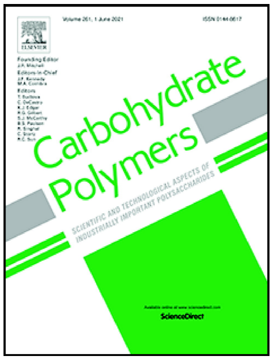


Production of rayon fibres from cellulosic pulps: state of the art and current developments

Inês S.F. Mendes, Dmitry V. Evtuguin

PII: S0144-8617(21)00853-5

DOI: https://doi.org/10.1016/j.carbpol.2021.118466

Reference: CARP 118466

To appear in: *Carbohydrate Polymers*

Received date: 20 April 2021

Revised date: 16 June 2021

Accepted date: 17 July 2021

Please cite this article as: I.S.F. Mendes and D.V. Evtuguin, Production of rayon fibres from cellulosic pulps: state of the art and current developments, *Carbohydrate Polymers* (2021), https://doi.org/10.1016/j.carbpol.2021.118466

Production of rayon fibres from cellulosic pulps: state of the art and current developments

Inês S. F. Mendes, Dmitry V. Evtuguin*

CICECO, Department of Chemistry, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

*Author to whom correspondence should be addressed.

E-mail address: Dmitrye@ua.pt

Phone: +351 234 401526

Fax: +351 234 380084

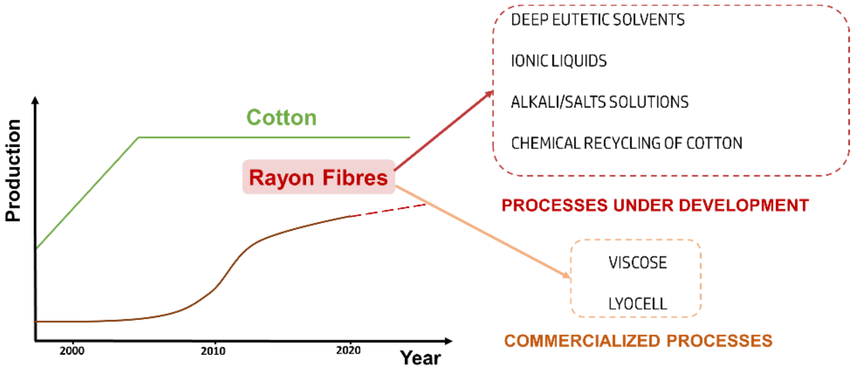
ORCID ID 0000-0002-6304-5105

Abstract

The increasing demand for cellulosic fibres is continuously driven by the growing earth population and requirements of the textile industry. The annual cotton production of *ca.* 25 million tons is no longer enough to meet the market demands. This market gap of cellulosic fibres is progressively filled by regenerated cellulosic fibres derived from the dissolving pulp. The conventional industrial process of viscose production is far from being environmentally friendly due to the use of hazardous reagents. Alternatively, new trends in the production of regenerated fibres are related to the direct dissolution of cellulose in appropriate environmentally sound recyclable solvents, allowing high quality rayon fibres. This article reviews the sources of dissolving pulps used for the production of viscose and its quality parameters related to the performance of viscose production. The prospective cellulose regeneration processes, both commercialized and under development, are reviewed regarding current and future developments in the area.

Keywords: Dissolving pulp; Rayon fibres; Cuprammonium; Viscose; Ionic liquid, Recycling, Textile fibres

Graphical abstract:



Highlights:

- Specific properties of dissolving pulps to produce rayon fibres are summarized
- Drawbacks of the conventional viscose process are highlighted
- Commercialized direct dissolution lyocell process has limitations
- Greener approaches include ionic liquids and deep eutectic solvents
- Chemical recycling of textile fibres is a challenging research topic

Contents

---

1. Introduction

Cellulose, the most abundant natural polymer, is a linear homopolymer composed by β-D-anhydroglucopyranose monomeric units linked by β-(1→4)-glycosidic bonds, with cellobiose as the repeating stereoregular unit (Fengel & Wegener, 1983; Klemm et al., 1998). Due to the strong inter- and intra-molecular hydrogen bonds and significant van der Waals forces, cellulose molecules are organized in fibrils, possessing an amorphous-crystalline physical structure, affording unique properties required for the construction of plant cells, as it is exemplified for wood in Fig. 1 (Fengel & Wegener, 1983; Klemm et al., 1998). Being a tough fibrous polymer, cellulose is insoluble in water and in common organic solvents (Feng & Chen, 2008; Luo & Zhang, 2013; Ramamoorthy et al., 2015; Swatloski et al., 2002; H. Wang et al., 2012; Zhao et al., 2012). It is the main material of cell wall skeleton in plants, bacteria, algae and even in the animal kingdom (Dunlop et al., 2018; Fengel & Wegener, 1983; Sixta, 2006; Sjöström, 1981). However, the abundance of cellulose in plant kingdom varies widely according to its origin: from up to with 95-99 % in seed-hairs (e.g. cotton) to nearly 20-25 % in grasses (e.g., horse-tails) (Fig. 2).

Depending on the cellulose content and fibre morphology (primary length), these plant species may have direct application in textile fibres with minimal processing, known as natural fibres (e.g., cotton, ramie and linen) or need deep processing with isolation of cellulose-rich fibres from plant (e.g., cellulosic pulp) that are first dissolved with or without chemical modification in appropriate solvent/solution to be further regenerated by filament precipitation, known as regenerated cellulosic fibres or rayon. Both natural and viscose fibres are the basis of the textile filaments for the production of various types of woven materials used for the production of clothing or for technical purposes.

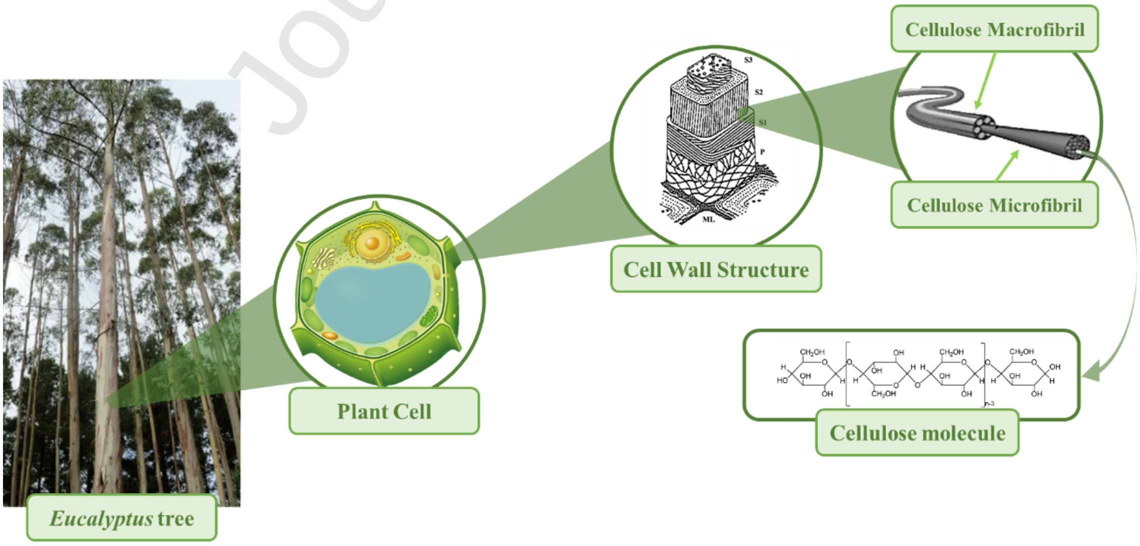


Fig. 1. The structural hierarchy of cellulose from a molecule to a wood tissue.

Fig. 2. Cellulose content in different plant sources (adapted from (Fengel & Wegener, 1983)).

Regarding the textile fibres in general, these can be classified into two main categories – natural and man-made fibres. Natural fibres are divided according to their origin (vegetable, animal, and mineral fibres) whereas man-made fibres can be classified in regenerated cellulosic, inorganic and synthetic fibres (Fig. S1, Supplementary data)

Nowadays, synthetic fibres still govern the textile market with around 70 million metric tonnes produced in the year 2019 (Textile Exchange, 2020). However, due to unique absorbency and moisture management, cellulosic fibres are still indispensable for textile applications (Ma, et al., 2019; Michud, et al., 2016). Among the natural fibres, cotton has the highest production, established at 25 million tons per year (Björquist et al., 2018). Despite being the preferred natural fibre, cotton has a highly negative environmental impact, mainly due to the use of excessive amount water and soil depletion, eutrophication and high ecotoxicity impacts (Shen et al., 2010). Accordingly, the significant growth in cotton production in the nearest future seems problematic. For these reasons, it can be expected that the consumption of dissolving pulp for the production of regenerated fibres will continue to grow in the coming years (Fig. 3).

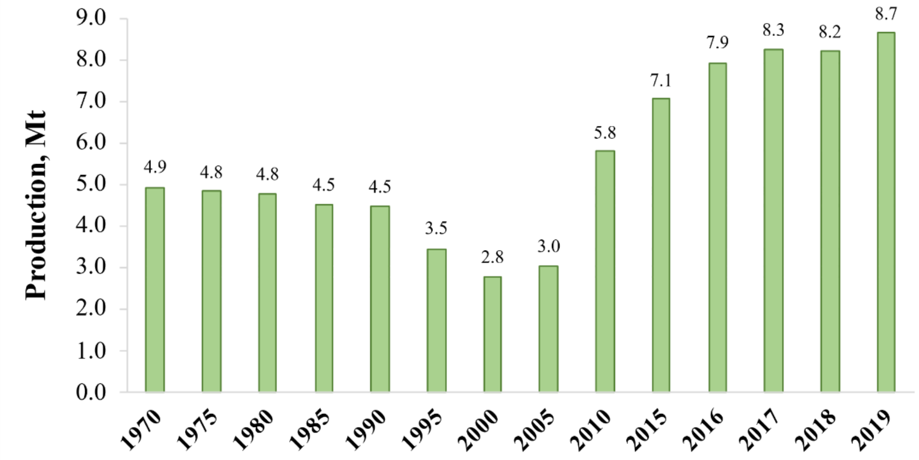


Fig. 3. World production of dissolving pulp from 1970 to 2019 (Food and Agriculture Organization of the United Nations, 2019).

The commonly use for the rayon fibre production viscose process involves the chemical modification of cellulose with hazardous CS_2 under strong alkaline conditions, followed by its dissolution and regeneration under strong acidic conditions (Ciechańska et al., 2009). Due to technical and environmental concerns, this process needs to be replaced with a more ecologically appropriate one. Over time, new prospective cellulose solvent systems have been developed, also considering environmental issues. In general, the approaches for the manufacturing of regenerated fibres can be divided into processes that include cellulose dissolution after its derivatization (e.g., the conventional viscose process) or direct dissolution of cellulose without its chemical derivatization (e.g., Lyocell® process) (Fig. S2, Supplementary data). The latter approach implies to use of specific solvents like *N*-methyl morpholine-*N*-oxide (NMMO) (Jedvert & Heinze, 2017; Wang et al., 2016), aqueous solutions combined with ZnO, urea and/or thiourea (Chen et al., 2007; Li et al., 2015; Luo & Zhang, 2013; Väisänen et al., 2021), lithium chloride solution in *N*,*N*-dimethylacetamide (DMAc/LiCl) (Hong et al., 1998; Matsumoto et al., 2001; C. Zhang et al., 2014), ammonia/ammonium thiocyanate (NH_3/NH_4SCN) (Cuculo et al., 1994), dimethyl sulfoxide/ tetrabutylammonium fluoride (DMSO/TBAF) (Köhler & Heinze, 2007; Wang et al., 2016), dimethyl sulfoxide/benzyl trimethylammonium fluoride (DMSO/BTMAF) (Köhler & Heinze, 2007), molten inorganic salt hydrates (e.g., $LiClO_4 \cdot 3H_2O$) (Fischer et al., 1999; Fischer & Thümmler, 2010; Leipner et al., 2000); second generation ionic liquids (Mohd et al., 2017; Morais et al., 2020; Wang et al., 2012; Xu & Wang, 2020), among others. Among direct cellulose solvents, only NMMO is currently commercialized in the Lyocell® process and for the production of Tencel® fibres by the Lenzing AG company (Wang et al., 2016). However, the conventional viscose process still dominates the industrial production of regenerated cellulose fibres with around 91% contribution, lyocell fibres (*ca*. 5 %), modal fibres (*ca*. 3 %) and *cupro* fibres (*ca*. 1%) (Textile Exchange, 2020).

Table 1 summarises the properties of cotton and different regenerated cellulose fibres used for the textile purposes. Physical properties of regenerated fibres are largely dependent on the rheological properties of cellulose solutions. There are a number of parameters that influence the rheological properties of the resulting cellulose solutions to spin, which includes the type of dissolution process and the solvent used, time and temperature to dissolve, coagulation medium, raw material, among others (El Seoud et al., 2020; Wawro et al., 2014).

Table 1 Properties of cotton and different regenerated cellulose fibres (Bartsch & Kling, 2001; Chavan & Patra, 2004; Cook, 2001; El Seoud et al., 2020; Fink et al., 2014; Jiang et al., 2020; Kamide & Nishiyama, 2001; Kreze & Malej, 2003; Yibo Ma et al., 2020; Shen et al., 2010; S. Wang et al., 2016; Wardman, 2018; Woodings, 1995; S. Zhang et al., 2018).

	Cotton	Viscose	Modal	Lyocell	Cuprammonium
Density (g/cm^3)	1.50-1.54	1.52-1.54	1.52-1.54	1.50	1.54
Tenacity (cN/tex)					
Wet	26-40	10-15	15-22	26-38	9-12
Dry	24-36	20-27	30-36	35-42	15-20
Tensile strength (cN/tex)					
Wet	25-40	10-15	19-24	34-38	18-22
Dry	20-36	22-26	34-36	38-42	26-30
Elongation (%)					
Wet	12-14	21-23	13-20	17-19	17-33
Dry	7-10	17-25	12-18	10-17	10-17
Water retention (%)	38-55	85-100	60-80	60-75	100
Moisture regain (%)	7-8[a]	12-14[a]	n.d.	n.d.	12.5[b]
DP value	2000-3000	235-350	300-650	500-640	450-550

[a] at 20 ºC and 65 % of relative humidity; [b] at standard conditions; n.d. not defined.

Comparing the data in Table 1, only lyocell fibres have a high enough tenacity and tensile strength comparable with cotton fibres. However, none of the regenerated fibres has a higher degree of polymerization (DP) than cotton. Taking into account that DP is directly related to the mechanical properties of fibres, further studies are needed to improve this parameter of regenerated fibres in order to approach cotton in all aspects of its application (De Silva & Byrne, 2017). Lyocell fibres are stronger and stiffer than conventional viscose fibres, because of both their higher degree of chains orientation and higher cellulose crystallinity (Gindl et al., 2006). The lyocell fibres also possess thinner and longer cellulose crystallites than the viscose fibres (Gindl et al., 2006). Modal fibres, exhibiting intermediate cellulose DP and structural order, shows intermediate strength properties between viscose and lyocell fibres (Table 1). Due to the lower tenacity and tensile strength, not to mention the hazardous auxiliary chemicals used in this expensive manufacturing process, cuprammonium rayon fibres find much less applicability in recent years than other regenerated fibres (Sayyed et al., 2019).

The main goal of this review was the overviewing of conventional commercialized processes of regenerated cellulose fibres manufacturing, such as cuprammonium, viscose, modal and lyocell, highlighting the quality of obtained rayon fibres and the environmental friendliness of the technologies involved. In addition, the prospective regeneration cellulose processes under development are listed regarding future developments in the area. These trends include the utilization of ionic liquids and the recycling of cotton/textile wastes.

2. Sources of dissolving pulps and quality demands

The major sources for the regenerated cellulosic fibres are cotton linters and high-grade cellulosic pulps called dissolving pulps, the latter being predominant

(Kvarnlöf et al., 2006; Sayyed et al., 2019; Wilkes, 2001). The quality parameters of dissolving pulps are greatly related to their processability to viscose in such operations as steeping, mercerization, pre-aging, xanthation, dissolution processes, filtration, ripening and also the fibre formability (Kvarnlöf et al., 2006; Wilkes, 2001). Dissolving pulps have usually low process yields, relatively uniform molecular weight distributions, high brightness (≥90% ISO) and α-cellulose content (> 91 %), low hemicelluloses (< 5 %) and lignin contents (< 0.1 %) (Bajpai, 2018; Gehmayr et al., 2011; Uddin et al., 2019). This type of pulps is commonly produced by acid sulphite (ASP) and pre-hydrolysis kraft (PHK) pulping contributing respectively to 42 % and 56 % of the worldwide production (Arce et al., 2020; Li et al., 2018). Typical pulping conditions of ASP and PHK and associated bleaching sequences are summarised in Table 2. Nevertheless, other processes such as Milox and Acetosolv organosolv pulping are shown to be suitable for the production of dissolving pulp (Bajpai, 2018; Dapía et al., 2003; Johansson et al., 1987). In addition, numerous attempts were made to transform conventional paper-grade sulphite/kraft pulps to high-purity dissolving pulps, by applying different purification steps such as cold/hot caustic extraction and enzymatic treatments (e.g., with endoglucanases) or the combination thereof (Carrillo-Varela et al., 2019; Ibarra et al., 2009; Li et al., 2018; Yang et al., 2019).

Table 2 Typical pulping conditions and bleaching sequences used for the production of acid sulphite (ASP) and pre-hydrolysis kraft (PHK) pulps (Arce, Llano, García, et al., 2020; Duan et al., 2016; Evtuguin, 2016; J. C. Ferreira et al., 2020; Llano et al., 2018; Magina et al., 2015; Sixta, 2006; Vieira et al., 2019; C.-J. Wu et al., 2018).

	ASP	PHK
Temperature (ºC)	140-145	160-180
pH	1-2	13-14
Chemicals	H_2SO_3 + HSO_3^- with Na^+, Ca^{2+}, Mg^{2+} and NH_4^+ bases	NaOH + Na_2S
Bleaching sequences	E_{op}-P Z-E_{op}-P_o E-O-Z-P O-D-E-D-P E-O-P	D_0-Eop-D_1 D_0-E-H-Ep-D_1 O-D-E-H-D-P-Q O-H-P

Both hardwoods and softwoods are involved in the production of dissolving pulp. Hardwoods differ from softwoods in density, fibre morphology and chemical composition, which affect their cooking/bleaching conditions to be applied and the processability of the final dissolving pulp (Li et al., 2018). Hardwoods are easier to cook and bleach than softwoods, and the former allow higher yields of dissolving pulps, although they have also a higher pentosan content than dissolving softwood pulps (Li et al., 2018). These facts are attributed to lower lignin content in hardwoods (18-24%) than in softwoods (25-32%) and its different chemical structure (Bajpai, 2018; Evtuguin, 2016; Fengel & Wegener, 1983; Sixta, 2006). Hardwood lignin is built mainly with syringyl-type structural units (S) and is easier to degrade during pulping than softwood lignin, which built essentially by guaiacyl units (G), and have a more recalcitrant network to be cooked. In addition, softwoods have some lower cellulose content than hardwoods, which implies lower yields of the dissolving pulp. Moreover, the main softwood hemicellulose (galactoglucomannan) retains easier in ASP than in PHK pulp, which affects negatively the quality of the pulp for the production of rayon fibre (Bajpai, 2018; Evtuguin, 2016; Fengel & Wegener, 1983; Sixta, 2006). At the same time, several studies demonstrated the possibility to produce lyocell fibres with paper-grade pulp containing a high hemicellulose content resulting in fibres even with better resistance to fibrillation than those obtained with dissolving pulp (Zhang et al., 2008). Hence, the pulp quality prerequisites for the production of lyocell fibre could be less demanding than for viscose fibres.

Among hardwoods, the *Eucalyptus*, *Fagus*, *Betula*, *Populus*, *Acacia*, *Quercus* and *Acer* genus and among softwoods the *Pinus*, *Picea*, *Larix*, *Cedrus* and *Tsuga* genus are the most employed in the production of dissolving pulp. Although wood is the main source to produce dissolving pulp (85 %, hardwoods being predominant), cotton linters

(10 %) and non-woody plants (5 %) like hemp (Paulitz et al., 2017; Zhou et al., 2006), bamboo (Basit et al., 2018; Ma et al., 2011; Wu et al., 2018; Wu et al., 2014), bagasse (Andrade & Colodette, 2014; Helmy & Abou-State, 1991), jute (Nayeem et al., 2017; Sarkar et al., 2018), alfa (Bouiri & Amrani, 2010), corn stalk (Behin et al., 2008; Reddy & Yang, 2005), among others, are suitable raw-materials for the same purpose.

The properties of the dissolving pulps used have a direct influence on the quality of the regenerated fibres produced. The suitability of a dissolving pulp for its processing to viscose by the conventional process involving xanthogenation is usually assessed by reactivity and filterability tests (Sixta, 2006; Strunk et al., 2011; Testova et al., 2014). The reactivity of the dissolving pulp refers to its ability to react with carbon disulphide under predefined alkaline conditions and is commonly determined by a Fock test (Fock, 1959; Tian et al., 2014). The reactivity relates to the accessibility of OH groups in the pulp and is affected by the structural characteristics of cellulose and the presence of non-cellulosic components hampering the xanthation (Sixta, 2006; Strunk et al., 2011). Thus, high reactivity of dissolving pulps avoid many operational problems during the production of viscose (Chen et al., 2016). In addition, the greater the reactivity, the lower the consumption of reagents (CS_2 and NaOH) during cellulose xanthogenation and the easier its dissolution in aqueous alkaline solution called dope (Arce, et al., 2020; Gondhalekar, Pawar, & Dhumal, 2019; Ibarra et al., 2010).

The reactivity depends on cellulose supramolecular structure and decreases with the increasing on the degree of crystallinity, the dimensions of the crystallites and the fibril aggregates (Engström et al., 2006; Ferreira et al., 2020; Strunk et al., 2011). Other factors that affect reactivity are related to the chemical composition of the pulps and the production history (e.g., sulphite dissolving pulps have higher reactivity than the pre-hydrolysis kraft dissolving pulps) (Gondhalekar, Pawar, & Dhumal, 2019; Li et al., 2018; Tian et al., 2014; Zhou et al., 2019). Numerous attempts were done studying the possibility to increase the dissolving pulp reactivity, for example, by modification with electron beam irradiation (Gondhalekar, Pawar, & Dhumal, 2019), enzymes (Duan et al., 2016; Ibarra et al., 2010; Miao et al., 2014), a post-treatment with pulp beating (Wu et al., 2014; Zhou et al., 2018), ultrasonic treatment (Zhou et al., 2019), treatment with an inorganic acid (Wang et al., 2018), mechanical treatment (Duan et al., 2019; Tian et al., 2014), pre-treatment with deep eutectic solvents (DES**)** (Arce, Llano, González, et al., 2020), by the addition of new stage after bleaching (e.g., cold caustic extraction and dilute acid hydrolysis) (Carrillo-Varela et al., 2019), or even by a combination of the methods described above (Qin et al., 2021). It is generally considered that Fock reactivity should be as high as 50 %, however, steady good results in viscose production appear when Fock reactivity is as high as 60 %.

Besides the reactivity, the filterability parameter of the dope is another important parameter of dissolving pulps to consider (Sixta, 2006; Strunk et al., 2011; Testova et al., 2014). In the industry, the filterability of the pulp is determined by the Treiber test (Treiber et al., 1962), which simulate the steps involved in the real conversion of pulp into viscose dope. However, this analysis is extremely complex, time-consuming and requires special equipment and substantial amounts of pulp. Therefore, this analysis is exceedingly difficult to perform on a laboratory scale. An alternative method was proposed by Chinese Technical and Engineering Association that omits several intermediate dope preparation steps (Chinese filterability, CF) and is commonly used in China (Chen et al., 2016). The CF reflects the efflux time of target volume of filtrated dope prepared under controlled procedure, e.g., 25 mL to 50 mL (t_1) and from 125 ml to 150 ml (t_2) ($\Delta t=t_2-t_1$). The last test is widely used both by academic and industrial communities. The Δt values below 30 s are suitable to produce viscose, but steady satisfactory results appear when CF is as lower as 10 s, at least for the hardwood dissolving pulps. The relationships between the Fock reactivity and CF looks contradictory, when clear correlation found for one set of ASP and PHK dissolving pulps (Duan et al., 2015) was not confirmed for another set of sulphite dissolving pulps (Ferreira et al., 2020).

Typical characteristics of dissolving pulps obtained by acid sulphite and pre-hydrolysis kraft processes are depicted in Table 3. Both reactivity and filterability are sensitive to the purity of dissolving pulps and the degree of cellulose polymerization. Thus, reactivity and filterability are vulnerable to intrinsic viscosity, which should vary approximately between 400 and 600 cm^3/g to meet the dissolving pulp prerequisites to produce viscose (Asaadi et al., 2016; Chen et al., 2016; Duan et al., 2015; Ferreira et al., 2020; Sixta, 2000, 2006; Strunk et al., 2011; Testova et al., 2014). The uniform molecular weight distribution (MWD) usually favours the homogeneous cellulose mercerization and xanthation and provides improved mechanical properties of final viscose fibres. The polydispersity index (PDI) is normally larger for ASP that for PHK dissolving

Table 3 Typical characteristics of dissolving pulps (Duan et al., 2015; J. C. Ferreira et al., 2020; Köpcke et al., 2010; Sango et al., 2018; Sixta, 2000, 2006; Peter Strunk et al., 2011)**.**

Cooking Process	ASP		PHK
Raw Material	Hardwood	Softwood	Hardwood
Brightness (% ISO)	91.0-92.9	90.2-90.8	90.6-98.1
α-cellulose (%)	91.8-93.5	92.4-94.8	94.2-96.3
Hemicelluloses (%)	2-4	3-5	2-3
Residual lignin (%)	<0.1	<0.2	<0.2
Extractives (%)*	<0.4	<0.3	<0.3
Ash (%)	0.1-0.2	0.1-0.2	0.1-0.2
Viscosity (cm^3/g)	500-600	420-780	430-600
R_{18} content (%)	93.4-97.8	95.1-95.2	96.4-98.2
R_{10} content (%)	86.8-91.4	87.3-93.8	92.9-97.7
Fock reactivity (%)	40-70	40-60	20-50
Chinese filterability (s)	2-10	n.d.	20-40
DP_w	1790-2390	4750	1400-2100
DP_n	277	450	460-650
PDI	6.5-7.6	10.6	3.0-4.5
DP<100 (wt. %)	9.0	0.5	2.5-2.0
DP>2000 (wt. %)	26.8	61.0	19.9-35.0

Degree of crystallinity (%)	54	n.d.	56

n.d. not defined; *extractives in acetone.

pulps (Chen et al., 2016; Duan et al., 2015; Strunk et al., 2011; Testova et al., 2014). This explains the lower yield of viscose fibres from ASP than PHK due to the loss of low- molecular weight cellulose fraction in the dope preparation.

The purity of dissolving pulps, expressed as α-cellulose content, normally exceed of 91 % and may reach up to 94-96 % for the PHK hardwood pulps (Table 3). Accordingly, unlike to ASP, PHK pulps can be used in the applications which require high content of α-cellulose (e.g., in cellulose esters, carboxymethyl cellulose, etc.). Other advantages of PHK over the ASP process is the recovery of hemicelluloses in the pre-extraction stage, the efficient extractives removal and also the tolerance for wood species (Gehmayr et al., 2011; Liu et al., 2016). Although PHK may seem a better process, some drawbacks as low reactivity and the formation of highly reactive degradation intermediates (which could undergo condensation reactions and produce sticky precipitates during drainage) make the ASP process preferable in some situations (Gehmayr et al., 2011; Li et al., 2018). The greater reactivity of ASP pulps is related to the acid conditions used during pulping, which are preferable to the alkaline conditions used by the PHK process (Li et al., 2018). It is worth mentioning that in addition to the α-cellulose content, the purity of the dissolved pulps can be expressed as the amount of cellulose resistant to dissolving in 10% NaOH (R_{10}), which is commonly used in industry.

It is generally assumed that the presence of extractives in the dissolving pulp negatively affects the viscose process, and its content should be kept at low levels (≤ 0.1 %) (Sixta, 2006). The negative effects of extractives are mostly related to the pitch formation that clods holes of spinnerets rather than hampering the cellulose xanthation. In fact, the increase of extractives to values as higher as 0.3-0.4 % did not affected the reactivity of dissolving pulps with carbon disulphide (Rodrigues et al., 2018; Strunk et al., 2011). Similar to the extractives, the presence of certain inorganic compounds (usually between 0.08 and 0.1 %), such as ferric ions, could have a negative effect in the processing of viscose (Cao et al., 2014; Sixta, 2006; Testova et al., 2014; Wu et al., 2018).

Depending on the type of wood and pulping process used, the hemicellulose content in dissolving wood pulps varies within 2-5% (Arce et al., 2020; Buurman, 1953). The amount of hemicelluloses in the dissolving pulps can be inferred based on the analysis of sugars or by the analysis of the pentosans content (valid for hardwood pulps). In the industry, the hemicellulose content is also commonly expressed by detecting a portion of polysaccharides resistant to dissolving in 18% NaOH (R_{18}), taking into account the predominant removal of hemicelluloses in these conditions (that is, the greater the R_{18} the lower the hemicellulose content). The content of hemicelluloses in the pulps as higher as 5% impairs the production of viscose by competing with cellulose to react with Na_2S and consuming NaOH (Arce et al., 2020; Sixta, 2006). The yield of viscose drops drastically at higher content of hemicelluloses in dissolving pulps. Despite the removal of these non-cellulosic polysaccharides through the viscose process (mostly in a steeping step), a certain amount remains in viscose and could affect the mechanical properties (e.g., tensile strength) of the final product (Buurman, 1953; Cao et al., 2014; Jahan et al., 2016; Mitchell, 1949). It is recognized that a high residual xylan content could (i) reduce the fibre swelling during the steeping stage and (ii) affect the xanthation due to the preferably reaction with carbon disulphide (CS_2) and, consequently, deteriorates the viscose filterability (Arce, Llano, García, et al., 2020; Sixta, 2006). In addition, hemicelluloses cause discoloration of the viscose products (Sixta, 2006).

3. Industrialized processes for rayon production

3.1. Cuprammonium process

The discovery of cuprammonium process remotes to the 1850's, when Matthias Eduard Schweizer found that cellulose could be dissolved in an aqueous solution of ammonia and copper (II) hydroxide generally described by Eq. 1 (Kamide & Nishiyama, 2001; Kauffman & Karbassi, 1985; Sayyed et al., 2019):

$$n[Cu(NH_3)_4]^{2+}+(C_6H_{10}O_5)_n+2nOH^- \rightleftharpoons \left[[Cu(NH_3)_2]C_6H_8O_5\right]_n+2nNH_3+2nH_2O \qquad (1)$$

The cuprammonium process consists on the dissolution of cellulose (concentration *ca.* 10 %) in a mixed solution of copper salts and ammonia at low temperature, followed by the extrusion of the solution into a coagulation bath (consisting of a dilute acid, an alcohol and a concentrated cresol solution) through small holes in a spinneret, allowing cellulose to regenerate in the shape of multifilament yarn (Ciechańska et al., 2009; Cook, 2001; Kamide & Nishiyama, 2001; Sayyed et al., 2019). This process allows the use of either wood pulp (with a α-cellulose content ≥ 96 %) or cotton linters as raw material (Ciechańska et al., 2009; Cook, 2001).

With extremely fine filaments, cuprammonium fibres (also known as *cupro* fibres) exhibit higher tensile strength and lower tensile elongation than viscose fibres (Cook, 2001; Kamide & Nishiyama, 2001; Sayyed et al., 2019). *Cupro* fibres could be used to produce a great variety of products, like chiffons, satins, and all manner of very sheer fabrics (usually used to produce underwear, dress fabrics and linings) (Cook, 2001; Wang et al., 2016). The obtained yarns are used to produce weft, dresswear, sportswear and fine drapery fabrics, whereas the yarn-dyed fabrics are addressed to produce high quality silk-like linings, dress and upholstery fabrics (Cook, 2001). Despite all the valuable applications, this process is becoming less used due to environmental issues, mainly related to the hazardous chemicals used in the dissolution process, and also because of the high costs of the entire process (Sayyed et al., 2019).

3.2. Viscose process

Viscose rayon, or simply viscose, is the most important and versatile artificial fibre existing, with the first patent appearing in the year of the 1892 granted to Cross, Bevan and Beadle (Germgård, 2007; Wilkes, 2001). The conventional viscose manufacturing process, schematically represented in Fig. 4, have four important operations, namely the steeping (has the dual function of purifying and mercerizing cellulose, under appropriate conditions), aging, xanthation and spinning (Germgård, 2007; Mitchell, 1949). The mercerization of cellulose in an aqueous solution of sodium hydroxide (17-19 %) and temperature ranging between 20 and 30 ºC results in alkali cellulose (Eq. 2), which is subsequently pressed out and drained off (i) for recovery and re-use of the excess of soda, and (ii) to provide an adequate surface areas for uniform reactions in the succeeding steps (Germgård, 2007; Wilkes, 2001). In order to improve the soda penetration and the swelling of the pulp, a small amount of a synthetic resin can be added to the dissolving pulp (Wilkes, 2001). Despite the well-known fact that increasing the mercerization temperature affects the quality of the alkali cellulose obtained, there are studies that proves that increasing temperature up to 105 ºC originate even better high-quality viscose solution (Pavlov et al., 1991).

$$(C_6H_{10}O_5)_n+nNaOH\rightarrow(C_6H_9O_4ONa)_n+nH_2O \qquad (2)$$

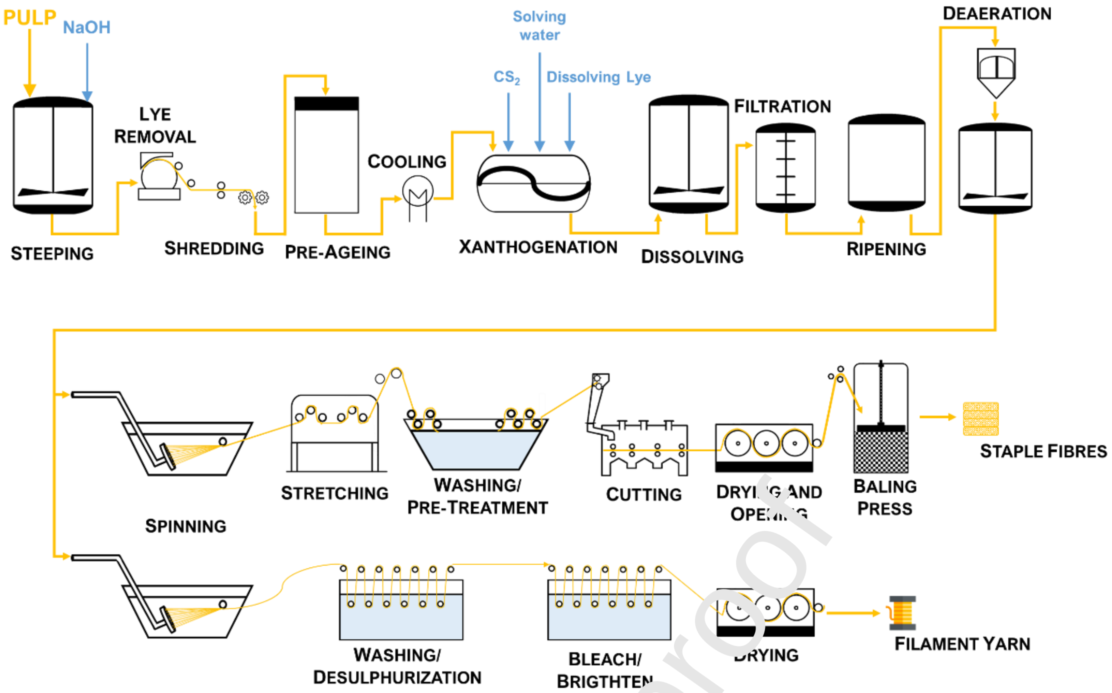


Fig. 4. Production of staple fibres and filament yarn through the viscose process.

The shredded alkali cellulose is then stored for 4-5h in air around 40 ºC to depolymerise the cellulose (dissolving pulps suitable for viscose process usually have a DP varying between 750 and 850) until the desired DP (pre-ageing step) (Germgård, 2007; Kvarnlöf et al., 2006; Mitchell, 1949; Wilkes, 2001). High hemicelluloses content and low fibre porosity hampers the pre-ageing process (Strunk et al., 2012). The next step, the most critical one, consists in the reaction of the degraded alkali cellulose with CS_2 at low temperature and pressure, to form cellulose xanthate according to the Eq. 3 (Ciechańska et al., 2009; Germgård, 2007; Gondhalekar et al., 2019; S. Wang et al., 2016; Wilkes, 2001). However, the yield of this reaction is inferior than expected due to the significant fraction of CS_2 lost in secondary reactions (Eqs 4 and 5), resulting in a degree of substitution (DS) between 0.5 and 0.7 (Germgård, 2007; Gondhalekar et al., 2019; Wilkes, 2001):

$$(C_6H_9O_4ONa)_n + nCS_2 \rightarrow \left(C_6H_9O_4O\text{-}SC\text{-}SNa\right)_n \tag{3}$$

$$3CS_2+6NaOH\rightarrow 2Na_2CS_3+Na_2CO_3+3H_2O \quad (4)$$

$$Na_2CS_3+6NaOH\rightarrow Na_2S+Na_2CO_3+3H_2O \quad (5)$$

In this step, the product is still in a fibre state (consistency around 10 %) which, when dissolved in a dilute sodium hydroxide solution under mechanical treatment forms a viscous solution called viscose dope (Germgård, 2007; Wilkes, 2001). The resulting solution is ripening for *ca.* 15h where the solution is slowly stirred, aiming the uniform distribution of the xanthate groups in cellulose (Ciechańska et al., 2009; Germgård, 2007). After that, viscose dope is filtrated to remove undissolved particles that could clog holes in the spinning jet and is deaerated to remove air bubbles (Ciechańska et al., 2009; Wilkes, 2001). Interestingly, adding a small amount of softwood pulp can improve dope drainage. Although, the use of either softwood or softwood pulp blends results in different reaction rates throughout the viscose process (Wilkes, 2001).

In the final stage, the viscose solution is extruded through small holes of a spinneret into a coagulation bath consisting in a mixture of acid and salts (sulfuric acid, sodium sulphate, zinc sulphate and water) at 45-55 ºC, being cellulose regenerated by the liberation of xanthate groups from the cellulose backbone (Ciechańska et al., 2009; Germgård, 2007; Mitchell, 1949; Shen et al., 2010; Wang et al., 2016; Wilkes, 2001). Besides the composition of the coagulation bath, many other manufacturing factors, such as a viscose dope feeding rate and a draw ratio (ratio of the take-up and extrusion velocities during the fibre spinning) have a crucial effect on the orientation and physical structure of regenerated cellulose in rayon fibres (Wilkes, 2001). Finally, the filaments formed are washed, desulfurized, and bleached, followed by a final washing and the finishing process (Ciechańska et al., 2009; Germgård, 2007; Wilkes, 2001).

Viscose fibres differ from natural cellulosic fibres, by being a polymorph of cellulose II, and not have an organized structure in fibrils as in native cellulose due to the lack of orientation of the rayon fibre and a lower degree of crystallinity (Compton, 1939; Mitchell, 1949; Wardman, 2018). Viscose fibres are hydrophilic, and their high water retention is an advantage during wet processing, which is related to the quick liquid absorption of the final product (Ramamoorthy et al., 2015).

When compared to cotton fibres, viscose fibres are weaker, especially when wet, and tend to shrink more easily (Ramamoorthy et al., 2015; Wardman, 2018). In the same way, when compared to lyocell fibres, viscose fibres exhibit lower crystallinity, tensile strength, Young modulus, and thermal stability (Ramamoorthy et al., 2015). These fibres are widely used in textile industry for the production of clothes, linings, furnishing fabrics and household fabrics (Ciechańska et al., 2009). Viscose dope also can be used to produce cellophane films (Wawro et al., 2014), tyre cords (Ramamoorthy et al., 2015), synthetic sponges and hygienic materials with high absorption properties (Ciechańska et al., 2009).

Despite being one of the few alternatives available to cotton, viscose fibres are produced by a process that is far from being ecologically sound and has some drawbacks, namely: (i) the large quantities of hazardous carbon disulphide, sodium hydroxide, sulfuric acid and water used in this process; (ii) the formation of side highly toxic chemicals and gases and (iii) the strong degradation of cellulose backbone (Chavan & Patra, 2004; Gondhalekar et al., 2019; Ingildeev et al., 2013; Michud, Tanttu, et al., 2016; Wang et al., 2012). Several approaches, like thermal oxidation or activated carbon adsorption with steam regeneration, have been developed to avoid the CS_2 emissions. However, these processes are still associated with high operating costs (Enneking, 2002).

In an attempt to reduce the CS_2 consumption, Butkova and co-workers proposed the activation of cellulose with liquid ammonia (Butkova et al., 1979), while few years later Abramova and co-workers suggested the activation of cellulose prior to xanthation with urea (Abramova et al., 1982). Kraft & Schelosky (2000) proposed the electron beam treatment of dissolving pulps to facilitate their xanthation. Recently, Gondhalekar and collaborators reported a kinetic study for the formation of cellulose xanthate and formed by-products, aiming to reduce the consumption of CS_2 and, consequently, to reduce the by-products emitted (Gondhalekar et al., 2019).

3.3. Modal process

Modal fibres, also known as high wet modulus rayon, are manufactured by a modified viscose process (e.g., using an increased load of CS_2 in dope preparation, spinning solutions with higher DP values, different spinning bath composition and with addition of modifiers), and currently commercialized by Lenzing AG with the brand name of Modal® (Albrecht, 1981; Ciechańska et al., 2009; Röder, 2017; Schaumann, 1996; Shen et al., 2010; Wang et al., 2016). The resulting rayon fibres are characterized for having a higher wet modulus, tenacity and strength (in both wet and conditioned state), a lower water retention capacity, and a higher resistance towards alkalinity than conventional viscose fibres (Albrecht, 1981; Llaudet, 1990; Schaumann, 1996). In addition, when compared to conventional viscose fibres, modal fibres have a higher ratio of wet to dry breaking tenacity, better washability, less swelling, a higher degree of cellulose polymerization and a more developed fibrillary structure (Albrecht, 1981; Ciechańska et al., 2009; Röder, 2017; Shen et al., 2010; Wang et al., 2016). At the same time, modal fibres exhibit a lower crystallinity when compared with lyocell fibres and also have both a higher moisture absorption and a lower thermal stability than lyocell and viscose fibres (Ramamoorthy et al., 2015). Due to the good mechanical and comfort properties of the modal fabrics, this type of fibres is widely used in the production of different woven fabrics, underwear, sportswear, terry products (towels) and knit material (Latif et al., 2019; Llaudet, 1990; Röder, 2017).

3.4. Lyocell process

Concerning the environmental issues and to improve the cost/performance profile, Lyocell® process emerges in 1939 with the first patent published by Charles Graenacher, In the earlier studies, Graenacher and Sallmann used an amine oxide to dissolve cellulose (Graenacher & Sallmann, 1939; Mbe, 2001). Later, in 1969 D.L. Johnson described the use of cyclic mono (*N*-methylamine-*N*-oxide) compounds, which include NMMO, as solvents that partially dissolve cellulose fibres and other natural polymers such as wool, silk and hair (Johnson, 1969a, 1969b).

Lyocell is a direct dissolution-type process (Fig. 5) without the formation of any intermediate cellulose derivative, that started to be commercialized in the 90's and consists mainly of three steps (Carrillo et al., 2004; Chavan & Patra, 2004; Ciechańska et al., 2009; Wang et al., 2012). The first step consists in the direct dissolution of cellulose in NMMO (suspension of *ca.* 13 % cellulose, 20 % water and 67 % NMMO) at 120 ºC with reduced pressure, resulting in an extremely viscous solution – the spinning dope (cellulose concentration between 8 and 20 %) (Chavan & Patra, 2004; Ciechańska et al., 2009; Hummel et al., 2016; Jiang et al., 2020; Sayyed, Mohite, et al., 2020; Zhang et al., 2018). Temperature plays an important role in the process, as low temperatures can result in undissolved particles, while high temperatures (≥120 ºC) can lead to cellulose degradation (Sayyed et al., 2020). In the next step, the solution is filtered and extruded via an air gap into a coagulation bath (water with a small NMMO content), being the fibres formed collected as a tow (Chavan & Patra, 2004; Ciechańska et al., 2009; Hummel et al., 2016; Jiang et al., 2020; Zhang et al., 2018). Fibres are then washed and proceed to the finishing process that includes bleaching, finishing and drying (Zhang et al., 2018). Finally, NMMO is recovered by evaporation of water from the regenerating and washing bath to 99.5 % purity and is reused in the process (Ciechańska et al., 2009; Hummel et al., 2016). NMMO effectively dissolves cellulose with moderate formation of adducts and with minimal degradation, being 99% recyclable (Haule et al., 2016b; Jiang et al., 2020).

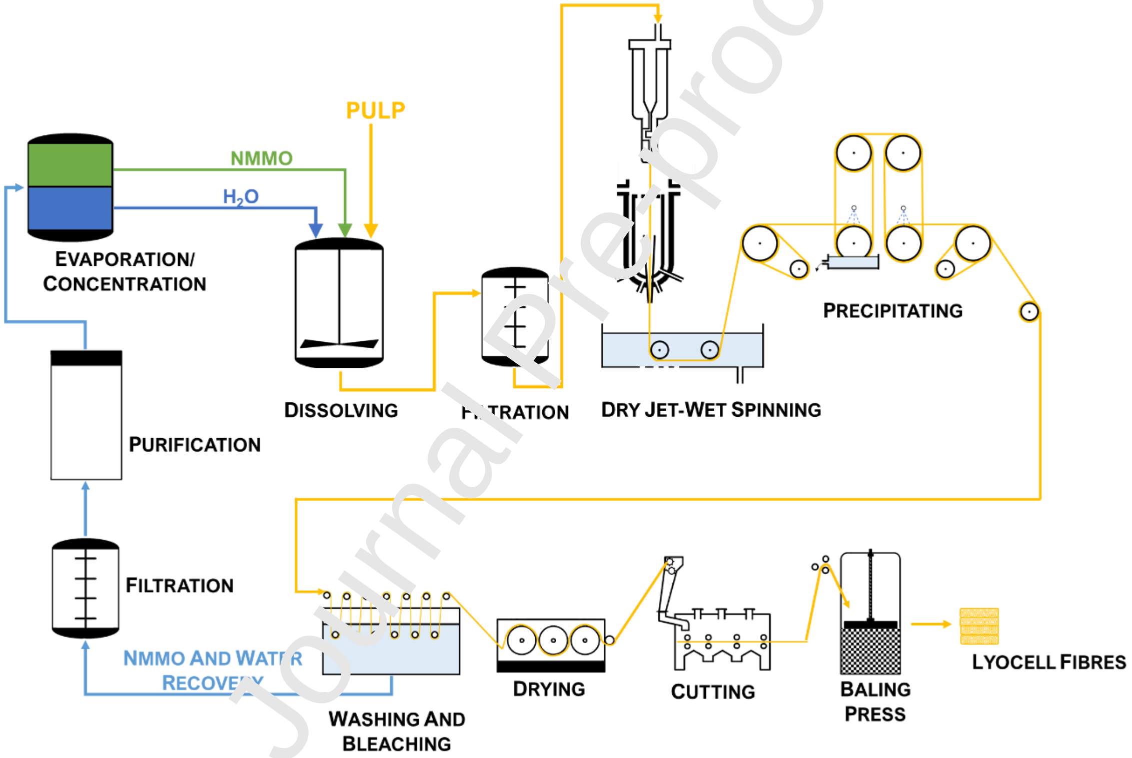


Fig. 5. Production of rayon fibres through the lyocell process.

As the lyocell process uses wood pulp as raw material, the chemical composition of lyocell fibres varies largely with the type of wood used (Ramamoorthy et al., 2015). Usually, hardwood dissolving pulps with high α-cellulose content are used to produce lyocell fibres. Typically, the dissolving pulp characteristics required to use in the lyocell process are a DP of 650-750 and a α-cellulose content of 96 %, which gives a high crystallinity lyocell fibres (Chavan & Patra, 2004; Jiang et al., 2020; Ramamoorthy et al., 2015). The intrinsic viscosity values ranging between 280 and 350 cm^3/g and brightness as higher than 90 %ISO are preferred (Jiang et al., 2020). Studies using pre-swelled pulps are already been developed, showing an intensification of the dissolution process by the reduction in energy and time consumed (Sayyed, Gupta, et al., 2020; Sayyed et al., 2020). In addition, studies using deep eutectic solvents as co-solvents have already been carried out, showing an improvement on the cellulose dissolution even at room temperature (Nguyen et al., 2020).

Lyocell fibres exhibit a relatively high crystallinity, a high degree of orientation of the fibrils, a low lateral holds within fibres, a quite large pore volume, a weak intrafibrillar hydrogen bonds and a high tenacity value ranging from 35 to 42 cN/tex (Carrillo et al., 2004; Chavan & Patra, 2004; Ciechańska et al., 2009; Haule et al., 2016b; Ingildeev et al., 2013). Lyocell fibres also reveal some unique features such as softness and absorption, as well as possess good textile properties (Edgar & Zhang, 2020; Ramamoorthy et al., 2015; Woodings, 1995). The highly crystalline structure of lyocell fibres plays an important role on fibrillation, the last occurring generally under stress along the long axis in wet condition (Chavan & Patra, 2004). Lyocell fibres show smooth surface, quasi-round cross-section as well as a homogeneous, dense fibre bundle structure (Hummel et al., 2016).

In terms of applications, lyocell fibres are suitable to produce an extensively range of products, since textile clothes, to wipes or filters, among others (Bartsch & Kling, 2001; Cafuta et al., 2019; Chavan & Patra, 2004; Wang et al., 2016). Being a direct dissolution process, lyocell has as an advantage the fact of avoiding toxic chemicals (Zhang et al., 2018). Another main advantage of this process consists on the recycling of NMMO (as higher as 99 % of the solvent can be recycled), which reduces the effluent produced, and make the process more environmental-friendly (Chavan & Patra, 2004; Ingildeev et al., 2013; Ramamoorthy et al., 2015; Zhang et al., 2018). However, it could not replace the conventional viscose process yet, mainly due to the costs of the process and the nature of the fibrillating fibre produced (strong tendency of fibres to undergo wet fibrillation, that could result in partial damage of the fibres during rope finishing/dyeing) (Ingildeev et al., 2013; Ma et al., 2020; Ramamoorthy et al., 2015; Wang et al., 2012). Lyocell process also have as drawbacks the side reactions in the cellulose-NMMO-water system (radical decomposition and degradation; deoxygenation; and the Polonovski reaction) and the formation of by-products that can affect the final properties of the fibres (Asaadi et al., 2016; Ingildeev et al., 2013; Michud, Tanttu, et al., 2016; Zhang et al., 2018).

4. Advanced rayon processes under development

Despite being the predominant approach for the production of regenerated cellulose, and all attempts to reduce CS_2 consumption, the viscose process continues to be an environmental concern. Therefore, new alternative processes are challenging and described in the following sections. These approaches include the use of ionic liquids, deep eutectic solvents, aqueous NaOH-based solvents, and the cotton waste recycling systems. Among all these processes, the use of advanced ionic liquids has already reached the pilot scale (e.g. Ioncell-F® process) and is close to reaching the industrial exploitation.

4.1. Processes using alkali and salt solutions

Considering the problems existing in the viscose process, numerous attempts have been made to find a direct solvent capable of dissolving cellulose and, at the same time, being environmentally friendly. In particular, these studies involve aqueous NaOH-, LiOH-based solutions, and molten inorganic salt hydrates.

The first report related to the dissolution of cellulose with aqueous NaOH system remotes to the 1930's by Davidson (Budtova & Navard, 2016). Later in the 1980's, Kamide and co-workers presented the dissolution of a steam pre-treated pulp in an aqueous 9 wt.% NaOH solution, followed by wet spinning and an aqueous H_2SO_4 coagulation bath (Kamide et al., 1984). However, this process results in fibres with inferior properties to those of viscose fibres.

Aqueous NaOH systems have a limited solubility power and, in order to facilitate the cellulose dissolution in these systems, numerous attempts were made to activate cellulose prior to it dissolution, namely by mechanical, physical, chemical and enzymatic methods (Budtova & Navard, 2016; Sixta et al., 2015). One of the alternatives to improve cellulose dissolution in aqueous NaOH systems lies in the addition some auxiliary additives like poly(ethylene glycol) (PEG), urea, thiourea or ZnO (Cuissinat & Navard, 2006; El Seoud et al., 2020; Harlin, 2019; Jedvert & Heinze, 2017; Sixta et al., 2015). However the addition of additives complicates the recovery system and, consequently, increases the solvent recovery costs (Sixta et al., 2015).

Studies using NaOH/urea aqueous solutions have been developed in the 1980th (Cai et al., 2004; Cai & Zhang, 2005; Cuissinat & Navard, 2006; Ekman et al., 1984; Sixta et al., 2015). The dissolution of cellulose in NaOH/urea is similar to the viscose conventional process, and could be a cheaper and also a non-toxic process that can recycle the by-products formed (Ekman et al., 1984; Harlin, 2019; Jedvert & Heinze, 2017; Luo & Zhang, 2013). Cellulose, even in high concentrations, can be dissolved quickly at room temperature (below 20ºC) using a pre-cooled 7 % NaOH/12 % urea aqueous solution system (Cai et al., 2007; Cai & Zhang, 2005). Cellulose multifilament's prepared by wet-spinning process at a pilot scale have already been performed, revealing to be quicker, cheaper and greener than the viscose process (Cai et al., 2007; R. Li et al., 2010). The resulting fibres reveal lower mechanical properties than viscose fibres, and simultaneously a larger crystallinity index and a higher DP than viscose fibres (Cai et al., 2007; R. Li et al., 2010). It is claimed that despite being similar to the viscose process, it differs from the latter by having a shorter production cycle, being a non-polluting process and also by having lower process costs (Cai et al., 2007).This process developed by Cai et al. (2007) also differs from the carbamate process. Although the NaOH/urea process is greener than the viscose, the resulting weak fibre properties limits its commercial application. To improve the fibre strength, studies introducing a lower percentage of ZnO (0.8 %) and a different composition of coagulation bath (15 wt.% citric acid/5 wt.% disodium citrate/40 wt.% glycol instead of H_2SO_4/Na_2SO_4) have been proposed, revealing an increase in the cellulose solubility and in the solution stability (Tu et al., 2020).

The carbamate process, also known as CarbaCell, differs little from the viscose process and consists on a reaction between cellulose and urea carried out at temperature ranging between 135 and 180 ºC, that results in the intermediate cellulose carbamate (El Seoud et al., 2020; Fink et al., 2014; Harlin, 2019). This intermediate is easily and readily dissolved in a dilute NaOH solution, with cellulose concentrations lower than 10 % (depending on the DP), and at low temperatures (around or below 0 ºC**)** (El Seoud et al., 2020; Fink et al., 2014; Harlin, 2019). The major advantages of the CarbaCell process over the viscose process are the (i) prolonged chemical stability of the cellulose carbamate either in wet or in dry states; (ii) faster dissolution of carbamate in NaOH; (iii) omission of heavy metals in the coagulation bath composition (it is only composed by H_2SO_4 and Na_2SO_4); (iv) absence of sulphur in the whole process and (v) spinning process is performed at room temperature (Fink et al., 2014). Combining these advantages with the good strength properties of the resulting fibres (tenacities as high as 26 cN/tex and elongation reaching 27 %), the carbamate process has potential to compete with the viscose process (El Seoud et al., 2020; Fink et al., 2014; Harlin, 2019; Sixta et al., 2015).

Cellulose dissolution studies using pre-cooled NaOH/thiourea aqueous solutions have been carried out and reached the pilot scale (Ruan et al., 2004, 2006). The resulting fibres revealed to be similar to lyocell fibres, exhibiting a tensile strength closer to the obtained by the viscose process and also a higher degree of crystallinity and more regular cross-section order than viscose fibres (Ruan et al., 2004, 2006).

In the 2000's, the cellulose carbonate process was proposed and consisted on the reaction of CO_2 with alkali cellulose in ethyl acetate (or $ZnCl_2$ and acetone) at -5 ºC and pressure around 40-50 bar (El Seoud et al., 2020; Sixta et al., 2015). The derivative formed is readily dissolved in a 8.5 wt.% NaOH/ZnO solution at 0 ºC and the solution is wet spun into continuous filaments in a coagulation bath using acid/water or acid/salt/water system (El Seoud et al., 2020; Sixta et al., 2015). However, the resulting fibres appeared to be weaker than viscose fibres (Sixta et al., 2015).

Studies using LiOH/urea aqueous solutions showed a higher dissolution power over the NaOH/urea aqueous solutions (Cai et al., 2006; Cai & Zhang, 2005). The dissolution of cellulose in this solvent system has as advantages being a non-toxic solvent and having substantially higher stability when compared with the cuprammonium solution (Cai et al., 2006). Although there are few studies using this solvent.

Molten salt hydrates are concentrated inorganic salt solutions that have a water-salt ratio near to the coordination number of the strongest hydrated ion (usually a cation) (Huang et al., 2020; Leipner et al., 2000; Sen et al., 2013). These liquids are able to dissolve cellulose without any activation or pre-treatment, resulting in significantly different regenerated cellulose (Leipner et al., 2000). The molten salt hydrates can be divided into five groups, according to their interaction with cellulose: (i) with no dissolution (e.g., $CaCl_2 \cdot 6H_2O$; $LiNO_3 \cdot 3H_2O$); (ii) fine dispersion (e.g., $NaCH_3COO \cdot 3H_2O$); (iii) partial decomposition (e.g., $Mg(ClO_4)_2 \cdot H_2O$); (iv) strong swelling (e.g., $Zn(NO_3)_2 \cdot 6H_2O$; $NaClO_4 \cdot H_2O$) and (v) dissolution (e.g., $ZnCl_2 \cdot 4H_2O$; $LiClO_4 \cdot 3H_2O$) (Fischer et al., 2003; Fischer et al., 1999; Fischer et al., 1999; Fischer & Thümmler, 2010; Fischer et al., 2002; Leipner et al., 2000; Sen et al., 2013).

The dissolution ability of molten salt hydrates is influenced by water content of the melt, acidity, composition/species, and also by the hydration deficiency of the coordination sphere (Fischer et al., 2003; S. Fischer & Thümmler, 2010; Steffen Fischer et al., 2002; Leipner et al., 2000; Sen et al., 2013). These inorganic molten salts are both an effective and efficient media for cellulose dissolution. They also have as advantages their excellent solvation ability and electrochemical performance, high thermal and chemical stability, a negligible vapour pressure, and they are also cheap and easy to prepare (Huang et al., 2020; Sen et al., 2013). Like other solvents (e.g., NMMO), the inorganic salts can be recovered by the evaporation of water, and further reuse (Huang et al., 2020; Sen et al., 2013).

Despite all studies using alkali/salt solutions, including those that have reached the pilot scale, none can overcome the properties of viscose fibres. Thus, further studies related to these or similar solvent systems are needed.

4.2. Processes using ionic liquids

Ionic liquids (ILs) are a combination of bulky organic cations with mostly inorganic anions, resulting in salts that are liquids at low temperatures (melting points below 100 ºC) (Brandt et al., 2013; Cao et al., 2017; Chiappe & Pieraccini, 2005; Hermanutz et al., 2019; Hummel et al., 2016; Verma et al., 2019; Wang et al., 2016). Due to their low melting point, low vapour pressure and relative thermal stability, ionic liquids become interesting to apply in industrial processes for the biomass processing (Cao et al., 2017; Chiappe & Pieraccini, 2005; Y. Li et al., 2018; Michud et al., 2016). A large number of ILs have been studied as cellulose solvents, which are briefly reviewed in Table S1 (Supplementary data). Among nearly 230 different IL systems, imidazolium ionic liquids with chloride anion have been found to be particularly suitable for cellulose spinning (the first generation of ionic spinning liquids) (Hummel et al., 2016; Michud, Tanttu, et al., 2016). This type of ILs is effective in dissolving cellulose, however can induce cellulose degradation at temperatures above 90 ºC, their regeneration causes problems, and the resulting fibres need to be purified due to the contamination with residual IL (Bodachivskyi et al., 2020; Hummel et al., 2016; Michud et al., 2016; Wawro et al., 2014; Zhou et al., 2020).

ILs have shown promising results in cellulose dissolution due to their ability to break the intermolecular hydrogen bonds present in the biopolymer (Mahadeva & Kim, 2012). The cellulose dissolution in ionic liquids is usually controlled by the anion selected, since it size and geometry plays an important role in cellulose dissolution (Brandt et al., 2013; Erdmenger et al., 2007; Ingildeev et al., 2013). The chlorine ion is one of the most promising anions found for IL systems. However, halides, carboxylates or phosphates anions also play an important role in cellulose dissolution, since they can hinder both the intramolecular and intermolecular hydrogen bonds formation between the polymer chains and sheets (Cao et al., 2017; Erdmenger et al., 2007; Ingildeev et al., 2013). Swatloski et al. (2002) studied seven different ILs on the dissolution of cellulose and found that both tetrafluoroborate and hexafluorophosphate-based ILs cannot dissolve cellulose, whereas chloride containing ILs appear to be the most effective for these purposes. Ohira and co-workers applied ILs with amino acids in cellulose dissolution and, among the ILs studied, $[N_{221ME}]$[Ala] (*N*,*N*-diethyl-*N*-(2-methoxyethyl)-*N*-methylammonium alanine) was the one that had a higher dissolution (12 wt.%). According to the results obtained, the authors proposed that amino acids may have some affinity with a specific part of cellulose, causing its dissolution in ionic liquids based on amino acids (Ohira et al., 2012).

There are some features to take into consideration when using ionic liquids to dissolve cellulose, namely: (i) the presence of water (may have a negative effect in cellulose dissolution) (Brandt et al., 2013; Ohira et al., 2012); (ii) the temperature (the DP has an inverse correlation with dissolution temperature (De Silva et al., 2015)); (iii) the source of cellulose, and (iv) the Kamlet-Taft parameters (α, β and π* parameters) (Chiappe & Pieraccini, 2005; Morais et al., 2020; Xu & Wang, 2020; Zhang et al., 2017). α and β parameters relates to the hydrogen-bond acidity and basicity of the ILs anions, respectively, having a strong direct correlation with cellulose solubility, while π* is related to the interactions through bipolarity and polarizability (Brandt et al., 2013; Chiappe & Pieraccini, 2005; Li et al., 2018; Morais et al., 2020; Xu et al., 2010; Xu & Wang, 2020). It is known that the reduction of ILs stability is associated with high hydrogen-bond basicity (Brandt et al., 2013). Moreover, the presence of hydroxyl groups either on the anion or the cation, affects negatively the solubility of cellulose, due to the increase on the hydrogen bond acidity of the IL (Brandt et al., 2013). Accordingly, in order to have a solvent capable of dissolving cellulose, it should has simultaneously a higher hydrogen-bond basicity and a lower hydrogen-bond acidity (Zhu et al., 2018).

Despite the large amount of ionic liquids studied in cellulose dissolution, only few of them are suitable to produce textile fibres (Table 4). ILs have some advantages over other processes, namely: (i) the ability to dissolve polymers in high concentrations, (ii) recover the solvents used after the regeneration of the cellulose fibre/film (in the case of the [DBNH][OAc] (1,5-diazabicyclo[4.3.0]non-5-ene acetate) ionic liquid, it recovery is higher than 95 % (Parviainen et al., 2015; Jinming Zhang et al., 2017)); (iii) the moderate water pollution caused and (iv) the higher fibrillation resistance of some fibres obtained with advanced ILs when compared to lyocell fibres (Cao et al., 2017; Ingildeev et al., 2013; Mahadeva & Kim, 2012; Michud et al., 2014; Wawro et al., 2014; Zhang et al., 2020). However, ionic liquids also have some drawbacks like slow rate of dissolution, high costs of solvents, some of them are toxic with undetermined end-effects on the environment (Magina et al., 2021) and non-biodegradable (e.g., imidazolium-based ILs), and also have high viscosity cellulose solutions (Chiappe & Pieraccini, 2005; Malaeke et al., 2018; Rinaldi, 2011). The later problem can be overcome by the addition of polar aprotic solvents to ILs (e.g., DMSO or DMF), lithium salts among others, which increases the cellulose solubility in ILs and reduce the dissolution time (Brandt et al., 2013; Cao et al., 2017; Ferreira et al., 2019; Grøssereid et al., 2019; Lethesh et al., 2020; Li et al., 2018; Ohira et al., 2012; Rinaldi, 2011; Sánchez et al., 2020; Satria et al., 2018; Verma et al., 2019; Xu et al., 2010; Zhang et al., 2017; Zhang et al., 2016; Zhu et al., 2018). It appears that the ideal IL for dissolving cellulose and producing spinnable rayon fibres has not yet been found and is a challenge for the scientific community.

Table 4 Ionic liquids suitable to produce textile fibres, with respective tenacity and elongation values (El Seoud et al., 2020; Elsayed et al., 2020; Hermanutz et al., 2019; Hummel et al., 2016; Michud et al., 2014; Jiaping Zhang, Yamagishi, et al., 2020).

Ionic liquid	IL concentration (wt. %)	Tenacity (cN/tex)[a]	Elongation (%)[a]
[Amim]Cl	10.0-12.5	26.8-41.6	8.4-12.2
[C_4mim][OAc]	13.2-18.9	44.0-48.6	12.6-15.5
[C_4mim]Cl	5.0-13.6	20.7-56.8	4.3-15.3
[C_2mim][OAc]	6.0-19.6	17.6-46.0	3.8-11.2
[C_2mim]Cl	15.8	43.0-53.1	9.6-13
[C_2mim][$(EtO)_2PO_2$]	10.0	26.4	4.6-6.5
[DBNH][OAc]	10.0-15.0	45.7-50.7	7.4-12.2
[DBUH][OAc][b]	n.m.	56.3	9.8
[mTBDH][OAc][c]	n.m.	49.9	9.8

[a] in the conditioned state; [b] 1,8-diazabicyclo[5.4.0]undec-7-ene acetate; [c] 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-enium acetate; n.m. not mentioned.

Recently, a research group from Aalto University and Helsinki University has been developing a new Ioncell-F® process allowing rayon fibres with strength properties equal or even better than those of lyocell (Asaadi et al., 2018; Hummel et al., 2016; *Ioncell*, n.d.; Michud et al., 2014; Michud, Hummel, et al., 2016; Michud, Tanttu, et al., 2016; Sixta et al., 2015). This new process uses the ionic liquid [DBNH] [OAc] to dissolve the cellulose with high concentrations at moderate temperatures (60-100 ºC), while the degradation of the polysaccharides is quite insignificant (Hummel et al., 2016; Michud et al., 2014; Michud et al., 2016). Ioncell-F®, also identified as a lyocell-type process, uses the ionic liquid as a direct cellulose solvent and the same dry-jet wet spinning method used in the lyocell process to manufacture rayon fibres (Guizani et al., 2020, 2021; Hummel et al., 2016; Michud et al., 2016; Stepan et al., 2016). [DBNH] [OAc] exhibited superior properties in the dissolution of cellulose and also in its subsequent regeneration in filaments than NMMO (Michud et al., 2016). The resulting fibres exhibit a high structural conformity, a dry tenacity superior to 35 cN/tex, and a crystallinity as higher as 45 % (Asaadi et al., 2018; Michud et al., 2014; Sixta et al., 2015). Moreover, studies using blends of different cellulose sources were made, revealing mechanical properties slightly higher than lyocell fibres, with wet tenacity values higher than 40 cN/tex, and Young’s modulus values higher than 20 GPa (Michud et al., 2015; Stepan et al., 2016). The Ioncell® process opens new opportunities for fibre engineering while combining cellulose with other natural compounds with specific properties, thus resulting in new functional fibres (Moriam et al., 2021). Currently, the Ioncell-F® process is on a pilot scale and aims to be introduced in industrial scale production from 2025 (*Ioncell*, n.d.).

4.3. Processes using deep eutectic solvents

Deep eutectic solvents (DESs) are formed by a hydrogen bond acceptor (usually an ammonium salt) and a hydrogen bond donor (e.g., amines, carboxylic acids, etc.), linked by hydrogen bonds at a certain molar ratio, that emerged to overcome the ILs drawbacks (Chen et al., 2019; Malaeke et al., 2018; Tan et al., 2020; Tang et al., 2017; Zdanowicz et al., 2018; Zhang et al., 2020). Despite having similar chemical and physical properties with ILs, DESs have lower production costs, higher biodegradability, safety and innocuous nature (Chen et al., 2019; Tan et al., 2020; Tang et al., 2017; Zdanowicz et al., 2018; Zhang et al., 2020). Also known as “designer solvents”, DESs have the ability to change their physicochemical properties by choosing the best DESs components in terms of chemical nature, ratio, and water content (Chen et al., 2019; Francisco et al., 2012). These solvents can be classified, depending on the components selected to form the solvent, in (i) organic salts and metal chlorides; (ii) organic salts and metal hydrates; (iii) organic salts and organic compounds and (iv) metal chlorides and organic compounds (Arce et al., 2020; Tan et al., 2020).

DES have been already applied to a wide range of steps of the biomass treatment as, for example, in pre-treatment (Arce et al., 2020; Ling et al., 2020), delignification (Jablonský et al., 2015), extraction (Cao et al., 2019; Tan et al., 2019), and many other purposes (Loow et al., 2017). Despite numerous attempts to dissolve cellulose in DESs (Table 5), the cellulose solubility falls far short from that for ionic liquids (Chen et al., 2019). This can be explained by the strong hydrogen bond network existing in DESs that results in a decrease of opportunities for interactions between cellulose and these solvents (Chen et al., 2019). Chen and co-workers suggest that compounds containing anions of high hydrogen bonding basicity (e.g., Cl^-, OAc^-) are an auspicious alternative to form DESs capable of dissolving cellulose (Chen et al., 2019).

Table 5 Cellulose solubility (wt. %) in different deep eutectic solvents for different cellulose sources.

DESs	Molar ratio	Cellulose source	Cellulose solubility (wt. %)	Reference
Acetamide/Caprolactam	1:1	Cotton-Ramie pulp	1.79 (T=50 °C)	(E. Zhou & Liu, 2014)
Acetamide/urea	2:1	Cotton-Ramie pulp	1.03 (T=50 °C)	(Y.-L. Chen et al., 2019; E. Zhou & Liu, 2014)
Betaine/Lactic acid	1:2	Cellulose, ≥ 90% mass fraction purity	Insoluble (T=60 ºC)	(Francisco et al., 2012; Lynam et al., 2017; Tang et al., 2017)
		Cellulose, fibrous, medium	<1 (T=60 ºC)	
Caprolactam/Urea	3:1	Cotton-Ramie pulp	2.[illegible]3 (T=50 °C)	(Y.-L. Chen et al., 2019; E. Zhou & Liu, 2014)
ChCl/Acetamide	1:2	Cotton linter pulp	0.22 (T=120 ºC after cellulose activation by ultrasound-assisted saturated calcium chloride solution)	(Y.-L. Chen et al., 2019; Ren, Chen, Wang, et al., 2016)
ChCl/Acetic acid	1:2	Cellulose, fibrous, medium	<1 (T=60 ºC)	(Lynam et al., 2017)
ChCl/Ammonium thiocyanate	1:1	Cotton linter pulp	0.85 (T=120 ºC after cellulose activation by ultrasound-assisted saturated calcium chloride solution)	(Y.-L. Chen et al., 2019; Ren, Chen, Wang, et al., 2016)
ChCl/Caprolactam	1:1	Cotton linter pulp	0.16 (T=120 ºC after cellulose activation by ultrasound-assisted saturated calcium chloride solution)	(Y.-L. Chen et al., 2019; Ren, Chen, Wang, et al., 2016)
ChCl/Formic acid	1:2	Cellulose, fibrous, medium	<1 (T=60 ºC)	(Lynam et al., 2017)
ChCl/Imidazole	3:7	Cotton linter pulp	2.48 (T=120 ºC after cellulose activation by ultrasound-assisted saturated calcium chloride solution)	(Y.-L. Chen et al., 2019; Ren, Chen, Wang, et al., 2016; Tang et al., 2017)
ChCl/Lactic acid	1:1.3	Cellulose, ≥ 90% mass fraction purity	Insoluble (T=60 ºC)	(Francisco et al., 2012; Lynam et al., 2017; Tang et al., 2017)
	1:2	Cellulose, ≥ 90% mass fraction purity	Insoluble (T=60 ºC)	
	1:5	Cellulose, ≥ 90% mass fraction purity	Insoluble (T=60 ºC)	
	1:10	Cellulose, ≥ 90% mass fraction purity	Insoluble (T=60 ºC)	
	1:10	Cellulose, fibrous, medium	<3 (T=60 ºC)	
ChCl/L-Lysine	1:2	Wheat straw cellulose (DP>3000)	<5.0 (T=90 °C, with ultrasonic irradiation)	(J. Wang et al., 2020)
		MCC	<8.0 (T=90 °C, with ultrasonic irradiation)	
ChCl/Maleic acid	1:1	Cellulose, ≥ 98% mass fraction purity	2.57 (T=90 °C, with ultrasonic irradiation)	(Y.-L. Chen et al., 2019; Malaeke et al., 2018)

ChCl/Malic acid	1:1	Cellulose, ≥ 90% mass fraction purity	Insoluble (T=100 ºC)	(Francisco et al., 2012; Tang et al., 2017)
ChCl/α-naphthol	1:1	Cellulose, ≥ 98% mass fraction purity	3.39 (T=90 °C, with ultrasonic irradiation)	(Y.-L. Chen et al., 2019; Malaeke et al., 2018)
ChCl/Oxalic acid dihydrate	1:1	Cellulose, ≥ 90% mass fraction purity	Insoluble (T=60 ºC)	(Francisco et al., 2012; Tang et al., 2017)
ChCl/phenol	2:1	Cellulose, ≥ 98% mass fraction purity	4.70 (T=90 °C, with ultrasonic irradiation)	(Y.-L. Chen et al., 2019; Malaeke et al., 2018)
ChCl/resorcinol	1:1	Cellulose, ≥ 98% mass fraction purity	6.[illegible]0 (T=90 °C, with ultrasonic irradiation)	(Y.-L. Chen et al., 2019; Malaeke et al., 2018)
ChCl/urea	1:2	AVICEL Cotton linter pulp	<0.2 (T=110 °C) 1.43 (T=120 ºC after cellulose activation by ultrasound-assisted saturated calcium chloride solution)	(Y.-L. Chen et al., 2019; Ren, Chen, Wang, et al., 2016; Tang et al., 2017; Q. Zhang et al., 2012)
ChCl/ZnCl$_2$	1:2	AVICEL	<0.2 (T=110 °C)	(Y.-L. Chen et al., 2019; Tang et al., 2017; Q. Zhang et al., 2012)
Lactic acid/Alanine	9:1	Cellulose, ≥ 90% mass fraction purity	Insoluble (T=60 ºC)	(Francisco et al., 2012)
Lactic acid/Glycine	9:1	Cellulose, ≥ 90% mass fraction purity	Insoluble (T=60 ºC)	(Francisco et al., 2012)
Lactic acid/Histidine	9:1	Cellulose, ≥ 90% mass fraction purity	Insoluble (T=60 ºC)	(Francisco et al., 2012)
Malic acid/Alanine	1:1	Cellulose, ≥ 90% mass fraction purity	0.11 (T=100 °C)	(Y.-L. Chen et al., 2019; Francisco et al., 2012)
Malic acid/Betaine	1:1	Cellulose, ≥ 90% mass fraction purity	Insoluble (T=100 ºC)	(Francisco et al., 2012)
Malic acid/Glycine	1:1	Cellulose, ≥ 90% mass fraction purity	0.14 (T=100 °C)	(Y.-L. Chen et al., 2019; Francisco et al., 2012; Tang et al., 2017)
Malic acid/Histidine	2:1	Cellulose, ≥ 90% mass fraction purity	Insoluble (T=85 ºC)	(Francisco et al.,

				2012)
Malic acid/Nicotinic acid	9:1	Cellulose, ≥ 90% mass fraction purity	Insoluble (T=85 ºC)	(Francisco et al., 2012)
Malic acid/Proline	1:1 1:2 1:3	Cellulose, ≥ 90% mass fraction purity	Insoluble (T=100 ºC) 0.24 (T=100 °C) 0.78 (T=100 °C)	(Y.-L. Chen et al., 2019; Francisco et al., 2012; Tang et al., 2017)
Oxalic acid dihydrate/Betaine	1:1	Cellulose, ≥ 90% mass fraction purity	Insoluble (T=60 ºC)	(Francisco et al., 2012)
Oxalic acid dihydrate/Glycine	3:1	Cellulose, ≥ 90% mass fraction purity	Insoluble (T=85 ºC)	(Francisco et al., 2012)
Oxalic acid dihydrate/Histidine	9:1	Cellulose, ≥ 90% mass fraction purity	0.25 (T=60 °C)	(Y.-L. Chen et al., 2019; Francisco et al., 2012)
Oxalic acid dihydrate/Nicotinic acid	9:1	Cellulose, ≥ 90% mass fraction purity	Insoluble (T=60 ºC)	(Francisco et al., 2012)
Proline/Lactic acid	1:2 1:3.3	Cellulose, ≥ 90% mass fraction purity Cellulose, fibrous, medium	Insoluble (T=60 ºC) <1 (T=60 °C)	(Francisco et al., 2012; Lynam et al., 2017; Tang et al., 2017)
Proline/Oxalic acid dihydrate	1:1	Cellulose, ≥ 90% mass fraction purity	Insoluble (T=60 ºC)	(Francisco et al., 2012; Tang et al., 2017)
Triethyl-allyl ammonia chloride/Oxalic acid	1:1	Cotton linter pulp	6.48 (T=110 °C)	(Y.-L. Chen et al., 2019; Ren, Chen, Guo, et al., 2016; Tang et al., 2017)

ChCl – choline chloride.

4.4. Cotton waste recycling

As already mentioned, cotton production is no longer sufficient to meet the demand for textile fibres, although this problem is mitigated with the appearance of man-made fibres (Asaadi et al., 2016; Björquist et al., 2018). In addition to the production of regenerated cellulose, the shortage of cotton fibre in the market can be compensated, considering that there is an enormous annual waste of textiles and the strategy would involve recycling cotton waste (Asaadi et al., 2016; Björquist et al., 2018). Cotton wastes are mainly mechanically recycled, leading to fibres with poor quality that are commonly blended with virgin cotton (De Silva & Byrne, 2017). In this way, a new approach emerges and consists on the chemical recycling of textile/cotton waste, with or without blending with dissolving wood pulps (Asaadi et al., 2016; Björquist et al., 2018; Peters et al., 2019). Some studies have already been developed in this context, using NMMO (Björquist et al., 2018; Haule et al., 2016a, 2016b) and other ILs as solvents (Asaadi et al., 2016; De Silva & Byrne, 2017; Ma et al., 2019a; Nasri-Nasrabadi et al., 2020). Studies were also carried out using alkaline hydrolysis (Peters et al., 2019), or even trials where cotton waste is used as a raw material in the carbamate process (Paunonen et al., 2019). The studies involving the dissolution of cotton wastes in NMMO showed that the fibres obtained have higher mechanical properties than typical lyocell fibres and similar supramolecular structure (Björquist et al., 2018; Haule et al., 2016a, 2016b).

Among the ILs used in rayon fibres production, only few were used in dissolution of cotton wastes, namely [DBNH][OAc] (Asaadi et al., 2016), [Amim]Cl (De Silva et al., 2014; De Silva & Byrne, 2017; Lv et al., 2015), and [C$_4$mim][OAc] (Ma et al., 2019a; Ma et al., 2019b; Nasri-Nasrabadi et al., 2020). These studies reveal that the fibres obtained have higher tenacities values than natural cotton fibres and higher crystallinity index than lyocell fibres (Asaadi et al., 2016). In addition, it was proved that it is possible to dissolve cotton wastes with high DP values in ionic liquids, and that exists a direct relation between the DP value and the mechanical properties of fibres (De Silva & Byrne, 2017). In order to improve the recycling of textile wastes Ma and co-workers proposed a closed loop process using a binary solvent ([C_4mim][OAc] as solvent and DMSO as co-solvent), where the resulting fibres reveal mechanical and morphological properties similar to those of viscose fibres (Ma et al., 2019a; Ma et al., 2019b).

Nowadays, a significant part of textiles comprises blend of fibres which difficult the recycling of these wastes. Accepting this challenge, studies were carried out to separate cotton from the blends with synthetic fibres by taking advantage of the ILs selectivity (De Silva et al., 2014; Haslinger et al., 2019; Lv et al., 2015), by the hydrothermal treatment of cellulose (Hou et al., 2018), or by the degradation of one of the components (e.g., PET) (Palme et al., 2017). It was also found that the dopes with cotton viscosities out of the 450-550 cm^3/g range are not spinnable, observing the formation of breaks and agglomerates that prevent the precise design of the fibres (Asaadi et al., 2016). According to the promising results of these recent works, the chemical recovery of textile waste has become an important path for its recovery, fulfilling the concepts of environmental safety and contributing to the circular economy in agreement with the biorefinery principles. Moreover, these results triggered new promising studies that fit the previous principles, and include the recycling of waste paper and cardboard (Ma et al., 2016), paper sludge (a by-product from paper industry) (Adu et al., 2021), or waste newsprint (Ma et al., 2018) to produce textile fibres.

5. Concluding remarks

Rayon fibres are a suitable substitute for natural textile fibres such as cotton, which are no longer sufficient to meet market demands. This explains the constant trend of increasing rayon fibre production by more than twice over two decades of the 21st century, inducing an annual consumption of dissolving pulp of up to almost 9 million tons. Although wood is the main source for the production dissolving pulp (*ca.* 85 %), the contribution of non-woody plants (e.g., cotton linters, hemp, bamboo, etc.) becomes quite remarkable. Nowadays, almost 95% of rayon fibres are produced by the conventional viscose process, which provide moderate quality rayon fibres and is far from being environmentally friendly. Consequently, alternative approaches are seeking to replace conventional viscose production. Novel processes dealing with the direct dissolution of cellulose in appropriate recyclable solvents have gained especial attention, being the lyocell process the only direct dissolution process currently commercialized. At the same time, high production costs, exploration limitations of lyocell fibers (e.g. excessive fibrillation under wet condition), cellulose and NMMO side reactions and by-products formed along this process have stimulated the development of alternative cost-competitive approaches with better technical performance. Proposed direct cellulose dissolution systems include advanced ionic liquids, deep eutectic solvents, alkali-based and concentrated inorganic salt solutions. Despite all the efforts to obtain rayon fibers using the aforementioned direct cellulose dissolution systems, the most outstanding results from the point of view of the technical and economic feasibility of the process and the strength of rayon fibers were obtained using few classes of ionic liquids. Chemical recycling of cotton waste represents another promising tool to complete the lack of natural fibres on the market, challenging researchers to new solutions.

Credit authorship contribution statement

Inês S. F. Mendes: Methodology, Investigation, Writing - original draft. **Dmitry V. Evtuguin**: Conceptualization, Supervision, Writing – review & editing, Project administration, Funding acquisition.

Acknowledgments

The financial support of this work by Caima – Indústria de Celulose S.A. within the scope of the PhD project of Inês S. F. Mendes and by CICECO-Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/50011/2020, financed by national funds through the Portuguese Foundation for Science and Technology/MCTES, are greatly acknowledged.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at https://doi.org/10.1016/j.carbpol.2021.xxxxxx.

6. References

Abramova, L. S., Trusova, S. P., & Rogovin, Z. A. (1982). Ripening of low-substitution cellulose xanthate solutions. *Fibre Chemistry, 13*(5), 327–328. https://doi.org/10.1007/BF00548233

Adu, C., Zhu, C., Jolly, M., Richardson, R. M., & Eichhorn, S. J. (2021). Continuous and sustainable cellulose filaments from ionic liquid dissolved paper sludge nanofibres. *Journal of Cleaner Production, 280*, 124503. https://doi.org/10.1016/j.jclepro.2020.124503

Albrecht, W. (1981). Achievements and prospects in the field of man-made fibre modification (review). *Fibre Chemistry, 12*, 207–218. https://doi.org/10.1007/BF00548708

Andrade, M. F., & Colodette, J. L. (2014). Dissolving pulp production from sugar cane bagasse. *Industrial Crops and Products*, *52*, 58–64. https://doi.org/10.1016/j.indcrop.2013.09.041

Arce, C., Llano, T., García, P., & Coz, A. (2020). Technical and environmental improvement of the bleaching sequence of dissolving pulp for fibre production. *Cellulose, 1*. https://doi.org/10.1007/s10570-020-03065-1

Arce, C., Llano, T., González, S., & Coz, A. (2020). Use of green solvents as pre-treatment of dissolving pulp to decrease CS_2 consumption from viscose production. *Cellulose, 3*. https://doi.org/10.1007/s10570-020-03465-3

Asaadi, S., Hummel, M., Ahvenainen, P., Gubitosi, M., Olsson, U., & Sixta, H. (2018).

Structural analysis of Ioncell-F fibres from birch wood. *Carbohydrate Polymers*, *181*(November 2017), 893–901. https://doi.org/10.1016/j.carbpol.2017.11.062

Asaadi, S., Hummel, M., Hellsten, S., Härkäsalmi, T., Ma, Y., Michud, A., & Sixta, H. (2016). Renewable High-Performance Fibers from the Chemical Recycling of Cotton Waste Utilizing an Ionic Liquid. *ChemSusChem*, *9*(22), 3250–3258. https://doi.org/10.1002/cssc.201600680

Bajpai, P. (2018). *Biermann's Handbook of Pulp and Paper: Raw Material and Pulp Making* (3rd ed.). Elsevier Inc. https://doi.org/10.1016/b978-0-12-814240-0.00014-8

Bartsch, P., & Kling, G. (2001). What Opportunities are Available to the Finisher From Today' s Point of View When It Comes to Dyeing and Finishing of Lenzing Lyocell®. *Lenzinger Berichte*, *80*, 40–48.

Basit, A., Latif, W., Baig, S. A., & Afzal, A. (2018). The Mechanical and Comfort Properties of Sustainable Blended Fabrics of Bamboo With Cotton and Regenerated Fibers. *Clothing and Textiles Research Journal*, *36*(4), 267–280. https://doi.org/10.1177/0887302X18782778

Behin, J., Mikaniki, F., & Fadaei, Z. (2008). Dissolving pulp (alpha-cellulose) from corn stalk by kraft process. *Iranian Journal of Chemical Engineering*, *5*(3), 14–28.

Björquist, S., Aronsson, J., Henriksson, G., & Persson, A. (2018). Textile qualities of regenerated cellulose fibers from cotton waste pulp. *Textile Research Journal*, *88*(21), 2485–2492. https://doi.org/10.1177/0040517517723021

Bodachivskyi, I., Page, C. J., Kuzhiumparambil, U., Hinkley, S. F. R., Sims, I. M., & Williams, D. B. G. (2020). Dissolution of Cellulose: Are Ionic Liquids Innocent or Noninnocent Solvents? *ACS Sustainable Chemistry and Engineering*, *8*(27), 10142–10150. https://doi.org/10.1021/acssuschemeng.0c02204

Bouiri, B., & Amrani, M. (2010). Production of dissolving grade pulp from alfa. *BioResources*, *5*(1), 291–302.

Brandt, A., Gräsvik, J., Hallett, J. P., & Welton, T. (2013). Deconstruction of lignocellulosic biomass with ionic liquids. *Green Chemistry*, *15*(3), 550–583. https://doi.org/10.1039/c2gc36364j

Budtova, T., & Navard, P. (2016). Cellulose in NaOH – water based solvents : a review. *Cellulose*, *23*(1), 5–55. https://doi.org/10.1007/s10570-015-0779-8

Butkova, N. T., Tokareva, T. I., Pakshver, A. B., Finger, G. G., Butyagin, P. A., & Shablygin, M. V. (1979). Reduction of carbon disulfide consumption in xanthation by ammonia-activation of cellulose. *Fibre Chemistry*, *10*(6), 570–571. https://doi.org/10.1007/BF00546099

Buurman, A. (1953). Hemicellulose in the Viscose Rayon Process: A Chromatographic Investigation. *Textile Research Journal*, *23*(12), 888–896. https://doi.org/10.1177/004051755302301206

Cafuta, D., Abu-Rous, M., Jary, S., Scheffelmeier, M., & Rijavec, T. (2019). Suitability of lyocell fiber for pillow fillings. *Textile Research Journal*, *89*(18), 3722–3743. https://doi.org/10.1177/0040517518819844

Cai, J., Liu, Y., & Zhang, L. (2006). Dilute solution properties of cellulose in LiOH/urea aqueous system. *Journal of Polymer Science Part B: Polymer Physics*, *44*(21), 3093–3101. https://doi.org/10.1002/polb.20938

Cai, J., & Zhang, L. (2005). Rapid dissolution of cellulose in LiOH/Urea and NaOH/Urea aqueous solutions. *Macromolecular Bioscience*, *5*(6), 539–548. https://doi.org/10.1002/mabi.200400222

Cai, J., Zhang, L., Zhou, J., Li, H., Chen, H., & Jin, H. (2004). Novel fibers prepared from cellulose in NaOH/urea aqueous solution. *Macromolecular Rapid Communications*, *25*(17), 1558–1562. https://doi.org/10.1002/marc.200400172

Cai, J., Zhang, L., Zhou, J., Qi, H., Chen, H., Kondo, T., Chen, X., & Chu, B. (2007). Multifilament fibers based on dissolution of cellulose in NaOH/urea aqueous solution: structure and properties. *Advanced Materials*, *19*(6), 821–825. https://doi.org/10.1002/adma.200601521

Cao, Q., Li, J., Xia, Y., Li, W., Luo, S., Ma, C., & Liu, S. (2019). Green extraction of six phenolic compounds from rattan (*Calamoideae faberii*) with deep eutectic solvent by homogenate-assisted vacuum-cavitation method. *Molecules*, *24*(1), 113–128. https://doi.org/10.3390/molecules24010113

Cao, S., Ma, X., Lin, L., Huang, F., Huang, L., & Chen, L. (2014). Morphological and Chemical Characterization of Green Bamboo (Dendrocalamopsis oldhami (Munro) Keng f.) for Dissolving Pulp Production. *BioResources*, *9*(3), 4528–4539. https://doi.org/10.15376/biores.9.3.4528-4539

Cao, Y., Zhang, R., Cheng, T., Guo, J., Xian, M., & Liu, H. (2017). Imidazolium-based ionic liquids for cellulose pretreatment: recent progresses and future perspectives. *Applied Microbiology and Biotechnology*, *101*(2), 521–532. https://doi.org/10.1007/s00253-016-8057-8

Carrillo-Varela, I., Retamal, R., Pereira, M., & Mendonça, R. T. (2019). Structure and reactivity of cellulose from bleached kraft pulps of different Eucalyptus species upgraded to dissolving pulp. *Cellulose*, *26*(9), 5731–5744. https://doi.org/10.1007/s10570-019-02491-0

Carrillo, F., Colom, X., Suñol, J. J., & Saurina, J. (2004). Structural FTIR analysis and thermal characterisation of lyocell and viscose-type fibres. *European Polymer Journal*, *40*(9), 2229–2234. https://doi.org/10.1016/j.eurpolymj.2004.05.003

Chavan, R. B., & Patra, A. K. (2004). Development and processing of lyocell. *Indian Journal of Fibre and Textile Research*, *29*(4), 483–492.

Chen, C., Duan, C., Li, J., Liu, Y., Ma, X., Zheng, L., Stavik, J., & Ni, Y. (2016). Cellulose (dissolving pulp) manufacturing processes and properties: A mini-review. *BioResources*, *11*(2), 5553–5564. https://doi.org/10.15376/biores.11.2.Chen

Chen, X., Burger, C., Wan, F., Zhang, J., Rong, L., Hsiao, B. S., Chu, B., Cai, J., & Zhang, L. (2007). Structure study of cellulose fibers wet-spun from environmentally friendly NaOH/Urea aqueous solutions. *Biomacromolecules*, *8*(6), 1918–1926. https://doi.org/10.1021/bm061186i

Chen, Y.-L., Zhang, X., You, T.-T., & Xu, F. (2019). Deep eutectic solvents (DESs) for cellulose dissolution: a mini-review. *Cellulose*, *26*(1), 205–213. https://doi.org/10.1007/s10570-018-2130-7

Chiappe, C., & Pieraccini, D. (2005). Ionic liquids: Solvent properties and organic reactivity. *Journal of Physical Organic Chemistry*, *18*(4), 275–297. https://doi.org/10.1002/poc.863

Ciechańska, D., Wesolowska, E., & Wawro, D. (2009). An introduction to cellulosic fibres. In S. J. Eichhorn, J. W. S. Hearle, M. Jaffe, & T. Kikutani (Eds.), *Handbook of textile fibre structure. Volume 2: Natural, regenerated, inorganic and specialist fibres* (1st ed., Vol. 66, Issue 5, pp. 3–61). Woodhead Publishing Limited. https://doi.org/10.2115/fiber.66.P_174

Compton, J. (1939). Structural Relation of Rayon to Natural Cellulosic Fibers: Study of the Viscose Process. *Industrial and Engineering Chemistry*, *31*(10), 1250–1259.

Cook, J. G. (2001). *Handbook of Textile Fibres. II. Man-Made Fibres* (5th ed.). Woodhead Publishing Limited.

Cuculo, J. A., Smith, C. B., Sangwatanaroj, U., Stejskal, E. O., & Sankar, S. S. (1994). A study on the mechanism of dissolution of the cellulose/NH_3/NH_4SCN system. I. *Journal of Polymer Science Part A: Polymer Chemistry*, *32*(2), 229–239. https://doi.org/10.1002/pola.1994.080320203

Cuissinat, C., & Navard, P. (2006). Swelling and dissolution of cellulose part II: Free floating cotton and wood fibres in NaOH-water-additives systems.

Macromolecular Symposia, *244*, 19–30. https://doi.org/10.1002/masy.200651202

Dapía, S., Sixta, H., Borgards, A., Harms, H., & Parajó, J. C. (2003). TCF bleaching of hardwood pulps obtained in organic acid media: Production of viscose-grade pulps. *Holz Als Roh - Und Werkstoff*, *61*(5), 363–368. https://doi.org/10.1007/s00107-003-0404-7

De Silva, R., & Byrne, N. (2017). Utilization of cotton waste for regenerated cellulose fibres: Influence of degree of polymerization on mechanical properties. *Carbohydrate Polymers*, *174*, 89–94. https://doi.org/10.1016/j.carbpol.2017.06.042

De Silva, R., Vongsanga, K., Wang, X., & Byrne, N. (2015). Cellulose regeneration in ionic liquids: factors controlling the degree of polymerisation. *Cellulose*, *22*(5), 2845–2849. https://doi.org/10.1007/s10570-015-0733-9

De Silva, R., Wang, X., & Byrne, N. (2014). Recycling textiles: the use of ionic liquids in the separation of cotton polyester blends. *RSC Advances*, *4*(55), 29094–29098. https://doi.org/10.1039/c4ra04306e

Duan, C., Li, J., Ma, X., Chen, C., Liu, Y., Stavik, J., & Ni, Y. (2015). Comparison of acid sulfite (AS)- and prehydrolysis kraft (PHK)-based dissolving pulps. *Cellulose*, *22*(6), 4017–4026. https://doi.org/10.1007/s10570-015-0781-1

Duan, C., Qin, X., Wang, X., Feng, X., Yu, H., Dai, L., Wang, W., & Zhao, W. (2019). Simultaneous mechanical refining and phosphotungstic acid catalysis for improving the reactivity of kraft-based dissolving pulp. *Cellulose*, *26*(9), 5685–5694. https://doi.org/10.1007/s10570-019-02461-6

Duan, C., Verma, S. K., Li, J., Ma, X., & Ni, Y. (2016). Viscosity control and reactivity improvements of cellulose fibers by cellulase treatment. *Cellulose, 23*(1), 269–276. https://doi.org/10.1007/s10570-015-0822-9

Dunlop, M. J., Acharya, B., & Bissessur, R. (2018). Isolation of nanocrystalline cellulose from tunicates. *Journal of Environmental Chemical Engineering*, *6*(4), 4408–4412. https://doi.org/10.1016/j.jece.2018.06.056

Edgar, K. J., & Zhang, H. (2020). Antibacterial modification of Lyocell fiber: A review. *Carbohydrate Polymers*, *250*(June), 116932. https://doi.org/10.1016/j.carbpol.2020.116932

Ekman, K., Eklund, V., Fors, J., Huttunen, J. I., Mandell, L., Selin, J.-F., & Turunen, O. T. (1984). Regenerated Cellulose Fibers From Cellulose Carbamate Solutions. *Lenzinger Berichte*, *57*, 38–40.

El Seoud, O. A., Kostag, M., Jedvert, K., & Malek, N. I. (2020). Cellulose Regeneration and Chemical Recycling: Closing the “Cellulose Gap” Using Environmentally Benign Solvents. *Macromolecular Materials and Engineering, 305*(4), 1900832. https://doi.org/10.1002/mame.201900832

Elsayed, S., Hummel, M., Sawada, D., Guizani, C., Rissanen, M., & Sixta, H. (2020). Superbase-based protic ionic liquids for cellulose filament spinning. *Cellulose*. https://doi.org/10.1007/s10570-020-03505-y

Engström, A.-C., Ek, M., & Henriksson, G. (2006). Improved accessibility and reactivity of dissolving pulp for the viscose process: Pretreatment with monocomponent edoglucanase. *Biomacromolecules*, *7*(6), 2027–2031. https://doi.org/10.1021/bm0509725

Enneking, J. C. (2002). Control of carbon disulfide emissions from viscose processes. *Environmental Progress*, *21*(3), 169–174. https://doi.org/10.1002/ep.670210314

Erdmenger, T., Haensch, C., Hoogenboom, R., & Schubert, U. S. (2007). Homogeneous tritylation of cellulose in 1-butyl-3-methylimidazolium chloride. *Macromolecular Bioscience*, *7*(4), 440–445. https://doi.org/10.1002/mabi.200600253

Evtuguin, D. V. (2016). Sulphite Pulping. In N. Belgacem & A. Pizzi (Eds.), *Lignocellulosic Fibers and Wood Handbook: Renewable Materials for Today's Environment* (1st ed., pp. 225–244). Scrivener Publishing LLC. https://doi.org/10.1002/9781118773727.ch8

Feng, L., & Chen, Z. (2008). Research progress on dissolution and functional modification of cellulose in ionic liquids. *Journal of Molecular Liquids*, *142*(1–3), 1–5. https://doi.org/10.1016/j.molliq.2008.06.007

Fengel, D., & Wegener, G. (Eds.). (1983). *Wood: Chemistry, Ultrastructure, Reactions* (1st ed.).

Ferreira, D. C., Oliveira, M. L., Bioni, T. A., Nawaz, H., King, A. W. T., Kilpeläinen, I., Hummel, M., Sixta, H., & El Seoud, O. A. (2019). Binary mixtures of ionic liquids-DMSO as solvents for the dissolution and derivatization of cellulose: Effects of alkyl and alkoxy side chains. *Carbohydrate Polymers*, *212*, 206–214. https://doi.org/10.1016/j.carbpol.2019.02.024

Ferreira, J. C., Evtuguin, D. V., & Prates, A. (2020). Effect of cellulose structure on reactivity of eucalyptus acid sulphite dissolving pulp. *Cellulose*, *27*, 4763–4772. https://doi.org/10.1007/s10570-020-03092-y

Fink, H.-P., Ganster, J., & Lehmann, A. (2014). Progress in cellulose shaping: 20 years industrial case studies at Fraunhofer IAP. *Cellulose*, *21*(1), 31–51. https://doi.org/10.1007/s10570-013-0137-7

Fischer, S., Leipner, H., Brendler, E., Voigt, W., & Fischer, K. (1999). Molten inorganic salt hydrates as cellulose solvents. In M. A. El-Nokaly & H. A. Soini (Eds.), *Polysaccharide Applications* (Vol. 737, pp. 143–150). American Cgemical Society. https://doi.org/10.1021/bk-1999-0737.ch010

Fischer, S., Leipner, H., Thümmler, K., Brendler, E., & Peters, J. (2003). Inorganic molten salts as solvents for cellulose. *Cellulose*, *10*(3), 227–236. https://doi.org/10.1023/A:1025128028462

Fischer, S., & Thümmler, K. (2010). Molten inorganic salts as reaction medium for cellulose. In T. F. Liebert, T. J. Heinze, & K. J. Edgar (Eds.), *Cellulose Solvents: For Analysis, Shaping and Chemical Modification* (Vol. 1033, pp. 91–101). ACS Symposium Series. https://doi.org/10.1021/bk-2010-1033.ch004

Fischer, S., Voigt, W., & Fischer, K. (1999). The behaviour of cellulose in hydrated melts of the composition LiX·nH_2O (X = I^-, NO^-_3, CH_3COO^-, CIO^-_4). *Cellulose*, *6*(3), 213–219. https://doi.org/10.1023/A:1009269614096

Fischer, Steffen, Thümmler, K., Pfeiffer, K., Liebert, T., & Heinze, T. (2002).

Evaluation of molten inorganic salt hydrates as reaction medium for the esterification of cellulose. *Cellulose*, *9*, 293–300. https://doi.org/10.1007/s10570-009-9344-7

Fock, W. (1959). Eine modifizierte method zur bestimmund der reaktivität von zellstoffen für die viskoseherstellund. *Das Papier*, *13*, 92–95.

Food and Agriculture Organization of the United Nations. (2019). *Forestry Production and Trade*. http://www.fao.org/faostat/en/#data/FO

Francisco, M., Van Den Bruinhorst, A., & Kroon, M. C. (2012). New natural and renewable low transition temperature mixtures (LTTMs): screening as solvents for lignocellulosic biomass processing. *Green Chemistry*, *14*(8), 2153–2157. https://doi.org/10.1039/c2gc35660k

Gehmayr, V., Schild, G., & Sixta, H. (2011). A precise study on the feasibility of enzyme treatments of a kraft pulp for viscose application. *Cellulose*, *18*(2), 479–491. https://doi.org/10.1007/s10570-010-9483-x

Germgård, U. (2007). From pure cellulose to CMC and viscose - some process and mechanistic aspects. *O Papel*, *9*(setembro), 68–88.

Gindl, W., Konnerth, J., & Schöberl, T. (2006). Nanoindentation of regenerated cellulose fibres. *Cellulose*, *13*(1), 1–7. https://doi.org/10.1007/s10570-005-9017-0

Gondhalekar, S. C., Pawar, P. J., & Dhumal, S. S. (2019). Use of electron beam irradiation for improving reactivity of dissolving pulp in viscose process. *Journal of Radioanalytical and Nuclear Chemistry*, *322*(1), 67–72.

https://doi.org/10.1007/s10967-019-06563-0

Gondhalekar, S. C., Pawar, P. J., Dhumal, S. S., & Thakre, S. S. (2019). Mechanism of xanthation reaction in viscose process. *Cellulose*, *26*(3), 1595–1604. https://doi.org/10.1007/s10570-018-2213-5

Graenacher, C., & Sallmann, R. (1939). *US Patent 2,179,181: Cellulose solutions and process of making same* (Patent No. 2,179,181).

Grøssereid, I., Lethesh, K. C., Venkatraman, V., & Fiksdahl, A. (2019). New dual functionalized zwitterions and ionic liquids; Synthesis and cellulose dissolution studies. *Journal of Molecular Liquids*, *292*, 111353. https://doi.org/10.1016/j.molliq.2019.111353

Guizani, C., Larkiala, S., Moriam, K., Sawada, D., Elsayed, S., Rantasalo, S., Hummel, M., & Sixta, H. (2021). Air gap spinning of a cellulose solution in [DBNH][OAc] ionic liquid with a novel vertically arranged spinning bath to simulate a closed loop operation in the Ioncell® process. *Journal of Applied Polymer Science*, *138*(5). https://doi.org/10.1002/app.49787

Guizani, C., Nieminen, K., Rissanen, M., Larkiala, S., Hummel, M., & Sixta, H. (2020). New insights into the air gap conditioning effects during the dry-jet wet spinning of an ionic liquid-cellulose solution. *Cellulose*, *27*(9), 4931–4948. https://doi.org/10.1007/s10570-020-03115-8

Harlin, A. (2019). Cellulose carbamate: production and applications. In *VTT Technical Research Centre of Finland*. VTT Technical Research Centre of Finland.

https://doi.org/10.32040/2019.978-951-38-8707-0

Haslinger, S., Hummel, M., Anghelescu-Hakala, A., Määttänen, M., & Sixta, H. (2019). Upcycling of cotton polyester blended textile waste to new man-made cellulose fibers. *Waste Management*, *97*, 88–96. https://doi.org/10.1016/j.wasman.2019.07.040

Haule, L. V., Carr, C. M., & Rigout, M. (2016a). Investigation into the supramolecular properties of fibres regenerated from cotton based waste garments. *Carbohydrate Polymers*, *144*, 131–139. https://doi.org/10.1016/j.carbpol.2016.02.054

Haule, L. V., Carr, C. M., & Rigout, M. (2016b). Preparation and physical properties of regenerated cellulose fibres from cotton waste garments. *Journal of Cleaner Production*, *112*, 4445–4451. https://doi.org/10.1016/j.jclepro.2015.08.086

Helmy, S. A., & Abou-State, M. A. (1991). Viscose Pulps from Egyptian Bagasse with High Chemical Reactivity. *Holzforschung*, *45*(6), 433–436. https://doi.org/10.1515/hfsg.1991.45.6.433

Hermanutz, F., Vocht, M. P., Panzier, N., & Buchmeiser, M. R. (2019). Processing of Cellulose Using Ionic Liquids. *Macromolecular Materials and Engineering*, *304*(2), 1800450. https://doi.org/10.1002/mame.201800450

Hong, Y.-K., Chung, K.-H., & Lee, W.-S. (1998). Structure of Regenerated Cellulose Fibers from DMAc/LiCl Solution. *Textile Research Journal*, *68*(1), 65–69. https://doi.org/10.1177/004051759806800108

Hou, W., Ling, C., Shi, S., Yan, Z., Zhang, M., Zhang, B., & Dai, J. (2018). Separation and characterization of waste cotton/polyester blend fabric with hydrothermal method. *Fibers and Polymers*, *19*(4), 742–750. https://doi.org/10.1007/s12221-018-7735-9

Huang, Z., Liu, C., Feng, X., Wu, M., Tang, Y., & Li, B. (2020). Effect of regeneration solvent on the characteristics of regenerated cellulose from lithium bromide trihydrate molten salt. *Cellulose*, *27*(16), 9243–9256. https://doi.org/10.1007/s10570-020-03440-y

Hummel, M., Michud, A., Tanttu, M., Asaadi, S., Ma, Y., Hauru, L. K. J., Parviainen, A., King, A. W. T., Kilpeläinen, I., & Sixta, H. (2016). Ionic Liquids for the Production of Man-Made Cellulosic Fibers: Opportunities and Challenges. In O. J. Rojas (Ed.), *Advances in Polymer Science* (1st ed., Vol. 271, pp. 133–168). Springer International Publishing. https://doi.org/10.1007/978-3-319-26015-0

Ibarra, D., Köpcke, V., & Ek, M. (2009). Exploring enzymatic treatments for the production of dissolving grade pulp from different wood and non-wood paper grade pulps. *Holzforschung*, *63*(November), 721–730. https://doi.org/10.1515/HF.2009.102

Ibarra, D., Köpcke, V., & Ek, M. (2010). Behavior of different monocomponent endoglucanases on the accessibility and reactivity of dissolving-grade pulps for viscose process. *Enzyme and Microbial Technology*, *47*(7), 355–362. https://doi.org/10.1016/j.enzmictec.2010.07.016

Ingildeev, D., Effenberger, F., Bredereck, K., & Hermanutz, F. (2013). Comparison of direct solvents for regenerated cellulosic fibers via the lyocell process and by means of ionic liquids. *Journal of Applied Polymer Science*, *128*(6), 4141–4150. https://doi.org/10.1002/app.38470

Ioncell. (n.d.). Retrieved November 22, 2019, from https://ioncell.fi/

Jablonský, M., Škulcová, A., Kamenská, L., Vrška, M., & Šíma, J. (2015). Deep Eutectic Solvents: Fractionation of Wheat Straw. *BioResources*, *10*(4), 8039–8047. https://doi.org/10.15376/biores.10.4.8039-8047

Jahan, M. S., Deb, R. C., Rahaman, M. M., & Quaiyyum, M. A. (2016). Dissolving pulp from white press cuttings. *Tappi Journal*, *15*(4), 277–282.

Jedvert, K., & Heinze, T. (2017). Cellulose modification and shaping - A review. *Journal of Polymer Engineering*, *37*(9), 845–860. https://doi.org/10.1515/polyeng-2016-0272

Jiang, X., Bai, Y., Chen, X., & Liu, W. (2020). A review on raw materials, commercial production and properties of lyocell fiber. *Journal of Bioresources and Bioproducts*, *5*(1), 16–25. https://doi.org/10.1016/j.jobab.2020.03.002

Johansson, A., Aaltonen, O., & Ylinen, P. (1987). Organosolv pulping - methods and pulp properties. *Biomass*, *13*(1), 45–65. https://doi.org/10.1016/0144-4565(87)90071-0

Johnson, D. L. (1969a). *US Patent 3,447,939: Compounds dissolved in cyclic amine oxides* (Patent No. 3,447,939).

Johnson, D. L. (1969b). *US Patente 3,447,956: Process for strengthening swellable* *fibrous material with an amine oxide and the resulting material* (Patent No. 3,447,956).

Kamide, K., & Nishiyama, K. (2001). Cuprammonium processes. In C. Woodings (Ed.), *Regenerated Cellulose Fibres* (1st ed., pp. 88–155). Woodhead Publishing Limited. https://doi.org/10.1533/9781855737587.88

Kamide, K., Okajima, K., Matsui, T., & Kowsaka, K. (1984). Study on the solubility of cellulose in aqueous alkali solution by deuteration IR and ^{13}C NMR. *Polymer Journal*, *16*(12), 857–866. https://doi.org/10.1295/polymj.16.857

Kauffman, G. B., & Karbassi, M. (1985). A demonstration of the cuprammonium rayon process. *Journal of Chemical Education*, *62*(10), 878. https://doi.org/10.1021/ed062p878

Klemm, D., Philipp, B., Heinze, T., Heinze, U., & Wagenknecht, W. (1998). Comprehensive Cellulose Chemistry: Volume I: Fundamentals and analytical Methods. In *Methods: Vol. l* (p. 260). https://doi.org/10.1002/3527601929

Köhler, S., & Heinze, T. (2007). New solvents for cellulose: Dimethyl sulfoxide/ammonium fluorides. *Macromolecular Bioscience*, *7*(3), 307–314. https://doi.org/10.1002/mabi.200600197

Köpcke, V., Ibarra, D., Larsson, P. T., & Ek, M. (2010). Optimization of treatment sequences for the production of dissolving pulp from birch kraft pulp. *Nordic Pulp and Paper Research Journal*, *25*(1), 31–38. https://doi.org/10.3183/npprj-2010-25-01-p031-038

Kraft, G., & Schelosky, N. (2000). Irradiation of dissolving pulp by elecron beams. *Lenzinger Berichte*, *79*(September), 65–70.

Kreze, T., & Malej, S. (2003). Structural Characteristics of New and Conventional Regenerated Cellulosic Fibers. *Textile Research Journal*, *73*(8), 675–684. https://doi.org/10.1177/004051750307300804

Kvarnlöf, N., Germgård, U., Jönsson, L. J., & Söderlund, C.-A. (2006). Enzymatic treatment to increase the reactivity of a dissolving pulp for viscose preparation. *Appita Journal*, *59*(3), 242–246.

Latif, W., Basit, A., Rehman, A., Ashraf, M., Iqbal, K., Jabbar, A., Baig, S. A., & Maqsood, S. (2019). Study of mechanical and comfort properties of modal with cotton and regenerated fibers blended woven fabrics. *Journal of Natural Fibers*, *16*(6), 836–845. https://doi.org/10.1080/15440478.2018.1441084

Leipner, H., Fischer, S., Brendler, E., & Voigt, W. (2000). Structural changes of cellulose dissolved in molten salt hydrates. *Macromolecular Chemistry and Physics*, *201*(15), 2041–2049. https://doi.org/10.1002/1521-3935(20001001)201:15<2041::AID-MACP2041>3.0.CO;2-E

Lethesh, K. C., Evjen, S., Venkatraman, V., Shah, S. N., & Fiksdahl, A. (2020). Highly efficient cellulose dissolution by alkaline ionic liquids. *Carbohydrate Polymers*, *229*(November 2019), 115594. https://doi.org/10.1016/j.carbpol.2019.115594

Li, H., Legere, S., He, Z., Zhang, H., Li, J., Yang, B., Zhang, S., Zhang, L., Zheng, L., & Ni, Y. (2018). Methods to increase the reactivity of dissolving pulp in the viscose rayon production process: a review. *Cellulose*, *25*(7), 3733–3753. https://doi.org/10.1007/s10570-018-1840-1

Li, R., Chang, C., Zhou, J., Zhang, L., Gu, W., Li, C., Liu, S., & Kuga, S. (2010). Primarily industrialized trial of novel fibers spun from cellulose dope in NaOH/Urea aqueous solution. *Industrial and Engineering Chemistry Research*, *49*(22), 11380–11384. https://doi.org/10.1021/ie101144h

Li, R., Wang, S., Lu, A., & Zhang, L. (2015). Dissolution of cellulose from different sources in an NaOH/urea aqueous system at low temperature. *Cellulose*, *22*(1), 339–349. https://doi.org/10.1007/s10570-014-0542-6

Li, Y., Wang, J., Liu, X., & Zhang, S. (2018). Towards a molecular understanding of cellulose dissolution in ionic liquids: anion/cation effect, synergistic mechanism and physicochemical aspects. *Chemical Science*, *9*(17), 4027–4043. https://doi.org/10.1039/c7sc05392d

Ling, Z., Guo, Z., Huang, C., Yao, L., & Xu, F. (2020). Deconstruction of oriented crystalline cellulose by novel levulinic acid based deep eutectic solvents pretreatment for improved enzymatic accessibility. *Bioresource Technology*, *305*(January), 123025. https://doi.org/10.1016/j.biortech.2020.123025

Liu, Y., Shi, L., Cheng, D., & He, Z. (2016). Dissolving Pulp Market and Technologies: Chinese Prospective - A Mini-Review. *BioResources*, *11*(3), 7902–7916. https://doi.org/10.15376/biores.11.3.Liu

Llano, T., Arce, C., Ruiz, G., Chenna, N., & Coz, A. (2018). Modelling and

Optimization of the Last Two Stages of an Environmentally-Compatible TCF Bleaching Sequence. *BioResources*, *13*(3), 6642–6662. www.geruc.es

Llaudet, J. M. (1990). Modal blends in knitted and woven fabrics - fashion and functional aspects. *Lenzinger Berichte*, *70*, 24–26.

Loow, Y. L., New, E. K., Yang, G. H., Ang, L. Y., Foo, L. Y. W., & Wu, T. Y. (2017). Potential use of deep eutectic solvents to facilitate lignocellulosic biomass utilization and conversion. *Cellulose*, *24*(9), 3591–3618. https://doi.org/10.1007/s10570-017-1358-y

Luo, X., & Zhang, L. (2013). New solvents and functional materials prepared from cellulose solutions in alkali/urea aqueous system. *Food Research International*, *52*(1), 387–400. https://doi.org/10.1016/j.foodres.2010.05.016

Lv, F., Wang, C., Zhu, P., & Zhang, C. (2015). Isolation and recovery of cellulose from waste nylon/cotton blended fabrics by 1-allyl-3-methylimidazolium chloride. *Carbohydrate Polymers*, *123*, 424–431. https://doi.org/10.1016/j.carbpol.2015.01.043

Lynam, J. G., Kumar, N., & Wong, M. J. (2017). Deep eutectic solvents' ability to solubilize lignin, cellulose, and hemicellulose; thermal stability; and density. *Bioresource Technology*, *238*, 684–689. https://doi.org/10.1016/j.biortech.2017.04.079

Ma, X., Huang, L., Chen, Y., Cao, S., & Chen, L. (2011). Preparation of bamboo dissolving pulp for textile production. Part 1. Study on prehydrolysis of green bamboo for producing dissolving pulp. *BioResources*, *6*(2), 1428–1439. https://doi.org/10.15376/biores.6.2.1428-1439

Ma, Y., Hummel, M., Kontro, I., & Sixta, H. (2018). High performance man-made cellulosic fibres from recycled newsprint. *Green Chemistry*, *20*(1), 160–169. https://doi.org/10.1039/c7gc02896b

Ma, Y., Hummel, M., Määttänen, M., Särkilahti, A., Harlin, A., & Sixta, H. (2016). Upcycling of waste paper and cardboard to textiles. *Green Chemistry*, *18*(3), 858–866. https://doi.org/10.1039/c5gc01679g

Ma, Yibo, Rissanen, M., You, X., Moriam, K., Hummel, M., & Sixta, H. (2020). New method for determining the degree of fibrillation of regenerated cellulose fibres. *Cellulose*. https://doi.org/10.1007/s10570-020-03513-y

Ma, Yibo, Rosson, L., Wang, X., & Byrne, N. (2019a). Upcycling of waste textiles into regenerated cellulose fibres: impact of pretreatments. *Journal of the Textile Institute*. https://doi.org/10.1080/00405000.2019.1656355

Ma, Yibo, Zeng, B., Wang, X., & Byrne, N. (2019b). Circular Textiles: Closed Loop Fiber to Fiber Wet Spun Process for Recycling Cotton from Denim [Research-article]. *ACS Sustainable Chemistry and Engineering*, *7*(14), 11937–11943. https://doi.org/10.1021/acssuschemeng.8b06166

Magina, S., Barros-Timmons, A., Ventura, S. P. M., & Evtuguin, D. V. (2021). Evaluating the hazardous impact of ionic liquids – Challenges and opportunities. *Journal of Hazardous Materials*, *412*, 125215.

https://doi.org/10.1016/j.jhazmat.2021.125215

Magina, S., Marques, A. P., & Evtuguin, D. V. (2015). Study on the residual lignin in *Eucalyptus globulus* sulphite pulp. *Holzforschung*, *69*(5), 513–522. https://doi.org/10.1515/hf-2014-0218

Mahadeva, S. K., & Kim, J. (2012). Influence of residual ionic liquid on the thermal stability and electromechanical behavior of cellulose regenerated from 1-ethyl-3-methylimidazolium acetate. *Fibers and Polymers*, *13*(3), 289–294. https://doi.org/10.1007/s12221-012-0289-3

Malaeke, H., Housaindokht, M. R., Monhemi, H., & Izadyar, M. (2018). Deep eutectic solvent as an efficient molecular liquid for lignin solubilization and wood delignification. *Journal of Molecular Liquids*, *263*, 193–199. https://doi.org/10.1016/j.molliq.2018.05.001

Matsumoto, T., Tatsumi, D., Tamai, N., & Takaki, T. (2001). Solution properties of celluloses from different biological origins in LiCl·DMAc. *Cellulose*, *8*(4), 275–282. https://doi.org/10.1023/A:1015162027350

Mbe, P. W. (2001). Lyocell: the production process and market development. In C. Woodings (Ed.), *Regenerated Cellulose Fibres* (1st ed., pp. 62–87). Woodhead Publishing Limited.

Miao, Q., Chen, L., Huang, L., Tian, C., Zheng, L., & Ni, Y. (2014). A process for enhancing the accessibility and reactivity of hardwood kraft-based dissolving pulp for viscose rayon production by cellulase treatment. *Bioresource Technology*, *154*, 109–113. https://doi.org/10.1016/j.biortech.2013.12.040

Michud, A., Hummel, M., & Sixta, H. (2015). Influence of molar mass distribution on the final properties of fibers regenerated from cellulose dissolved in ionic liquid by dry-jet wet spinning. *Polymer*, *75*, 1–9. https://doi.org/10.1016/j.polymer.2015.08.017

Michud, A., Hummel, M., & Sixta, H. (2016). Influence of process parameters on the structure formation of man-made cellulosic fibers from ionic liquid solution. *Journal of Applied Polymer Science*, *133*(30), 1–9. https://doi.org/10.1002/app.43718

Michud, A., King, A., Parviainen, A., Sixta, H., Hauru, L., Hummel, M., & Kilpeläinen, I. (2014). *WO Patent 2014/162062 A1: Process for the production of shaped cellulose articles* (Patent No. 2014/162062 A1).

Michud, A., Tanttu, M., Asaadi, S., Ma, Y., Netti, E., Kääriainen, P., Persson, A., Berntsson, A., Hummel, M., & Sixta, H. (2016). Ioncell-F: ionic liquid-based cellulosic textile fibers as an alternative to viscose and Lyocell. *Textile Research Journal*, *86*(5), 543–552. https://doi.org/10.1177/0040517515591774

Mitchell, R. L. (1949). Viscose Processing of Cellulose: changes in basic properties. *Industrial & Engineering Chemistry*, *41*(10), 2197–2201. https://doi.org/10.1021/ie50478a033

Mohd, N., Draman, S. F. S., Salleh, M. S. N., & Yusof, N. B. (2017). Dissolution of cellulose in ionic liquid: A review. *AIP Conference Proceedings*, *1809*(February), 020035. https://doi.org/10.1063/1.4975450

Morais, E. S., Da Costa Lopes, A. M., Freire, M. G., Freire, C. S. R., Coutinho, J. A. P., & Silvestre, A. J. D. (2020). Use of ionic liquids and deep eutectic solvents in polysaccharides dissolution and extraction processes towards sustainable biomass valorization. *Molecules*, *25*(16), 3652. https://doi.org/10.3390/molecules25163652

Moriam, K., Rissanen, M., Sawada, D., Altgen, M., Johansson, L.-S., Evtyugin, D. V., Guizani, C., Hummel, M., & Sixta, H. (2021). Hydrophobization of the Man-Made Cellulosic Fibers by Incorporating Plant-Derived Hydrophobic Compounds. *ACS Sustainable Chemistry and Engineering*, *9*(13), 4915–4925. https://doi.org/10.1021/acssuschemeng.1c00695

Nasri-Nasrabadi, B., Wang, X., & Byrne, N. (2020). Perpetual colour: accessing the colourfastness of regenerated cellulose fibres from coloured cotton waste. *Journal of the Textile Institute*, *111*(12), 1745–1754. https://doi.org/10.1080/00405000.2020.1728182

Nayeem, J., Sarkar, M., Quadery, A. H., & Jahan, M. S. (2017). High purity dissolving pulp from jute. *Nordic Pulp and Paper Research Journal*, *32*(4), 623–629. https://doi.org/10.3183/npprj-2017-32-04_p620-629_jahan

Nguyen, H. V. D., Vries, R. De, & Stoyanov, S. D. (2020). Natural Deep Eutectics as a “Green” Cellulose Cosolvent. *ACS Sustainable Chemistry and Engineering*, *8*, 14166–14178. https://doi.org/10.1021/acssuschemeng.0c04982

Ohira, K., Abe, Y., Kawatsura, M., Suzuki, K., Mizuno, M., Amano, Y., & Itoh, T.

(2012). Design of Cellulose Dissolving Ionic Liquids Inspired by Nature. *ChemSusChem*, *5*(2), 388–391. https://doi.org/10.1002/cssc.201100427

Ohira, K., Yoshida, K., Hayase, S., & Itoh, T. (2012). Amino acid ionic liquid as an efficient cosolvent of dimethyl sulfoxide to realize cellulose dissolution at room temperature. *Chemistry Letters*, *41*(9), 987–989. https://doi.org/10.1246/cl.2012.987

Palme, A., Peterson, A., de la Motte, H., Theliander, H., & Brelid, H. (2017). Development of an efficient route for combined recycling of PET and cotton from mixed fabrics. *Textiles and Clothing Sustainability*, *3*, 4. https://doi.org/10.1186/s40689-017-0026-9

Parviainen, A., Wahlström, R., Liimatainen, U., Liitiä, T., Rovio, S., Helminen, J. K. J., Hyväkkö, U., King, A. W. T., Suurnäkki, A., & Kilpeläinen, I. (2015). Sustainability of cellulose dissolution and regeneration in 1,5-diazabicyclo[4.3.0]non-5-enium acetate: a batch simulation of the IONCELL-F process. *RSC Advances*, *5*(85), 69728–69737. https://doi.org/10.1039/c5ra12386k

Paulitz, J., Sigmund, I., Kosan, B., & Meister, F. (2017). Lyocell fibers for textile processing derived from organically grown hemp. *Procedia Engineering*, *200*, 260–268. https://doi.org/10.1016/j.proeng.2017.07.037

Paunonen, S., Kamppuri, T., Katajainen, L., Hohenthal, C., Heikkilä, P., & Harlin, A. (2019). Environmental impact of cellulose carbamate fibers from chemically recycled cotton. *Journal of Cleaner Production*, *222*, 871–881. https://doi.org/10.1016/j.jclepro.2019.03.063

Pavlov, P., Valtcheva, E., Makaztchieva, V., & Lozanov, E. (1991). Kinetics of xanthogenation after high- temperature mercerization. *Acta Polymerica*, *42*(9), 462–465. https://doi.org/10.1002/actp.1991.010420914

Peters, G. M., Sandin, G., & Spak, B. (2019). Environmental Prospects for Mixed Textile Recycling in Sweden. *ACS Sustainable Chemistry and Engineering*, *7*(13), 11682–11690. https://doi.org/10.1021/acssuschemeng.9b01742

Qin, X., Duan, C., Feng, X., Zhang, Y., Dai, L., Xu, Y., & Ni, Y. (2021). Integrating phosphotungstic acid-assisted prerefining with cellulase treatment for enhancing the reactivity of kraft-based dissolving pulp. *Bioresource Technology*, *320*, 124283. https://doi.org/10.1016/j.biortech.2020.124283

Ramamoorthy, S. K., Skrifvars, M., & Persson, A. (2015). A review of natural fibers used in biocomposites: plant, animal and regenerated cellulose fibers. *Polymer Reviews*, *55*(1), 107–162. https://doi.org/10.1080/15583724.2014.971124

Reddy, N., & Yang, Y. (2005). Structure and properties of high quality natural cellulose fibers from cornstalks. *Polymer*, *46*(15), 5494–5500. https://doi.org/10.1016/j.polymer.2005.04.073

Ren, H., Chen, C., Guo, S., Zhao, D., & Wang, Q. (2016). Synthesis of a Novel Allyl-Functionalized Deep Eutectic Solvent to Promote Dissolution of Cellulose. *BioResources*, *11*(4), 8457–8469. https://doi.org/10.15376/biores.11.4.8457-8469

Ren, H., Chen, C., Wang, Q., Zhao, D., & Guo, S. (2016). The properties of choline chloride-based deep eutectic solvents and their performance in the dissolution of cellulose. *BioResources*, *11*(2), 5435–5451. https://doi.org/10.15376/biores.11.2.5435-5451

Rinaldi, R. (2011). Instantaneous dissolution of cellulose in organic electrolyte solutions. *Chem. Commun.*, *47*(1), 511–513. https://doi.org/10.1039/C0CC02421J

Röder, T. (2017). *The Viscose Process – Scope and Limitations*. http://costfp1205.com/wp-content/uploads/2017/04/13. Roder_final_COST_Stockholm_March_2017.pdf

Rodrigues, P. F., Evtyugin, D. D., Evtuguin, D. V., & Prates, A. (2018). Extractive Profiles in the Production of Sulfite Dissolving Pulp from *Eucalyptus Globulus* Wood. *Journal of Wood Chemistry and Technology*, *38*(5), 397–408. https://doi.org/10.1080/02773813.2018.1513037

Ruan, D., Zhang, L., Lue, A., Zhou, J., Chen, H., Chen, X., Chu, B., & Kondo, T. (2006). A rapid process for producing cellulose multi-filament fibers from a NaOH/thiourea solvent system. *Macromolecular Rapid Communications*, *27*(17), 1495–1500. https://doi.org/10.1002/marc.200600232

Ruan, D., Zhang, L., Zhou, J., Jin, H., & Chen, H. (2004). Structure and properties of novel fibers spun from cellulose in NaOH/thiourea aqueous solution. *Macromolecular Bioscience*, *4*(12), 1105–1112. https://doi.org/10.1002/mabi.200400120

Sánchez, P. B., Tsubaki, S., Pádua, A. A. H., & Wada, Y. (2020). Kinetic analysis of microwave-enhanced cellulose dissolution in ionic solvents. *Physical Chemistry*

Chemical Physics, *22*(3), 1003–1010. https://doi.org/10.1039/c9cp06239d

Sango, C., Kaur, P., Bhardwaj, N. K., & Sharma, J. (2018). Bacterial cellulase treatment for enhancing reactivity of pre-hydrolysed kraft dissolving pulp for viscose. *3 Biotech*, *8*(6), 271. https://doi.org/10.1007/s13205-018-1293-0

Sarkar, M., Nayeem, J., Popy, R. S., Quadery, A. H., & Jahan, M. S. (2018). Dissolving pulp from jute wastes. *Bioresource Technology Reports*, *4*(September), 96–100. https://doi.org/10.1016/j.biteb.2018.09.008

Satria, H., Kuroda, K., Tsuge, Y., Ninomiya, K., & Takahashi, K. (2018). Dimethyl sulfoxide enhances both the cellulose dissolution ability and biocompatibility of a carboxylate-type liquid zwitterion. *New Journal of Chemistry*, *42*(16), 13225–13228. https://doi.org/10.1039/c8nj01912f

Sayyed, A. J., Deshmukh, N. A., & Pinjari, D. V. (2019). A critical review of manufacturing processes used in regenerated cellulosic fibres: viscose, cellulose acetate, cuprammonium, LiCl/DMAc, ionic liquids, and NMMO based lyocell. *Cellulose*, *26*(5), 2913–2940. https://doi.org/10.1007/s10570-019-02318-y

Sayyed, A. J., Gupta, D., Deshmukh, N. A., Mohite, L. V., & Pinjari, D. V. (2020). Influence of intensified cellulose dissolution process on spinning and properties of lyocell fibres. *Chemical Engineering and Processing - Process Intensification*, *155*, 108063. https://doi.org/10.1016/j.cep.2020.108063

Sayyed, A. J., Mohite, L. V., Deshmukh, N. A., & Pinjari, D. V. (2020). Intensification of lyocell dissolution process and dope characteristics using pre-swelled cellulosic pulp. *Chemical Engineering and Processing - Process Intensification*, *148*, 107826. https://doi.org/10.1016/j.cep.2020.107826

Schaumann, W. (1996). Properties of Lenzing Viscose and Lenzing Modal Applied to Finishing. *Lenzinger Berichte*, *75*, 81–90.

Sen, S., Martin, J. D., & Argyropoulos, D. S. (2013). Review of cellulose non-derivatizing solvent interactions with emphasis on activity in inorganic molten salt hydrates. *ACS Sustainable Chemistry and Engineering*, *1*(8), 858–870. https://doi.org/10.1021/sc400085a

Shen, L., Worrell, E., & Patel, M. K. (2010). Environmental impact assessment of man-made cellulose fibres. *Resources, Conservation and Recycling*, *55*(2), 260–274. https://doi.org/10.1016/j.resconrec.2010.10.001

Sixta, H. (2000). Comparative evaluation of TCF bleached hardwood dissolving pulps. *Lenzinger Berichte*, *79*, 119–128.

Sixta, H. (Ed.). (2006). *Handbook of pulp* (1st ed.). Wiley-VCH Verlag GmbH & Co. KGaA.

Sixta, H., Michud, A., Hauru, L., Asaadi, S., Ma, Y., King, A. W. T., Kilpeläinen, I., & Hummel, M. (2015). Ioncell-F: A high-strength regenerated cellulose fibre. *Nordic Pulp and Paper Research Journal*, *30*(1), 43–57. https://doi.org/10.3183/npprj-2015-30-01-p043-057

Sjöström, E. (1981). Wood Polysaccharides. In *Wood Chemistry: Fundamentals and Applications* (1st ed., pp. 49–67). Academic Press, Inc.

https://www.sciencedirect.com/book/9780080925899/wood-chemistry

Stepan, A. M., Michud, A., Hellstén, S., Hummel, M., & Sixta, H. (2016). IONCELL-P&F: Pulp Fractionation and Fiber Spinning with Ionic Liquids. *Industrial and Engineering Chemistry Research*, *55*(29), 8225–8233. https://doi.org/10.1021/acs.iecr.6b00071

Strunk, P., Lindgren, Å., Eliasson, B., & Agnemo, R. (2012). Chemical changes of cellulose pulps in the processing to viscose dope. *Cellulose Chemistry and Technology*, *46* (9–10), 559–569.

Strunk, Peter, Eliasson, B., Hägglund, C., & Agnemo, R. (2011). The influence of properties in cellulose pulps on the reactivity in viscose manufacturing. *Nordic Pulp and Paper Research Journal*, *26*(1), 81–89.

Swatloski, R. P., Spear, S. K., Holbrey, J. D., & Rogers, R. D. (2002). Dissolution of Cellose with Ionic Liquids. *Journal of the American Chemical Society*, *124*(18), 4974–4975. https://doi.org/10.1021/ja025790m

Tan, Y. T., Chua, A. S. M., & Ngoh, G. C. (2020). Deep eutectic solvent for lignocellulosic biomass fractionation and the subsequent conversion to bio-based products – A review. *Bioresource Technology*, *297*(October 2019), 122522. https://doi.org/10.1016/j.biortech.2019.122522

Tan, Y. T., Ngoh, G. C., & Chua, A. S. M. (2019). Effect of functional groups in acid constituent of deep eutectic solvent for extraction of reactive lignin. *Bioresource Technology*, *281*(January), 359–366.

https://doi.org/10.1016/j.biortech.2019.02.010

Tang, X., Zuo, M., Li, Z., Liu, H., Xiong, C., Zeng, X., Sun, Y., Hu, L., Liu, S., Lei, T., & Lin, L. (2017). Green Processing of Lignocellulosic Biomass and Its Derivatives in Deep Eutectic Solvents. *ChemSusChem*, *10*(13), 2696–2706. https://doi.org/10.1002/cssc.201700457

Testova, L., Borrega, M., Tolonen, L. K., Penttilä, P. A., Serimaa, R., Larsson, P. T., & Sixta, H. (2014). Dissolving-grade birch pulps produced under various prehydrolysis intensities: quality, structure and applications. *Cellulose*, *21*(3), 2007–2021. https://doi.org/10.1007/s10570-014-0182-x

Textile Exchange. (2020). *Preferred Fiber & Materials Market Report 2020*. https://textileexchange.org/wp-content/uploads/2020/06/Textile Exchange_Preferred-Fiber-Material-Market-Report_2020.pdf%0Ahttps://textileexchange.org/2020-preferred-fiber-and-materials-market-report-pfmr-released/

Tian, C., Zheng, L., Miao, Q., Cao, C., & Ni, Y. (2014). Improving the reactivity of kraft-based dissolving pulp for viscose rayon production by mechanical treatments. *Cellulose, 21*(5), 3647–3654. https://doi.org/10.1007/s10570-014-0332-1

Treiber, E., Rehnström, J. A. C., & Kolos, F. (1962). Über eine laboratoriums- viskose-kleinstanlage zur testing von chemiefazerzellstoffen. *Das Papier*, *16*(3), 85–94.

Tu, H., Xie, K., Ying, D., Luo, L., Liu, X., Chen, F., Duan, B., Fu, Q., & Zhang, L. (2020). Green and Economical Strategy for Spinning Robust Cellulose Filaments.

ACS Sustainable Chemistry and Engineering, *8*(39), 14927–14937. https://doi.org/10.1021/acssuschemeng.0c04890

Uddin, M. N., Nayeem, J., Islam, M. S., & Jahan, M. S. (2019). Rapid determination method of dissolving pulp properties by spectroscopic data and chemometrics. *Biomass Conversion and Biorefinery*, *9*(3), 585–592. https://doi.org/10.1007/s13399-019-00383-8

Väisänen, S., Kosonen, H., Ristolainen, M., & Vuorinen, T. (2021). Cellulose dissolution in aqueous NaOH-ZnO : effect of pulp pretreatment at macro and molecular levels. *Cellulose*, *28*, 4385–4396. https://doi.org/10.1007/s10570-021-03779-w

Verma, C., Mishra, A., Chauhan, S., Verma, P., Srivastava, V., Quraishi, M. A., & Ebenso, E. E. (2019). Dissolution of cellulose in ionic liquids and their mixed cosolvents: A review. *Sustainable Chemistry and Pharmacy*, *13*, 100162. https://doi.org/10.1016/j.scp.2019.100162

Vieira, F. R., Colodette, J. L., & Andrade, M. F. (2019). Ozone application in the dissolving pulp bleaching. *Scientia Forestalis*, *47*(123), 404–420. https://doi.org/10.18671/scifor.v47n123.03

Wang, H., Gurau, G., & Rogers, R. D. (2012). Ionic liquid processing of cellulose. *Chemical Society Reviews*, *41*(4), 1519–1537. https://doi.org/10.1039/c2cs15311d

Wang, J., Wang, Y., Ma, Z., & Yan, L. (2020). Dissolution of highly molecular weight cellulose isolated from wheat straw in deep eutectic solvent of Choline/L-Lysine hydrochloride. *Green Energy and Environment*, *5*(2), 232–239. https://doi.org/10.1016/j.gee.2020.03.010

Wang, S., Lu, A., & Zhang, L. (2016). Recent advances in regenerated cellulose materials. *Progress in Polymer Science*, *53*, 169–206. https://doi.org/10.1016/j.progpolymsci.2015.07.003

Wang, X., Duan, C., Zhao, C., Meng, J., Qin, X., Xu, Y., & Ni, Y. (2018). Heteropoly acid catalytic treatment for reactivity enhancement and viscosity control of dissolving pulp. *Bioresource Technology*, *253*(December 2017), 182–187. https://doi.org/10.1016/j.biortech.2018.01.022

Wardman, R. H. (2018). Textile Fibres. In *An Introduction to Textile Coloration: Principles and Practice* (1st ed., pp. 47–105). John Wiley & Sons Ltd. https://doi.org/10.1002/9781119121619

Wawro, D., Hummel, M., Michud, A., & Sixta, H. (2014). Strong cellulosic film cast from ionic liquid solutions. *Fibres and Textiles in Eastern Europe*, *105*(3), 35–42.

Wilkes, A. G. (2001). The viscose process. In C. Woodings (Ed.), *Rege* (1st ed., pp. 37–61). Woodhead Publishing Limited.

Woodings, C. R. (1995). The development of advanced cellulosic fibres. *International Journal of Biological Macromolecules*, *17*(6), 305–309. https://doi.org/10.1016/0141-8130(96)81836-8

Wu, C.-J., Zhang, J.-C., Yu, D.-M., & Li, R.-G. (2018). Dissolving pulp from bamboo-willow. *Cellulose*, *25*(1), 777–785. https://doi.org/10.1007/s10570-017-1596-z

Wu, C., Zhou, S., Zhao, C., & Wang, D. (2014). Improved Reactivity of Bamboo Dissolving Pulp for the Viscose Process: Post-Treatment with Beating. *BioResources*, *9*(2), 3449–3455. https://doi.org/10.15376/biores.9.2.3449-3455

Xu, A., & Wang, F. (2020). Carboxylate ionic liquid solvent systems from 2006 to 2020: thermal properties and application in cellulose processing. *Green Chemistry*, *22*(22), 7622–7664. https://doi.org/10.1039/d0gc02840a

Xu, A., Wang, J., & Wang, H. (2010). Effects of anionic structure and lithium salts addition on the dissolution of cellulose in 1-butyl-3-methylimidazolium-based ionic liquid solvent systems. *Green Chemistry*, *12*(2), 268–275. https://doi.org/10.1039/b916882f

Yang, S., Yang, B., Duan, C., Fuller, D. A., Wang, X., Chowdhury, S. P., Stavik, J., Zhang, H., & Ni, Y. (2019). Applications of enzymatic technologies to the production of high-quality dissolving pulp: A review. *Bioresource Technology*, *281*(March), 440–448. https://doi.org/10.1016/j.biortech.2019.02.132

Zdanowicz, M., Wilpiszewska, K., & Spychaj, T. (2018). Deep eutectic solvents for polysaccharides processing. A review. *Carbohydrate Polymers*, *200*(July), 361–380. https://doi.org/10.1016/j.carbpol.2018.07.078

Zhang, C., Liu, R., Xiang, J., Kang, H., Liu, Z., & Huang, Y. (2014). Dissolution mechanism of cellulose in N,N-dimethylacetamide/lithium chloride: Revisiting through molecular interactions. *Journal of Physical Chemistry B*, *118*(31), 9507–9514. https://doi.org/10.1021/jp506013c

Zhang, Heng, Lang, J., Lan, P., Yang, H., Lu, J., & Wang, Z. (2020). Study on the dissolution mechanism of cellulose by ChCl-based deep eutectic solvents. *Materials*, *13*(2), 278. https://doi.org/10.3390/ma13020278

Zhang, Huiru, Zhang, H., Tong, M., Shao, H., & Hu, X. (2008). Comparison of the Structures and Properties of Lyocell Fibers from High Hemicellulose Pulp and High α-Cellulose Pulp. *Journal of Applied Polymer Science*, *107*(1), 636–641. https://doi.org/10.1002/app

Zhang, Jiaping, Tominaga, K., Yamagishi, N., & Gotoh, Y. (2020). Comparison of regenerated cellulose fibers spun from ionic liquid solutions with lyocell fiber. *Journal of Fiber Science and Technology*, *76*(8), 257–266. https://doi.org/10.2115/fiberst.2020-0029

Zhang, Jiaping, Yamagishi, N., Gotoh, Y., Potthast, A., & Rosenau, T. (2020). High performance cellulose fibers regenerated from 1-butyl-3-methylimidazolium chloride solution: Effects of viscosity and molecular weight. *Journal of Applied Polymer Science*, *137*(19), 48681. https://doi.org/10.1002/app.48681

Zhang, Jinming, Wu, J., Yu, J., Zhang, X., He, J., & Zhang, J. (2017). Application of ionic liquids for dissolving cellulose and fabricating cellulose-based materials: State of the art and future trends. *Materials Chemistry Frontiers*, *1*(7), 1273–1290. https://doi.org/10.1039/c6qm00348f

Zhang, Q., Benoit, M., De Oliveira Vigier, K., Barrault, J., & Jérôme, F. (2012). Green and inexpensive choline-derived solvents for cellulose decrystallization. *Chemistry - A European Journal*, *18*(4), 1043–1046. https://doi.org/10.1002/chem.201103271

Zhang, S., Chen, C., Duan, C., Hu, H., Li, H., Li, J., Liu, Y., Ma, X., Stavik, J., & Ni, Y. (2018). Regenerated cellulose by the Lyocell process, a brief review of the process and properties. *BioResources*, *13*(2), 4577–4592. https://doi.org/10.15376/biores.13.2.Zhang

Zhang, X., Zhao, W., Li, Y., Li, C., Yuan, Q., & Cheng, G. (2016). Synergistic effect of pretreatment with dimethyl sulfoxide and an ionic liquid on enzymatic digestibility of white poplar and pine. *RSC Advances*, *6*(67), 62278–62285. https://doi.org/10.1039/c6ra14206k

Zhao, D., Li, H., Zhang, J., Fu, L., Liu, M., Fu, J., & Ren, P. (2012). Dissolution of cellulose in phosphate-based ionic liquids. *Carbohydrate Polymers*, *87*(2), 1490–1494. https://doi.org/10.1016/j.carbpol.2011.09.045

Zhou, E., & Liu, H. (2014). A novel deep eutetic solvents synthesized by solid organic compounds and its application on dissolution for cellulose. *Asian Journal of Chemistry*, *26*(12), 3626–3630.

Zhou, L., Pan, F., Liu, Y., Kang, Z., Zeng, S., & Nie, Y. (2020). Study on the regularity of cellulose degradation in ionic liquids. *Journal of Molecular Liquids*, *308*, 113153. https://doi.org/10.1016/j.molliq.2020.113153

Zhou, S., Li, Y., Huang, L., Chen, L., & Miao, Q. (2018). Enhanced reactivity of kraft-based viscose-grade dissolving pulp by hollander beating treatment. *BioResources*, *13*(2), 2861–2870. https://doi.org/10.15376/biores.13.2.2861-2870

Zhou, S., Li, Y., Huang, L., Chen, L., Ni, Y., & Miao, Q. (2019). Ultrasonic treatment for enhancing the accessibility and reactivity of softwood rayon-grade kraft-based dissolving pulp. *Cellulose*, *26*(17), 9287–9294. https://doi.org/10.1007/s10570-019-02719-z

Zhou, Y.-K., Cao, L., & Zhang, J.-C. (2006). Discussion on the process and performance research of hemp viscose fiber. *Advanced Materials Research*, *11–12*, 529–534. https://doi.org/10.4028/www.scientific.net/amr.11-12.529

Zhu, C., Koutsomitopoulou, A. F., Eichhorn, S. J., van Duijneveldt, J. S., Richardson, R. M., Nigmatullin, R., & Potter, K. D. (2018). High Stiffness Cellulose Fibers from Low Molecular Weight Microcrystalline Cellulose Solutions Using DMSO as Co-Solvent with Ionic Liquid. *Macromolecular Materials and Engineering*, *303*(5), 1800029. https://doi.org/10.1002/mame.201800029