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RECYCLING CELLULOSIC FIBRES FROM WASTE TEXTILE BY CELLULOSE CARBAMATE TECHNOLOGY (CCA)

ABSTRACT

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As the new transition of energy is obviously motivated forward which applies technology and constructs closed-loop materials, the textile industry has to confront a massive issue – where solid waste should be administered cautiously. Hence, eco-friendly materials and circular techniques are utilized to improve the performance of the textile industry, whereas cellulose-based fibre and their chemically recycled pathways are concerned. Cellulose carbamate (CCA) technique is especially implemented to recover discarded cotton and dissolving pulp cellulosic fibres. To recover cellulosic fibre in waste cotton or viscose products, the pre-treatments are carried out to withdraw silicate, impurities such as metal and ash by applying alkali, ozone, peroxide and acidic washing prior to the actual carbamation process. The CCA mixture is formed by reacting with urea, small amount of H_2O_2 and kneader. The cellulose intermediate is soluble in NaOH solution with the aid of ZnO as additive. It is precipitated subsequently into fibres in acidic coagulation baths with Na_2SO_4 and $Al_2(SO_4)_3$. The reacted urea attached to cellulose is removed in mild NaOH solution and performed after completing the spinning process. The CCA fibres possess the similar properties but it is more sustainable compares to viscose products. This thesis demonstrated the literature review of CCA production, which has been gradually developed by diverse inventions to acquire the appropriate methods synthesizing CCA fibres from reacting cellulose with urea, or alternative agents to urea aqueous during the CCA formation and dissolution, or alternative baths in the spinning dopes. This thesis also comprised of the mass balance of CCA production by implementing chemical charge and utilized water during the process as the main sources to evaluate GWP, recommending the suitable locations for the factory of CCA and circulation pathway of significant chemicals used to dissolute and regenerate CCA fibres.

Key words
Cellulose carbamate, alkali soluble cellulose, carbamation, intermediate cellulose, cellulose/urea mixture, alkali dissolution, acidic coagulation bath, CCA fibres.

ACKNOWLEDGEMENT

ABBREVIATIONS

Word Abbreviations

AGU	Anhydroglucose unit
CCA	Cellulose carbamate
CL	Cotton linter
DES	Deep eutectic solvent
DP	Degree of polymerization
DS	Degree of substitution
DTA	Differential thermal analysis
EU	European union
FTIR	Fourier-transform infrared spectroscopy
GWP	Global warning potential
IL	Ionic liquid
IR	Infrared
ISO	International organization for standardization
LCA	Life-cycle assessment
NIR	Near-infrared spectroscopy
NTP	Normal temperature and pressure
PET	Polyester
$scCO_2$	Supercritical carbon dioxide
SEM	Scanning electron microscope
UFF	U-landshjälp från Folk till Folk i Finland rf (a non-profit, non-governmental humanitarian organization)
wt%	Weight-percent

Formula of chemicals compound

$Al_2(SO_4)_3$	Aluminium sulphate
CO_2	Carbon dioxide
CS_2	Carbon disulphide
H_2O_2	Hydrogen peroxide
H_2SO_4	Sulphuric acid

HCl	Hydrogen chlorine	
HNCO	Isocyanic acid	
KOH	Potassium hydroxide	
N	Nitrogen	
Na_2CO_3	Sodium carbonate	
Na_2SO_4	Sodium sulphate	
NaOH	Sodium hydroxide	
NH_3	Ammonia	
NMMO	N-Methylmorpholine N-oxide	
O_3	Ozone	
ZnO	Zinc oxide	

Equation symbols and units

C_M	Molarity	mol L^{-1}
DF	Dilution factor	h odt^{-1}
E	Efficiency factor	
E_{10}	The modified efficiency factor	
K_a, K_{a1}, K_{a2}	The equilibrium constant	
L_{out}	Liquor flow rate in pulp discharge	t h^{-1}
m	Mass	g, kg
M	Molar mass	kg kmol^{-1}, g mol^{-1}
n	Mole	mol
N_{out}	Discharge consistency	%
P	Pulp production capacity	odt h^{-1}
pH	Power of hydrogen or potential for hydrogen	
V	Volume	L
WL	Wash liquor flow rate	t h^{-1}
ρ	Density	kg L^{-1}

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1 INTRODUCTION

Textile is one of the necessities providing household covering to filtering in scientific progress and industry. Likewise, for human beings, textile contributes protection, comfort and individuality expression that significantly affects the economic growth. In 2007, EU was the largest consumers of fibres that it consumed 10 million tons of fibre in the total of 72 – 75 million tons of fibres in the world. By 2020, the consumption of fibres is rated to achieve 110 million tons globally. (Bojana 2014) Alongside with those values, the textile industry implies to the production of yarn, textiles and fabrics. It also contains extending discouragements as textile waste solid and hazardous substances getting off the secure zone to landfill and incineration facility that damage both inhabitants and their habitats. Recently, the new transition of energy which applies technology and constructs closed-loop materials is strongly motivated forward. The textile industry has to confront a massive issue – where solid waste should be administered cautiously. Recycling is not a novel affair to the textile manufacture yet it needs to be advanced because the economic and environmental necessity. Therefore, eco-friendly materials and circular techniques are utilized to improve the performance of the textile industry, whereas cellulose-based fibre and chemically recycled technique are considerably applied.

Cellulose-based fibre is accounted for one-third in the textile-fibres-apparel industry, where cotton, viscose, Lyocell (so called dry jet-wet spinning process that generates a form of rayon including cellulosic fibres) are the commercially significant manufactures. Cellulosic fibre is known as biodegrading, safe and futuristic. (MacArthur 2017, 120.) Due to those positive impacts of cellulose-based fibre, the cellulose-based fibre industry is predicted to extend its quantities substantially to 19.0 million tons in 2030 from 5.7 million tons in 2013. (Määttänen, Asikainen, et al. 2019.) Another cause to enlarge cellulose-based fibre production comes forward the issue with production of virgin materials that relate to the land area for fibres cultivation and climate condition. Particularly, land is prioritized to cultivate food than being consumed for cotton manufacture, where the demand for food increases by 43% in 2030. For cotton production, it only consumed about 2% of the world's arable land but mainly located in climatic regions. Nevertheless, many cotton-growing countries are highly populated with a tremendous necessity to

extend food production. The continuous land loss by soil degradation reduces the overall arable land available. Those matters intensify the desperate shortage of fertile farmland in the near future and arable land on which non-food crops are growing these days and indicate that food crops should be prioritised to cotton cultivation (Haemmerle 2011). Dissolving pulp thus is the key factor to compensate cotton manufacture, where its production was already 6.6 million tons in 2014 worldwide, proving its significance in textile industry in the future. (Yishan, Liuxin and Dong Cheng and Zhibin 2016.) Otherwise, it is essential to fabricate additional technical inventions to create a closed-loop system where textile waste is not an exception. Dissolving pulp and cotton waste textile therefore are the potential raw materials for advanced cellulosic fibre production.

Cellulose carbamate (CCA) technique is implemented to recover recycled cotton and wood based-cellulosic fibres (Harlin 2019, 5). It has been an emerging consideration by enabling products of sophisticated material and applying environmentally friendly technology, where cellulose carbamate represents as an intermediate to be stored and transported before entering to dissolution. This technology possesses greater benefits than other commercial processes and carries sustainable solution for textile industry. (Saxell, Ratamäki and Ekaman 2017.) CCA production economises washing water and solvent power consumption compared to Lyocell technology. And it is environmental friendlier than viscose production with thorough applicability for high absorbent products as nonwoven hollow fibres, sponges, and carpet cleaners under solvent-free and catalyst-free conditions. (Fu, et al. 2014.)

By applying CCA technology to recycle cellulosic fibre, the global warming potential (GWP) of the manufacturing process will reduce 35% and the water consumption is lower 98% than cotton production. (Määttänen, Harlin, et al. 2019, 209.) This thesis includes the collection of waste textile to sorting cellulose-based material and significant cellulose carbamate production. Those studies are reviewed as literature survey in which initial mass balance is executed by calculating the fibre production in weight with chemical charges during CCA production using approximate collected data from different reports in European countries.

2 COLLECTING & SORTING CELLULOSE-BASED TEXTILE WASTE

Textile recycling is not only beneficial for economy, but also a route to implement the circular economy such as close loop production system (Filho, et al. 2019). The quatity of reusable clothes decreased based on a flow analysis in the period of 2015 – 2017. Energy consumption such as gas and electricity have been increasing, yet the quality of textile has been on downtrend for the last decade, which consequently reflects to the second-hand clothes would further undergo fine sorting. (Nørup, et al. 2019.) The scope of collection and sorting waste textile mainly revolve around Scandinavian countries, especially Finland, where textile consumption was 13.5 kg per capita. Most of the unworn clothes end up in the back of wardrobe, or land fill and incinerator, only a small portion of them are reused and recycled. (Palm, et al. 2014, 9.) For instance, annually in Finland approximately 72 million kg of waste textile is consumed. From this data, the calculated home textile for reusing was 12 million kg, it accounted for 16.5% of total amount. A small portion for mechanical recycling was 1.1 million kg, it accounted for 1.5% of the total amount, and others 2% went to the energy production. (Heikkilä and Fontell 2017, 11.) There are four main techniques among recycling technologies as shown in Figure 1. The pathways comprise of mechanical, chemical and thermal technology, other waste textile would require mixed technology to produce carpet or composites. Yet chemical recycling is the only considered technology in this thesis that minor mechanical technology is also utilized in the sorting and removing non-textile materials. (Palm, et al. 2014, 131.)
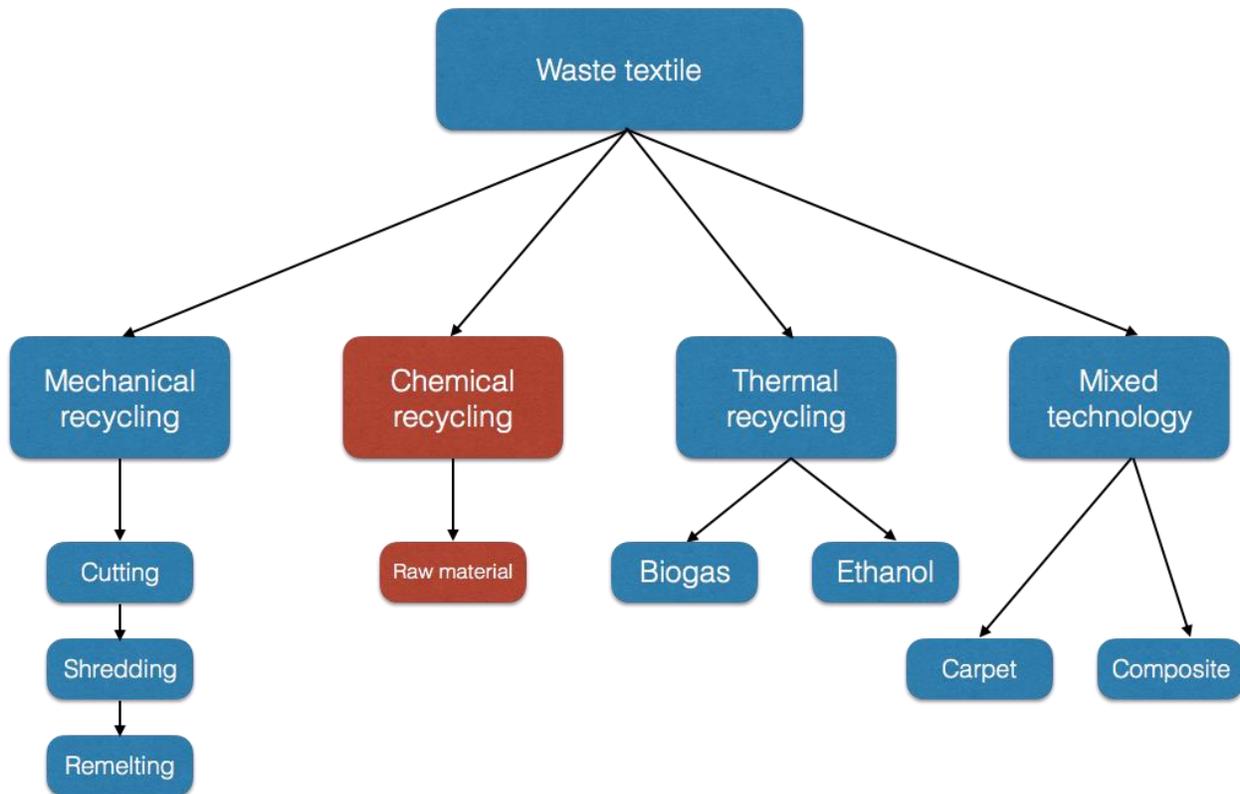
FIGURE 1. Main technology pathways used for recycling textile waste today (adapted from (Palm, et al. 2014, 131)).

2.1 Collecting pre-customer and post-consumer textile

During fabric and garment production, 25 – 30% of textile material is lost from the supply chain. This pre-consumer waste is mainly from mill waste and cutting, which is excluded from the deadstock when the production season is changing. (Määttänen, Harlin, et al. 2019, 24.) Unworn pre-consumer textile residuals are already mechanically recycled on an industrial scale, where it is typically cut into shorter lengths of fibre (Wanassi 2016). Cellulosic fibres recycled by mechanical technique are bleached 10 – 30% with raw textile fibre, but 100% recycled fibre yarns are also commercially available (Määttänen, Harlin, et al. 2019, 204). A Finnish company named Pure Waste Textile established in India – the company manufacture yarns and other knitwear and fabrics from waste cutting textile in factories. The mechanical is available for both natural and synthesis fibres and feasible to operate worldwide. (Heikkilä and Fontell 2017, 37.)

The current post-customer textile collection is mainly accomplished by voluntary basis such as charity organizations (Nørup, et al. 2019), which is dominated by 4 charity organizations (UFF, Red Cross, Fida International and Salvation Army). The collection system is crucially operated through the container, where it is placed in large population areas and/or next to local waste collection sites, which is separated from other waste sources. The location of collection site is obligated to obtain permission from municipality or retail groups. The container sites should be sheltered since the waste textile is occasionally stolen, but this status does not usually happen. Particularly, some textile is collected either via second-hand shop maintained by charity organizations with provided pickup service. Municipal waste management companies and municipalities gather waste textile both via recycling centres and individually owned companies from both industry and customers. (Palm, et al. 2014, 37.)

2.2 Sorting

In Figure 2, "good as new" and "homogeneous" are categorized as the easiest textile to be reused. As the material is generally unsold and undergone any wearing and washing cycle, hence it is eligible for being macroscopically and microscopically reused, reducing the identification sorting efforts. (Määttänen, Harlin, et al. 2019, 201.) Parallelly, the combined characteristic of "good as new" and "inhomogeneous" alongside with "worn" and "homogeneous" with "worn" and "inhomogeneous" are feasible to be recycled chemically. Because "worn" and "homogeneous" textile is not possible to be recycled mechanically without the aid of virgin material. However, nonwoven garment is a beneficial material to recycle chemically cotton, since the quality of nonwoven garment is similar to dissolving pulp products compares to the virgin cotton fibre. By expanding simultaneously the collection and sorting with development of novel processes and products, Telaketju project tries to solve the discarded (post-consumer) textile issues, where many actors are involved in the waste textile collection activities such as H&M, The Helsinki Metropolitan Area Reuse Centre, Finlayson. During the sorting, the non-reusable textile fraction is processed on an industrial scale. Depending on the cleanliness and the microscopic damaging of textile, reutilization is separated into 4 categories. The most difficult to be reutilized textile is

the most suitable input for chemically recycling process because it is both inhomogeneous and worn. (Heikkilä and Fontell 2017, 34.)
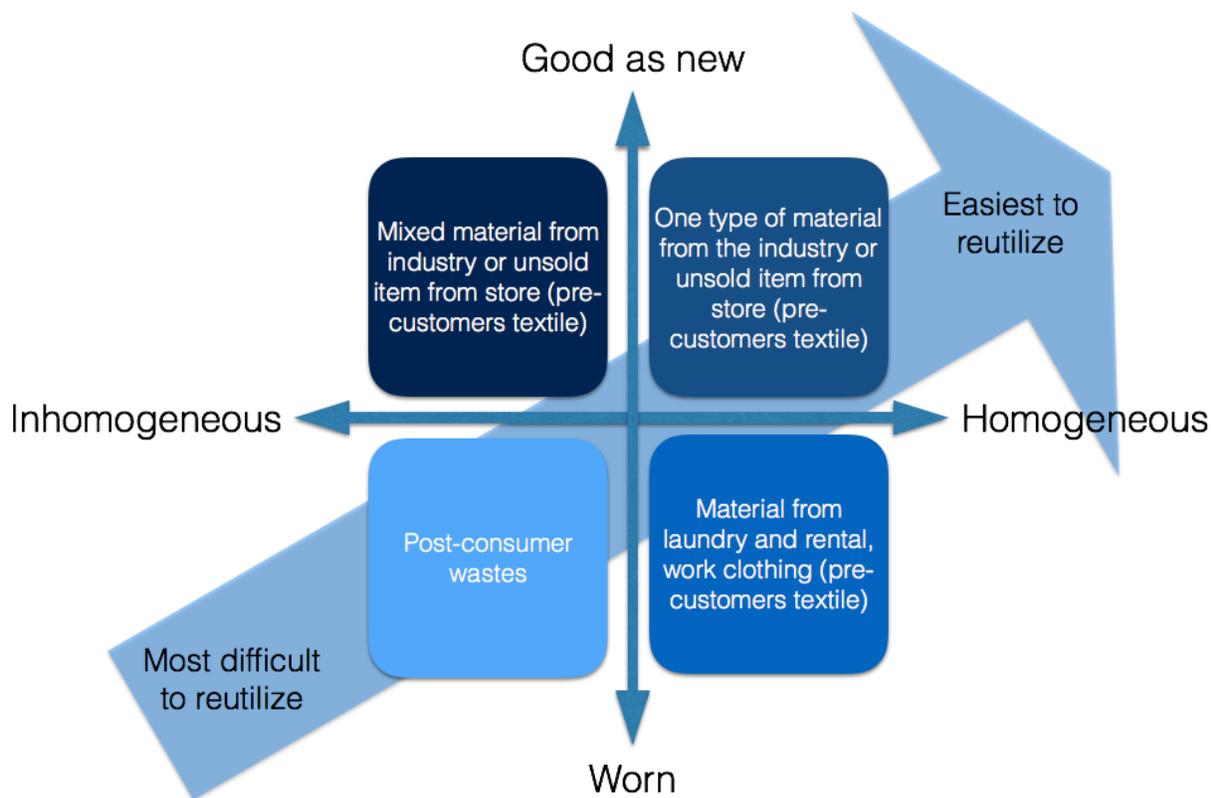
FIGURE 2. Raw material sources for reutilization in textile applications based on homogeneity and wear of materials (adapted from (Heikkilä and Fontell, Model of circular business ecosystem for textiles 2017, 33)).

The sorting system of waste textile is commonly characterized by 3 techniques: manual, semi-automatic and spectroscopic methods sorting (Palm, et al. 2014, 111-116). The manually sorting technique is traditionally used to identify accurately different waste textile materials. However, this method dissipates several hours since it is based on the attached tags in the waste textile and the waste textile condition is not always perfect to be readable. (Heikkilä, et al. 2019, 28.) Semi-automatic sorting is also utilized, where the conveyor belts transport waste textile and the textile is manually sorted. This type of sorting is used for compact sorting fraction before further

transportation. (Palm, et al. 2014, 113.) Nowadays, automated sensor-based material identification is utilized to improve the efficiency and capacity of waste textile sorting. This identification method involves the context of quality control, historical studies (archaeology, conservation) and forensic sciences. The sensors functioned based on the spectroscopic methods such as FTIR and NIR. The input material is fast, accurate and non-destructive during the analysis since there is no interaction with the materials. NIR sensor detects the organic compounds that chemical bonds absorbed light in the NIR wavelength range. The textile fibres are identified in the range of 700 – 2500 nm. The sensor still is a section in the sorting system, which it should be synchronous with the line conveyors and divided into different textiles depending on the identified material composition. (Heikkilä, et al. 2019, 29.) The FTIR and NIR, however, can cause major inaccuracy to classify diverse types of textile since they are not capable to categorize waste textile with a high re-sale value, such as a well-known brand clothes. (Määttänen, Harlin, et al. 2019, 202)

3 WASTE VEGETABLE CELLULOSE-BASED FIBRES AS RAW MATERIAL

Cellulosic fibre-based textiles are strong, tough that can provide fibre-based products for industrial end uses. A popularised example is fibres used in tire cord. In addition, it is an ideal source of textile fibres for high-end products, such as commodity, and fashion oriented markets such as rayon. It is an outstanding candidate because of its strong intermolecular bonds, and as it does not dissolve in ordinary solvents. Researchers have been studying in advanced to the derivatives of cellulose to deliver them to be soluble and processable. (Kotek 2007, 667.) The chemical compositions of some typical cellulose-containing materials are shown in Table 1, whereas those sources are harvested sources such as high cellulose yield presenting in cotton or many types of wood. (Sixta 2006, 24)

TABLE 1. Chemical composition of some typical cellulose-containing materials (adapted from (Klemm, Shmauder and Heinze 2005)).

Sources	Composition (%) cellulose	Hemicellulose	Lignin	Extract
Hardwood	43–47	25–35	16–24	2–8
Softwood	40–44	25-29	25-31	1–5
Bagasse	40	30	20	10
Coir	32–43	10–20	43–49	4
Corn cobs	45	35	15	5
Corn stalks	35	24	35	5
Cotton	95	2	1	0.4
Flax (retted)	71	21	2	6
Flax (unretted)	63	12	3	13
Hemp	70	22	6	2
Jute	71	14	13	2
Sisal	73	14	11	2
Wheat Straw	30	50	15	5

As producing 1.5×10^{12} tons per year, cellulose is the most abundant biopolymer globally, comparable to fossil fuel and mineral sources-based polymers. Cellulose is utilized as biodegradable to renewable raw materials in various applications nowadays. Cellulose is distributed over natural plants, animal, fungi, algae and mineral (tunicine) yet the major source of cellulose is plant fibre, which contributes approximately 40% to the carbon fractions. (Rojas 2016, 2.) The cellulose sources are also indicated in Table 1, where cotton contained more than 90 wt% of cellulose are accommodated. Other sources of cellulose are bacterial cellulose fungi and green algae cellulose. (Klemm, Shmauder and Heinze 2005.)

3.1 Molecular, supramolecular, and morphological structure of cellulose

Cellulose structure consists of linear homopolymer β-D-glucopynarose rings acting as a basic building block (Kovula 1996, 12). D-glucopyranose ring units in the chair $^4C_1$ configuration and linked by β-1,4-glyocsidic bonds resulting to an alternative turning of the cellulose chain axis by 180° (Rojas 2016, 4), as displayed in Figure 3 and 2-fold symmetry to each other (Kovula 1996, 12). The repeating unit of cellulose is known as cellobiose with 1.3 nm. In the ring plane position, 3 hydroxyl groups exist in each AGU are appeared reactively 3 times within a cellulose chain at C2, C3 and C6. (Rojas 2016, 4.)
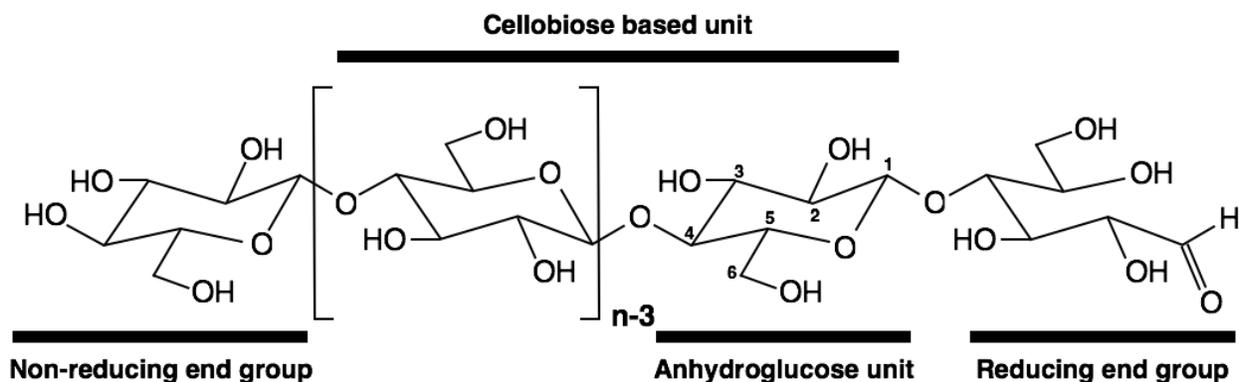
FIGURE 3. Structure of cellulose molecule (n = value of DP) (adapted from (Poletto and Ornaghi Jr. 2015)).

Depending on the plant sources, the amount of DP is from 1 000 to 30 000. Being present as ordered crystalline fibres, this corresponds to a length of 500 – 15 000 nm. It is substantial to

prompt hydrogen bonds in cellulose structure since it impacts the properties of cellulose, restricts the solubility and reactivity in most solvents and of the hydroxyl group in AGU. (Rojas 2016, 5.)

Cellulose I (native fibre) and cellulose II (regenerated fibre) are the most common polymorphs that describe the crystallite supramolecular structure of cellulose as shown in Figure 4 (Bredereck and Hermanutz 2005). The other cellulose (III and IV) polymorphs are obtained by special treatments of cellulose I and are of minor significance (Sixta 2006, 27). They are included in the category of supramolecular structure, which characterizes crystalline and amorphous regions of cellulosic fibres – one of the factors which determines the physical properties of textile cellulosic fibres parallel to the molecular structure, pore structure and inner surface of cellulose. (Bredereck and Hermanutz 2005.) Hydrogen bonding system of the cellulose II is more compacted and stronger intermolecular bonded hence it is less reactive than the cellulose I. Hydrogen bonding leads to the formation of fibres in cellulose morphology which is arranged in parallel assemblies of elementary crystallites. (Rojas 2016, 5.)
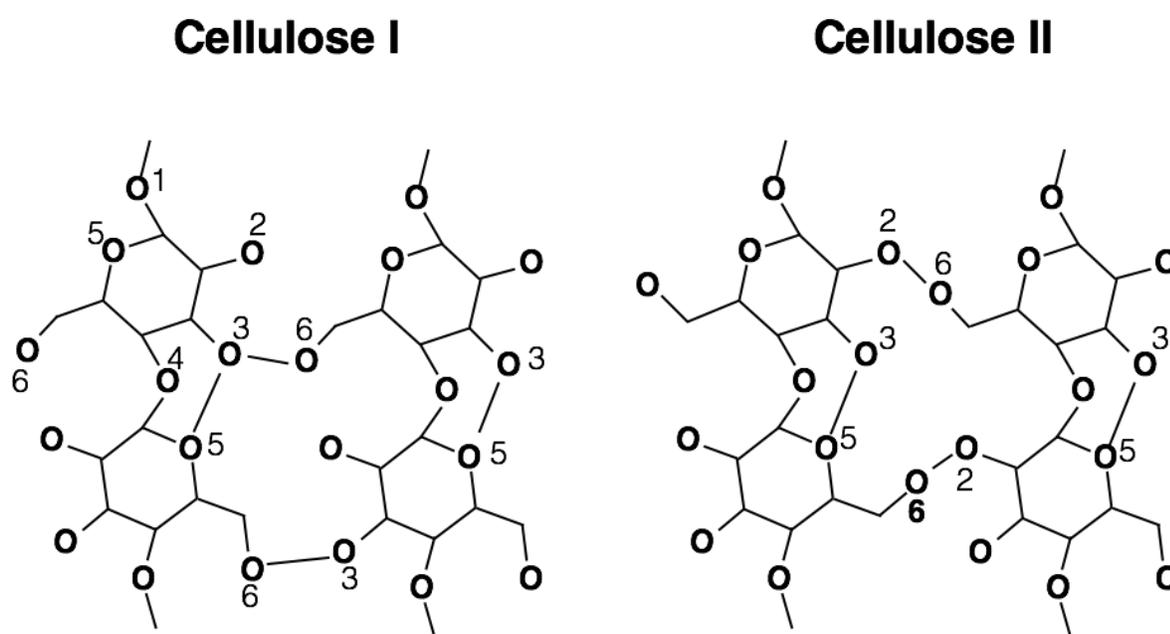
FIGURE 4. Hydrogen bond system of cellulose I and cellulose II (adapted from (Kontturi 2015)).

3.2 Dissolving pulp products

Dissolving pulp refers to pulp having a high content of cellulose (90% of α-cellulose) with low hemicellulose content. Dissolving pulp is comprised of purified cotton linters and wood from softwood (spruce, pine) or hardwood (beech, eucalyptus) compared to paper-grade pulp that it was produced until World War II. (Sixta 2006, 7,11.) Furthermore, the cotton linters regulate the residual amount of dissolving pulp. They are attached into the cotton seed and removed in the delintering process to generate diverse length. The shortest fibres or second-cut linters are used as chemical input. Purification is achieved by a combination of mechanical and chemical steps, consisting of mild alkali treatment at elevated temperature to remove proteins, waxes, pectins and other polysaccharides and bleaching to achieve the desired brightness level. (Sixta 2006, 1022.)

Dissolving pulp is characterized as its "reactivity" over solvents or derivatizing chemicals. The reactivity connects to accessibilities of chemicals to the cellulose, which the hydroxyl groups are reached by reactants. The structure and morphology characterize the conversion process homogeneity and last products. Moreover, the reactivity relates to the pore system that associates to the molecular structure of cellulose, the qualitative and quantitative determination of organic or inorganic component impurities of their inputs. (Sixta 2006, 1023.)

Dissolving pulps are chemically refined bleached pulps, for which the pulp is manufactured with 2 main processes: the prehydrolysis kraft and the acid sulfite process. Application of the prehydrolysis kraft process results into a pulp with $94 - 96\%$ of α-cellulose while the sulfite process results into a pulp having $90 - 92\%$ of α-cellulose. For specified alkali purification treatments, the yield of α-cellulose can achieve a yield of 96% and 98% for sulfite and prehydrolysis kraft, respectively. (Sixta 2006, 7,11.) By implementing viscose, Lyocell and cuprammonium rayon commercialized processes, dissolving pulp is the raw material to produce viscose staple, textile; technical filaments via viscose process; and textile, non-wovens through the Lyocell process. (Sixta 2006, 1025.)

3.3 Discarded cotton textile

Cotton fibres are seed hairs from plants of the order Malvales, family Malvaceae, tribe Gossypieae, and genus Gossypium. The commercial cotton products are almost all white (creamy yellow to bright white). The natural colour of cotton has disappeared for more than 50 years because of the appearance of inexpensive dyes and high demand of cotton production. The yields of natural cotton are too low and the fibres are too short and weak to be spun. Therefore, numerous researchers over the years have improved the quality, yield, strength and length of fibres. The cottons available today are usually shorter, weaker, and finer than regular Upland cottons but they can be spun into ring and rotor yarns for many applications. They can be blended with themselves or with normal white cottons. The utilization of dye and chemicals can be eliminated in textile finishing for a limited number of colours, possibly generating some savings, which can compensate for the higher raw material prices. (Kotek 2007, 525.)

Cotton fibre production requires intensive work, energy and labour. Many of the key cotton-producing countries are under high water stress, including China, the United States, India, Pakistan and Turkey. For instance, 80 – 90% of fabric, yarn and plastic-based fibres in China are made in water-scarce or water-stressed water. The productive land and freshwater resources are the main consequences of global population growth beside the hazardous chemicals used during the cotton cultivation. The emerged circular economy thus is employed broadly including recycle project of cotton textile. The current promising small-scale collaboration is operated in Finland and called "Relooping Fashion". This pilot is an unique production experiment of cotton recycling and has been developed into a cross-chain-value business ecosystem in line with the principles of the circular economy. (MacArthur 2017, 27.)

Cotton raw material accounts for 26% in the total virgin feedstocks (97%) in 2015 (MacArthur 2017, 20). Also, less than 1% of the used garments is recycled back into clothes. Within that 1%, waste cotton is regenerated from two main sources: pre-consumer (scrap from yarn, fabric by-products) and post-consumer (household items to be repurposed such as garments, upholstery, towels) (Cottonworks 2020). The term of "cotton-based" or "cotton blend" means that the material obtains at least 40% cotton. It is referred to utilize at least 70% cotton, if the textile tags are labelled

"100% cotton", it means the textile cotton contains approximately 90% of cellulose and 10% of other materials (Harlin, Määttänen, et al. 2018.) "100% cotton" is selected to be the only input material for the mass balance section in this thesis. Particularly, for polyester/cotton blended, if the cotton yield is higher than 20% of the total weight, cellulosic fibre is recovered, PET is removed for other process, such as synthesis recovery. (WRAP, et al. 2017, 21.)

4 PRE-TREATMENT OF DISCARDED CELLULOSE-BASE TEXTILES

The defining idea of activating cellulose during pre-treatment is to weaken the interconnections of cellulose structure and loosen its crystallinity to increase the accessibility of cellulose, namely cellulose activation. The most common procedure to activate cellulose is to unfasten supramolecular structure by decreasing the interchain hydrogen bonds with swelling agents, such as dimethyl sulfoxide (DMSO) and N, N-dimethyl formamide (DMF). (Huang, et al. 2019, 1.)

Diverse techniques such as degradative, mechanical, and swelling methods are applied as the essential prerequisites to activate cellulosic fibre and known as pre-treatments stage in recycling cellulose-based textiles (Engström, Ek and Henriksson 2006). The surface area, reactivity, activity as well as the DP modification and impurities removal of cellulose are enhanced to prepare the cellulose for the subsequent cellulose dissolution stage. The impurities removal such as silica and decolouring are progressed mechanically following the hot alkali treatment step to intensify the surface area of cellulose at elevate temperature and remove PET fibres. (Harlin, Määttänen, et al. 2018.) Agent selectivity is due to the unsustainability, hazardousness and energy demand of all manufacture, purification and recycling technologies (Huang, et al. 2019, 1). For example, if the viscosity of waste cotton does not reach the target figure, the dyed cotton materials need to be treated with endoglucanase treatment to reduce high viscosity (Määttänen, Vehviläinen, et al. 2018). The pre-treatment is followed by these steps removal of metal (button, zipper), mechanical preparation (shredding, grinding), chemical treatment (metal and impurities removal) (Tubito, et al. 2016).

The schematic of pre-treatment stage is illustrated in Figure 5. It involves many mechanical objects and chemical substances from ball or ham mill to operate wet milling, hot alkali treatment and followed by enzymatic activation if the dyed materials obtained high viscosity. Or else would be treated by bleaching agent – O_3 with or without any disk refining. Both enzymatic and O_3 steps are followed by H_2O_2 and acidic treatment to remove all undesired chemical substances in the waste cotton. (Harlin, Määttänen, et al. 2018.)
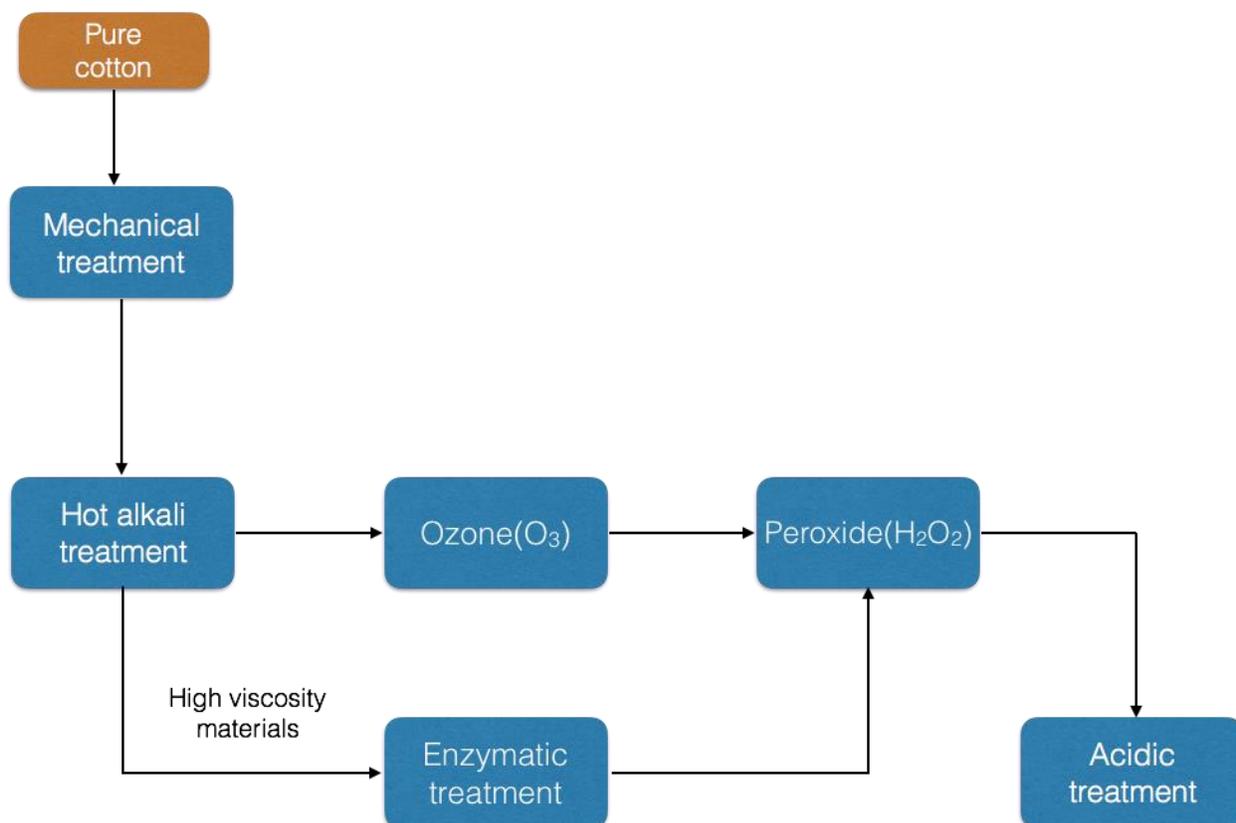
FIGURE 5. Schematic of pre-treatment stage to activate and decolour cellulose-based textile waste (adapted from (Harlin, Määttänen, et al. 2018)).

4.1 Mechanical treatment

One of the purest cotton garments such as denim jeans is indispensable to remove zipper, studs, rivet and buttons. This step is either operated in the recycler or sorter as they may interfere with fragmentation or with later stages in the process. After hard compounds are removed, the garments are broken down through hammer milling, in which a 10 mm screen is used and refined with a Bauer disk refiner (wet milling) (Määttänen, Vehviläinen, et al. 2018.), or ball milling. Those mechanical operations are physical techniques to fracture the cellulose interchain. Ball milling technique modifies supramolecular cellulose structures by the disintegration at the macroscopic level, diminishes crystallinity and destructs the fibrillar architecture of fibre structure. The activation of cellulose structure is achieved by grinding fibre into smaller pieces for coming steps. (Huang, et al. 2019, 2.) Depending on the demand, there are several types of ball mill. Generally, it consists of steel, stainless steel, ceramic or rubber. Figure 6(a) and Figure 6(b) show tumbler

ball mills, vibratory mills and planetary mills. Derivative microcrystalline cellulose from cotton linter are placed in a ball milling at 200 rpm from 4-8 hours in dry and wet condition with water, toluene and 1-butanol solvents. (Piras, Fernández-Prieto and M. 2019.) The wet milling also reduces the ISO brightness of un-dyed cotton fabric and produces different colours (Määttänen, Asikainen, et al. 2019).
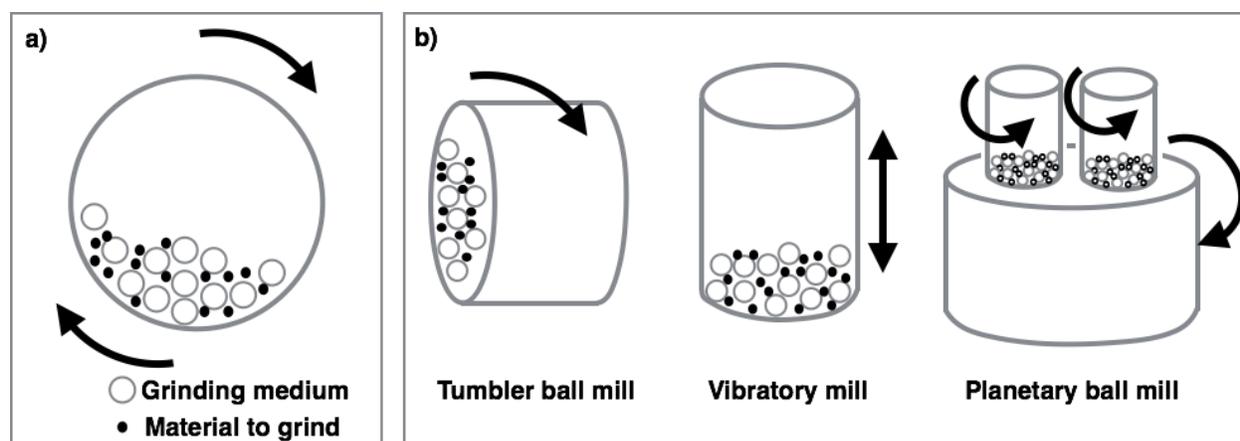
FIGURE 6. (a) Schematic representation of a ball mill (horizontal section); (b) different types of instruments (adapted from (Piras, Fernández-Prieto and DeBorggraeve 2019)).

The demolition of cellulose structure leads to the diversity of morphology, polymorphism and crystallinity, which is influenced by optional media. The cellulose nanofibre formation identifies the chemically functionalized preparation of ball mill technique. Most of the reported studies were experimented in wet conditions, as they were found to be most favourable for fibrillation. This factor relates to fibre swelling matters that cellulose is swollen in water or organic solvent thus it prevents excessive grinding problem by hydrogen bond disruption. It is favourable combination between ball mill and chemical treatment enhancing product quality at minimal effort. (Piras, Fernández-Prieto and DeBorggraeve 2019.)

For cotton linter, planetary ball mill is used as a class of mechanical techniques that the artificial gravity caused by the centrifugal force can be obtained to the grinding medium. The main aim of utilizing planetary ball mill is to break down the crystallinities. Cellulose powder with acid hydrolysis H_2SO_4 at low concentration and acid hydrolysis process are discontinued by adding 4°C distilled water until the suspension reaches neutralized pH (Phanthong, et al. 2015). The

mixing time, temperature and reaction ratio rely on ball weight and cellulose size along with the mill type. In another representation, ball mill is operated by Spex 8000 shaker mill and applied to dried softwood-based materials to loosen hydrogen bonds. An aqueous suspension of cellulose nanofibers with the concentration of 0.2 wt% is prepared and the weight ratio between the grinding balls and original fibres was 50:1 (Zhang, Tsuzuki and Wang 2010.) Ball mill provides comprehensively an effective grinding approach for activating cellulose. Despite the advantageous consequence of physical activation, it still carries complex process parameter such as filling ratio, rotation speed, ball diameter, initial moisture content that impacts the size of final product. (Huang, et al. 2019, 8.)

4.2 Chemical treatments

Generally, cellulosic fibres are dyed. Reactive dye is accounted for 50%, vat dye for 17%, indigo and sulphur for 7% of the use of dyes. Other dyes utilized are direct dye and naptoles dye. Depending on the dye type, the suited decolouring technique is selected based on the oxidation and reduction mechanism. (Božič and Kokol 2006.) The bright colour of textile is the consequence of the chromophoric system of reactive dyes, where the fasten properties of reactive dyes on cellulosic fibres are influenced, leading to moderate to good light fastness of dyeing. Covalent bond between the reactive dye and cellulose polymer are strong and stable. Dye molecule with two reactive groups cross-links two different cellulose chains. (Broadbent 2001, 339.) The benefit of using alkali reductive stripping process, which the strength and weight loss percentage increased. The study revealed that under optimal alkali conditions, bi-hetero type reactive dyes can be stripped out of the dyed cotton, made chance of releasing hydroxyl group, resulting in the strength loss of textile as well as high water absorbency. (Uddin, Mazedul and Rashedul 2015.)

Traditionally, bleaching is a prerequisite step acquiring high-quality white goods or if the textile will be dyed with pale bright colours. The original purpose of bleaching cotton is to whiten by decomposing yellow-brown pigment as well as removing the seed fragments. (Eren and Yetişir 2017.) In this process, the oxidation stage involves the emergence of O_3 and/or H_2O_2 treatments that occur after alkali treatment with NaOH. For PET/cotton, alkali treatment should be fulfilled at an elevated temperature to remove the presence of PET in the materials. It also causes the

mercerization of cellulose and decoloring to waste textile. Between stages, an optional refining is included, either before or after alkali treatment or before or after O_3 treatment to increase the available surface area of cellulose interchain. Both alkali reductive treatment and oxidation stages can be substituted by hot alkali extraction and applying hydrothermal activation with wetting agents, followed by enzymatic and acidic treatments. (Harlin, Määttänen, et al. 2018.)

The bleaching process with the aid of refining enlarges cellulose reactivity, modifies viscosity, removes impurities and ensures high-quality dyeing to manufacture cellulosic fibres. This step also restores the waste materials back to their original cleanliness, white state. Because dye is also a significant impurity in recycling process, it might alter the chemical characteristics and unpredictable behaviours according to the dye-type. Bleaching can be operated either before or after the spinning. The textile waste without prior bleaching would create the greyish – brownish shades in the spinning dope, then it is treated in the finishing stage by the conventional technique such as dyeing. Although the purpose of this technique is to create dark or back colour in the final textile, it is still not preferably suggested as a commercial product. (Määttänen, Asikainen, et al. 2019.)

4.2.1 Alkali treatment

During the step of stripping dye, alkali loosens crystalline structure of cellulose in addition to the amorphous as a swelling agent. Alkali solution is correspondingly known as an effective reactive agent, where the bonds of hydroxyl groups are released. By setting less than 2% of NaOH solution with hydrose ($Na_2S_2O_4$; reducing agent for the reduction of vat dyes and sulphur containing dyes) and experimenting at various ratio conditions at elevated temperature of 100°C for 20 minutes, the alcohol groups on the glucose unit of cellulose backbones present as a weak acid and ionized under alkali solution. Fabric strength loss takes place and increases accordingly to the elevated temperature in alkali condition. (Uddin, Mazedul and Rashedul 2015.) Another reductive agent for stripping bio-functional reactive dye is thiourea dioxide ($CH_4N_2O_2S$). The stripping is achieved at 4g/l and 8g/l of thiourea dioxide and hydrose, respectively. As stripping is a bond breaking process utilizing harsh chemicals, the adverse effect on quality of fabric is not thoroughly eradicated.

Therefore, the quality of cellulosic fibres is less damaged if an appropriate stripping agent is selected. (Ghosh, Fatema and Munni 2018.)

The alkali treatment can be followed through both at room temperature and elevated temperature and it is feasibly worked in a reactor having an anchor blade mixer. Especially, hot alkaline treatment is utilized in PET/cotton textile to withdraw PET and silicate, which are presented in recycled textile. Hot alkaline treatment sufficiently removes the reactive and direct dye out of the waste textile. These dyes are degraded in the alkali solution at high temperature hence the dye molecules are broken, causing to decolour the fabrics. The NaOH concentration lower than 2% is suitable for the dissolution of recycled PET in another process. (Määttänen, Asikainen, et al. 2019.) NaOH can hydrolyse the PET fibre surface at 90°C for the most favourable temperature, can remove some impurities as well as immature fibres and improve some fabric properties such as fabric pilling and absorbency. PET is gradually degraded in alkali solution by saponification of its ester linkages thus it results in a loss in weight of the fabric. To achieve the most stable and strong fibre condition for dying, the pH level is adjusted to 6 for a blend of PET/cotton. (Ibrahim 2014.)

4.2.2 O_3; H_2O_2 as oxidative treatments – bleaching chemicals

Oxidative agents are well-known chemicals for desizing cotton and they are applicable widely to various fabrics. (Karmakar 1999, 75) In addition, the oxidative bleaching treatment can adjust the brightness of colour cotton waste material, which improve the ISO higher than 80%. (Weilach, et al. 2019) The target intrinsic viscosity is 500 ml/g after decolouring when it is applied in the case of waste cotton pre-treatment. In the report of (Wedin, et al. 2018, 16), the intrinsic viscosity of cellulose is successfully improved, the ISO brightness though does not reach the desired commercial goal as shown in Table 2.

TABLE 2. Intrinsic viscosity and ISO brightness of pulps after decolourization (adapted from (Wedin, et al. 2018)).

Sample	Intrinsic viscosity (ml/g)	ISO brightness (%)
Dyed	490	68
Dyed and wrinkle free	470	73
Dyed and soft	510	68
Dyed, wrinkle free and soft	500	77

O_3 is known as a strong oxidizing agent having an oxidation potential of 2.07 V among other oxidizing agents (Powar, et al. 2020). Hence, it is feasible to oxidize both organic and inorganic compounds that the amount of energy, chemicals and water consumption are considerable (Eren and Yetişir 2017). Ozonation is one of the methods to degrade dyes that destroy the chromophoric system as well as eliminate the issues extend during the reaction (Sharma, et al. 2013). The oxidation stage can be executed with both O_3 or H_2O_2 to compare the decolouring yield to other pilot processes. However, when the practical case was completed, the efficient combination of O_3 and H_2O_2 with prior alkali treatment is greater when there was only O_3 or H_2O_2 before applying the alkali step. (Harlin, Määttänen, et al. 2018.)

The reaction mechanisms of ozonalytic decomposition followed by two possible degradation pathways: direct reaction consists of the attack the molecular O_3 and indirect reaction comprises of the free radical reaction mechanism. Both mechanisms occur simultaneously during the ozonation process. (Sharma, et al. 2013.) At the pH of 3, 98% of reactive dye is removed with 85 g/m^3 NTP O_3, at treatment time lasts for 30 minutes. Those parameters conclude the conventional O_3 treatment, where acidic pH contributes satisfying decolourization results and less mechanical damage. O_3 reacts directly in the molecular form at low pH. At higher pH, the ozone becomes more unstable because of the hydroxyl ions reaction, thus it creates free radicals. When pH is higher than 4, the occurrence of indirect oxidation mechanism prompts the great increase in discoloration kinetics. (Powar, et al. 2020.)

On the contrary, O_3 oxidative bleaching is preferably worked at pH 10 – 11 between 80 – 100°C for about 60 – 90 minutes. In addition to the oxidation stage, H_2O_2 is added preceding to the acidic washing treatment. It is also preferably conducted at pH 10 – 11 with temperature between 70 –

80°C for 30 – 60 minutes at 3 – 6 bar. The peroxide dose is recommended to be 5 – 15kg/otdp (ovendry ton per day) of wood. In the oxidative stage, it is also referable to employ a stabilizing agent such as silicate, complexing agents or Mg-salt. (Weilach, et al. 2019.) Above the pH of 10.8 and over 80°C, the formation of HO_2^- ions is rapid as a result of O_2 liberation and the bleaching power. In alkali medium, H_2O_2 will be decomposed into perhydroxy ion (OOH^-) in the alkali condition and generate nascent oxygen. (Patnaik and Patnaik 2020, 162,163.)

When treating O_3 under cold water of 30°C, the whiteness is higher than treating the pulp at temperature of 80°C. At the elevated temperature, the whiteness is affected by the poor dissolution of O_3. During the whitening process, desizing also takes place, as H_2O_2 causes desizing of cellulose at 95°C. Even though O_3 improves the whiteness of cellulose, it still removes less starch size than the conventional H_2O_2. Furthermore, the tensile strength of cotton is reduced during the oxidation process, in which H_2O_2 damages the tensile properties more than O_3. At higher temperatures, the cellulose-based fibres lose weight since the fibres are desized. The weight loss is dependent on the reaction time and high temperature. At the same reaction time, higher temperature results to more weight loss, which usually aids the extraction of impurities. (Eren and Yetişir 2017.)

4.3 Remove metals from waste cellulose-based textiles as acidic washing

The waste cotton is subjected to the acidic treatment to lower the metal content after the decolouring process. High content of silicate, calcium and magnesium originates likely from dust and sand. High content of metal particulates will negatively influence the quality in spinning dope. If the particle yield is high, the filtration system becomes completely blocked. And these tiny particles cannot be eliminated by filtration hence the acidic treatment is necessitated to augment the fibre quality in the spinning dope. The acidic washing technique (H_2SO_4) to remove metals in waste cotton, viscose and Lyocell textile, where pre- and post-customer waste textile are both reclaimed from. In the current invention, the pH value is modified between 1.5 and 5 at 100°C, preferably pH 2 – 3 at 50 – 70°C while the optimum time was between 15 to 60 minutes. During this process, the DP is preferably changed less than 5% compared to the initial DP. (Weilach, et al. 2019.) After washing metals remained in the waste cotton, the H_2SO_4 wastewater is used as hydrolysate in waste water system of the CCA production, where wastewater is neutralized after

washing out unwanted substances from the recycled cellulose-based materials (Kantola, et al. 2019).

4.4 Enhancing reactivity of cellulosic fibres by enzymatic treatment

Another method to desize cellulosic fibre is to apply enzymes. The starch-based sizing materials are not soluble in water and demand amylase enzymes for their removal. In comparison to oxidative agents, enzymatic treatment causes no damage to the cellulosic fibres. Accordingly, aggressive chemicals are not utilized in the enzymatic treatment, enzymes are highly biodegradable and they are widely used in diverse applications. (Hussain 2016, 6.) Enzymatic treatment aims to shorten cellulosic fibre waste by hydrolysis of cellulosic chains. The cotton, Lyocell and viscose fibres encounter weight loss, length changes and moister regain if the enzymatic treatment is applied. The cotton and Lyocell fibre notably obtain less weight loss yield than viscose fibre, the length of viscose fibres are shorter than Lyocell and cotton fibre. The moister regain in cellulose-based textile waste is reduced, yet the regain percentage is more diminished in viscose and Lyocell fibres. (Shojaei, Dadashian and Montazer 2015.)

Many different enzymes are applied to increase the reactivity of cellulosic fibre in cotton, viscose and Lyocell. The starting material is dissolving pulp, which is treated with a mono-component C-type endoglucanase according to Engström, Ek and Henriksson in 2006. To acquire a homogenous enzyme distribution, it was added in phosphate buffer before the buffer is added into the pulp. The intention is to modify the never-dried pulp to neutralized state, when the pH is 7, the final pulp concentration is 3%. The enzymatic incubation is carried out in a bath for less than 20 minutes (usually 10 minutes for mostly 100% pulp reactivity) and periodically taken out of bath and kneaded to mix for 10 – 15s. To deactivate the enzyme, the sample is washed and filtered on Büchner funnel by deionized water at 90°C and transferred to 80°C water bath. (Engström, Ek and Henriksson 2006.)

The reactivity of cellulose is determined by Fock's method and normally applied in viscose pre-treatment to obtain the optimal effect of dissolving pulp. The enzyme attacks on amorphous regions between the crystalline microfibrils, which contributes into swelling. Endoglucanase

generally attacks on the less ordered region of the fibril surface. The endoglucanase preferably breaks down amorphous rather than crystalline cellulose and splits the cellulose at random within the chain. Hence, the endoglucanase treatment causes swelling of the cell wall since the amorphous regions exist on the surface and between the microfibrils. (Engström, Ek and Henriksson 2006) The enzymatic treatment goes beyond the ordinary CCA activation, whereby cellulose pulp is activated by alkaline, hydrothermal and enzymatic activation prior to the reaction between the cellulose pulp with aqueous urea solution. Especially, water presented in urea is replaced by organic liquid carrier. The molar ration of urea to endoglucanase units is 0.25:1 – 3:1, which a virtually stoichiometric ratio is more preferred. (Struszczyk, et al. 1999.) The enzymatic treatment is used to adjust the DP, provide a pre-version of BioCelSol fibres in surplus of a mechanical treatment, and enzymatic treatment is usually applied prior to the H_2O_2 treatment and subsequently to the alkali treatment. (Määttänen, Asikainen, et al. 2019.)

4.5 Applying modified environments

Traditionally, an alkali solution is used to reduce cellulose DP reduction. However, irradiation can either be carried out at the cellulose mill at the drying phase or at an earlier phase of the CCA process. The production of CCA from cellulose in web form and urea with the liquid NH_3 additive is exposed to a radiation dose of preferably 0.5 – 10 Mrad from a radiation source. (Turunen, Mandell, et al. 1984.) Or else, hydrothermal under urea/cellulose reaction can improve the solubility of the mixture in alkali aqueous (Gan, et al. 2017), and/or combined with enzymatic treatment, intercalation with urea in aqueous solution (Struszczyk, et al. 1999). The modified environments also involve the reactivity enhancement by adding liquor prior to the cellulose/urea reaction, which is collected through distillation and can be reused. (Hermanutz and Oppermann 1996.)

4.5.1 Hydrothermal activation

Under hyperbaric pressure, cellulose pulp suspension is heated at the temperature range of 100 – 170°C in water or methanol. The reactivity of cellulose is enhanced after the pulp is reacted in hot compressed water. (Ciechańska, Wesołowska and Wawro 2009.) For example, cellulose is mixed

with water with a catalyst for 0.5 – 10h at 120 – 160°C and 5 bar. The catalyst can be e.g organic and/or inorganic acids as well as organic salts of an inorganic and/or organic acids, which directs the activation process and the degradation. The hydrothermal activation controls the polydispersity of activated pulp to be less than 2.7. (Struszczyk, et al. 1999.) The hydrolysis treatment is employed hydrothermally as an intermediate during the cellulose/urea reaction and resolution for CCA production after washing unreacted urea in the cellulose/urea mixture, where washed and dried CCA obtains an average DP of 400. The hydrolysis treatment can be carried out with acidic liquid (1-2 N hydrochloric acid) under autogenous pressure and at temperatures above 100°C. The upper limit of the hydrolytic action on the cellulose carbamate is a decrease of the N content of 50% of the initial value. The intensity of this treatment is also selected based on the enhancement of the CCA solubility and the reduction of DP might be dispensed to an additional step to regulate its number, which is not lower than 200. The further advantageous factors regarded to the hydrolysis treatment of CCA. CCA product quality is specifically improved including the decrease of insoluble particles associated with the amendment of filterability and the change of rheological characteristics of the solution. (Schleicher, et al. 1994.)

4.5.2 Substituting alkali pre-treatment by irradiation

In this operation, starting cellulose is dosed by irradiation between 0.05 – 10 Mrad to diminish the DP to an appropriate level. DP level is modified by time and intensity of the irradiation. These factors are not selected because of the economic consideration. It can be an alternative method to eliminate multistage process of alkali treatment. The regulation quality or the properties of requisite CCA utilized for the preparation of the end product, is controlled by the ultimate end product of CCA. This technique therefore contributes to the flexibility of the overall CCA fibre. (Selin, et al. 1985) Irradiation perfects the non-soluble cellulose in web or in form of loose fibre. It is feasible to treat CCA in the prior step to shape the continuous web to simplify the CCA process. Ionization radiation is utilized in this patent, comprising gamma radiation and electron rays, where the conventional apparatus can apply either gamma radiation or electron rays in the procedure. (Turunen, Mandell, et al. 1984.) An original gamma emitter is defined as an electromagnetic radiation, or photons, consisting of radiation shield, to transport arrangement for the emitted materials cobalt-60 operated as an irradiation source. Meanwhile, electron radiation

conventionally involves a tungsten filament cathode to generate electrons, in which an electron field with the support of vacuum can produce electron irradiation at range between 0.1 – 4 MeV. (Selin, et al. 1985.)

4.5.3 Additional liquor (Hermanutz and Oppermann 1996)

Hermanuts and Oppermann (1996) proposed in their patent that an alcohol should be applied in the washing step prior to cellulose/urea reaction and be subsequently distilled off the solution. Cellulose ester at 5 – 80°C with DS of 0.1 – 0.4, preferably 12 – 30 wt%, is swollen in alkali or alkali metal hydroxide, preferably 16 – 22 wt%. After being rinsed with alcohol, the moist-cellulose alkali mixture can directly react with urea at around 140°C, or be substituted in pure acetic anhydride or propionic anhydride, and washed with water, dried and then reacted with urea. Cellulose treated by this method is completely de-crystallised, and hence the urea reactivity is extended. The excess alkali solution is squeezed then rinsed with a fresh liquor (methanol) and separated via distillation. For suspended alkali cellulose, methanol is collected by filtration while the mixture is being pressed dry. If the cellulose would react directly with urea, the suspended alkali cellulose is also treated by methanol to react with urea and distilled off. The remaining alcohol acquired in cellulose pulp after the reaction between cellulose and urea is distilled afterwards at the temperature range between 135 – 150°C and can be recycled.

5 CCA FORMATION

Cellulose carbamate is an ester of cellulose and carbamic acid, and typically is the product of cellulose and urea reaction (Vo, et al. 2010). It is also a stable derivative of cellulose that is soluble in alkali solution and conventional organic solvents (Gan, et al. 2017), at a DS of 0.1 – 0.3 (Valta, et al. 2011). The reaction between cellulose and urea results in CCA formation, which can be stored after washing and drying, or used directly to the dissolution (Selin, et al. 1985). The dissolution solution is spinnable in diluted acid or alkali solutions to produce CCA fibres or regenerated cellulose or the mixture of the two (Vo, et al. 2010). So, carbamate process does not require any special organic solvent or impacts negatively the environment (Huttunen, et al. 1983). CCA is a potential alternative to petroleum based-polymer, which can be spun into filaments, membranes, sponges, foils and other products (Vo, et al. 2010). Figure 7 is drawn to display the various methods that possibly improve the carbamation performance, but the chosen additive to the mass balance for cellulose/urea reaction is H_2O_2 and kneader.
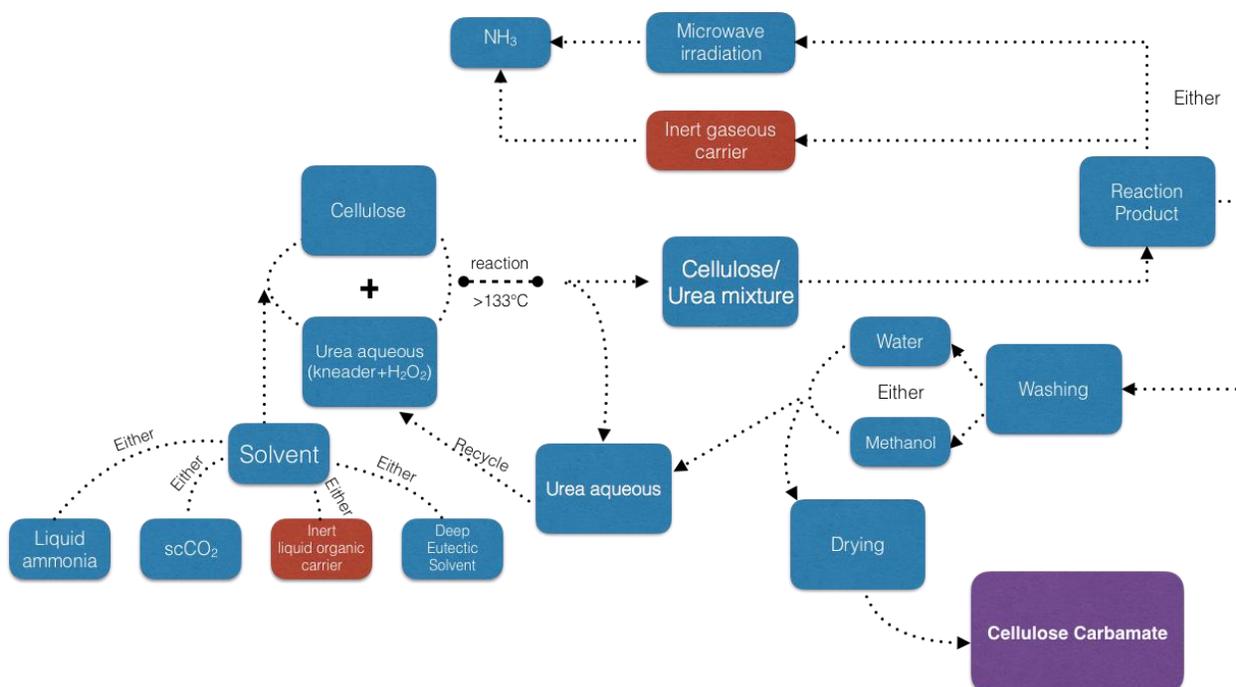
FIGURE 7. The cellulose carbamate formation route .

5.1 Carbamation with urea

The CCA product is made from a heterogeneous reaction between cellulose and urea reaction at high temperature above the urea melting point (>133°C). Overall, the formation of CCA is not theoretically complex, beyond functions as an alkali soluble cellulose derivative. The practical applications are still under development. (Klemm, et al. 1998, 161.) In the repeating cellulose unit, hydroxyl group at C6 position mostly reacts with isonyanic acid (HNCO; a colourless substance that is volatile and poisonous) as shown in Figure 8, and some other hydroxyl groups substitution occur at C2 and C3. Among HNCO sources, urea is selected because it is the least inexpensive chemical. (Kotek 2007, 703,704.) The initial purpose was to avoid gelling in such solution on standing by aqueous caustic alkali solutions of low substituted cellulose derivatives (Schreiber 1938).
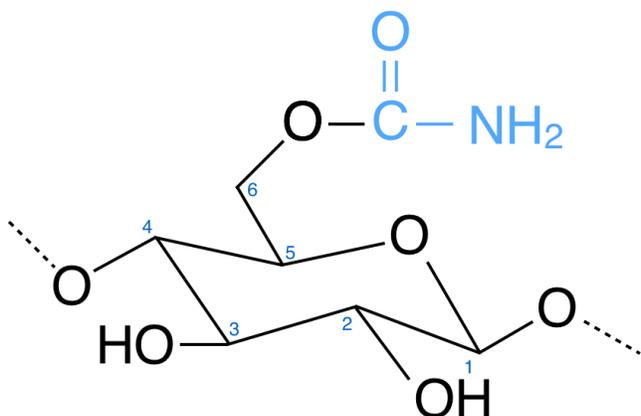
FIGURE 8. Cellulose carbamate molecules (adapted from (Hummel 2015)).

The initial knowledge of urea activation began with Hill and Jacobson (1938). The product of cellulose and urea solutes in an aqueous caustic soda that are useful for spinning filament and sizing textile. This cellulose derivative generally contains 1 – 2.5% of N and it exhibits many of the properties of the other low-substituted cellulose derivatives such as alkyl cellulose ethers. The new cellulose derivative was prepared as steeping cellulose such as wood pulp or cotton linters with at least 15% of urea aqueous. (Hill and Jacobson 1938). Recently, Saxell, Ratamäki and Ekaman (2017) have researched that the cellulose prepared as the never-dried pulp is more active than dried pulp when reacting with urea. Once the cellulosic fibres are dried, the fibres change irreversibly their properties as the internal volume of the fibre shrink. This phenomenon is known

as hornification. Never-dried fibres are hence fibres that not have been dried, so those are non-hornificated fibres. The never-dried pulp is operated with 8% consistency of cellulose and diluted into 35% solid content in the cellulose/ urea mixture with other additives or/and auxiliary agents. It shows that using smaller urea dose for never-dried pulp is much more efficient compared to for dried pulp. (Saxell, Ratamäki and Ekaman 2017.)

The schematic carbamation reaction and urea by-product formation is presented in Figure 9. When urea approaches its melting point, it starts to decompose and form NH_3 with HNCO. The most significant formation of HNCO is alkali-soluble-cellulose compound when HNCO decomposes and reacts with cellulose. At elevated temperature, HNCO has a chance to attach hydroxyl group of cellulose in surplus of uniform DS, then a soluble product is made. HNCO tends to be unstable and becomes trimerized to HNCO and reacts with urea to create biuret. Other significant concern is that the solubility adjustment of urea in liquid NH_3 will be increased along with the temperature rises. (Huttunen, et al. 1983.) The gathered NH_3 gas in the addition of CO_2, which can be obtained from the flue gas stream, can be utilized as reactants under elevated pressure in an urea synthesis tower or reactor for the production of urea. (Ennenbach and Koss 2013.) Another resolution is that the formed NH_3 can be removed from the carbamation reaction to reduce the nitrogen oxide emissions if it is integrated with a pulp mill flue-gas system. NH_3 can be in gaseous form or in dissolved solution form when it is treated with nitrogen oxide. (Kantola, et al. 2019.)

Cellulose carbamate
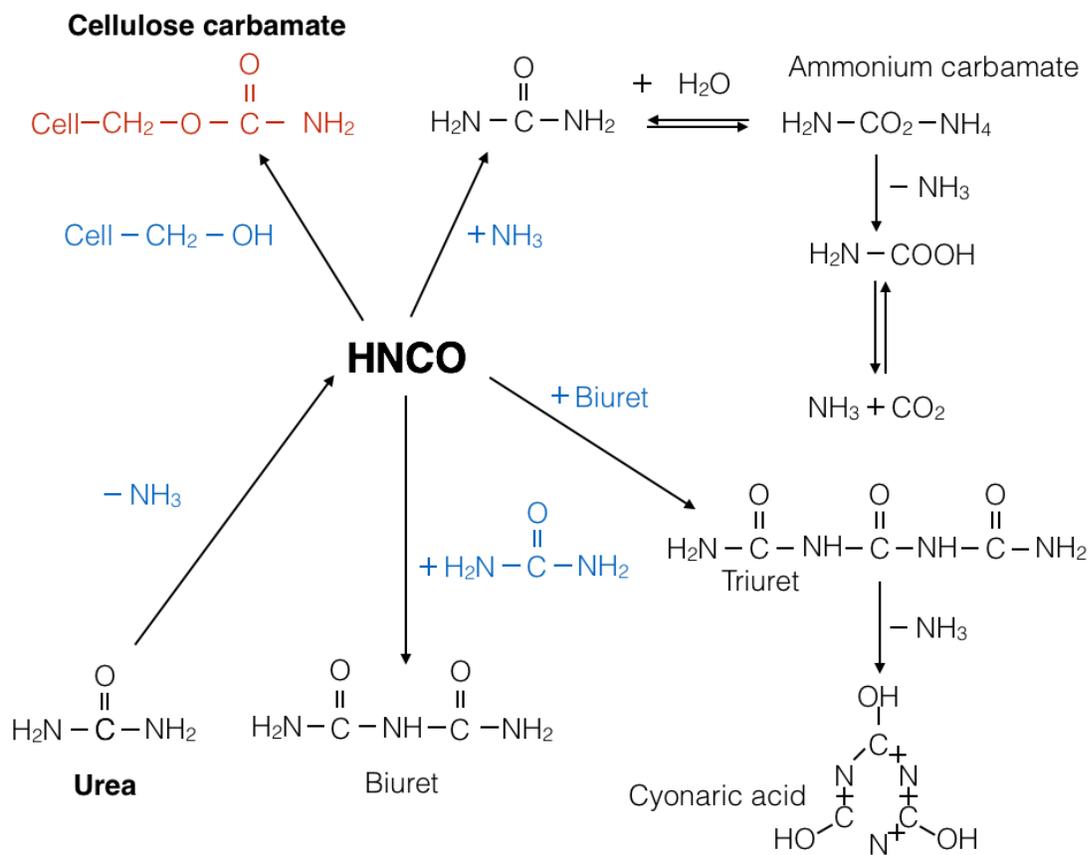
FIGURE 9. Schematic chemical reactions of urea and carbamation (adapted from (Kotek 2007), (Harlin, Cellulose carbamate: production and applications 2019), (Ennenbach and Koss 2013)).

5.2 IR spectrum of CCA

As can be observed in Figure 10 and Figure 11, CCA and ordinary cotton linter (CL) obtain almost the same line in IR spectrum except the absorption band around 1710 cm^{-1} in the CCA. This new band is based on the carbonyl stretching vibration in the urethane groups. The 1710 cm^{-1} band diminishes mildly when applying CCA technology and increased due to the increased amount of N in the CCA. In Figure 10, (1) demonstrates the IR spectra of cotton itself and (2) displays spectra of the CL swollen in NaOH solution. The relative absorbance of hydroxyl group at 3420 and 1035 cm^{-1} in Figure 10, the treated CL in alkali solution is higher than the untreated ones. Therefore, it is stated that the relative absorbance of hydroxyl group bands at 3421 and 1035 cm^{-1} decrease while the N content is increased. These specifics can be comparable to the growth of urea reactivity with the primary hydroxyl group in the cellulose chain. (Nada, Kamel and Mohamed 2000.)
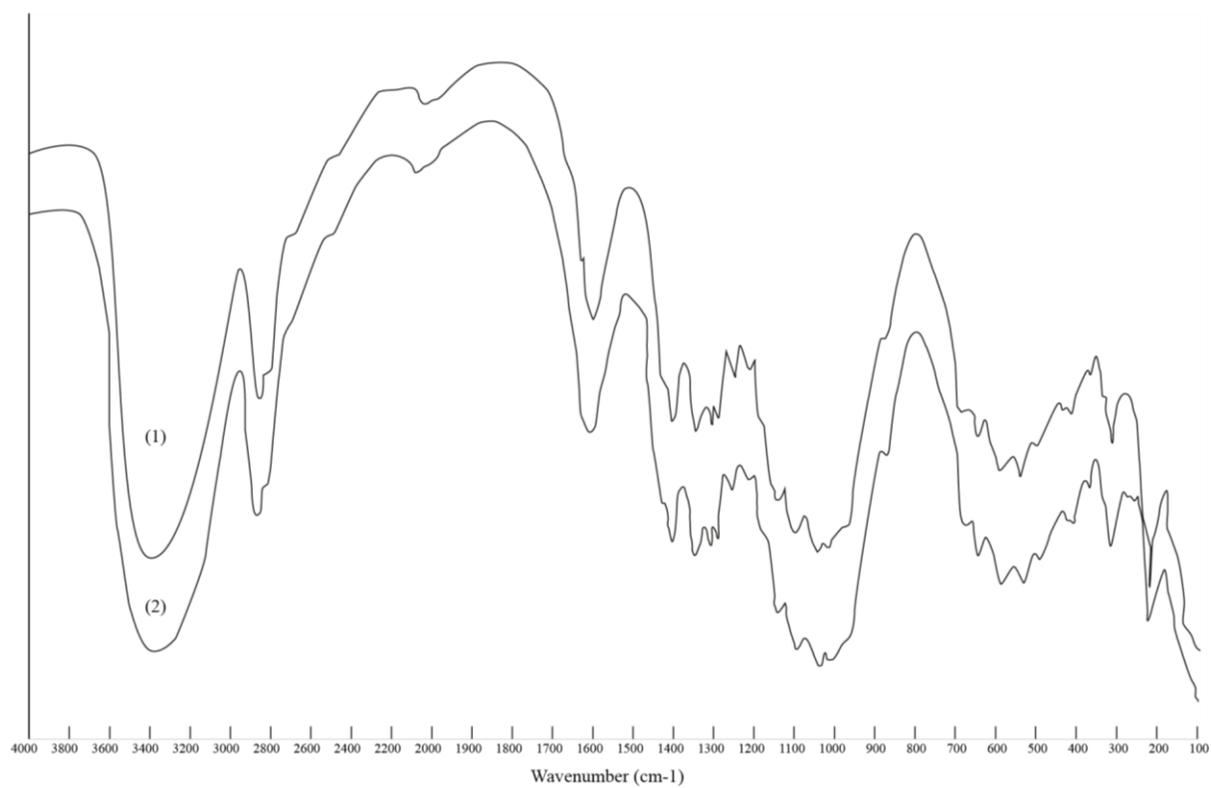
 FIGURE 10. IR spectra of cotton (1) and cotton swollen with sodium hydroxide (2) (adapted from (Nada, Kamel and Mohamed 2000)).
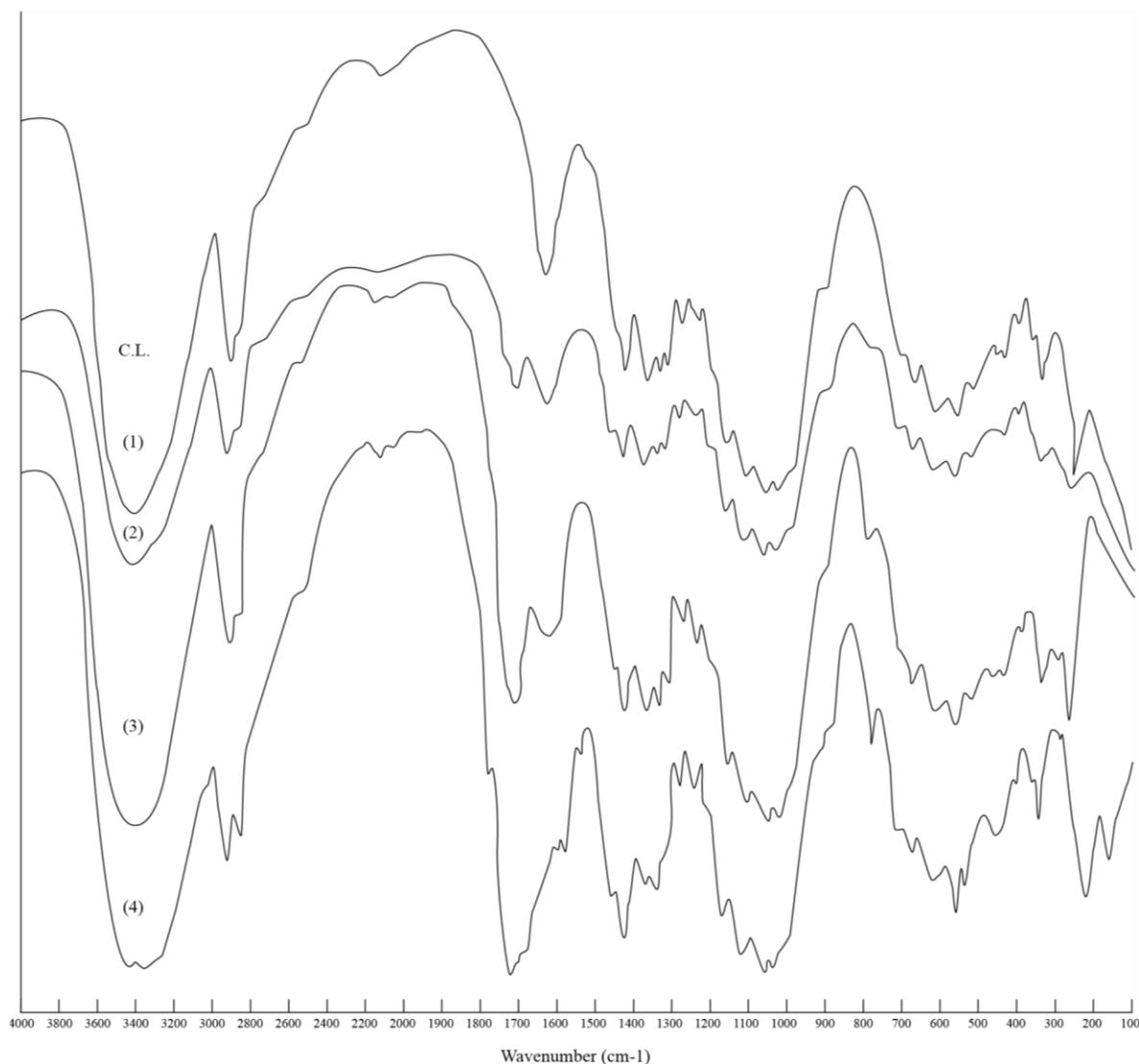
FIGURE 11. IR spectra of cotton (1) and cotton carbamates of different N content. (2) 1.29%N; (3) 3.28%N; (4) 8.29%N (adapted from (Nada, Kamel and Mohamed 2000)).

The minor and major decomposition temperature of the treated cellulose is lower than the untreated ones. It is ascribed to the rise of swellability of swollen cellulose upon the growth of the amorphous or disordered region in the cellulose chains, which decomposes quicker than the crystalline region. According to Figure 12, the swelled cellulose obtained lower endothermic peaks than untreated CL. It is then appropriately higher in disorder structure content in the swelled CL thence it leads to the rapid decompose of CL, which can be calculated from the crystallinity index. Furthermore, the maximum decomposition of CCA depends on the N content that the decomposed temperature

is relatively lower than CL's. (Nada, Kamel and Mohamed 2000.) In a different study, the X-ray crystallography sample of CCA also indicates that the higher urea content, the lower of crystallinity index of the CCA membrane. The crystallinity index and morphology therefore are influenced by the urea amount and solubility of CCA. (Gan, et al. 2017.)
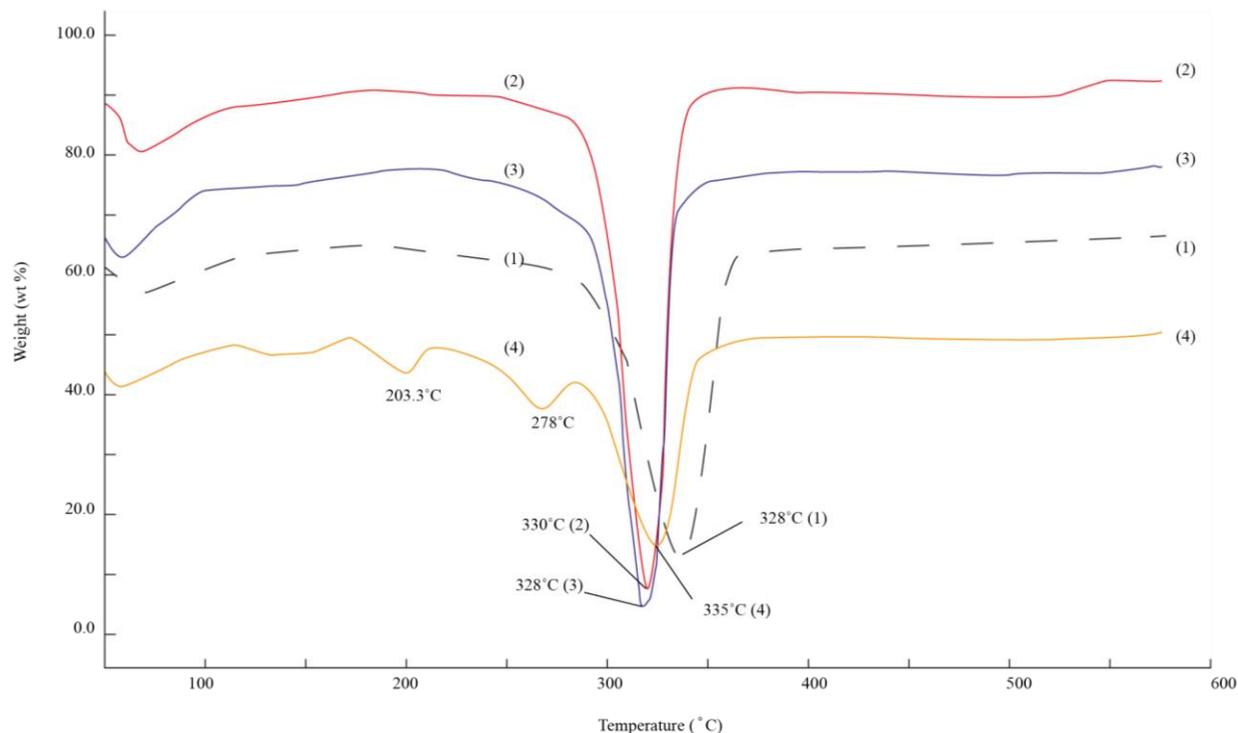
FIGURE 12. DTA curves of cotton (1) and cotton carbamates of different N content. (2) 1.29%N; (3) 3.28%N; (4) 8.29%N. (adapted from (Nada, Kamel and Mohamed 2000)).

5.3 Degree of Substitution and degree of Polymerization of CCA fibres

Because CCA contained hydroxyl groups in the repeating unit are substituted with carbamate groups. The DS in surplus specifies the average amount of substituted hydroxyl groups per AGU. (Chunilall, Bush and Larsson 2012.) The carbamate group also includes the N atoms, hence the DS relates to the value of N content in the carbamate groups that substitute hydroxyl groups, which can be calculated using the formula (1) (Vo, et al. 2010):

$$DS = \frac{M_{AGU} \times N(\%)}{M_N \times 100 - 43 \times N(\%)} \tag{1}$$

Where M_{AGU} is the molecular weight of the (AGU) = 162, M_N is the molecular mass of N atom = 14 and 43 is the net increment in the AGU for every substituted carbamate group, and N(%) is the N content of modified cellulose determined by elemental analysis. Hence, in the synthesis of CCA, N increases due to the increase of DS with the length of reaction time. (Vo, et al. 2010.)

The solubility of CCA in alkali solution is determined by the DS of cellulose. The increase in the DS of CCA subsequently decreases the crystallinity of cellulose because the hydroxyl groups are substituted, and the density of hydrogen bonds is reduced to permit the dissolution of CCA in alkali solution. (Sirviö and Heiskanen 2017.) Still, a high DS does not always guarantee satisfied distributed solution with NaOH in dissolution if the distribution of carbamate groups along the cellulose backbone is not uniform. CCA is obtained at a small DS range of 0.15 – 0.25 (or more), which corresponds to N content of 1.2 – 2.0% in the CCA. (Määttänen, Vehviläinen, et al. 2018.) If the DS exceedingly increases, a growing tendency of crosslink formation counteracts the solubilizing action of the hydrophilic substituents, which is against the improvement of CCA solubility (Klemm, et al. 1998, 161).

Because cellulosic fibres are generated for various applications, it is essential to modify DP for each particular purpose (Selin, et al. 1985). The average DP of the native cellulose is decreased approximately to 1000 – 350. By controlling this DP level, the following spinning step would minimize the mechanical issues. In detail, the tensile strength of fibre varied from 290 to 480, for instance 430 would specify the optimum tensile properties. (Coley 1953.) In another embodiment, the DP also regulates critically the viscosity of the end product. In Table 3, the strating mateirals such as cotton or wood-based cellulose are commonly resulting such a high viscosity and low cellulose content in the solution. To achieve high content of cellulose product, for example 18% of NaOH is added to adjust the DP level, at the desirable point of DP, the process is cut off by wash the pulp with water and dried. Or the DP is modified by the influence of oxygen and air after alkali aid. (Huttunen, et al. 1983.) DP is determined through the intrinsic viscosity of CCA, which is represented in the formula (2) (Vo, et al. 2010):

$$\eta = 4.85 \times DP^{0.61} \tag{2}$$

Where η is intrinsic viscosity of CCA

DP is degree of polymerization

α is constant, $= 0.905$.

The intrinsic viscosity of CCA is calculated by the equation: (Vo, et al. 2010)

$$\eta = \frac{(\eta_{rel}-1)/c}{1+k\times(\eta_{rel}-1)} \qquad (3)$$

Where η (ml/g) is the intrinsic viscosity

c (g/ml) is the concentration of CCA in the solution

k is constant, $=1.33$

η_{rel} is relative viscosity

The relative viscosity, which can be determined by the formula below: (Vo, et al. 2010)

$$\eta_{rel} = \frac{t}{t_o} \qquad (4)$$

Where t is the efflux time of the solution

t_o is the efflux time of the solvent

TABLE 3. Molecular weight parameters (DP_w and DP_n) and polydispersity (DP_w/DP_n) of cellulosic fibres (adapted from (Bredereck and Hermanutz 2005)), w and n relate to the weight and number averages, respectively.

Fibres	DP_w	DP_n	DP_w/DP_n
Dissolving Pulp	1500	172	8.7
Alkalicellulose (after pre-aging)	410	171	2.4
Viscose	348	145	2.4
Tencel	708	181	3.9
Cotton	3345	328	10.2

5.4 Alternative options to improve urea/cellulose reaction

As shown in Figure 7, the urea/cellulose reaction performance is essential to be enhanced for more profitable and efficient values. The additional solvents and microwave irradiation enlisted below would assist the reaction whether they function in the urea preparation step or both in the urea solvent, and remove NH_3 by-product for further reuse in the washing step. The other supplemental methods have been developed to minimize reaction time, and increase both the quality and product yield. The supplemental methods applied such as inert liquid organic carrier, $scCO_2$, DES and auxiliary agent are also included in this section.

5.4.1 Liquid NH_3

Liquid NH_3 is one of the techniques improving the performance of carbamate technology. In this supplemental method, the reaction between urea and cellulose occurs in an organic liquid in which urea is substantially insoluble. This reaction produces cellulose carbamate, which acts as an intermediate and is able to solute in alkali solution. This technique is found with numerous problems about the organic solvent that purification and recovery of waste water connection are the main matters. Cellulose reacts with urea dissolved in liquid NH_3, which is performed as a medium and the mixture are together heated at 135°C. The NH_3 liquid penetrates cellulose through its crystalline element with dissolved urea. This advantage is extremely beneficial to the cellulose/urea reaction because of the DS uniformity, which requires urea/cellulose ratio of 0.5 – 3. The DS of CCA product are essentially uniformed to reach the perfect state of solubility. Even though the DS is low, a uniform penetration can cause a readily soluble solution. Excessive urea used would be consumed and lost in side reaction. The quantity of urea used relates to the reaction time and temperature. The steeping time required normally varies from few minutes to 10 hours. (Huttunen, et al. 1983.)

During the reaction of cellulose and urea with the appearance of liquid NH_3, the temperature is lower than the actual reaction in the aim of distributing urea throughout the cellulose. The NH_3 is then withdrawn by evaporation, and leaves cellulose with urea at heating temperature forming cellulose carbamate. NH_3 liquid is not only eco-friendlier than organic solvent, but it is also simpler

in recovering steps for all unused reactants. When the NH_3 is removed, the cellulose reacts with urea at elevated temperature not lower than 110°C but not necessarily higher than 150°C for at least 1 hour. (Huttunen, et al. 1983.) Urea are left with cellulose as a residue through cellulose. Liquid NH_3 is preferably recovered and reused by vacuum evaporation and/or heating. The reaction of urea and cellulose is accomplished once it is washed by methanol several times before being dried. The mixture can be washed also by liquid NH_3 to advantageously covert biuret into urea for reuse. (Huttunen, et al. 1983.) Instead, water extraction can be used in the washing step with methanol (Selin, et al. 1985) since cellulose carbamate is not soluble in water so the by-products can be collected. Afterwards, CCA is dried and transported or stored or both for a long period. (Kotek 2007, 707.)

5.4.2 Inert liquid organic carrier

In this alternative CCA is produced based on the conversion of excess urea with inert liquid organic reaction carrier at 130 – 160°C temperature range. This technique tackles the recycling matters of excess urea in the carbamation process. During the CCA formation, the organic reaction carrier and the aqueous liquid exchange before and after the conversion because of the disturbance of water in CCA process. CCA/urea reaction requires excess urea and it is washed by methanol and water. However, the treatment demands low temperature since the boiling point of NH_3 is –33°C. The CCA/urea mixture needs problematically controlled techniques, where required resident time and concerned capacity of reactors in the process would enlarge the financial issues. If NH_3 and water still remain in the urea aqueous after washing, it should not be reused. The addition of inert liquid organic carrier therefore is involved in urea solution. And the by-product NH_3 is removed with the aid of inert gaseous carrier, resulting in the withdrawal of the utilized liquid NH_3 and washed free urea. (Arnold, Butzke and Keunecke 1995.)

With the support of inert organic carrier, the water is evaporated with a portion of organic carrier. The inert gaseous is generated by boiling the reaction carrier in the reaction zone, which is to transport agent for removing NH_3 formation in the CCA reaction. Preferably, the inert liquid organic reaction carrier is an aliphatic hydrocarbon or alkyl aromatic hydrocarbon that the sum of carbon atoms in alkyl group is in the range of 1 to 4, or a mixture obtaining boiling temperature

between 90 and 185°C atm. The improvement of CCA solubility by utilizing a plurality of reactions that the reaction temperature of each subsequent reactor is 5 to 30°C higher than the previous reactor. (Keunecke 1998.) In the case of Arnold, Butzke and Keunecke in 1995, organic reaction carrier is xylene or toluene. Urea is added into xylene or toluene as reaction carrier in granular form. As being insoluble in xylene, urea obtains low conversion rate, even with stirring. Xylene or toluene thus is vapoured and possibly drawn off the reactor. In an economic objective, the exchanges of organic carrier are carried out by those steps: the first portion of organic carrier is removed mechanically and the remaining product is mixed with aqueous urea solution. Then the remaining reaction carrier is vaporized together with a portion of water in the aqueous urea solution. CCA product is driven off the urea solution, the other CCA with solid urea and some undesirable biuret formations, are washed by water. (Arnold, Butzke and Keunecke 1995.)

Carbacell technology is a special process to synthesize CCA and it was introduced by Fraunhofer IAP, which characterizes the homogenous and smooth fracture surface (Fraunhofer-IAP 2000). In this process, xylene functions as an inert organic carrier (Volkert, Lehmann and Hettrich 2014, 426). It is advantageous in retaining the use of the viscose spinning technology while eliminating the utilization of hazardous sulphur-containing compounds for derivatization. Cellulose materials are first alkalized and pre-ripened with the occurrence of partial chain degradation. CCA is then obtained from the alkali cellulose in xylene (as a transfer medium) and result in being dissolved in NaOH solution. (Fu, et al. 2014.)

5.4.3 Supercritical CO$_2$

In this technique, urea is impregnated into the cellulose pulp by supercritical CO_2(scCO_2) as solvent and carrier, followed by the esterification of cellulose. scCO_2 is eco-friendly, clean and more affordable than other fluids and recovered easily after being utilized. It has low viscosity, and its density and dielectric constant change rapidly accompanied by temperature and pressure. (Yin and Shen 2007.) scCO_2 performs both the property of gas-like diffusivity and liquid-like density in a supercritical phase. This solvent thus is applied among several processes in the polymer industry (Nalawade, Picchioni and Janssen 2005), and also assisted CCA synthesis (Zhang, et al. 2013).

The solubility in green solvent scCO$_2$ of urea is enhanced by ethanol. The reaction is conducted in high-pressure chemical reactor. Urea and cotton cellulose are placed in the upper part of the autoclave while ethanol is placed in the lower part to avoid contacting each other. CO$_2$ is also introduced twice into the autoclave until vapour–liquid equilibrium is reached. In the reaction, the temperature of autoclave is 150 – 170°C with the pressure range is between 2600 – 3200 psig and the reaction lasts from 2 to 10 hours. The product at that time has high N content and inherent solubility. The mixture is taken out from the autoclave and cooled down, it is followed by washing with an excess of warm water at 60°C until the washed water is neutral. (Yin and Shen 2007.) Since scCO$_2$ swells cellulosic fibres, the accessibility of cellulose therefore is expanded towards esterification. The cellulosic fibres production can eliminate contamination and toxicity thanks to this technique. (Zhang, et al. 2013.)

5.4.4 Deep eutectic solvent

Since the green chemistry has been setting new targets to upgrade industrial chemical process for cellulose versatile modification, IL is considered as an optimal option in wide range of applications despite its unsatisfied biodegradability and hazardous toxicity (Willberg-Keyriläinen, Hiltunen and Ropponen 2017). ILs are constituted from systems composed primarily of one type of discrete anion and cation. Otherwise, among IL analogues, deep eutectic solvents (DESs) are now broadly noticed as a new class since they share many characteristics and properties with ILs. DESs are systems formed from an eutectic mixture of Lewis or Brønsted acids and bases that can include a diversity of anionic and/or cationic species. It means that DES and IL obtain similar physical properties yet DES chemical properties prefer distinguished requisition. (Smith, Abbott and S. 2014.)

DES mixture comprises of a at least two components and a hydrogen bond donor and a hydrogen bond acceptor (halide salt) obtaining the low melting point than individual component (Willberg-Keyriläinen, Hiltunen and Ropponen 2017), because of the low lattice energy of nonsymmetric ions. For instances a common mixture is urea as hydrogen bond donor (melting point 132°C) and chlorine chloride as hydrogen bond acceptor (melting point at 302°C) creating a mixture with melting point of 12°C. DES possesses many beneficial influences such as affordability and ease

of preparation as well as less chemical inert generally. So, DES is significantly emerging as an appropriate media for the shape-controlled synthesis of nanoparticles that could be crucial in applications such as electrocatalysts, electrochemical sensors, air batteries, and fuel cells. (Smith, Abbott and S. 2014.) By applying selected DES in urea as solvent, CCA preparation does not acquire additional solvent at low temperature. N% is adjusted by tuning consistency temperature according to Kjeldahl method and N% increases from 5 to 20% due to the cellulose consistency increase. Beyond urea/ chlorine chloride, urea/betaine and urea/betaineHCl also modify N%, where highest N content belongs to urea/betaine DES system. DES loosens the cellulose crystallinities when CCA reaction use 20% of cellulose consistency and high-consistency reactor. CCA yield is endowed upon high N content. Urea prepared with chlorine chloride in ratio as 2:1 and 4:1 at 120°C are relatively higher than other ratios at lower temperature. (Willberg-Keyriläinen, Hiltunen and Ropponen 2017.)

5.4.5 Microwave irradiation (Guo, et al. 2010)

During the last decade, microwaves have been using as a non-conventional form in synthesis chemistry. Microwave can penetrate and heat the particles simultaneously to lower the heat transfer issues and provide rapid non-contact heating and better control over the heating process., This work synthesizes CCA under solvent and catalyst-free after drying cellulose/urea mixture for 2 – 5 minutes at 255W. The NH_3 gas produced is absorbed into an acidic solution. Being dried under vacuum, the white or slight yellow samples are collected. The microwave irradiation thus assists the CCA production to be a greener process. If the mixture is pulsed at low power level (170W), it will elongate the mixture reaction time. Under other conditions, the product is accompanied with carbonization and cross-linking at too high energy level (425W), drawing to poor-quality products. This technique shortens the reaction time from hours to minutes, which is a great improvement in CCA production. Moreover, the microwave-assisted reaction provides a possibility to operate in an open vessel thus the high pressure is eliminated, and the reaction can be up-scaling.

5.4.6 Auxiliary agent

Alongside additional solvents in urea/cellulose reaction, alkalization agent also acts as an auxiliary agent such as alkali metal hydroxide (sodium hydroxide or magnesium hydroxide) or H_2O_2, NH_3 or enzyme (Saxell, Ratamäki and Ekaman 2017). It is unnecessary to add other chemicals except a modest water as a medium (less than 40% to mechanical working). H_2O_2 is partially or totally replaced with alkali metal hydroxide before urea, at the same time or after urea. An additional mechanical device is an essential factor in this technique that lets auxiliary agent absorption activate the fibre and extend urea penetration by opening fibre pores and infiltrating liquid into fibres. The homogenous stage of chemical pulp, the penetration of the chemical into fibres, the DP adjustment and the pulp crystallinity reduction and partly also the reaction are induced by mechanical working. Urea aqueous solution is premixed with auxiliary agent in cellulose in atomized form. Due to high dry content, the mixture can be transferred to elevated temperature passing the drying step to complete cellulose/urea reaction. The drying and reaction relies on the temperature and time adjustment. Nevertheless, this patent is limited to laboratory scale and remains numerous matters from the residue organic auxiliary agent recovery, the product homogeneity, the high operation expense to the properties of end-product. (Valta and Sivonen 2010.)

6 DISSOLUTION OF CCA

Aqueous NaOH has been studied as a solvent to dissolute CCA formed in urea solution. The dissolution mechanism basically is similar to the mercerization, which soda hydrates can penetrate the amorphous area of cellulose, destroy the neighbouring crystalline area. For low to moderate DP of cellulose, the highest solubility happens at 8 – 10% soda solution. (Zhao, Deng and Wang 2007.) The prepared NaOH in the dissolution is feasible to be recovered with electrodianalysis technology with H_2SO_4 used in the coming coagulation bath. The chemicals are recycled if the CCA is washed before the dissolution, and unreacted urea can be recovered and reused. (Fu, et al. 2014.)

The conventional technique takes 2 hours for the completely mixed solution, yet it is shortened to few minutes when applying the new dissolution procedure. In the typical method, the first step is carried out by using NaOH solution that is stronger than the final solution, and the next step is diluted with water and/or an aqueous NaOH solution. However, the novel technique has been studied recently, which shortens the mixing time from hours to few minutes. The new dissolution method is performed in 2 batches: 1% of the NaOH solution is premixed including free water and cooled down to 0°C. The CCA powder is added to the solution to create a moist CCA pulp. In the next step, 18% of NaOH is dosed into the dissolving mixture. The solution has been pre-cooled to the temperature about – 20°C and the final temperature is set at – 6°C. The final content of NaOH in the solution involving CCA is approximately 8%. This method is a novel invention to prepare dissolution for spinning dope. (Valta, et al. 2011.) It is first vital to identify the properties and mechanism between NaOH and cellulose. The principles involve the mechanism of swelling to dissolution, the stability and temperature influences on CCA fibre prior to the spinning dope.

6.1 From mercerization to dissolution mechanism

Mercerization is ordinarily achieved by immersing the solid cellulose in NaOH solutions with or without mechanical tension prior to the dissolution (Duchemin 2015). The earliest invention was proposed by John Mercer already in 1850, who treated cotton clothes with 20% NaOH solution

and subsequently washed the cellulose, and the process was completed without any tensions. Later in 1890s, the material was held under tension during the treatment until most of NaOH had been washed out. Therefore, the process has no shrinkage and the fibres develope an attractive, subdued lustre. (Broadbent 2001, 88.)

The concept of mercerization, furthermore, is to improve strength, luster and dyeability as well as to fabricate swelling cellulose, which maximizes the dissolution of cellulose in the following step. This technique is commonly applied in textile industry as a step prior to the preparation of cellulose gaining cellulose derivatives and regenerated fibres. (Duchemin 2015.) Generally, mercerization step is involved in textile industry, where dry cellulose pulp is soaked into alkali solution improving the accessibility of the crystalline regions. This method is time-consumed and it has high energy demand. After mercerization, the partly dewatered or dried cellulose is formed subsequently and so called ripening, the cellulose afterwards is degraded to desirable DP. (Saxell, Ratamäki and Ekaman 2017.)

Cellulose is swelled and hydrophilic in the existence of water (Wakelyn, et al. 2007, 587). The swelling specifically can take place in some exclusive zones only along the fibre. It is a precursor step of dissolution cellulose or cellulose derivatives such as CCA. In certain swelling agent, the raw material of cellulose causes the radical expansion of secondary wall of cellulose so the primary will be burst. (Poletto and Ornaghi Jr. 2015.) Particularly, in the first step of mercerization, the alkali solution penetrates amorphous regions (Budtova and Navard 2016), which exist in the interface of the cellulose between crystallites and causes cellulosic fibre swelling. Besides the impact of the amount NaOH solution, the cellulose chains in amorphous zones are repositioned into antiparallel Na-cellulose I while at this point crystalline regions are hard affected. Alkali continuously penetrates into crystalline regions and cellulose mobility chain is extended (Wang 2008, 22), and eventually configures an antiparallel crystalline soda-cellulose complex called Na-Cell II, hence the size of crystalline cellulose can be diminished (Budtova and Navard 2016).

The significant phenomenon in the cellulose swelling influence is ballooning, where the first wall is pressurized by the secondary wall of the cellulose and ultimately burst. The tear in the primary wall expands the swollen cellulose to latter rolls up in a way as to form helices and collars which

limit the fibre uniform expansion and create balloons. (Le Moigne 2008, 43.) Still, the secondary wall is the easiest wall to be dissolved because the DP and the crystallinity increase during the fibre development. And the primary wall is in localised regions when being broken and forms helices, it cannot be swollen and thus it does not dissolve easily. (Le Moigne 2008, 51.)

6.2 Effect of NaOH aqueous with temperature on CCA solubility

Due to the phase diagram in Figure 14, the most optimal temperature for NaOH concentration is 7 – 8 wt% (Sobue, Kiessig and Hess 1939). The solubility of cellulose reaches 91% with the NaOH concentration that peaks at 8%. The hydrodynamic diameters of NaOH-water hydrates may be too large to penetrate into the cellulose crystalline area if the concentration of alkali aqueous is too low. The dissolution also does not occur when the alkali concentration is not high enough considering the cellulose yield. If NaOH is higher than 18 – 20%, cellulose chains are close to NaOH molecules as the mercerization modifies the cellulose structure. Therefore, the dissolution is not succeeded because of the Na/cellulose crystals in the mercerization process. (Zhang, et al. 2010.)

By dissolving cellulose in aqueous alkali solution, macromolecular solution can be regenerated into various shapes such as fibres. Corresponding to different NaOH concentration and temperature combinations, different complex formation of cellulose is generated, which is known as Na-cell I, Na-cell II and Na-cell III. Noticeably, in Figure 13, there is a modest region (red circle) represented for NaOH concentration at 6 – 10% at temperature from –10 to 4°C. Cellulose in this region is distinctly swollen. NaOH consequently can cause swelling to cellulose and dissolve cellulose in modest DP. (Wang 2008, 23.) The relatively low temperature is due to the strengthened entropic driving force with increasing temperature. The sub-zero temperature is required in dissolution with soda. At low temperature, polymer is more polar, increases the attractive interactions with the polar solvents and the more polar configurations would be preferred at low temperature. (Medronho and Lindman 2014.)
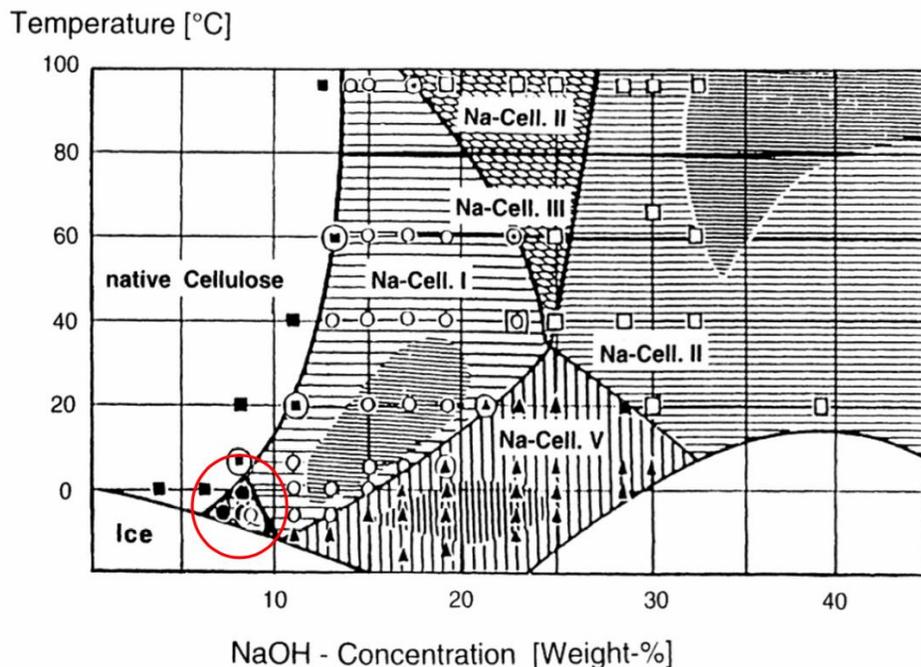
FIGURE 13. Phase diagram of cellulose-NaOH-water system (adapted from (Sobue, Kiessig and Hess 1939)).

The feasible indication of aggregations in dilute solution implies on the measurement of cellulose/NaOH aqueous viscosity. The temperature increases and decreased intrinsic viscosity cannot form the gelation because the viscosity increases with gelation and dilute solutions do not form gelation. (Roy, Budtova and Navard 2003.) The decrease of the intrinsic viscosity with temperature is conditional on the hydrophobic interactions with the increased temperature. Gels formed from cellulose/9% NaOH solution are not thermo-reversible, it means the solution does not re-dissolve at any temperature after being cool, including the cellulose dissolution temperature (– 6°C). (Budtova and Navard 2016.)

The interchain hydrophobic interactions with temperature increase will conclude the compact condition of cellulose agglomerates. The new compact agglomerates are produced with the hydrodynamic volume by the inter-agglomerates interaction. The agglomerates are smaller than the additive sum of the initial agglomerate volumes. And its formation is similar to the interpolymer complex between oppositely charged macromolecules. The aggregate compactization therefore is created by the increasing role of intra- and interchain hydrophobic interaction with temperature above 20°C. This interaction illustrates the semi-dilute behaviour of

the solution without any additives. (Roy, Budtova and Navard 2003.) Figure 14 demonstrates the overall cellulose coil in dilute and semi-dilute solution. At a constant temperature, the solution of cellulose/NaOH will turn from a viscous liquid into an elastic network. At a more or less determined temperature, hydrogen bonding and hydrophobic association can both form gelation. The local chain segregation with local phase can be a possible mechanism governing thermos-induced changes, which conduces to the slightly turbid cellulose/NaOH gels. (Budtova and Navard 2016.)
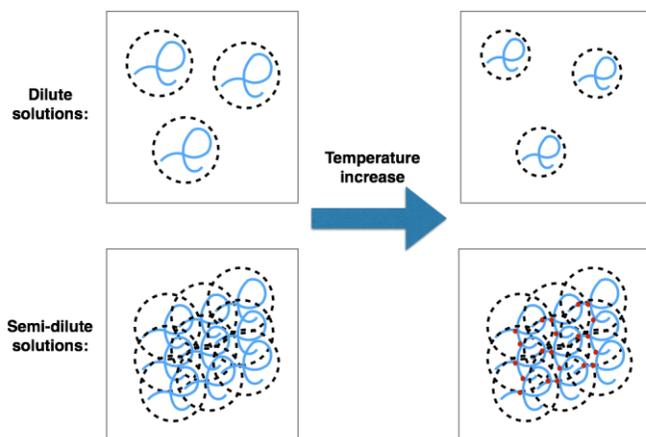
FIGURE 14. Schematic presentation of cellulose coil dimension changes with temperature increase in dilute and semi-dilute solutions (adapted from (Budtova and Navard 2016)).

In the dissolution process, the alkali solubility quality is measured by clogging value or filter value (K_w). This is a general quantification for the quality of a solution, and particularly a measure for the clotting tendency of a fibre nozzle. K_w describes the filterability of cellulose, the higher of the K_w value, the better quality for the spinning dope. For the fibre application, the suitable K_w is normally < 2000. (Huttunen, et al. 1983) The clogging value is depended on the filter cloth type and indicates the insoluble content in the solution. (Valta, et al. 2011.) The cellulose concentration is greatly achieved to 9% at very low DP 216. High temperature also extends the K_w value, results in the poor quality of CCA fibres. Higher DP 300 can lower the concentration below 6%. The N content is lower as being influenced by DP parameters, where DP enhancement decreases the N content and DP value reduction results in the higher N yield in contrast. (Harlin 2019, 16.)

6.3 Additives to aqueous NaOH

Because it is complex to identify the accurate temperature for dissolution step, additives thus is applied to increase the solubility and stability of CCA in aqueous NaOH, some intensively considered additives are ZnO, urea or thiourea. Because hydroxyl breaks the inter- and intra-molecular hydrogen bonds in the NaOH solvent, the hydration ions and free water number correspondingly impacts the CCA dissolution. Aqueous NaOH is easily gelling and unstable at low DP of CCA. Cellulose hydrophobic parts undergo large repulsion from the surrounding and intend to connect together during the dissolution. This matter therefore is unfavourable for the energy system though the NaOH is strong enough to break cellulose hydrogen bonds, but it still limites the dissolution capacity. (Xiong, et al. 2014.) These next steps are studied to analyse how the additives improve CCA dissolution performance.

6.3.1 ZnO as an additive to NaOH solution

The initial purpose of ZnO additive was to prevent unstable and gelling state or viscose of the solution. NaOH with a small portion of ZnO and berrylium oxide is prepared for the dissolution step. The solution is then called sodium hydroxide sodium zincate solution with the overall concentration of 7% NaOH, 1.4% ZnO. For example, the portions of each element are respectively determined as 82.6% weight of water, 7% of urea/cellulose, 8% NaOH and 2.4% ZnO to avoid undissolved materials. The solution is not allowed to freeze upon the gelling solution formation. During the process, viscosity is reduced depends on the viscosity characteristic of initial steep cellulose with degradation promoter such as dilute hydrogen peroxide or ferric chloride during the reaction or after pressing and baking urea/cellulose at 55°C for 3 hours. Drying and baking technique also decrease the NaOH viscosity. Cotton linter or dissolving pulp as steeping cellulose is placed in an excessive aqueous and consists of 2 – 10% sodium hydroxide and minimum 15% of urea with a small amount of wetting agent such as cresol or sodium "Lorol" (the fraction of saturated alcohol obtained by hydrogenation of coconut oil, and involving mainly of C_{13} and C_{14} alcohol) sulfate at the temperature equal or lower than room temperature. The impregnated cellulose is pressed, dried and baked at 120 – 150°C until the product is soluble in aqueous caustic

alkali, CCA would become insoluble in if the baking process was still ongoing. (Hill and Jacobson 1938)

The solution of 0.84% ZnO is added into 7.8% aqueous NaOH with 6% cellulose to prepare for the spinning dope. The temperature is maintained at 3°C by setting the cooling agent. The tenancy of spun fibres is 1.8 cN/dtex with elongation of 15%. (Vehviläinen, et al. 2008.) This solution is developed for the novel fibre, Biocelsol, where cellulose is pre-treated by enzyme. In another study, they explored that with the addition of 0.5 wt% ZnO in the cellulose/NaOH/urea solution, the hydrogen bond formation between cellulose is stronger than cellulose with hydrated NaOH, ZnO existed as $Zn(OH)_4^{2-}$ plus hydroxyl groups are possible to form new stronger hydrogen bonds with cellulose, loosens the intermolecular hydrogen bonds of cellulose and its larger steric hindrance keeps the cellulose chains farther apart from each other. The cellulose solubility therefore is enhanced in the system including zincate. (Yang, et al. 2011.)

6.3.2 Urea as an additive to NaOH solution

The cold NaOH/urea solution in the dissolution step with CCA after the enzymatic pre-treatment step. The de-crystalinity is not increased yet the total solubility of alterative NaOH/urea solution is improved 30% for untreated cellulosic fibres and 65% for enzymatic treated fibres. (Zhao, Deng and Wang 2007.) For example, 6% of NaOH/urea can increase the solubility up to 31% at –15°C, or–20°C (Wang 2008, 66). The NaOH/urea solutions are non-derivatizing solvents for cellulose to form true solution. NaOH works as a destroyer of inter-hydrogen and intra-hydrogen bonds between cellulose molecules. Meanwhile, the urea is responsible as a hydrogen donor and receptor between solvent molecules and eliminates the re-association of cellulose molecules, therefore it results in a good dispersion of cellulose to form an actual solution. (Cai and Zhang 2005.) In another explanation, urea molecules occupied the faces of the hydrophobic pyranose rings to prevent dissolved cellulose molecules from regathering. In the cellulose/NaOH/urea solution, hydroxyl groups break the hydrogen bonds, hydrated Na^+ stabilizes the hydrophilic hydroxyl groups and urea stabilizes the hydrophobic part of cellulose. (Xiong, et al. 2014.) Low solubility implies the high molecule weight, thus it produces high viscosity, leads to gelation that is sterically

hindered in the dissolution and unbroken molecule parts for chemicals accessibility (Wang 2008, 67).

Cellulose is steeped into NaOH/Urea solvent with small amount of ZnO and berrylium oxide. The CCA product would become insoluble if the baking time is too long since the baking time easily turns to critical condition if naOH is withdrawn from urea solution. (Hill and Jacobson 1938.) In a different article, the solubility is improved respectively by the easy penetration and shortened length if the NaOH/urea solution and pre-treated cotton are utilized by enzymatic treatment (Zhao, Deng and Wang 2007). Alkali lye and urea solution with the reactive extrusion are also responsible to form CCA. Cellulose is immersed into an aqueous urea solution with the aid of NaOH and glycerine, the reaction is executed at elevated temperature, and the mixture is centrifuged and pressed by reactive extruder. (Weigel, Fink and Loth 2005.)

The CCA preparation is completed with low concentration of NaOH in the steeping cellulose, with less satisfactory filterability and high viscosity (Hill and Jacobson 1938). Thus, it is inconvenient to produce cellulose textile fibre, where fibre spinning process is completed by passing solution via nozzles that have numerous small holes. Applying NaOH as a solvent with urea to treat cellulose can cause some undesirable properties to the end-product because of the partial soluble in alkali solution. NaOH influences the reduction of DP because it still remains in the fibres when operated as a solvent for the urea. (Huttunen, et al. 1983.)

6.3.3 Thiourea as an additive to NaOH solution

NaOH/thiourea solution is intensively investigated because it enhances indeed the solubility of cellulose in NaOH aqueous solution and reduces the formation of cellulose gel. The lower cost and less toxicity of the NaOH/urea (thiourea) solvent and its simplicity for wet spinning exhibits some virtue promises for the CCA manufacturer. (Chen, et al. 2006.) In a different investigation, 8.0 – 12 wt% of NaOH accompanies by 3 – 6 wt% of thiourea of the total weight of the aqueous is used for spinning by a two-step coagulation bath spinning device in lab-scale. The NaOH/thiourea solution can also be used to produce regenerated cellulose films, comprises of CCA technology and granulation through film-making and granulating devices. (Zhang, et al.

2011.) Thiourea is studied with variable temperatures in NaOH/urea solution. Cellulose in the mixture of NaOH/urea/thiourea is more soluble than in binary mixture of NaOH/urea or NaOH/thiourea. (Bochek, et al. 2015.) Since the spinning solutions contain high concentration of immersed cellulose are unstable in NaOH/urea or NaOH/thiourea, which is unbeneficial in industrial applications. Furthermore, the dissolution mechanism for cellulose in ternary solvents systems is unapparent. The combination of NaOH/urea/thiourea thus is more stable to dissolute cellulose. (Jin, Zha and Gu 2007.)

7 SPINNING INTO FIBRES

Before being spun, the CCA solution is filtrated three times: first with coarse filter to remove larger undissolved particles, second with fine filter to enhance the quality of the solution and final wash with spinneret filtration to prevent clogging (Paunonen, et al. 2019), and the solution is filtered through absolute-rated polypropylene filter cartridges (50 μm + 10 μm or 50 μm + 20 μm) (Määttänen, Vehviläinen, et al. 2018, 14). The spinning process of CCA usually consists of 3 steps: degassing of CCA solution, coagulation of CCA liquid jets and hydrolysis of CCA fibres (Kotek 2007, 707).

In degassing, air is removed after being filtrated, the CCA solution afterwards is precipitated in the coagulation bath (Paunonen, et al. 2019). Being treated by acidic coagulation bath in the second step, CCA fibres is precipitated with the substituent groups intact (Määttänen, Vehviläinen, et al. 2018, 6), where the solution of CCA contact with an aqueous alkali solution containing several cations selected from the group: sodium, aluminium, magnesium, zinc, and calcium cations (Mandell, et al. 1984). The CCA fibres can be regenerated back to cellulose by hot alkali treatment if it is essential (Määttänen, Vehviläinen, et al. 2018, 6). In the final treatment stage before being washed by water and dried (Morgan 2005, 153). Acidic bath is a commercial coagulant, other considerable coagulation baths such as methanol or $Al_2(SO_4)_3$ or Na_2CO_3 can also be applied to form CCA fibres. The hydrolysis of the CCA fibres are conducted at the temperature of $80 - 90°C$ hydrolysing carbamate groups, although the carbamate groups are released from the regenerated cellulosic fibres, a small amount of N content always remains in the CCA fibre. (Kotek 2007, 707.) After the spinning process, 0.02 to 0.85 carbamate groups are presented in the cellulosic fibres or sheet per AGU unit, corresponding to the N content of 0.17 to 6% by weight, depending on the conditions of the synthesis. (Gärh and Hermanutz 2001.)

7.1 Coagulation bath and wet spinning line

The fibres are spun utilizing 10% of H_2SO_4 bath involving Na_2SO_4 and $Al_2(SO_4)_3$. $Al_2(SO_4)_3$ is added to the coagulation bath to improve the fibres tenacity and elongation (Määttänen,

Vehviläinen, et al. 2018, 6). $Al_2(SO_4)_3$ causes a substantial improvement in the dry matter content of the fibre. CCA is stable in acid conditions and does not easily decompose into cellulose on precipitating as in the viscose process, in the form of film or fibres. During the process, alkali solution of the carbamate with H_2SO_4 induces precipitation of the cellulose carbamate and formation of Na_2SO_4 as NaOH is neutralized. (Mandell, et al. 1984.) $Al_2(SO_4)_3$ is chosen since its trivalent cations are more powerful than the bivalent or monovalent cations (Mandell, et al. 1984).

The recovery of alkali solution is also researched to recycle the remaining chemicals in precipitating the cellulose. The process includes the following steps: the solution comprised of CCA and NaOH is prepared for the dissolution step, the solution contacts with a precipitation aqueous solution containing Na_2CO_3, where CCA is precipitated and can be removed, and Na_2CO_3 is recycled by crystallizing and returning to the precipitant solution as cooling through various steps. The substantial liquor NaOH is recovered back to the dissolution and continues to dissolve CCA. (Turunen, Huttunen and Selin, et al. 1987.) Similar to the manufacture of viscose fibre cellulose, the common precipitating solution includes some compounds such as H_2SO_4, Na_2SO_4 and $Al_2(SO_4)_3$. In Figure 15, the spinning line of CCA fibres comprises of 3 godet rolls, one stretching bath with hot demineralized water and 2 washing baths with cold demineralized water and finally a fibre collector (Asikainen, Määttänen, et al. 2013). The fibres generated from waste cotton have a tenancy of 16 cN/tex with an elongation of 18% using a spinneret with 1000, 2000 or 2100 orifices of 50μm. (Määttänen, Vehviläinen, et al. 2018, 6,14) And the desired initial speed of the spinning pump is calculated according to formula (5) (Vehviläinen, et al. 2008):

$$Q = \frac{T \times n \times v_{III}}{\rho_{dope} \times \frac{\alpha}{100} \times 10000} \tag{5}$$

Where $\quad$ Q $\quad\quad\quad$ is capacity of pump, mL/min

$\quad\quad\quad\quad$ T $\quad\quad\quad$ is desired titre of fibre $= 16$ cN/tex

$\quad\quad\quad\quad$ n $\quad\quad\quad$ is the number of spinneret orifices

$\quad\quad\quad\quad$ v_{III} $\quad\quad\quad$ is the speed of III godet $= 20$ m/min

$\quad\quad\quad\quad$ ρ_{dope} $\quad\quad\quad$ is the density constant of spin dope $= 1.4$ g/mL

$\quad\quad\quad\quad$ α $\quad\quad\quad$ is the cellulose concentration of spin dope
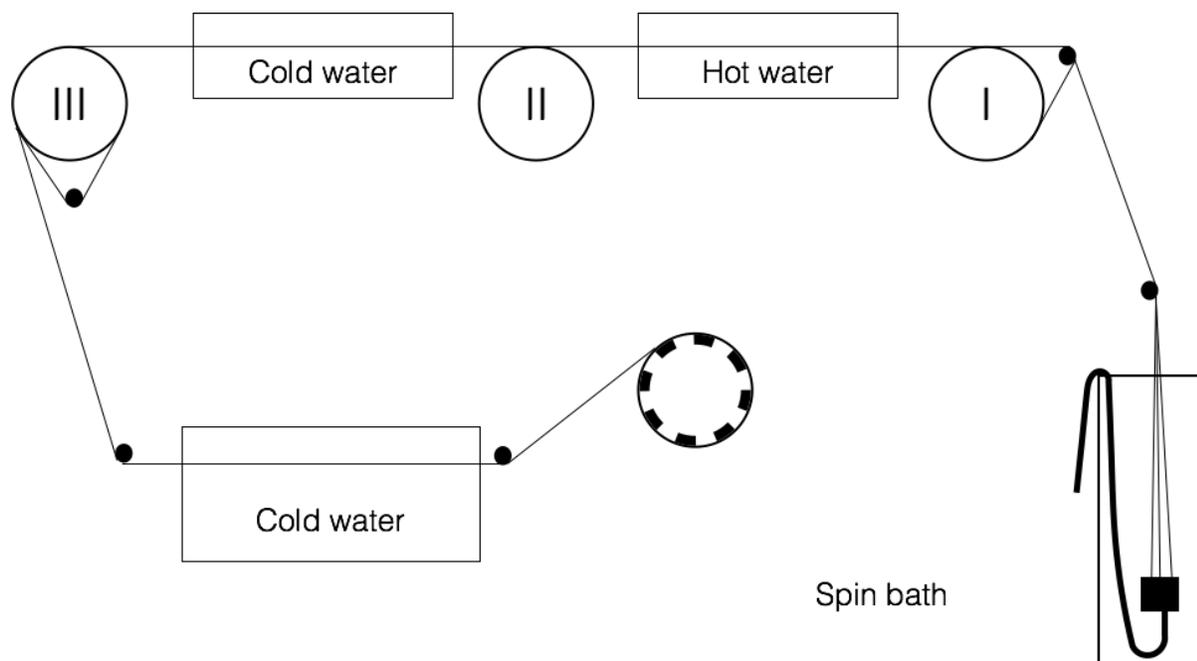
FIGURE 15. Schematic of spinning line preparation (adapted from (Vehviläinen, et al. 2008)).

7.2 Final treatments stage

Because it is a mandatory production of artificial fibers that obtain sufficiently high wet tenacity, the carbamate groups have to be subtracted by a subsequent alkaline treatment (Klemm, et al. 1998, 163). In viscose rayon, fibres contaminated by acid and free sulphur are removed by treating under washing steps, which incorporate respectively with water and alkaline treatment by 0.3% NaOH (Morgan 2005, 153). Similarly, it is possible that half of the original carbamate groups are still in the fibres when the process is at cold temperature. The solution consequently requires high alkali solution and the carbamate groups should be removed from the fibres. The existence of carbamate groups characterizes antimicrobial properties for the final products. (Määttänen, Vehviläinen, et al. 2018, 6.)

The said treatment involves alkali solution which is less than 10% NaOH or KOH, or an organic base for substantially removing the CCA group from the fibres such as tetramethylammonium hydroxide ($N(CH_3)_4{}^+OH^-$) and ethylene diamine ($C_2H_4(NH_2)_2$). However, the most powerful agent is NaOH with the quantity range of 0.1 – 2%. The treating time is depended on the

proportional CCA groups desired to be removed. The time is shortened by raising the temperature, in practical case it can reach 100°C if treatment means capable of containing pressure at disposal. By applying 0.5 and 2% NaOH solution at elevated temperature to CCA fibres or filaments, the N content decreases from 1.15 to 0.3 and 0.2%, respectively. The results positively affect the properties of ultimate CA fibres which thus remain in solid state, thereby increasing wet strength and reducing wet stretchability of the fibres. (Turunen, Huttunen and Ekman, et al. 1986.) After the alkalizing stage, the soft finishing step is carried out with ethoxylated alcohol (AE3) chemical (Paunonen, et al. 2019). Since it is known as a fabric softener compound (Baker, et al. 1996). Washing stages are taken between these steps to release the remaining chemicals within the fibres.

7.3 Characteristic of spun CCA fibres

The tenacity of fibres is tested among different origins. The CCA fibres from pre-treated pre-treatment have lower tenacity. The main reason is due to the compact layered structure of fibres that eliminates cellulosic fibres to be completely dissolved in alkali solution. It is also because of the residue impurities coming from the textile printing stage of recycled raw materials. These issues influence the flow properties of the spinning process and restrict the operation in stretching bath, and consequently make the CCA fibres hold low tenacity. The characteristic of CCA fibres are listed in Table 4. (Määttänen, Vehviläinen, et al. 2018, 17.)

TABLE 4. Characteristics of CCA spun fibres (adapted from (Asikainen, Määttänen, et al. 2013), (Määttänen, Vehviläinen, et al. 2018)).

Sources	N content %	Titre, dtex	Tenacity cN/dtex	Elongation %
Dissolving pulp	1.2	2.0	2.10	15.2
Recycled paper	2.2	1.9	2.10	16.2
Recycled board	1.5	2.2	2.0	15.4
Recycled cotton	1.1	2.3	1.15	20

The surface and cross section structure fibres spun from CCA method, cold sodium hydroxide dissolution method and viscose process are displayed in Figure 16 by SEM. These fibres obtain similar structures compared to each other, and the surfaces are formed from axial stripes with transversal fine morphology. Different from other fibres, viscose's cross-section shape is more

oval than round and has serrated structure. However, the fine structure of the surface of CCA fibres made the fibres softer so it possesses better absorption of water and dyestuff leading to more efficient dyeing of fibres even though the fibres have circular cross section. (Määttänen, Vehviläinen, et al. 2018.)
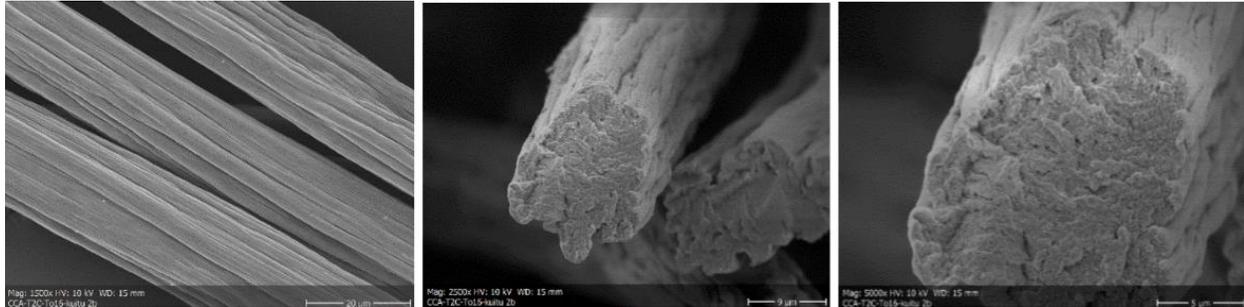
a) Fibres spun by CCA technique
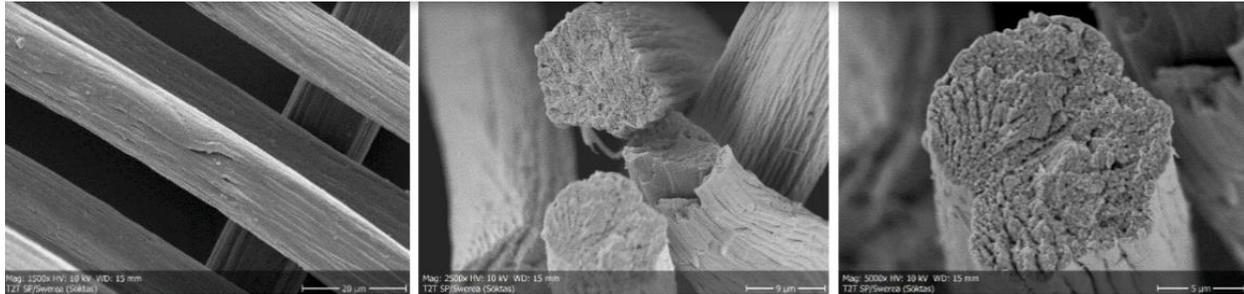
b) Fibres spun with cold sodium hydroxide dissolution method
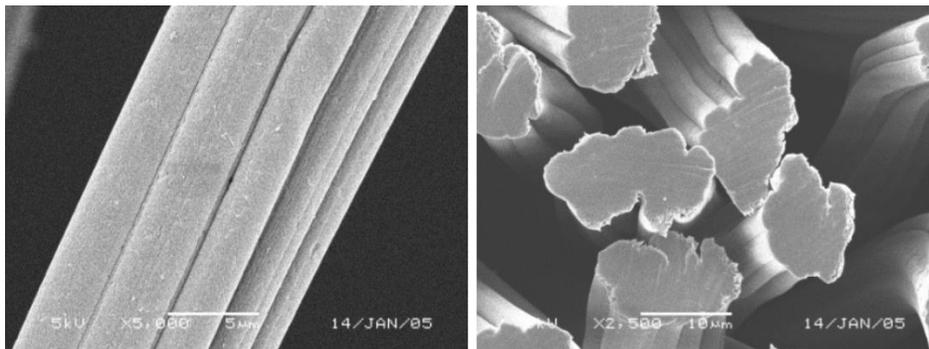
c) Commercial nonwoven type viscose fibre

FIGURE 16. SEM of regenerated fibres by different methods (adapted from (Määttänen, Vehviläinen, et al. 2018))

7.4 Alternative spinning bath and dissolution agent

Alcohol or water coagulation bath are the other options where the cellulose or cellulose derivative are precipitated from. The procedure of CCA fibre production is considered as a typical diffusion

process. When the cast cellulose solution immersed into alcohol, the components of both cellulose solution and coagulation bath were exchanged by diffusion with liquid-liquid de-mixing. (Yu, Zhang and Li 2010.) A typical bath is produced by 75% methanol, 22.5% water and 2.5% NaOH. The fibres produced have the elongation and tenacity based on the stretchability. When applying the same stretching, the tenacity is lower than using acidic bath and the higher alcohol contents also decrease both tenacity and wet modulus. (Harlin 2019, 22.)

NMMO solution is used to substitute NaOH solution to develop high-strength fibres and improve the financial feature of CCA production. The DP and DS of CCA fibres can be adjusted by modifying temperature, dwell time, raw material charge and cellulose concentration. CCA fibres from NMMO are characterised by a tensile strength up to 6 cN/dtex and a modulus of maximum 0.25 cN/dtex. The thermal stability of CCA solution is attained by using the system NaOH–NH_2OH–propyl gallate. N content is reduced from 3% in the primary product to 0.5% in the spin fibres. However, the generated gases such as NH_3 and CO_2 produce insecure spinning behaviour by diminishing the N content and breaking the filaments. Therefore, during the spinning, the loss of carbamate groups is decreased by pH adjustment, which is resolved by adding acidic medium. The pathway is described as setting the pH value in the coagulation bath and directly in the cellulose carbamate/NMMO solution. (Wendler, et al. 2012.)

8 MASS BALANCE

Figure 17 describes the cellulose carbamate production route, which comprises of 3 crucial stages: pretreatment, CCA formation and spinning. In pre-treatment, the button and zippers from cotton denims are removed by hand before the waste cotton is cut and shredded by aT4T machine. The alkali agent used for alkali treatment is 2% NaOH at 110°C, pH 7. (Määttänen, Asikainen, et al. 2019.) O_3 is operated at pH 10 – 11, 80 – 100°C for 60 – 90 minutes. In peroxide treatment, cellulose is treated with the similar pH 10 – 11 but the temperature is reduced to 70 – 80°C. (Weilach, et al. 2019.) H_2SO_4 (95 – 97%) is utilized (Haslinger, et al. 2019), and diluted to a solution of 0.39 M. The acidic washing step overall is carried out in pH 2.5 (Asikainen, Määttänen, et al. 2013). After each treatment, the cellulose is washed with cold deionized water to stop the reaction (Haslinger, et al. 2019). After washing, the pulp is dried or diluted into 8% consistency and centrifugated to 35% consistency for preparing the never-dried-pulp in carbamation reaction (Saxell, Ratamäki and Ekaman 2017).

In the carbamation, the pre-mixing is prepared by adding urea, 0.3 – 1.0 wt% of peroxide with a kneader. The required urea is 25.1 wt% or lower based on the quantity of the pulp. The solid content of cellulose is 35 wt%, the remaining content is water, the pH range is about 6 – 7.5 at elevated temperature 140°C, and the mixture is dried until the solid content is at least 70% and preferred temperature is below 60°C. (Saxell, Ratamäki and Ekaman 2017.) The dissolution solution is prepared in two batches. In the first batch, the pre-mixing is performed at 1% NaOH including the free water in advanced down to the temperature of about 0°C. In the second batch, 18% NaOH is measured into the dissolving mixer and operated below –15°C to attain 8% NaOH in the actual solution, the solution is therefore mixed for few minutes only. (Valta, et al. 2011.) The dissolution conditions are operated at 8.0 wt% NaOH/ 1.6 wt% ZnO to result roughly 6% cellulose content (Ahokas 2019).

The undissolved CCA content is filtrated by the coarse filtration and improved its quality by fine filtration in cold temperature. The solution thereafter is degassed before being spun in the coagulation bath. In the spinning bath, the solution includes 10% H_2SO_4 (Määttänen, Vehviläinen,

et al. 2018), with calculated 12% Na_2SO_4 and 12% $Al_2(SO_4)_3$. The fibres are wet spun as continuous filament and manually cut to 55 – 60 mm prior to rinsing with hot water (Määttänen, Vehviläinen, et al. 2018), and alkalizing treatment, where carbamate groups stayed in the CCA fibres are removed (Paunonen, et al. 2019). The treated products are washed and ethoxylated alcohol is utilized as soft finishing to complete the after-treatments process and the CCA fibres are prepared to the drying and bailing process. During the drying process, water is evaporated and oxygen is released in degassing stage before entering to the coagulation bath.
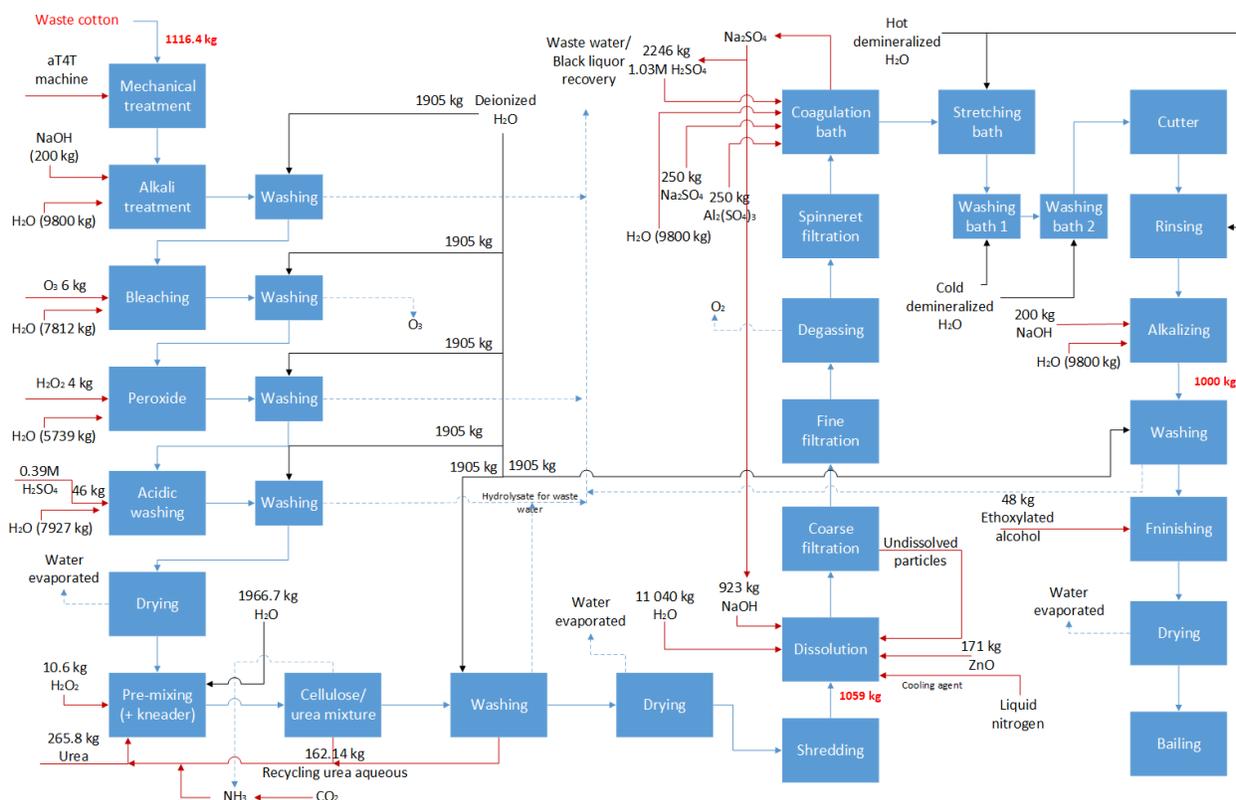
FIGURE 17. Aggregates of the CCA process.

Table 5 displays all the parameters such as chemicals used, mass and conditions in teach step of CCA production. Na_2SO_4 is recycled back to H_2SO_4 and NaOH by electrodialysis, the H_2SO_4 and NaOH thus are recycled back to the operation 80% yet H_2SO_4 utilized in the pre-treatment is not possible to be recycled (Paunonen, et al. 2019), and acts as hydrolysate in the wastewater system (Kantola, et al. 2019). The mass of waste cotton needed to produce 1000 kg of CCA fibres is 1116.4 kg, which includes the mass of buttons, zippers, metals, ash, extractives, dyes and rejection cellulose in the dissolution and spinning process.

TABLE 5. Chemical charge of individual CCA mill.

Chemicals used	Amount (kg)	Stage consumption	References
Waste cotton	1 116.4	-	Calculated in this thesis
NaOH	1 323	Pre-treatment (200kg)	(Harlin, Määttänen, et al. 2018)
		Dissolution (923 kg)	Calculated in this thesis
		After-treatment (200kg)	Calculated in this thesis
Urea	265.8	Carbamation	Calculated in this thesis
ZnO	171	Dissolution	Calculated in this thesis
0.39 M H_2SO_4	46	Pre-treatment	Calculated in this thesis
1.03 M H_2SO_4	2246	Spinning bath	Calculated in this thesis
$Al_2(SO_4)_3$	250	Spinning bath	(Paunonen, et al. 2019)
Na_2SO_4	250	Spinning bath	(Paunonen, et al. 2019)
O_3	6	Pre-treatment	(Harlin, Määttänen, et al. 2018)
H_2O_2	14.18	Pre-treatment (4 kg)	(Harlin, Määttänen, et al. 2018)
		Carbamation (10.6 kg)	Calculated in this thesis
Ethoxylated alcohol	48	Finishing	(Paunonen, et al. 2019)
Product CCA fibres	1000	-	Calculated in this thesis

The amount of process water and washing water is calculated and enlisted in Table 6. The total water used is 93.74 m^3, where process water is 61.74 m^3 and washing water is 32 m^3. Cooling water is not comprised in the table since the cooling chemical used in the dissolution is liquid nitrogen (Paunonen, et al. 2019). The washing water is the estimation of water consumed by medium TwinRoll Press (Roll Press) and excluded from two washing baths after spinning as reported from (Asikainen, Määttänen, et al. 2013), and rinsing with hot water as reported from (Paunonen, et al. 2019). The process water also involved the water used to dilute concentrated chemicals such as H_2SO_4 and NaOH. By using the roll press washer, the average feed consistency is 10% and discharge consistency is 35%. The feed consistency is maintained at 10% in the following step by fulfilling the process water. In some stages such as acidic washing and dissolution, the molarity of H_2SO_4 is modified according to the optimal pH, which reported by (Asikainen, Määttänen, et al. 2013), and mass reported by (Paunonen, et al. 2019). The amount of

process water is calculated based on the room temperature condition (25°C) and the washing water is preferred as deionized water.

TABLE 6. The calculated water consumption in CCA process.

Stages	Process water (m^3)	Washing water (m^3)
Alkali treatment	9.80	5.4
Ozone	7.81	5.4
Peroxide	5.74	5.4
Acidic washing	7.97	5.4
Carbamation	7.44	5.4
Dissolution	11.04	-
Spinning bath	2.03	-
After-treatment	9.80	5.4
Total	61.74	32

8.1 Washing stage

To calculate the proximate washing liquor for pre-treatment step, the washing step after acidic washing is chosen since it contains high amounts of impurities in the total unwanted substance remaining in the waste cotton. According to Sixta (2016), medium TwinRoll Press (Roll Press) is the considered washer for this mass balance because of its high consistency, which makes the temperature and pH adjustment in the subsequent dilution step an easier task. In Table 7, the feed and discharge consistency values (N_{in}, N_{out}) are selected as the highest value in its range from. The pulp production capacity (P) self-proposed is roughly of 1 ton. The E_{10} is between $3 - 5$ with the E is 1, (Sixta 2006, 556,557) $E_{10} = 4.8$ is chosen to minimize the washing liquor used.

TABLE 7. Known specifications of medium Roll Press washer (adapted from (Sixta 2006, 556,557)).

Specification	Unit	Amount
N_{in}	%	10
N_{out}	%	35
E_{10}	-	4.8
E	-	1
P	odt/h	1

The E_{10} value is calculated as: (Sixta 2006, 546)

$$E_{10} = E \frac{\log\left(1+\frac{DF}{1/N_{out}-1}\right)}{\log\left(1+\frac{DF}{9}\right)} \tag{5}$$

$$4.8 = 1 \frac{\log\left(1+\frac{DF}{1/0.35-1}\right)}{\log\left(1+\frac{DF}{9}\right)}$$

$$\rightarrow DF = 0.045 \text{ t odt}^{-1}$$

The liquid flow rate out is calculated as: (Sixta 2006, 530)

$$L_{out} = P\left(\frac{1}{N_{out}}-1\right) \tag{6}$$

$$\rightarrow L_{out} = 1\left(\frac{1}{0.35}-1\right) = 1.86 \text{ t h}^{-1}$$

The dilution factor is determined as: (Sixta 2006, 545)

$$DF = \frac{WL - L_{out}}{P} \tag{7}$$

The wash liquor flow rate is therefore:

$$\rightarrow WL = DF.P + L_{out} = 0.045 \text{ t odt}^{-1} \times 1 \text{ odt t}^{-1} + 1.86 \text{ t h}^{-1} = 1.905 \text{ t h}^{-1} \approx 5.4 \text{ m}^3\text{h}^{-1}$$

There are 5 washing stages including the pre-treatments and carbamation process, plus one other washing stage in the after-treatment, the corresponding amount of washing water used is: $5.4 \text{ m}^3 \text{ h}^{-1} \times 6 = 32 \text{ m}^3 \text{ h}^{-1}$

8.2 In dissolution

The target CCA fibres mass produced is 1000 kg. And the dissolution condition is: 8.0 wt% NaOH/1.6 wt% ZnO, the determined cellulose content for cotton, which is pre-treated by enzyme-

extruded is 5.88% (Ahokas 2019). The undissolved CCA content is filtrated by the coarse filtration stage. The mass of cellulose before dissolution therefore is 1059 kg.

$$1000 + 1000 \times \left(\frac{5.88}{100}\right) = 1059 \text{ kg}$$

It is assumed that 923 kg and 171 kg of NaOH and ZnO respectively reported by (Paunonen, et al. 2019) is represented for 8.0 wt% NaOH / 1.6 wt% ZnO solution. The water required in this solution is:

$$0.08 = \frac{923}{\frac{923}{2.13} + \frac{\text{mass of water}}{0.997} + \frac{171}{5.61}}$$

$\rightarrow$ mass of water = 11 040 L

8.3 In carbamation

According to Saxell, Ratamäki and Ekaman (2017), small amount of urea is added to never dried pulp containing 8% consistency to 35% of solid content in the solution of cellulose/urea mixture. It is assumed that H_2O_2 used is 1 wt% of the pulp, the H_2O_2 therefore is 10.6 kg (Saxell, Ratamäki and Ekaman 2017). The urea is dosed 25.1 wt% of the pulp, which is equal to 265.809 kg and the urea efficiency is 39%, all the urea recycled from NH_3 is assumed that 61% of 265.809 is 162.14 kg.

8.4 In pre-treatment

The total weight is lost from metal and ash removal, the mass of waste cotton before the acidic treatment. The average metal content on dry based of 4 types of waste cotton is calculated as 0.52% from (VTT 2015). The metal content also includes dye components such as Ca, Cu, Fe, etc (Wedin, et al. 2018). The average ash content is 1.175% of the waste cotton, which is calculated from data given in Table 8 (VTT 2015). Ash content also included metals but excluded the metal content on dry base. (*)

TABLE 8. Chemical compositions of waste pure cotton from both pre- and post-customers (VTT 2015).

Waste materials	Limited viscosity (ml/g)	Ash content on dry weight (wt%)	Metal on dry base (mg/kg)
Pre-consumer uncoloured cotton fibres	1890±172	1.6	7486.72
Pre-consumer colour cotton printed with non-fixated dye	860±37	1.7	1685.42
Pre-consumer colour cotton printed with fixated reactive dye	970±8	0.3	7094.22
Post-consumer colour cotton denim garment	910±19	1.1	4644.7

The selected pre-treatments are hot alkali treatment, wetting agents and acidic treatment. Therefore, the estimate metal weight loss is 90.68% (Harlin, Määttänen, et al. 2018). It is assumed that 90.68% metal removal is applied for both ash (metals included) and metal on dry base content of waste cotton (**).

The extractive content is 0.6% and elastane content is 3.3% (***) (VTT 2015). It is supposed that the mass of post-consumer colour cotton denim garment is one-fourth the total mass of waste cotton input. The relative cotton content in denim textile is 83.9% (VTT 2015). The polyester content in denim textile thus is: $100 - 83.9 - 0.52 - 1.175 - 0.6 - 3.3 = 10.505\%$, it is assumed that all PET is eliminated in the pre-treatment. (****)

From (*), (**), (***), (****):

$$\rightarrow 1059 + (5.2 \times 10^{-3}y + 0.01175y)0.9068 + 6 \times 10^{-3}y + \frac{y}{4} \times \frac{10.505}{100} = y$$
$$\rightarrow y = 1105 \text{ kg}$$

The weight loss percentage of handpicking button and zipper in waste cotton is 1.03% in the initial mass of waste pure cotton (Paunonen, et al. 2019) The initial waste cotton is therefore $1105 + 1105 \times 0.0103 = \textbf{1116 kg.}$

8.4.1 In alkali treatment

The NaOH is weighted as 200kg to treat roughly 1 ton of cellulose (Määttänen, Vehviläinen, et al. 2018), the water used for this stage is therefore:

$$2\% = \frac{200kg}{(200+m)} \times 100 \text{ (m is the weight of water)}$$

$\rightarrow$ m = 9800 kg = 9800 L

8.4.2 In acidic treatment

The pH is between 1.5 to 5, for at least 90% of metallic compounds released during the acidic washing (Weilach, et al. 2019). pH 2.5 is the common acidic condition to determine the water required for this process. The H_2SO_4 consumed in the pre-treatment is 46 kg (Paunonen, et al. 2019). Hence, 46 kg of H_2SO_4 solution is supposedly applied to achieve a solution of 2.5 pH and 10% consistency, the molarity (C_M) of H_2SO_4 is determined based on resulting pH 2.5:

$$pH = 2.5 \rightarrow [H^+] = 10^{-2.5} = 3.16 \times 10^{-3} \frac{mol}{L}$$

u is the molarity of H_2SO_4 in the final solution, v is the molarity change during the reaction, u and v are calculated based on the 2 dissociation of H_2SO_4, where the K_{a1} is considered to be completed, K_{a2} is weaker therefore the ICE table is set as:

	$H_2SO_4^-$	$\rightleftharpoons$	H^+	+	SO_4^-
I	u		u		0
C	$-v$		$+v$		$+v$
E	$(u-v)$		$(u+v)$		$+v$

$$[H^+] = u + v = 3.16 \times 10^{-3} \frac{mol}{L} \text{ (')}$$

$$K_a = \frac{(u+v)\,v}{(u-v)} = 0.012 \text{ ('')}$$

Based on ('), and (''), the equation is made:

$$\begin{cases} u + v = 3.16 \times 10^{-3} \\ 0.012u - (0.012v + 3.16 \times 10^{-3}v) = 0 \end{cases}$$

$$\Leftrightarrow \begin{cases} u = 1.765 \times 10^{-3} = C_M \\ v = 1.4 \times 10^{-3} \end{cases}$$

The total water volume at 10% consistency is: $\frac{1116 \text{ kg}}{0.1} - 1116 kg = 10\,044 \text{ kg} = 10\,044 \text{ L}$

The mole of concentrated H_2SO_4 used is calculated as: $n = C_M \times V = 1.765 \times 10^{-3} \frac{mol}{L} \times 10\,044 \text{ L} = 17.68 \text{ mol}$

The mass of concentrated H_2SO_4 used is: (McMurry and Fay 2003, 84)

$$m = n \times M \tag{8}$$

$$= 0.01768 \text{ kmol} \times 98.079 \frac{\text{kg}}{\text{kmol}} = 1.73 \text{ kg}$$

In 46 kg of H_2SO_4 solution, 1.73 kg of concentrated H_2SO_4 is included. The volume of concentrated H_2SO_4 therefore is: (McMurry and Fay 2003, 17)

$$V = \frac{m}{\rho} \tag{9}$$

$$= \frac{1.73 \text{ kg}}{1.83 \frac{\text{kg}}{\text{L}}} = 0.945 \text{L}$$

$$\rightarrow V_{\text{water in the solution}} = 46 \text{ kg} - 1.73 \text{ kg} = 44.27 \text{ kg}$$

The molarity of H_2SO_4 solution is (McMurry and Fay 2003, 92):

$$C_M = \frac{n}{V} \tag{10}$$

$$= \frac{\left(\frac{1.73 \text{ kg}}{98.079 \text{ kg}/\text{kmol}}\right) \times 10^3}{0.945 \text{ L} + 44.4 \text{ L}} = 0.388 \text{ M}$$

The extra volume of solution needed from 35% consistency in previous washing step to 10% consistency in acidic washing: $(\frac{1116 \text{ kg}}{0.1} - 1116) - (\frac{1116 \text{ kg}}{0.35} - 1116) - 44.27 \text{ kg} = 7927 \text{ kg}$

8.5 In coagulation bath

In the spinning bath, the precipitating solution contains 10 wt% H_2SO_4, $Al_2(SO_4)_3$ and Na_2SO_4 (Määttänen, Vehviläinen, et al. 2018). The molarity of H_2SO_4 should be determined for spinning bath, $Al_2(SO_4)_3$ and Na_2SO_4 are added equally at 250 kg (Paunonen, et al. 2019), and their concentrations are also calculated. The reported weight of H_2SO_4 is 2246 kg and the concentration of the precipitation solution is 10%. So, a and b are the mass (kg) of acid and process water, respectively, the equation is presented as:

$$\begin{cases} a + b = 2246 \\ \dfrac{a}{a/1.83 + b/0.997 + \dfrac{250}{2.66} + \dfrac{250}{2.67}} = 0.1 \end{cases}$$

$$\Leftrightarrow \begin{cases} a + b = 2246 \\ \dfrac{a}{(1 - 0.1/1.83)a - 0.1b/0.997} = 1.876 \end{cases}$$

$$\Leftrightarrow \begin{cases} a = 217.23 \text{ kg} \\ b = 2028 \text{ kg} \end{cases}$$

The molarity of H_2SO_4 is:

$$C_M = \frac{n}{V} = \frac{\left(\dfrac{217.23 \text{ kg}}{98.079 \text{ kg}/\text{kmol}}\right) \times 10^3}{\dfrac{217.23 \text{ kg}}{1.83 \frac{\text{kg}}{\text{L}}} \text{ L} + 2028 \text{ L}} = 1.03 \text{ M}$$

The concentration of $Al_2(SO_4)_3$ and Na_2SO_4 are:

$$C\% = \frac{250 \text{ kg}}{2028 \text{ L}} \times 100 = 12.33\%$$

9 DISCUSSION AND LIMITATION

CCA technology is evaluated with viscose and cultivation cotton that against three pillars of sustainability. CCA fibres produce due to the reaction of cellulose with urea, which is widely utilized as synthetic fertilizer and produced in large volume. The unreacted and NH_3 are also feasible to recycled back to the operation, decrease the raw urea input to the process. The Na_2SO_4 formed in the coagulation bath between $NaOH$ and H_2SO_4 is also possible to recycle. Those alternatives chemicals are socially and economically advantageous for CCA technology that the sustainable chemicals and CCA intermediate are secure to be stored and transported in long-term. (Paunonen, et al. 2019.) The cotton cultivation necessitates high water consumption, farming fertilizers, pesticides and requires large deforestation to fulfill human demand. It thus creates water scarcity areas and contaminates food and drinking water in nearby regions as well. Since it is natural fibres and depends on seasonal crops, the price thus is also not stable. The cotton cultivation industry therefore is not a sustainable operation compared to viscose and CCA production. Whereas, the CCA production completely creates sulphur free, improves the environmental impacts instead of using poisonous and harmful CS_2. (Määttänen, Harlin, et al. 2019, 209.) Remarkably, the total cost to produce 1 ton of CCA fibres is estimated to save 15 – 20% when compared to the traditional viscose process (Fu, et al. 2014).

Comparing to other designated cases, the CCA fibre has been researched to illustrate the environmental aspects by showing the GWP as evaluation indicator (Heikkilä, Kamppuri, et al. 2018). The GWP (CO_2 eq.) is calculated with stand-alone factory and without heat energy (integrated with pulp factory). The stand-alone factory uses fossil fuel and presents non-optimized process, without any recycling of chemicals, the raw materials are utilized for the first time (Paunonen, et al. 2019). Meanwhile, the CCA factory integrated with pulp mill and chemicals are recycled, resulting in the lowest GWP among other factories (Heikkilä, Kamppuri, et al. 2018). However, in both cases all the water vaporized from the drying step cannot be circulated. The process water and washing water are recycled when CCA production integrating with pulp factory, the water thus is not optimized when the CCA manufactory is stand-alone (Paunonen, et al. 2019).

Specifically, the used water is circulated by black liquor recovery process (Sixta 2006, 967). NaOH and H_2SO_4 are recycled up to 80% by electrodialysis from coagulation bath (Paunonen, et al. 2019). And urea is recycled from unreacted urea in cellulose/urea mixture and NH_3 vapourized from HNCO is also returned back to urea by reacting NH_3 with CO_2 (Ennenbach and Koss 2013), or using inert organic gas (Arnold, Butzke and Keunecke 1995). Although recycling chemicals increase significant electricity, the plant utilizes renewable energy and it is also integrated into a spinning factory hence the total GWP is one third of the stand-alone factory. In the pre-treatment processes in CCA integrated factory, O_3 is used from circulated O_3 in pulp mill and H_2O_2 after using is also circulated to the process. The O_3 and H_2O_2 are not recycled back to the operational system in the stand-alone factory. During the bleaching, the input and output O_3 is equal while H_2O_2 is partly lost during the operation, the bleaching agents are recycled in case of integrating with pulp mill. (Paunonen, et al. 2019.) The mass consumption of NaOH and H_2SO_4 used in dissolution and spinning are greater than other chemicals. When the chemicals cannot be recycled, it will increase the GWP level as enhancing the CO_2 eq. The non-recycled problem from pre-treatment to carbamation, dissolution and spinning in the stand-alone factory causes higher GWP level, plus the fossil fuel utilized to run the manufactory, the CCA integrated with pulp mill factory is ultimately eco-friendlier than other designated factories.

The CCA production still attains some boundaries in spite of the beneficially environmental impacts. This designated factory is limited in the scope of EU countries from collecting, sorting and generating into fibres. CCA production project and environmental analysis are halted at the CCA fibres products. The textile materials and product manufacture should be characterized and widen their scope for the references-based feasibility of the further LCA studies. The expansion of this technology can be analyzed profoundly on water footprint and the most consumed chemicals during the dissolution and spinning process. The raw materials of this technology are one of the most challenging tasks among other stages because without discarded cotton textile reported from several projects, in practical case they are collected after being sorted to be reused. In 2012, only 1.5% discarded textile was recycled and natural based-fibres were accounted for small amount in those fractions, around 20% of the collected textile eventually arrived at the landfill and the separation of collected textile was mostly focalized on reusable clothes. The collection of discarded textile therefore has diverted from municipal waste since 2016. European

Commission furthermore announced in 2017 that its member states should organize separate collection of textile waste by 2025. All of the foundations construct a novel business system around circular economy and textile should be initiated. (Heikkilä, et al. 2019, 28.) Another consideration is related to the defined properties of CCA fibres, in which the quality of CCA fibres and viscose fibres are alike and CCA fibres can substitute viscose ones. The cut off modelling should be chosen because the man-made fibres are assumed to have the same properties as virgin fibres and can be used many times. Still, there is no consensus currently about the allocation principle to recycle used chemicals in man-made fibers manufacture that have the identical properties as virgin fibers. Therefore, the comparison of quality of CCA fibres to virgin item can define the allocation principle to appreciate this project. (Paunonen, et al. 2019.)

10 CONCLUSION

From the 1980s, CCA technology has been an alternative way to produce regenerated fibres compared to conventional viscose process (Selin, et al. 1985). Because the CCA fibre acquire similar properties and retain the spinning process as the viscose products, but the process to manufacture CCA fibres is non-toxic and environmental friendlier than viscose production. Since then, the CCA production has been gradually developed by several inventions to gain the convenient methods synthesizing CCA fibres from alternatives urea aqueous to auxiliary agents during the CCA formation and dissolution, or alternative baths in the spinning dopes as reviewed in the thesis. So far, the only application of CCA is to perform as an intermediate for solubilizing cellulose in alkali solution in artificial fibres (Klemm, et al. 1998, 164). But it is practiced in pilot scale in Asia (mostly China) (Fu, et al. 2014), and EU countries (Määttänen, Vehviläinen, et al. 2018). The CCA technology thus can be concluded as a futuristic production in recycling textile industry. According to the mass balance and evaluation of CCA production, it clearly testifies the most optimized location of CCA manufactory, where it should be integrated with pulp mill or feasibly existing viscose factories without xanthate production. When the CCA production becomes more sustainable as being established more articles related to the quality of fibres compared to viscose's and to discover the most optimum pathway, it is possible to broaden the production scale without major capital investment (Paunonen, et al. 2019).

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