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# Influence of the molecular weight of cellulose on the solubility in ionic liquid-water mixtures

**Master's thesis for the degree of Master of Science in Technology**

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**Espoo, Finland**

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# Abstract

**Aalto University**
**School of chemical technology- Department of forest product technology**
**Master's Programme in Process System Engineering**

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**Abstract:**

Ionic liquids (ILs) are a novel class of solvents which have been in the focus of interest during the last few years due to their desirable properties such as high thermal stability or low vapor pressures. Some of them have the ability to dissolve cellulose without any derivatization. Different mechanisms are presented in the literatures for the dissolution of cellulose in ILs. However, the effect of the molecular weight of cellulose on the solubility in ionic liquid-water mixtures hasn´t been studied yet.

The IONCELL-P is a process, which can quantitatively separate pulps into pure cellulose and hemicellulose fractions using IL-water mixtures. In this work we aim to explain the mechanism of the IONCELL-P fractionation. Ozone treatment was used to degrade cotton linter (CL) to a lower molecular weight range which is the same molecular weight range as the hemicelluloses and low molar mass cellulose in commercial pulps. The ozone treated CLs were treated with the IONCELL-P process using 1-ethyl-3-methylimidazolium acetate ([emim]OAc) and water mixtures. Different IL-Water ratios with water content between 13.5 and 19 wt% in the mixture were tested. The MMD of dissolved and undissolved cellulose were evaluated. According to these results, the effect of the molecular weight of cellulose in IL-water mixture is determining and the hypothesis of cellulose dissolution in ILs being based on the size of the polymers is supported.

To validate this effect, the thesis also compares the results of the experimental data with that reported earlier by Carmen et al [30] for IONCELL-P fractionation in [emim] OAc-water using birch pulp, which contains numerous biopolymers of various chemical structures, such as cellulose and hemicellulose.

Keywords: Ionic Liquid, Cellulose, Hemicellulose, IONCELL-P, Ozonation, Cellulose degradation, MMD, Cellulose Fractionation, IL-Water system

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# Table of contents

# List of abbreviations

| | |
|---|---|
| **BC** | bacterial cellulose, |
| **BMCC** | bacterial microcrystalline cellulose |
| **BH** | Sodium borohydride |
| **CL** | cotton linters |
| **CED** | cupriethylenediamine |
| **DP** | Degree of Polymerization |
| **DMAc** | Dimethylacetamide |
| **[emim] OAc** | 1-Ethyl-3-methylimidazolium acetate |
| **EDA** | Electron donor/electron acceptor |
| **GPC** | Gel Permeation Chromatography |
| **IL** | Ionic Liquid |
| **LODP** | leveling off degree of polymerization |
| **LCC** | lignin carbohydrate complex |
| **MMD** | Molar Mass Distribution |
| **MCC** | microcrystalline cellulose |
| **MALLS** | Multiangle laser light scattering |
| **PDI** | polydispersity index |
| **RI** | refractive index detector |
| **SEC** | Size-exclusion chromatography |

# 1. INTRODUCTION

Over the last centuries, rapid progress in the health sciences and life style improvements have led to a dramatic increase in the world's population. This has significantly increased the demand for food and textiles. Since available fertile farmland is restricted, new sources of raw materials will be required to meet the demand of the textile and food industry [1].

Traditionally, cotton has been a key plant due to its vast number of applications. Recently, the price of the cotton fiber have risen significantly because of the growing demand rate for cotton fiber and limitation of supply sources [2]. For several years, this growing trend in fiber demand has been met by petroleum based synthetic fibers. However, the new approach to clean technologies and the environmental issues have pushed some industries to invest in finding new sources and more environmentally friendly methods to produce high purity biopolymers.

One potential alternative to cotton is to use wood as a biopolymer source. Wood grows generally in forests on marginal land using natural irrigation and as a consequence wood has a smaller carbon footprint than cotton in addition to different environmental benefits. These all turned the interest of many industries towards wood derived dissolving pulps. Such pulps can be produced by using acid sulfite and pre-hydrolysis Kraft treatments, the two most common processes. . However, for these processes further poet-treatment is required to achieve an adequate degree of purity. The degree of purity is typically specified as the content of residual hemicelluloses and alkali resistance. Based on the harsh condition of the treatment in the mentioned processes, severe losses of cellulose (15-30%) that is caused by peeling-off reactions is reported. [3].

The classic methods for xylan (a group of hemicelluloses) removal include hydrolysis by using steam and elevated pressure, enzymatic treatments/oxidative and reductive treatments. These methods are often accompanied by a certain degree of biopolymer degradation [4]. Defining a new environmentally friendly, economically

attractive process that allows recovery of hemicelluloses and dissolving pulps with high yields and high purity is a topic of interest in the field of biorefinery. IONCELL-P process shows the same desirable advantages in order to use in different cellulose applications. IONCELL-P is a dissolution process in which the hemicellulose and cellulose are selectively separated by using ionic liquid (IL)-water mixture. Treatment of the cellulose by using ionic liquids (ILs) is often applied as a pretreatment or as a complete dissolution of cellulose. Treatments of cellulose with different ILs such as NMMO,[emim] DMP, [emim] OAc, DBNH OAc have been studied over the last decades. 1-Ethyl-3-methylimidazolium acetate - [emim] OAc - is one of the most researched ILs for cellulose. [emim]OAc presents properties such as low viscosity and selectively fractionation which facilitates cellulose dissolution tremendously compared to several other ILs.

Thus, understanding of the principle behavior of cellulose in ionic liquid solutions is essential to improve the IONCELL-P process and to commercialize this process in the near future. However, the effects of chemical and physical properties of biopolymers in ILs had not been evaluated at the time that this thesis was written.

The aim of this thesis is to experimentally determine the effect of biopolymer molecule size on the dissolution of cellulose in [emim] OAc-water system under different water concentration. To validate this effect, the thesis also compares the results of the experimental data with that reported earlier by Carmen et al [30] for IONCELL-P fractionation in [emim] OAc-water using birch pulp, which contains numerous biopolymers of various chemical structures, such as cellulose and hemicellulose.

# 2. LITERATURE REVIEW

This chapter describes the principles of cellulose, Ionic liquids(ILs) and the effect of cellulose dissolution in Ionic Liquid (IL) with different water contents as a co-solvent. Thus, the first section of this chapter (2.1) describes the structure of cellulose. Sections 2.2 and 2.3 introduce wood and cotton linter as two most common sources for cellulose. Dissolution of these two cellulose's sources in IL, as well as the specification and structure of ILs are discussed in Section 2.4. Different mechanisms for cellulose degradation are introduced in Section 2.5. Ozonation which is the selected degradation method in this thesis to mimic the desired cellulose substrate is discussed more in detailed. The final section of this chapter describes the method used to determine the molar mass distribution (MMD) of cellulose.

## 2.1 INTRODUCTION TO CELLULOSE

Cellulose is the world's most abundant natural polymeric raw material with fascinating structure and properties. It took about a century before the molecular structure of cellulose was established [5]. Cellulose shows great chemical variability based on linear macromolecular chain of 1-4 linked β-D-glucopyranose structure.

Cellulose has four different crystalline forms named cellulose I-IV. The crystal structure of cellulose I in native cellulose can be converted to cellulose II by dissolution and regeneration or mercerization [6]. The original parallel-chain crystal structure of cellulose I changes to anti-parallel chains of cellulose II during the process of regeneration or mercerization. This phenomenon happens when cellulose fibers are converted into swollen state and micro fibers assembly and orientation are disrupted. [7]. The most studied forms of cellulose are Cellulose I and II. The natural crystal is made up of metastable cellulose I with all cellulose stands in a highly ordered parallel arrangement [8].

An anhydroglucose is the monomer of cellulose; The β(1-4)-linked dimer of two glucose residues is called cellobiose, which is the structural repetitive unit of the cellulose chain. The hydroxyl groups on the cellulose units enable hydrogen bonding between two adjacent polymer chains and intra molecular bonding as well. The

degree of polymerization is determined by the number of monomers which compose each cellulose chain (Brown et al., 1996).

In the $^4C_1$ chair conformation, the equatorial orientation of the hydroxyl groups of the polysaccharide chain units makes the glucose monomers very stable. Each cellulose chain contains a reducing and a non-reducing end: a hemiacetal structure and an alcoholic hydroxyl group respectively [9]. The structure of the cellulose is shown in Figure 1.

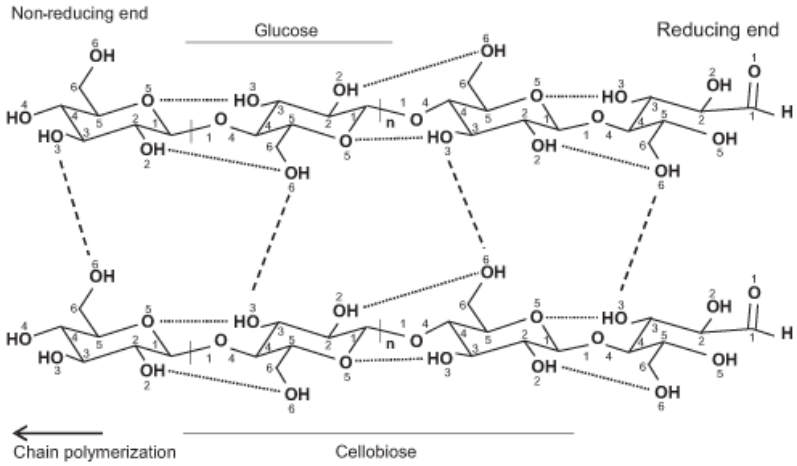


*Figure 1. The structure and the inter- and intra-chain hydrogen bonding pattern in cellulose I. Dashed line: inter-chain hydrogen bonding. Dotted lines: intra-chain hydrogen bonding. [10]*

Degree of the crystallinity, accessibility and reactivity of the cellulose chains are important properties of the cellulose. The high degree of crystallinity, the hydrogen bonded structure and hydrophobic interactions contribute to the recalcitrance of cellulose towards dissolution in water and common organic solvent.

Cellulose can be provided from different sources, and this thesis will use and discuss two major sources: wood and cotton plant.

## 2.2 WOOD

Wood is known as one of the best alternatives for cotton plant substitution to provide the growing demand for cellulose. Cellulose, hemicelluloses and lignin are three

major biopolymers of wood's structure. In addition to these three main components, small amount of pectin, protein, extractive and ash are defined in wood's structure as well. Depending on the source of wood, different relative proportions of cellulose (40-50%), hemicelluloses (20-40%) and lignin(18-25%) content are reported in pulp and paper references as shown in Figure 2[11]. Hemicelluloses are a branched heteropolymers, consisting of different sugar monomers including glucose, xylose, mannose, galactose and etc., with 500-3000 sugar units per molecule depending on their sources [12]. Lignin is relatively hydrophobic and aromatic in nature, but lacks a defined primary structure. Softwood lignin is mainly composed of guaiacyl units and hardwood lignin is composed of both guaiacyl and syringyl units [10].

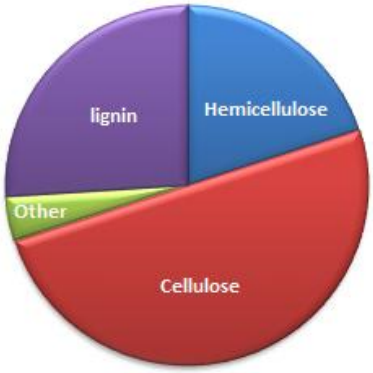


*Figure 2. General composition of wood [11]*

## 2.3 COTTON LINTER

The cotton linter is used as a raw material in this study. Cotton linters are considered as a world-wide valuable cellulose raw material for paper manufacture, cellulose derivatives and regenerated fibers. Bleached cotton linter fibers are used for many applications in paper industry. The cotton linter usually is used alone or mixed with other pulps, for special application like technical papers, security paper, insulating paper, filter paper and fine paper such as art paper. Beside the use of cotton fibers in paper industry, cotton is also used to make a number of textile products with different quality and uses, these include: terrycloth, denim, cambric, corduroy, seersucker, cotton twill and etc. Due to the high purity of cellulose in cotton linter which is more than 99%, it is used in this study as a cellulose substrate that represents a single chemical structure.

The cotton plant – botanically Gossypium – is categorized as part of the Mallow Family (Malvaceae). By the blooming of the ripe cotton capsules the cotton fibers have passed three development stages known as: elongation, thickening and maturation to get ready for harvesting.

The cross section of the ready cotton seed is shown in Figure 3. As it can be seen from this figure, there are two kind of different fibers from each cotton seed that are called lint and linter. The long-fibers which develop first are called lint or staple cotton. When the lint is formed, the shorter and thick-walled fibers are developed and appear as fuzz, known as linter [9].

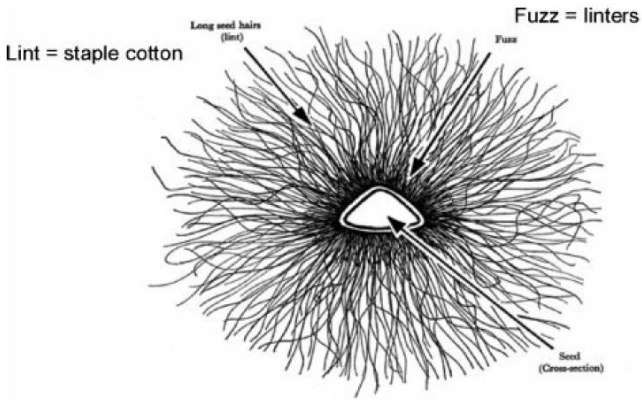


*Figure 3. Cross-section view of cotton seed [2]*

Many varieties of cotton seeds based on different cotton species can be grown under various conditions in different environments. The most common specie is G.hirsutum which accounts for about 87 % of world production [13].

### 2.3.1 Morphology of Cotton linter fibers:

Development of the cotton fibers can be divided into two stages; During the first stage of development that is known as elongation period, the thin membrane identified as ‘’Primary wall’’ is produced. By establishing the fiber length, the fiber stops growing and from this point, the second stage of fiber formation takes place. During the second stage which is identified as the ‘’ thickening stage’’ a different layer is produced on the inner surface of the primary wall. The secondary wall (S2) is formed during the thickening stage and is shown in Figure 4.

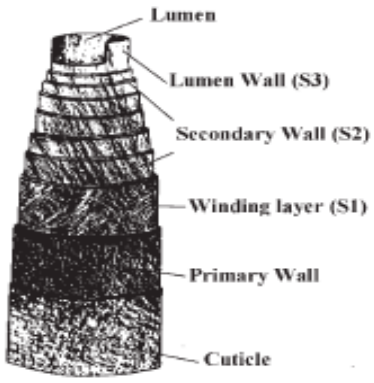


*Figure 4. Morphology of a cotton linters fiber. [14]*

The cuticle layer on the fiber consists of wax and pectin material. The primary is a layer composed of cellulosic fibers. The majority of the secondary wall (S2) also consists of cellulose. The rest of the cellulose can be found in the lumen wall [15].

### 2.3.2 Cotton linter processing technologies

The cotton linter processing technologies can be summarized in four main stages:

1. The cotton is harvested manually or by machine. The product in this stage is the cotton balls.
2. In roller ginning the staple fibers are separated from cotton balls.
3. The separated staple fibers are sent to spinning and the residual cotton seed that contains linter fuzz is delivered to oil mills.
4. The oil mills final product is the cotton seed oil, but besides the final product there are also byproducts of the process such as cotton linter, seed hulls and seed cake.

Depending on type of the oil mill three different kinds of linter fibers are generated: first-cut, second cut and millrun. The first delinting stage results to first-cut, the product after a second delinting stage results to second-cut and if the oil mills contains only one delinting stage the produced product will be millrun linter.

### 2.3.3 Raw Cotton Components

The overall composition of the cotton fiber can be found as Table 1:

*Table 1. Composition of linters [13]*

| | |
|---|---|
| **Cellulose** | 80-90% |
| **Water** | 6-8% |
| **Waxes and fats** | 0,5-1% |
| **Proteins** | 0-1,5% |
| **Hemicelluloses and pectin's** | 4-6% |
| **Ash** | 1-1,8% |

The cellulose purity of the cotton fibers is typically around 80% and the natural components, such as pectins, hemicelluloses, proteins, fat, and waxes are the remaining percentage. A large amount of these natural and often non-natural contaminates are released during the linter treatment processes which consists of mechanical cleaning, alkaline cooking and bleaching. After the treatment and releasing the impurities from the linters, the natural contaminants are removed by boiling the linters with dilute aqueous sodium hydroxide in an inert atmosphere. After cooking and bleaching, the fiber is 99% cellulose. The degree of polymerization of cellulose from cotton is 9,000-15,000 [16]. The degree of polymerization (DP) of the cellulose can be adjusted by the selection of temperature and caustic soda concentration during the alkaline cooking. The final cotton linter cellulose is free of lignin, low in ash, carbonyl, carboxyl and aldehyde groups [9,17].

### 2.3.4 The Degree of Polymerization of cellulose

The degree of polymerization (DP) for some natural cellulose samples may reach value of more than 15000. The pre-treatments and other main treatments may cause change in this value. The DP of different types of cellulose is shown in Figure 5.

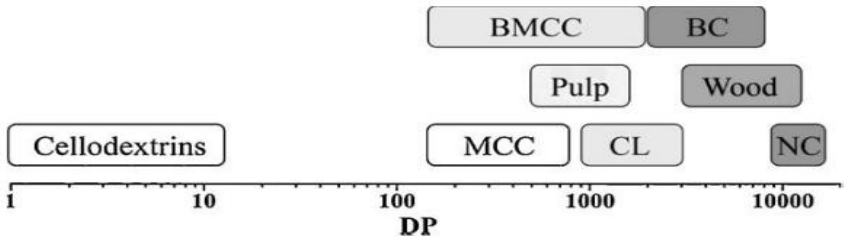


*Figure 5. Degree of polymerization (DP) of different types of cellulose [18] (BC: bacterial cellulose, BMCC: bacterial microcrystalline cellulose, MCC: microcrystalline cellulose, CL: cotton linters, NC: natural cotton).*

High molecular weight celluloses are often used in industrial application as polymeric component due to their rheological and structure-forming properties. However, studying the phenomena related to dissolution processes and the interaction of cellulose with other biomolecules cannot be done with high molecular weight samples. In addition, a higher DP will mean a longer chain length of the cellulose and consequently increase different accessibility of hydroxyl groups for reagents. Thus, to study the cellulose behavior in different systems, low molecular weight (lmw) mimics with low DP is highly required. These lmw celluloses should be well suitable for the analytical characterization of IONCELL-P process.

## 2.4 IONIC LIQUIDS (ILs)

Recently, finding new alternatives to solvents with serious environmental problems has attracted much research interest. Solvents are usually used in large amounts and most of them are volatile liquids. In contrast, ionic liquids are room temperature salt fluids containing only ions; IL usually consists of large organic cations and small inorganic anions. Since the vapor pressure of ILs is very low and they are non-volatile, using ILs in high-vacuum systems can help to avoid containment problems in the systems [19]. Due to these specifications, ILs are suitable candidates to replace current solvents used in several novel applications and pushes these processes towards clean technologies. Target applications for ILs include catalytic synthesis [20]; separation [21]; cellulose treatment, polymerization [22] and nanotechnology [23].

Since ILs has been used in several different processes, various articles have been published which are focused on synthesis of ILs for specific use such as cellulose fractionation. ILs have many desirable properties as a cellulose solvent which is very attractive from an industrial point of view. Some of the desirable properties of ILs include different alternatives for anion and cation combinations, low hydrophobicity and viscosity, enhanced electrochemical and thermal stability [24].

The chemical and physical properties of ILs such as viscosity or melting points are strongly dependent on their type of cations and anions specs, for instance, some ILs are in liquid phase at room temperature. 1-alkyl-3-methylimidazolium cations,

abbreviated [Cnmim+] where n is the number of carbon atoms in a linear alkyl chain, is the most commonly cation used to produce room temperature IL for different cellulose applications. Anions are preferably halide (chloride, bromide), perchlorate, thiocyanate and cyanate or C1-C6 carboxylate. For example, using carboxyl acid and phosphate anions would cause low melting points, low viscosity and high hydrogen bonding acceptor abilities for the IL [19,25]. The chosen IL for this study was 1-ethyl-3-methylimidazolium acetate ([C2mim]OAc or [emim] OAc), and its structure is shown in Figure 6 [26].

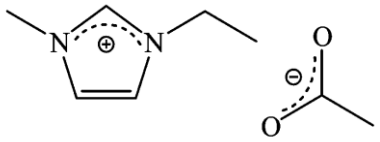


*Figure 6. Structure of 1-ethyl-3-methylimidazolium acetate or ([C2mim] OAc).*

The most important characteristics of the 1-ethyl-3-methylimidazolium acetate are listed in Table 2.

*Table 2. Characteristics of 1-ethyl-3-methylimidazolium acetate [27]*

| | |
|---|---|
| **Molar mass** | 170.22 |
| **Melting point (◦C)** | <-20 |
| **Viscosity at RT (mPas)** | 93 |
| **Viscosity at 80 ◦C (mPas)** | 10 |
| **Density at 80 ◦C (g/cm$^3$)** | 1.07 |
| **Electrochemical window (Volt)** | -2.3/+0.9 |
| **Electric Conductivity (µS/cm)** | 2500 (25◦C) |
| **Flash-point ◦C** | 164 |
| **Solubility in water** | ∞ |

### 2.4.1 Wood dissolution in ILs

Separation of the major component of biomass by direct dissolution of lignocellulosic biomass leads to direct integral usage of feedstock including the direct use of the resulting wood components in their polymeric form. Direct dissolution of lignocellulosic biomass and separation of its major components opens a door to an integral usage of feedstock, including the direct use of the resulting

wood components in their polymeric form. Homogenous dispersion and amorphous forms of the biopolymers allow more ready chemical derivatization or depolymerization into other chemicals. Thus, finding a clean and easily technology for biopolymers separation from any lignocellulosic source and utilize these biopolymers as a feedstock are now in high interest of the industry not only for base chemicals and fuels but also in polymeric forms.

Firmly cross-linked network of lgnin and carbohydrate, also called as lignin carbohydrate complex (LCC), is caused by covalent bondes between these two component. Due to this sepecification, fractionation of biomass is not easy task. LCC precluding undegraded carbohydratesrecovery from direct dissolution or fractionation of wood in conventional solvents.

In general, ILs can dissolve the wood components; For instant, in 2006, Patrick and Moyana et.al published that the IL [C4mim]Cl could dissolve cellulose and lignin from different sources of wood with both softwood and hardwood; treatment performed for 5% wood mixing with [C4mim]Cl/DMSO (86:16 wt.%) [28].

Dissolved cellulosic materials could be recovered with addition of precipitating solvents such as acetone/water, dichloromethane, or acetonitrile. The extracted celluloses showed physical properties, TGA and IR analysis, including processing characteristics and thin film preparation comparable to that of pure cellulose samples subjected to the same treatment conditions.

Moreover, recent study has shown that under the same operation conditions [emim] OAc is an even more desirable solvent for wood dissolution than [C4mim]Cl [29]. Both softwood (southern yellow pine) and hardwood (red oak) could be completely dissolved in [C2mim] OAc after mild grinding and partial separation is achieved by regeneration in the selected solvent-acetone/water.

The dissolution process in which the hemicellulose and the cellulose are selectively separated by using IL-water mixture is known as IONCELL-P process (Figure 7). During the IONCELL-P process, a pulp sample is mixed with IL-water solution at optimum temperature and pressure for specific time. The process is followed by separating the undissolved cellulose and dissolved hemicellulose in a filtration unit where the residual filter cake contains mostly cellulose. The hemicellulose in IL-

water solution can be recover by adding more water to the filtrate phase; By recovering the hemicellulose and separating the excess water from IL the whole process cycle is completed.[30]

The process scheme of the IONCELL-P on birch pulp can be found as Figure 7:

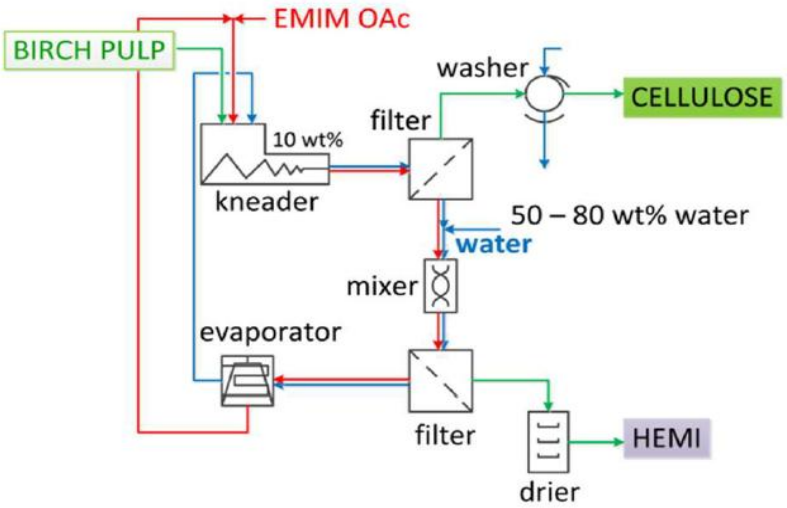


*Figure 7.The process scheme of the IONCELL-P [30]*

### 2.4.2 Dissolution of cellulose in ionic liquids

In IONCELL-P process, cellulose is dissolved in IL and mechanism of this dissolution is discussed here. Cellulose consists of polydisperse linear glucose polymer chains which form hydrogen-bonded supramolecular structures and hydrophobic interactions which render cellulose insoluble in water and most common organic liquids. Dissolution of cellulose in IL results to a homogeneous mixture which the different advance material can be generated by utilizing simple separation methods and strategies. However, prior to dissolution, process can get advantages of various pretreatment methods that would increase the access of enzymes or chemicals to react with cellulose. The direct dissolution and ready separation of the wood biopolymers will help to decrease the variations between biomass sources and could provide polymeric feedstocks for further processing and products. Various methods for conversion of cellulose biomass into sugar have been developed for IL solution which would provide suitable condition to produce more valuable products

To date the viscose and NMMO (N-methylmorpholine N-oxide) processes are the two common industrial processes used to manufacture regenerated cellulose fibers from dissolved cellulose. In both processes, disadvantages have been pointed out; the polluting carbon disulfide ($CS_2$) that is used in the viscose process and high demand of energy beside the runaway reactions in the presence of certain transition metal in NMMO process are the major disadvantages of both methods [31].

These unfavorable conditions have induced further research in order to develop a new ecofriendly regeneration processes.

Cellulose is difficult to dissolve in conventional solvents but due to the unique properties of IL's, they are considered as a potential substitute to the current cellulose solvents in use.

### 2.4.3 Dissolution mechanism of cellulose

In general, five different modes of dissolution can describe cellulose behavior in different solvents: [32]

Mode 1: Fast dissolution by disintegration into rod-like fragments.

Mode 2: Large swelling by ballooning, and then dissolution of the whole fiber.

Mode 3: Large swelling by ballooning, and partial dissolution of the fiber, still keeping its fiber shape.

Mode 4: Homogeneous swelling, and no dissolution of any part of the fiber.

Mode 5: No swelling and no dissolution (case of a non-solvent)

Compared to the other kind of solvents, ILs are considered as direct solvents for cellulose fractionation. The dissolution of cellulose in ionic liquids involves the cleavage of the extensive hydrogen bonding network. The oxygen and hydrogen atoms of cellulose hydroxyl groups form electron donor and electron acceptor (EDA) complexes which interact with the ionic liquid. Oxygen atoms behave as an electron pair donor and hydrogen atoms act as an electron acceptor. In ionic liquid, the cations act as the electron acceptor centre and the anions as electron donor centre. The interaction can only occur if the two centres are close enough in space leading to

the formation of the complexes. The oxygen and hydrogen atoms from the hydroxyl groups of cellulose are separated permitting the opening of the crystalline structure and consequently the dissolution of cellulose.

The cellulose characteristic and the IL type, play important roles in the efficiency of the process. It has also been shown that an increase in anions basicity makes the disruption of the inter- and intra-molecular hydrogen bonding more efficiently. Choosing IL with shorter carbon chain results in lower viscosity and melting point that facilitate the better dissolution of cellulose and handling of the solution. Different studies show that the degree of polymerization of cellulose has an impact on the dissolution rate and efficiency besides the effect of other variable parameters for the dissolution process like temperature, stirring or pre-treatment. At room temperature, cellulose just swells in ionic liquids known also as ballooning effect and only a minor fraction of the cellulose might be dissolved [32]. The dissolution of cellulose in ILs within a reasonable time requires a sufficient energy input in terms of heat. Therefore the sample is typically heated to a temperature of 60-80 °C for total dissolution [33].

Residual water in ILs decreases the efficiency of cellulose dissolution; water may form competitive hydrogen bonds to the macromolecular chains of cellulose. The removal of the residual water is thus necessary before dissolving cellulose [34].

### 2.4.4 Regeneration of cellulose from ILs

Structure, morphology and properties of regenerated cellulose are strongly influenced by the precipitation process and how the cellulose-IL solution and the regenerating solvent are contacted. The degree of crystallinity can be for example controlled by the regeneration techniques. Cellulose can be regenerated in a large variety of structural forms like: powder, fibers, tubes and films. Thin fibers and rods can be prepared by extrusion of the cellulose-IL solution into water whereas a rapid mixing of the solution with an aqueous stream leads to powdery flocs of cellulose. In both cases the regenerated cellulose is type II [25,33].

In the IONCELL-P process the regenerated cellulose can be separated from dissolved cellulose in IL by filtration. Washing the filtrated by using hot water can help to remove the remaining IL in the regenerated cellulose.

A large part of the water can be released from the ionic liquid by e.g. partial phase separation using $K_3PO_4$ to bind water before the enriched ionic liquid phase can be collected and further purified by the energy consuming evaporation of the water, ionic exchange or reverse osmosis are some of the other purification techniques that can be used [35]. Therefore, finding an efficient recycling process is a key factor to eliminate the environmental and consumption problems of IL based processes.

However, due to the hygroscopic nature of the ionic liquids and the relatively high boiling point of water, the recycle step will require high energy costs especially in industrial scale applications. Thus, studying the effect of the water content in ionic liquid aided fractionation is a major factor in scaling up these processes.

## 2.5 CELLULOSE DEGRADATION

Several different methods are available for cellulose degradation and the most widely use methods are introduced below:

### 2.5.1 Acid hydrolysis

Under the acid hydrolysis condition cellulose would degraded either heterogeneously or homogeneously.

Homogeneity condition may results to degradation of the entire structure. For homogenous degradation high acid concentration is required that would disrupt and degrade the crystalline part of the cellulose. Heterogeneous acid hydrolysis required low concentration of acids and the residue is not susceptible for degradation. Two kinetically different phases were suggested for the heterogenous degradation reaction of cellulose. The easily accessible region of cellulose would be degraded at the first phase. The reaction rate declines during the second stage of the reaction, until the degree of polymerization (DP) of the cellulosic residue approaches the leveling-off-

degree of polymerization (LODP). The LODP is defined as the DP at which no further acid hydrolysis takes place, and is around of 100-300 units [36].

### 2.5.2 Alkaline degradation

Degradation of the cellulose under alkaline condition starts from the reducing end group of the cellulose at moderate temperature (80-100 °C). This first phase of degradation is known as first peeling reaction. In first peeling reaction a β-alkoxy elimination takes place and provides a soluble "monosaccharide unit" and a shortened polysaccharide chain with a new reducing end group.

By increasing the temperature to around 140 °C, an alkaline hydrolysis cleaving randomly the glycosidic linkages of the cellulose chains results in new reducing end groups which is followed with secondary peeling. Treatment at this temperature will result in significant change in DP and yield losses.

### 2.5.3 Ozonation

Ozone is a pale blue gas, slightly soluble in water and much more soluble in inert non-polar solvents. The human immune system can detect about 0.01 ppm of ozone in air as it has a very specific sharp odor. Physical properties of the Ozone can be found in table 3.

*Table 3 Ozone physical properties*

| | |
|---|---|
| **Molecular formula** | $O_3$ |
| **Molar mass** | 47.998 g·mol$^{-1}$ |
| **Density** | 2.144 g/L (0 °C), gas |
| **Melting point** | 80.7 K, −192.5 °C |
| **Boiling point** | 161.3 K,−111.9 °C |
| **Solubility in water** | 0.105 g/100mL (0 °C) |

Ozone is a bent molecule, similar as the water molecule. The oxygen bond's distance and angle are shown in Figure 8. The bonding can be expressed as a resonance hybrid with a single bond on one side and double bond on the other producing an overall bond order of 1.5 for each side.

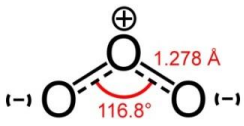


*Figure 8. Ozone molecular Structure*

### 2.5.3.1 Ozone reaction with Carbohydrates

In many saturated compounds carbon-hydrogen bonds are susceptible to cleavage by ozone, including the activated anomeric carbon-hydrogen bonds in carbohydrates.

Degradation of the cellulose by ozone resembles the degradation of cellulose by other oxidizing agents in acidic medium condition. Due to the polymeric character of cellulose and by knowing that one anhydroglucose unit contains three hydroxyl groups that are available for oxidation; various structural changes are possible during the ozonation.

The two important oxidized functions in cellulose are carbonyl and carboxyl group. The only naturally occurring carbonyl function is the reducing end group in cellulose (figure 9). By further oxidation, the reducing end groups would convert to the corresponding aldonic acids. The reducing ends are very likely to be present as hemiacetals in pyranose units, but only to a small extent as aldehydes and aldehyde hydrates [37].

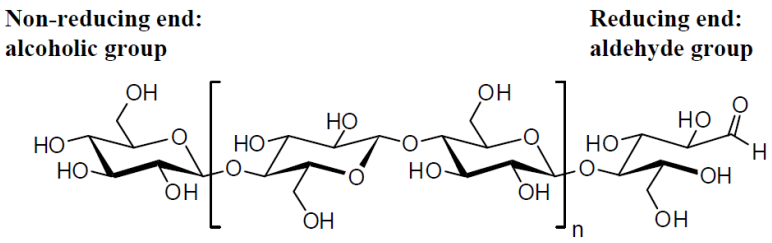


*Figure 9. Cellulose's structure showing non-reducing and reducing ends.*

Ozonation of cellulose, in general, like some hydrolysis, is a heterogeneous reaction. Attack occurs more rapidly in the amorphous region of cellulose; followed by slower attack on the more ordered region.

During the ozonation of cellulose two primary reactions take place: [38]

- The cleavage of the glycosidic linkage which is occurred base on insertion mechanism and results to formation of corresponding lactone as it is shown in figure 10.

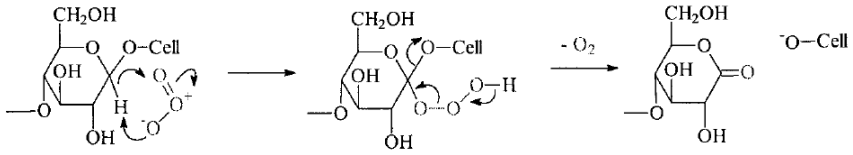

*Figure 10. Cleavage of the glycosidic linkage [10]*

- And the oxidation of the primary and secondary hydroxyl group to carbonyl groups and further to carboxyl groups as it is depicted in figure 11.

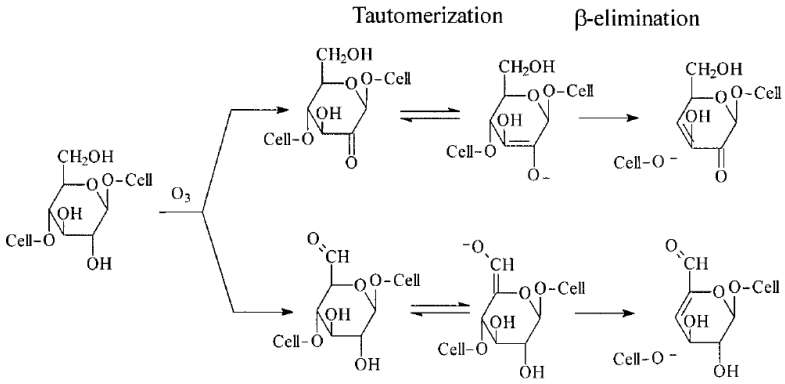


*Figure 11. Oxidation of the primary and secondary hydroxyl groups [39]*

The carbonyl groups are highly alkali sensitive, which results to bond cleavage due to a series of keto-enol tatumers and β elimination.

In some publications it is reported that a substantial amount of carbon dioxide ($CO_2$) was detected during the ozonation and the amount of produced $CO_2$ has a liner relation to ozone charged flow rate [39]. Comparing the carboxyl group content before and after the ozonation showed a lack of change. So regarding to the $CO_2$ generation during the treatment indicates that the ozonotion mechanism likely occurred in the following three stages:

- The formation of carbonyl group
- Oxidation of carbonyl group to carboxyl group
- Decarboxylation; this mostly happens to the C-6 position with concurrent β elimination (Figure 12, bottom pathway).

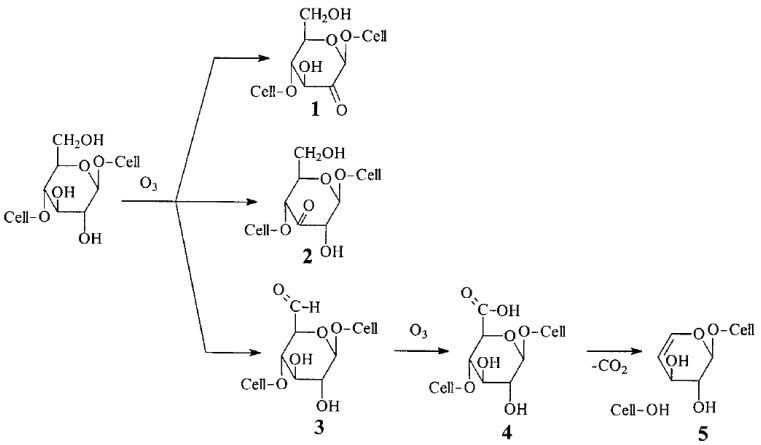


*Figure 12. Ozonation mechanism*

The sample treated with ozone will be highly sensitive to alkali conditions. This is a problem for the viscosity measurement using cupriethylenediamine (CED) solution, which would result to lower measured viscosity value than the sample's true viscosity. To eliminate further degradation after ozonation under alkaline condition, a reducing stage known as ''R'' stage and post treatment stage known as ''P'' stage should be applied to the treated samples.

During the R stage the carbonyl groups which are produced at the reducing end group of cellulose, are reduced to hydroxyls/alcohols [28]. A typical compound for selectively reducing carbonyl groups to alcohols is sodium borohydride (BH). The BH treatment has been used commonly in pulp bleaching to reduce the carbonyl groups which affect the pulp yellowing [40]. The R stage is then followed by the P stage with hydrogen peroxide as a reducing agent.

In contrast to dioxygen, which contains a double bond between the O atoms, hydrogen peroxide has only one bond, which can be easily broken. During the P stage the hydrogen peroxide attacks electron-poor structures (e.g., carbonyl structure) with conjugated double bond and will reduce the activity of the sample. Using high temperature and high charge of hydrogen peroxide will improve the efficiency of the stabilization treatment [3].

### 2.5.4 Kinetics of cellulose degradation

The kinetics of ozonation reaction is a first order reaction and small changes in pH will not affect the rate constant [41]. When analyzing the kinetics of the cellulose

degradation, the first step is to define the degradation variable, because the degradation cannot be quantified directly. After defining the degradation variables, the effect of the degradation variables should be defined. In the final stage the established variables are used to predict the degree of degradation of cellulose at the given conditions [42].

According to the definitions that are presented in previous sections, the degradation of the cellulose is essentially due to the scission of cellulose polymer chain. The Chain Scission number (CSN) or the Scission Fraction of cellulose unit (SFCU) are used in different literature for characterizing cellulose degradation. CSN is defined as the average number of chain scission per cellulose chain unit and (SFCU) corresponds to the ratio of broken glucose units to the total glucose units of a cellulose chain [43,44].

- CSN = $\frac{DP_0}{DP} - 1$ (1)
- SFCU = $\frac{CSN}{DP_0} = \frac{1}{DP} - \frac{1}{DP_0}$ (2)

Where:

$DP_0$ is the degree of polymerization before degradation

DP is the degree of polymerization after degradation.

The degree of polymerization can be obtained from the intrinsic viscosity [η] of the non-degraded and degraded pulp assuming a relatively constant polydispersity index (PDI) throughout the chain scission.

- DP = $\left(\frac{[\eta]}{2.28}\right)^{(1/0.76)}$ if [ŋ]> 410 ml/g (3)
- DP = $\left(\frac{[\eta]}{0{,}42}\right)$ For smaller [ŋ] (4)

Where:

[ŋ] Is the intrinsic viscosity (mL/g) according to the standard method SCAN-CM 15:99.

The kinetic of cellulose degradation is commonly described by the Ekenstam's equations by assuming the SFCU as a function of reaction time (t). To derive the equation, first the chain degradation can be followed through a random zero-order chain scission reaction.

- $\frac{dn}{dt}$ = -k (5)

Where:

k is the rate constant of the degradation ($s^{-1}$)

n is the number of glucosidic bonds

The integration of equation 5 gives:

- $n - n_0 = -kt$ (6)

The number of bond can also be expressed by:

- $n = A.(1 - \frac{1}{DP_n})$ (7)

Where:

A is the number of sugar units

$DP_n$ is the number average degree of polymerization

$DP_n$ can be approximated by $DP_v$, viscosity average degree of polymerization, assuming there is no significant change in polydispersity.

By assuming A is constant, equation 7 can be replaced by

- $n = (1 - \frac{1}{DP_v})$ (8)

Equation 8 can then be inserted in the integrated rate equation 9:

- $\frac{1}{DP} - \frac{1}{DP_0} = kt$ *Ekenstam's equation* (9)

The first-order equation of the chain scission process would be

- $\ln(1-\frac{1}{DP_0}) - \ln(1-\frac{1}{DP}) = kt$ (10)

k, presenting the reaction rate constant, can be expressed by an Arrhenius-type of equation:

- $k = A.\exp(\frac{-E_a}{RT})$ (11)

where:

$E_a$ is the activation energy of the degradation of cellulose (kJ/mol)

R is the universal gas constant (kJ/K.mol)

T is the degradation temperature (K)

The activation energy of cellulose degradation can be determined from the equations 9 and 11.

After the determination of k at different temperatures (equation 9), $E_a$ can be calculated from the slope of the plot ln(k) against 1/T.

$$\ln(k) = \ln(A) - \frac{Ea}{RT} \quad (12)$$

## 2.6 MOLAR MASS DISTRIBUTION (MMD)

The intrinsic viscosity measurement is a fast and convenient method to estimate the average DP of cellulose.

Polymers are in general characterized by the average molecular weight determined from the elution of the different molecular mass constitutes.

In linear polymers the individual polymer chains have usually different degree of polymerization and molar mass. Therefore, the characterization of a polymeric sample is better defined by Molar Mass Distribution (MMD) than by single values. The MMD describes the relationship between the number of moles of every polymer constituents and the molar mass of those constituents [45].

Size-exclusion chromatography (SEC) is an analytical method widely used to provide the molar mass distribution of a polymer. Number average ($M_n$), weight average ($M_w$) and centrifuge average ($M_z$) molecular weight are the most common values of molecular mass used to describe a polymeric sample's molecular size distribution [4].

The number average molecular weight $M_n$ is defined as the ratio of the total weight of polymer and the number of polymer molecules. $M_n$ deals with the number of the molecules without using the mass of the molecules with a molar mass $M_i$ [4].

- $$M_n = \frac{\sum_i n_i M_i}{n_i} \quad (13)$$

Where:

i is a subscript representing the different molecular mass in a chain

$n_i$ is the number of polymer of molecular mass $M_i$

The weight average molecular weight $M_w$, considers not only the number of polymer molecules but also the size or weight of each polymer molecule. In this case, the

number $n_i$ of polymer of molar mass $M_i$ is replaced by the weight $n_iM_i$ of polymer of molar mass $M_i$ [4].

- $M_w = \frac{\sum_i n_i M_i^2}{\sum_i niMi}$ (14)

The centrifuge average molecular weight $M_z$ used in ultracentrifugation experiment corresponds to $M^2$.

In case of monodisperse samples, all the above presented factors will be equal. However, for other range of polymers the order is as shown below:

- $Mn \leq Mw \leq Mz \leq Mz+1$ (15)

The ratio of the weight average molecular weight to the number average molecular weight describes the polydispersity index (PDI). It gives an indication on the distribution profile.

- $PDI = M_w/M_n$ (16)

The PDI can change differently during degradation processes according to the types of degradation mechanisms occurring (random or systematic). In the case of a random degradation, the ratio does not change and the molar mass distribution keeps the same profile. The ratio decreases if scissions near the center are favored and increases if scission is formed near the ends [46]. In the following section, the most common method for MMD analysis is described.

### 2.6.1 Gel Permeation Chromatography (GPC)

Size-exclusion chromatography (SEC) is an analytical method which separates macromolecules according to their size. This separation technique is named gel permeation chromatography (GPC) when applied to polymers.

The principle of the GPC is based on the permeation of molecules into the standard gel with pores of a certain size that is placed in chromatography columns. The small molecules permeate through the gel and interact with the inner surface of the gel while larger ones go through the column without any retention [45].

The cellulose should be dissolved as a monodisperse solution, which is a solvation of each individual cellulose molecule to achieve a reliable separation of cellulose molecules according to their molecular weights. Solvent systems like cadoxen or

DMAc/LiCl can be used for this purpose. In some methods for preparing samples, some pretreatment and activation like using water, acetone and DMAc, prior to dissolution is recommended.

In order to detect different molar mass and plot the molar mass distribution (MMD), several detectors with different sensitivity are used. The refractive index detector (RI) and the multiangle laser light scattering detector (MALLS) are two kind of detecting instrument usually used for GPC analysis. RI is one of the least sensitive liquid chromatography detectors. MALLS detectors show a higher sensitivity than RI detectors. From MALLS detection, low molar masses as well as very high molecular masses can be detected [45].

For indirect detection (RI) the column has to be calibrated. The first stage is to select the calibrating substances similar to the studied substances. In the second stage, the elution volume (or retention time) of those substances are correlated with their corresponding molecular weights. MALLS can detect the molar mass directly and does not require calibration with standard substances. The intensity of the signal is directly proportional to the concentration of the respective polymer in the eluent fraction. The relative amount of each polymer can then be plotted against its molecular mass $M_i$ whereby the total sum of all fractions (area under the curve) is normalized to one.

## 2.7 AIM OF THE STUDY

During the recent years by introducing the room temperature ILs, the idea of using this green solvent in cellulose treatment and selective separation of the cellulose and hemicellulose has been suggested in different publications [30,33]. A recent publication by Carmen Froschauer et al. presented a new methodology for the quantitative separation of bleached paper-grade pulps into cellulose and hemicellulose fractions, both of high purity without significant yield losses [30]. By testing the effect of different cosolvents with [emim] OAc, water turned out to be an ideal cosolvent for the fractionation, since the cellulose solubility was hindered, while the hemicelluloses were still soluble in the mixture. The dissolution of the polysaccharides can be controled by changing the water content [47]. The scheme of the IONCELL-P process can be found as figure 13.

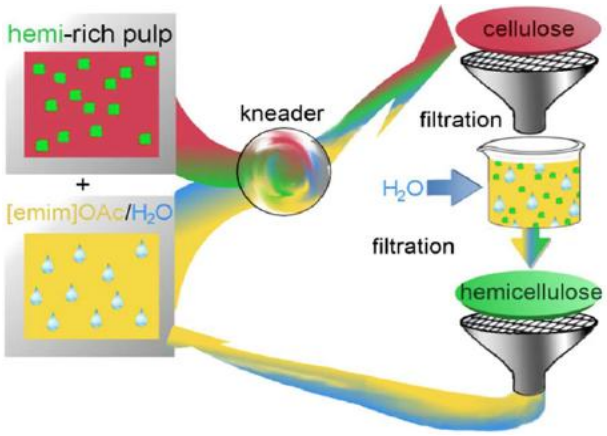


*Figure 13. The Ion-Cell dissolution process using [emim] OAc [30]*

The molar mass distribution of the filtrated cellulose and the precipitated hemicellulose fractions from their experiment is presented in Figure 14.

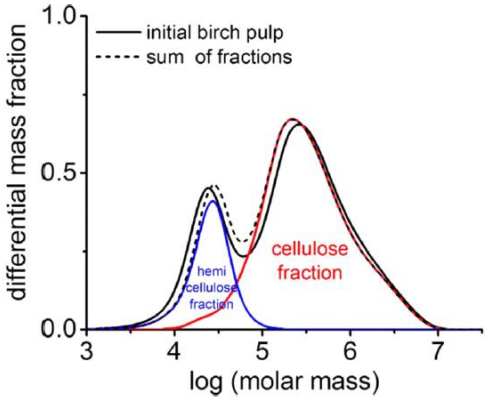


*Figure 14. Molar mass distribution of the initial birch Kraft pulp, the separated cellulose fraction, the precipitated hemicellulose fraction, and the calculated sum of the fractions (treatment, 15 wt % water, 60 °C, 3 h; consistency, 10.5 wt %). [30]*

This figure depicts that during the extraction using [emim] OAc no degradation is observed for cellulose and hemicellulose fractions which result to recovery of the polymers after fractionation without yield losses or degradation.

The effect of the chemical and physical properties of the cellulose components in IL-water solution is still unknown. The aim of this study is to research the effect of the $M_w$ on the IONCELL-P process in respect to various water contents in this IL system. The results of this study aim to help the understanding of the cellulose dissolution in ILs in general and will help to improve the IL fractionation process. The details of the experiments, results and discussion are presented in the following chapters of this study.

# 3. MATERIALS AND METHODS

In this chapter, specification of the used material and equipment are discussed in the section 3.1. Method of degradation of cellulose by using Ozone as degradation agent and the stabilization stae are explained in the section 3.2 and 3.3. The degraded cotton linter is then fractionated with [emim]OAc and water. The final part of this chapter ,section 3.5 and 3.6, describes the method for GPC analysis and viscosity measurement that are used in this study.

## 3.1 MATERIALS

The used cotton linter in this study was purchased from Solvay Rhodia with cellulose purity higher than 99.5%. The used [emim] OAc was purchased from IoLiTec and synthesized by Helsinki University. Ozone is produced by a Wedeco GSO30 device using oxygen (Figure 15). The KI, $Na_2S_2O_3$ and CED Solutions were prepared by the laboratory staff in Aalto university- Department of Forest Product Technology. The MMD of the samples were measured by UltiMate 3000 device with analytical column 4 X PL gel 20µm mixed using RI detector by and used 9 g/L LiCl/DMAc as eluent at 25 °C. Two different kinds of filters, polyethylene and metal mesh filters with the porosity size of 20µm and cutoff size of 5-6 µm respectively, were used in this study.

## 3.2 METHODS

### 3.2.1 Degradation of the CL by ozone

The cotton linter pulp was degraded by ozone to decrease the intrinsic viscosity from the initial value of 580 mL/g to lower than 200 mL/g. The detailed specification of the untreated cotton linter can be found in Table 4.

*Table 4. Specification of the used untreated CL*

| **Molecular weight** | | | | **Viscosity** |
|---|---|---|---|---|
| **Mn** kg/mol | **Mw** kg/mol | **DP** | **PDI** | mL/g |
| 92887.9 | 253773.49 | 1429.5 | 2.2 | 579.2 |

Ozonation of the untreated cotton linter was done in the ozonator. Due to the lack of information on the ozone treatment of cotton linter, the required amount of ozone

to degrade the sample to the desire DP levels was unknown. Therefore, the optimal ozonation conditions had to be determined.

The ozone treatment was performed at ambient temperature and high cellulose consistency of 55-60 wt% and the initial pH level was adjusted to 5±0.5, to prevent the formation of undesired byproducts and reduce the yield losses.

The treatment started with the pH adjustment. The cotton linter's pH was adjusted by sulfuric acid to the range of 4.5 - 5 at 3 wt% consistency. After the pH adjustment the excess water was removed from the sample by centrifugation to reach the consistency close to 55-60 wt%. For the ozonation trials aiming to determine the optimal condition to reach the required $DP_V$, 5 gr of dried sample was used for each treatment. Once optimal conditions were established, 50 grs of dried sample was treated and was used as a reference sample for all of the fractionation experiments, except for those experiments in which non-treated cotton linter directly fractionated..

### 3.2.2 Ozone generator

Ozone is produced by a Wedeco GSO30 device using oxygen (figure 15). Theoretical Ozone production capacity is 100 g/h and theoretical ozone concentration is about 7 wt%. Ozone is generated in high voltage which is produced by electrodes that are cooled in a water flow. The minimum oxygen flow is 100 L/h on this device.

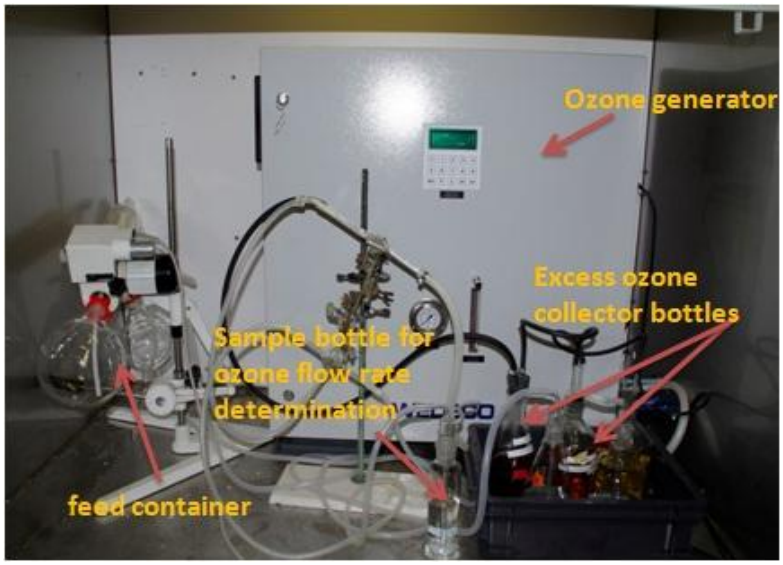


*Figure 15 Wedeco GSO30 ozonator*

The ozone production rate is measured always before starting the treatment and at the end of the treatment. Ozone production rate may change during the trial, so an average value of 3-4 measurements is used in the calculations; changes in pressure, flow rates and reaction temperature are parameters effecting the ozone production.

The rate of generated ozone should be calculated before starting the treatment. For calculating the rate of produced ozone, ozone was collected in the sample unit bottle that consist of a bottle containing 150 ml of 2-10 wt% KI solution, for a controlled time period. The recommended time for this step is two minutes. Reaction of ozone with KI solution is as below:

$$O_3 + 2I^- + H_2O \longrightarrow I_2 + O_2 + 2\,OH^- \quad (17)$$

Then, the solution is emptied into a 300 mL Erlenmeyer and the solution is acidified by adding 10 mL of 2M HCl. The released iodine is titrated with 0.1-0.2 N of $Na_2S_2O_3$ solution until the solution changes to bright yellow. After adding a few drops of starch to the solution, the titration is continued until the solution became colorless.

### 3.2.3 Ozone Calculation

**Ozone amount**

The amount of ozone generated by the device can be calculated by eq.18 :

- $m = n*a*E$ (18)

Where

m ozone amount (mg)

n thiosulphate normality

a thiosulphate consumption (ml)

E Equivalent weight of ozone (48/2=24)

**Ozone production**

The rate of ozone production is calculated by eq.19

- $M = m/t$ (19)

Where

M Ozone production rate (mg/h)

t time(h)

**Ozone concentration**

- $c = M/Q$ (20)

Where

c ozone concentration (mg/l)

Q Gas flow in ozone generator (l/h)

**Ozone concentration in oxygen gas (cw/w)**

- $c_{w/w} = [c/(D_{o2} + 0.33\ c)]*100\%$ (21)

Where

$D_{o2}$ = density of oxygen gas (in 20◦C about 1310 mg/l)

After repeating the ozone flowrate measurement 3-4 times and defining the average of generated ozone rate, the pH adjusted cotton linter is placed in the round bottom flask and the ozone is injected to the sample through a tube while the bottle is rotated (Figure 16).

*Figure 16 feed container*

### 3.2.4 Ozone treatment

The Wedeco GSO30 ozonator has a high production capacity. With the flow rate of 0.25 $m^3$/h (4.17 l/min) and 50% efficiency (power), ozonator generates about 667 mg/min of ozone. The amount of ozone consumed by the sample is calculated as a

difference of the inlet and outlet rate of the ozone to the sample container (rotary bottle). The inlet is the measured ozone rate generated and the outlet is determined by the same titrating procedure for the ozone that comes out of the feed container and dissolves in the KI solution in the ozone collector bottles.

However, due to the minor unexpected leakage and the restricting safety instruction, the flowrate and the efficiency (power) of the ozonator was set at a low value, the power was set to 33 W and the power consumption set to 1% for all of the experiments. By fixing the produced ozone rate, the only variable factor in the treatment is the time of the treatment. To reduce the calculation error when long time treatment is required, it is recommended to divide the treatment into different shorter time stages and the consumed ozone should be measured in between. Thus, with these ozonator settings the 50 g batch was ozonated for at least 70 minutes in 12 stages.

## 3.3 STABILIZATION

As explained in chapter 5, for the viscosity measurement and the IONCELL-P fractionation the treated cotton linter needs to be stabilized by applying two more stages which were introduced as R and P stages.

### 3.3.1 R Stage

Sodium borohydride (BH) is a typical compound for selectivity reducing carbonyl groups to alcohols. Intermediate treatment with BH was carried out at 70°C with fixed BH concentrations, a liquid-to-solid ratio of 15 ml/g and isothermal treatment duration is set to 60 minutes. The stabilization agent can cause yield loss of the sample. The relation of the BH concentration and the cellulose yield can be found as Figure 17 [47]. According to these data, sever yield loss of cellulose is only expected at concentration below 0.75 g/L; Therefore, 0.75 g/L was the used BH concentration in this study.


*Figure 17 relation of the BH concentration and the cellulose yield* [48]

Equation 22, shows the relation of the BH half-life with pH and temperature in aqeous condition.

$$\log t_{1/2} = pH - (0.034T - 1.92) \quad (22)$$

The pH in the BH treatment was adjusted to 13 with NaOH, where the BH half-life of 30.3 h at 70 ◦C was acceptable for the selected treatment time.

### 3.3.2 P Stage

The P stage was carried out using hydrogen peroxide and sodium hydroxide with the ratio of 8 kg/t and 10 kg/t of cellulose, respectively. The temperature was set at 75 ◦C and the initial pH was set to 5 for the P stage stabilization. After applying the stabilization to the treated cotton linter, the samples were dried at room temperature overnight for further processing with IL.

## 3.4 FRACTIONATION OF THE TREATED COTTON LINTER IN [emim] OAc-WATER SYSTEM

1-Ethyl-3-methylimidazolium acetate [emim] OAc is one of the most researched solvent for polysaccharides.

For this study, different [emim] OAc –water wt% solutions were prepared with water molar fractions of 0.595, 0.605, 0.625, 0.659 and 0.689 (equivalent to 13.5, 14, 15,17 and 19 wt% respectively) in [emim] OAc for performing IONCELL-P on ozone treated and untreated CL samples. In each experiment, one gram of the oven dried ozone treated cotton linter was mixed with 20g of prepared IL solution (resulting in 5 wt % cellulose consistency) in a 50 ml Falcon tube which was being heated in a

water bath at 60 ◦C for 3 hours. These conditions are the optimum condition for hemicellulose removal from Birch pulp presented in the previously discussed study by C. Froschauer [30].

After 3 hours, the IONCELL extraction process is followed by filtering the Cellulose/IL-water mixture. For the samples that are treated with the IL solution containing water above 15 wt% a syringe filter of 20 µm porosity is used, and for the samples fractionated with lower water content mixtures which would need more applied back pressure for filtration, another filtration unit was used. The filter unit used high pressure nitrogen gas and contains a metal mesh filter with a cutoff size of 5-6 µm that was supported with a strong metal mesh.(Figure 18)

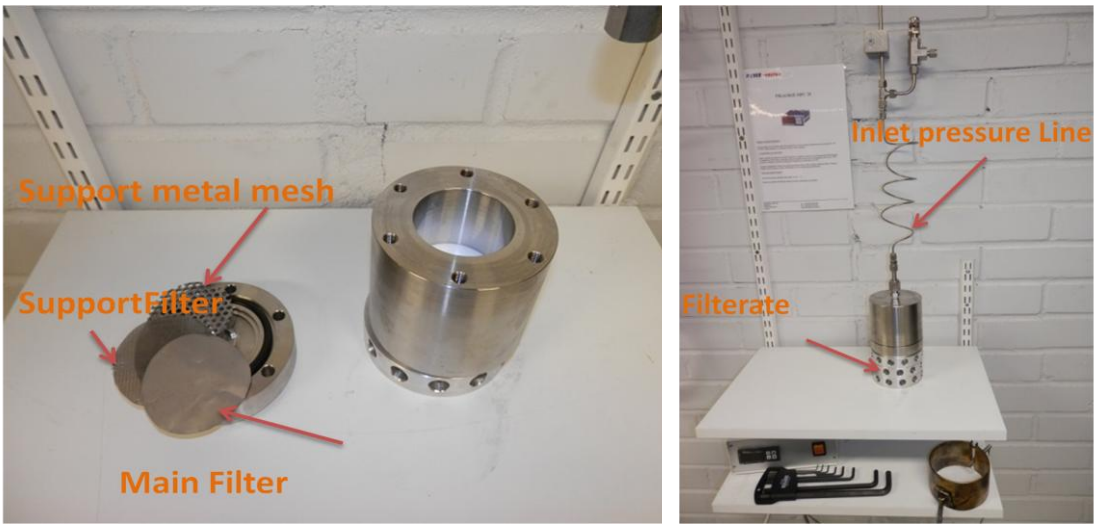


*Figure 18 the filter unit*

The cellulose residue was then washed with 20 g of the [emim] OAc-water mixture as used in the extraction step in order to remove residual dissolved cellulose from the fibers without inducing cellulose precipitation.

Subsequently, the extracted pulp was washed three times with hot water to remove all traces of ionic liquid. All filtrates were then combined to induce their precipitation by excess water.

The precipitated cellulose was collected via centrifugation and the pellets washed three times with hot water. The gravimetrical yield and MMD of both retentate and filtrate fractions were analyzed.

In addition, two more fractionations using untreated cotton linter with water molar fraction of 0.574 and 0.585 in IL solution was done. These mole fractions correspond

to 12.5 and 13 wt%. Thus, the total range of investigated water content was 12.5-19 wt% in the IL-water mixtures.

The residual cellulose and the precipitated cellulose were dried at room temperature overnight for further GPC analysis.

## 3.5 GPC ANALYSIS OF FRACTIONS

The molecular weight characterization was performed by gel permeation chromatography.

As it is described in section 2.6, cellulose samples should be dissolved in LiCl/DMAc solution to inject in the GPC column. Prior to this stage the samples were prepared according to a standard operating procedure explains here:

The first stage of the preparation process is activation in water. For this purpose 6 ml polypropylene tube that is connected to a vacuum manifold with a 20 µm PE-frit as filter at the bottom open end was used. A 50±5 mg of each sample was weighted into these tubes accurately. 4 ml of milliQ-water was added to the sample and the tube was covered with plastic stopper and kept for more than 6 hours at ambient temperature. Then, water was released by using vacuum manifold and 2 ml of acetone was added to the sample and removed by vacuum instantly. Thereafter, 4 ml of acetone was added to the sample and the sample was kept in acetone at ambient temperature for more than 2 hours until the acetone absorb the residual water remaining in the samples. After the dewatering stage, 4 ml of pure DMAc was added to the sample and the mixture was kept overnight. Activation in DMAc was followed by the dissolution step where the sample was transfer to glass bottles and 5 ml of 90g/l LiCl/DMAc was added to sample and dissolved at room temperature under a constant low magnetic stirring. Depending on the sample, the complete dissolution could take up to several hours. Then, 0.5 ml of dissolved sample was diluted with 4.5 ml of pure DMAc and was filtered into vials using 0.2 µm syringe filter. The samples were then injected into an analytical column 4 X PL gel 20µm with the flow rate of 0.75 ml/min and injection volume of 100 µm.

## 3.6 VISCOSITY MEASUREMENT

The intrinsic viscosities (mL/g) were measured according to the standard method SCAN-CM 15:99 using CED solution as a solvent and capillary tube for viscosity measurement.

# 4. RESULTS AND DISCUSSION

The first three section of this chapter presents the basic measurement data of the ozone flow rate, ozonation results of different samples and stabilization stage respectively. Results of the MMD for treated CLand the IONCELL-P treatment can be found in section 4.4 and 4.5. In the final section (4.7) , collected data in this study is compared to the birch pulp fractionation described in literature.

## 4.1 OZONE FLOWRATE DETERMINATION

The produced ozone flowrate before and after the ozonation was measured and the results are presented in Table 5:

*Table 5. Ozone flowrate trials*

| No | Trials | t (s) | a (ml) | n ($Na_2S_2O_3$) | m (mg) | M (g/min) | Q10% (L/h) | c (mg/L) | c w/w (%) | Power (W) | SET (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 1 | 120 | 35.75 | 0.203 | 174.17 | 0.086 | 150 | 34.74 | 2.62 | 33 | 1 |
| | 2 | 120 | 31.25 | 0.203 | 152.25 | 0.076 | 150 | 30.45 | 2.30 | 33 | 1 |
| | 3 | 120 | 30.51 | 0.203 | 148.64 | 0.073 | 150 | 29.58 | 2.24 | 33 | 1 |
| | 4 | 120 | 31.44 | 0.203 | 153.17 | 0.076 | 150 | 30.48 | 2.30 | 33 | 1 |
| **Mean** | | | | | 151.35 | 0.075 | | 30.17 | 2.28 | | |
| **2** | 1 | 120 | 29.69 | 0.203 | 144.57 | 0.072 | 150 | 28.81 | 2.18 | 33 | 1 |
| | 2 | 120 | 28.57 | 0.203 | 139.12 | 0.069 | 150 | 27.73 | 2.10 | 33 | 1 |
| | 3 | 120 | 28.36 | 0.203 | 138.10 | 0.068 | 150 | 27.48 | 2.08 | 33 | 1 |
| **Mean** | | | | | 138.61 | 0.069 | | 27.60 | 2.09 | | |
| **3** | 1 | 121 | 30.44 | 0.203 | 148.23 | 0.073 | 150 | 29.28 | 2.21 | 33 | 1 |
| | 2 | 120 | 29.25 | 0.203 | 142.43 | 0.071 | 150 | 28.43 | 2.15 | 33 | 1 |
| | 3 | 120 | 28.68 | 0.203 | 139.66 | 0.069 | 150 | 27.88 | 2.11 | 33 | 1 |
| | 4 | 120 | 27.37 | 0.203 | 133.28 | 0.066 | 150 | 26.52 | 2.01 | 33 | 1 |
| **Mean** | | | | | 138.45 | 0.069 | | 27.61 | 2.09 | | |
| **4** | 1 | 300 | 59.62 | 0.206 | 294.76 | 0.058 | 150 | 23.55 | 1.78 | 140 | 1 |
| | 2 | 300 | 73.81 | 0.206 | 364.91 | 0.072 | 150 | 29.17 | 2.21 | 33 | 1 |
| | 3 | 300 | 72.67 | 0.206 | 359.28 | 0.071 | 150 | 28.68 | 2.17 | 33 | 1 |
| | 4 | 300 | 72.75 | 0.206 | 359.67 | 0.071 | 150 | 28.70 | 2.17 | 64 | 1 |
| **Mean** | | | | | 361.29 | 0.072 | | 28.85 | 2.18 | | |
| **5** | 1 | 300 | 76.03 | 0.206 | 375.89 | 0.075 | 150 | 30.07 | 2.27 | 33 | 1 |
| | 2 | 300 | 75.54 | 0.206 | 373.46 | 0.074 | 150 | 29.84 | 2.26 | 33 | 1 |
| | 3 | 300 | 71.9 | 0.206 | 355.47 | 0.071 | 150 | 28.43 | 2.15 | 33 | 1 |
| **Mean** | | | | | 368.27 | 0.073 | | 29.45 | 2.23 | | |

***Note*** ***t:*** *period of the measurement,* ***a:*** *Na2S2O3 consumption (ml),* ***n:*** *Na2S2O3 normality,* ***m:*** *produced ozone,* ***M:*** *rate of the produced ozone,* ***Q****: Gas flow rate* ***c:*** *ozone concentration,* ***cw/w:*** *Ozone concentration in oxygen gas,*

As it can be seen from Table5, the ozone flow rates fluctuate between the 0.069 – 0.075 mg/min, so for each ozone treatment this predetermination of ozone flow should be repeated to minimize the error in calculations.

❖ **Calculation example for No.5-trial 1:**

m = n*a*E = 0.206*76.03*(48/2) = 375.892 mg

M = m*(1/t)*60*(1/1000) = 375.892*(1/300)*(1/1000) = 0.0751 g/m

c = m*(1/t)*3600*(1/Q) = 375.892*(1/300)*3600*(1/150) = 30.071

$c_{w/w} = [c/(D_{o2} + 0.33\ c)]*100 = [30.071/(1310+0.33*30.071)]*100 = 2.278$

## 4.2 OZONATION

The above mentioned calculations were used to calculate the amount of ozone charge based on the reaction time of the treatments. The detailed data regarding the ozone treatment before the R and P stage are presented in Table 6.

*Table 6. Cotton linter ozonation before applying P and R treatment*

| Sample | C | t | W | m | a | R | TOC | Y | DP | ŋ |
|---|---|---|---|---|---|---|---|---|---|---|
| | Wt% | min | gr | gr/min | ml | (%) | mg | % | | mL/g |
| **CL-1** | 32.7 | 10 | 3 | 0.0754 | 143 | 1.935 | N/A | N/A | 987 | 430 |
| **CL-2** | 27.49 | 10 | 5 | 0.069 | 130.7 | 0.693 | N/A | N/A | 1023 | 442 |
| **CL-3** | 52.48 | 5 | 5 | 0.069 | 62.9 | 0.378 | 4.927 | 0.222 | 1125 | 475 |
| **CL-4** | 55.49 | 70 | 10 | 0.072 | 933.2 | 4.392 | 44.7 | 1.0062 | 405 | 170 |
| **CL-5** | 59.31 | 89 | 50 | 0.073 | 1321.8 | 3.893 | 270 | 1.2162 | 435.7 | 183 |

***Note*** ***C:*** *Consistency* ***t:*** *period of the measurement,* ***W:*** *Oven Dried Weight* ***m:*** *produced ozone* ***a:*** *Na2S2O3 consumption (ml)* ***R:*** *The ratio of consumed ozone to sample* ***TOC:*** *Total Organic Carbon* ***Y:*** *yield losses* ***ŋ:*** *intrinsic viscosity*

To reach the desired DP for the degraded cotton linter , time of the treatment was set to more than 70 minutes. Treating the CL for 70 minutes all at once might cause major error in the consumed ozone calculations and so it is recommended to divide the treatment into different stages in a row. Since the CL-1 to CL-3 haven't reached the required viscosities, CL-4 and CL-5 were performed with 7-8 times longer treatment times. These samples had promising premeasured intrinsic viscosity. Thus only these two samples were stabilized for the further IONCELL-P experiments. The consumed ozone per gram of sample is also very informative in the sense that we see

the first three samples did not consume much ozone so we expect less degradation as well.

### 4.3 STABILIZATION

As it is discussed earlier, the target of the ozonation was to degrade the cotton linter sample to have a viscosity lower than 200 ml/g, equivalent to $DP_V$ of 470 or lower. To save time during the experiments, the intermediate stage ''R'' and post treatment stage ''P'' were not applied to those samples which have not satisfied the required viscosity level. According to preliminary viscosity measurements the two last samples, CL-4 and CL-5 were the best candidate since they degraded to the molecular weight to the range that we wanted to study.

According to section 2.5, to eliminate further degradation after ozonation, two stabilization stages (R and P) were applied to the treated samples marked as CL-4 and CL-5 in Table 6. In some publications the sequence of the treatment is R-P but in this study the reverse order P-R also gave acceptable results. Detailed data regarding the conditions of the R and P treatment can be found in Table 7.

*Table 7. P and R stage's detailed data*

| **Sample** | **C** Wt% | **pH** | **pH** in filtrate | **T** ◦c | **t** h | **W** gr | **$R_{H2O2}$** (kg/t) | **$R_{NaOH}$** (kg/t) | **$M_{NaBH4}$** (gr) | **DPv** | **ŋ** mL/g |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **P stage** | | | | | | | | | | | |
| **CL-4** | 3 | 4.4 | 3.8 | 95 | 3 | 5 | 8 | 10 | N/A | N/A | N/A |
| **CL-5** | 10 | 5 | 3.6 | 75 | 3 | 16 | 8 | 10 | N/A | N/A | N/A |
| **R stage** | | | | | | | | | | | |
| **CL-4** | 6.6 | 13 | 12 | 70 | 1 | 5 | N/A | N/A | 0.0562 | 350 | 147 |
| **CL-5** | 6.6 | 13 | 12 | 70 | 1 | 16 | N/A | N/A | 0.18 | 364.3 | 153 |

***Note*** ***C:*** *Consistency* ***t:*** *period of the measurement,* ***W:*** *Oven Dried Weight* ***$R_{H2O2}$:*** *The ratio of consumed $H_2O_2$ to sample* ***$R_{NaOH}$:*** *The ratio of consumed NaOH to sample* ***$M_{NaBH4}$:*** *weight of sodium borohydride* ***ŋ:*** *intrinsic viscosity*

Viscosity measurement after the borohydride stabilization shows an average 15% decrease (see last two rows of Table 6 and Table 7). This can be explained by the fact that the alkali sensitivity introduced by ozone on cellulose during the ozonation is manifested in DP loss during the R stage that takes place at alkaline condition (pH=13). The post treated samples will have a lower viscosity which can be

determined more accurately with the intrinsic viscosity measurements and is close to the true value calculated by physical measurement.

## 4.4 MOLAR MASS DISTRIBUTION OF TREATED CL

The molecular weight characterization was performed by gel permeation chromatography. Table 8 summarizes the number, weight and centrifuge average molecular weight, the polydispersity and the different molecular weight fractions of the ozone treated cotton linters.

*Table 8. Molecular characterization of the original and degraded pulps*

| **Sample** | **ŋ** | **DP** | **Mn** | **Mw** | **Mz** | **PDI** | **$W_{(DP<50)}$** | **$W_{(DP<100)}$** |
|---|---|---|---|---|---|---|---|---|
| | ml/g | | (kg/mol) | (kg/mol) | (kg/mol) | (Mw/Mn) | (%) | (%) |
| **CL** | 570 | 1429.5 | 92.88 | 253.77 | 497.19 | 2.732 | 0.00743 | 0.01828 |
| **CL-3** | 475 | 1125 | 79.54 | 197.88 | 376.95 | 2.5 | 0.00840 | 0.02351 |
| **CL-4** | 153 | 364.28 | 32.50 | 75.72 | 123.93 | 2.329 | 0.04153 | 0.10395 |
| **CL-5** | 147 | 350 | 31.41 | 78.96 | 131.89 | 2.513 | 0.04504 | 0.10726 |

***Note*** ***ŋ:*** *intrinsic viscosity Number average* ***(Mn)****, weight average* ***(Mw)*** *and centrifuge average* ***(Mz)*** *molecular weight* ***PDI:*** *polydispersity index* **$W_{(DP<50)}$:***Ratio of polymers with DP<50* **$W_{(DP<100)}$** *: Ratio of polymers with DP<100*

By ozonation of the CLs, the amount of high molecular weight fraction of cellulose is reduced and the low molecular fraction of cellulose is slightly increased. The polydispersity index depicts the quality of the degradation. No changes in index value means that random degradation of polysaccharides chains can be consider as a dominant degradation mechanism. Decrease in the index value means that polymer scissions mostly occurring near the center of the chains is the dominant degradation mechanism. However, in all of the degraded cotton linter in Table 8, a decrease in polydispersity index is observed, thus the second degradation mechanism is libely.

The profiles of the MMD of the original and degraded cotton linters are plotted in Figure 19. By degrading the cotton linter, the MMD shifted towards lower molecular weight. Moreover, according to the polydispersity index and Figure 19, the MMD profiles for CL-4 and CL-5 get narrower and at the same time the peak increased to a higher value, possibly due to the cleavage of the higher molecular weight polymers.

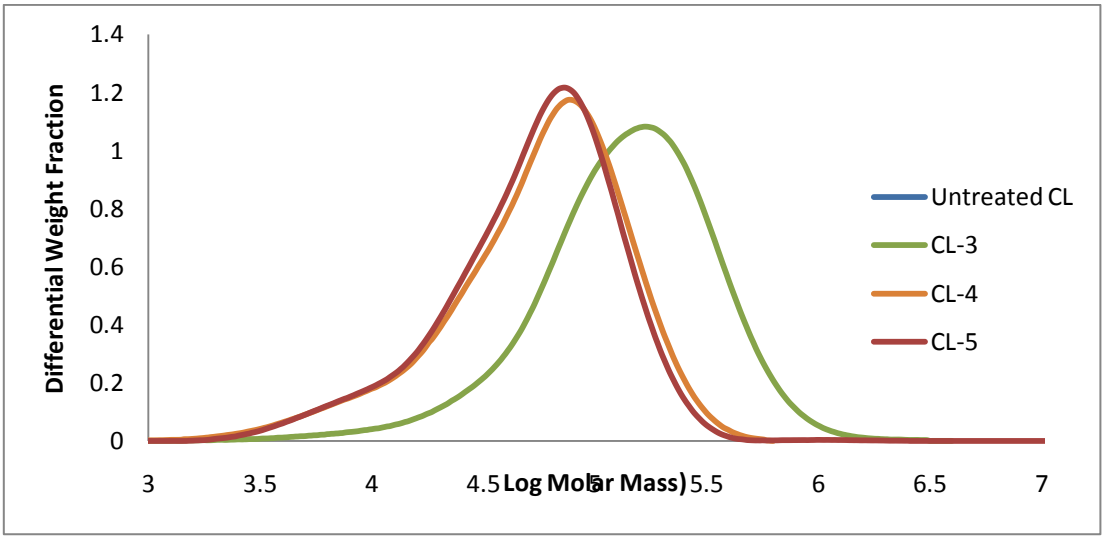


*Figure 19. Molar mass distribution of the original and degraded cotton linters.*

The CL-4 was selected as a reference material for further processing by ionic liquid.

## 4.5 IONCELL-P TREATMENT OF THE OZONE TREATED CL

The IONCELL-P process was explained in detailed in the first part of this study. The yield and MMD's data of the residual (undissolved) and the precipitated (dissolved) fractions from IL-Water solution for different water content - 13.5-19 wt % - are collected in Table 9. The MMD of each fraction is plotted separately in Figures 20-24. The sum curves in these graphs were calculated based on the gravimetrical yield of the undissolved and dissolved cellulose fractions by equation 26.

SUM = (undissolved cellulose's MMD) * (Solid residue yield) + (26)
(dissolved cellulose's MMD) * (precipitated cellulose yield)

Overlapping these sum curves with the treated CL's MMD curve before the fractionation, confirmed that no degradation happened during the IONCELL-P process.

*Table 9. IONCELL fractionation data*

| | | | | | | Residual | | | precipitated | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **EDUCT** | **water** | **C** | **W** | **T** | **t** | **Y** | **Mn** | **Mw** | **Y** | **Mn** | **Mw** |
| | wt% | wt% | Odg | °C | h | wt% | kg/mol | kg/mol | wt% | kg/mol | kg/mol |
| CL-4 | 13.5 | 5 | 1 | 60 | 3h | 60.6 | 61.3 | 98.3 | 37.81 | 17.5 | 37.4 |
| CL-4 | 14 | 5 | 1 | 60 | 3h | 72.7 | 59.4 | 93.8 | 26.60 | 15.1 | 30.8 |
| CL-4 | 15 | 5 | 1 | 60 | 3h | 78.8 | 53.8 | 86.8 | 22.32 | 12.4 | 24.5 |
| CL-4 | 17 | 5 | 1 | 60 | 3h | 87.3 | 47.8 | 82.5 | 12.35 | 10.2 | 18.2 |
| CL-4 | 19 | 5 | 1 | 60 | 3h | 91.1 | 41.7 | 79.5 | 4.21 | 9.1 | 16.3 |

***Note*** ***C:*** *Consistency* ***W:*** *Oven Dried Weight* ***t:*** *period of the treatment* ***Y:*** *Yield Number average* ***(Mn)*** *and weight average* ***(Mw))*** *molecular weight*

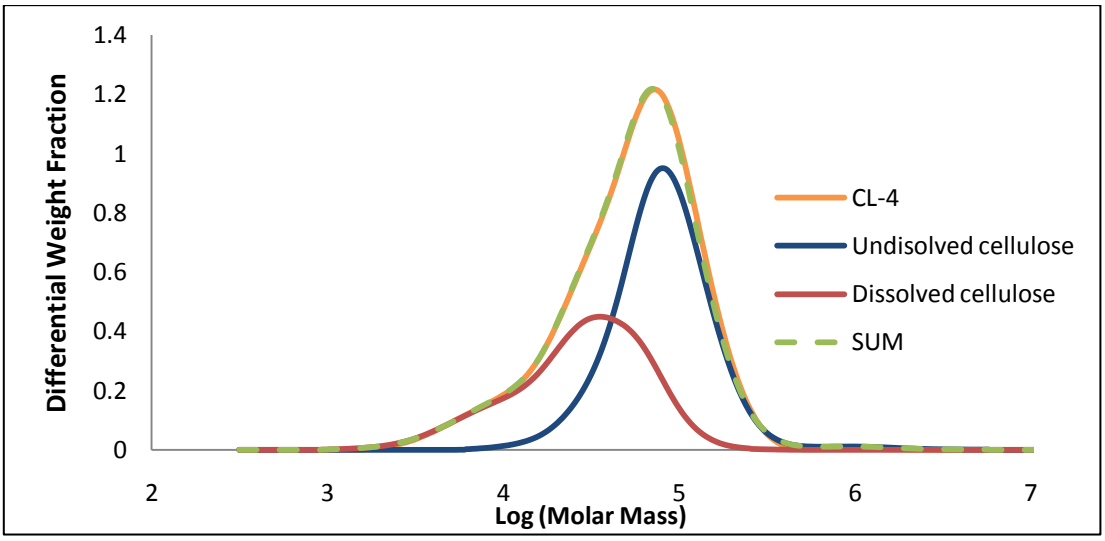


*Figure 20. IONCELL fractionation using [emim] OAc with 13.5 wt% of water*

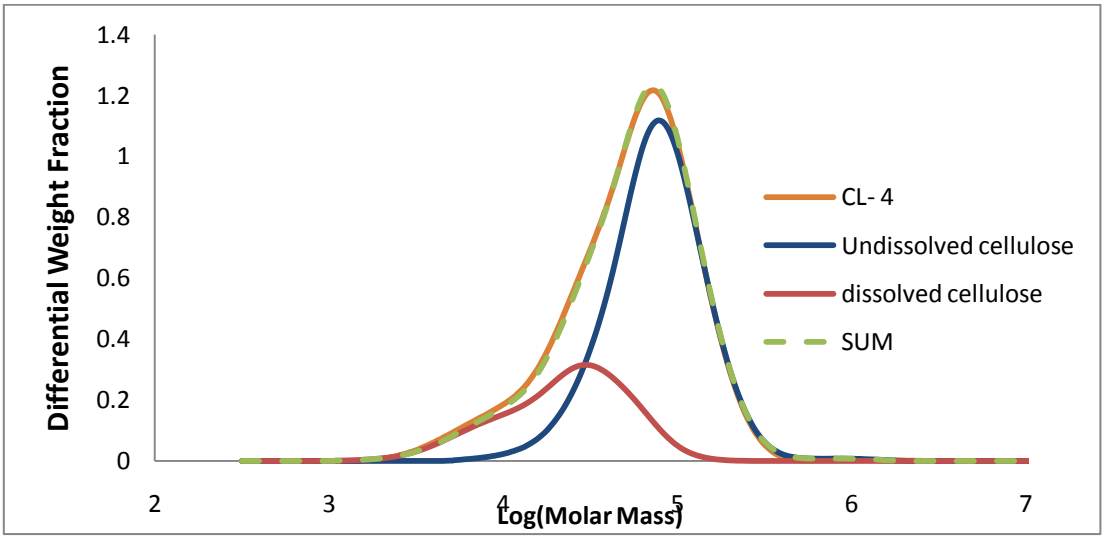


*Figure 21. IONCELL fractionation using [emim] OAc with 14 wt% of water*

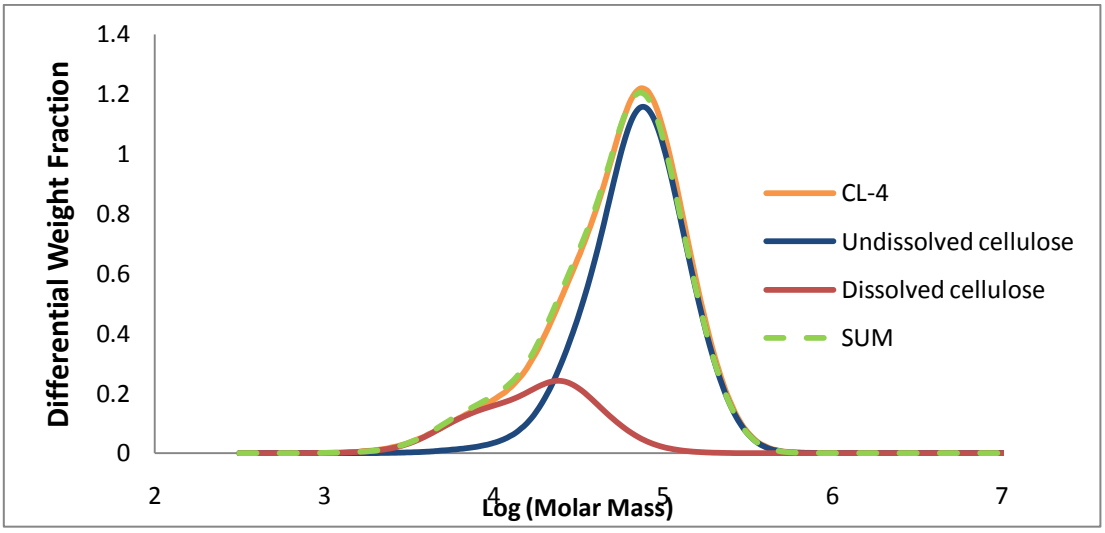


*Figure 22. IONCELL fractionation using [emim] OAc with 15 wt% of water*

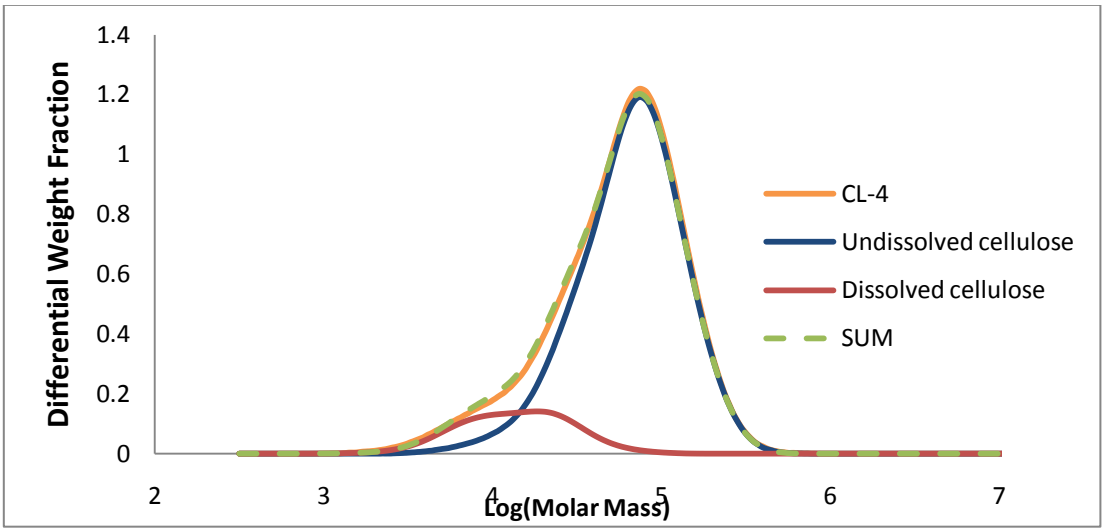


*Figure 23. IONCELL fractionation using [emim] OAc with 17 wt% of water*

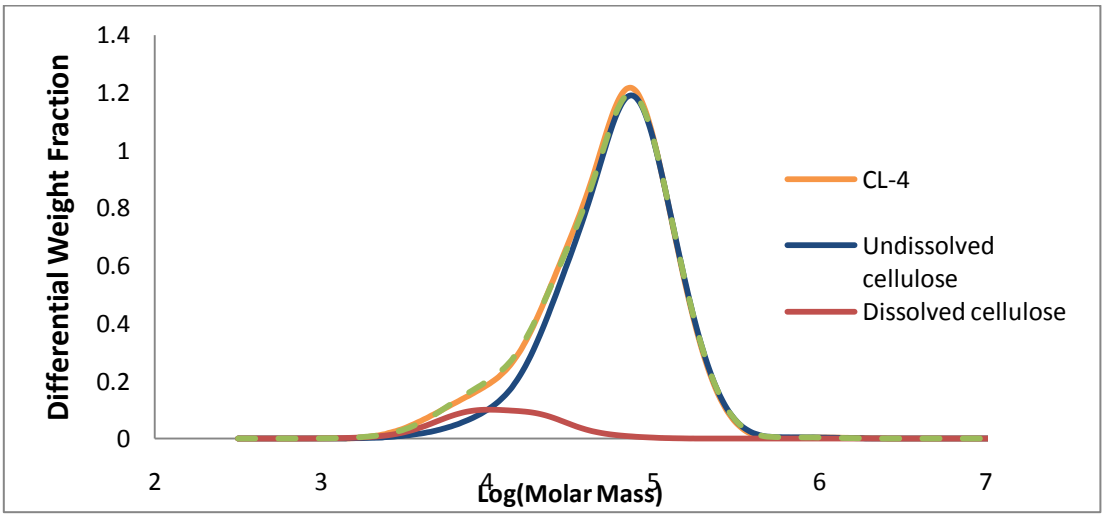


*Figure 24. IONCELL fractionation using [emim] OAc with 19 wt% of water*

Increasing the water content in the IL results in decreased dissolution capacity of the IL because created hydrogen bonds between the water and IL moleculs would caused competitive environment for cellulose to dissolve; So, by increasing the water content we expected that the fraction of dissolved cellulose in the IL would be decreased, since only even lower Mw range of cellulose is possible to dissolve in such high water content mixtures, and this range of molecular size is a smaller fraction of the total sample. The results of the experimental data supports this hypothesis, Figure 25 depict this trend.

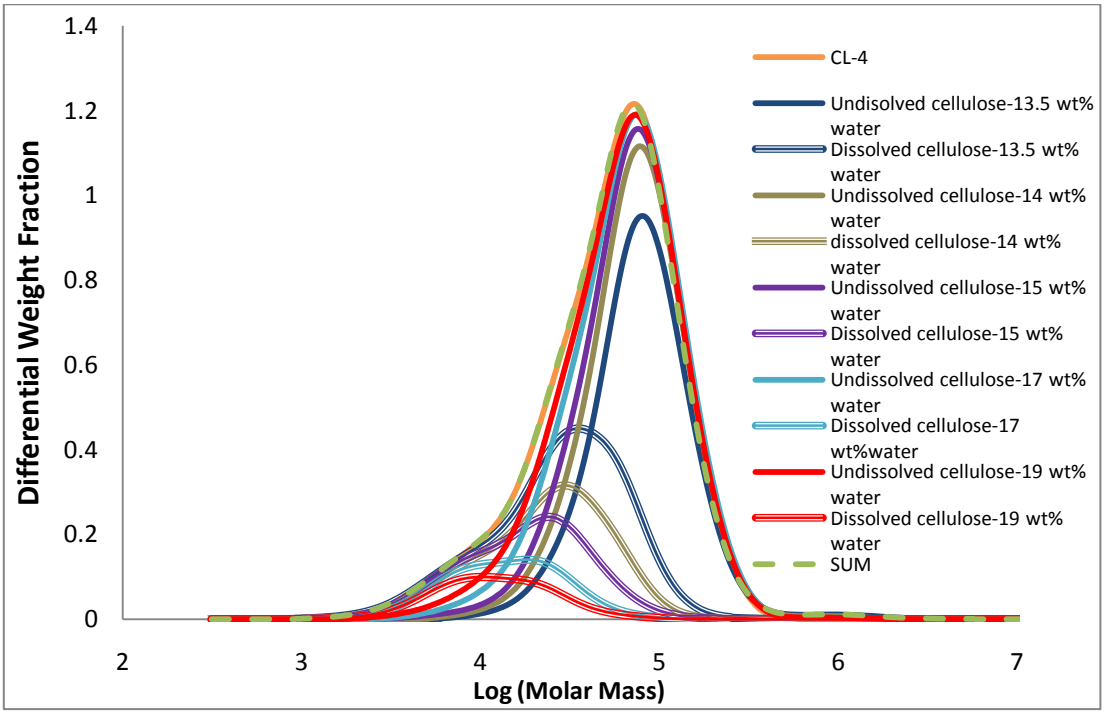


*Figure 25. IONCELL fractionation using [emim] OAc with 13.5-19 wt% of water*

The target of this study is to investigate the effect of the molecular weight on the fractionation of different polysaccharides with IL-Water mixture. By using the treated CL which is pure cellulose with a single chemical structure for the IL fractionation the effect of the chemical structure is eliminated.

From figure 25 we can clearly see the trend of the different Mw ranges being dissolved to a different extent in [emim] OAc-water mixtures with different water content. By studying this pattern we can conclude that in the absence of the different chemical structures (like hemicellulose, lignin and etc) the IL dissolved the cellulose polymer based on the molecular size of the polymer.

## 4.6 IONCELL-P TREATMENT OF NON-TREATED CL

To support the previous study lower water content of the mixture was tested for fractionation as well. Decreasing the water content in IL solution will result to enhance the cellulose solubility in IL and consequently more cellulose with higher molecular weight will be dissolved in IL and this phenomenon will cause some difficulties in filtration. In addition to the presented results for IONCELL-P process using degraded CL, two more fractionation with the 12.5 and 13 wt% of water were done using untreated cotton linter. The fractionation data and MMD results are presented in Table 10; MMD of both fractions and the sum curves are potted in Figure 26 and 27.

Table-10 IONCELL fractionation data

| | | | | | | Residual | | | precipitated | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **EDUCT** | **Co-Solv** | **C** | **W** | **T** | **t** | **Y** | **Mn** | **Mw** | **Y** | **Mn** | **Mw** |
| | wt% | wt% | Odg | °C | h | wt% | kg/mol | kg/mol | wt% | kg/mol | kg/mol |
| CL | 12.5 | 5 | 1 | 60 | 3h | 84.9 | 156.4 | 277.3 | 16.62 | 37.1 | 79.3 |
| CL | 13 | 5 | 1 | 60 | 3h | 87.8 | 139.6 | 267.2 | 7.79 | 32.9 | 70.9 |

***Note*** ***C:*** *Consistency* ***W:*** *Oven Dried Weight* ***t:*** *period of the treatment* ***Y:*** *Yield Number average* ***(Mn)*** *and weight average* ***(Mw))*** *molecular weight*

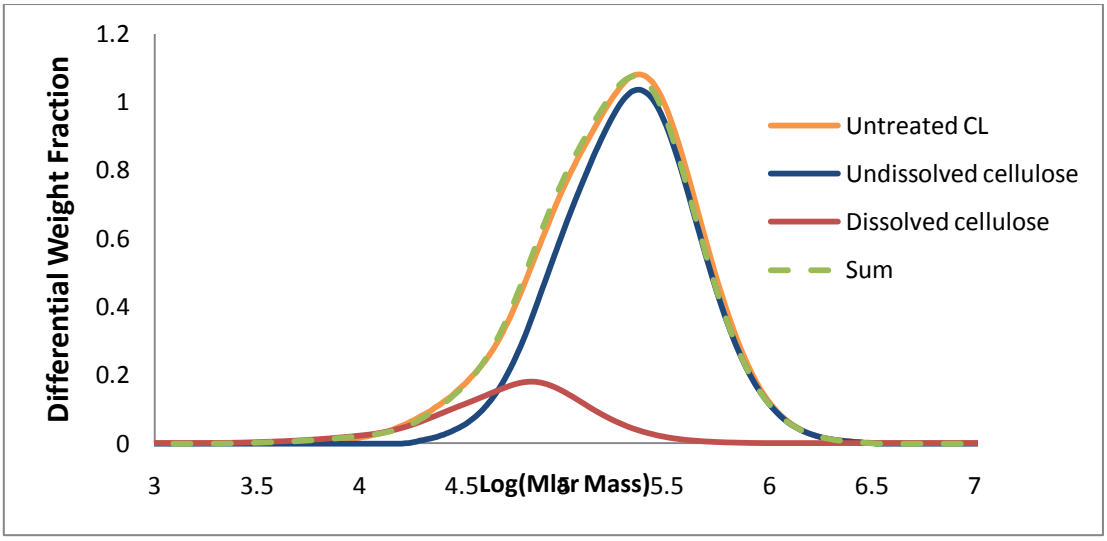


*Figure 26. IONCELL fractionation using [emim] OAc with 12.5 wt% of water*

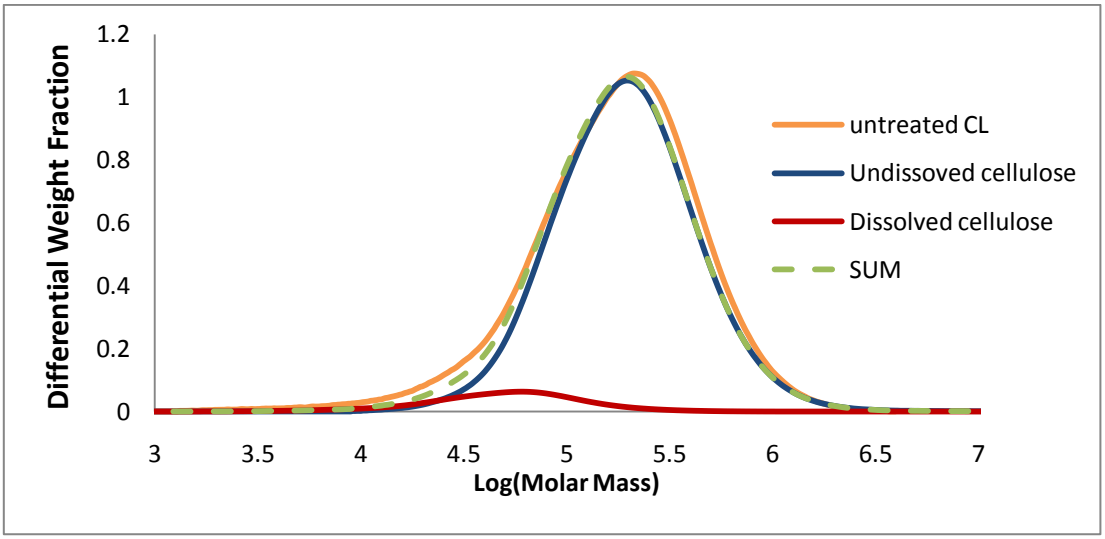


*Figure 27. IONCELL fractionation using [emim] OAc with 13 wt% of water*

These two samples showed similar trend to the samples summarized on figure 25. By decreasing the water content in ILs, cellulose polymers with higher molar mass are also dissolved in the IL-water mixture and the range of the dissolved cellulose will increase until the point that this range overlapping with the used sample's MMD; According to these data we can conclude that there is not an accurate limit for water wt% in IL that cellulose can be dissolved completely. This limit may vary according to the range of the molecular weight that is available in the sample. For example, the treated CL in this study may be dissolved completely in IL-water mixture with higher water fraction compare to the untreated CL which may require lower water fraction in IL to dissolve completely.

Considering the results, figure 29 depict schematically how the IONCELL-P process worked in this study for fractionating of pure cellulose.

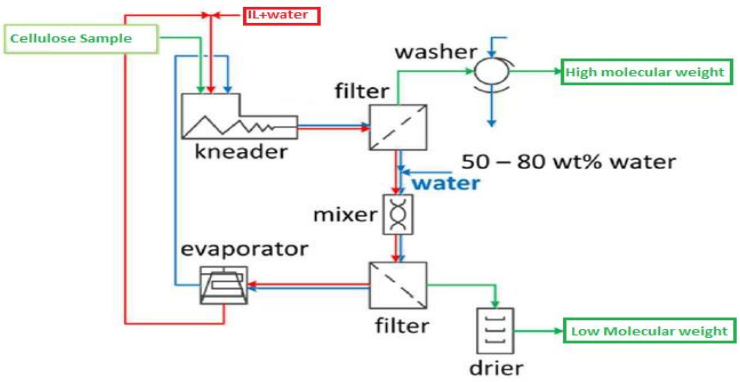


*Figure 28 – IONCELL-P process by using pure cellulose*

## 4.7 COMPARING THE IONCELL-P TREATMENTS OF CL TO THE BIRCH PULP FRACTIONATION DESCRIBED IN LITERATURE

By comparing the results of this study with the available result of the Birch pulp fractionation in *[emim] OAc* with 15 wt% water at the same conditions that is presented in the Carmen et al publication [30] Figure 29, we can predict that in the presence of different chemical structure like the hemicellulose structure that is available in Birch pulp, the IL-water mixture acts the same way and dissolves the same molecular size of the hemicellulose of pure low molecular weight cellulose. Based on this comparison ILs dissolves cellulose and most likely other polysaccharides based on the molecular size and the chemical structure of the molecules has no major effect on the dissolution efficiency, but the same sets of experiment are needed to be done with hemicelluloses to prove this hypothesis.

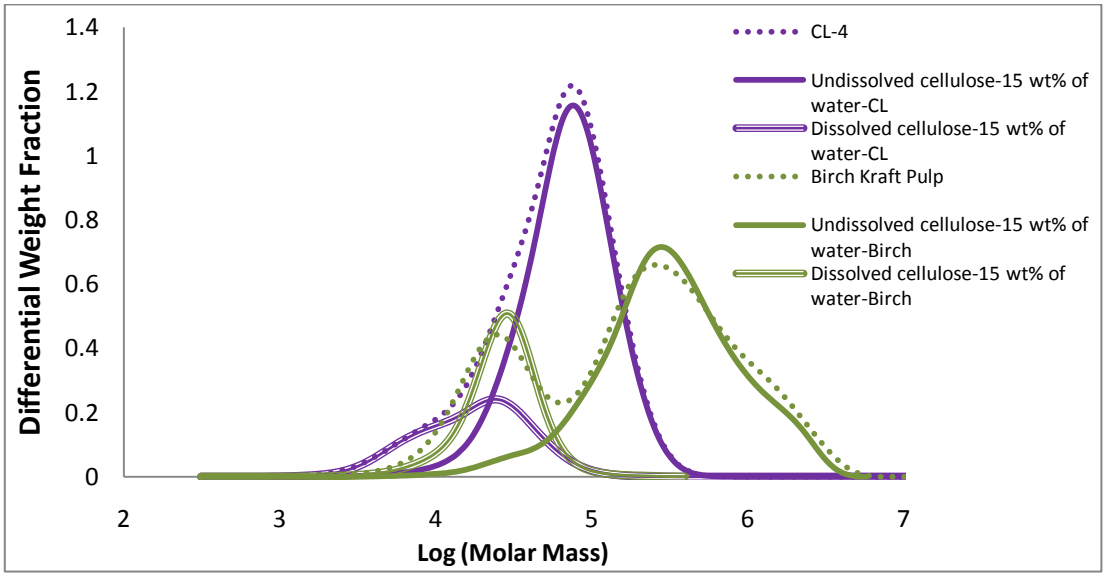


*Figure 29 Comparision of achived data of this study with data presented by Carmen et al* [30]

# 5. CONCLUSION

The influence of the molecular weight of cellulose on the solubility in ionic liquid-water mixtures has been investigated during this Diploma's thesis. The study consists of two parts; Ozone treatment was selected as a degradation method for cotton linters in first part and IONCELL-P treatment was applied to the treated samples in the second part. In the first part the viscosity of the untreated cotton linter was decreased from 580 mL/g to less than 200 mL/g. During the second part the treated and untreated cotton linter samples were treated with [emim] OAc-water solutions with different water contents varied between 12.5 and 19 wt% at fixed temperature (60◦C) and time (3h).

The molar mass distribution of the filtrated and the precipitated cellulose were determined. According to the presented MMD's results it can be concluded that the used IL [emim] OAc, dissolved cellulose based on the molecular size of the cellulose polymers. However, due to the single chemical structure of the cotton linter which is practically pure cellulose, from this data we cannot judge the chemical effect of polysaccharides in IL-water mixtures.

Carmen et al [30] has published the results for selective separation of the hemicellulose and cellulose in Birch Kraft pulp using [emim]OAc at the optimum fractionation conditions (60◦c ,15 wt% of water in [emim]OAc for 3hrs reaction time). The results of separation of low and high molecular weight of cellulose using [emim] OAc is presented in this study by applying the same fractionation conditions. From the present study it can be concluded that the used IL-water systems dissolved cellulose based on the molecular size since the fractionated molecules had the same chemical structure, all of them being pure cellulose. In both the present study and in the work of Carmen et al., the dissolved fractions had comparable MMD, which supports the hypothesis of polysaccharide fractionation in IL-water systems being molecular weight driven and less influenced by the chemical structure of the polysaccharides. However more experiments are needed to clarify the effect of chemical structures on the fractionation process.

## FUTURE WORK

Due to the lack of information on this specific topic, the experiments were done for cotton linter at first. But, to get a better vision and study the chemical effect of different cellulose structures in more detailed, it is recommended to repeat the same experiments by using xylans and galactoglucomannans as raw materials.

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