

Lappeenranta-Lahti University of Technology LUT
School of Engineering Science
Master's Program in Chemical and Process Engineering

Joonas Liikanen

**PRODUCTION OF HYDROXY CARBOXYLIC ACIDS FROM WASTE
CELLULOSIC MATERIAL**

Examiners: Professor Tuomo Sainio

D.Sc. (Tech) Jari Heinonen

TIIVISTELMÄ

Lappeenrannan-Lahden teknillinen yliopisto LUT

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Master's Programme in Chemical and Process Engineering

Joonas Liikanen

Hydroksikarboksylihappojen valmistus jäte selluloosa materiaaleista

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Tarkastajat: Professori Tuomo Sainio

TkT. Jari Heinonen

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Halpojen ja helposti saatavilla olevien vaatteiden kulutus on lisääntynyt viime vuosina. Tämä on kasvattanut tekstiilikuitujen tuotantoa ja markkinoita. Kasvava kulutus on johtanut tekstiilijätteen määrän kasvuun ja yleisimmät hävitystavat aiheuttavat ilmastopäästöjä, joten uusille hävitysmenetelmille on tarvetta. Tekstiilien ja niiden komponenttien kierrätys uuteen käyttöön pidentäisi tuotteen elinkaarta ja tukisi kiertotalouteen siirtymistä.

Yksi yleisimmistä tekstiilikuiduista on puuvilla, joka koostuu pääosin selluloosasta. Selluloosan hajoaminen alkaliliuoksessa on kirjallisuudessa hyvin tunnettu reaktio. Tässä diplomityössä hyödynnetään aikaisemmista tutkimuksista saatua tietoa ja tutkitaan selluloosan sekä puuvillan hajoamista. Puhdasta selluloosaa ja puuvillakankaita testataan hajoamiselle sopivissa olosuhteissa, hydroksikarboksylihappojen tuottamiseksi. Selluloosan peeling-reaktion päätuote on glukoisosakkariinihappo, GISA. Koska tekstiilijäte koostuu useista materiaaleista, tässä diplomityössä tutkitaan myös muita tekstiilimateriaaleja, kuten regeneroitua selluloosaa ja synteettisiä kuituja.

Tässä diplomityössä esitetään prosessi, jonka avulla puuvillaa voidaan kierrättää kemikaaleiksi. Prosessissa käytetään vahvaa natriumhydroksidia ja korkeaa lämpötilaa. Sopivien olosuhteiden määrittämiseksi kokeita tehdään ensin puhtaalla selluloosalla. Saatuja tuloksia voidaan hyödyntää puuvillatekstiileihin. Puuvilla hajoaa prosessissa karboksylihapoiksi ja tuoteliuos analysoidaan HPLC-laitteistolla. Tehdyt kokeet luovat perustan tekstiilien alkaaniselle hajoamisprosessille ja antavat suunnan jatkotutkimuksia varten.

ABSTRACT

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Joonas Liikanen

Production of hydroxy carboxylic acids from waste cellulosic material

Master's thesis

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65 pages, 26 figures, 13 tables, 1 appendix

Examiners: Professor Tuomo Sainio

D.Sc. (Tech) Jari Heinonen

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Textile fiber production and market has seen a growth in recent years, with the growing consumption in cheap and easily accessible clothing. As a result, the amount of textile waste generated has increased and there is a need for new textile waste disposal methods. Most common disposal practices cause emissions and ends the product life cycle. Recycling fabric or its components to new use, would extend product lifecycle and would support circular economy.

One of the most common textile fibers is cotton, that is mostly consisted of cellulose. Cellulose degradation in alkali solution is a well-known reaction in pulping industry and in literature. In this thesis, literature-based knowledge on cellulose degradation is utilized to work with cotton fabrics. Pure cellulose and cotton fabrics are tested in suitable degradation conditions, to produce hydroxy carboxylic acids. Main product of the cellulose peeling reaction is glucoisosaccharinic acid, GISA. Textile waste consists of various materials, so also other textile materials such as regenerated cellulose and synthetic fibers are studied through literature and tests.

This thesis proposes a process to recycle cotton material to chemicals with strong NaOH and high temperature. Pure cellulose is tested to establish suitable conditions that can be utilized for cotton fabrics. Cotton textile is degraded to various carboxylic acids and the product solution is analyzed with HPLC. Cotton behaved at same way as pure cellulose, producing GISA as the key product. These experiments laid a foundation for the process and give a direction for further studies on the topic.

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Helsinki, May 24, 2020

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ABBREVIATIONS

GISA	Glucosiosaccharinic acid
HLW	High-level waste
ILW	Intermediate-level waste
LLW	Low-level waste
L/S	Liquid to solid
MMCF	Man-made cellulosic fibers
MSW	Municipal solid waste
mt	Metric tons
NaOH	Sodium hydroxide
Na ₂ CO ₃	Sodium carbonate
Na ₂ S	Sodium sulfide
TPA-Na ₂	Disodium terephthalate salt
NMMO	M-methylmorpholine N-oxide
PAN	Polyacrylonitrile
PET	Polyethylene terephthalate
XISA	Xyloisosaccharinic acid
2-HBA	2-hydroxybutanoic acid
2,5-DHPA	2,5-dihydroxypentanoic acid

1 INTRODUCTION

1.1 Background

Textile wastes are piling up around the world and there is a need for optional recycle methods for these materials. World production and consuming of textile materials in the form of clothes and household materials are growing each year, as the trend of consumerism and fast fashion are growing. At this moment the most used end disposal has been landfill and combustion, both of which may have a negative impacts on the environment. A process that could break down these textile materials to useful chemicals would provide an environmentally friendly option to fight the growing textile waste piles. Majority of textile consumption is due to cotton and growing use of polyester. Cotton mainly consists of cellulose, a polymer which behavior is widely researched in alkaline conditions, due to similar conditions in paper industry (Kraft process) and geological disposal facilities. Specifically cotton in alkaline solutions has also been briefly researched by Niemelä and Sjöström (Niemelä & Sjöström 1986). Under alkaline conditions, cellulose undergoes a peeling reaction and other side reactions. Peeling reaction forms GISA, which may further on degrade to other smaller molecule acids. Waste could be transformed to hydroxy carboxylic acids, that could be used in other applications.

1.2 Objectives and research questions

The aim of the thesis was to study the production of hydroxy carboxylic acids from textile wastes. The objective is to create a base understanding of the process and how different textile materials react in alkali environment. Objective was not to optimize the process, but to explore conditions that may be effective for the most common textile materials, such as cotton and polyester. The main research question was that can hydroxy carboxylic acids be produced from textile waste material by alkaline (NaOH) cooking. This study explores the possibility of producing useful substances of a variety of fabrics. Idea for the process comes from the fact that one the most common fabrics used is cotton, which is mostly made from cellulose and

for the knowledge that cellulose can be degraded in alkali environments. Therefore, one of the main focuses will be GISA (glucoisosaccharinic acid) that is the main degradation product of cotton.

Beginning of the study focuses on textile wastes, to give a background for the issue that this study is aiming to help with. After highlighting the problem related to the growing amount of textile wastes, this study explores what materials are present in textile wastes and the basic information of the different fibers that are produced globally. Fourth and fifth chapter turns the aim to the process, exploring the written knowledge on material behavior in alkaline conditions and the possible degradation products. Fourth chapter is particularly focusing on cellulose degradation reactions and products. Giving a knowledge of what will and could happen in our process. Chapter 6 reveals the process equipment, conditions and analytics that is used. In the last chapters, results and conclusions of the experiments are discussed.

2 GLOBAL AND FINNISH TEXTILE WASTE SITUATION

Textile wastes piling up around the world, have been a growing concern in recent years. This is due to an increase in textile consumption and therefore in growing fiber production. Global fiber production surpassed the 100 million metric tons (mt) mark in 2017, and it has doubled since 1990 and seems to continue the growth to reach 145 million mt in the next 10 years. (Textile Exchange 2018). Figure 1 shows the growth of global fiber production over the last two decades.

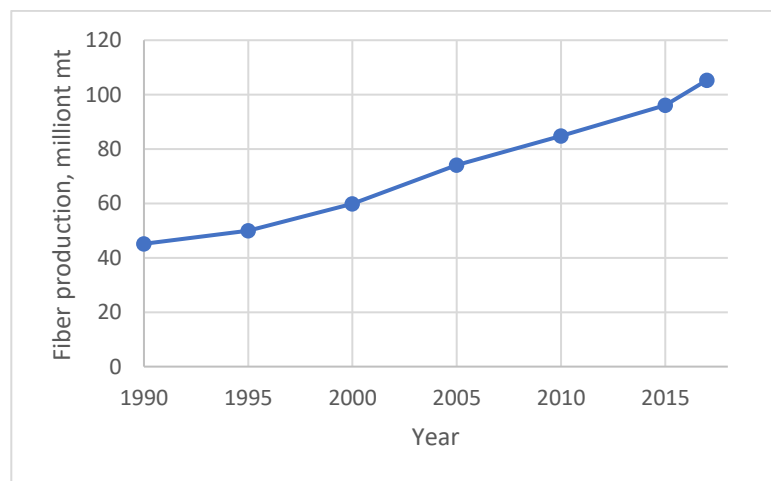


Figure 1 Data from Textile Exchange 2018, showing the growth in fiber production.

Rise of textile supply responds to growing global demand. Households in European Union spent 40% more on clothes in 2012 than 1996, after the data was reflected with changes in clothing prices. This increase made clothing one of the world's most traded manufactured products. Consumption increase can be explained by many reasons. Production networks have changed: improved transport and removal of tariffs and trade barriers. (EAA, 2014) Another reason for the increase is globalization and consumerism that gives rise to "fast fashion", in other words, low price clothing that consumers consider disposable. Marketing and season depended clothing affects especially young people to spend more in clothes. (Claudio 2007) Old clothing goes out of fashion in a short time and is replaced with new clothing lines. Often these garments are low-value clothing that has low durability and retention, that also lowers consumers threshold of disposal. Expanding wardrobes of cheap disposable clothes leads to increase in global textile waste. In summary,

more clothes are bought and used for a shorter period of time. It is also inevitable that consumerism is going rise globally when purchasing power of people in developing-countries increases, not forgetting the growing middle class.

Clothing consumption was 70% of total textile consumption by weight in EU (EAA, 2014). A research made by WRAP (Waste and Resources Action Program) in 2017 examines environmental impacts of clothing to support ECAP (European Clothing Action Plan). Their calculations and estimations show the total consumption of clothing to be 6,4 million mt in EU. Breakdown of clothing consumption and waste in some of the examined EU countries are shown in Table 1. In the US, the situation is much worse as they generate 16.9 million tonnes (2017) of textile waste every year which is 52kg per capita (calculated with USA population of 325 million) (EPA 2017).

Table 1 Clothing consumption and waste in EU countries. (WRAP 2017)

	Consumption (tonnes)	Consumption per capita (kg)	Clothing waste (tonnes)	Clothing waste per capita (kg)
Netherlands	230 887	13.66	71 374	4.2
Denmark	72 801	12.86	15 735	2.8
UK	992 040	15.29	302 000	4.7
Germany	1 123 210	13.83	280 972	3.5
Italy	881 811	14.50	440 179	7.2

In addition to clothing and household textiles, the market of technical textiles has grown. Technical textiles consist of materials and products produced not for their looks but for their properties. Examples of application areas are transport, medical, agriculture, construction, packaging and geotextiles. (Horrocks & Anand 2000) The technical textile market is projected to grow from 217,178 million (2017) to 309,933 million euros (2025) (Allied Market Research 2020). This of course would add some amount to the textile waste globally, as some of technical textile structures (e.g. composites) can differ largely from typical textiles.

Dahlbo *et al.* defined the annual amount of discarded textile in Finland to be about 71 300 tons based on textile and textile flows. In the same way as elsewhere in Europe, textile waste amount and share in solid municipal waste has increased. Clothing purchases grew 28% from 1996 to 2012 and Finnish consumers own double the amount of clothes that they did before. (Dahlbo *et al.* 2017)

2.1 End use and disposal

Textile waste problem can be tackled throughout the whole life cycle, from product design and manufacturing to its use and disposal. In this study the main focus will be on the end disposal and recycling possibilities. Textile waste recycling stream can be represented well with the pyramid model, that was introduced by Wang in 2006. I present this model to give a general idea how gathered textile waste is treated. The model consists of 5 categories as seen in Figure 2, where categories are in order of volume, decreasing to the top.



Figure 2 Textile waste pyramid model, adapted from Wang (2006).

Most of recycled waste is sorted for used clothing markets, mainly to developing countries. Some of the recycled textiles are converted to new products. Fabrics are cut down to fibers through mechanical and chemical processes and then re-engineered into new products. Clothing that don't have use in previous categories

can be recycled as wiping and polishing cloths for industrial use, but this mainly concerns cotton t-shirts. One percent of recycled textile can be treated as “diamonds” if they have a value being vintage clothes, valuable fibers, couture clothing or antique. (Wang 2006) All recycled textiles cannot be used for purposes previously mentioned and they end up in landfills or incineration where also other non-recycled waste ends.

End disposal options for textile waste changed in 2016. A Finnish government decree (Decree 331/2013) on restricting biodegradable and other organic waste on landfills was approved in 2013 and applied from the beginning of 2016. Purpose of the decree is to prevent pollution of surface waters, groundwater, soil and air. (Ministry of Environment 2013) Textile wastes fall into this category and therefore are restricted from landfills. Clothes and other textiles biodegrade to methane, a greenhouse gas.

Changes in waste law and decrees come from the European Union’s objective to move towards circular economy. Council of the European Union approved a waste package in 2017. It sets new rules and targets on waste management and recycling. Circulation would reduce pollution, littering and the valuable materials would be used more efficiently. Waste package includes targets for municipal solid waste recycling and landfilling limits. Each EU country must have a separate collection for textiles waste until 1. January 2025. (Council of the European Union 2018) This will enhance the possibility to take make use of textile waste and move towards circular economy.

The solution to textile waste has been and is still today (depending on location) incineration and landfill. These end uses lead to loss of energy and raw materials that could be recycled to continue textile materials lifetime. Two thirds of textile waste are collected from mixed waste and most are incinerated to recover energy in Nordic countries. (Schmidt *et al.* 2016) Incineration became preferable option after the landfill ban in absence of effective recycling practices. Energy is recovered by combustion in high temperature to recover energy as power or electricity. Incineration has environmental risks as it produces toxic compounds. Currently these risks are decreased by energy recovery and emissions control, but this is not the case globally. (Enis *et al.* 2019) Main concern in incineration has been the emission of organic compounds (dioxins) and heavy metals. There are cases made

for incineration and against as higher concentrations of mentioned substances has been detected but no significant health effects have been found. (Giusti 2009) Debate on behalf and against will continue.

Landfill offers the least favored option for textile waste disposal and some countries like Finland, have banned it from landfills as mentioned before. Landfill is still one of the most used disposal methods globally, in United States 85% of textile waste is landfilled. Landfill capacities are a problem as they take up a lot of land space. In the landfills synthetic fibers don't decompose and biodegradable material such as cotton produce methane and carbon dioxide, thus promoting global warming. (Enis *et al.* 2019) Increasing landfill plans and targets for a greener future, leads to an increasing need for textile waste recycling methods as consumption of fabrics seems to increase year after year.

In Finland, previously mentioned annual production of 71 000 tons of textile waste, originates 60% from household waste and the rest from industry and service sectors (Tojo 2012). Textile waste considers 5.9% of total municipal solid waste in average, from which clothes are 2.6% in average (JLY, 2019) Following Figure 3 shows how the textile waste is divided to different end uses in Finland. Finland does not have a national textile waste collection system, only non-governmental organizations (NGOs) and charity organizations (such as UFF and Red Cross) have clothing collection points. Collected reusable clothing's treatment is determined on material condition. Good condition clothing is resold in second-hand shops, donated or sent abroad. As an alternative, textiles can be are also mechanically teared or modified so the material can be reused. Large quantities clothing is also reused by consumers themselves, through flea markets and internet. Non-reusable collected low grade textiles are recycled as raw materials for industries or incinerated. (Tojo *et al.* 2012) But in general the separate collection focuses more on re-usable textile and non-usable low-grade material is ending up in mixed municipal waste. As seen from the figure most of the waste are not collected, ending up in mixed municipal waste. Data in the figure is old (from 2010), so the waste ending to landfill does not reflect the current situation. As mentioned before landfilling textile waste is restricted, so the 26 000 tons are now either incinerated or recycled.

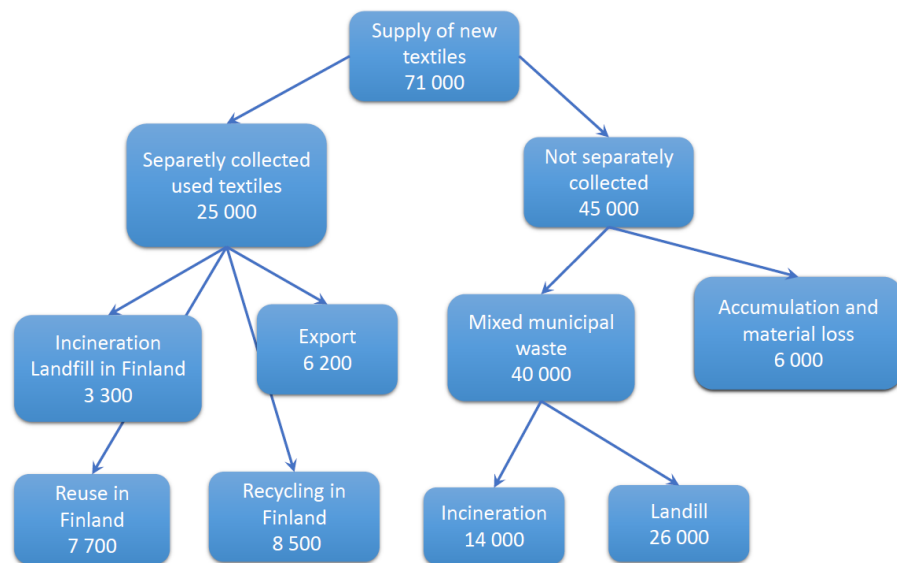


Figure 3 Textile waste in Finland (2010), in tonnes. Adapted from Schmidt et al. (2016).

2.2 Challenges in circular economy

Why textile recycling is not done effectively already? This is due to many challenges during the whole life cycle of textiles. Transition from linear to circular economy is ongoing, aiming to reduce waste amounts and more efficient use of resources. With textiles this means reducing textile waste and maintaining material value throughout the life cycle, keeping the value after disposal. Transition to circular economy needs new networks, processes and technologies to respond on growing waste piles. Koszewska (2019) divides main factors influencing practicality and viability of recycling to three sections. Product design and development consists of decisions made before manufacture, such as raw material, dye, solvent, finishing process selections. These selections determine product lifetime and disposal possibilities. Selection of more easily recyclable fibers would ease the recycling possibilities, but it might not please consumers demand for product features and performance. The second and third factors are technological possibilities and disposal practices. Consumers should be educated on built disposal infrastructure. Although one problem is that there is a shortage of viable and scaled up collecting and sorting of textile waste (especially low-grade textiles), that could be traced to lack of viable fiber separation processes and recycling technologies.

(Koszewska 2018) In Finland, VTT is leading a project called Telaketju in cooperation with the Ministry of Environment and Economy, Business Finland and with various other organizations. The project targets to enhance utilization of textile waste and to help Finland transfer from linear to circular economy of textiles. (Heikkilä *et al.* 2019)

3 FIBERS AND CHEMICALS FOUND IN COMMON TEXTILES

Textiles are made of natural or manufactured fibers, which are described as being 100 times longer than its diameter. Fibers can be used to form different fabrics, composites and other textiles, but in this work, composites are disregarded because their structure differs from fabrics. Fabrics are formed from yarn, which are usually spun from fibers. Most common fabric forming method is weaving, but also braiding, knitting, felting, tufting, and nonwoven is used. Various kinds of fabrics are manufactured with different properties and quality, based on used fibers and manufacturing process. These processes use various chemicals to enhance and modify qualities of the textile, leaving small amounts to product as components or residues. Left over chemicals are due to textile dyeing, bleaching, printing, washing, and others.

Textile fibers are divided by source to natural and manufactured. They exist and are manufactured with different shape, contour, chemical structure, and color. Natural fibers can be found as such in nature, recovered from plants and animals. Manufactured fibers are manmade from natural or synthetic polymers. Synthetic fibers do not exist in nature, they are made from chemicals. (Houck 2009)

According to Textile Exchange's Preferred Fiber and Materials report synthetic fibers account for over 51,5% of the 2018 fiber production. Synthetics have dominated fiber industry from 1990's and popularity the keeps growing. Figure 4 presents global fiber production in 2018. (Textile Exchange 2019) Here it must be noted that all of fiber production does not go to clothing and household textile industry, as many synthetic fibers are popular in technical textile industry.

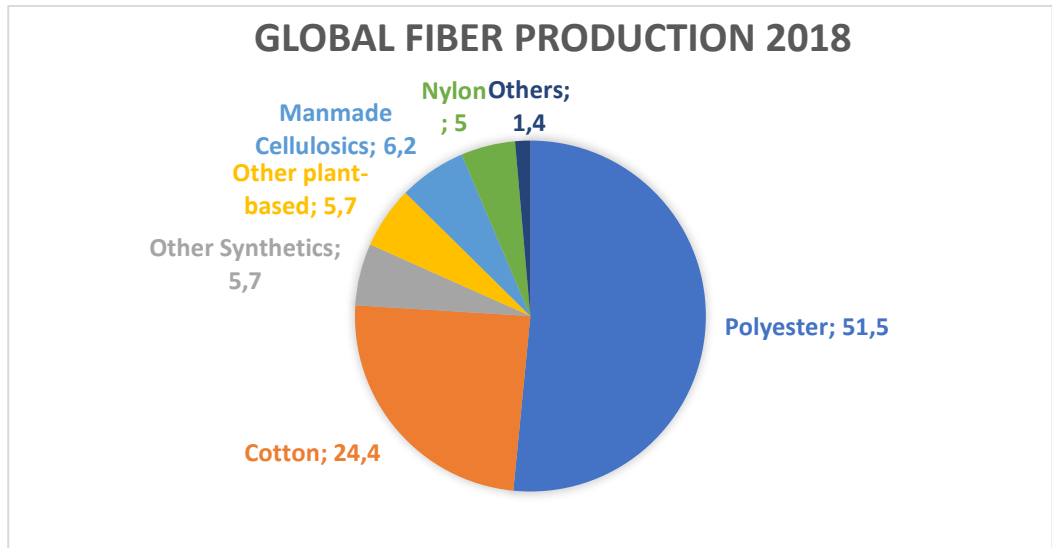


Figure 4 Data from Textile Exchange 2019 report, "others" are wool, silk and down. (Textile Exchange 2019)

European commission published a study in 2014 about environmental improvement potential of textiles. Their study concluded textile consumption breakdown of textile products in 2007. From total consumption, clothing textile covered 70% and household textile covered the rest. Most of clothing consumption was tops (of which almost half was made of synthetic fibers). The next largest consuming products were underwear and bottoms. In household textiles, the biggest share in consumption was floor coverings. Figure 5 shows material breakdown of clothing and household textiles. Cotton is the most used fiber in both categories and polyester is the second most used. (Beton *et al.*2014)

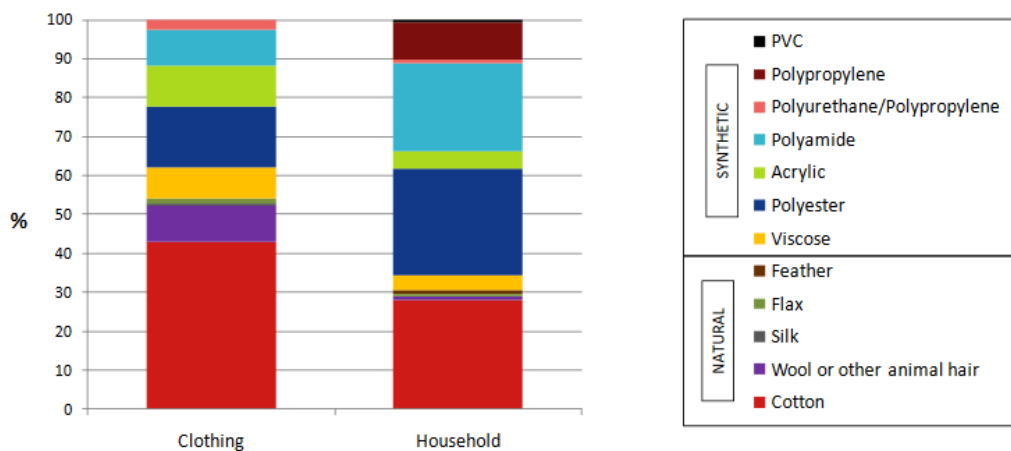


Figure 5 Composition breakdown. (Beton et al.2014)

Data used in their study was gathered in 2007, so we can assume that in 12 years these figures have changed. Especially the share of synthetic fibers has grown from 2007, but this study gives a good overview of the most used materials. Polyesters forecast from 2019 to 2026 is estimated to be 8.5% (CAGR, Compound Annual Growth Rate). Polyester has excellent qualities in important areas of fashion industry, such as in resistance and strength properties. Especially sportswear segment has seen a growth in polyester usage. (Pulidini & Chakraborty 2019)

3.1 Natural fibers

Natural fiber sources are various plants and animals. Plants can provide fibers from the seed, leaf and stem, depending on the plant species. Animal fibers are usually animal hair/fur and silk, also down and feathers are gathered and used in textile industry. (Houck 2009)

Yearly production of plant-based fibers is dominated by cotton. Other plant-based fibers reached 6 million mt annual production in 2018 (Textile Exchange 2019). Most of it was for bast fibers, which are obtained from various plant stems that can be collected annually. Most common cultivated plants for bast fiber production are flax, hemp, jute, ramie and kenaf. Bast fibers have a much larger cellulose content than wood but lower than cotton. Their cellulose content is from 59% up to 76%, rest is mostly made up of hemicellulose and proportions of pectin, lignin (except jute that has 11.8-12.9% lignin), and wax. Bast fibers are mainly used for high strength materials: ropes, carpets, curtains and sacks. (Yu 2015) Another type of plant fiber is coir, that is extracted from coconut husk and is used mainly in home textiles. Also, agricultural residues are a rising field of applicable material, e.g. rice straw and pineapple leaves (Textile Exchange 2019).

Animal fibers used in textile industry are most commonly mammal hair like sheep wool and camel hair, but silk fiber is an exception. Silk fibers are obtained from specific insect larvae, silkworms. The worms produce silk cocoons to protect themselves during transformation to a moth. Silk is composed mostly of fibroin and small portion of sericin proteins, so 95% of it is protein and the rest are composed of waxes, salts and ash. (Basu 2015) Yearly silk production is 159 648 mt. Other

commonly used animal fiber is wool, with annual production of one million mt. (Textile Exchange 2019) Classification of wool can be wide, as it may imply to all animal hair, such as goat (cashmere/angora), camel, vicuna, alpaca or yak hair. Generally, it does refer to hair of various sheep breeds. Like silk, wool consists of proteins, more specifically α -keratins. (Simpson & Crawshaw 2002) In addition to the animal fibers, duck and goose feathers and down is used in textile industry as insulator and padding.

Cotton production globally is 25 million mt per year, with India, China and United States being largest producers. Cotton is collected around the seeds of *Gossypium* genus plants and then spun into yarn or thread (Wakelyn *et al.* 2007). The fiber structure from the outermost to inside consists of cuticle, primary wall, secondary wall and lumen (Wakelyn *et al.* 2007). Cotton fiber, similarly as other plant fibers consists mostly of cellulose. More precisely 88-96.5% of cotton is α -cellulose and the rest are mainly proteins, water, pectins, waxes, the latter two causing hydrophobicity in raw cotton fibers. (Gordon, Hsieh 2006) Noncellulosic content portion varies with the fiber maturity, being larger in immature fibers.

Cellulose is a polymer that is a linear chain of hundreds or thousands linear β -D-glucopyranose units linked joined by β -1,4-glucosidic bonds. As Figure 6 shows, cellulose has a reducing end with a unsubstituted hemiacetal and a non-reducing end with an additional hydroxyl group. (Wertz *et al.* 2010)

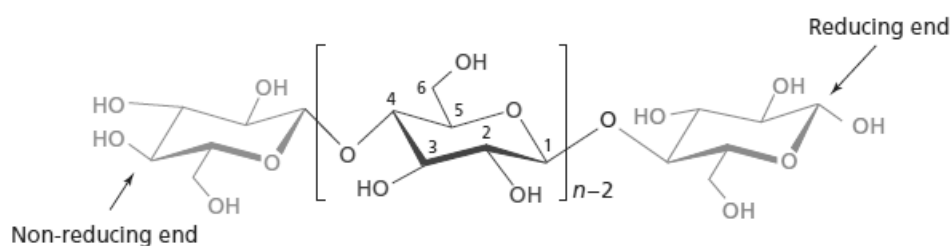


Figure 6 Cellulose structure. (Wertz *et al.* 2010)

Cellulose can occur as four different crystalline forms, polymorphs or as amorphous, without a crystalline structure. Cotton cellulose has a wide molecular weight distribution that prevents high-crystallinity and allows amorphous forms to exist. Cellulose chains are joined together by intermolecular hydrogen bonds and

hydrophobic bonds. These cluster together to form microfibrils which in turn form macrofibrils that are eventually organized into fibers. (Wakelyn *et al.* 2007)

3.2 Man-made cellulosic fibers

Man-made cellulosic fibers (MMCF) are made from natural polymers, which are derived from wood pulp and agricultural products. MMCFs are regenerated or acetylated cellulose fibers, of which the most used ones are viscose, lyocell and acetates. Annual production of MMCFs reached 6,7 million mt in 2018 and viscose covered almost 80% of the production, therefore being one of the most important fibers after polyester and cotton (Textile Exchange 2019). Regenerated fibers are simply a regenerate of natural polymers into a fibrous form. These manufacturing processes can be modified to add properties, which are required by today's demand. (Woodings 2001) MMCFs chemical structure is like cotton and other natural fibers, therefore it is used in similar applications.

Basic principle of the **viscose** process is dissolving pulp in sodium hydroxide and carbon disulphide, followed by wet spinning to fiber. Pulp is introduced to sodium hydroxide solution (17-19%), resulting in alkali cellulose. After this it is pressed and aged to get the desired alkali to cellulose ratio and degree of polymerization. Next the alkali cellulose is reacted with carbon disulphide, to produce sodium cellulose xanthate. The final solution is formed by dissolving xanthate with dilute sodium hydroxide. After ripening and filtration, the solution is ready for spinning, where the solution is pressed through fine holes to a coagulation bath. The bath consists of salts and acids that neutralizes the alkali content and regenerates cellulose. (Woodings 2001) **Lyocell** offers a similar fiber but it's manufactured differently. Pulp is dissolved to N-methylmorpholine N-oxide (NMMO) and heated. This solution is pressed through a spinnerette into a coagulation bath, where NMMO is dissolved and cellulose fiber is precipitated. (Chen 2015)

Where viscose and lyocell were regenerated cellulose fibers, **acetate fibers** are acetylated cellulose fibers (Figure 7). They are second most produced MMCFs with 14% margin of total MMCFs production (Textile Exchange 2019). Diacetate (also known as acetate) and triacetate are the two types of acetate fibers produced.

Cellulose triacetate is similar to normal acetate but has a bigger acetylation (substituting active hydrogen atom with acetyl group) rate. Most common manufacturing processes are acetic acid systems where the acid acts as a solvent for acetylation. (Matama *et al.* 2010) Wood pulp (or other cellulose based product) is mixed to acetic acid and acetic anhydride. Acetylation occurs and triacetate is formed, which is afterwards precipitated in water, dissolved to methylene chloride and pressed through the spinnerette. Diacetate is produced by the same method, but for lower acetylation rate the triacetate is reacted with water for hydrolysis. Every sixth acetate group are replaced by hydroxyl group. (Chen 2015)

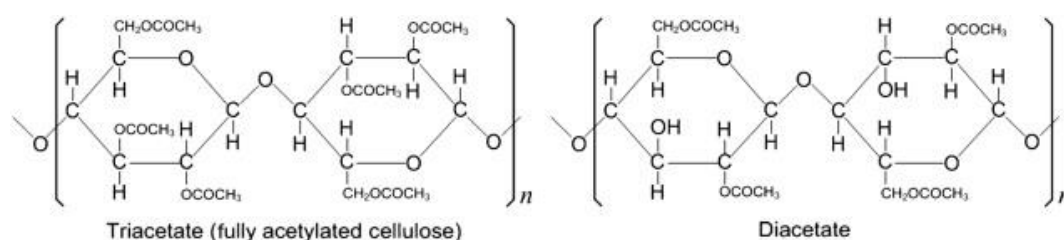


Figure 7 Triacetate and Diacetate chemical structure. (Chen 2015)

3.3 Synthetic fibers

Synthetic fibers have risen to be the most produced fiber, with polyester being produced 55 million mt annually. Their development has grown over time and there are a large variety of commercial synthetic fibers that are derived from crude oil. Here are introduced the most common synthetic fibers that are often seen in textiles.

Polyester fibers are classified as synthesized polymers, containing ester functional group. All polyesters are produced by condensation reaction and the most common fiber produced is polyethylene terephthalate (PET), with annual production of 55 million mt (Textile Exchange 2019). PET structure is presented in Figure 8. Large production is due to the unique properties caused by the aliphatic and aromatic structure elements of the fiber, economic viability and ability to be easily modified by spinning, drawing and heat treatment (Militky 2009). PET is produced by ethylene glycol (ethane-1,2-diol) and terephthalic acid (benzene 1,4-dicarboxylic acid) esterification reaction. In the reaction these two monomers split a water

molecule and form an ester bond. It can be also produced by a transesterification between ethylene glycol and DMT (dimethyl terephthalate). Either way, the process continues with polycondensation and various treatments (melting, drawing, spinning) that give specific properties to the fiber. (Lewin & Pearce 1998)

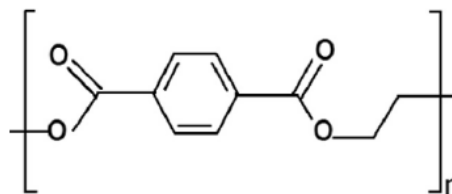


Figure 8 PET structure. (Lu et al. 2015)

Polyamides are the second most produced synthetic fiber with yearly global production of 5,4 million mt in 2018 (Textile Exchange 2019). Polyamide fibers are more commonly known as Nylon, more specifically called Nylon 6 and Nylon 6.6 (Figure 9). Numbers in the name presents the number of carbons in the molecule. Polyamides in general are produced with various structures, but when it comes to textile fiber Nylons, they are aliphatic. The two fibers mentioned differ in the way they are processed and in their final structure (Figure 9). As seen in the Figure 9, polyamides are molecules linked with an amide bond. Nylon 6 is made of polycaprolactam that is formed by ring-opening polymerization, instead of nylon 6.6 which is made by polycondensation of hexamethylenediamine and adipic acid. (Cook 1984) Nylon has higher tear and tensile strength, flexibility, abrasion strength and durability than cotton and viscose, therefore it is usually used in military textiles and survival equipment etc. that demand higher strength and lighter fiber properties. (Adanur 2017)

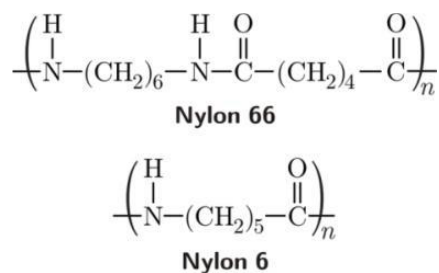


Figure 9 Nylon 6 and 66 structure. (Zakarta et al. 2012)

Elastane fibers that is also known by their trade names Spandex or Lycra, is a polyether-polyurea copolymer. Commonly known as polyurethane, is made by reaction of a glycol with di-isocyanate to form prepolymer which is further reacted with diamine to form a spinning solution. Depending on the polymer type (linear, branched etc.) the solution is spanned in different ways to form elastane fiber. (Cook 1984) The molecule can be divided to two segments giving the molecule its specific properties, as is shown in Figure 10. Soft segment is due to amorphous polyether and hard segments consists of aromatic diisocyanate and diamine urea with segment linking urethane groups (Quye 2014). Spandex which is an elastomer is used in general athletic wear and garments as a part of textile mixture. Its elastomeric properties are required for durability and high abrasion and flexibility strength (Chawla 1998).

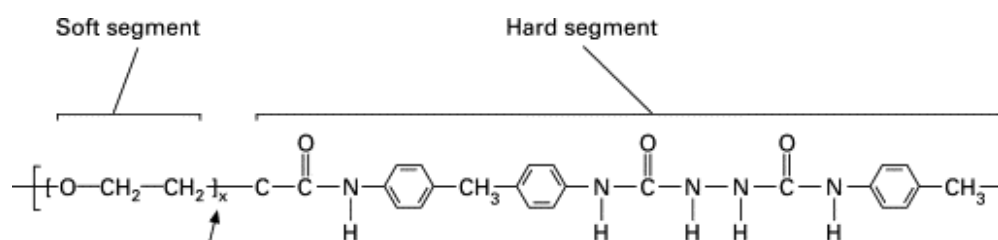


Figure 10 Polyether-polyurea copolymer structure. (Otaigbes & Madbouly 2009)

Acrylic fibers are constructed of liner polyacrylonitrile (PAN), and some amounts of comonomers such as methylacrylate, vinylacetate and methylmethacrylate (Figure 11). Comonomers affect the physical properties and processability (e.g. solubility, dyeing) of the fiber, thus giving variety to the product by comonomer selection. It needs to contain at least 85% of acrylonitrile to be considered as an acrylic fiber. Containing less, but at least 35% of acrylonitrile, the fiber is called as modacrylic. (Kim 2009) Acrylic fibers are produced with various of ways, for example via acetylene and hydrogen cyanide or via propylene and ammonia. Fibers are spun by wet-spinning form metallic salts or organic solvents. (Clark 2011) Acrylic fibers are mainly used in apparel textiles, as it can mimic natural fibers like wool.

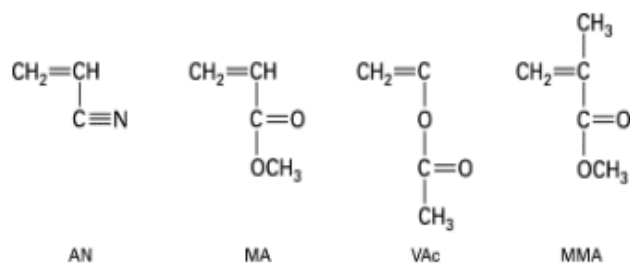


Figure 11 Chemical structure of acrylonitrile (AN) and comonomers mentioned. (Kim 2009)

Polyolefins contain at least 85% olefin (alkene) units such as thermoplastics ethylene or propylene, which are presented in Figure 12. These two mentioned olefins are the most used in polyolefin textile applications. Polyethylene and polypropylene fibers offer good strength, toughness and abrasion resistance, but with a downside of low melting point. Fibers are polymerized from monomers with Ziegler-Natta complex metal catalyst. (Moody & Needles 2004) Polyolefins are mainly used as technical textiles in various industrial applications, but also in hometextiles (e.g. carpets and rugs).



Figure 12 Structure of most used fiber polyolefins. (Moody & Needles 2004)

3.3 Chemicals

In manufacturing the textile undergoes various treatments to achieve the final product properties. Many of these treatments involve chemicals that modify or add features. Chemicals are used for example in pretreatment, dyeing, printing and finishing. Some of the chemicals can remain in the product, but it must be kept in mind that concentrations are low, and chemicals are washed away due washing and wearing. Unintentionally added and auxiliary chemicals may remain in the final product unintentionally but in minor quantities that are hard to detect. Textiles do contain functional chemicals that are added to remain in textile intentionally such

as color and easy-care chemicals. In the following Table 2, examples of these substances are shown. (Swedish Chemicals Agency 2014)

Table 2 Chemical substances found in textiles. (Swedish Chemicals Agency 2014)

Functional	Auxiliary	Unintended
<ul style="list-style-type: none"> • Dyes • Pigments • Anti-shrinking agents • Oil, soil • Plasticizers • Flame retardants • Biocides • Stabilizers • Stiffening agents • Reactive resins 	<ul style="list-style-type: none"> • Organic solvents • Surfactants • Softeners • Salts • Acid/Bases • Biocides 	<ul style="list-style-type: none"> • Formaldehyde (from reactive resins) • Polyaromatic hydrocarbons (in pyrolyzed products) • Arylamines (derived from dyestuff and pigments) • Toxic metals (impurities from raw material)

Unintended chemicals are contaminants or degradation products that are not used in production and not intended to be in the final product. Auxiliary chemicals are important for the textile processes but as the previous, they are not designed to be present in the final product. These substances may cause concern for health and environment but are present in very low concentrations. (Swedish Chemicals Agency 2014)

It can be said that a large portion of used chemicals in textile industry are due to dyeing processes. Dyeing process can require different dispersants, levelling agents, thickeners, binders and others to make dyeing more effective. Dyeing can be done with various methods and dyes depending on material and desired product. Three main methods are exhaust dyeing, continuous dyeing, and printing. Most used textile dyes are direct, reactive, disperse, acid, azoic, vat and sulphur. (Clark 2011)

4 CELLULOSE IN ALKALINE ENVIRONMENT

Object of our study was to break down textiles in an alkali solution. Main focus will be in cellulose-based textiles, such as cotton. Cellulose in different alkali environments has been a researched topic for its occurrence in pulping, textile industry and in radioactive waste disposal in underground repositories. Different aspects, reactions and process variables in literature of previously mentioned occurrences are covered in this chapter.

4.1 Kraft process

Kraft process converts wood to wood pulp with white liquor. The main goal for the process is to remove lignin by delignification and retain carbohydrates such as cellulose. In addition to delignification, cellulose degradation takes place in Kraft pulping, when cellulose contacts alkaline pulping liquor, resulting in peeling reaction. Cellulose degradation is an important reaction in our study and is covered more closely in chapter 5.1.

Kraft process uses a cooking liquor that is a mixture of white and weak black liquor. White liquor is a strongly alkaline (pH 14) mixture of NaOH and Na₂S with small portions of other sodium compounds; Na₂CO₃, NaCl, accumulated salts and non-process elements. NaOH and Na₂S are so called active species in this process, they dissociate in water in the following way because they are strong electrolytes.



The sulphide forms more hydroxide ions by reaction with water. Main active components in the process are OH⁻ and HS⁻ groups. The process takes place in a digester that is heated up to 150-170 °C after liquor and wood is added. First the initial delignification starts at 150 °C. Only little of lignin is dissolved (20-25%) but carbohydrates (hemicelluloses such as xylan) are degraded in the initial phase. Hydrosulphide sorption improves lignin penetration and protects cellulose from

degrading in the initial phase. The temperature is increased to 170 °C where the bulk delignification starts, and the delignification rate increases.

Hemicellulose degrades mainly in initial phase, slowing down in the bulk stage. Resulting degradation products are carboxylic acids that consume alkali. Higher degree of polymerization and crystallinity of cellulose protects it from dissolution. During the cooking, cellulose is degraded by 10-15%, especially in the residual phase when almost all the lignin is dissolved (>90%). The selectivity to lignin is low and carbohydrate degrade risk is increasing the longer the residual phase is continued. Carbohydrate reactions consists of primary and secondary peeling reactions, stopping reaction, alkaline hydrolysis of glycosidic bonds.

Primary peeling starts already at 100 °C temperature, reducing end groups one monomeric unit a time. When temperature is above 150 °C alkaline hydrolysis starts to split the cellulose chain in random positions. Hydrolysis forms new reducing end groups that degrades by secondary peeling reaction. The reducing end group will further on form isosaccharinic acid, lactic acid and 2-hydroxybutanoic acid. Carbohydrate that is dissolved in peeling converts to hydroxy, formic, acetic and dicarboxylic acids, all of them consuming alkali. Kraft pulping liquors can contain 100kg of glucoisosaccharinic acid per ton (Ek *et al.* 2009).

Stopping reactions are more significant at higher temperatures slowing down the degradation. It starts after 50-60 glucose units have been peeled, end group forms an alkali stable metasaccharinic acid end group. Alkaline hydrolysis, so called scission takes place between oxygen atom and glucosyl group. This depolymerization of the polysaccharide gives new end groups that are subjected for peeling.

In the end of the process the desired delignification degree is reached, and the content is discharged, screened and washed. Screening separates incompletely delignified wood and underfibrated chips, which will be returned to process.

Kraft process has many process variables, but we are interested in liquor-to-wood ratio, alkali charge, time and temperature. Liquor-to-wood ratio is the ratio between cooking liquor and dry chips of wood in the digester. Usually around 3.5-5 ton of liquor to ton of wood in a batch cook. Variations of the liquor-to-wood ratio is

affected by wood density and packing density. Too low ratio may slow down the circulation and too high needs a bigger energy input.

Kraft process uses a NaOH concentration of 140-170 g/l in the white liquor as active alkali. Usually the batch cooking time is 3-4 hours and cooking temperature 170°C. These control variables are calculated for the best delignification but gives good starting values for our process. (Pedro Fardim 2011)

4.2 Mercerization

Mercerization is a treatment used in textile industry to enhance features of cotton fabrics with sodium hydroxide. The treatment is done in low temperature, so our objective for cotton degradation does not occur. However, despite not degrading the cotton, the literature on mercerization tells us how cotton behaves in strongly alkaline solutions and at low temperature.

In short, cotton yarn or fabric is introduced to 22-27% caustic soda in room temperature while being under tension and subsequently dried and washed (with water and acid) (Horrocks & Anand 2000). Treatment conditions vary depending on the material and objective. Temperature in normal mercerization is generally is 15-18 °C (hot mercerization higher 70-100°C) and the dwell time is 55 s on average. (Karmakar 1999) Main target is to enhance color depth, making coloring more effective and therefore cost saving. It also changes properties so that it increases lustre (if treated while in tension), tensile strength, moisture regain, water sorption. (Horrocks & Anand 2000)

When cotton is introduced to strong caustic soda solution, it modifies it chemically, physico-chemically and structurally. The alkali diffuses and causes swelling in the fibers. Swelling may occur in mercerization to almost 150%, this makes the fiber more compact and the caustic soda is inhibited to penetrate the fiber. In the cases of high concentration solutions there is less water molecules to formate hydrates. This will lead to smaller hydrodynamic diameter, allowing them to penetrate the fiber structure and to form hydrogen bonds with cellulose, hydrate ion pairs and dipole hydrates. Swelling diminishes the cross-sections changing the shape from

kidney shaped to round. Occurring swelling causes crystalline parts of molecular structure to become amorphous. (Karmakar 1999)

Most of the modified properties are due to the short alkali treatment, tension on fabric, washing (water and acid) and drying of hydrogen bonds breaking and re-bonding during the post-treatment. Swelling is a phenomenon happening in our studies when cotton textiles are introduced to room temperature caustic soda before the reactor is heated. Swelling effects, the amount cotton can be put in the reactor as it takes a higher volume.

4.3 Geological disposal facility

Geological disposal facilities are established for radioactive waste that exceeds the limits for regular disposal. Waste is collected from nuclear power plants, research facilities and others that contain radioactive material. Radioactive waste is categorized to three levels: low-(LLW), intermediate-(ILW) and high-level wastes (HLW). High-level wastes contain spent nuclear fuel but LLW and ILW contains radioactive material but also high quantities of cellulose, such as wood, clothes. (Glaus 1998) Alkaline conditions in repositories are due to alkaline cement pore water in the cementitious facilities that will lead to cellulose degradation in long term. (Pavasars *et al.* 2003) This is because all the waste isn't located inside cement capsules, allowing low pH environment to effect cellulose content. Waste containers are made from steel that will be affected by corrosion leading to oxygen removal. This enables alkaline environment in the repository. Cellulose will degrade in alkaline and anoxic conditions by peeling reaction, producing isosaccharinic acid (ISA) and other organic acids. (Rout *et al.* 2014) ISA formation has been a studied subject because ISAs have ability to form complexes with radionuclides, that increases the aqueous solubility and mobility of radionuclides into the ground water. (Almond *et al.* 2016) Next chapter takes a closer look to cellulose degradation and its products.

5 CHEMISTRY OF ALKALINE DEGRADATION OF TEXTILE FIBERS

5.1 Cotton

In the previous chapters was stated the fact that cotton mostly consist of cellulose and cellulose can be degraded by strong alkali solution. Cellulose breaks down mainly by peeling reaction producing organic acids, isosaccharinic acid being the most abundant.

In degradation, the glucose units are removed one at a time from reducing end of the cellulose chain. Peeling reaction is started with aldose isomerization to ketose. Cellulose polymer is eliminated by β -alkoxycarbonyl elimination and leads to 4-deoxy-2,3-hexodilulose, which is 1,2-diketone. This undergoes benzylic acid rearrangement to a hydroxyl-carboxylic acid, isosaccharinic acid (ISA). Peeling reaction as described is presented in Figure 13. The reaction doesn't completely degrade the cellulose chain as there is an inhibiting stopping reaction, which is due to formation of alkali-stable end group. It results when β -hydroxycarbonyl elimination occurs in place of β -alkoxycarbonyl elimination and therefore forming Metasaccharinic acid (MSA), one of the possible stopping end groups. (Shaw 2014)

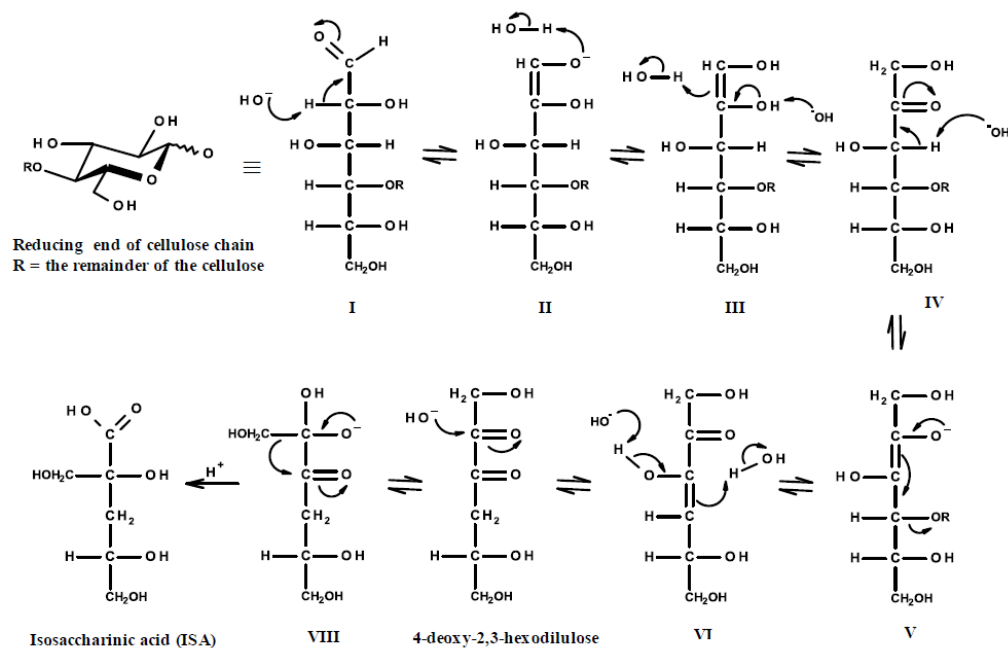


Figure 13 Peeling reaction of cellulose, picture from Shaw (2013).

Degradation rate is controlled by the peeling reaction and is affected by the concentration of reducing end groups. Alkaline hydrolysis of glycosidic linkages becomes the rate-limiting step. Glycosidic (1→4)-linkages are stable in alkaline environment when temperature is under 170. (Knill & Kennedy 2003)

5.1.2 Degradation products

Isosaccharinic acids (ISA) have been under research for its occurrence as waste product in alkaline pulping of wood and in radioactive waste storage as told in previous chapters. ISA, 3-deoxy-2-C-(hydroxymethyl)-pentanoic acid (alpha and beta form) is the most common degradation product in a peeling reaction, as shown in figure 13, with stopping reaction product 3-deoxy-hexanoic acid, also known as metasaccharinic acid. (Pavasars *et al.* 2003) Saccharinic acids are interesting for their ability to act as metal chelating agent. They are enantiomerically pure, so they are useful as carbon skeletons with predefined stereochemistry. This kind of molecule can be functionalized for synthesis purposes. (Almond *et al.* 2016)

Klaus Niemelä and Eero Sjöström (1986) researched the topic concerning cotton cellulose degradation in 1986. They treated cotton linters with 1 or 3M NaOH solution at 170-190°C, in nitrogen atmosphere. Total acid yields were obtained between 40-80%, detecting 65 degradation products, majority detected as hydroxyl-monocarboxylic and dicarboxylic acids. Best results concerning total acid yield (79%) and ISA formation (168mg out of 1g cellulose) was obtained with 3M NaOH with the temperature of 190°C. Glucoisosaccharinic acid was the main product in all cases, next largest quantities were obtained for formic, lactic, 3,4-dideoxyhexaric and 3,4-dideoxypentonic. Niemelä and Sjöstrom also considers possible applications for the acid mixture formed. The likes of dispersing agents, detergents and sacrificial agents could be possible applications. (Niemelä & Sjöström 1986)

Niemelä made another similar study concerning the cellulose degradation into carboxylic acids, this time nitrogen atmosphere was replaced by oxygen. In this study 170 and 180°C gave almost the same acid yields. Biggest differences to the study made in nitrogen atmosphere that only a trace of GISA was detected, considering that it was the main product in nitrogen atmosphere. Although few

substances that are formed from the same intermediate as GISA were detected, according to them it would imply that GISA is formed and rapidly degraded to more resistant compounds. Another difference between the tests was the little effect of alkali concentration to carboxylic acid formation. Major monocarboxylic acids formed were formic, glycolic, lactic acids due to several fragmentation reactions. According to Niemelä (1987) oxygen atmosphere accelerated glycolic acid formation in comparison to previous tests. Main dicarboxylic acid detected were oxalic acid and other dicarboxylic acid quantities increased with higher alkali concentration. In conclusion Niemelä (1987) states that oxygen atmosphere results major changes in acid mixture composition, in comparison to nitrogen atmosphere. (Niemelä 1987)

Niemelä (1989) made further studies on the same subject in 1989 in a much higher temperature 260°C and 280°C. Higher temperature resulted to over 95% low-molecular-weight carboxylic acids. Most of the founded hydroxy monocarboxylic acids (25 compounds) were α -hydroxy acids, lactic acid being the most abundant of these. In these temperatures high amount of anhydroisosaccharinic acids are formed in expense of GISA because benzylic arrangement that produces GISA is replaced by the dehydration of 4-deoxy-2,3-hexodiulose intermediate. Niemelä also considers the possibility that GISA is degraded further in such high temperatures. 2,3-dideoxypentanic, 3,4-dideoxyhexanic, and 3,4,5-trideoxyheptanic were the most abundant dicarboxylic acids found. Niemelä's studies has the full lists of all detected monocarboxyl, dicarboxyl acids and cyclic compounds. The most abundant compounds were mentioned in this study but as it seems various reactions takes place in the process resulting in a big variety of carboxylic acids. (Niemelä 1989)

Machell and Richards (Machell & Richards 1960) published an article in 1960 also concerning saccharinic acid formation trough alkaline degradation. Their study concluded few 4-O-substituted glucose derivatives including cellulose. They used a dilute solution of limewater (CaOH_2) (0,04N) or NaOH (0,5N). Lime-water results showed that it accelerated the alkaline degradation. But in later stages of experiments greater yield of acid was obtained with NaOH. They considered the possibility that calcium was catalyzing some stage in isosaccharinic acid formation, in expense of fragmentation. They also state that presence of calcium favors

isosaccharinic acid formation. Dilute limewater in 25°C and 100°C produced respectively 88% and 65% D-glucosaccharinic, while NaOH in same temperatures produced 32 and 30% D-glucosaccharinic. (Machell & Richards 1960)

5.2 Other materials in alkali environment

Although this study focuses more on experiments done to cotton, textile waste consists various fibers with different features, so other textile materials needs to be explored also. Knowledge of their behavior in alkali conditions gives a better understanding what is expected to happen and what can be achieved.

5.2.1 Synthetic fibres

Most used polyester in fabrics is polyethylene terephthalate (PET). In general polyester is very resistant to alkaline hydrolysis, because of the benzene ring that stabilizes the molecule (Johansson, Somasundaran 2007). Despite that, polyester can be degraded with strong alkaline hydrolysis under suitable conditions. Pitat and Bacak applied for a patent concerning PET hydrolysis in 1957. Their patent describes that the hydrolysis is done by the following conditions: 18% solution of NaOH with 20:1 ratio to polyester, 100 °C and with a reaction time of 2 hours. The method forms alkali metal terephthalate salt that precipitates out of the solution, that can be filtered and rest of the polyester forms ethylene glycol that remains in the filtrate. (Pitat, Bacak 1957) Figure 14 shows the chemical reaction happening to polyethylene terephthalate in strong sodium hydroxide. PET is hydrolyzed to disodium terephthalate salt (TPA-Na₂) and ethylene glycol. TPA-Na₂ can be neutralized and precipitated with 98% sulphuric acid. (Das *et al.* 2006)

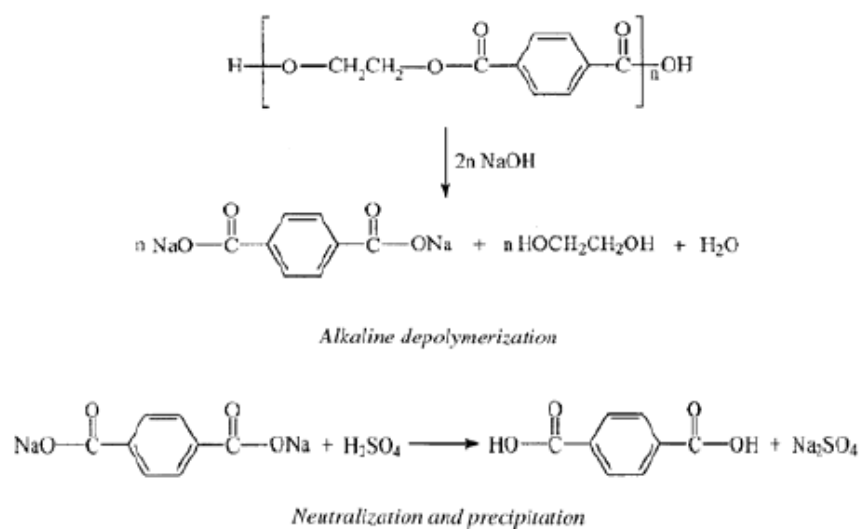


Figure 14 PET hydrolysis reactions (Das et al. 2006)

Alkaline depolymerization has also been enhanced with the help of a phase-transfer catalysts to get higher reaction rates. Polk *et al.* used a catalyst that has cationic and organic character that could cause the catalyst and an anion to divide into the organic phase with higher reactivity. The catalyst involves the system by transferring a reactant to normal phase of to the other reactant. Adding a catalyst, it alleviates the method conditions to only 80°C and atmospheric pressure. Polk at al. tried out various catalyst and according to them trioctylmethylammonium chloride and bromide (TOMAC and TOMAB) performed the best. (Polk *et al.* 1999)

Nylon 6 and 6.6 have melting points of 220°C and 265°C, respectively. Nylon polymers have a better resistance to alkaline solutions than acids. Nylon can be depolymerized as Miller (1958) patent of nylon hydrolysis, describes nylon depolymerization to diamines and diacids with superatmospheric pressure and temperature of 160-220°C. His invention uses aqueous alkaline medium with aliphatic alcohol. (Miller 1958). Polk *et al.* study of nylon depolymerization was able to form oligomers and a monomer with alkaline phase transfer catalyst, using 50% sodium hydroxide and benzyltrimethylammonium bromide. Nylon 66 would depolymerize to hexamethylenediamine and adipic acid. (Polk *et al.* 1998)

Study made by Bhattacharya *et al.* (2004) tells that acrylic fibers undergoes partial transformation under alkaline hydrolysis. Nitrile groups of acrylonitrile transform to amide groups and further on to carboxyl groups that may link to sodium to form

sodium salt (sodium acrylate). Further on carboxylic groups may transform to other stable groups. In the study 22% of nitrile undergoes this transformation with 100 °C temperature. The fibers are not soluble in this temperature because of the hydrophobic nature of nitrile groups. (Bhattacharya *et al.* 2004) Siskin *et al.* (1994) patent for polyacrylonite depolymerization, described decomposing in hot water. Temperature of 200°C to critical temperature, in autogenous pressure would depolymerize it to water soluble by-products. (Siskin *et al.* 1994) Polyacrylonite degrades before melting in 320°C.

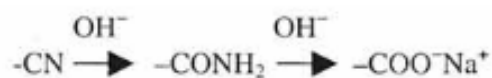


Figure 15 Hydrolysis of acrylic fibers (Bhattacharya *et al.* 2004)

Synthetic fibers most resistant to alkaline degradation seems to be elastane and polyolefins. Yao and Wang (2013) were able to dissolve spandex fibers from a spandex/nylon fabric by solvent extraction in N, N-dimethylformamide (DMF) (Yao & Wang 2013). Also, thermal degradation is possible above 170 °C (Hu & Lu 2015). Polyolefins polypropylene and polyethylene are very chemical resistant thus resistant to hydrolysis. Polyolefins can be depolymerized with catalytic cracking with temperatures ranging from 400 to 800 °C (Wolosiewicz-Glab *et al.* 2016) and degraded with oxidative degradation (Joshy *et al.* 2016).

5.2.2 Natural fibers

Plant-based natural fibers contain mainly cellulose, so their behavior in strong alkaline follows the same path as cotton. Most abundant animal-based fibers are composed of other substances. Silk is easily damaged by even dilute alkali in higher temperatures. Low resistance to alkali conditions lead to hydrolyzing of polypeptide bonds in fibroin. A boiling 5% sodium hydroxide solution can dissolve silk fibers rapidly. (Basu 2015) Wool keratin is not affected by dilute alkaline but is sensitive to strong alkaline and destroys the polymer into aminoacids. (Carr 2012)

5.2.3 Man-made cellulose fibers

Man-made viscose and lyocell are regenerated cellulose, acetate fibers are a derivative of cellulose. They are similar by composition to cotton excluding manufacturing process and degree of polymerization (DP). Effects of alkaline degradation can be mostly equated to cotton. Difference in DP can affect the degradation rate as cotton has a much larger DP of 15 000 while viscose and lyocell has DP of 235 and 642 respectively (Kreze *et al.* 2001 & Kozlowski 2012). Lyocell fibers has also a much higher degree of crystallinity than viscose fibers, 80% and 41% respectively. A study Colom & Carrillo (2001) studied the effect of mercerization to these fibers. Viscose fibers tend to dissolve in higher sodium hydroxide concentrations due to crystalline cellulose transformation to amorphous cellulose. Higher degree of crystallinity of lyocell prevents dissolution in low temperatures. (Colom & Carrillo 2002)

Acetate fibers are formed of cellulose acetate, where most of the hydroxyl groups are acetylated by acetylation process. Reverse process deacetylation removes the acetyl group and has been done for cellulose acetate membranes with alcoholic NaOH solution as the study of Liu & Hsieh (2002) implements. They also studied the deacetylation with dilute aqueous NaOH (0.05M) solution and revealed it to occur in fiber surfaces but being unable to penetrate the the fiber. The deacetylation leaves the surface hydroxyl rich and the core acetyl rich. (Liu & Hsieh 2002)

6 MATERIALS AND METHODS

6.1 Raw materials

Experiments in this study can be divided to two section, first part of the experiments were done for pure cellulose and the second part was done for various textile materials. Cellulose used in the experiments was microcrystalline cellulose (100%, Alfa Aesar) TM. Textile materials consisted of 100% cotton t-shirts and viscose, polyester, and polyamide textile fabrics. Alkali solutions used was diluted from sodium hydroxide pellets (98,8%, VWR chemicals).

6.2 Equipment

Experiments were done in a 500ml batch autoclave presented in Figure 16, 2/3 of the autoclave could be filled. The autoclave was connected to nitrogen line to allow nitrogen atmosphere and a sampling valve, that enabled sampling during the experiments. The system had temperature, pressure sensors and a mixer, that could be controlled.



Figure 16 Autoclave used for the experiments.

6.3 Analyses

Samples were analyzed with high-performance liquid chromatography HPLC-DAD, Agilent Technologies 1260 Infinity. Phenomex fully porous silica column, Luna® Omega 5 µm Polar C18 100Å was used with 0,1% phosphoric acid as the eluent and gradient grade methanol as secondary eluent. Methanol eluent was used in later stage of the 40 min run time. Samples were taken during the tests through a sampling pipe and the samples were acidified with HCl to pH 1-2, as the used column separated measured acids better in low pH.

NaOH concentrations were analyzed by Mettler Toledo titrator, to measure amount of NaOH consumed during the tests. The end product samples were titrated to pH 9 with 0,1 M HCL.

6.4 Experiments

Experiments for pure cellulose degradation in alkaline solution were done to study what amount of carboxylic acids could be achieved and what process conditions are suitable for degradation. For textiles, the fabric was cut down with scissors to about 1-2cm pieces by diameter. Sodium hydroxide pellets were diluted to 20% solution, by dissolving 200g of NaOH pellets to 1l bottle and filling it with purified water. Desired masses of solution and cellulose/textiles were added to the autoclave. After closing the autoclave tightly, oxygen was replaced with nitrogen in the reactor by filling and emptying the reactor several times with nitrogen. Due to the results of Niemelä (1987), it was more desirable to use nitrogen atmosphere for larger amount of GISA. Nitrogen atmosphere accounted for pressure of ~10 bar, rising to 14-20 bar depending on the test temperature. Heater and mixer were set for desired values. Heating to 190°C usually took 20-25min and the mixer was set to ~400rpm. Following Tables 3 and 4 shows the process conditions for different tests that were carried out for pure cellulose and for textiles. Different combinations of critical parameters temperature, L/S ratio, NaOH solution strength and reaction time was tested to figure out a suitable condition for fabric tests. Liquid to solid ratio is

presented as L/S ratio that describes the NaOH solution ratio to solid cellulose in mass.

Table 3 Tests for pure cellulose.

Test	Temperature, °C	L/S ratio	NaOH solution, wt%	Reaction time, h
Test 1	150	11	20	6
Test 2	170	11	20	6
Test 3	190	6	20	6
Test 4	210	6	20	6
Test 5	150	6	20	24
Test 6	190	6	20	24
Test 7	190	6	10	24

Table 4 Tests for textile materials.

Test	Temperature, °C	L/S ratio	NaOH solution, wt%	Reaction time, h
Cotton (white)	190	10	20	8
Cotton (blue)	190	10	20	8
Cotton (blue)	210	10	20	6
Viscose	190	10	20	8
Polyester	190	11,7	20	8
Polyester	210	15	20	8
Polyamide	190	8,5	20	8
Cotton/Polyester	190	10	20	8

After the desired reaction time was reached the autoclave was stopped and cooled down with cold water circulating the system, to be able to handle the system safely. Equipment cool down to 40°C usually took 5 minutes. If the solid residues remained, the solutions were centrifuged and decanted to separate from the liquid phase. Usually the product solution was too thick to be able to successfully filter with suction. Different L/S ratios in the table are due to different materials used in

test. Materials different behavior in strong alkaline caused variation on how much material could be put in the autoclave.

7 RESULTS

7.1 Pure cellulose

First tests were done in lower temperatures of 150°C and 170°C with a high L/S ratio of 11, in other words larger amount of liquid (300g) to pure cellulose (30g). Test results are shown in Figure 17, that shows the overall acid yield produced from the 30g of cellulose used. Higher temperature clearly gives better yield reaching 21,5% in comparison to the other (12,5%). The higher temperature also resulted in more GISA as a proportion to all end products, 28% in comparison to lower temperature result of 11%. From this it can be concluded that a higher temperature degrades the cellulose more effectively to GISA and overall, to smaller acids. It must be reminded that after the raw material was put to the autoclave, the heating took 20-25min and the timing started when the desired temperature was reached. Therefore, the zero sample already contains carboxylic acids.

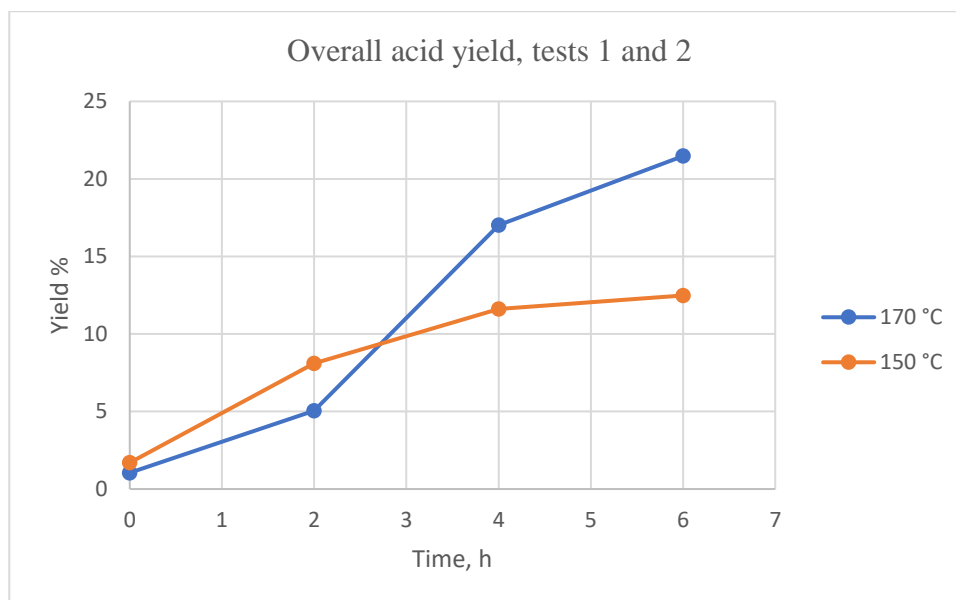


Figure 17 Overall acid yield growth during test 1 (150°C) and 2 (170°C)

For the next tests solid content was increased to 50g and solution reduced to 250g, giving a L/S ratio of 6. This ratio is closer to the ton of liquor to ton of wood in a Kraft process batch cook. It was clearly visible how cellulose swells when in contact

with room temperature NaOH. First samples taken were thick but as the tests continued the samples became more fluid. Figures 18 and 19 represents the next tests done with smaller L/S ratio in different temperatures and reaction times. Figure 18 shows how the even higher temperatures of 190°C and 210°C results in much better yields in total acids, achieving 59,8% (in 6 hours) and 52,9% (in 3 hours) respectively. Notable in test 4, done in 210°C is the decreasing yield after peaking at 3 hours. The decrease is due to decreasing amount of GISA after 2-hour sample, while amount of other substances remained about the same. Test 3 in 190°C seemed to be getting better results going further in reaction time.

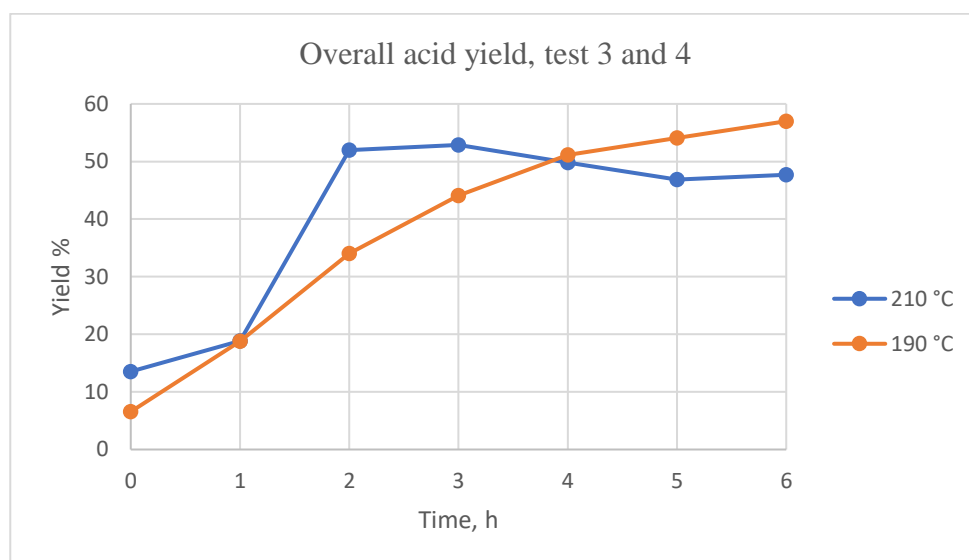


Figure 18 Overall acid yield growth during test 3 (190°C) and 4 (210°C).

Previous test indicated that total acid yield could be growing after 6 hours. Tests 5 and 6 were done to study the reaction with a longer reaction time, with 24h. As seen in Figure 19 the same decrease of yield as in the previous test 4 occurs between 5-10 hours. Test done in 150°C was not able to reach same results even in 24 hours.

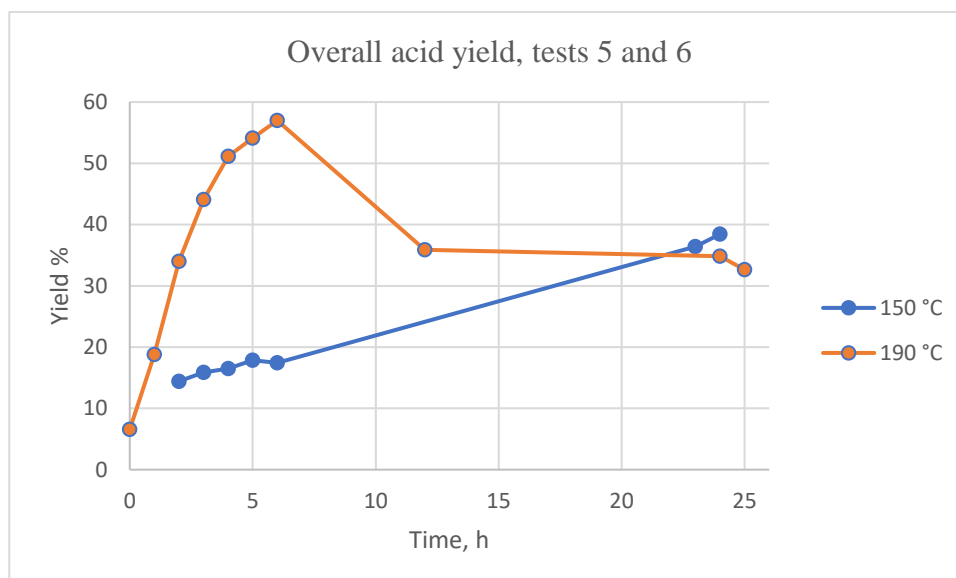


Figure 19 Overall acid yield growth during test 5 and 6, that were done for 24-25h.

In conclusion best results according to overall acid yields are obtained with 190°C in 6 hours, possibly reaching better yield between 6-10 hours. Smaller L/S ratio produces better results comparing the first tests to the latter.

Tests giving the highest yield from the tests were chosen to present the degradation products in Table 5. In case of the test done in 210°C the results are from the sample taken in 2 hours, as it resulted with the biggest amount of GISA. The tests are comparable with each other for the fact that they were done under the same conditions except for the temperature. Measured substances in Table 5 were the most abundant in the samples. It is possible that there are many smaller acids that are present but in a marginal portion which are harder to detect. Analyzed substances in the tests were: oxalic acid, glycolic acid, formic acid, glucoisosaccharinic acid (GISA), xyloisosaccharinic acid (XISA), lactic acid, acetic acid, 2,5-dihydroxypentanoic acid (2,5 DHPA), succinic acid, 2-hydroxybutanoic acid (2-HBA).

Table 5 Results from the best performed tests, with 50g input cellulose. Both tests were done with L/S ratio of 6 and 20 wt% NaOH solution. Reaction times of these samples were: 6h for 190°C test and 3h for the 210°C test.

Components	190 °C, g	210 °C, g
Oxalic acid	0,09	0,10
Glycolic acid	0,34	0,40
Formic acid	2,27	2,21
GISAs	13,88	10,25
XISA	2,47	2,12
Lactic acid	3,81	3,65
Acetic acid	0,18	1,20
2,5-DHPA	1,45	0,64
Succinic acid	1,41	1,66
2-HBA	5,41	5,42
Total	29,91	25,98

Test 7 was carried out with a 10 wt% solution of NaOH instead of 20 wt%. Other experimental conditions were same as in test 6. Total acid yield growth is presented in Figure 20. Next chapter focuses on fabric experiments, which product solution NaOH concentration was also measured. It showed that only ~2 mol/l is consumed with a 5 mol/l starting solution. Because of that the test 7 for pure cellulose was done with 10 wt% solution that is equal to 2,5 mol/l. Analysis revealed that the end solution has a concentration of 0,3633 mol/l, this subject will be discussed more in the end of next chapter. First sample taken when the autoclave achieves the desired temperature of 190°C, shows already a larger amount of acids when compared to previous tests. Ultimately the test achieves similar results regarding the total acid yield.

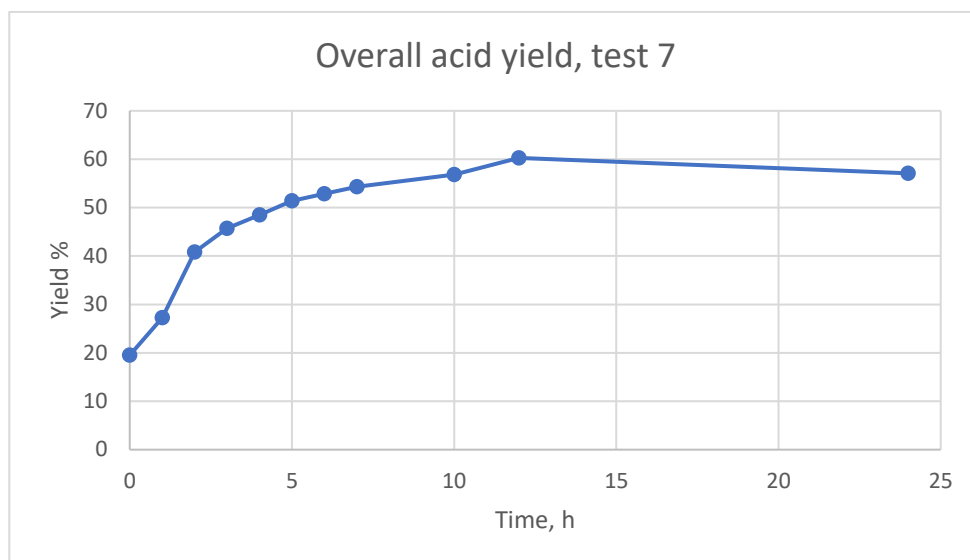


Figure 20 Overall acid yield growth in test 7, done with more dilute NaOH solution

To sum up the results from the tests with pure microcrystalline cellulose, Table 6 presents experiment conditions, highest acid yield and highest GISA yield achieved during the rest. Reaction time shown is the time that achieved these results, not the overall time of the test. When compared, the test done in 190°C produced the best result for pure cellulose. Product solutions were brown, turbid and no larger solids were visible. Next chapter focuses on cotton experiments.

Table 6 Summary of the cellulose tests. Reaction time is the moment of time that the results were at the best

Test	Temperature, °C	L/S ratio	NaOH solution, wt%	Reaction time, h	Total acid yield, %	GISA yield, %
Test 1	150	11	20	6	12,5	1,4
Test 2	170	11	20	6	21,5	6,0
Test 3	190	6	20	6	59,8	27,8
Test 4	210	6	20	2	52,9	8,3
Test 5	150	6	20	24	38,4	13,9
Test 6	190	6	20	6	57,0	23,7
Test 7	190	6	10	12	60,3	29,1

7.2 Cotton

Three different tests were carried out for cotton fabrics, based on the previous results. For the two first tests temperature was set to 190°C, L/S ratio to 10 and a process time of 8h. It was difficult to keep the L/S ratio of 6 with the equipment used. Large amount of fabric pieces would have blocked the sampling pipe, so the ratio was raised to make the mix more fluid. From this point forward ~30g of textile is mixed with 270g of NaOH solution. Other conditions corresponded to previous tests: nitrogen atmosphere and 400 rpm mixing. Two different 100% cotton fabrics were used: white and blue. Third tests were done in an elevated temperature of 210°C and a shorter process time 6h. According to previous tests it would reach peak already after few hours.

Table 7 shows the degradation products resulted from the experiments and Figure 21 presents the growth over the time period. Results obtained from the higher temperature (210°C) test, are from the sample taken at 1.5 hours (degradation products amount peak at that moment).

Table 7 Cotton degradation results. with ~32g input cellulose. Tests were done with L/S ratio of 10 and 20 wt% NaOH solution. Reaction times of these samples were: 8h for 190°C tests and 1,5h for the 210°C test.

Components	Cotton, white (190°C), g	Cotton, blue (190°C), g	Cotton, blue (210°C), g
Oxalic acid	0,04	0,03	0,05
Glycolic acid	0,20	0,33	0,37
Formic acid	1,28	1,36	1,31
GISAs	6,90	6,17	4,58
XISA	2,06	1,95	1,93
Lactic acid	2,99	2,72	2,86
Acetic acid	0,37	0,45	0,09
2,5-DHPA	0,70	0,76	0,72
Succinic acid	0,07	0,12	0,16
2-HBA	4,67	4,51	5,54
Total	19,2	18,41	17,62
Yield, %	59,9	56,9	54,2

GISA can be confirmed as the main product of the process. GISA covered 35% of the total carboxylic acids in the product solution. Second most abundant was 2-HBA. Total acid yields achieved are similar to pure cellulose results, about 60%. It may be possible that not all the cellulose degraded. Realistically few factors reduce the yield achieved. Some smaller portions of acids are not measured, as they are hard to detect. Errors during experiment and for example, when assembling the reactor with raw material. Two tests done in same temperature and with 100% cotton, but with different cloth, followed a similar growth pattern to each other. There is some fluctuation probably due to errors in sampling. Higher temperature test follows the same pattern as did the previous pure cellulose test in the same temperature. The amount of GISA drops after 1.5 hours, but no significant growth in other measured acids.

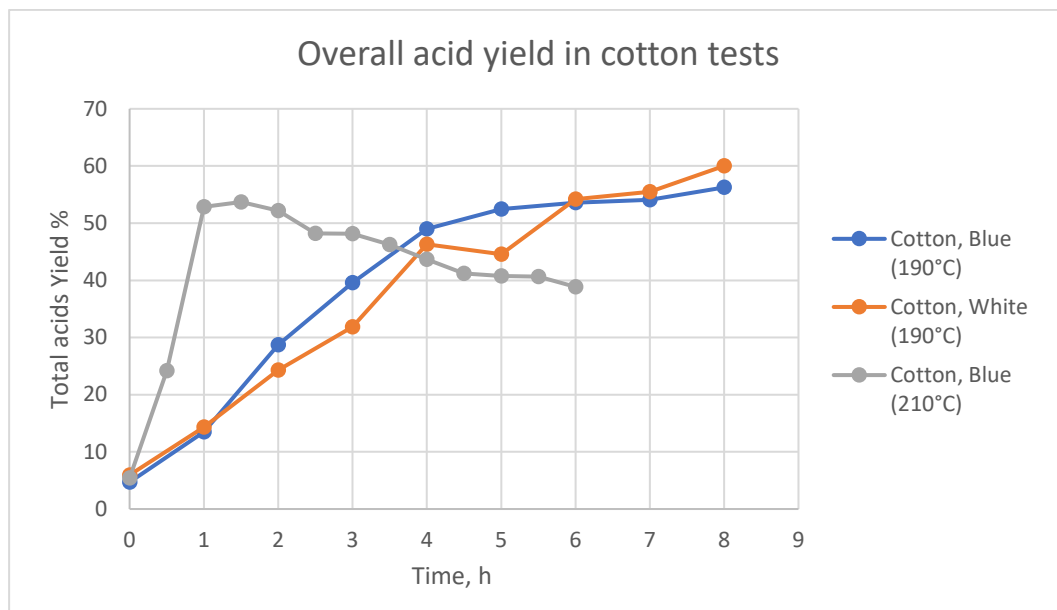


Figure 21 Overall acid yield growth during cotton degradation.

The product is similar to pure cellulose tests: brown and turbid, but in textiles there are some solids left in the product solution. Not visible textile pieces, but dark brown soft solids. Following Figure 22 shows the development from textile pieces to product solution. The cut cotton pieces degrade during the process and in the end, we have a 60% yield solution of different carboxylic acids.

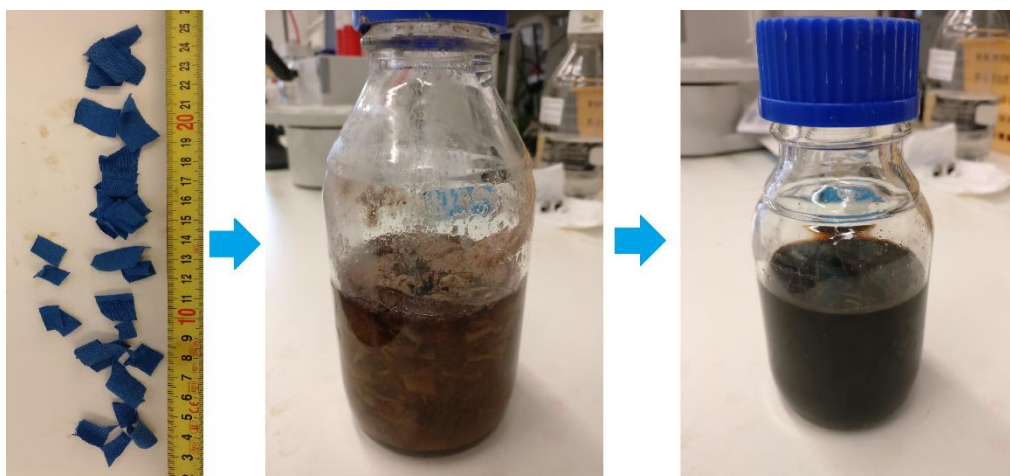


Figure 22 Cotton degrades from fabric pieces into a product liquid. First picture shows the raw material used, middle picture shows what the process solution looks like in the middle stages of the process and the last picture shows what the product solution looks like.

Larger solids in the product solution was centrifuged and decanted. Dried solid was weighted and compared to textile mass put in (Table 8). As filtering the solution was troublesome the amounts are not accurate, but still tells the bigger picture.

Table 8 Solid mass change before and after the process.

Test	Mass before, g	Mass after, g	Mass lost, g	Mass lost %
Cotton 190°C (white)	32,93	16,03	16,9	51,3
Cotton 190°C (blue)	32,45	14,21	18,24	56,2
Cotton 210°C	32,5	5,15	27,35	84,2

Higher temperature resulted in smaller amount of solids, but this does not mean a bigger acid yield as previous results reveal. It seems that the mass degrades to some smaller unmeasured substances. For the two tests in 190°C, a similar amount of solid was left in the product solution.

The experiments were done in a 20 wt% NaOH solution, which is equal to 5 mol/l. Analyses with titrator gave results of the molarity of the product solution. Formed carboxylic acids consume NaOH that is present in the solution and according to results, the process consumes ~2mol/l. The same result was obtained with the pure cellulose test done with 10 wt% solution, as 0,3633 mol/l is left. This starting concentration seems optimal for cellulose content in this study.

Table 9 NaOH concentration left in the product solution, from the original 5mol/l.

Test	c (NaOH), mol/l
Cotton 190°C (white)	2,6254
Cotton 190°C (blue)	3,0681
Cotton 210°C	3,3105

7.2 Viscose

Viscose was discussed in Chapter 5, it was explained that it should behave like cotton in strong alkaline. Viscose as cotton, is mostly made of cellulose, so similar results were expected. Viscose test was carried out in same experimental conditions as the first tests with cotton (190°C). Total acid yield 56,7% was measured at 4 hours, slightly declining afterwards. Degradation progress is presented in Figure 23. Viscose achieved its peak yield faster than cotton; one decisive factor could be thinness of the viscose textile pieces compared to cotton.

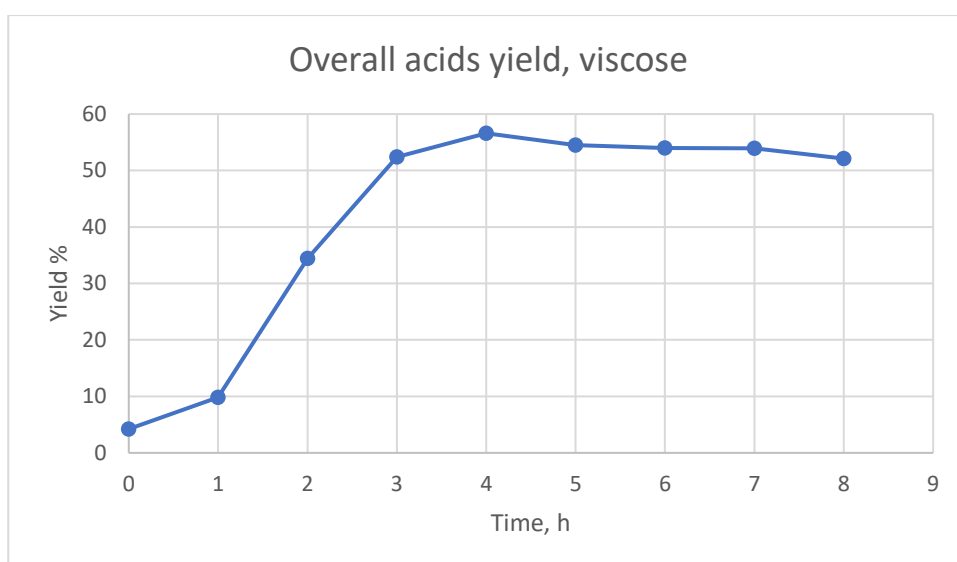


Figure 23 Overall acids growth over time with viscose

Specific results of the tests are in Table 10. They also resemble cotton results, overall acid content at peak sample was similar to cotton tests, but GISA content was a bit higher.

Table 10 Viscose degradation products at 4h peak sample with 32g viscose input

Component	Viscose, g
Oxalic acid	0,05
Glycolic acid	0,19
Formic acid	1,41
GISAs	7,80
XISA	1,47
Lactic acid	2,41
Acetic acid	0,43
2,5-DHPA	0,88
Succinic acid	0,04
2-HBA	3,70
Total	18,35
Yield, %	56,72

Almost all the solid fabric material was broken down, so nearly no solids could be retained (Table 11). As for the remaining molarity, there was almost 2 mol/l decrease that also resembles to cotton tests.

Table 11 Viscose mass loss and remaining NaOH concentration in end solution.

Test	Mass before, g	Mass after, g	Mass lost, g	Mass lost %	c (NaOH), mol/l
Viscose	32,35	~2	30,35	93,8	3,1895

7.3 Synthetic fibers

Synthetic fibers were studied just understand how they would behave under strongly alkaline conditions. First tested synthetic fiber material was polyester, using same conditions as previous: temperature of 190°C, 20 wt% NaOH solution

and 8 hours process time in nitrogen atmosphere. Solution recovered after 8 hours contained large amounts of solids. Visually the recovered mass contained textile pieces and salt. Trying a higher temperature of 210°C resulted in a similar result visually. As told in chapter 5.2.1, polyester should degrade to TPA-Na₂ and ethylene glycol in much milder conditions. TPA-Na₂ seemed to precipitate as a salt also in this study and covering the majority of the recovered mass. In lower temperature the collected mass even increased, but with higher temperature the mass was decreased slightly. The recovered mass was dissolved to water, with purpose to dissolve the salt and filter it, so that remaining fabric pieces would be separated. Polyester pieces broke down during dissolving and no bigger pieces were not possible to collect. The filtrate was acidified with 98% H₂SO₄ and terephthalic acid precipitated fast. Second synthetic fabric tested was polyamide, which resulted a far better break down, as 83,8% of the fabric mass was degraded. Results are shown in Table 12 and Figure 23 shows the retained solid mass.

Table 12 Polyester and polyamide mass reduction/gain

Test	Mass before, g	Mass after, g	Mass lost, g	Mass lost %
Polyester 190°C	28,03	29,77	-1,74	-6,2
Polyester 210°C	20	16,57	3,43	17,2
Polyamide 190°C	29,46	4,76	24,7	83,8



Figure 23 Leftover mass of polyester (left) and polyamide (right)

NaOH solution concentrations in polyester tests were 5 mol/l, and they decreased to 3,7 mol/l in the end. This can be explained by TPA- Na_2 salt formation, which consumes Na^+ ions. Polyamide process products did not consume a lot of NaOH that was present, although majority of the mass did break down. 5 mol/l concentration was decreased to 4,4 mol/l. Process can break down the fabric but perhaps the polyamide molecules will not depolymerize completely in these conditions.

Final synthetic fiber test was done for acrylics, again in the same conditions as previous ones. No visible acrylic textile fabric pieces were left in the end solution. Very thick solution was recovered as the following Figure 24 shows.



Figure 24 Acrylic fibers resulted in a thick liquid with no visible textile pieces.

7.4 Cotton/polyester mix

Two of the most used textile materials are cotton and polyester as stated in chapter 3. This results in most of the general textile waste cotton and polyester, which are also a common combination in modern clothing. After experimenting on cotton and polyester, a test was done for this combination, with a t-shirt consisting of 60% cotton and 40% polyester. Same conditions were used for the test as in the previous. Difference in this test was that this time the degradation product amounts were compared to the total cotton mass in the textile (19,2g) instead of the total textile mass (32g). Results in Figure 25 and Table 13 were similar to those of cotton tests.

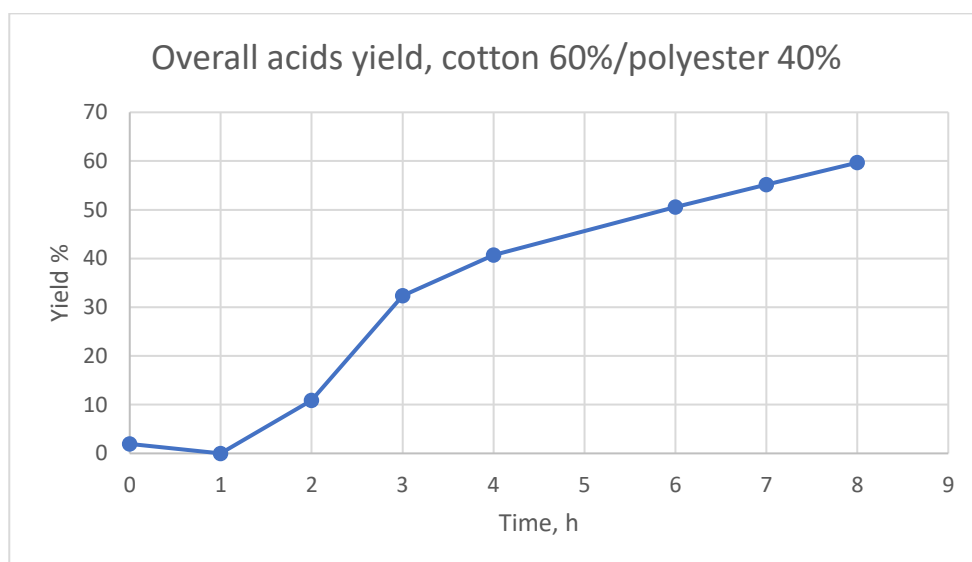


Figure 25 Overall carboxylic acid yield growth overtime with a mix fabric of cotton and polyester.

Polyester presence and its own decomposition did not affect the carboxylic acid generation. Total carboxylic acid yield from original cotton content was again nearly 60% with GISA as the most abundant substance.

Table 13 Degradation products from 32g cotton/polyester fabric. Cotton content corresponded for 19,2g of the input.

Component	M, G
Oxalic acid	0,01
Glycolic acid	0,16
Formic acid	0,65
GISAs	4,09
XISA	1,25
Lactic acid	2,19
Acetic acid	0,68
2,5-DHPA	0,18
Succinic acid	0,50
2-HBA	1,75
Total	11,46
Yield, %	59,67

Following Figure 26 shows the different layers in the product solution. Brown liquid has resulted from the cellulose degradation, resembling cotton tests end product. Bottom solids are disodium terephthalate salt (TPA- Na_2) precipitated in these conditions, resembling the polyester test.



Figure 26 Cotton/polyester degradation product solution.

8 CONCLUSIONS

Concern over textile waste piling up globally, has raised a need for alternative methods to recycle waste material. Cotton, mainly consisting of cellulose is widely known to degrade through peeling reaction to different carboxylic acids in alkali environment. Peeling reaction could be used to recycle excess cotton waste to useful chemicals, that could be separated for other uses.

Experiments done to pure cellulose set the conditions for cotton textile waste tests. It turned out that cotton fabrics, that was cut to pieces could be degraded at the same efficiency as pure cellulose. Total carboxylic acid yield of ~60% was achieved in 190°C with GISA covering 35% of the total carboxylic acids. The next most abundant acids were 2-HBA, lactic acid and XISA in that order. Cellulose degraded as the peeling reaction described to GISA and further on degraded to smaller carboxylic acids. The process reached the results in 8 hours or little bit lower results (54%) in higher temperature of 210°C. NaOH solution of 20 wt% and nitrogen atmosphere were used in the process. NaOH consumption revealed that a lot of excess NaOH remained in the product solution. From the starting 5 mol/l concentration, the process consumed ~2 mol/l. It would have been enough to use a 10 wt% NaOH solution to degrade ~30g of cotton fabric. With a larger cellulose content, the alkali consumption would have been greater, hence it would have consumed more than 2 mol/l.

Main objective of the work was to study cotton fabric processing, but textile waste in general contains many other types of fiber material used today. Study showed that cellulose based viscose behaved at the same way as cotton, and similar results were obtained. Similar results can be derived to happen for other cellulose based fibers that were not tested, for example lyocell, jute and hemp. Animal fibers were not tested since literature review showed that they would easily degrade in alkaline environment.

Difference especially in synthetic fiber compositions is a challenge for strong alkaline to break down. Polyester, polyamide and acrylic textile material were tested to see how synthetic fabrics would withstand the conditions. Polyester tests produced a mix of remaining textile pieces, TPA-Na₂ salt and probably ethylene

glycol in the solution. Polyamide textile degraded more effectively in the conditions as a smaller amount of fabric pieces was retained, but it was visible that neither of the synthetic fibers decomposed completely. No visible pieces of acrylic fiber were left after 8 hours in strong alkaline, resulting in a thick solution. In the end a test with the most abundant textile materials in industry, 60% cotton and polyester 40% could be performed with similar carboxylic acid yields as cotton alone.

It was established that cotton could be processed in strong NaOH solution to achieve at least 60% yield. For future developments, the process conditions in terms of temperature, L/S ratio and textile piece size should be optimized to achieve possibly better results for total and GISA yield. As was shown in viscose testing, the thinner fabric degraded faster. More effective way to cut textile to smaller pieces would be able to start degradation faster as cellulose would be exposed to alkaline faster. Also, the factors contributing to the stopping of degradation should be clarified. Synthetic fibers were shown to at least break down in high temperature and NaOH, but a wider study on degradation products should be done. General textile waste consists of various materials, so it is important to study in practice all the possible degradation products of all fibers in alkaline environment. Modifications in the process and optimal conditions could be established to recycle a mix of textile waste or at least big portion of waste. A solution with textile waste degradation chemicals could be further on separated to other uses, in order for the circular economy to continue.

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Table A1 100% cellulose degradation results over time. Process parameters: T=150°C, m(cellulose)=30g, c(NaOH)=20 wt%.

Test 1	1h	2h	3h	4h
Oxalic acid	0,00	0,01	0,00	0,01
Glycolic acid	0,14	0,60	0,09	0,31
Formic acid	0,00	0,00	0,75	0,49
GISAs	0,00	0,00	0,24	0,41
XISA	0,00	0,24	0,65	0,44
Lactic acid	0,00	0,39	0,00	0,53
Acetic acid	0,30	0,10	0,07	0,14
2,5-DHPA	0,08	0,88	0,75	0,72
2-HBA	0,00	0,20	0,94	0,69
Total:	0,51	2,43	3,48	3,74
Yield,%	1,70	8,10	11,61	12,48

Table A2 100% cellulose degradation results over time. Process parameters: T=170°C, m(cellulose)=30g, c(NaOH)=20 wt%.

Test 2	1h	2h	3h	4h
Oxalic acid	0,01	0,00	0,05	0,00
Glycolic acid	0,00	0,06	0,10	0,40
Formic acid	0,00	0,19	0,85	0,28
GISAs	0,00	0,06	0,56	1,79
XISA	0,09	0,09	1,02	0,54
Lactic acid	0,05	0,05	0,00	1,00
Acetic acid	0,00	0,06	0,09	0,22
2,5-DHPA	0,00	0,74	0,74	0,91
2-HBA	0,17	0,27	1,69	1,29
Total:	0,31	1,51	5,11	6,44
Yield,%	1,05	5,05	17,02	21,47

Table A3 100% cellulose degradation results over time. Process parameters: T=190°C, m(cellulose)=50g, c(NaOH)=20 wt%.

Test 3	0h	1h	2h	3h	4h	5h	6h
Oxalic acid	0,01	0,05	0,07	0,08	0,08	0,10	0,09
Glycolic acid	0,00	0,04	0,10	0,24	0,30	0,33	0,34
Formic acid	0,46	0,93	1,32	1,77	2,09	2,25	2,27
GISAs	0,39	1,12	12,53	14,05	14,45	13,09	13,88
XISA	0,01	0,61	1,24	1,76	2,21	2,37	2,47
Lactic acid	0,44	0,61	1,40	2,14	3,09	3,46	3,81
Acetic acid	0,12	0,17	0,19	0,03	0,09	0,10	0,18
2,5-DHPA	0,84	0,95	1,08	1,23	1,39	1,69	1,45
2-HBA	0,26	0,49	2,06	3,31	4,61	5,20	5,41
Total:	2,53	4,96	19,97	24,61	28,32	28,61	29,91
Yield,%	5,07	9,92	39,94	49,22	56,64	57,21	59,82

Table A4 100% cellulose degradation results over time. Process parameters:
T=210°C, m(cellulose)=50g, c(NaOH)=20 wt%.

Test 4	0h	1h	2h	3h	4h	5h	6h
Oxalic acid	0,07	0,01	0,10	0,12	0,13	0,13	0,14
Glycolic acid	0,08	0,48	0,40	0,49	0,51	0,50	0,53
Formic acid	1,17	0,92	2,21	2,50	2,60	2,57	2,64
GISAs	0,16	0,22	10,25	8,26	6,52	5,68	5,65
XISA	0,97	1,17	2,12	2,36	2,43	2,38	2,43
Lactic acid	1,05	1,93	3,65	4,47	4,85	5,01	5,29
Acetic acid	0,84	1,04	1,20	1,24	1,24	1,11	1,12
2,5-DHPA	0,44	0,31	0,64	0,92	1,10	1,19	1,54
2-HBA	1,99	3,35	5,42	6,08	5,54	4,85	4,52
Total:	6,77	9,43	25,98	26,44	24,91	23,44	23,86
Yield,%	13,54	18,86	51,95	52,88	49,83	46,88	47,71

Table A5 100% cellulose degradation results over time. Process parameters:
T=150°C, m(cellulose)=50g, c(NaOH)=20 wt%.

Test 5	2h	3h	4h	5h	6h	23h	24h
Oxalic acid	0,03	0,03	0,03	0,04	0,03	0,07	0,07
Glycolic acid	0,03	0,03	0,03	0,03	0,05	0,12	0,16
Formic acid	0,44	0,49	0,51	0,58	0,55	1,19	1,24
GISAs	5,56	6,06	6,15	6,63	6,53	13,36	13,95
XISA	0,21	0,24	0,27	0,31	0,32	0,73	0,83
Lactic acid	0,24	0,25	0,26	0,30	0,31	0,70	0,77
Acetic acid	0,05	0,05	0,20	0,17	0,07	0,15	0,15
2,5-DHPA	0,48	0,48	0,49	0,50	0,49	1,16	1,12
2-HBA	0,17	0,29	0,32	0,37	0,38	0,72	0,92
Total:	7,21	7,92	8,26	8,93	8,73	18,20	19,21
Yield,%	14,42	15,85	16,52	17,86	17,46	36,39	38,42

Table A6 100% cellulose degradation results over time. Process parameters:
T=190°C, m(cellulose)=50g, c(NaOH)=20 wt%.

Test 6	0h	1h	2h	3h	4h	5h	6h	11h	12h	24h	25h
Oxalic acid	0,03	0,05	0,07	0,08	0,09	0,09	0,09	0,10	0,10	0,12	0,12
Glycolic acid	0,04	0,04	0,10	0,15	0,18	0,34	0,36	0,37	0,38	0,39	0,38
Formic acid	0,69	0,96	1,39	1,76	2,00	2,26	2,33	2,34	2,34	2,40	2,36
GISAs	0,82	4,85	9,05	10,52	10,65	11,07	11,87	10,49	2,00	1,87	0,82
XISA	0,33	0,60	1,39	1,95	2,34	2,45	2,51	2,48	2,60	2,53	2,50
Lactic acid	0,42	0,70	1,59	2,40	3,24	3,56	3,77	4,07	4,35	4,75	4,82
Acetic acid	0,57	0,74	0,96	1,12	1,32	1,26	1,28	1,22	1,10	1,13	1,11
2,5-DHPA	0,25	0,81	0,25	0,43	0,55	0,60	0,66	0,85	0,95	1,26	1,61
2-HBA	0,14	0,63	2,19	3,62	5,18	5,42	5,61	5,25	4,13	2,97	2,61
Total:	3,28	9,39	17,00	22,03	25,56	27,06	28,50	27,17	17,95	17,42	16,32
Yield,%	6,56	18,77	34,00	44,06	51,12	54,11	56,99	54,33	35,89	34,85	32,64

Table A7 100% cellulose degradation results over time. Process parameters:
T=190°C, m(cellulose)=50g, c(NaOH)=10 wt%.

Test 7	0h	1h	2h	3h	4h	5h	6h	7h	8h	10h	12h	24h
Oxalic acid	0,02	0,06	0,05	0,05	0,05	0,06	0,06	0,06	0,06	0,06	0,06	0,06
Glycolic acid	0,03	0,09	0,30	0,35	0,39	0,41	0,45	0,47	0,47	0,55	0,59	0,71
Formic acid	1,33	1,53	2,15	2,30	2,45	2,57	2,69	2,78	2,85	3,11	3,22	3,46
GISAs	5,03	8,88	12,70	14,12	14,81	15,31	15,43	15,63	11,25	14,50	14,03	13,57
XISA	0,33	0,41	0,63	0,71	0,76	0,80	0,84	0,87	0,93	0,95	0,96	0,92
Lactic acid	0,96	1,24	1,84	2,05	2,26	2,43	2,66	2,84	3,03	3,33	3,60	4,13
Acetic acid	0,92	1,07	1,36	1,43	1,48	1,54	1,59	1,63	1,68	1,73	1,79	1,88
2,5-DHPA	1,22	0,04	0,63	0,94	1,01	1,43	1,31	1,31	1,68	2,04	1,63	1,22
2-HBA	0,16	0,66	1,28	1,46	1,64	1,78	2,06	2,24	2,52	2,82	3,13	3,54
Total:	10,00	13,97	20,93	23,41	24,85	26,33	27,09	27,83	24,48	29,10	29,02	29,50
Yield,%	20,00	27,95	41,87	46,82	49,69	52,67	54,18	55,67	48,96	58,21	58,04	59,01

Table A8 Cotton degradation results over time. Process parameters: T=190°C,
m(cotton)=32g, c(NaOH)=20 wt%.

Cotton 1	0h	1h	2h	3h	4h	5h	6h	7h	8h
Oxalic acid	0,02	0,02	0,02	0,02	0,03	0,03	0,04	0,04	0,04
Glycolic acid	0,00	0,03	0,06	0,07	0,13	0,15	0,17	0,18	0,20
Formic acid	0,10	0,29	0,51	0,65	0,93	0,99	1,14	1,19	1,28
GISAs	0,97	2,15	3,36	4,51	6,10	4,85	6,83	5,98	6,90
XISA	0,09	0,35	0,73	0,96	1,49	1,64	1,82	1,96	2,06
Lactic acid	0,21	0,60	1,22	1,42	1,96	2,13	2,42	2,64	2,89
Acetic acid	0,03	0,09	0,17	0,21	0,27	0,26	0,33	0,32	0,37
2,5-DHPA	0,11	0,28	0,37	0,52	0,70	0,73	0,65	0,69	0,69
Succinic acid	0,02	0,05	2,23	2,23	0,04	2,09	0,06	0,05	0,07
2-HBA	0,36	0,79	1,31	1,81	3,22	3,49	3,96	4,19	4,67
Total:	1,93	4,64	10,00	12,41	14,86	16,35	17,41	17,23	19,17
Yield,%	6,03	14,50	31,24	38,79	46,45	51,11	54,41	53,85	59,90

Table A9 Cotton degradation results over time. Process parameters: T=190°C,
m(cotton)=32,35g, c(NaOH)=20 wt%

Cotton 2	0h	0.5h	1h	1.5h	2h	2.5h	3h	3.5h	4h	4.5h	5h	5.5h	6h
Oxalic acid	0,02	0,02	0,03	0,05	0,05	0,03	0,04	0,04	0,05	0,06	0,06	0,07	0,07
Glycolic acid	0,00	0,08	0,34	0,37	0,32	0,34	0,39	0,34	0,32	0,41	0,32	0,40	0,34
Formic acid	0,10	0,46	1,26	1,31	1,32	1,34	1,40	1,40	1,39	1,44	1,41	1,56	1,53
GISAs	0,77	2,75	4,54	4,58	4,28	3,58	3,94	3,64	3,33	3,01	2,75	2,68	2,50
XISA	0,24	0,81	1,92	1,93	1,97	1,96	1,97	1,98	1,95	1,91	1,97	1,95	1,96
Lactic acid	0,19	0,92	2,68	2,86	2,99	3,07	3,09	3,15	3,15	3,11	3,23	3,25	3,32
Acetic acid	0,00	0,30	0,04	0,09	0,09	0,11	0,14	0,16	0,18	0,21	0,31	0,32	0,24
2,5-DHPA	0,08	0,36	0,72	0,72	0,72	0,71	0,68	0,71	0,68	0,64	0,79	0,79	0,68
Succinic acid	0,21	0,16	0,15	0,16	0,18	0,17	0,19	0,20	0,22	0,22	0,23	0,22	0,22
2-HBA	0,36	2,16	5,65	5,54	5,22	4,53	4,00	3,63	3,14	2,62	2,42	2,18	2,00
Total:	1,97	8,02	17,33	17,62	17,14	15,84	15,84	15,24	14,40	13,62	13,48	13,43	12,86
Yield,%	6,05	24,68	53,33	54,20	52,73	48,75	48,75	46,89	44,31	41,90	41,46	41,31	39,56

Table A10 Cotton degradation results over time. Process parameters: T=210°C, m(cotton)=32,5g, c(NaOH)=20 wt%

Cotton 3	0h	1h	2h	3h	4h	5h	6h	7h	8h
Oxalic acid	0,02	0,02	0,02	0,02	0,03	0,03	0,03	0,03	0,03
Glycolic acid	0,00	0,00	0,07	0,13	0,18	0,20	0,21	0,23	0,33
Formic acid	0,09	0,27	0,60	0,89	1,06	1,14	1,20	1,23	1,36
GISAs	0,58	1,66	3,65	4,89	5,98	6,33	6,45	6,33	6,17
XISA	0,18	0,50	0,99	1,50	1,71	1,82	1,89	1,90	1,95
Lactic acid	0,15	0,48	1,09	1,64	2,07	2,31	2,45	2,58	2,72
Acetic acid	0,00	0,10	0,24	0,21	0,36	0,40	0,41	0,43	0,45
2,5-DHPA	0,13	0,28	0,54	0,60	0,71	0,72	0,74	0,84	0,76
Succinic acid	0,14	0,07	0,11	0,08	0,10	0,20	0,12	0,13	0,12
2-HBA	0,36	1,06	2,09	2,92	3,75	4,03	3,95	4,06	4,51
Total:	1,66	4,43	9,39	12,88	15,94	17,18	17,46	17,74	18,41
Yield,%	5,14	13,70	29,04	39,82	49,26	53,10	53,96	54,84	56,90

Table A11 Viscose degradation results over time. Process parameters: T=190°C, m(viscose)=32,35g, c(NaOH)=20 wt%.

Viscose	0h	1h	2h	3h	4h	5h	6h	7h	8h
Oxalic acid	0,01	0,01	0,03	0,05	0,05	0,06	0,06	0,06	0,07
Glycolic acid	0,00	0,03	0,10	0,16	0,19	0,19	0,20	0,21	0,20
Formic acid	0,12	0,28	0,91	1,30	1,39	1,40	1,40	1,46	1,46
GISAs	0,81	1,65	4,82	7,18	7,80	7,08	6,95	7,21	6,98
XISA	0,07	0,00	0,87	1,35	1,47	1,48	1,47	1,49	1,48
Lactic acid	0,09	0,34	1,30	2,11	2,41	2,50	2,55	2,65	2,69
Acetic acid	0,05	0,08	0,29	0,40	0,43	0,41	0,41	0,43	0,43
2,5-DHPA	0,12	0,25	0,63	0,84	0,88	0,87	0,86	0,87	0,86
Succinic acid	1,96	2,06	2,09	2,12	0,04	0,02	2,08	0,06	0,06
2-HBA	0,09	0,54	2,20	3,56	3,70	3,63	3,56	3,47	3,32
Total:	3,33	5,25	13,23	19,07	18,35	17,65	19,54	17,91	17,53
Yield,%	10,28	16,22	40,90	58,94	56,72	54,56	60,41	55,37	54,19

Table A12 Cotton 60%/ Polyester 40% degradation results over time. Process parameters: T=190°C, m(total)=32g, m(cotton)=19,2g, c(NaOH)=20 wt%

Cotton/Polyester	0h	1h	2h	3h	4h	5h	6h	7h	8h
Oxalic acid	0,01	0,00	0,04	0,08	0,00	0,03	0,01	0,01	0,01
Glycolic acid	0,00	0,00	0,02	0,13	0,15	0,07	0,20	0,24	0,16
Formic acid	0,00	0,00	0,15	0,42	0,55	0,53	0,66	0,71	0,65
GISAs	0,22	0,00	0,42	2,63	3,53	0,27	4,03	4,19	4,09
XISA	0,00	0,00	0,27	0,64	0,82	1,03	1,06	1,16	1,25
Lactic acid	0,00	0,00	0,00	0,62	0,84	1,12	1,23	1,37	2,19
Acetic acid	0,00	0,00	0,11	0,20	0,27	0,35	0,45	0,59	0,68
2,5-DHPA	0,00	0,00	0,05	0,09	0,10	0,14	0,13	0,15	0,18
Succinic acid	0,07	0,00	0,55	0,17	0,24	0,13	0,34	0,44	0,50
2-HBA	0,08	0,00	0,47	1,24	1,32	1,64	1,59	1,73	1,75
Total:	0,38	0,00	2,09	6,22	7,82	5,31	9,71	10,59	11,46
Yield,%	1,97	0,00	10,90	32,39	40,73	27,65	50,57	55,15	59,67