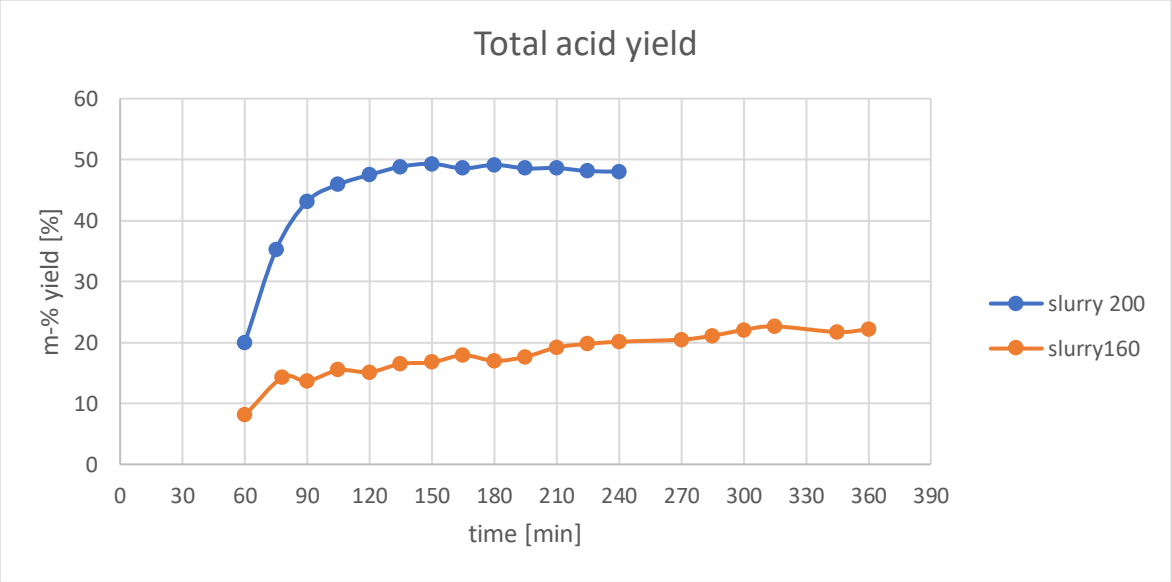

Figure 38 Total acid yield of slurry experiments. See table VI for more information.

Total acid yield of 200°C experiment was over two times higher than the on conducted at 160°C. This greatly shows the importance of high temperature when the DP of cellulosic raw material increases as also the crystallinity increases. The 160°C experiment has an upward trend and there is no reason why the degradation would not reach similar yields as the 200°C if given enough time. This experiment also shows why the alkaline scission/hydrolysis is described as a slow reaction compared to the peeling (when in near temperatures where the scission begins).

This is also greatly illustrated in figure 39 where 1h sample from both experiments are shown. The 200°C sample is very liquid like and viscose and when watch glass is rotated to 90 degree it falls at the bottom. The 160°C sample however is very sticky and viscose and has threadlike darker areas indicating that still quite long chain cellulose is present.

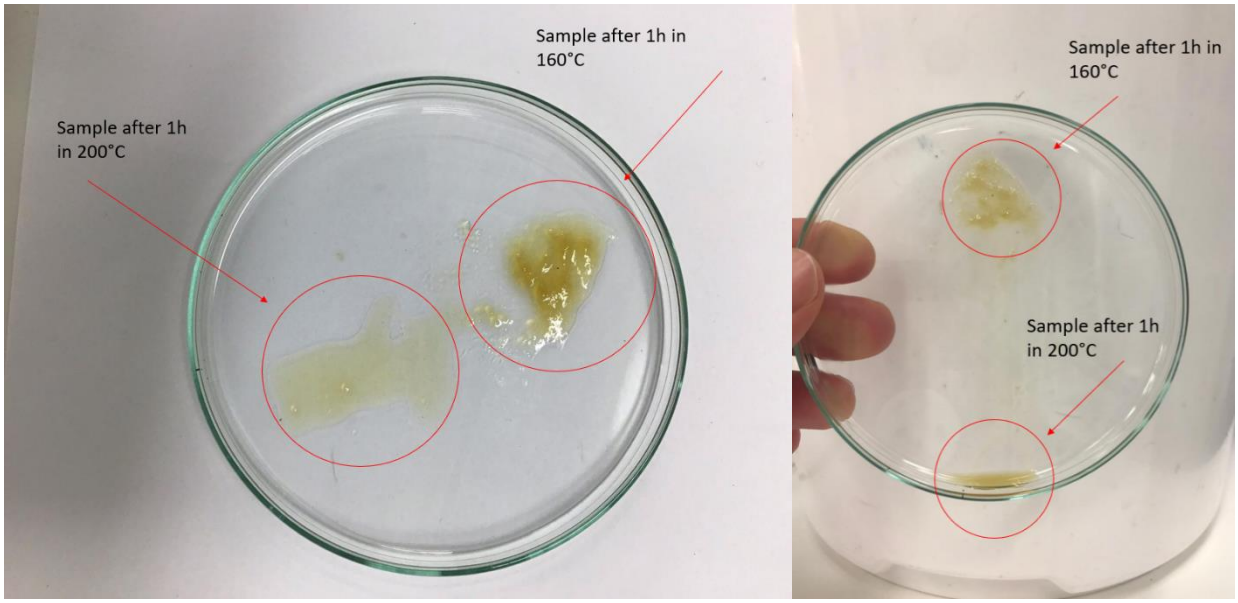

Figure 39 1h samples on the watch glass. The watch glass is held horizontally on the left and held vertically on the right

The total acid yield with slurry at 200°C was 48% when in the case of microcrystalline cellulose which is described as low DP material the yield was 66% at 200°C. More interestingly the total acid yield with slurry at 160°C was only 22% after 7h when with microcrystalline cellulose 50% yield was achieved in same temperature after 2h 43minutes.

Similarly, as in microcrystalline cellulose experiments with low total acid yield the GISA's proportional yield is higher. The higher experiment temperature seems to increase the amount of lactic acid and 2,5-DHPA. In addition, three times more alkali was consumed while the acid yield was only doubled when temperature was increased to 200°C.

Table XIII Acid end composition of the artificial slurry experiments. See table VI for details and experiment conditions.

Experiments	GISA [%]	Formic acid [%]	Lactic acid [%]	2,5-DHPA [%]	Acetic acid [%]	Glycolic acid [%]	**total acid yield [%]**	**Consumed alkali [mol]**
slurry 200°C	51	14	19	12	2	2	**48**	**0,6**
slurry 160°C	61	11	15	9	2	2	**22**	**0,2**

9. Conclusion

Lactose hydrolysis produces similar acids as does cellulose hydrolysis with GISA being the main product. Sugar analysis showed that the reaction seems to obey the proposed mechanism so that the lactose reducing end glucose is peeled off and galactose molecule is left in the solution to further react to mainly lactic acid. The lactose use for modelling purposes was not suitable due to unknown intermediate, that in the analysis with HPLC caused inaccuracy as the unknown intermediates had similar retention time as GISA.

Cellobiose hydrolysis proved the complex nature of cellobiose/cellobiulose alkali system with glucose/fructose monosaccharides involved. Total acid yield of cellobiose alkali degradation was 70% with GISA and lactic acid being the most abundant products.

Microcrystalline cellulose was degraded in varying temperature with highest acid yield being 66% in 200°C which was only temperature where total degradation was found to happen before 3h. It was shown that for total degradation of mcellulose either high enough temperature 200°C or longer reaction time (7h) at slightly lower temperature (180°C) is required. The existence of alkaline hydrolysis at elevated temperature (160-180°C) is as important for the acid production as the peeling off reaction.

The effect on NaOH concentration on the degradation was studied with 10, 5 and 2.5wt% NaOH solution and there showed to be no differences in the total degradation while the temperature of the experiment was 160°C and under. When the temperature is increased to 200°C the alkaline hydrolysis becomes reaction limiting step and to that the NaOH concentration seems to have an effect. Moreover, the alkali must be available for the reaction to continue.

Toilet paper experiments and artificial slurry experiments laid the foundation for what could be a potential raw material for acid production in industrial size. Toilet paper was fully degraded in hot alkali with 50% yield. GISA, formic acid, lactic acid and 2,5-DHPA being the most abundant products.

In this work reaction mechanism as well as affecting parameters on the alkali degradation of cellulosic material was discussed. More work is still needed, to study the behaviour of authentic cellulosic samples in alkali and the effect of higher temperature >200°C.

10. Appendixes

Appendix I Lactose experiments

Appendix II Cellobiose experiments

Appendix III mcellulose experiments

Appendix IV mcellulose experiments in dilute NaOH

Appendix V shredded/milled toilet paper experiments and slurry experiments

Appendix VI Image of the used toilet paper

References

Adibi Larijani, A.H., 2020. Oxidative reactions of cellulose under alkaline conditions. Jyväskylän yliopisto, Jyväskylä.

Alén, R., 2011. Papermaking science and technology. Book 20, Biorefining of forest resources. Paperi ja puu, Helsinki.

Atalla, R., 1986. Effects of physical structure on the alkaline degradation of hydrocellulose.

Badea, G.I., Radu, G.L., 2018. Introductory Chapter: Carboxylic Acids - Key Role in Life Sciences, Carboxylic Acid - Key Role in Life Sciences. IntechOpen. https://doi.org/10.5772/intechopen.77021

Berg, H.E., 1993. Reactions of lactose during heat treatment of milk : a quantitative study. https://edepot.wur.nl/203007

Bonn, G., Binder, H., Leonhard, H., Bobleter, O., 1985. The alkaline degradation of cellobiose to glucose and fructose. Monatsh Chem 116, 961–971. https://doi.org/10.1007/BF00809189

Budtova, T., Navard, P., 2016. Cellulose in NaOH–water based solvents: a review. Cellulose 23, 5–55. https://doi.org/10.1007/s10570-015-0779-8

Chakar, F.S., Ragauskas, A.J., 2004. Review of current and future softwood kraft lignin process chemistry. Industrial Crops and Products, 6th International Lignin Institute conference 20, 131–141. https://doi.org/10.1016/j.indcrop.2004.04.016

Chen, J., Yuan, Z., Zanuso, E., Trajano, H., 2017. Hydrothermal Processing in Biorefineries-Production of Bioethanol and High Added-Value Compounds of Second and Third Generation Biomass.

Dinand, E., Vignon, M., Chanzy, H., Heux, L., 2002. Mercerization of primary wall cellulose and its implication for the conversion of cellulose I → cellulose II 12.

Duchemin, B., 2015. Mercerisation of cellulose in aqueous NaOH at low concentrations. Green Chemistry 17, 3941–3947. https://doi.org/10.1039/C5GC00563A

Eugene, A.D., 2020. carbohydrate | Definition, Classification, & Examples | Britannica [WWW Document]. URL https://www.britannica.com/science/carbohydrate (accessed 1.6.22).

Faruk, O., Ain, M.S., 2013. Biofiber reinforced polymer composites for structural applications, in: Developments in Fiber-Reinforced Polymer (FRP) Composites for Civil Engineering. Elsevier, pp. 18–53. https://doi.org/10.1533/9780857098955.1.18

Galadima, M.S., 2018. Chemistry of Glucoisosaccharinic Acids 194.

Glaus, M.A., Van Loon, L.R., 2004. Cellulose Degradation at Alkaline Conditions: Long-Term Experiments at Elevated Temperatures.

Greenfield, B.F., Holtom, G.J., Hurdus, M.H., O'Kelly, N., Pilkington, N.J., Rosevear, A., Spindler, M.W., Williams, S.J., 1994a. The Identification and Degradation of Isosaccharinic Acid, a Cellulose Degradation Product. MRS Online Proceedings Library 353, 1151–1158. https://doi.org/10.1557/PROC-353-1151

Greenfield, B.F., Holtom, G.J., Hurdus, M.H., O'Kelly, N., Pilkington, N.J., Rosevear, A., Spindler, M.W., Williams, S.J., 1994b. The Identification and Degradation of Isosaccharinic Acid, a Cellulose Degradation Product. MRS Proc. 353, 1151. https://doi.org/10.1557/PROC-353-1151

Haas, D.W., Hrutfiord, B.F., Sarkanen, K.V., 1967. Kinetic study on the alkaline degradation of cotton hydrocellulose. Journal of Applied Polymer Science 11, 587–600. https://doi.org/10.1002/app.1967.070110408

Isikgor, F.H., Becer, C.R., 2015. Lignocellulosic Biomass: A Sustainable Platform for Production of Bio-Based Chemicals and Polymers 61.

Johansson, M.H., Samuelson, O., 1974. The formation of end groups in cellulose during alkali cooking. Carbohydrate Research 34, 33–43. https://doi.org/10.1016/S0008-6215(00)80367-5

Kaylor, R.M., Dimmel, D.R., Ragauskas, A.J., Liotta, C.L., 1995. A New Model Compound for Studying Alkaline Cellulose Chain Cleavage Reactions. Journal of Wood Chemistry and Technology 15, 431–452. https://doi.org/10.1080/02773819508009519

Khondakar, R.H., Yu, Y., Wu, H., 2021. Cellobiulose as a Key Intermediate during Biomass Hydrothermal Conversion into Biofuels and Biochemicals: Fundamental Decomposition Mechanisms. Energy Fuels 35, 12200–12207. https://doi.org/10.1021/acs.energyfuels.1c01636

Khuwijitjaru, P., Milasing, N., Adachi, S., 2018. Production of D-tagatose: A review with emphasis on subcritical fluid treatment 12. https://doi.org/10.14456/sehs.2018.15

Knill, C., Kennedy, J., 2003. Degradation of Cellulose under Alkaline Conditions. Carbohydrate Polymers 51, 281–300. https://doi.org/10.1016/S0144-8617(02)00183-2

Lai, Y.-Z., Ontto, D.E., 1979. Effects of alkalinity on endwise depolymerization of hydrocellulose. J. Appl. Polym. Sci. 23, 3219–3225. https://doi.org/10.1002/app.1979.070231107

Lai, Y.-Z., Sarkanen, K.V., 1969. Kinetic study on the alkaline degradation of amylose. J. polym. sci., C Polym. symp. 28, 15–26. https://doi.org/10.1002/polc.5070280105

Lai, Y.-Z., Sarkanen, K.V., 1967. Kinetics of alkaline hydrolysis of glycosidic bonds in cotton cellulose. Cellulose chemical technology 1, 517–527.

Lindstrom, L.A., Samuelson, O., 1977. Alkali and oxygen alkali treatment of 4 deoxy 2,3 hexodiulose and 3 deoxy erythro pentose. Acta Chem Scand Ser B Org Chem Biochem. https://scholar.google.com/scholar_lookup?title=Alkali+and+oxygen+alkali+treatment+of+4+deoxy+2%2C3+hexodiulose+and+3+deoxy+erythro+pentose&author=Lindstrom%2C+L.A.&publication_year=1977

Loon, L.R., Glaus, M.A., 1997. Review of the kinetics of alkaline degradation of cellulose in view of its relevance for safety assessment of radioactive waste repositories. J Environ Polym Degr 5, 97–109. https://doi.org/10.1007/BF02763593

Loon, L.R.V., Glaus, M.A., 1998. Experimental and Theoretical Studies on Alkaline Degradation of Cellulose and its Impact onthe Sorption of Radionuclides 156.

Loon, L.R.V., Glaus, M.A., Laube, A., Stallone, S., 1999. Degradation of Cellulosic Materials Under the Alkaline Conditions of a Cementitious Repository for Low- and Intermediate-Level Radioactive Waste. II. Degradation Kinetics. Journal of Environmental Polymer Degradation, Vol. 7, No. 1, 1999 11.

Machell, G., Richards, G.N., 1960. 384. Mechanism of saccharinic acid formation. Part I. Competing reactions in the alkaline degradation of 4-O-methyl-D-glucose, maltose, amylose, and cellulose. Journal of the Chemical Society (Resumed) 1924–1931. https://doi.org/10.1039/jr9600001924

MacLaurin, D.J., Green, J.W., 1969. Carbohydrates in alkaline systems. II. Kinetics of the transformation and degradation reactions of cellobiose, cellobiulose, and 4- *O* -β- D -glucopyranosyl- D -mannose in 1 *M* sodium hydroxide at 22 °C. Can. J. Chem. 47, 3957–3964. https://doi.org/10.1139/v69-659

Macleod, J.M., Schroeder, L.R., 1982. Alkaline Degradation of Cellobiose, 3.6-Anhydro-4-O-(β-D-Gluc0pyranosyl)-D-Glucose, 3,6-Anhydr0-4-0-Methyl-D-Glucose, and D-Glucose1. Journal of Wood Chemistry and Technology 2, 187–205. https://doi.org/10.1080/02773818208085129

Mattonai, M., Pawcenis, D., del Seppia, S., Łojewska, J., Ribechini, E., 2018. Effect of ball-milling on crystallinity index, degree of polymerization and thermal stability of cellulose. Bioresource Technology 270, 270–277. https://doi.org/10.1016/j.biortech.2018.09.029

Mohd Shafie, Z., Yu, Y., Wu, H., 2014. Insights into the Primary Decomposition Mechanism of Cellobiose under Hydrothermal Conditions. Ind. Eng. Chem. Res. 53, 14607–14616. https://doi.org/10.1021/ie5027309

Montet, E., 2021. Investigation of the consequences of the use of ozone in the bleaching of cellulosic fibres.

Mozdyniewicz, D.J., Nieminen, K., Sixta, H., 2013. Alkaline steeping of dissolving pulp. Part I: cellulose degradation kinetics. Cellulose 20, 1437–1451. https://doi.org/10.1007/s10570-013-9926-2

Niemelä, K., 1990. The formation of hydroxy monocarboxylic acids and dicarboxylic acids by alkaline thermochemical degradation of cellulose. J. Chem. Technol. Biotechnol. 48, 17–28. https://doi.org/10.1002/jctb.280480103

Niemelä, K., Sjöström, E., 1986. The conversion of cellulose into carboxylic acids by a drastic alkali treatment. Biomass 11, 215–221. https://doi.org/10.1016/0144-4565(86)90068-5

Ouellette, R.J., Rawn, J.D., 2018. Carbohydrates, in: Organic Chemistry. Elsevier, pp. 889–928. https://doi.org/10.1016/B978-0-12-812838-1.50028-1

Paananen, M., 2016. High-yield Pulping of Scots Pine under Strongly Alkaline Conditions. Aalto University.

Petersson, G., Samuelson, O., 1976. Formation of 1,4-anhydro-3-deoxypentitol-2-carboxylic acids by alkaline degradation of cellulose. Acta Chemica Scandinavica B 30, 27–30. https://research.chalmers.se/en/publication/111866

Pulidindi, I., 2014. Isosaccharinic Acid Mediated Fine Chemicals Production from Cellulose. Journal of Fundamentals of Renewable Energy and Applications 4, 143. https://doi.org/10.4172/2090-4541.1000143

Reyes, L., Nikitine, C., Vilcocq, L., Fongarland, P., 2020. Green is the new black – a review of technologies for carboxylic acid recovery from black liquor. Green Chem. 22, 8097–8115. https://doi.org/10.1039/D0GC02627A

Richards, E.L., Chandrasekhara, M.R., 1960. Chemical changes in dried skim-milk during storage. Journal of Dairy Research 27, 59–66. https://doi.org/10.1017/S0022029900010128

Shaw, P.B., 2013. Studies of the Alkaline Degradation of Cellulose and the Isolation of Isosaccharinic Acids 271.

Speck, J.C., 1958. The Lobry De Bruyn-Alberda Van Ekenstein Transformation, in: Wolfrom, M.L. (Ed.), Advances in Carbohydrate Chemistry. Academic Press, pp. 63–103. https://doi.org/10.1016/S0096-5332(08)60352-5

Stenius, P., 2000. Papermaking science and technology. Book 3, Forest products chemistry. Fapet, Helsinki.

Van Loon, L.R., Glaus, M.A., 1997. Review of the kinetics of alkaline degradation of cellulose in view of its relevance for safety assessment of radioactive waste repositories. J Environ Polym Degr 5, 97–109. https://doi.org/10.1007/BF02763593

W.pratt, C., Cornely, K., 2017. Essential Biochemistry, 4th Edition | Wiley [WWW Document]. Wiley.com. URL https://www.wiley.com/en-us/Essential+Biochemistry%2C+4th+Edition-p-9781119319337R120 (accessed 1.6.22).

Table A 1 Lactose test 1. Process parameters: T=80°C, m(lactose)=31,08g c(NaOH)=10wt%

T [°C]	t (min)	Glycolic [g]	Formic [g]	GISA [g]	Lactic [g]	Acetic [g]	2,5-DHPA [g]	2-HBA [g]	**total [g]**	**total yield [%]**
29	3	0,01	0,00	0,00	0,00	0,00	0,00	0,00	**0,02**	**0,1**
37	6	0,01	0,00	0,01	0,00	0,00	0,00	0,00	**0,02**	**0,1**
50	9	0,01	0,00	0,08	0,00	0,00	0,00	0,00	**0,10**	**0,3**
65	12	0,00	0,15	1,94	0,02	0,00	0,00	0,00	**2,11**	**6,8**
80	15	0,00	0,78	8,85	0,89	0,00	0,00	0,00	**10,52**	**33,9**
80	75	0,17	0,99	7,19	2,59	0,04	0,00	0,00	**10,97**	**35,3**
80	135	0,23	0,82	3,83	2,70	0,03	0,00	0,00	**7,62**	**24,5**

Table A 2 Lactose test 2 Process parameters: T=100°C, m(lactose)=31,05g c(NaOH)=10wt%

T [°C]	t (min)	Glycolic [g]	Formic [g]	GISA [g]	Lactic [g]	Acetic [g]	2,5-DHPA [g]	2-HBA [g]	**total [g]**	**total yield [%]**
27	3	0,01	0,01	0,15	0,04	0,03	0,00	0,00	**0,25**	**0,80**
38	6	0,01	0,00	0,11	0,03	0,03	0,00	0,00	**0,18**	**0,58**
51	9	0,01	0,00	0,19	0,01	0,03	0,01	0,00	**0,26**	**0,83**
66	12	0,00	0,24	1,55	0,03	0,07	0,16	0,00	**2,05**	**6,60**
85	15	0,00	0,98	6,82	1,26	0,19	0,34	0,00	**9,59**	**30,89**
100	18	0,15	0,78	6,30	2,47	0,24	0,05	0,00	**10,00**	**32,19**
100	78	0,24	0,91	11,19	2,79	0,23	0,00	0,00	**15,36**	**49,48**
100	138	0,25	0,78	10,86	2,80	0,21	0,00	0,00	**14,89**	**47,95**

Table A 3 Lactose test 3 Process parameters: T=120°C, m(lactose)=31,05g c(NaOH)=10wt%

T [°C]	t (min)	Glycolic [g]	Formic [g]	GISA [g]	Lactic [g]	Acetic [g]	2,5-DHPA [g]	2-HBA [g]	**total [g]**	**total yield [%]**
31	3	0,0	0,0	0,1	0,0	0,0	0,0	0,0	**0,2**	**0,5**
43	6	0,0	0,0	0,1	0,0	0,0	0,0	0,0	**0,1**	**0,3**
56	9	0,0	0,0	0,4	0,0	0,0	0,0	0,0	**0,5**	**1,4**
72	12	0,0	0,4	3,1	0,1	0,0	0,4	0,0	**3,9**	**12,6**
94	15	0,1	0,8	7,4	1,9	0,0	0,2	0,0	**10,4**	**33,2**
105	18	0,2	0,4	6,4	2,6	0,1	0,0	0,0	**9,8**	**31,3**
113	21	0,2	0,9	9,5	2,8	0,0	0,0	0,0	**13,6**	**43,4**
120	24	0,2	0,9	11,9	2,8	0,0	0,0	0,0	**16,0**	**51,2**
120	84	0,2	0,8	10,6	2,9	0,0	0,0	0,0	**14,5**	**46,6**
120	144	0,2	0,9	10,3	2,9	0,0	0,0	0,0	**14,3**	**46,0**

Table A 4 Lactose test 4 Process parameters: T=140°C, m(lactose)=32,58g c(NaOH)=10wt%

T [°C]	t (min)	Glycolic [g]	Formic [g]	GISA [g]	Lactic [g]	Acetic [g]	2,5-DHPA [g]	2-HBA [g]	**total [g]**	**total yield [%]**
26	3	0,0	0,1	0,0	0,0	0,0	0,0	0,0	**0,1**	**0,3**
36	6	0,0	0,1	0,0	0,0	0,0	0,0	0,0	**0,1**	**0,5**

50	9	0,0	0,1	0,0	0,0	0,0	0,0	0,0	**0,1**	**0,4**
64	12	0,0	0,3	1,4	0,0	0,0	0,0	0,0	**1,7**	**5,2**
83	15	0,0	0,8	5,9	0,8	0,0	0,2	0,0	**7,8**	**23,8**
100	18	0,1	0,9	8,7	2,1	0,0	0,0	0,0	**11,8**	**36,4**
108	21	0,2	0,9	7,0	2,6	0,0	0,0	0,0	**10,8**	**33,1**
116	24	0,3	1,0	7,8	2,7	0,0	0,0	0,0	**11,8**	**36,2**
125	27	0,3	1,0	12,0	2,8	0,0	0,0	0,0	**16,1**	**49,4**
134	30	0,3	1,1	11,0	2,8	0,0	0,0	0,0	**15,1**	**46,5**
140	33	0,2	0,9	9,7	2,5	0,0	0,0	0,0	**13,3**	**40,8**
140	93	0,2	1,1	11,0	3,0	0,0	0,0	0,0	**15,3**	**47,0**
140	153	0,2	0,9	9,0	2,5	0,0	0,1	0,0	**12,7**	**38,9**

Table A 5 Lactose test 5 Process parameters: T=160°C, m(lactose)=31,04g c(NaOH)=10wt%

T [°C]	t (min)	Glycolic [g]	Formic [g]	GISA [g]	Lactic [g]	Acetic [g]	2,5-DHPA [g]	2-HBA [g]	**total [g]**	**total yield [%]**
27	3	0,0	0,1	0,5	0,0	0,0	0,0	0,0	**0,7**	**2,2**
37	6	0,0	0,1	0,3	0,0	0,0	0,0	0,0	**0,4**	**1,4**
49	9	0,0	0,1	0,0	0,0	0,0	0,0	0,0	**0,1**	**0,3**
64	12	0,0	0,2	1,1	0,0	0,0	0,0	0,0	**1,3**	**4,3**
82	15	0,0	0,5	4,0	0,5	0,0	0,1	0,0	**5,1**	**16,5**
100	18	0,1	0,7	8,0	1,8	0,0	0,1	0,0	**10,7**	**34,4**
108	21	0,2	0,4	6,8	2,5	0,0	0,0	0,0	**9,9**	**31,7**
113	24	0,2	1,0	7,3	2,6	0,0	0,0	0,0	**11,2**	**36,0**
123	27	0,3	1,0	12,0	2,7	0,0	0,0	0,0	**16,0**	**51,3**
133	30	0,2	1,0	10,6	2,8	0,0	0,0	0,0	**14,6**	**47,1**
142	33	0,2	1,0	10,8	2,8	0,0	0,0	0,0	**14,8**	**47,5**
150	36	0,2	0,9	9,2	2,4	0,0	0,0	0,0	**12,7**	**40,7**
157	39	0,2	0,8	8,2	2,3	0,0	0,0	0,0	**11,6**	**37,1**
160	99	0,2	0,8	8,8	2,4	0,0	0,1	0,1	**12,3**	**39,4**
160	159	0,2	0,9	9,4	2,6	0,0	0,1	0,1	**13,3**	**42,6**

Table A 6 Lactose test 6 Process parameters: T=180°C, m(lactose)=30,97g c(NaOH)=10wt%

T [°C]	t (min)	Glycolic [g]	Formic [g]	GISA [g]	Lactic [g]	Acetic [g]	2,5-DHPA [g]	2-HBA [g]	**total [g]**	**total yield [%]**
25	3	0,0	0,1	0,3	0,0	0,0	0,0	0,0	**0,3**	**1,1**
35	6	0,0	0,1	0,2	0,0	0,0	0,0	0,0	**0,3**	**1,0**
48	9	0,0	0,1	0,3	0,0	0,0	0,0	0,0	**0,4**	**1,3**
63	12	0,0	0,1	0,7	0,0	0,0	0,0	0,0	**0,9**	**2,9**
82	15	0,0	0,5	4,4	0,6	0,2	0,0	0,0	**5,7**	**18,4**
100	18	0,1	0,6	6,8	1,6	0,0	0,0	0,0	**9,2**	**29,8**
108	21	0,1	0,3	4,8	1,8	0,0	0,0	0,0	**7,1**	**22,8**

116	24	0,2	0,7	5,3	1,9	0,0	0,0	0,0	**8,0**	**25,9**
126	27	0,2	0,7	7,2	1,8	0,0	0,0	0,0	**9,9**	**31,9**
135	30	0,2	0,8	8,6	2,3	0,0	0,0	0,0	**11,9**	**38,4**
144	33	0,2	0,8	9,0	2,3	0,0	0,0	0,0	**12,4**	**39,9**
153	36	0,2	0,8	9,0	2,3	0,0	0,0	0,0	**12,4**	**40,0**
161	39	0,1	0,6	6,4	1,7	0,0	0,0	0,0	**8,8**	**28,4**
169	42	0,2	0,9	9,0	2,4	0,0	0,0	0,0	**12,5**	**40,2**
176	45	0,2	0,8	8,3	2,2	0,0	0,0	0,0	**11,6**	**37,3**
180	48	0,2	0,9	9,1	2,4	0,0	0,0	0,0	**12,7**	**40,9**
180	108	0,2	0,8	8,5	2,4	0,0	0,1	0,0	**12,1**	**39,1**
180	168	0,3	0,8	8,0	2,3	0,0	0,2	0,0	**11,6**	**37,5**

Table A 7 Lactose test 7 Process parameters: T=200°C, m(lactose)=31g c(NaOH)=10wt%

T [°C]	t (min)	Glycolic [g]	Formic [g]	GISA [g]	Lactic [g]	Acetic [g]	2,5-DHPA [g]	2-HBA [g]	**total [g]**	**total %**
24	3	0,0	0,0	0,0	0,0	0,0	0,0	0,0	**0,1**	**0,2**
34	6	0,0	0,1	0,0	0,0	0,0	0,0	0,0	**0,1**	**0,2**
48	9	0,0	0,1	0,0	0,0	0,0	0,0	0,0	**0,2**	**0,5**
63	12	0,0	0,9	1,8	0,0	0,0	0,0	0,0	**2,8**	**8,9**
82	15	0,0	3,7	6,2	0,9	0,2	0,0	0,0	**11,1**	**35,7**
100	18	0,1	3,3	8,4	2,0	0,1	0,0	0,0	**13,9**	**44,9**
109	21	0,2	0,8	6,8	2,5	0,0	0,0	0,0	**10,2**	**32,9**
116	24	0,2	1,0	8,0	2,7	0,0	0,0	0,0	**12,0**	**38,5**
125	27	0,3	1,0	11,5	2,8	0,0	0,0	0,0	**15,6**	**50,4**
135	30	0,2	1,0	11,4	2,7	0,0	0,0	0,0	**15,4**	**49,6**
145	33	0,2	1,0	11,3	2,9	0,0	0,0	0,0	**15,4**	**49,5**
155	36	0,2	1,0	10,9	2,9	0,0	0,0	0,0	**15,1**	**48,6**
164	39	0,2	1,0	10,6	2,6	0,0	0,0	0,0	**14,5**	**46,8**
172	42	0,2	1,1	11,3	2,7	0,0	0,0	0,0	**15,4**	**49,6**
178	45	0,2	1,1	10,5	2,6	0,0	0,0	0,0	**14,5**	**46,6**
185	48	0,2	1,2	10,9	2,6	0,1	0,0	0,0	**15,0**	**48,4**
192	51	0,3	1,2	10,7	2,6	0,1	0,0	0,0	**14,9**	**47,9**
197	54	0,3	1,1	10,5	3,0	0,1	0,0	0,0	**15,0**	**48,3**
200	57	0,3	1,2	11,2	2,7	0,1	0,0	0,0	**15,5**	**49,9**
200	117	0,4	0,9	10,9	3,1	0,3	0,0	0,0	**15,5**	**50,0**
200	177	0,4	0,8	9,8	3,3	0,4	0,0	0,0	**14,7**	**47,5**

Table A 8 Lactose test with sugar analysis Process parameters: T=120°C, m(lactose)=31,2g c(NaOH)=10wt%

t (min)	T [°C]	Glycolic [g]	Formic [g]	GISA [g]	Lactic [g]	Acetic [g]	2,5-DHPA [g]	2-HBA [g]	Lactose [g]	Galactose [g]	**total acid [g]**	**total yield [%]**
3	27	0,0	0,1	0,9	0,1	0,0	0,0	0,0	36,6	0,8	**1,1**	**3,6**
6	36	0,0	0,1	0,7	0,0	0,0	0,0	0,0	33,6	2,4	**0,8**	**2,6**
9	49	0,1	0,1	0,6	0,0	0,0	0,0	0,0	37,6	0,6	**0,8**	**2,5**

12	63	0,0	0,2	1,8	0,0	0,0	0,0	0,0	36,2	2,2	**2,0**	**6,5**
15	82	0,1	0,4	6,3	0,7	0,2	0,1	0,0	7,3	7,7	**7,8**	**24,9**
18	100	0,1	0,7	8,3	1,5	0,3	0,3	0,0	2,2	6,7	**11,3**	**36,2**
21	108	0,2	0,5	5,9	2,5	0,4	0,5	0,0	0,6	2,4	**9,9**	**31,9**
24	115	0,2	1,0	12,8	2,5	0,4	0,5	0,0	0,4	1,4	**17,4**	**55,8**
27	120	0,2	1,1	10,6	2,6	0,4	0,5	0,0	0,0	1,1	**15,4**	**49,3**
87	120	0,2	1,1	10,5	3,3	0,3	0,5	0,0	0,0	0,0	**15,9**	**50,9**
147	120	0,2	1,0	10,5	3,3	0,3	0,6	0,0	0,0	0,0	**15,9**	**51,0**

Table A 9 galactose test Process parameters: T=120°C, m(Galactose)=30,05g c(NaOH)=10wt%

T [°C]	t (min)	Glycolic [g]	Formic [g]	GISA [g]	Lactic [g]	Acetic [g]	2,5-DHPA [g]	2-HBA [g]	Galactose [g]	total acid [g]	total yield [%]
25	3	0,0	0,1	0,4	0,0	0,0	0,0	0,0	24,7	0,4	1,5
35	6	0,0	0,1	0,4	0,0	0,0	0,0	0,0	24,8	0,5	1,6
48	9	0,0	0,1	0,3	0,0	0,0	0,0	0,0	25,2	0,4	1,3
63	12	0,0	0,1	0,3	0,2	0,0	0,0	0,0	0,0	0,6	1,9
84	15	0,1	0,0	0,6	2,0	0,3	0,0	0,0	0,0	3,1	10,2
100	18	0,2	0,0	1,5	4,5	0,4	0,0	0,0	0,0	6,6	22,1
108	21	0,2	0,0	0,3	5,2	0,6	0,1	0,0	0,0	6,4	21,2
115	24	0,3	0,0	0,3	5,4	0,4	0,1	0,0	0,0	6,5	21,5
120	27	0,3	0,1	0,3	5,5	0,4	0,1	0,0	0,0	6,5	21,7
120	57	0,3	0,1	0,3	5,4	0,4	0,0	0,0	0,0	6,4	21,4
120	87	0,3	0,1	0,3	5,4	0,4	0,0	0,0	0,0	6,4	21,2
120	117	0,3	0,1	0,3	5,3	0,3	0,0	0,0	0,0	6,2	20,7
120	147	0,3	0,1	0,3	5,2	0,3	0,0	0,0	0,0	6,2	20,5

Table A 10 Cellobiose test 1 Process parameters: T=100°C, m(Cellobiose)=15,31 c(NaOH)=10wt%

T [°C]	t (min)	Glycolic [g]	Formic [g]	GISA [g]	Lactic [g]	Acetic [g]	2,5-DHPA [g]	2-HBA [g]	Cellobiose [g]	Glucose [g]	Fructose [g]	total acid [g]	total yield [%]
49	9	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,1	0,7
64	12	0,0	0,0	0,5	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,6	4,2
75	15	0,0	0,1	2,5	0,4	0,1	0,0	0,0	0,1	0,0	0,0	3,2	21,5
95	18	0,0	0,2	5,4	1,9	0,3	0,1	0,0	0,5	0,1	0,0	8,0	53,2
100	21	0,1	0,5	7,1	3,0	0,4	0,3	0,0	0,7	0,1	0,1	11,3	75,2
100	36	0,1	0,6	6,7	3,1	0,3	0,4	0,0	0,8	0,1	0,1	11,1	74,3
100	51	0,1	0,6	6,8	3,2	0,3	0,4	0,0	0,8	0,1	0,1	11,3	75,1
100	66	0,1	0,6	6,9	3,2	0,2	0,4	0,0	0,8	0,1	0,1	11,4	76,2
100	81	0,1	0,6	6,9	3,2	0,2	0,4	0,0	0,8	0,1	0,1	11,3	75,5
100	96	0,1	0,6	6,9	3,2	0,2	0,4	0,0	0,8	0,0	0,1	11,3	75,3
100	111	0,1	0,6	7,0	3,2	0,2	0,4	0,0	0,8	0,0	0,1	11,4	76,0
100	126	0,1	0,6	7,0	3,2	0,2	0,4	0,0	0,8	0,0	0,1	11,4	76,1
100	141	0,1	0,6	7,0	3,2	0,2	0,4	0,0	0,8	0,0	0,1	11,3	75,6

Table A 11 Cellobiose test 2 1 Process parameters: T=100°C, m(Cellobiose)=15,3 c(NaOH)=5wt%

T [°C]	t (min)	Glycolic [g]	Formic [g]	GISA [g]	Lactic [g]	Acetic [g]	2,5-DHPA [g]	Cellobiose [g]	Glucose [g]	Fructose [g]	total acid [g]	total yield [%]
47	9	0,0	0,0	0,1	0,0	0,0	0,0	10,0	1,8	0,4	0,2	1,3
61	12	0,0	0,0	0,3	0,0	0,0	0,0	8,8	2,0	0,5	0,3	2,3
76	15	0,1	0,1	1,9	0,1	0,1	0,0	5,7	2,0	0,8	2,2	15,0
92	18	0,1	0,2	3,3	0,7	0,3	0,1	3,0	1,9	1,3	4,7	31,1
100	21	0,1	0,5	5,5	2,1	0,5	0,3	0,9	0,5	0,3	8,9	59,7
100	36	0,1	0,7	5,9	2,8	0,6	0,5	0,2	0,0	0,0	10,3	68,9
100	51	0,1	0,8	6,3	2,9	0,6	0,5	0,2	0,0	0,0	10,9	72,6
100	66	0,2	0,8	6,3	2,9	0,5	0,5	0,0	0,3	0,0	10,7	71,5
100	81	0,2	0,8	6,4	2,9	0,5	0,5	0,0	0,0	0,0	10,8	72,2
100	96	0,2	0,8	6,4	2,9	0,5	0,5	0,0	0,5	0,0	10,8	71,8
100	111	0,1	0,8	6,4	2,9	0,4	0,5	0,0	0,4	0,0	10,7	71,0
100	126	0,2	0,8	6,4	2,9	0,4	0,5	0,0	0,2	0,0	10,6	71,0
100	141	0,2	0,8	6,5	2,9	0,4	0,5	0,0	0,1	0,0	10,6	70,8

Table A 12 Cellobiose test 3 Process parameters: T=80°C, m(Cellobiose)=15,31 c(NaOH)=5wt%

T [°C]	t (min)	Glycolic [g]	Formic [g]	GISA [g]	Lactic [g]	Acetic [g]	2,5-DHPA [g]	2-HBA [g]	Cellobiose [g]	Glucose [g]	Fructose [g]	Total acid [g]	Total yield [%]
48	9	0,0	0,0	0,2	0,0	0,0	0,0	0,0	12,1	0,7	0,1	0,2	1,4
61	12	0,0	0,0	0,1	0,0	0,0	0,0	0,0	11,6	0,9	0,1	0,1	0,9
75	15	0,0	0,0	0,6	0,1	0,1	0,0	0,0	6,7	1,6	0,4	0,8	5,7
80	18	0,1	0,1	3,5	0,6	0,3	0,1	0,0	4,0	2,1	1,2	4,9	32,6
80	33	0,1	0,5	5,5	2,2	0,5	0,3	0,0	0,7	0,6	0,3	9,5	63,3
80	48	0,1	0,7	5,4	2,7	0,6	0,5	0,0	0,2	0,1	0,1	10,2	68,0
80	63	0,1	0,7	5,6	2,6	0,6	0,5	0,0	0,1	0,1	0,1	10,3	68,8
80	78	0,1	0,7	5,6	2,6	0,6	0,5	0,0	0,0	0,1	0,0	10,3	68,4
80	93	0,1	0,7	5,7	2,7	0,6	0,5	0,0	0,0	0,1	0,1	10,4	69,6
80	108	0,1	0,7	5,7	2,7	0,6	0,5	0,0	0,0	0,1	0,0	10,4	69,4
80	123	0,1	0,7	5,8	2,8	0,6	0,5	0,0	0,0	0,1	0,0	10,5	69,8
80	138	0,1	0,7	5,8	2,8	0,6	0,5	0,0	0,3	0,1	0,0	10,4	69,6

Table A 13 Cellobiose test 4 Process parameters: T=60°C, m(Cellobiose)=15,31 c(NaOH)=5wt%

T [°C]	t (min)	Glycolic [g]	Formic [g]	GISA [g]	Lactic [g]	Acetic [g]	2,5-DHPA [g]	2-HBA [g]	Cellobiose [g]	Glucose [g]	Fructose [g]	total acid [g]	total yield [%]
47	9	0,0	0,0	0,0	0,0	0,0	0,0	0,0	12,3	0,7	0	0,0	0,3
60	12	0,0	0,0	0,0	0,0	0,0	0,0	0,0	11,8	0,9	0	0,1	0,4
60	27	0,0	0,1	2,1	0,4	0,2	0,0	0,0	9,5	1,7	1,1	3,0	20,0
60	42	0,0	0,3	4,9	1,5	0,4	0,1	0,0	4,1	2,1	1,1	7,5	49,9
60	57	0,1	0,5	5,4	2,2	0,4	0,2	0,0	0,7	0,6	0,7	9,0	59,7
60	72	0,1	0,5	5,1	2,6	0,4	0,3	0,0	0,2	0,1	0,4	9,1	60,9
60	87	0,1	0,6	5,3	2,7	0,4	0,4	0,0	0,1	0,1	0,3	9,6	63,9
60	102	0,1	0,6	5,4	2,8	0,4	0,4	0,0	0,0	0,1	0,1	9,8	65,4
60	117	0,1	0,6	5,4	2,9	0,4	0,4	0,0	0,0	0,1	0,1	9,9	65,9
60	132	0,1	0,6	5,5	2,9	0,5	0,4	0,0	0,0	0,1	0,1	10,0	66,8

Table A 14 mcellulose test 1 Process parameters: T=100°C, m(mcellulose)=30,10 c(NaOH)=10wt%

T [°C]	t (min)	Glycolic [g]	Formic [g]	GISA [g]	Lactic [g]	Acetic [g]	2,5-DHPA [g]	total [g]	total yield [%]
24	3	0,0	0,1	0,2	0,0	0,0	0,0	0,3	1,2
36	6	0,0	0,4	0,5	0,0	0,0	0,0	0,8	2,7
54	9	0,0	0,1	0,2	0,0	0,0	0,0	0,3	1,0
72	12	0,0	0,1	0,2	0,0	0,0	0,0	0,3	1,2
92	15	0,0	0,3	0,4	0,0	0,0	0,0	0,6	2,1
100	18	0,0	0,3	0,4	0,0	0,1	0,0	0,8	2,6
100	48	0,0	0,5	5,5	0,2	0,1	0,0	6,3	20,9
100	78	0,0	0,6	6,3	0,3	0,1	0,5	7,7	25,7
100	108	0,0	0,7	7,5	0,3	0,1	0,6	9,2	30,5
100	138	0,0	0,8	8,8	0,3	0,1	0,6	10,7	35,5

Table A 15 mcellulose test 2 Process parameters: T=140°C, m(mcellulose)=30,18 c(NaOH)=10wt%

T [°C]	t (min)	Glycolic [g]	Formic [g]	GISA [g]	Lactic [g]	Acetic [g]	2,5-DHPA [g]	2-HBA [g]	total [g]	total yield [%]
25	3	0,0	0,1	0,1	0,1	0,0	0,1	0,0	0,4	1,3
34	6	0,0	0,0	0,2	0,1	0,0	0,1	0,0	0,5	1,5
47	9	0,0	0,0	0,1	0,0	0,0	0,1	0,0	0,3	1,1
60	12	0,0	0,1	0,0	0,0	0,0	0,1	0,0	0,2	0,6
74	15	0,0	0,1	0,1	0,0	0,0	0,1	0,0	0,3	0,9
87	18	0,0	0,0	0,2	0,0	0,0	0,1	0,0	0,3	1,1
100	21	0,0	0,1	1,0	0,1	0,0	0,0	0,0	1,2	4,0
110	24	0,0	0,2	2,3	0,1	0,0	0,1	0,0	2,8	9,3
120	27	0,0	0,5	4,7	0,2	0,1	0,4	0,0	5,8	19,2
132	30	0,0	0,7	6,0	0,3	0,1	0,5	0,0	7,5	25,0
140	33	0,1	0,9	6,9	0,4	0,1	0,6	0,0	8,8	29,1
140	63	0,1	1,2	8,4	0,5	0,0	0,7	0,0	10,7	35,4
140	93	0,1	1,4	9,6	0,6	0,1	0,9	0,0	12,5	41,4
140	123	0,1	1,6	10,3	0,7	0,1	1,0	0,0	13,4	44,3
140	153	0,1	1,5	9,8	0,7	0,1	1,0	0,0	12,7	42,2

Table A 16 mcellulose test 3 Process parameters: T=160°C, m(mcellulose)=30,05 c(NaOH)=10wt%

T [°C]	t (min)	Glycolic [g]	Formic [g]	GISA [g]	Lactic [g]	Acetic [g]	2,5-DHPA [g]	2-HBA [g]	total [g]	total yield [%]
84	18	0,0	0,0	0,4	0,1	0,0	0,0	0,0	0,5	1,6
105	23	0,0	0,1	1,6	0,1	0,0	0,1	0,0	2,0	6,5
125	28	0,0	0,5	4,9	0,2	0,1	0,4	0,0	6,2	20,5
139	33	0,1	0,9	7,4	0,4	0,1	0,6	0,0	9,5	31,6
153	38	0,1	1,2	9,0	0,5	0,1	0,8	0,0	11,6	38,7
160	43	0,1	1,3	9,5	0,6	0,1	0,9	0,0	12,2	40,7
160	58	0,1	1,4	10,3	0,7	0,1	1,0	0,0	13,3	44,4
160	73	0,1	1,4	10,7	0,8	0,1	1,1	0,0	13,9	46,4
160	91	0,1	1,5	10,8	0,8	0,1	1,2	0,0	14,1	46,9
160	103	0,1	1,5	11,0	0,8	0,1	1,2	0,0	14,3	47,7
160	118	0,1	1,5	11,1	0,9	0,1	1,2	0,0	14,5	48,3
160	133	0,1	1,5	11,2	0,9	0,1	1,3	0,0	14,8	49,1
160	148	0,1	1,5	11,2	0,9	0,1	1,3	0,0	14,8	49,1
160	163	0,1	1,6	11,5	0,9	0,1	1,4	0,0	15,2	50,5

Table A 17 mcellulose test 4a Process parameters: T=180°C, m(mcellulose)=30,05 c(NaOH)=10wt% t=2h48min

T [°C]	t (min)	Glycolic [g]	Formic [g]	GISA [g]	Lactic [g]	Acetic [g]	2,5-DHPA [g]	2-HBA [g]	total [g]	total yield [%]
85	18	0,0	0,0	0,5	0,0	0,0	0,0	0,0	0,5	1,8
107	23	0,0	0,1	2,0	0,0	0,0	0,1	0,0	2,4	7,8
123	28	0,0	0,3	3,3	0,2	0,1	0,2	0,0	4,2	13,9
141	33	0,1	0,6	6,0	0,3	0,1	0,4	0,0	7,6	25,5
156	38	0,1	0,8	6,9	0,4	0,0	0,6	0,0	9,0	30,0
169	43	0,1	1,0	9,2	0,5	0,0	0,8	0,0	11,9	39,7
179	48	0,1	1,2	10,3	0,6	0,0	0,9	0,0	13,5	45,0
180	63	0,1	1,4	11,5	0,9	0,0	1,2	0,0	15,4	51,3
180	78	0,1	1,5	12,0	1,0	0,0	1,3	0,0	16,3	54,4
180	93	0,1	1,6	12,2	1,1	0,0	1,5	0,0	16,9	56,1
180	108	0,1	1,7	12,7	1,2	0,0	1,5	0,0	17,6	58,6
180	123	0,1	1,8	13,1	1,3	0,1	1,6	0,0	18,1	60,3
180	138	0,2	1,8	12,8	1,4	0,1	1,6	0,0	18,0	59,8
180	153	0,2	1,8	13,1	1,3	0,1	1,6	0,0	18,3	60,8
180	168	0,2	1,9	13,0	1,5	0,1	1,6	0,0	18,3	61,0

Table A 18 mcellulose test 4b Process parameters: T=180°C, m(mcellulose)=30,03 c(NaOH)=10wt% t=5h

T [°C]	t (min)	Glycolic [g]	Formic [g]	GISA [g]	Lactic [g]	Acetic [g]	2,5-DHPA [g]	2-HBA [g]	total [g]	total yield [%]
81	18	0,0	0,0	0,2	0,0	0,0	0,0	0,0	0,3	1,0
103	23	0,0	0,1	1,5	0,0	0,0	0,1	0,0	1,7	5,8
119	28	0,0	0,3	2,6	0,0	0,0	0,2	0,0	3,2	10,6
136	33	0,0	0,6	4,6	0,3	0,0	0,4	0,0	5,9	19,8
150	38	0,1	0,9	6,6	0,4	0,0	0,6	0,0	8,5	28,3
162	43	0,1	1,1	7,7	0,5	0,0	0,7	0,0	10,1	33,5
175	48	0,1	1,3	8,4	0,5	0,0	0,8	0,0	11,1	36,9
180	63	0,1	1,5	9,0	0,7	0,0	0,9	0,0	12,1	40,2
180	78	0,2	1,8	10,6	1,0	0,1	1,2	0,0	14,6	48,5
180	93	0,2	1,9	10,8	1,0	0,1	1,4	0,0	15,1	50,2
180	108	0,2	1,9	11,0	1,1	0,1	1,4	0,0	15,4	51,3
180	123	0,2	2,0	11,4	1,2	0,1	1,5	0,0	16,1	53,7
180	138	0,2	2,1	11,6	1,3	0,1	1,6	0,0	16,6	55,1
180	153	0,3	2,1	11,9	1,4	0,1	1,6	0,0	16,9	56,1
180	168	0,3	2,2	11,9	1,4	0,1	1,7	0,0	17,0	56,5
180	181	0,3	2,2	11,9	1,5	0,1	1,6	0,0	17,1	56,8
180	240	0,3	2,3	12,4	1,6	0,1	1,7	0,0	17,8	59,4
180	300	0,3	2,4	12,8	1,8	0,1	1,7	0,0	18,4	61,4

Table A 19 mcellulose test 4c Process parameters: T=180°C, m(mcellulose)=30,01 c(NaOH)=10wt% t=7h

T [°C]	t (min)	Glycolic [g]	Formic [g]	GISA [g]	Lactic [g]	Acetic [g]	2,5-DHPA [g]	2-HBA [g]	total [g]	total yield [%]
180	300	0,2	2,2	13,1	1,8	0,1	1,9	0,0	19,3	64,2
180	360	0,2	2,2	12,8	1,7	0,1	2,0	0,0	18,9	63,0
180	420	0,3	2,3	13,4	1,9	0,1	2,0	0,0	19,9	66,3

Table A 20 mcellulose test 5 Process parameters: T=200°C, m(mcellulose)=30,01 c(NaOH)=10wt%

T [°C]	t (min)	Glycolic [g]	Formic [g]	GISA [g]	Lactic [g]	Acetic [g]	2,5-DHPA [g]	2-HBA [g]	total [g]	total yield [%]
25	3	0,0	0,0	0,1	0,0	0,0	0,0	0,0	0,1	0,3
33	6	0,0	0,0	0,1	0,0	0,0	0,0	0,0	0,2	0,7
45	9	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,1	0,4
58	12	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,1	0,2
71	15	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,1	0,3
84	18	0,0	0,0	0,1	0,0	0,0	0,0	0,0	0,1	0,4
97	21	0,0	0,1	0,7	0,1	0,0	0,0	0,0	0,9	3,0
110	24	0,0	0,1	1,1	0,1	0,0	0,1	0,0	1,3	4,4
121	27	0,0	0,5	4,6	0,2	0,0	0,4	0,0	5,8	19,2

130	30	0,1	0,7	5,7	0,3	0,0	0,4	0,0	7,0	23,4
139	33	0,1	1,0	7,6	0,4	0,0	0,6	0,0	9,5	31,6
149	36	0,1	1,1	8,2	0,4	0,0	0,7	0,0	10,3	34,3
157	39	0,1	1,2	8,6	0,5	0,0	0,8	0,0	10,8	36,1
165	42	0,1	1,3	9,1	0,5	0,0	0,9	0,0	11,5	38,5
172	45	0,1	1,4	9,5	0,6	0,0	1,0	0,0	12,2	40,7
178	48	0,1	1,5	10,2	0,7	0,1	1,1	0,0	13,2	43,9
184	51	0,1	1,6	10,5	0,7	0,1	1,2	0,0	13,7	45,8
190	54	0,2	1,6	10,6	0,7	0,1	1,2	0,0	13,9	46,2
195	57	0,2	1,6	10,9	0,8	0,1	1,3	0,0	14,3	47,8
199	60	0,2	1,7	11,2	0,9	0,1	1,3	0,0	14,8	49,3
200	90	0,3	2,3	12,7	1,6	0,1	1,6	0,0	17,9	59,6
200	120	0,4	2,6	13,6	2,0	0,1	1,7	0,0	19,6	65,2
200	150	0,4	2,7	13,5	2,3	0,1	1,7	0,0	19,9	66,4
200	180	0,4	2,9	13,2	2,5	0,2	1,8	0,0	20,1	66,8

Table A 21 dilute mcellulose test 1 Process parameters: T=100°C, m(mcellulose)=30,82 c(NaOH)=5wt%

T [°C]	t (min)	Glycolic [g]	Formic [g]	GISA [g]	Lactic [g]	Acetic [g]	2,5-DHPA [g]	2-HBA [g]	total [g]	total yield [%]
26	3	0,0	0,0	0,1	0,1	0,0	0,1	0,0	0,3	0,8
36	6	0,0	0,0	0,3	0,1	0,0	0,1	0,0	0,5	1,5
49	9	0,0	0,0	0,1	0,0	0,0	0,1	0,0	0,2	0,8
63	12	0,0	0,0	0,0	0,0	0,0	0,1	0,0	0,1	0,4
76	15	0,0	0,0	0,1	0,0	0,0	0,1	0,0	0,2	0,7
90	18	0,0	0,0	0,3	0,0	0,0	0,0	0,0	0,4	1,4
100	21	0,0	0,1	1,3	0,1	0,0	0,1	0,0	1,8	5,8
100	51	0,0	0,5	4,5	0,3	0,1	0,5	0,0	5,9	19,1
100	81	0,0	0,9	7,3	0,4	0,1	0,8	0,0	9,6	31,0
100	111	0,0	1,1	8,5	0,5	0,1	0,9	0,0	11,1	36,0
100	141	0,0	1,1	8,9	0,5	0,1	1,0	0,0	11,6	37,7

Table A 22 dilute mcellulose test 2 Process parameters: T=160°C, m(mcellulose)=30,17 c(NaOH)=5wt%

T [°C]	t (min)	Glycolic [g]	Formic [g]	GISA [g]	Lactic [g]	Acetic [g]	2,5-DHPA [g]	2-HBA [g]	total [g]	total yield [%]
95	20	0,0	0,1	1,2	0,1	0,0	0,1	0,0	1,6	5,1
111	25	0,0	0,3	3,4	0,2	0,1	0,3	0,0	4,3	14,4
126	30	0,0	0,8	6,4	0,4	0,1	0,7	0,0	8,5	28,2
142	35	0,1	1,3	8,7	0,6	0,1	1,0	0,0	11,7	38,7
154	40	0,1	1,4	9,9	0,7	0,0	1,1	0,0	13,2	43,6
160	60	0,1	1,6	10,3	0,9	0,0	1,2	0,0	14,0	46,3
160	80	0,1	1,6	10,2	0,9	0,0	1,3	0,0	14,0	46,3
160	100	0,2	1,6	10,2	0,9	0,0	1,4	0,0	14,1	46,6
160	120	0,2	1,6	10,4	1,0	0,1	1,3	0,0	14,3	47,5
160	140	0,2	1,6	10,3	1,0	0,1	1,3	0,0	14,2	47,0
160	160	0,2	1,7	10,5	1,0	0,1	1,4	0,0	14,5	48,1
160	190	0,2	1,7	10,8	1,0	0,1	1,3	0,0	14,7	48,8
160	220	0,2	1,7	10,6	1,0	0,1	1,4	0,0	14,7	48,6

Table A 23 dilute mcellulose test 3 Process parameters: T=200°C, m(mcellulose)=30,07 c(NaOH)=5wt%

t (min)	T [°C]	Glycolic [g]	Formic [g]	GISA [g]	Lactic [g]	Acetic [g]	2,5-DHPA [g]	2-HBA [g]	total [g]	total yield [%]
3	25	0,0	0,1	0,7	0,1	0,0	0,1	0,0	0,9	3,1
6	34	0,0	0,1	0,8	0,1	0,0	0,1	0,0	1,6	5,2
9	47	0,0	0,0	0,3	0,0	0,0	0,0	0,0	0,4	1,3
12	61	0,0	0,0	0,2	0,0	0,0	0,0	0,0	0,3	1,0
15	74	0,0	0,0	0,1	0,0	0,0	0,0	0,0	0,2	0,8
18	88	0,0	0,0	0,2	0,0	0,0	0,0	0,0	0,4	1,2
21	101	0,0	0,1	0,7	0,1	0,0	0,0	0,0	0,9	3,0
24	109	0,0	0,1	1,3	0,1	0,1	0,1	0,0	1,7	5,7

27	118	0,1	0,5	4,4	0,3	0,1	0,5	0,0	5,8	19,4
30	128	0,2	1,0	7,2	0,5	0,1	0,8	0,0	9,5	31,6
33	137	0,2	1,2	8,2	0,6	0,1	1,0	0,0	11,0	36,6
36	146	0,2	1,4	9,0	0,7	0,1	1,1	0,0	12,2	40,7
39	154	0,2	1,5	9,4	0,8	0,1	1,2	0,0	12,8	42,7
42	162	0,3	1,6	9,2	0,9	0,1	1,2	0,0	12,9	43,0
45	170	0,3	1,7	9,5	0,9	0,1	1,3	0,0	13,3	44,3
48	176	0,3	1,6	10,0	0,9	0,1	1,3	0,0	13,8	46,0
51	183	0,3	1,7	10,2	0,9	0,1	1,4	0,0	14,1	46,8
54	188	0,2	1,6	10,2	0,9	0,1	1,3	0,0	14,0	46,4
57	194	0,3	1,8	10,3	1,0	0,1	1,5	0,0	14,4	47,7
60	199	0,3	1,8	11,0	1,1	0,1	1,5	0,0	15,3	50,8
90	200	0,3	1,8	10,3	1,2	0,1	1,5	0,0	14,6	48,6
120	200	0,3	1,9	9,2	1,7	0,1	1,4	0,0	14,0	46,6
150	200	0,4	2,2	10,6	1,8	0,1	1,6	0,0	16,1	53,5
180	200	0,5	2,7	11,2	2,0	0,1	1,9	0,0	17,7	58,8

Table A 24 dilute mcellulose test 4 Process parameters: T=100°C, m(mcellulose)=30,01 c(NaOH)=2,5wt%

T [°C]	t (min)	Glycolic [g]	Formic [g]	GISA [g]	Lactic [g]	Acetic [g]	2,5-DHPA [g]	2-HBA [g]	total [g]	total yield [%]
24	3,00	0,0	0,0	0,1	0,0	0,0	0,0	0,0	0,2	0,6
32	6,00	0,0	0,0	0,1	0,0	0,0	0,0	0,0	0,2	0,6
46	9,00	0,0	0,0	0,1	0,0	0,0	0,0	0,0	0,2	0,8
59	12,00	0,0	0,1	0,2	0,0	0,0	0,0	0,0	0,4	1,2
73	15,00	0,0	0,0	0,1	0,0	0,0	0,0	0,0	0,2	0,7
86	18,00	0,0	0,1	0,2	0,0	0,0	0,0	0,0	0,3	0,9
99	21,00	0,0	0,1	0,3	0,0	0,0	0,0	0,0	0,5	1,7
100	51,00	0,1	0,7	4,2	0,4	0,0	0,6	0,0	6,0	19,9
100	81,00	0,1	1,1	5,0	0,6	0,0	0,9	0,0	7,7	25,8
100	111,00	0,1	1,4	5,9	0,7	0,0	1,1	0,0	9,2	30,7
100	141,00	0,1	1,5	6,0	0,7	0,0	1,2	0,0	9,6	31,9

Table A 25 dilute mcellulose test 5 Process parameters: T=200°C, m(mcellulose)=30,01 c(NaOH)=2,5wt%

T [°C]	t (min)	Glycolic [g]	Formic [g]	GISA [g]	Lactic [g]	Acetic [g]	2,5DHPA [g]	2-HBA [g]	total [g]	total yield [%]
25	3	0,0	0,0	0,1	0,0	0,0	0,0	0,0	0,2	0,7
36	6	0,0	0,0	0,2	0,0	0,0	0,0	0,0	0,3	0,9
49	9	0,0	0,1	0,2	0,0	0,0	0,0	0,0	0,4	1,3
63	12	0,0	0,0	0,1	0,0	0,0	0,0	0,0	0,2	0,7
76	15	0,0	0,0	0,1	0,0	0,0	0,0	0,0	0,2	0,6
89	18	0,0	0,1	0,3	0,0	0,0	0,0	0,0	0,4	1,4
101	21	0,0	0,1	0,5	0,0	0,0	0,0	0,0	0,6	2,1

109	24	0,0	0,3	1,6	0,0	0,0	0,1	0,0	1,9	6,5
119	27	0,0	0,6	2,9	0,0	0,0	0,3	0,0	3,8	12,6
128	30	0,0	0,7	3,7	0,0	0,0	0,4	0,0	4,8	16,0
138	33	0,1	1,6	5,2	0,0	0,0	1,0	0,0	7,9	26,4
146	36	0,2	1,9	5,8	0,0	0,0	1,2	0,0	9,0	30,0
153	39	0,2	2,1	6,1	0,0	0,0	1,3	0,0	9,5	31,7
162	42	0,2	2,2	6,2	0,0	0,1	1,4	0,0	9,8	32,7
170	45	0,2	2,2	6,3	0,0	0,0	1,4	0,0	10,0	33,3
177	48	0,3	2,3	6,5	0,1	0,1	1,4	0,0	10,4	34,5
183	51	0,3	2,4	6,4	0,9	0,1	1,5	0,0	11,2	37,3
189	54	0,3	2,4	6,4	1,0	0,1	1,6	0,0	11,4	38,0
193	57	0,4	2,5	6,5	1,0	0,1	1,5	0,0	11,6	38,7
197	60	0,4	2,5	6,5	1,1	0,1	1,7	0,0	11,7	39,1
200	90	0,4	2,5	6,5	1,1	0,1	1,6	0,0	11,7	38,8
200	120	0,4	2,5	6,4	1,1	0,1	1,6	0,0	11,6	38,5
200	150	0,5	2,6	6,4	1,1	0,1	1,6	0,0	11,8	39,4
200	180	0,5	2,6	6,2	1,1	0,1	1,6	0,0	11,6	38,6
200	210	0,5	2,8	6,4	1,2	0,1	1,8	0,0	12,3	41,0

Table A 26 Toiletpaper 1 shredded Process parameters: T=200°C, m(Toiletpaper)=14,46 c(NaOH)=10wt%

T [°C]	t (min)	Glycolic [g]	Formic [g]	GISA [g]	Lactic [g]	Acetic [g]	2,5-DHPA [g]	2-HBA [g]	total [g]	total yield [%]
194	53	0,1	0,6	2,4	0,6	0,1	0,4	0,1	4,2	28,8
200	90	0,1	0,9	3,9	1,2	0,1	0,8	0,4	7,4	51,1
200	120	0,1	1,0	4,2	1,3	0,1	0,9	0,3	8,0	55,5
200	150	0,1	1,1	4,1	1,4	0,1	0,9	0,2	8,0	55,5
200	180	0,1	1,0	4,2	1,5	0,1	0,9	0,1	8,1	55,9

Table A 27 Toiletpaper 2 shredded Process parameters: T=200°C, m(Toiletpaper)=14,51 c(NaOH)=10wt%

T [°C]	t (min)	Glycolic [g]	Formic [g]	GISA [g]	Lactic [g]	Acetic [g]	2,5-DHPA [g]	2-HBA [g]	total [g]	total yield [%]
65	18	0,0	0,3	1,8	0,3	0,1	0,2	0,2	2,9	20,0
200	180	0,1	1,1	4,1	1,5	0,1	0,9	0,2	8,0	55,4

Table A 28 Toiletpaper 3 milled Process parameters: T=200°C, m(Toiletpaper)=14,49 c(NaOH)=10wt%

T [°C]	t (min)	Glycolic [g]	Formic [g]	GISA [g]	Lactic [g]	Acetic [g]	2,5-DHPA [g]	2-HBA [g]	total [g]	total yield [%]
85	18	0,0	0,0	0,1	0,0	0,0	0,0	0,0	2,6	18,3
105	23	0,0	0,0	0,2	0,0	0,1	0,0	0,0	0,3	2,2
117	28	0,0	0,0	0,5	0,1	0,1	0,0	0,0	0,7	4,9
131	33	0,0	0,1	0,8	0,1	0,1	0,1	0,0	1,0	7,0
146	38	0,0	0,1	1,0	0,1	0,1	0,1	0,0	1,3	9,2
161	43	0,0	0,1	1,2	0,1	0,1	0,1	0,0	1,6	11,3
175	48	0,0	0,1	1,3	0,2	0,1	0,1	0,0	1,8	12,4
188	53	0,0	0,2	1,7	0,3	0,1	0,2	0,1	2,5	17,1
198	58	0,0	0,4	2,4	0,5	0,1	0,4	0,1	3,9	26,7
200	73	0,0	0,6	3,1	0,7	0,1	0,6	0,2	5,2	35,8
200	88	0,1	0,9	4,2	1,0	0,1	0,8	0,3	7,2	49,7
200	103	0,1	0,9	4,4	1,1	0,1	0,8	0,3	7,6	52,4
200	118	0,1	1,0	4,4	1,2	0,1	0,8	0,3	7,7	53,4
200	133	0,1	1,0	4,4	1,3	0,1	0,8	0,3	7,9	54,5
200	148	0,1	1,0	4,5	1,3	0,1	0,9	0,4	8,0	55,3
200	163	0,1	1,0	4,4	1,4	0,1	0,8	0,4	7,9	54,6
200	178	0,1	1,0	4,5	1,3	0,1	0,9	0,4	8,1	56,0

Table A 29 Slurry test 1 Process parameters: T=160°C, m(slurry)=319g c(NaOH)=10wt%

T [°C]	t (min)	Glycolic [g]	Formic [g]	GISA [g]	Lactic [g]	Acetic [g]	2,5-DHPA [g]	2-HBA [g]	total [g]	total yield [%]
160	60	0,1	0,1	0,6	0,2	0,1	0,1	0,0	1,0	8,2
160	78	0,1	0,2	1,1	0,2	0,1	0,1	0,0	1,9	14,5
160	90	0,1	0,2	1,1	0,2	0,1	0,1	0,0	1,8	13,8

160	105	0,1	0,2	1,3	0,3	0,1	0,1	0,0	2,0	15,6
160	120	0,1	0,2	1,2	0,3	0,1	0,1	0,0	2,0	15,3
160	135	0,1	0,2	1,3	0,3	0,1	0,1	0,0	2,1	16,5
160	150	0,1	0,2	1,3	0,3	0,1	0,1	0,0	2,2	16,9
160	165	0,1	0,2	1,5	0,3	0,1	0,1	0,0	2,3	18,2
160	180	0,1	0,2	1,4	0,3	0,1	0,1	0,0	2,2	17,2
160	195	0,1	0,3	1,4	0,3	0,1	0,2	0,0	2,3	17,9
160	210	0,1	0,3	1,6	0,4	0,1	0,1	0,0	2,5	19,4
160	225	0,1	0,3	1,6	0,4	0,1	0,2	0,1	2,6	20,5
160	240	0,1	0,3	1,7	0,4	0,1	0,1	0,1	2,6	20,5
160	270	0,1	0,3	1,7	0,4	0,1	0,1	0,1	2,7	21,0
160	285	0,1	0,3	1,7	0,4	0,1	0,2	0,1	2,7	21,5
160	300	0,1	0,3	1,8	0,5	0,1	0,2	0,0	2,9	22,4
160	315	0,1	0,3	1,8	0,5	0,1	0,2	0,1	2,9	23,1
160	345	0,1	0,3	1,7	0,5	0,1	0,2	0,1	2,8	22,1
160	360	0,1	0,3	1,8	0,4	0,1	0,2	0,1	2,9	22,7

Table A 30 Slurry test 2 Process parameters: T=200°C, m(slurry)=303g c(NaOH)=10wt%

T [°C]	t (min)	Glycolic [g]	Formic [g]	GISA [g]	Lactic [g]	Acetic [g]	2,5-DHPA [g]	2-HBA [g]	total [g]	total yield [%]
195	60	0,1	0,3	1,4	0,4	0,1	0,2	0,1	2,5	21,0
200	75	0,1	0,5	2,4	0,7	0,1	0,5	0,2	4,5	36,9
200	90	0,1	0,7	2,9	0,9	0,1	0,5	0,3	5,5	45,4
200	105	0,1	0,7	3,1	1,0	0,1	0,6	0,3	5,9	48,5
200	120	0,1	0,8	3,1	1,1	0,1	0,6	0,3	6,1	50,0
200	135	0,1	0,8	3,2	1,2	0,1	0,6	0,3	6,3	51,5
200	150	0,1	0,8	3,2	1,1	0,1	0,7	0,3	6,3	52,0
200	165	0,1	0,8	3,1	1,2	0,1	0,7	0,3	6,2	51,3
200	180	0,1	0,8	3,1	1,2	0,1	0,6	0,3	6,3	51,7
200	195	0,1	0,8	3,1	1,1	0,1	0,7	0,3	6,2	51,2
200	210	0,1	0,8	3,1	1,2	0,1	0,6	0,3	6,2	51,1
200	225	0,1	0,8	3,0	1,2	0,1	0,7	0,3	6,2	50,6
200	240	0,1	0,8	3,0	1,1	0,1	0,7	0,3	6,2	50,9

Figure A 1 Image of toilet paper used in experiments . Serla, Metsä Tissue recycled fibre, yellow