

UNIVERSIDAD DE CANTABRIA

PROGRAMA DE DOCTORADO EN INGENIERÍA INDUSTRIAL:
TECNOLOGÍAS DE DISEÑO Y PRODUCCIÓN INDUSTRIAL



TESIS DOCTORAL

Estudio y mejora de la reactividad de la pasta *dissolving*
orientado a la producción de fibra de viscosa

PhD Thesis

Research and improvement of reactivity of dissolving pulp
towards viscose fiber production



Carlos Arce Gutiérrez

Director: Alberto Coz Fernández

Escuela de Doctorado de la Universidad de Cantabria

Santander 2020

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Santander Noviembre 2020

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PREFACE

This Thesis is the result of a three years' work and the cooperation with a dissolving pulp mill. Additionally, to this thesis, three scientific papers were published showing the results that were obtained:

- 1 Llano T, Arce C, Ruiz G, et al. (2018) Modelling and optimization of the last two stages of an environmentally compatible TCF bleaching sequence. *BioResources* 13:6642-6662.
- 2 Arce C, Llano T, García P, Coz A (2020) Technical and environmental improvement of the bleaching sequence of dissolving pulp for fiber production. *Cellulose*. <https://doi.org/10.1007/s10570-020-03065-1>
- 3 Arce C, Llano T, González S, Coz A (2020) Use of green solvents as pre-treatment of dissolving pulp to decrease CS₂ consumption from viscose production. *Cellulose*.

The first publication was done in 2018 and published in the journal *Bioresources* which is ranked as in the second quartile (Q2) of the Journal Citation Reports (JCR) in the topic Material Science, paper & wood. The other two publications were both published in 2020, in the journal *Cellulose*, which is ranked: Q1 on the topics: Materials science, paper & wood, Materials Science, textiles and Polymer science.

To obtain the International Doctorate Mention, the author of the thesis spent three months (January-April 2018) in the Faculty of Biotechnical Systems Engineering, "Politehnica" University of Bucharest (Romania) under the supervision of Prof. Edmond Maican. This stay was done in the framework of the Cost Action FP 1306: Valorisation of lignocellulosic biomass side streams for sustainable production of chemicals, materials & fuels using low environmental impact technologies. This Cost Action granted the author a grant as part of the STSM program.

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The biggest thank to my family, especially my parents. These last years have not been the best, but the force of will and braveness they showed me during these years, have been my driving force and making me realize that everything is possible.

RESUMEN

La pasta *dissolving* es una importante fuente de celulosa que puede obtenerse a partir de la **purificación** de casi cualquier material vegetal presente en la naturaleza, eliminando la lignina y las hemicelulosas que forman parte de los mismos, ya sea de origen vegetal o arbóreo, o mediante **conversión de fábricas papeleras**.

La importancia de este material, precursor de un sinnúmero de productos, radica en la pureza en relación con el contenido en celulosa. Esta característica hace que la pasta *dissolving* sea capaz de compensar la alta demanda de celulosa que proviene directamente del algodón (fuente natural de celulosa), empleado fundamentalmente para producción de fibra textil.

Este tipo de fibra es uno de los muchos productos que se pueden obtener a partir de la pasta dissolving, pero para ello es necesario disolver este material mediante un compuesto (NMNO, ácido trifluoro acético, amoníaco, hidróxido de sodio) o proceso determinado (Lyocell, Tencel, Akzo), para luego regenerarlo en un medio adecuado (celulosa regenerada).

La fibra de viscosa (también denominada rayón) es un tipo de fibra textil que se obtiene a partir de celulosa. Además, dentro de la variedad de productos que se pueden obtener a partir de la misma, la producción de viscosa es la mayor consumidora de celulosa dissolving, es más, **el 70 % de la producción es destinada a la fabricación de esta**. Siendo China el mayor productor de fibra de viscosa con un 62% de la producción mundial.

El proceso productivo de viscosa fue patentado por primera vez a finales del siglo XIX. Consta de varias etapas que deben ser cuidadosamente controladas, ya que cualquier variación producirá cambios en el producto final. De hecho, la producción de diferentes tipos de fibras, dentro de un mismo proceso, se realizan añadiendo pequeñas modificaciones a las condiciones de operación. Las **etapas** más importantes para la producción de viscosa son: **mercerización**, la celulosa se transforma en álcali celulosa mediante tratamiento con NaOH, la **xantogenación**, en la cual la álcali celulosa reacciona con disulfuro de carbono (CS₂) para obtener el xantato de celulosa que posteriormente se transformará en viscosa, y por último **la regeneración**, la disolución de viscosa se hace pasar por un pequeño orificio y a través de un baño ácido, que hace que la viscosa se vuelva a transformar en celulosa, pero esta vez en forma de fibra.

El mayor inconveniente de este proceso de fabricación es, sobre todo, los compuestos que se emplean, especialmente el CS₂, que es un compuesto tóxico e inflamable, por ello es necesario que el uso de ese compuesto sea reducido, en la medida de lo posible.

Para la evaluación de la calidad de la pasta que será utilizada para la producción de viscosa, se emplean fundamentalmente dos métodos: la **reactividad de Fock** y **filtrabilidad China**. Ambos métodos son una reproducción a escala laboratorio del proceso de viscosa, sin embargo, el primero evalúa la cantidad de fibra regenerada y el segundo la facilidad de la viscosa para pasar a través de un tamaño de filtro determinado, medida en tiempo de filtrado. **A mayor reactividad y menor tiempo de filtrado, mejor es la calidad de la pasta.**

En cuanto a la reactividad de Fock, está directamente relacionada con la cantidad de CS₂ necesaria para disolverla, cuanto mayor es la reactividad menor será la cantidad de CS₂ necesaria para producir la viscosa. Por ello es necesario que la reactividad sea lo más alta posible, siempre y cuando no se vean comprometidas otras cualidades de la pasta, como el contenido en celulosa, la viscosidad o el contenido en lignina.

De ahí el objetivo de esta Tesis: mejorar la calidad de la pasta para que la producción de viscosa, a partir de la misma, sea más compatible con el medio ambiente. Para ello se evaluará, por un lado, **modificar el proceso de blanqueo** y, por otro, **añadir un pre-tratamiento** de la pasta para aumentar la reactividad.

ABSTRACT

Dissolving pulp is a significant cellulose source and can be obtained from the **purification** of nearly any lignocellulosic material present in nature, removing lignin and hemicelluloses that conform them, either vegetal or tree, or by **conversion of paper mills**.

The importance of this material, from which many products can be manufactured, is based on cellulose purity. This characteristic makes dissolving pulp able to compensate the cellulose gap that comes mainly from cotton (natural source of cellulose), used mainly to produce textile fibers.

This kind of fiber es one of many products that can be obtained from dissolving pulp, but for that to happen, pulps needs to be dissolved first either employing certain compounds (NMMO, trifluoroacetic acid, ammonia, sodium hydroxide) or a specific process (Lyocell, Tencell, Akzo) and then regenerated using an adequate medium (regenerated cellulose).

Viscose fibers (also known as Rayon) is a kind of textile fiber that is obtained from cellulose. Furthermore, among the variety of products that can be obtained from it, the production of viscose is the biggest dissolving pulp consumer in the world, in fact, **70 % of dissolving pulp produced is used for viscose production**, being China the biggest viscose producer, with a 62 % of global production.

The viscose process was firstly patented in the late 19th century. It involves several stages that must be carefully controlled because the smallest variation will make the final product characteristics to change. In fact, the production of different qualities, within the same process, is done by small changes in the process. The most **critical stages** of the process are: **mercerization**, cellulose is stepped in sodium hydroxide to be transformed into alkali cellulose; **xanthation**, alkali cellulose reacts with carbon disulfide (CS₂) to obtain cellulose xanthate that will be later be transformed into viscose, and **regeneration**, viscose solution is pushed through small holes and through an acid bath, that makes viscose to transformed back into cellulose, but fiber-shaped.

The biggest drawback of this process is, above all, the reactants that are used, especially CS₂, that is toxic and flammable; therefore, its use should be reduced.

To assess pulp quality to be used for viscose production, two methods are mainly used: **Fock's reactivity and Chinese filterability**. Both methods are a microscale viscose process, however, the first measures the number of regenerated fibers that can be obtained and the second one the ease of viscose solution to pass through a particular filter, measured as effusion time. **The higher the reactivity and the lower the filtration time, the better the pulp quality.**

Regarding Fock's reactivity, it is directly related to the quantity of CS₂ need for it to be dissolved, the higher the reactivity, the lower the quantity of CS₂ needed. For this reason, it is a need that cellulose pulp has the highest reactivity possible, but without compromising other pulp quality parameters, such as cellulose content, viscosity or lignin content.

As a result, the objective of this thesis would be to improve the quality of pulp for viscose production, to make it more environmentally friendlier, using either **modifying the bleaching process**, before the final product, or **add a pre-treatment** in the final stage to increase pulp reactivity.

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ABBREVIATIONS

List of abbreviations

$[\eta]$	Intrinsic viscosity of pulp
AS	Acid Sulfit
ADT	Air Dried Ton
c_1	concentration of $K_2Cr_2O_7$ used in Fock's analysis
c_2	concentration of $Na_2S_2O_3$ used in Fock's analysis
CA	Cellulose acetate
ChCl	Chlorine Chloride
C_{NaOH}^{EOP}	Dosage of NaOH in the EOP stage
C_{NaOH}^{PO}	Dosage of NaOH in the PO stage
$C_{H_2O_2}^{EOP}$	Dosage of H_2O_2 in the EOP stage
$C_{H_2O_2}^{PO}$	Dosage of H_2O_2 in the PO stage
$Cost_{energy}^{EOP}$	Energy-derived costs from the EOP stage
$Cost_{energy}^{PO}$	Energy-derived costs from PO stage
$Cost_{H_2O_2}^{EOP}$	H_2O_2 -derived costs from the EOP stage
$Cost_{H_2O_2}^{PO}$	H_2O_2 -derived costs from PO stage
$Cost_{NaOH}^{EOP}$	NaOH-derived costs from the EOP stage
$Cost_{NaOH}^{PO}$	NaOH-derived costs from PO stage
$Cost_{O_2}^{EOP}$	O_2 -derived costs from the EOP stage
$Cost_{O_2}^{PO}$	O_2 -derived costs from PO stage
CrI	Crystallinity Index
DES	Deep Eutectic Solvents
EC	Elemental Chlorine

ECF	Elemental Chlorine Free
EOP	Alkali Extraction
h	Constant of viscosimeter
I_{200}	Intensity of signal in XRD at 22°
I_{18}	Intensity of signal in XRD at 18°
LA	Lactic Acid
M	molecular weight of a glucose unit
m	oven dried weight of pulp sample
MA	Malic Acid
MFC	Microfibrillated cellulose
MWD	Molecular Weight Distribution
NC	Nitrocellulose
NCC	Nanocrystalline cellulose
NFC	Nanofibrillated cellulose
o.d.	Oven dried
ODT	Oven Dried Ton
OxA	Oxalic Acid
PO	Peroxide Delignification
PHK	Pre-hydrolysis kraft
RCF	Ratio of CS_2 consumption per quantity of fibers
T	Temperature of solution for kappa analysis
T	Normality of the $Na_2S_2O_4$ used in kappa analysis
t_v	Effusion time
T^{EOP}	Temperature in the EOP stage
T^{PO}	Temperature in the PO stage
t_R^{EOP}	Residence time in the EOP stage

t_R^{PO}	Residence time in the PO stage
TF	Theoretical quantity of fibers
TCF	Totally Chlorine Free
Ur	Urea
V	Volume of $Na_2S_2O_4$ in blank kappa analysis
V'	Volume of $Na_2S_2O_4$ in kappa analysis
v_1	Volume of $K_2Cr_2O_7$ used in Fock's analysis
v_2	Volume of $Na_2S_2O_3$ used in Fock's analysis
XRD	X-ray Diffraction

1. Introduction

1.1. Cellulose morphology

Cellulose is the most abundant natural polymer on earth. It is the main component of plant cell walls, and it is formed by units of glucose (Wada et al. 2010) linked together by β -(1 \rightarrow 4) glycosidic bonds between the C1 and C4 of adjacent glucose units $(C_6H_{10}O_5)_n$ where n can have values from 10000 to 15000 depending on the nature of the source material (Moon et al. 2011). Due to the interaction between hydroxyl ends of the molecule, hydrogen-bond interaction occurs, and these chains can be packed as a result (Kuang et al. 2020). Figure 1 shows the molecular structure of cellulose.

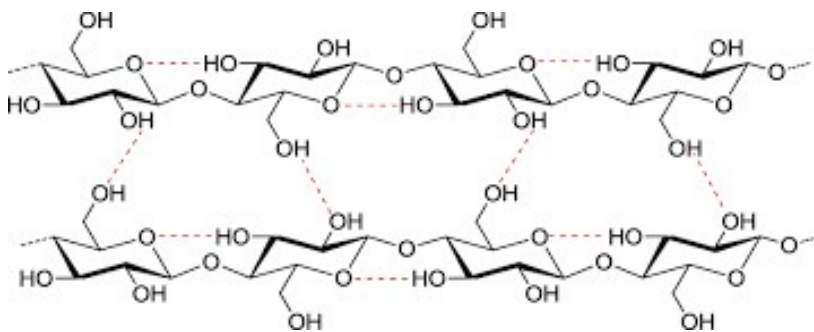


Figure 1 Structure of the cellulose molecule with intra and intermolecular bonds (Li and Liu 2015)

These hydrogen-bond interactions between the hydroxyl groups of cellulose make cellulose chain to arrange in a crystalline-like structure (Trache et al. 2017). However, there are also parts of the cellulose chain that cannot be ordered in this crystalline structure, and as a result, non-ordered segments exist as well, linked to the cellulose crystals, classified as amorphous cellulose.

Depending on how the molecules are oriented and the hydrogen-bond network, cellulose can have different allomorphs classified as cellulose I, II, III and IV (Xing et al. 2020).

Cellulose I is also called native or natural cellulose and is the result of the formation of cellulose within the plants and algae, without any processing. This allomorph is not as stable as cellulose II, and it can be converted into

cellulose II or III (Moon et al. 2011). This type of cellulose also has two types of allomorphs: I α and I β (Langan et al. 2001). The major difference between them is the source and the lattice system. I α is not as common as I β and only exists in combination with I β in some green algae, on the other hand, I β exists, mostly pure, in every plant or algae (Wada et al. 2010). Regarding the lattice system, cellulose I α has a triclinic structure, and cellulose I β has a monoclinic structure. The microfibrils in cellulose I are oriented in a parallel formation (Wu et al. 2020).

As it was stated before, cellulose II can be obtained from cellulose I by mercerization, intracrystalline swelling of cellulose by concentrated sodium hydroxide solution, or regeneration, dissolution of cellulose in a determine media and then coagulation and recrystallization (Langan et al. 2001). The change from cellulose I to cellulose II is irreversible; therefore, it can be concluded that cellulose II allomorph is more stable than cellulose I In this type of allomorph, the microfibrils are aggregated in an antiparallel formation (Köpcke 2008).

Cellulose III can be obtained from the treatment of both cellulose I and II with ammonia or amines, obtaining what is known by cellulose III₁ and cellulose III₂, respectively, this change is reversible. If both allomorphs of cellulose III are subjected to a heat treatment, they are converted into cellulose IV₁ and cellulose IV₂ (Zugenmaier 2001). Figure 2 shows the schematic changes of the different allomorphs of cellulose. It should be noted that there are no differences between cellulose I α and cellulose I β since the latter is the major allomorph of cellulose I.

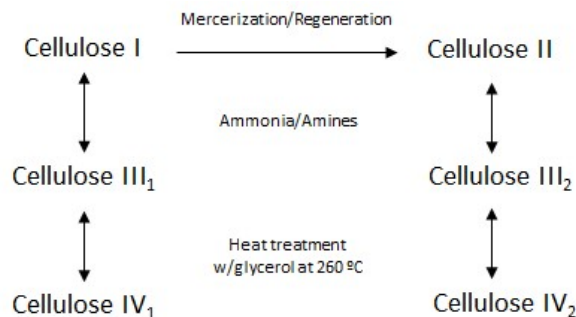


Figure 2 Schematic reaction path between cellulose allomorphs

1.2. Cellulose end-use products

Depending on the cellulose structure, it can be transformed into a wide variety of materials by altering the hydroxyl groups available in the glucose unit (Strunk 2012) or regenerating dissolved cellulose. These cellulose-based products are also called cellulose derivatives. The main sources of cellulose are cotton linters when cellulose purity is a must, and dissolving pulp. However, dissolving pulp is mainly used nowadays, for its availability. Regarding the production of these derivatives, they can be classified as: Ethers, nitrates, acetates and xanthates. The main characteristics of these derivatives will be shown next.

Dissolving pulp and cotton linters are the main sources of cellulose

1.2.1. Cellulose ethers

Cellulose ethers production is increasing, even though there are a wide variety of cellulose derivatives available, due to their availability, efficiency, processability and different types (Bhatt et al. 2011). Cellulose ethers can be used in whole different areas: Pharmacy, cosmetics, food, paint, textiles, construction and adhesives (Tosh 2014). The main reaction pathway, with commercial relevance, of these derivatives is the Williamson ether synthesis. In this type of reaction, cellulose is transformed into alkali-cellulose first and then reacts with an alkyl chloride (Granström 2009). Among all the possible cellulose ethers, three are the most industrially produced: Carboxymethylcellulose, methylcellulose and hydroxyethylcellulose (Klemm et al. 1998).

1.2.2. Cellulose nitrate

Cellulose nitrate, also commonly known as nitrocellulose (NC) is the first cellulose derivative obtained, synthesized in 1832 by Braconnot (Trache et al. 2016). This cellulose derivative is a type of cellulose ester, produced by the reaction of pure cellulose (either from cotton or high purity dissolving pulp) with a nitrating agent (a mixture of HNO_3 and H_2SO_4) (Klemm et al. 1998). It should be noted that cellulose nitrate application depends on the quantity of nitrogen if nitrogen content is below 12.5 %, applications are coatings, lacquers, inks and adhesives, whereas is higher than 12.5 %, is mostly used as propellant, fireworks, explosives and gas generator (Trache et al. 2016). Figure 3 shows the chemical structure of nitrocellulose.

However, due to its characteristics such as high impact sensitivity, poor chemical stability, flammability and explosive hazards (Chai et al. 2019), NC needs to be used with chemical stabilizers that hinders the decomposition products from the degradation of NC produced during storage (Fryš et al. 2011).

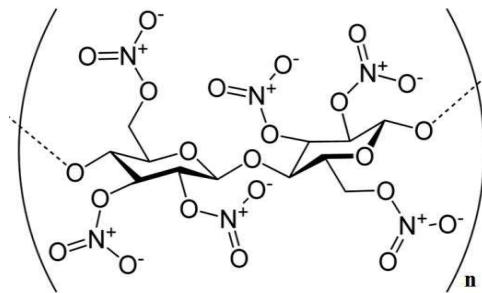


Figure 3 Chemical structure of nitrocellulose (Varis 2015)

1.2.3. Cellulose acetates

Cellulose acetates (CA) are industrially produced by making cellulose react with an excess of acetic anhydride catalyzed by sulfuric or perchloric acid (Lewin 2006) in a two-step process of acetylation, followed by hydrolysis (Wan Daud and Djuned 2015). As well as NC, CA are a type of cellulose ester; however, CA has lower flammability (Candido et al. 2017). Depending on the degree of substitution of the hydroxyl groups, cellulose acetates can be classified as diacetates (two hydroxyl groups per glucose unit) or tri acetates (three hydroxyl groups per glucose unit). The CA mostly used is diacetate or secondary acetate because it can be dissolved in acetone for further processing (Sun et al. 2013), when compared with triacetates, because of their limited solubility, commercial applications for this CA have not been found or studied (Cao et al. 2007). CA can be used in several fields such as: cigarette filters, textiles, camera films, surface coatings and inks (Cheng et al. 2010). Figure 4 shows the structure of cellulose acetate, more specifically, cellulose diacetate.

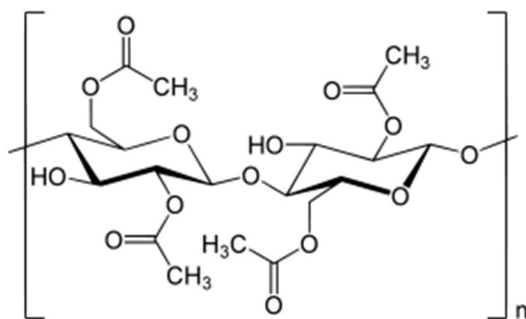


Figure 4 Chemical structure of cellulose diacetate

1.2.4. Cellulose xanthate

To form this cellulose derivative, dissolving pulp or high purity cellulose substrate is first treated with sodium hydroxide (mercerization), to produce alkali cellulose and then carbon disulfide (CS_2) is introduced to form the xanthate (Östberg 2012). This cellulose derivative is used mostly to form viscose fibers, also called rayon. The first commercial production of viscose fibers was achieved by Count Hilaire de Bernigaud de Chardonnet (Lewin 2006). Even though CS_2 is a hazardous component, rayon technology has not changed since it was first used in late 19th century; therefore research has focused on reducing the usage of this chemical in this technology or the development of new fiber spinning techniques such as Lyocell (Rosenau et al. 2001) or Ioncell process (Sixta et al. 2015).

CS_2 is a hazardous component; however, rayon technology has not changed since it was first used in the late 19th century

Even though xanthate is mostly used for viscose production (not as a derivative but as an intermediate), recent studies have used it for the detection of metal ions, by the ability of xanthate groups to form coloured complexes (Greis et al. 2019) and combined with cellulose carbamate to form cellulose films and possibly shed some light on cellulose-cellulose interactions (Weißl et al. 2019). Figure 5 shows the reactions involved in rayon production.

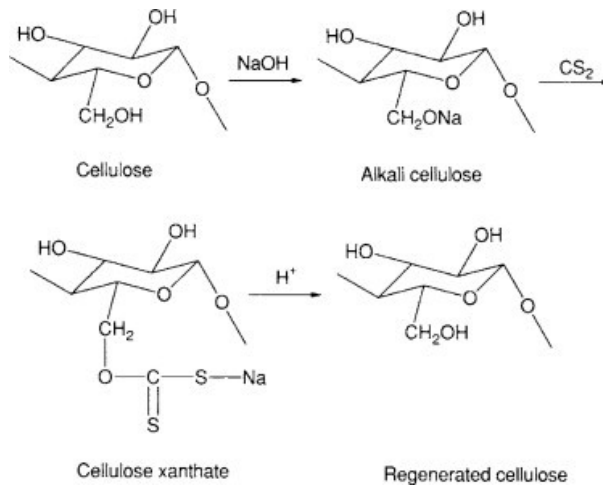


Figure 5 Reactions involved in the production of rayon

1.2.5. Other cellulose derivatives

Other cellulose derivatives are produced from cellulose, but their production is not as high as the ones presented before. They are produced either by derivatization of cellulose with other chemicals: cuprammonium (Sayyed et al. 2019), NMMO to produce lyocell fibers (Sayyed et al. 2018), LiCl/DMAc (*N,N*-dimethylacetamide) (Medronho and Lindman 2014) or by other treatments that include a combination of chemical and mechanical treatment: microfibrillated cellulose (MFC) or nano fibrillated cellulose (NFC) (Kumar et al. 2020; Oh et al. 2020; Singh et al. 2020) or just mechanical treatment (grinding) (Alotabi et al. 2020; Shao et al. 2020).

Cellulose ethers, cellulose nitrates, cellulose acetates and viscose, are the most produced end-use products from dissolving pulp. In fact, they accounted the 97.00 % of cellulose derivatives in the world, and 97.68 % in China. With viscose, being the most produced from dissolving pulp, 63.00 % of dissolving pulp was used to produce viscose worldwide, and 91.32 % in China (Liu et al. 2016).

Viscose is the most produced end-product from dissolving pulp with a 63 % of the total dissolving pulp worldwide and 91 % in China

1.3. Dissolving pulp production processes

Traditionally, pure cellulose was obtained from cotton linters; however, due to the increase of cellulose demand, new sources of cellulose needed to be found. Therefore, dissolving pulp became the most important alternative to compensate this gap and meet the requirements of cellulose demand (Chen et al. 2016). Dissolving pulp is a high-grade cellulose pulp (90 % to 98 % α -cellulose content), with low contents of hemicellulose, lignin and resin, and can achieve very high brightness (> 90 % ISO). The raw material used to obtain dissolving pulp is mainly woody lignocellulosic material; either softwood or hardwood (Chen et al. 2016), in fact about 85% is produced from this raw material (Li et al. 2018a). There are several **processes to obtain dissolving pulp**: Acid sulfite (AS), pre-hydrolysis kraft (PHK), SO₂-ethanol-water process (Iakovlev et al. 2011; Yamamoto et al. 2014; Yadollahi et al. 2018), pre-hydrolysis soda-anthraquinone (Sixta and Schild 2009) or by even purification of paper grade pulp (Duan et al. 2017), however, two of them, **AS and PHK, are the most used** (Sixta et al. 2013) and will be the ones explained in this thesis.

1.3.1. Acid sulfite (AS)

This process was first patented in 1867 by Benjamin Chew (Sixta 2006), who used aqueous solutions of calcium hydrogen sulfite and sulfur dioxide in pressurized reactors. This process has maintained practically unchanged through the years (Sixta et al. 2013), the main change in the process is the use of different chemicals, i.e. the cation employed. Initially, calcium was used; however, several drawbacks appeared over time, mainly the formation of calcium sulfite and its low solubility. Therefore, the principal cation employed in the production of dissolving pulp nowadays is magnesium (Sixta 2006; Strunk 2012).

Regarding the raw material, AS process can only be used with some hardwoods because some of the components of wood (pine or larch) can lead to condensed structures or decrease the stability of the chemicals (Chen et al. 2016). This process involves several steps. Initially, wood is debarked, and size is reduced mechanically into chips. The reactor is then loaded with the chips, and after that, cooking liquor is charge as well. Impregnation step comes next, so the reactants can reach the pores present in the wood by maintaining a constant pressure. Then before SO₂ dosage, excess liquor is withdrawn to maintain a constant liquid to solid ratio. Then the temperature is increased at a constant rate until the desired value reached, and it is maintained at a

constant value (140 °C) for about 4 hours. Finally, the reactor pressure is relieved, and liquor is displaced so the pulp can be discharged from the reactor. In this process, the non-desirable compounds of wood are removed from the raw material and dissolved in the liquor. These compounds, mainly lignin derivatives, can be converted into value-added compounds (Magdzinski 2006).

Composition of dissolving pulp is an important parameter to be accounted for since hemicelluloses can lead to undesirable effects in the subsequent processes it might be involved into, i.e. low filterability of viscose or incomplete reactions (Ibarra et al. 2010b), so α -cellulose content in AS dissolving pulp ranges between 92 % and 94 %, for a typical rayon grade dissolving pulp. Pulp viscosity is another critical property for dissolving pulp processing. Usually, it should be between 400 and 600 mL/g (Duan et al. 2015) because low viscosity value may cause filtration problems and high viscosity reduces the yield, both cases when dissolving pulp needs to be further processed. Viscosity is related to the molecular weight distribution (MWD); generally, MWD should be as narrow as possible. AS process gives a high MWD dissolving pulp, this is produced by the acid hydrolysis non-uniform reactions that take place in the process. As a result, AS dissolving pulp has a high amount of short-chain cellulose. All pulp properties will be further discussed in other sections of the thesis.

1.3.2. Pre-Hydrolysis Kraft (PHK)

In contrast with AS, Kraft process uses alkaline liquor, formed by sodium hydroxide and sodium sulfide, to eliminate lignin and hemicellulose. Although Kraft pulp is the most used process to produce pulp, this pulp is not suitable to be called dissolving pulp, since alkaline conditions cannot remove short-chain hemicelluloses and as a result of only a 86 % α -cellulose content can be achieved (Sixta 2006). Therefore, a pre-hydrolysis stage needs to be added (PHK). This pre-treatment is performed usually with water at 160 °C or 180 °C. As a result, acetic acid is formed, and at this pH (3-4) hemicellulose are solubilized and thus eliminated from wood. Then, the wood chips and the cooking liquor, are added to the reactor, and the cooking is carried out at temperatures between 140 and 175 °C. After cooking, wood hemicelluloses are eliminated, and hydrolysis of cellulose also occurs (Lahnammi et al. 2018). It should be noted that the main advantage of PHK process is that almost any kind of wood or lignocellulosic material can be used (Strunk 2012). Regarding pulp properties, PHK dissolving pulps can achieve α -cellulose content from 94 to 96 % (Li et al. 2015), since alkali reactions leave the primary

wall of the pulp fibers almost intact (Duan et al. 2015). MWD of PHK dissolving pulp is more uniform when compared with AS dissolving pulp, as a result of the swelling of the fibers when alkali liquor is used; thus a uniform reaction is produced (Duan et al. 2015).

Several processes can be used to produce dissolving pulp; however the most used are acid sulfite and pre-hydrolysis kraft

1.3.3. Bleaching process

In order to obtain a high-quality dissolving pulp to be used to produce viscose fiber and others, the pulp needs to be purified. After its production, the pulp is sent then through the bleaching process, which objective is not only to increase brightness but also to increase purity, removing lignin and hemicelluloses, adjusting the viscosity and molecular weight distribution of the cellulose (Liu et al. 2016). Such improvements on pulp quality allow it to meet the requirements of end-use products such as viscose, acetates, cellulose nitrate or cellulose ether.

The bleaching process increases the environmental impact of pulp mills. The quantity of chemicals employed in this part is very high. Most of the organic load, coming from the elimination of residual lignin and hemicelluloses, is generated in this process. Additionally, water demand is the highest of the pulp mill since pulp needs to be washed to eliminate excess chemicals. Depending on the reactants employed, bleaching sequences can be classified as: elemental chlorine (EC) (Tripathi et al. 2019); elemental chlorine free (ECF) (Jour et al. 2015; Kaur et al. 2017) and totally chlorine free (TCF) (Bahrami et al. 2018; Li et al. 2018b).

EC bleaching uses chlorine-based compounds to perform the purification process (Sixta, 2006). Despite the advantages of these compounds, such as selectivity towards lignin elimination and low cost, they contribute to the formation of halides, which has a negative impact on the environment. Therefore, research on **alternative bleaching sequences started to gain attention** and, as a result, chlorine-based sequences began to be replaced by oxygen-based sequences. The main alternatives developed were **ECF and TCF bleaching sequences**. On the one hand, ECF technology replaces Cl_2 by other compounds that are not as harmful; however it still uses ClO_2 as the main bleaching agent, research of this kind of technology focuses on reducing the quantity of this compound using additional treatments (Loureiro et al. 2010; Huang et al. 2012; Salazar et al. 2012). On the other hand, TCF bleaching replaces all chlorine-based compounds with oxygen-based ones such as:

Ozone, oxygen, sodium hydroxide and oxygen peroxide. The main advantage of TCF sequences is that they have a lower environmental impact than ECF or EC sequences; however, one disadvantage is that selectivity towards impurities is not as high as ECF or EC (Shatalov and Pereira 2008).

The bleaching process increases the environmental impact of pulp mills. Totally chlorine free bleaching is a good alternative with a lower impact; however, the selectivity of the process is also lower

PHK dissolving pulp provided 56 % of dissolving pulp production and AS process the 42 % of dissolving pulp production (Sixta et al. 2013). Pulp production by the processes mentioned before accounted for 85 % all over the world (Chen et al. 2019), the rest was produced by cotton linters. With China being the biggest consumer of dissolving pulp. Even though, more than 50 % of the dissolving pulp used in China is imported it is estimated that dissolving pulp production in this country will increase by 700,000 to 1,000,000 tons/year, in the following years (Chen et al. 2019).

1.4. Dissolving pulp quality parameters

Pulp quality parameters refer to the requirements dissolving pulp must meet, depending on the end-use product. These properties may be different depending on the type of raw material employed (cotton linter or wood) or the type of wood (hardwood or softwood).

1.4.1. α -cellulose content

α -cellulose content refers to the fraction of cellulose that is not degraded. For dissolving pulp quality, without considering the type of wood or the end-use product, should be higher than 90 %. There are other fractions of cellulose called β and γ cellulose; these fractions correspond to degraded cellulose and hemicelluloses, respectively. For viscose purposes, this parameter should range between 90 and 94.5 %, according to the Chinese standard FZ/T 51001-2009. For other applications, such as cellulose acetates or ether, α -cellulose content should be higher (Strunk 2012).

1.4.2. Lignin content

Lignin is present in every lignocellulosic material and needs to be eliminated in the cooking and bleaching processes. It is a complex phenolic polymer and is the most abundant polymeric organic substance in plants, after cellulose (Sixta 2006). Its presence in wood varies from 25 % to 31 % in softwood and from 16 % to 24 % in hardwood (Heinze and Liebert 2001).

1.4.3. *Pentosan content*

Pentosan is a heteropolysaccharide formed by pentoses present in dissolving pulp. It needs to be as low as possible since its presence may cause yield reduction in further processes. According to the Chinese standard FZ/T 51001-2009, pentosan content needs to be between 3 and 4 %, for viscose purposes. For another application, pentosan content should even be lower, especially for cellulose acetate production, which should be 0.9 for PHK from softwood and 0.2 for cotton linters (Strunk 2012).

1.4.4. *Viscosity*

Pulp viscosity in pulp is calculated by the increase of viscosity, of a suitable solvent, when the pulp is dissolved in it, and it is mainly influenced by the presence of cellulose (Sixta 2006). This parameter is related to the degree of polymerization of cellulose (Borrega et al. 2018), which is essential to determine the suitability of dissolving pulp to be further processed. As it was stated before, viscosity needs to be between 400 and 600 mg/L.

1.4.5. *Brightness*

For dissolving pulp, this parameter should be very high (>90 % ISO). When cotton linters are used as a cellulose source, brightness can have lower values (87.9 %). Chinese standard FZ/T 51001-2009, states that for second-grade viscose hardwood dissolving pulp brightness can be 82 %.

Dissolving pulp parameters determine which end-use product can be obtained. Therefore, these and other parameters of pulp need to be controlled through the process and in the final product stage. In order to predict the values of the pulp quality parameter through the process, this thesis focuses on the improvement of the properties of dissolving pulp from an acid sulfite process and how they vary through the different stages of the bleaching process when operating conditions are modified. Additionally, a final product pre-treatment, prior to its transformation into viscose, is also assessed.

Dissolving pulp parameters determine which end-use product can be obtained. Therefore, control of these and other parameters of pulp need to be controlled through the process and in the final product stage

2. Objective and hypothesis

The research work presented in this thesis has been carried out at the Chemistry and Process & Resource Engineering Department from the University of Cantabria, more specifically at the Green Engineering & Resource (GER) group (www.geruc.es). In addition, the framework of the thesis is within a sulfite pulp mill located in Cantabria, Sniace S.A. Additionally, a 3-month stay at the Universitate Politehnica Din Bucuresti, Faculty of Biotechnical Systems Engineering, is included in the thesis, under the FP 1306 Cost Action, by means of a Short-Term Scientific Mission (STSM) grant under the supervision of Prof. Edmond Maican.

The thesis hypothesises that pulp quality parameters can be controlled, predicted and upgraded, through the bleaching process and other novel processes, to tune in dissolving pulp properties and choose the suitable end-use product. Studying the operational conditions of the industrial bleaching process and understanding how these changes affect the quality of pulp, it can be helpful for the studied pulp mill in order to increase the possibilities of the final dissolving pulp to be used in different applications and also reducing energy and chemical consumption. In addition, other novel processes can be studied as pre-treatment prior to the viscose production to decrease the use of CS₂ in the process.

To achieve the main objective explained before, the next partial objectives have been completed:

- **State of the art** of different dissolving pulp end-use products, for the development of a mathematical model of the bleaching stage. The main end-use products studied were used to fix the characteristics of dissolving pulp.
- Further study of the **bleaching process**, focused on specific pulp parameters for viscose production, to obtain recommendations of operating conditions to modify the bleaching process.
- Study of the different of **dissolving pulp treatments prior to viscose** production to enhance specific pulp quality parameters, without compromising the others.
- Assessment of the chosen pretreatment using Deep Eutectic Solvents to reduce the use of CS₂ and NaOH in the viscose process.

3. Methodology

In this chapter of the thesis, the experimentation carried on will be explained. Figure 6 is a general flow diagram to show the main steps taken while doing the research. This research was organized in 3 main blocks.

The **first block** included all the steps to obtain the optimization of the bleaching process. Initially, a factorial experimental design is performed, employing the software Statgraphics Centurion XII.II, to configure the experimental procedure and include all the experiments needed to obtain the mathematical model. After all the experiment and analyses are done, it is possible to obtain a mathematical model that helps to predict how changes on the operational variables affect pulp properties. When the equations of the mathematical model are obtained, it needs to be validated with additional data, and if the model fits adequately, optimization of the process can be done.

The **second block** focuses on increasing the possibilities for viscose production. Bleaching step adjusts pulp quality parameters so it can be used to produce the desired end-use product. Since viscose production is the industry that uses most of the dissolving pulp, bleaching experiments were performed, focused on obtaining the best quality dissolving pulp to be transformed into viscose and make viscose process environmentally friendlier.

Finally, the **third block** focuses on pre-treatments that improves dissolving pulp quality parameters for viscose purposes and the possible use of DES as a pretreatment to increase the reactivity of dissolving pulp to produce viscose.

In addition, all of the processes related to the bleaching steps have been added in blue, quality parameters of the pulp have been added in red and other specific properties of the processes, depending on the step, have also been added in orange. In the end, the tasks related to the pre-treatments, especially the use of novel and greener solvents have been added in green.

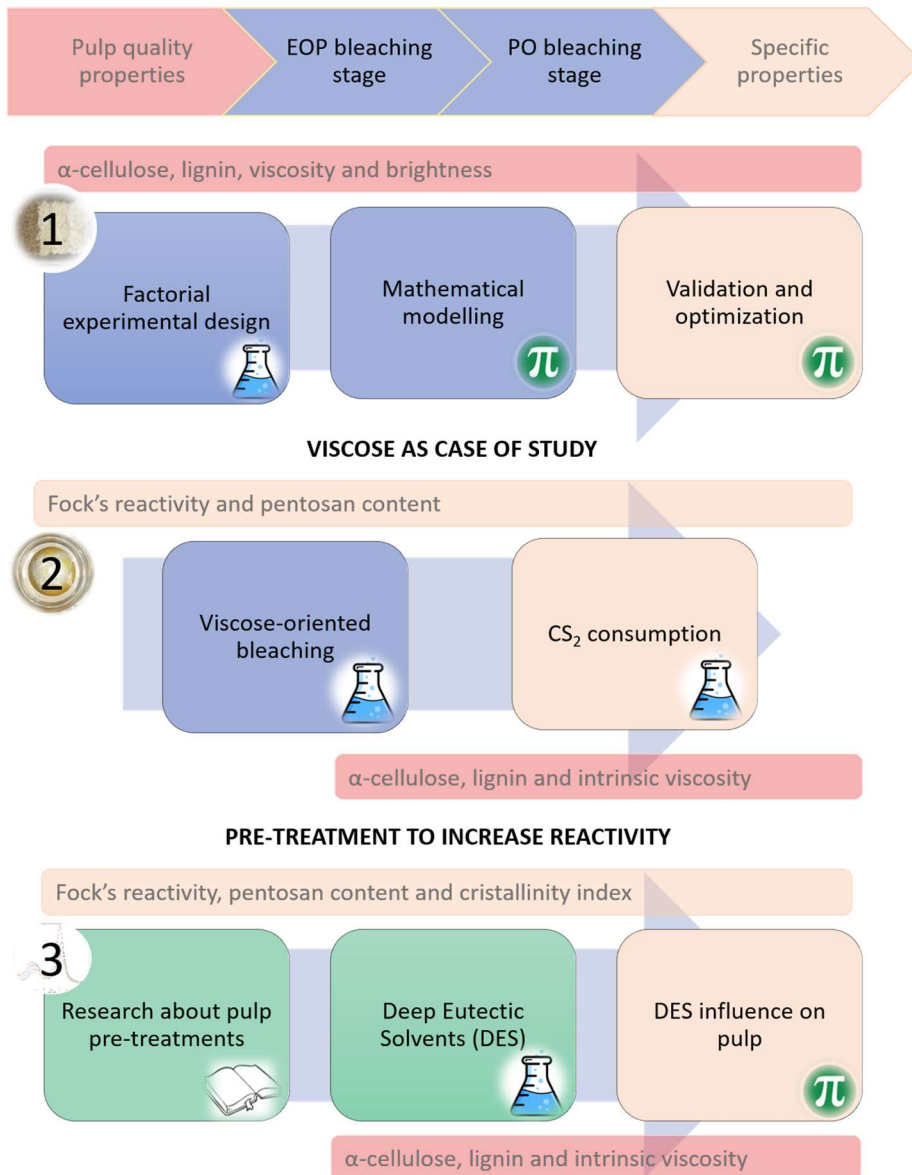


Figure 6 Flow diagram of the main steps

3.1. Bleaching Optimization

This section will show the steps taken to obtain the mathematical model and optimization of the bleaching process, through experiments at a lab scale. Figure 7 shows the main steps followed.

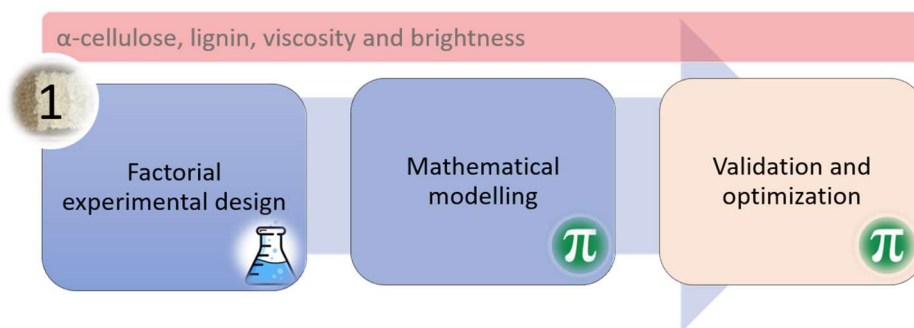


Figure 7 Main steps followed for the optimization

3.1.1. Experimental design

Dissolving pulp is an intermediate product and is further used to obtain value-added products so that additional information would be needed. Therefore, other experiments were performed to obtain a mathematical model focused on some of the end-use products mentioned previously. To obtain a mathematical modelling, the experiments carried out need to meet specific requirements. As a result, a design of experiments needs to be carried out by using Statgraphics Centurion XII software.

The experimental design helped to organize and cover all the combinations of the independent variables chosen. The two stages of the bleaching process studied were EOP and PO.

The chosen independent variables of the experimental design were the operating conditions used in the bleaching process: NaOH dosage, H_2O_2 dosage, time, and temperature. The values of the variables were configured in accordance to a statistically-design three-level, four-factor factorial experimental design and were evaluated at three levels: low (-1), medium (0) and high (+1). Values for each independent variable were given and assigned to the levels. The lowest value was assigned a (-1), the intermediate (0) and the highest (+1). The dependent variables were the pulp quality parameters (α -cellulose, kappa number, intrinsic viscosity, and brightness). The number of experiments, n , needed to cover all the combinations is obtained by Equation 1.

$$n=2^{(k-p)}+2\cdot k+n_c \quad (1)$$

Where k is the number of variables considered and equal to 4, p is a constant value that depends on the number of variables, and it is equal to 0 if $k < 5$ or 1 if $k > 5$ and n_c is the number of central points considered which is equal to 1. As a result of applying Equation 1, the total number of experiments should be 25, for each stage. The values for the independent variables of the first set of experiments are shown in Table 1.

Table 1 Codification for the independent variables in each stage of the bleaching process for the first set of experiments

Normalized value of the EOP stage	-1	0	1
NaOH (kg/ADT)	20	40	60
H ₂ O ₂ kg/ADT)	0	20	40
Time (min)	60	120	180
Temperature (°C)	90	115	140
Normalized value of the PO stage	-1	0	1
NaOH (kg/ADT)	0	30	60
H ₂ O ₂ kg/ADT)	20	40	60
Time (min)	60	120	180
Temperature (°C)	80	110	140

Conditions tested with the experimental design for the EOP stage were: 5, 10, 20, 30, 40, and 60 sodium hydroxide (NaOH) dosage expressed as kg/air-dried tonne (ADT); reaction times of 15, 30, 60, 90, 120 and 180 min; reaction temperatures of 80, 90, 120, 130 and 140 °C; and hydrogen peroxide (H₂O₂) dosages of 0, 5, 10, 15, 20 and 40 kg/ADT.

In the case of PO stage, the conditions tested were: 5, 10, 30, 40 and 60 NaOH dosage expressed as kg/ADT; reaction times of 30, 60, 90, 120, 150 and 180 min; reaction temperatures of 80, 100, 110, 120, 130 and 140 °C; and H₂O₂ dosages of 5, 10, 20, 30, 40 and 60 kg/ADT.

3.1.2. Bleaching procedure

Bleaching procedure was performed as propose by Llano et al. (2018). The pulp used in EOP and PO experiments were carried out in 1 L stainless steel vessels. EOP uses NaOH as the main bleaching compound, boosted by the addition of H₂O₂ and PO, uses H₂O₂ as the main bleaching agent, coupled with the addition of NaOH, both stages are pressurized with oxygen. Inlet pulp was

washed with tap water until the wastewater pH was 7. Pulp was then hand dried and kept in the refrigerator to avoid any further degradation (Yaqoob et al. 2010). Firstly, the moisture content of the pulp is measured and then 300 g of pulp, calculated as oven-dried (o.d.), is weighed. Then hot water, between 65-70 °C, is added to the pulp to obtain a moisture content of 11 %. Finally, the reactants are added; the quantity depends on the experiment carried out. The vessel is then pressurized with oxygen at 1.65 bar (EOP stage) and 2.5 bar (PO stage). When the reaction finishes, the pulp is retrieved from the reactor and washed until the pH of the washing wastewater is 7.

3.1.3. Pulp analyses

Pulp was analyzed before and after the bleaching experiments, in order to have an inlet value of the pulp and see the changes that the experiment produced on it. Figure 8 shows images of different analyses.



Figure 8 Images from the different analyses

- Sample preparation

Before making any analysis, the pulp handsheets were prepared as described in TAPPI T205 sp-02 (2002). Cellulose pulp was disintegrated in a rotary stirrer to homogenize the sample, filtered with a Büchner funnel and oven-dried at 105 °C. Afterwards, pulp handsheets were left to get moisture equilibrium in the air atmosphere.

- Intrinsic Viscosity

Intrinsic viscosity was determined by the standard ISO 5351(2010). 0.25 g. oven-dried pulp was dissolved in 25mL of cupriethyldiamine solution and 25 mL of UP water for half an hour. The mass of the sample depends on the viscosity value predicted. Since the pulp used in the experiments comes from the bleaching stage, viscosity values are assumed to be between 650 and 400 mL/g. Table 2 shows the ranges of viscosity and mass sample.

Table 2 Viscosity and mass ranges considered in the analysis

Viscosity (mL/g)	Mass sample (mg/50 mL)	Concentration (g/mL)
<400	250	0.005
401-650	250	0.005
651-850	200	0.004
851-10000	150	0.003
1001-1400	120	0.0024

After this, the sample was left in a water bath at 25 °C for 15 minutes and passed through Cannon-Fenske 150 viscometer at 25 °C. The time that takes the liquid to pass through the lines in the viscosimeter is noted. A blank analysis is also performed to calibrate the viscosimeter and to obtain its constant. Equation 2 is used.

$$\frac{\eta}{\eta_0} = h \cdot t_v \quad (2)$$

Where h (s^{-1}) is the constant of the viscosimeter and t_v is the effusion time (s). When $\frac{\eta}{\eta_0}$ is calculated, table B from the standard is used to obtain a numerical value called η_{ratio} then Equation 3 is applied to calculate the viscosity of the sample $[\eta]$ (mL/g).

$$\eta_{ratio} = [\eta] \cdot c \quad (3)$$

Where c is the concentration obtained from Table 2

- α -cellulose

α -cellulose was determined according to TAPPI T203 cm-99 (1999). Oven-dried pulp samples were weighed to an equal of 1.6 ± 0.1 g. Pulp was consecutively extracted with 17.5 % NaOH solutions at 25 ± 0.2 °C for a total extraction time of 60 ± 5 min. Then, pulp samples were stirred and filtered. 25 mL of the filtrate were taken and mixed with 10 mL of 0.5 N $K_2Cr_2O_7$ and 50

mL of 96 % H₂SO₄. After 15 minutes, samples were cooled by adding 50 mL of water and titrated with 0.1 N (NH₄)₂Fe(SO₄)₂·6H₂O using ferroin indicator. A blank analysis is also performed, and the volume is noted. After the titration, the volume spent of (NH₄)₂Fe(SO₄)₂·6H₂O is also noted. The percentage of α-cellulose is obtained using Equation 4.

$$\alpha\text{-cellulose}(\%)=100-\left[\frac{6.85\cdot(EB1-V)\cdot2}{25\cdot m\cdot CS}\right] \quad (4)$$

Where EB1 is the volume of (NH₄)₂Fe(SO₄)₂·6H₂O spent in the blank analysis, V is the volume spent of (NH₄)₂Fe(SO₄)₂·6H₂O when using the sample, m is the mass of the sample in grams and CS is the dry content of the sample in percentage

- Kappa

Kappa is an index that estimates the amount of residual lignin and hexenuronic acid by measuring the oxidant demand of the pulp. TAPPI UM 246 (1991) method was implemented to obtain the micro kappa number of high-purity pulp from the final stages of the bleaching process. Micro kappa was chosen because pulp used in this work possess high purity and therefore, has low lignin content and using kappa number would translate in errors regarding measurement.

Between 1 and 2 grams of the sample are weighed. The sample was previously dried for 15 min. 150 mL of UP water is added to the sample and stirred at 300 rpm. While stirring 20 mL of KMnO₄ mixed with 20 mL of H₂SO₄ (4 N), finally the glass is cleaned with an additional 10 mL of UP water and added to the stirring sample. When the reaction time is finished, 10 mL of KI are added to stop the reaction. The sample is then titrated with Na₂S₂O₄ using starch as an indicator. The titration finishes when the dissolution is transparent. A blank analysis, using only the reactants, is also needed. Lignin content is calculated using Equations 5 and 6.

$$G_d = \frac{P \cdot f}{E} \cdot [1 + 0.013 \cdot (25 - t)] \quad (5)$$

Where P is calculated as follows

$$P = \frac{(V - V') \cdot T}{0.1} \quad (6)$$

Where V is the volume of Na₂S₂O₄ spent in the blank analysis, V' is the volume of Na₂S₂O₄ spent when using the sample, T is the normality of the Na₂S₂O₄, t is the reaction temperature, and f and E are factors from the standard.

- Brightness

Brightness represents the numerical value of the reflectance factor of a sample concerning blue light of specific spectral and geometric characteristics. The method is described in the TAPPI T452 om-02 (2002) and is known as GE (or TAPPI) brightness. The equipment required consists of a reflectometer employing 45° illumination and 0° viewing geometry (45°/0°) using light with an effective wavelength of 457±0.5 nm.

3.1.4. *Mathematical modelling and validation*

Once the pulp quality parameters are obtained from the bleaching experiments, it was possible to construct a second-order polynomial equation, which allows predicting the values of pulp quality parameters when the operating conditions of the stage changed. Equation 7 shows the generic second-order polynomial equation.

$$y_k = a_0 + \sum_{i=1}^n (b_i x_i) + \sum_{i=1}^n (c_i x_i^2) + \sum_{i < j} \sum (d_{ij} x_i x_j) \quad (7)$$

Where x are the values of the independent variables; y_k is the values of the dependent values; n the number of the independent variables; and k is the number of dependent variables. The terms a , b , c and d are the coefficients for the intercept of y_k , linear interaction, quadratic interaction and binary interaction respectively. These coefficients are obtained when the experimental results are obtained, and only the coefficients with a confidence level of 95% are considered for the mathematical modelling. Every mathematical model needs to be validated, to observe if the equations obtained can predict how pulp quality parameters vary when the operational variables change. To validate the equations obtained from the experimental design, the results from a preliminary study were used.

3.1.5. Optimization

Once the model is validated the optimization of the process, can be performed. To optimize the process, costs associated with energy and chemicals, restrictions for pulp quality needed to be considered. Three different scenarios were studied, depending on the quality of the pulp: viscose, NCC and NFC. The generic objective function to be minimized is shown next (Equation 8)

$$Z = \sum \text{costs}_{\text{energy}} + \sum \text{costs}_{\text{chemicals}} \quad (8)$$

Restrictions for pulp quality are shown in Table 3. The EOP stage had the same restrictions for the three scenarios studied. PO stage constraints were different for each scenario since the configuration studied; it is the last stage of the bleaching process.

Table 3 Constrains for the optimization of the model

	EOP	Viscose	NCC	NFC
α-cellulose (%)	89 to 90	92 to 94	94 to 96	92.2 to 96
Brightness (ISO %)	70 to 80	90 to 92	80	92 to 94
Viscosity (mL/g)	550 to 610	400 to 600	250 to 588	500 to 600
Kappa	1.0 to 2.0	0.2 to 0.5	0.5 to 0.6	>0.7

Optimization towards viscose was performed because it is the end-use product, from dissolving pulp, that is produced the most. NCC and NFC were chosen since the restriction of some of the pulp quality parameters is lower than other end-use products.

3.2. Viscose oriented bleaching experiments

This section will show the steps taken to obtain CS₂ consumption reduction when the operational variables of the bleaching process change. This time bleaching was performed with the objective to upgrade the final dissolving pulp, that would be later be transformed into viscose. To assess this effect, two additional pulp quality parameters were added: Fock's reactivity and pentosan content. Both analyses will be explained in this section. Figure 9 shows the main steps of this phase.

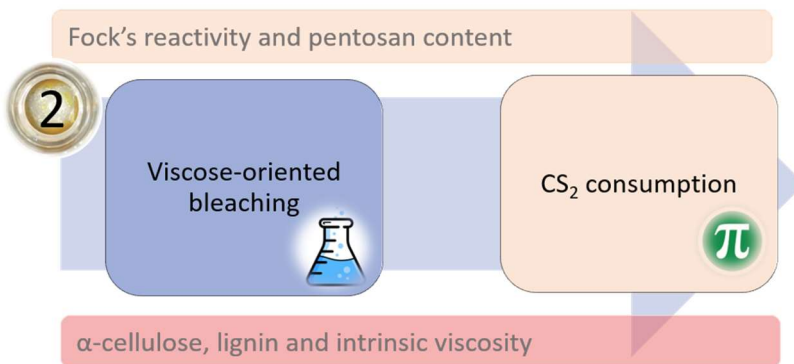


Figure 9 Steps taken for the bleaching towards viscose

Once the optimization was complete and all the experiments were carried out, it was decided to deepen the information that could be obtained from the bleaching process. Therefore, as viscose is, by far, the main end-use product obtained from dissolving pulp, literature research was done, but this time focused on viscose. It was found that research, in general, has focused over the years, on adding a pretreatment of dissolving pulp rather than studying the bleaching process. So, it was decided to study how bleaching affected the properties of dissolving pulp, but this time additional properties were added: **reactivity and pentosan content**. These properties are essential to control because they have a direct impact (economic and environmental) on xanthation since reactivity can lower the quantity of CS₂ used in this stage and pentosan content can affect the quantity of NaOH, used in the said stage of the viscose process.

CS₂ is one of the leading chemical compounds used in the viscose industry. This compound is used in the xanthation stage to dissolve alkali cellulose, which results in viscose, which will be later transformed in viscose fiber or rayon. The use of this compound needs to be controlled and, if possible, reduced, due to the environmental issues. It was found on a bibliography that one of the most important parameters to assess the quality of dissolving pulp for viscose production is reactivity, more specifically Fock's reactivity. This method is a microscale viscose process that measures the quantity of reacted cellulose after xanthation with CS₂ under alkaline conditions. The higher the reactivity, the lower the quantity of CS₂ needed to produce viscose. Pentosan content, which is a polymer formed of C5 sugars, was also measured as it can hinder the conversion of pulp into viscose. The objective of these set of bleaching experiments was to observe how the operating conditions of the bleaching process affect the reactivity of the pulp and to increase it as much

as possible without compromising the quality of the pulp. The effect of reactivity on CS₂ was also assessed on the PO stage. The bleaching will not be explained in this section since is the same procedure explained in section 3.1.2.

3.2.1. Pulp Analyses

These analyses were performed before and after each treatment to quantify the changes produced. Two additional analyses were added to the pulp quality parameters to focus on the pulp to be used for viscose purposes: Fock's reactivity and pentosan content. In this section of the thesis, the additional analyses will be explained. Figure 10 shows pictures of the different analyses.

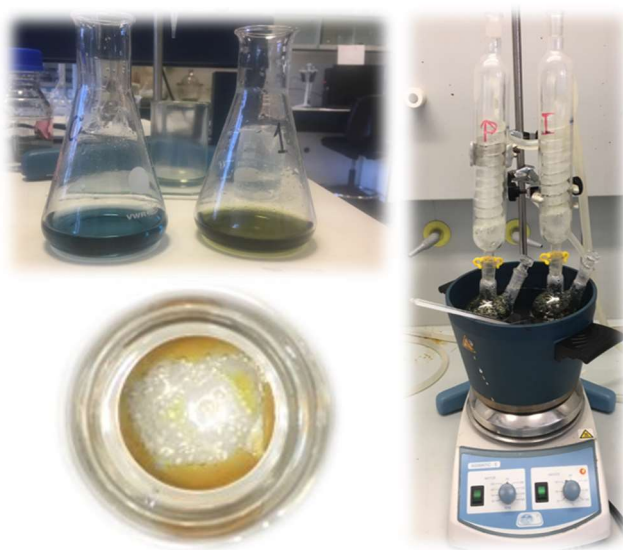


Figure 10 Example of the analyses performed

- Fock's reactivity

Reactivity of pulp samples was measured by the method described by which is based on (Tian et al. 2014; Fock 1959).

First, 0.5 g of pulp calculated as oven-dried (o.d.) were weighed and put into a 250 mL Erlenmeyer flask. Then, 50 mL of NaOH 9% (w/w) were added and stirred for 10 min at 19 °C. 1.3 mL of CS₂ were added, sealed with plastic parafilm, and stirred at 250 rpm for 3 h at 19 °C. This is the xanthation phase in which cellulose-xanthate is formed. When reaction time finishes, water was

added until a total mass of 100 g, the solution was then agitated and centrifuged at 5000 rpm for 15 min. Afterwards, 10 mL of the supernatant were poured in a 100 mL flask, and 3 mL of sulfuric acid 20% (w/w) was added to regenerate the dissolved cellulose. The flasks were left in a fume hood for 15 h-20 h for the CS₂ excess to be removed.

Dissolved cellulose was measured by oxidation with K₂Cr₂O₇. Firstly, 20 mL of sulfuric acid 68 % (w/w) were added and stirred at 250 rpm for 1 h. When the stirring time was set, 10 mL of 1/6 M K₂Cr₂O₇ was added, and the mixture was reflux-boiled for 1 h. Finally, the flasks were left to cool at room temperature and then diluted to a total volume of 100 mL. 40 mL of the solution were pipetted into a 250 mL Erlenmeyer flask and 5 mL of 10 % (w/w) KI were added and titrated with 0.1 N sodium thiosulfate using starch as an indicator. The volume of sodium thiosulfate was used for the calculation of the dissolved cellulose (DC) presented in Equation 9.

$$DC(\%) = \frac{[v_1 \cdot c_1 - (v_2 \cdot c_2 \cdot \frac{100}{40}) \cdot \frac{1}{6}] \cdot M \cdot \frac{1}{4} \cdot \frac{100}{10.4}}{m} \cdot 100 \quad (9)$$

Where M is the molecular weight of a glucose unit (180,156 g/mol) m is the o.d. weight of the pulp sample (g), v₁ and c₁ are the volume and the concentration of K₂Cr₂O₇, respectively. v₂ and c₂ are the volume (mL) and the concentration of sodium thiosulfate, respectively.

- Pentosan

The moisture content of the pulp was measured, and 1.6 g of pulp was weighed, and 100 mL of NaOH 5% (w/w) was added. Then, it was stirred for 3 min and left in a water bath for 1 hour, the suspension was filtered, and 15 mL of the filtrate was added to a 250 mL Erlenmeyer flask and mixed with 10 mL of K₂Cr₂O₇, and 35 mL of H₂SO₄ was added. It was left to cool for 15 min, and 50 mL of distilled water was added. The solution was titrated with (NH₄)₂Fe(SO₄)₂·6H₂O 0.1 N using ferroin as an indicator.

3.2.2. CS₂ consumption calculation

To see how increasing reactivity would affect the process, CS₂ consumption was evaluated. It was calculated using Fock reactivity, α-cellulose content and the stoichiometric value required for the xanthation phase (23.5 % w CS₂/w cellulose)(Gondhalekar et al. 2019b). Considering Fock's reactivity as a reaction yield of xanthation, and the α-cellulose content of the pulp, the **theoretical quantity of fibers (TF)** is obtained using Equation 10. The **CS₂ consumption** (Equation 11) is calculated using the stoichiometric value of CS₂

and α -cellulose content. This procedure is the same as the one proposed by Arce et al. (2020).

$$TF(\%) = \frac{\alpha\text{-cellulose}(\%) \cdot \text{Reactivity}(\%)}{100} \quad (10)$$

$$CS_2\text{ usage}(\%) = \frac{\alpha\text{-cellulose}(\%) \cdot 23.5}{100} \quad (11)$$

The quantity of CS_2 used to obtain viscose need to be calculated not only considering the reactivity of the sample but also the quantity of total fiber in the sample because it depends on the α -cellulose content. Therefore, a CS_2 usage /TF ratio, called the **ratio of consumption per fiber (RCF)** was measured and then, with the objective of comparing all the results, the final reduction of CS_2 usage was calculated using as reference the ratio RCF from the inlet pulp. Equation 12 shows the calculation.

$$RCF = \frac{CS_2\text{ usage}(\%)}{TF(\%)} \quad (12)$$

3.3. Novel pre-treatment

Finally, once the bleaching study was concluded, another research to increase the reactivity of dissolving pulp was considered; however, this time, it was focused on the pre-treatment of dissolving pulp. Figure 11 shows the main steps taken for the pretreatment and the assessment of its effects on dissolving pulp.

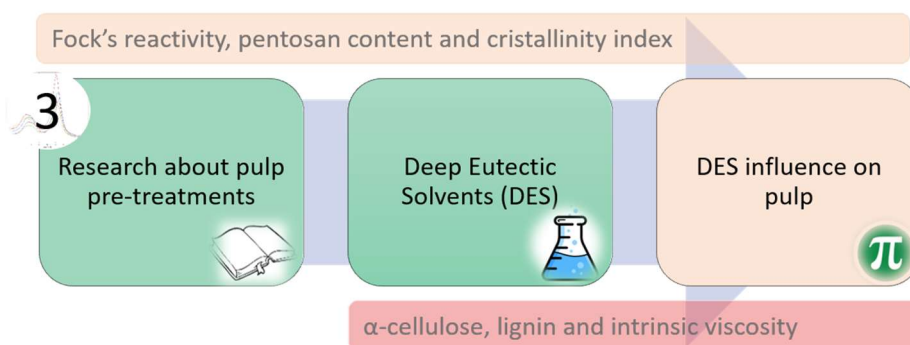


Figure 11 Steps taken for the pre-treatment of dissolving pulp with DES

3.3.1. Literature Research

Several methods, to increase the reactivity of dissolving pulp, were found, however, they are either expensive, consume energy or use additional chemicals.

Table 4 Literature research on pre-treatment to improve reactivity

Keyword(s)	Number of references	Years	Kind of Pre-treatment	Aim	Advantage/drawbacks
Enzymes	9	2005-2018	Traditional (biological)	Pentosan reduction	<ul style="list-style-type: none"> ■ High efficiency ■ High investment and maintenance costs
Mechanical	5	2013-2018	Traditional	Remove primary cell wall	<ul style="list-style-type: none"> ■ High yield ■ Energy consuming
Combination	7	2008-2018	Chemical/ Mechanical	Pentosans reduction Lignin reduction	<ul style="list-style-type: none"> ■ High reactivity ■ Improvement ■ High yield ■ High investment and maintenance costs
Novel	4	2017-2019	Chemical/ Morphological	Removal of undesirable compounds	<ul style="list-style-type: none"> ■ High efficiency ■ Difficult to scale-up

As a result, it was decided to use DES to increase the reactivity of pulp, since DES are not as expensive as other treatments and the reactants can be biocompatible.

3.3.2. DES pre-treatment

Pulp pre-treatment was performed as showed by Majová et al. (2017). Initially, the pulp was soaked and stirred in water to obtain a consistency of 4 %. The mole ratio for each DES were: ChCl:LA (1:9), ChCl:MA (1:1), ChCl:OxA (1:3) and ChCl:Ur (1:2) obtained from bibliography (Jablonský et al. 2015; Pan et al. 2017a). These DES are widely used with lignocellulosic material because of their ability to delignify (Zdanowicz et al. 2018). Reactants were weighed and mixed. The mixture was heated at 80 °C and magnetically stirred, until a clear liquid was formed. Finally, the pulp and the DES are put together in a flask and placed in a water bath at 60°C for one hour. When the treatment finishes, the pulp is washed with tap water, until the pH of washing wastewater is around 7.

Pulp analyses are not explained in this section of the thesis because they have been explained in the previous section of the methodology.

3.3.3. X-ray diffraction and crystallinity index

The crystallinity of pulp is a characteristic that researches point out as having a relationship with Fock's reactivity. It is quantified by the crystallinity index (CrI) and can be measured by several techniques. One of them is X-Ray diffraction (XRD). Characterization of the untreated pulp and DES-treated pulps at 1/20 S/L ratio were performed in air atmosphere on a Bruker D8 Advance diffractometer, using Cu K α radiation and a LynxEye detector. Diffraction patterns were collected with an angular 2 θ range between 10° and 70° with a 0.03° step size and measurement time of 3 s per step, and a graphite monochromator.

The XRD spectra obtained were used to calculate de CrI using Equation 13, proposed by Segal et al. 1959.

$$\text{CrI}(\%) = \frac{(I_{200} - I_{\text{am}})}{I_{200}} \cdot 100 \quad (13)$$

Where I_{200} is the intensity of the crystalline plane (200) at around 22° and I_{am} is the intensity of the amorphous cellulose at 18°.

DES treatment of pulp is not well-know, therefore X-Ray diffraction was performed only on DES-treated pulp, to observe any additional change on the morphology, apart from CrI. DES treatment might transform dissolving pulp

(native cellulose) into another allomorph, i.e. cellulose II. This change can be seen using this technique. Figure 12 shows a generic native cellulose diffractogram, corresponding to the raw pulp (dissolving pulp) used in DES pre-treatment, and the data used to calculate the CrI.

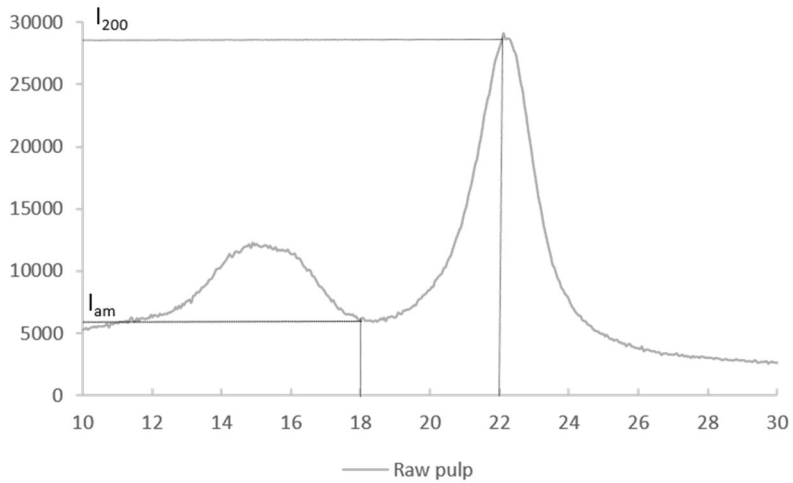


Figure 12 Example of the calculation of CrI

4. Results

In this section of the thesis, the results obtained from the different experiments performed will be discussed. It will be organized, as showed in Figure 6. Therefore, first, the optimization of the bleaching stage in terms of costs will be discussed. Then, the viscose oriented bleaching and finally the pre-treatment of dissolving pulp with DES will be discussed. Three scientific papers have been published in relation to the three steps.

4.1. Bleaching optimization

4.1.1. Experimental design and mathematical modelling

From the experimental design explained previously, a second-order polynomial equation could be constructed, with the selected independent variables. These models fitted the data well; the regression coefficients of the statistical surface models, F-values and the coefficients of the mathematical adjustment are provided in Tables 5 and 6. The expression is given by Equation 14.

$$\begin{aligned} y_i = & a_{1,i}[\text{NaOH}] + a_{2,i}\text{Time} + a_{3,i}\text{Temperature} + a_{4,i}[\text{H}_2\text{O}_2] + a_{5,i}[\text{NaOH}]^2 + a_{6,i}\text{Time}^2 + \\ & + a_{7,i}\text{Temperature}^2 + a_{8,i}[\text{H}_2\text{O}_2]^2 + a_{9,i}[\text{NaOH}]\text{Time} + a_{10,i}[\text{NaOH}]\text{Temp} + a_{11,i}[\text{NaOH}] \\ & [\text{H}_2\text{O}_2] + \\ & + a_{12,i}\text{Time Temp} + a_{13,i}\text{Time}[\text{H}_2\text{O}_2] + a_{14,i}\text{Temp} \\ & [\text{H}_2\text{O}_2] + a_{0,i} \end{aligned} \quad (14)$$

Statistical analyses revealed how well the data fitted with a second-order polynomial. These empirical models describe end-quality pulp properties as a function of the operational variables of the EOP and PO stages (*i.e.*, reaction time, reaction temperature, NaOH dosage, and H₂O₂ dosage). Only significant factors giving a *p*-value less than 0.05 were considered in the final response surface models. Three-dimensional graphs of each dependent variable against the two most influential variables are displayed in Figure 13 for EOP and PO stages.

Table 5 Coefficients for Each Independent Variable in the Models to Predict Dependent Variables for the EOP stage with ANOVA Analyses

EOP Stage Factors (j)	Coefficient ($a_{j,i}$ of Eq.)			
	Kappa No.	α -Cellulose	Intrinsic Viscosity	GE Brightness
[NaOH]	-0.0692	-0.221	0.565	-0.0578
Time	-0.0179	-0.0218	-1.23	$-8.64 \cdot 10^{-3}$
Temperature	-0.0353	-0.0692	1.89	-0.0670
[H ₂ O ₂]	-0.0311	-0.0303	-8.02	0.426
[NaOH] ²	-	-	-	-
Time ²	-	-	-	-
Temperature ²	-	-	-0.0302	-
[H ₂ O ₂] ²	$8.36 \cdot 10^{-4}$	$2.08 \cdot 10^{-3}$	0.128	-0.0105
[NaOH]·Time	$1.07 \cdot 10^{-4}$	-	-0.0628	-
[NaOH]·Temp	$4.14 \cdot 10^{-4}$	$2.45 \cdot 10^{-3}$	0.0795	-
[NaOH]·[H ₂ O ₂]	-	-	-0.111	$1.55 \cdot 10^{-3}$
Temp·Time	$1.32 \cdot 10^{-4}$	$1.47 \cdot 10^{-4}$	0.0212	-
[H ₂ O ₂]·Time	$-1.71 \cdot 10^{-4}$	$-7.61 \cdot 10^{-4}$	$6.40 \cdot 10^{-3}$	$-5.03 \cdot 10^{-4}$
[H ₂ O ₂]·Temp	-	-	-	$3.65 \cdot 10^{-3}$
Intersection	6.51	98.5	639	78.7
Statistical Data	-	-	-	-
No. experiments	48	48	48	48
R ²	0.888	0.972	0.987	0.970
R	0.943	0.986	0.993	0.985
R ² adjusted	0.878	0.969	0.9858	0.968
Standard Error	0.189	0.309	16.9	1.39
F-Value	350	$4.42 \cdot 10^5$	$4.79 \cdot 10^3$	$1.53 \cdot 10^4$
Weighted residual sum of squares	1.35	3.73	$1.02 \cdot 10^4$	75.7

Table 6 Coefficients for Each Independent Variable in the Models to Predict Dependent Variables for PO stage with ANOVA Analyses

PO Stage Factors (j)	Kappa No.	α -Cellulose	Intrinsic Viscosity	GE Brightness
[NaOH]	0.0275	0.152	6.76	0.127
Time	$-1.46 \cdot 10^{-3}$	-0.133	-3.27	0.114
Temperature	-0.0584	0.321	-0.374	1.02
[H ₂ O ₂]	-0.0290	0.0446	-9.32	0.180
[NaOH] ²	-	-	-	$-1.40 \cdot 10^{-3}$
Time ²	-	-	0.0111	$-2.71 \cdot 10^{-4}$
Temperature ²	$2.22 \cdot 10^{-4}$	$-2.26 \cdot 10^{-3}$	-	$-3.97 \cdot 10^{-3}$
[H ₂ O ₂] ²	-	-	-	-
[NaOH]·Time	$-9.2 \cdot 10^{-5}$	$7.02 \cdot 10^{-4}$	-0.0319	-
[NaOH]·Temp	-	$-2.71 \cdot 10^{-3}$	-0.0164	$-1.37 \cdot 10^{-3}$
[NaOH]·[H ₂ O ₂]	$3.97 \cdot 10^{-4}$	-	-	$2.49 \cdot 10^{-3}$
Temp·Time	-	$1.60 \cdot 10^{-3}$	-	$-8.29 \cdot 10^{-4}$
[H ₂ O ₂] ²	-	$-4.7 \cdot 10^{-4}$	0.0417	$1.34 \cdot 10^{-3}$
[H ₂ O ₂] ²	$3.81 \cdot 10^{-4}$	-	-	$-4.81 \cdot 10^{-3}$
Intersection (a _{0,i})	4.35	78.9	793	30.6
Statistical Data	-	-	-	-
No. experiments	51	48	49	51
R ²	0.957	0.966	0.959	0.961
R	0.978	0.983	0.979	0.980
R ² adjusted	0.953	0.963	0.955	0.958
Standard Error	0.0764	0.796	18.5	1.27
F-Value	$1.02 \cdot 10^3$	$4.87 \cdot 10^5$	$3.09 \cdot 10^3$	$1.51 \cdot 10^4$
Weighted residual sum of squares	0.245	24.1	$1.37 \cdot 10^4$	61.53

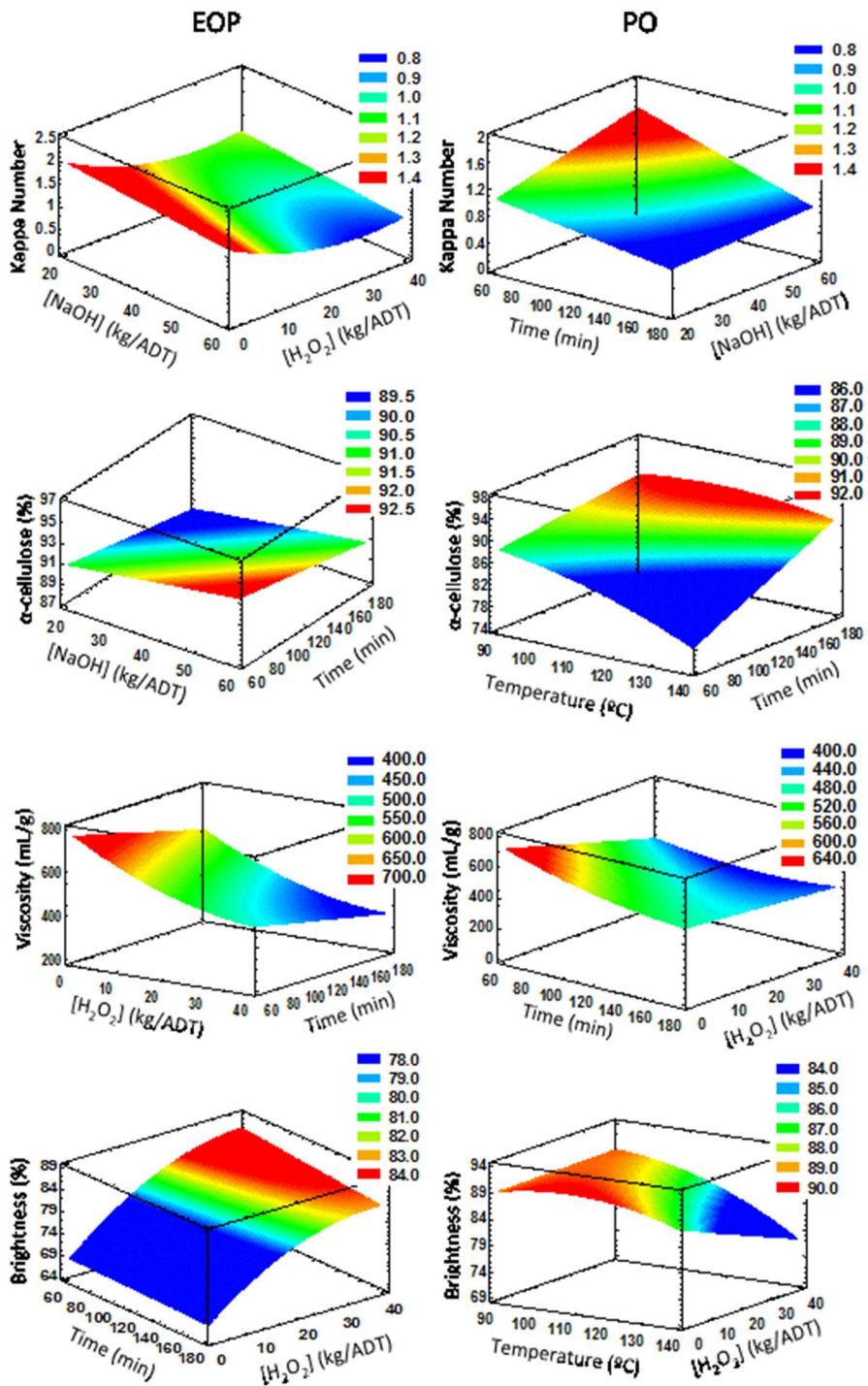


Figure 13 Response surfaces for kappa number, α -cellulose content, intrinsic viscosity, and brightness after the EOP and the PO stage

Response surface graphs made it possible to visualize the optimum operating range under the conditions explored. Such graphs were generated by considering the independent variables that had the most significant cumulative effect ($p < 0.05$) with a statistical confidence level of 95% for each stage.

As can be seen in Figure 13 optimal operating range conditions are: (i) kappa values below 0.8 in both stages operating with high dosages of NaOH and H₂O₂ in EOP and high residence time in PO; (ii) α cellulose content higher than 92 % using high NaOH dosages and intermediate time (between 60 and 100 min) in EOP and low temperatures and long residence time in PO; (iii) for the intrinsic viscosity the normal range of dissolving pulp is represented in the green zone. Such values were reached with H₂O₂ dosages from 10 up to 30 kg/ADT and residence time between 60 and 120 min for EOP. The same green zone in PO was achieved with low H₂O₂ dosages (no more than 10 Kg/ADT) and residence time in the range of 120 to 180 min; (iv) for the brightness the red area is the optimal value giving above 84% and 90% GE at EOP and PO stage.

The results obtained from the experiments of this research are similar to those reported by Matin et al. (2015) for dissolving jute pulp made by the PHK process. The authors noted α -cellulose content of 91 to 92% and GE brightness of 88.3 to 89.5%. Furthermore, Duan et al. (2015) reported that an AS pulp made from eucalypt had an α -cellulose content in the range of 91.34 to 92.90%, and intrinsic pulp viscosities between 498 and 505 mL/g. Finally, Perrin et al. (2017) indicated that the brightness of a eucalypt PHK pulp bleached with different bleaching sequences ranged between 88.5% and 89.8% ISO. Pareto charts represented in Figure 14 indicated the most influential variables affecting the end-quality pulp characteristics. The standardized effect (positive or negative) for each independent variable is also represented in the Pareto charts. Such diagrams quantify which of the effects have major significance impacts. In general, the linear terms have larger effects on the values of the dependent variables in comparison to the quadratic terms.

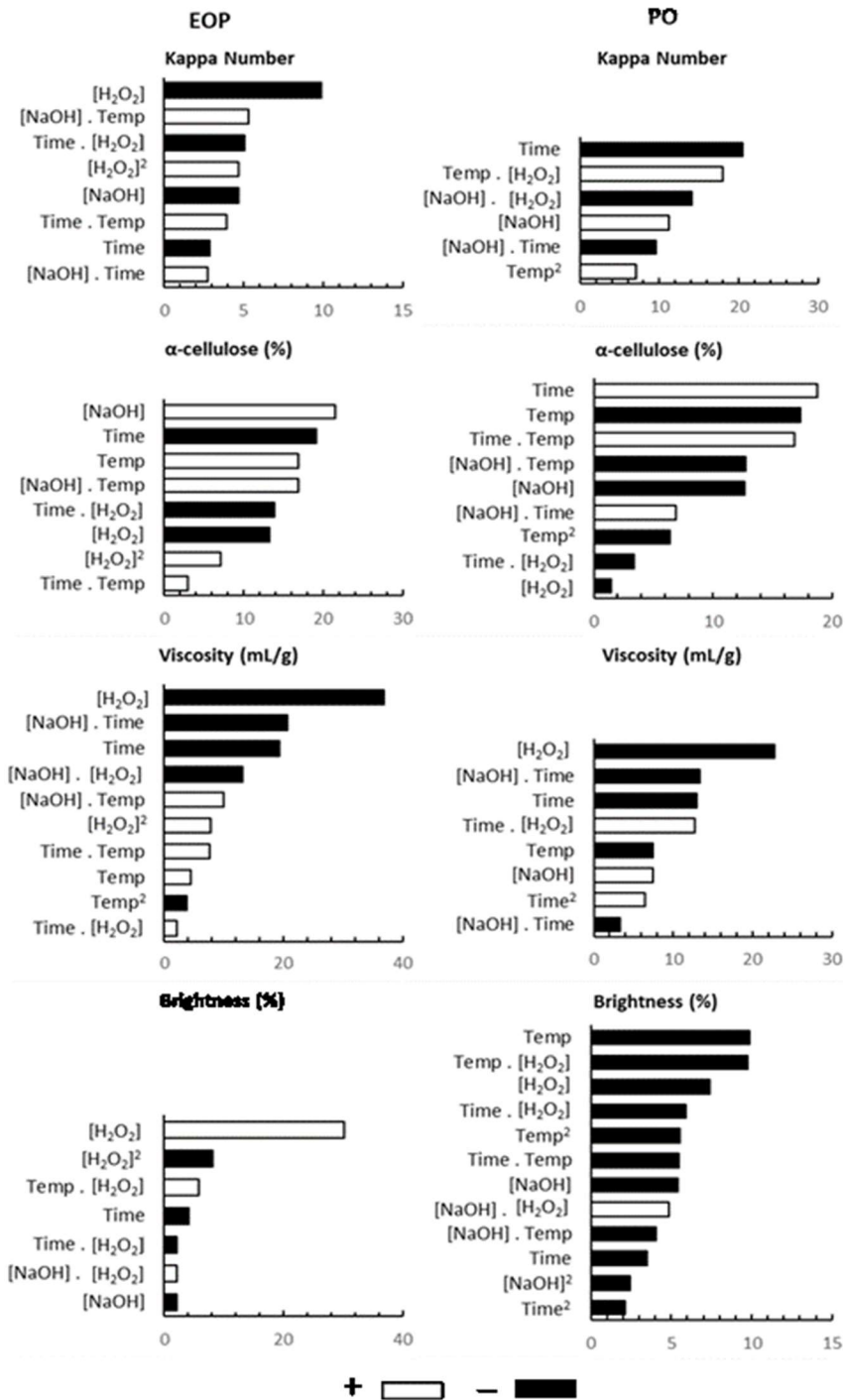


Figure 14 Pareto charts of standardized effects for EOP and PO stages

According to Figure 14, major effects at the EOP stage were primarily H₂O₂ and NaOH dosages, except for pulp brightness where H₂O₂ dosage and temperature were the variables with the higher impacts. Time and temperature played a more critical role for the PO stage, except for intrinsic pulp viscosity, which was more influenced by H₂O₂ dosage and time.

4.1.2. Model validation and optimization

From the preliminary study data regarding how the operational variables of the process affected the pulp quality parameters was obtained. This study was performed by varying one operational variable while maintaining the others constant. These results were compared to the ones obtained from the experiments of the factorial design. In Figure 11, it was observed that the surface response models fit very well with the experimental data obtained in the Preliminary study. These results confirmed that it is possible to predict which variables affect more to the pulp quality requirements. Figure 15 shows how the equations of the mathematical modelling (continuous black line) fitted well with the experimental data (represented in black and white points for EOP and PO, respectively) considering the small deviation under the tested conditions. When examining Figure 15, it was observed that the following variables have greatest influence: (1) H₂O₂ and NaOH dosages in EOP, and time and NaOH dosages in PO for the kappa number; (2) time and NaOH dosage in EOP, and time and temperature in PO for the α -cellulose content; and (3) H₂O₂ dosage and time for the intrinsic viscosity in both EOP and PO.

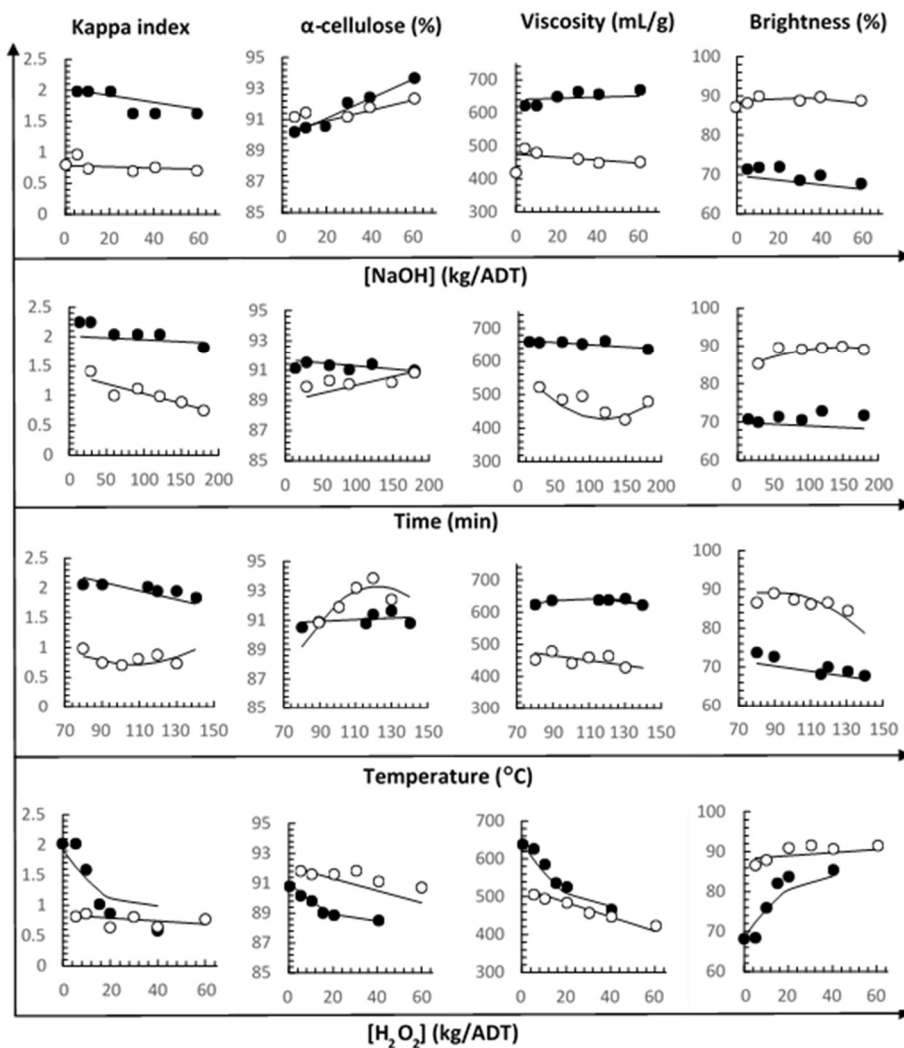


Figure 15 . Comparison of experimental data from the second set of experiments (symbols) to the response surface models for the EOP stage (represented by ●) and the PO stage (represented by ○)

A recent study with the Z-EOP-PO bleaching sequence (Llano et al. 2015) showed an increase of intrinsic pulp viscosity from 560 mL after the Z stage to 610 mL/g after the EOP stage. The study also showed that the hemicelluloses in the AS eucalypt pulp decreased from 5.1% to 2.2%, and the xylan decreased from 4.5% to 1.7% when going through the EOP stage.

Looking at Figure 15, the intrinsic viscosity was barely affected by time, temperature, or NaOH dosages. Both EOP and PO were observed to have large intrinsic pulp viscosity losses when the H₂O₂ dosage is increased. This is probably due to the degradation of γ- and β-cellulose chains by oxidation. A

decrease of glucan levels was observed in a previous study (Llano et al. 2015) of the same bleaching sequence from 88.8% to 87.3%, which was attributed to γ - and β -cellulose degradation. It is desirable that the intrinsic viscosity of dissolving pulp be around 400 to 600 mL/g (Duan et al. 2015; Chen et al. 2016). An increase in the intrinsic viscosity during the bleaching stage is thought to be caused by the removal of short-chain carbohydrates, particularly hemicelluloses (Duan et al. 2016a). This effect was mostly observed during the EOP stage, which solubilizes and extracts oxidized lignin and hemicelluloses.

Figure 15 indicated that variables with the most influence over pulp purity were NaOH and time for the EOP, and time and temperature for the PO. In the case with PO, the temperature had the highest impact, resulting in a maximum α -cellulose content of 94%. An α -cellulose content of 93.5 % was also reached by adding high amounts of NaOH.

The trends observed for the kappa number, which is related to lignin content, were similar for both EOP and PO stages. Increasing the reaction time, NaOH dosage or H_2O_2 dosages for either EOP or PO caused the kappa number to decrease, whereas the reaction temperature had little effect. These observations were hypothesized to be due to the attack of carbonyl groups in the oxidized lignin, which enhanced delignification. Among the selected independent variables, H_2O_2 dosages in EOP with peroxide loads over 20 Kg/ADT yielded a kappa number of 0.6 or less, which indicated that hemicelluloses extraction (typically occurring in EOP) and lignin extraction are happening at the same time.

Pulp brightness and kappa number are indirectly proportional to one another, whilst the pulp brightness and α -cellulose content have the same trend. The PO bleaching stage preferably attacks the chromophores of the trace lignin that results in higher pulp brightness. Pulp brightness was always higher after the PO versus after the EOP regardless of bleaching conditions (Figure 15); GE brightness values after PO reached maximum values of 91 to 92%.

Figure 16 shows the parity plots of the laboratory data from the factorial experiments and the validation experiments to the predictions of the response surface models. These graphs show that the models fitted well the experimental data, with prediction errors being lower than the experimental errors.

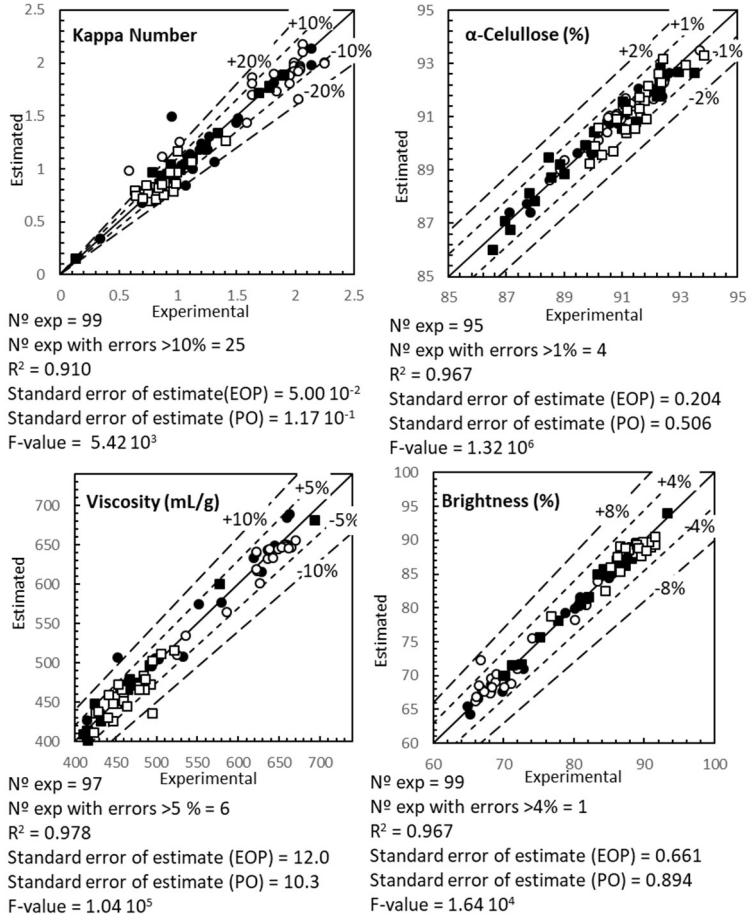


Figure 16 Parity plots comparing the two experimental data sets with the predictions of the response surface models derived from the factorial design experiments: EOP represented by ● (factorial design data) and ○ (validation data), and PO represented by ■ (factorial design data) and □ (validation data).

Parity plots are useful for the validation of the model at any bleaching time, temperature, NaOH dosage, and H₂O₂ dosage. The models fitted the data well with a global coefficient of determination, R^2 , of 0.929 and a global F-value of $9.61 \cdot 10^4$, which indicated that the models explained most of the observed variances. Individual R^2 and F-value were also calculated and shown in Figure 16. It was concluded that the proposed models should be able to predict the bleaching behavior of the acid sulfite pulp through EOP-PO partial sequence for the ranges examined. The correlation coefficient, R, were above 0.91 for the pulp property parameters (*i.e.*, 0.99, 0.95, 0.97 and 0.99 for kappa number, α -cellulose, intrinsic viscosity, and GE brightness, respectively). Furthermore, only a few predictions differed from the experimental data with the prediction errors were higher than the experimental errors.

The mathematical model developed from the statistical design-of-experiments was used for the optimization of the bleaching process with the GAMS software. Not all end-cellulose products have the same pulp specifications; hence, three different models were developed for optimum bleaching for producing: (i) viscose; (ii) nanocrystalline cellulose; and (iii) nanofibrillated cellulose grades. The general objective function (Z) for the three scenarios is the same and consists of minimizing the expression showed as Equation 8.

Costs related to energy ($costs_{energy}$) and chemical ($costs_{chemical}$) consumption for each stage were considered since they are significant contributors to bleaching costs. Energy costs for EOP and PO stages were calculated by Equations. 15 and 16, respectively:

$$Cost_{energy}^{EOP} (\text{€}) = 7.16 \left(\frac{ODT}{h} \right) \cdot \frac{1}{0.9} \left(\frac{ADT}{ODT} \right) \cdot \frac{1}{3600} \left(\frac{h}{s} \right) \cdot 1.55 \cdot \left(\frac{kW \cdot s}{AD \text{ kg} \cdot ^\circ C} \right) \cdot 0.083 \left(\frac{\text{€}}{kW \cdot h} \right) \cdot \frac{1}{60} \left(\frac{h}{min} \right) \cdot \frac{1000}{1} \left(\frac{AD \text{ kg}}{ADT} \right) \quad (15)$$

$$\cdot t_R^{EOP} (\text{min}) \cdot (T^{EOP} - 65) (^{\circ}C) = 0.00491 \cdot t_R^{EOP} \cdot (T^{EOP} - 65)$$

$$Cost_{energy}^{PO} (\text{€}) = 6.3 \left(\frac{ODT}{h} \right) \cdot \frac{1}{0.9} \left(\frac{ADT}{ODT} \right) \cdot \frac{1}{3600} \left(\frac{h}{s} \right) \cdot 1.55 \cdot \left(\frac{kW \cdot s}{AD \text{ kg} \cdot ^\circ C} \right) \cdot 0.083 \left(\frac{\text{€}}{kW \cdot h} \right) \cdot \frac{1}{60} \left(\frac{h}{min} \right) \cdot \frac{1000}{1} \left(\frac{AD \text{ kg}}{ADT} \right) \cdot t_R^{PO} (\text{min}) \cdot (T^{PO} - 65) (^{\circ}C) = 0.00432 \cdot t_R^{PO} \cdot (T^{PO} - 65) \quad (16)$$

Individual chemical costs for the EOP stage ((Equations. 17, 18, and 19) and the PO stage (Equations 20, 21 and 22) were calculated. For the chemical costs, they were considered consumptions of NaOH, H₂O₂ (process variables studied in this work) and oxygen (considered as a constant in this work) but also consumed during the bleaching sequence.

$$\begin{aligned}
\text{Cost}_{\text{NaOH}}^{\text{EOP}} (\text{€}) &= 7.16 \left(\frac{\text{ODT}}{\text{h}} \right) \cdot \frac{1}{0.9} \left(\frac{\text{ADT}}{\text{ODT}} \right) \cdot \frac{1}{60} \left(\frac{\text{h}}{\text{min}} \right) \\
&\cdot 0.195 \left(\frac{\text{€ NaOH}}{\text{kg NaOH}} \right) \cdot C_{\text{NaOH}}^{\text{EOP}} \left(\frac{\text{kg NaOH}}{\text{ADT}} \right) \cdot t_{\text{R}}^{\text{EOP}} (\text{min}) \\
&= 0.0259 \cdot C_{\text{NaOH}}^{\text{EOP}} \cdot t_{\text{R}}^{\text{EOP}}
\end{aligned} \tag{17}$$

$$\begin{aligned}
\text{Cost}_{\text{H}_2\text{O}_2}^{\text{EOP}} (\text{€}) &= 7.16 \left(\frac{\text{ODT}}{\text{h}} \right) \cdot \frac{1}{0.9} \left(\frac{\text{ADT}}{\text{ODT}} \right) \cdot \frac{1}{60} \left(\frac{\text{h}}{\text{min}} \right) \\
&\cdot 0.560 \left(\frac{\text{€ H}_2\text{O}_2}{\text{kg H}_2\text{O}_2} \right) \cdot C_{\text{H}_2\text{O}_2}^{\text{EOP}} \left(\frac{\text{kg H}_2\text{O}_2}{\text{ADT}} \right) \cdot t_{\text{R}}^{\text{EOP}} (\text{min}) \\
&= 0.0743 \cdot C_{\text{H}_2\text{O}_2}^{\text{EOP}} \cdot t_{\text{R}}^{\text{EOP}}
\end{aligned} \tag{18}$$

$$\begin{aligned}
\text{Cost}_{\text{O}_2}^{\text{EOP}} (\text{€}) &= 7.16 \left(\frac{\text{ODT}}{\text{h}} \right) \cdot \frac{1}{0.9} \left(\frac{\text{ADT}}{\text{ODT}} \right) \cdot \frac{1}{60} \left(\frac{\text{h}}{\text{min}} \right) \cdot 0.065 \left(\frac{\text{€ O}_2}{\text{kg O}_2} \right) \\
&\cdot 3 \left(\frac{\text{kg O}_2}{\text{ADT}} \right) \cdot t_{\text{R}}^{\text{EOP}} (\text{min}) = 0.0259 \cdot t_{\text{R}}^{\text{EOP}}
\end{aligned} \tag{19}$$

$$\begin{aligned}
\text{Cost}_{\text{NaOH}}^{\text{PO}} (\text{€}) &= 6.3 \left(\frac{\text{ODT}}{\text{h}} \right) \cdot \frac{1}{0.9} \left(\frac{\text{ADT}}{\text{ODT}} \right) \cdot \frac{1}{60} \left(\frac{\text{h}}{\text{min}} \right) \\
&\cdot 0.195 \left(\frac{\text{€ NaOH}}{\text{kg NaOH}} \right) \cdot C_{\text{NaOH}}^{\text{PO}} \left(\frac{\text{kg NaOH}}{\text{ADT}} \right) \cdot t_{\text{R}}^{\text{PO}} (\text{min}) \\
&= 0.0228 \cdot C_{\text{NaOH}}^{\text{PO}} \cdot t_{\text{R}}^{\text{PO}}
\end{aligned} \tag{20}$$

$$\begin{aligned}
\text{Cost}_{\text{H}_2\text{O}_2}^{\text{PO}} (\text{€}) &= 6.3 \left(\frac{\text{ODT}}{\text{h}} \right) \cdot \frac{1}{0.9} \left(\frac{\text{ADT}}{\text{ODT}} \right) \cdot \frac{1}{60} \left(\frac{\text{h}}{\text{min}} \right) \cdot 0.560 \left(\frac{\text{€ H}_2\text{O}_2}{\text{kg H}_2\text{O}_2} \right) \\
&\cdot C_{\text{H}_2\text{O}_2}^{\text{PO}} \left(\frac{\text{kg H}_2\text{O}_2}{\text{ADT}} \right) \cdot t_{\text{R}}^{\text{PO}} (\text{min}) = 0.0653 \cdot C_{\text{H}_2\text{O}_2}^{\text{PO}} \cdot t_{\text{R}}^{\text{PO}}
\end{aligned} \tag{21}$$

$$\begin{aligned}
\text{Cost}_{\text{O}_2}^{\text{PO}} (\text{€}) &= 6.3 \left(\frac{\text{ODT}}{\text{h}} \right) \cdot \frac{1}{0.9} \left(\frac{\text{ADT}}{\text{ODT}} \right) \cdot \frac{1}{60} \left(\frac{\text{h}}{\text{min}} \right) \cdot 0.065 \left(\frac{\text{€ O}_2}{\text{kg O}_2} \right) \\
&\cdot 3 \left(\frac{\text{kg O}_2}{\text{ADT}} \right) \cdot t_{\text{R}}^{\text{PO}} (\text{min}) = 0.0228 \cdot t_{\text{R}}^{\text{PO}}
\end{aligned} \tag{22}$$

Equations 15 to 22 were developed by considering data provided by the pulp mill and considering the mass balances, reagent prices, production, and consumption per Air Dried Tonne (ADT) of dissolving pulp. Regarding the energy cost of 0.083 €/KW·h, this data was taken from the Ministry of Commerce Industry and Tourism (MINCOTUR 2018). The only costs considered in the three optimization models were the major contributors to the bleaching costs, which correspond to reagent and energy costs. Water consumption or labor costs were not introduced in the models.

Pulp production rates of oven-dried tonne (ODT) basis were converted to air-dried tonne (ADT) basis assuming a 10% moisture content. Costs Equations (Equations 15 to 22) were expressed as functions of the independent variables of t_R^{PO} , t_R^{EOP} , C_{NaOH}^{PO} , C_{NaOH}^{EOP} , $C_{H_2O_2}^{PO}$, $C_{H_2O_2}^{EOP}$, T^{PO} , and T^{EOP} , which were bleach stage reaction times, sodium hydroxide and peroxide dosages, and reaction temperatures for PO and EOP, respectively. Apart from the costs, equations of the response variables (kappa number, α -cellulose content, intrinsic pulp viscosity and pulp brightness) as a function of the operational variables (reaction time, peroxide dosage, sodium hydroxide dosage and reaction temperature) were also introduced in the GAMS software. These equations are presented in Tables 5 and 6. The whole system of equations constitutes a non-linear problem (NLP) for optimization.

Bleached chemical pulps to high brightness require a multi-stage bleaching sequence. The first stage or two of the sequence focuses on removing residual lignin in the pulp and are known as delignification stages. The subsequent stages in the sequence are the brightening stages in which the chromophores in the pulp are eliminated (Sixta 2006). In this study, the optimization of Z-EOP-PO focused on the EOP-PO partial sequence, where the models for the EOP and PO stages were considered together when optimizing for the three different scenarios.

Once the objective function was defined and established with the rest of equations, some restrictions were incorporated to refine the objective function. Such restrictions vary as a function of the pulp grade and are summarized in Table 3. These restrictions should be accomplished at the end of the EOP-PO partial sequence to meet the product specifications of the dissolving pulp grade.

Constraints applied to the EOP stage are the same for all dissolving pulp grades. EOP restrictions were: 89 to 90% α -cellulose content, 70 to 80% brightness (GE), intrinsic pulp viscosity of 550 to 610 mL/g, and kappa number of 1.0 to 2.0. In the case of the PO stage, the product specifications for viscose, NCC and NFC pulp grades were taken from the literature (Abraham et al. 2011;

Sehaqui et al. 2011; Tonoli et al. 2012; Wang et al. 2012; Barbash et al. 2017a, b; Zhao et al. 2017). These PO stage constraints for each pulp grade are shown in Table 3.

For a standard rayon grade, the dissolving cellulose has an α -cellulose content of 92 to 94% for the acid sulfite pulping process; the desirable intrinsic viscosity for this grade is 400 to 600 mL/g (Duan et al. 2015; Chen et al. 2016). Dissolving pulps with lower α -cellulose levels are predominantly used to manufacture viscose grades, whereas higher α -cellulose levels are used for cellulose acetate, cellulose ether, and other speciality product grades (Sixta 2006). Additionally, the presence of excessive amounts of hemicelluloses can have adverse effects when the dissolving pulp is converted to rayon (*i.e.*, incomplete xanthation of the cellulose). Brightness should be higher than 90% ISO for viscose grade (Sixta 2000). In the case of nanocellulose products (NFC and NCC), the dissolving pulp quality parameters are not as strict as those in the cases of rayon. Results of the optimization of the energy and chemical costs associated with EOP and PO stages obtained for the three pulp grade scenarios are shown in Table 7. As was explained earlier, there is one model used for the EOP stage for all pulp grades, whereas different PO models are used for each pulp grade.

Table 7 Operating Conditions and Optimized Costs for Each End-Cellulose Product

	(i), (ii), (iii)	(i) viscose	(ii) NCC	(iii) NFC
	EOP	PO	PO	PO
t_R (min)	180	50.9	15.5	47.5
T (°C)	80.0	97.2	99.4	96.8
NaOH (kg/ADT)	30.0	30.0	30.0	30.0
H ₂ O ₂ (kg/ADT)	-	30.0	40.0	30.0
Kappa No.	1.86	0.500	1.38	1.00
Intrinsic viscosity (mL/g)	550	509	500	516
α -Cellulose (%)	90.0	92.0	94.0	92.2
Brightness (% GE)	70.1	90.0	83.5	90.0
$Costs_{energy}$ (€)	13.23	7.10	2.30	6.53
$Costs_{chemicals}$ (€)	144	136	51.3	127
Total Costs (€)	157	143	53.6	134

All calculated pulp grade costs were significantly lower than the current costs of the pulp mill, with 292.80 € for the EOP stage and 499.50 € for the PO stage (total 792.3 €). In comparison with the pulp mill costs, the three proposed models significantly reduce both the energetic and the chemical costs of bleaching. The cheapest dissolving pulp grade is the NCC with an EOP-PO bleach cost of 211 € per ton of air-dried pulp, whereas the viscose has a cost of 300 € per ton of air-dried pulp.

The most affecting operational variables to pulp quality parameter are NaOH and H₂O₂ dosages. Predicted results obtained with the mathematical model adjusted well to the experimental ones.

4.2. Viscose oriented bleaching

With the knowledge acquired by the bleaching optimization and since viscose is the end-use product, from dissolving pulp, that is produced the most, the viscose oriented bleaching was performed. The main differences from the bleaching optimization are that in this section, two additional pulp properties are added: Pentosan and Fock's reactivity, which are crucial for viscose quality. The results of that research will be shown next. Table 8 shows the inlet pulp quality parameters.

Table 8 Inlet pulp quality values for each stage

Bleaching stage	α- cellulose (%)	Viscosity (mL/g)	Kappa	Reactivity (%)	Pentosan (%)
EOP	89.87	476.4	6.54	63.38	4.06
PO	89.75	565.3	2.6	81.09	3.38

4.2.1. Effect of bleaching on pentosan and reactivity

Figure 17 and 18 show the influence of the operating conditions (NaOH and H₂O₂ dosages, time, and temperature) over pulp reactivity in both EOP and PO stages. Square and triangle-shaped points represent the best value of the operating conditions studied for EOP and PO stage respectively and was fixed for the following experiments. To choose these conditions, not only reactivity and pentosan content values were considered, but also α -cellulose content, viscosity and kappa number were considered.

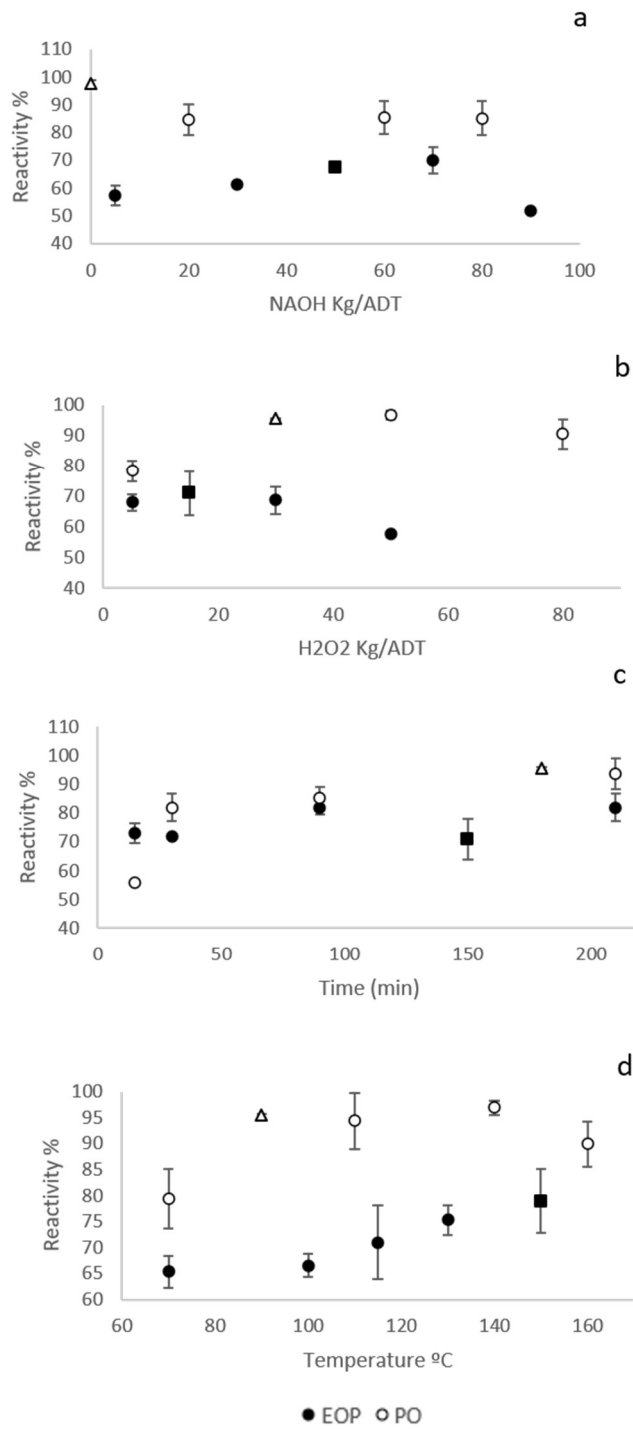


Figure 17 Influence of the process variables on reactivity: a) NaOH dosage (kg/ADT), b) H₂O₂ dosage (kg/ADT), c) time (min) and d) Temperature (°C)

Figure 17.a shows the influence of NaOH dosage on pulp reactivity. In the EOP stage, reactivity increases while NaOH dosage increases, reaching a maximum of 70 % at 70 kg/ADT (Air Dried Tonnes), further increasing the dosage of NaOH leads to a reduction in reactivity. (Wang et al. 2014), reported this reduction as a result of the hornification effect, which reduces the pore volume of the pulp and the accessibility of the chemicals (Dinand et al. 2002). Rebutzi and Evtuguin (2006), found a relationship between pentosan content and hornification, when using 10 % KOH extraction, the higher the pentosan content, the lower the hornification. On the other hand, Kaur et al. 2017, found that alkali dose higher than 8% increases the hornification effect, which can be seen in the experiments when 90 kg/ADT of NaOH (9 % w/w) was used, both trends are in accordance with this study. Recent studies also reported that increasing NaOH makes cellulose I (parallel orientation) transform into cellulose II (antiparallel orientation), and as a result, reactivity is lower (Li et al. 2018a). Therefore, an excess of NaOH is undesirable to obtain a good quality pulp to be processed into viscose. In fact, when no NaOH is used high reactivity pulp is obtained (>90 %), showed by the triangle in Figure 17.a. As a result, the addition of NaOH in the PO stage might be eliminated, reducing the quantity of chemicals used, in the bleaching process, and economic and environmental impacts.

The effect of H₂O₂ is shown in Figure 17.b. In the PO stage reactivity increases initially until 30 kg/ADT, further increasing the dosage of H₂O₂ lead to low reactivity values, even below inlet pulp values. H₂O₂ degrades the cellulose chain making it more accessible for chemicals to react, as a result of the degradation of the surface of the fibrils (Strunk 2012). Although further increasing H₂O₂ dosage might lead to good reactivity, low viscosity values, below 400 mL/g are obtained, which are undesirable. In fact, at 50 kg/ADT and 80 kg/ADT, good reactivity values are obtained; however, viscosity values were 328 mL/g and 295 mL/g respectively, leading to low-quality viscose.

The effects of time and temperature on reactivity are shown in Figures 17.c and 17.d, respectively. Time has a similar effect on both bleaching stages, in the EOP stage when time is below 50 min, there is no increase of reactivity; however, residence times higher than 50 min caused reactivity increases up to 81 % to remain constant for higher reaction times (higher than 100 min).

For the PO stage kinetics are faster than for EOP stage. In fact, below 40 min reactivity reaches a nearly constant value to increase when time is set to 210 min. In regards to temperature, it has a positive effect on reactivity on both stages. In the EOP stage, reactivity does not increase until temperature

reaches a value higher than 100 °C to reach the equilibrium at 130 °C, meaning that further increasing temperature would not increase reactivity. The pulp in the PO stage behave differently, reactivity remains constant until 110 °C, and increasing temperature increases reactivity up to a value higher than 90 % at 140 °C. However, when the temperature is higher than 140 °C reactivity decreases. This effect is produced by the degradation of hemicelluloses (Kolar 1997). Besides, a research study stated that at studied temperatures, some of the glycosidic bonds are broken, thus pentosan content increases (Sixta 2006). Pentosans react with NaOH used in the production of viscose and compete with cellulose.

Figure 18 shows the influence that the operating conditions: NaOH and H₂O₂ dosages, time, and temperature, both for the EOP and PO stages have on the pentosan content.

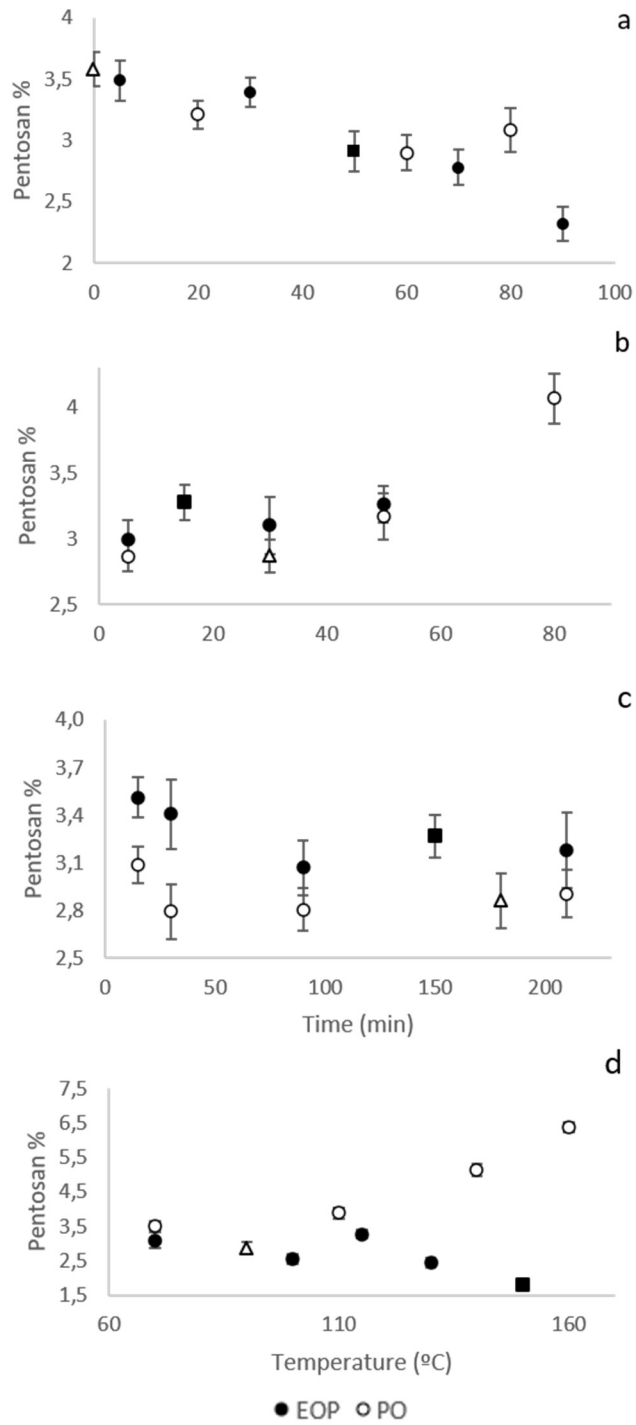


Figure 18 Influence of the process variables on pentosan content: a) NaOH dosage (kg/ADT), b) H₂O₂ dosage (kg/ADT), c) time (min) and d) Temperature (°C)

As shown in Figure 18.a, pentosan content decreases with the addition of NaOH since hemicellulose and pentosan are known to be dissolved by NaOH. In the PO stage, pentosan content decreases with the addition of NaOH until 60 kg/ADT are used, where it reaches a minimum of 2.98 %. Pulp quality requires pentosan content to be below 4 % (FZ/T 51001-2009), therefore it is in accordance within the range studied. Figure 18.b shows the evolution of the pentosan content with the H₂O₂. In the EOP stage, pentosan content increases because H₂O₂ reacts with hemicelluloses, thus liberating pentosan that cannot be dissolved by NaOH. However, in the PO stage, this parameter remains constant until 30 kg/ADT, and it increases for higher dosages. It must be noted that when varying H₂O₂ dosage, NaOH was not used; therefore, the pentosan liberated by the action of hydrogen peroxide could not be dissolved.

Pentosan content has a similar trend, in both stages, decreasing initially until reaching a constant value, however kinetic is different between each other. On the one hand, in the EOP stage, the equilibrium is achieved for reaction times lower than 100 min and, on the other hand, for the PO stage, the equilibrium is achieved at a reaction time of 30 min; therefore, pentosan kinetics in the PO stage are faster than in EOP stage.

Temperature has nearly no effect on pentosan content in the EOP stage; however, in the PO stage, the trend changes significantly for temperatures higher than 120 °C. Pentosan content increases up to 6.38 %, which is undesirable for pulp quality to be transformed into viscose. Hemicellulose released by the effect of temperature, cannot be removed because no NaOH was used in these experiments. Therefore, it is recommended that in the PO stage, the temperature below 120 °C to be used.

Reactivity is higher in the PO stage than in the EOP stages. This agrees with the configuration of the bleaching sequence studied since the PO stage is the last one in the industrial process. Therefore, the bleaching process has a positive effect on pulp reactivity. However, this is not enough for pulp to be suitable for viscose production. α -cellulose, pentosan content and viscose, need to meet specific values. Additionally, the reactivity of pulp in the EOP stage cannot be increased to meet the required values for viscose purposes; therefore, to obtain pulp to be transformed into viscose, both stages are needed.

To decide which operating variable affected pulp quality the most, a statistical analysis was performed with Stat Graphics Centurion XVII.II. Figure 19 and 20 show the response surface obtained with the information provided by the program.

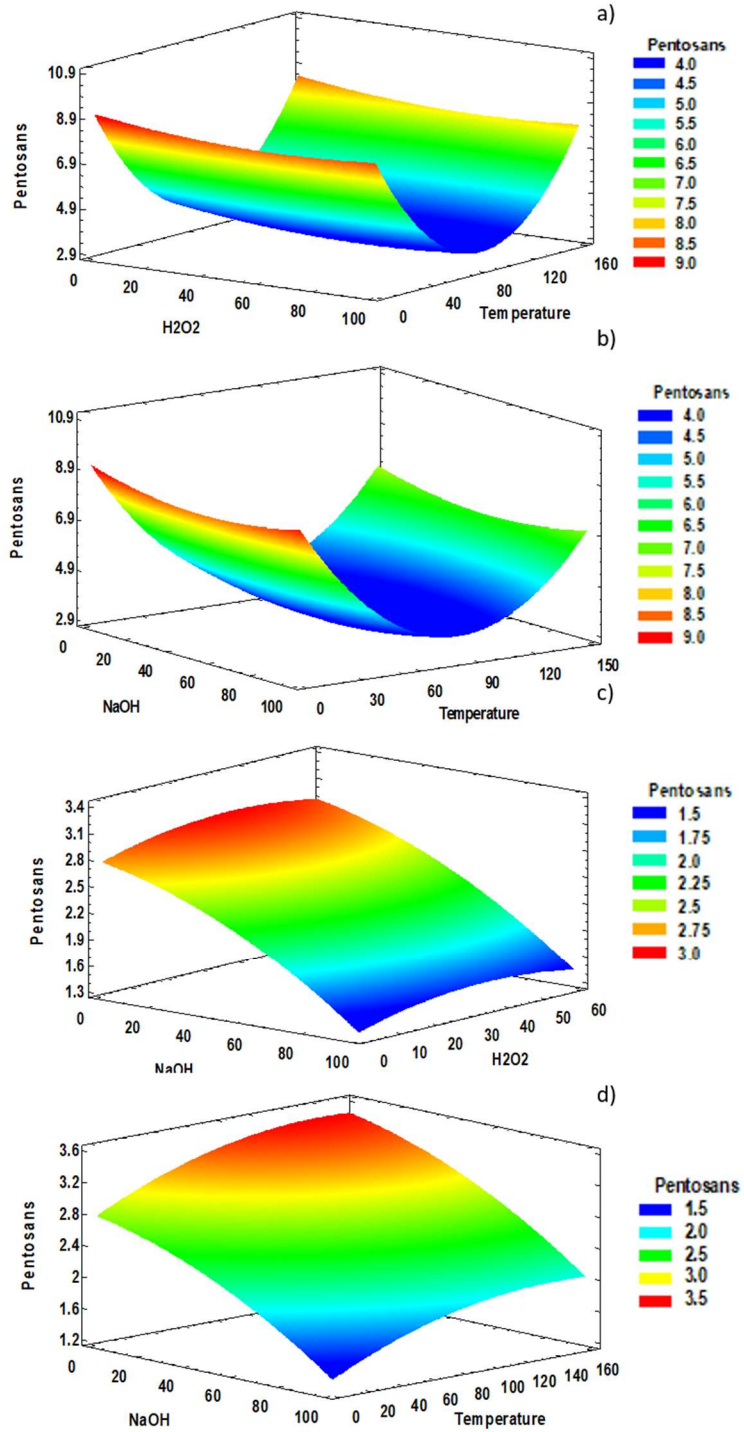


Figure 19 Response surfaces of the most affecting variables vs pentosan: a), b) PO stage and c), d) EOP stage

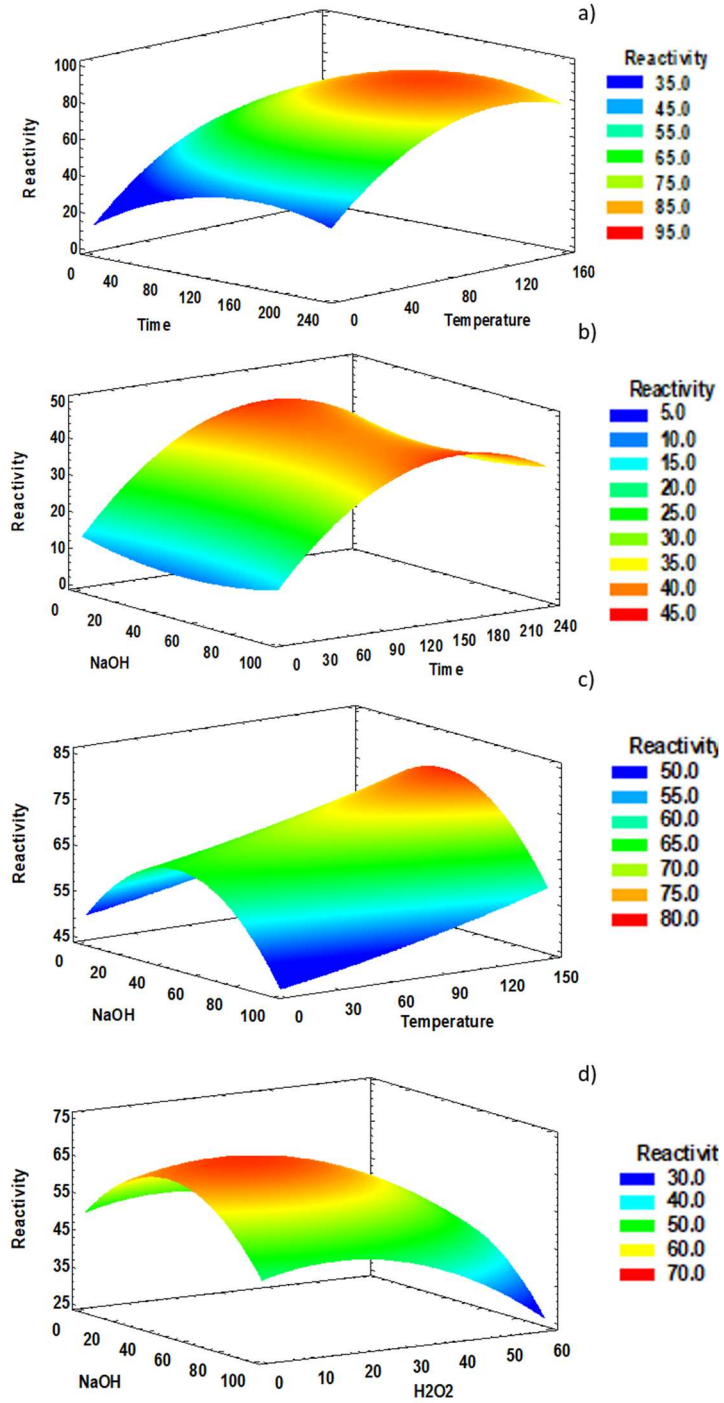


Figure 20 Response surfaces of the most affecting variables vs reactivity: a), b) PO stage and c), d) EOP stage

Regarding the PO stage, the variables that affect the most the pentosan content are temperature, H_2O_2 and NaOH dosages (Figures 19.a and 19.b). As stated before, pentosan content needs to be as lower as possible, so the blue range is the area for good pentosan content values. Therefore, mild conditions, regarding temperature, are recommended, since the pentosan content remains low (4 %). This shows that the degradation reaction of pentosan is temperature-dependent. Figure 19.b shows the evolution of pentosan with NaOH dosage and temperature, the low temperature has no significant effect on pentosan content, however, combined with increasing dosages of NaOH pentosan content reduces to a minimum of 4 %, represented by the blue surface. Increasing temperature further leads to an increase in pentosan, but it degrades cellulose so much that NaOH cannot eliminate the released pentosan from hemicellulose.

Figures 20.a and 20.b show the dependence of reactivity with: time, temperature and NaOH, in the PO stage. Reactivity values need to be as high as possible; recommended values have not been found on bibliography, however commercial dissolving pulp has about 70 % reactivity (Wang et al. 2014), so recommended values should be chosen following this condition. As can be seen in Figure 20.a, mild to high-temperature conditions are recommended, as reactivity higher than 90 % can be achieved, shown by the red area. Regarding NaOH dosage, reactivity above 45 % cannot be achieved; this fact shows that NaOH does not affect reactivity as much as the temperature does. The residence time of the process should be established at between 120 min and 180 min.

Regarding the EOP stage, Figures 19.c and 19.d represent the variation of the pentosan content with temperature, NaOH and H_2O_2 dosages. On the one hand, pentosan decreases while increasing NaOH dosage, since pentosan and hemicellulose are known to be dissolved by NaOH. On the other hand, pentosan content increases while increasing H_2O_2 dosage. However, when both compounds are added to the reactor, pentosan decreases (blue area). Figure 19.d shows the effect of both NaOH dosage and temperature. High temperature degrades cellulose and hemicellulose, releasing pentosan from the pulp. In fact, even adding up to 100 kg/ADT, does not reduce pentosan content, as is it shown by the green area. The recommended values are the ones which belong to the dark blue area; however, the temperature needs to be at least 100 °C, because some reactions are activated by temperature.

Figures 20.c and 20.d, show the change of reactivity with the most affecting variables in the EOP stage: temperature, NaOH and H_2O_2 dosage. As can be

seen, by Figure 20.c, high and low NaOH dosages result in low reactivity values, shown by the blue areas. At around 50 kg/ADT, reactivity reaches a value of 65 %, represented by the light green area. Increasing temperature, increase reactivity further, up to around 80 %, represented by the red area. Figure 20.d shows the influence of the chemical compounds used in the bleaching sequence. As stated before, low, and high NaOH dosages, result in low reactivity values around 50 %, represented by the green area. Mild dosage of NaOH is recommended in this stage about 50 kg/ADT. H₂O₂ dosage is recommended to be low, at about 15 kg/ADT, represented by the red area. Increasing the dosage further leads to low reactivity. The dosage of the reactants (H₂O₂ and NaOH) were the most affecting variables for both reactivity and pentosan content. In a previous study performed in this thesis, chemical dosages were the most affecting parameters as well.

Therefore, the recommended values of NaOH and H₂O₂ dosages would be 50 kg/ADT and 15 kg/ADT. Table 9 shows the values of the recommended operating conditions for these bleaching stages.

Table 9 Recommended operating conditions for the EOP and PO stages, respectively.

Variable	Recommended value (EOP)	Recommended value (PO)	Units
NaOH dosage	50	0	kg/ADT
H₂O₂ dosage	15	30	kg/ADT
Time	150	180	min
Temperature	150	90	°C

Recommended values by this work are different from the values used in the industry, which cannot be shown because they are confidential. The main difference from industrial operating conditions is that in the PO stage, NaOH is used; however, as can be seen in Table 9, recommended NaOH dosage in this stage is zero. It should be noted that operating conditions in the industry are sometimes adjusted, because the raw material is heterogeneous, regarding its properties. Therefore, pulp properties will also be different.

4.2.2. CS₂ consumption after bleaching

CS₂ is one of the leading chemical compounds used in the viscose industry. This compound is used in the xanthation stage to dissolve alkali cellulose, which results in viscose, which will be later transformed in viscose fiber or rayon. The quantity of this compound used in the industry ranges from 32 % to 34 % w/w of cellulose (Gondhalekar et al. 2019b). The use of this compound needs to be controlled and, if possible, reduced, due to the environmental issues (Östberg et al. 2012). Table 10 shows the CS₂ consumption in the PO stage. Negative values mean that the consumption of CS₂ is higher when compared with commercial values. The calculation is done with Equations 10, 11 and 12.

Table 10 CS₂ consumption in the PO stage.

Experiment	NaOH-kg/ADT H ₂ O ₂ -kg/ADT Time-min Temperature-°C	α-cellulose (%)	Reactivity (%)	CS ₂ (%)	TF (%)	RCF	CS ₂ reduction (%)
Commercial	-	91.52	83.98 ± 6.47	21.51	76.85	0.28	-
PO 1.1	0/0/180/90	88.51	97.35 ± 1.53	20.80	86.16	0.24	13.74
PO 1.2	20/0/180/90	92.02	84.63 ± 5.48	21.62	77.88	0.28	0.770
PO 1.3	60/0/180/90	90.81	85.37 ± 6.02	21.34	77.52	0.28	1.630
PO 1.4	80/0/180/90	92.68	85.07 ± 6.10	21.78	78.84	0.28	1.280
PO 4.1	0/5/180/90	88.58	78.33 ± 3.43	20.82	69.38	0.30	-7.210
PO 4.2	0/30/180/90	91.17	95.3 ± 0.46	21.42	86.89	0.25	11.88
PO 4.3	0/50/180/90	86.87	96.57 ± 1.37	20.41	83.89	0.24	13.04
PO 4.4	0/80/180/90	83.07	90.43 ± 4.80	19.52	75.12	0.26	7.130
PO 2.1	0/30/15/90	91.40	56.02 ± 0.46	21.48	51.20	0.42	-49.91
PO 2.2	0/30/30/90	91.30	81.89 ± 4.85	21.46	74.77	0.29	-2.550
PO 2.3	0/90/90/90	91.75	85.42 ± 3.79	21.56	78.37	0.28	1.690
PO 2.4	0/30/210/90	88.19	93.53 ± 5.26	20.72	82.48	0.25	10.21
PO 3.1	0/30/180/70	89.62	79.32 ± 5.73	21.06	71.09	0.30	-5.870
PO 3.2	0/30/180/110	89.40	77.21 ± 5.47	21.01	69.03	0.30	-8.770
PO 3.3	0/30/180/140	89.74	96.89 ± 1.44	21.09	86.95	0.24	13.33
PO 3.4	0/30/180/160	89.81	89.94 ± 4.35	21.11	80.78	0.26	6.630

CS₂ consumption is calculated considering, not only the reactivity but also the α-cellulose content. It can be noted that the consumption is lower when operating conditions are more severe. This is explained because reactivity increases when the pulp is more degraded. The operating conditions chosen as the best, are the ones that correspond to experiment 4.2, leading to a CS₂ usage reduction of 11.88 %. This is not the higher reduction obtained, however pulp parameters are in accordance with FZ/T 51001-2009 norm, for viscose purposes.

A new methodology to calculate the potential reduction of CS₂ has been developed. The highest CS₂ was obtained when no NaOH was used in the PO stage

4.3. Deep Eutectic Solvents pre-treatment

Dissolving pulp is mostly used for viscose production, as it was said previously. Therefore, research focused on viscose was carried out. Reactivity was found to be one of the essential characteristics of pulp when used for viscose production. This parameter is defined as the ability of chemicals to dissolve cellulose. Therefore, additional research to improve this parameter was done. Some of the treatments found are shown in Table 11.

4.3.1. Literature research of pulp pre-treatments

Table 11 Methods of increasing Fock's reactivity

Pulp type	Treatment	Highlights	Reference
Mechanical			
Bamboo dissolving pulp	PFI Refiner	*Decrease from 240.9 s to 128 s	<i>ChaoJun et al. 2014</i>
Softwood kraft pulp	Hollander beating	Increase from 54.4 % to 68.4 %	<i>Zhou et al. 2018</i>
Hardwood PHK dissolving pulp	Grinding	Increase from 49.27 % to 71.75 %	<i>Tian et al. 2014b</i>
	PFI refiner	Increase from 49.27 % to 58.32	
Enzymatic			
Hardwood PHK dissolving pulp	Cellulase	Increase from 48.9 % to 85.6 %	<i>Duan et al. 2017b</i>
Eucalptus kraft pulp	Endoglucanase	Increase from 31.5 % to 59.6 %	<i>Köpcke et al. 2008</i>
	Endoglucanase + Xylanase	Increase from 31.5 % to 70.7 %	
Birch kraft pulp	Endoglucanase	Increase from 42.1 % to 65.6 %	
	Endoglucanase + Xylanase	Increase from 42.1 % to 70.7 %	
Mixed kraft pulp	Xylanase	Pentosan reduction from 18.6 % to 6 %	<i>Kaur et al. 2016</i>
	Xylanase SEB	Pentosan reduction from 18.6 % to 7 %	
Sulfite Eucalyptus pulp	Endoglucanase	Increase from 65 % to 85 %	<i>Ibarra et al. 2010a</i>
	Endoglucanase	Increase from 65 % to 67 %	
	Endoglucanase	Increase from 65 % to 77 %	
Sulfite mixed softwood pulp	Endoglucanase	Increase from 70 % to 86 %	<i>Ibarra et al. 2010a</i>
	Endoglucanase	Increase from 70 % to 72 %	
	Endoglucanase	Increase from 70 % to 80 %	

Table 11. Cont. Methods of increasing Fock's reactivity

Pulp type	Treatment	Highlights	Reference
Enzymatic			
Sulfite mixed softwood pulp	Endoglucanase	Increase from 77.5 % to 90.9 %	<i>Henriksson et al. 2005</i>
Sulfite mixed softwood pulp	Endoglucanase	Increase from 70 % to nearly 100 %	<i>Engström et al. 2006</i>
Semi-bleached PHK pulp	Endoglucanase	Increase from 37.2 % to 72 %	<i>Duan et al. 2016</i>
Hardwood kraft dissolving pulp	Cellulase	Increase from 47.6 % to 87.87 %	<i>Miao et al. 2014</i>
Mixed softwood sulfite pulp	Cellulase	Increase from 67.3 % to 95.8 %	<i>Quintana et al. 2015</i>
Acid treatment			
Hardwood dissolving pulp	Phosphotungstic acid	Increase from 49.1 % to 74.1 %	<i>Wang et al. 2018</i>
Bamboo dissolving pulp	DTPA	Increase from 67.23 to 74.12 %	<i>Chen et al. 2017b</i>
Combination of treatments			
PHK hardwood dissolving pulp	PFI refiner + Phosphotungstic acid	Increase from 47.2 % to 75.8 %	<i>Duan et al. 2019</i>
PHK hardwood dissolving pulp	Cellulase + PFI Refining + PDADMAC	Increase from 41.5 % to 82.8 %	<i>Yang et al. 2018</i>
PHK hardwood dissolving pulp	PFI refining + cellulase	Increase from 75.8 % to 89.2 %	<i>Wang et al. 2020</i>
Maple kraft pulp	PFI refining + CCE + Endoglucanase	Increase from 46.7 % to 81 %	<i>Duan et al. 2016b</i>
Eucalpitus kraft pulp	CCE + Endoglucanase	**FV from 425 to 108	<i>Gehmayr et al. 2011</i>
Sisal soda/AQ pulp	CCE + Xylanase + Endoglucanase	Increase from 34.8 % to 66.2 %	<i>Ibarra et al. 2010b</i>
Eucalpitus kraft pulp	Xylanase + CCE	Increase from 31.5 % to 70.3 %	<i>Köpcke et al. 2008</i>
Birch kraft pulp	Xylanase + CCE	Increase from 42.1 % to 66 %	

Table 11. Cont. Methods of increasing Fock's reactivity

Pulp type	Treatment	Highlights	Reference
Other novel alternatives			
Softwood kraft pulp	Ultrasound	Increase from 53.3 % to 73.2 %	Zhou et al. 2019
Bamboo dissolving pulp	Electron Beam Radiation	Increase from 69.5 % to 98.3 %	Chen et al. 2017

* Reactivity measured by the Chinese filterability method

** Reactivity measured by the filtering clogging value (FV)

As can be seen from Table 11, research on increasing reactivity towards viscose production has been performed throughout the years. Increasing reactivity of pulp translates in less use of a very hazardous component used in the production of viscose, particularly in the xanthation phase, called carbon disulfide (CS₂). Lowering the impact that viscose production produces on the environment. The most used pre-treatment has been the utilization of enzymes (Henriksson et al. 2005; Engström et al. 2006; Köpcke et al. 2008; Ibarra et al. 2010a; Miao et al. 2014; Quintana et al. 2015; Duan et al. 2016b, 2017; Kaur et al. 2016). The reason behind this fact is that enzymes remove certain compounds from the pulp selectively and adjust pulp viscosity. Xylanases eliminate pentosan thus, increase the conversion of cellulose to alkali cellulose which will be later transformed in viscose. Endoglucanases degrade the cellulose chain, and as a result, the internal structure of the fibers is broken down. The degree of polymerization (DP) is reduced, and the accessibility of reagents is increased. Mechanical treatments (ChaoJun et al. 2014; Tian et al. 2014; Zhou et al. 2018) similarly affect the pulp, in the sense that they can affect both the internal and external structures of the fiber. For the internal structures, the hydrogen-bond like interactions are broken, and pores are created (Li et al. 2018a). These methods have a significant drawback in terms of costs. Enzymes are expensive and mechanical treatments are energy-consuming, therefore taking it to an industrial scale might be accessible in design but may not be cost-efficient. Acid treatment is another pre-treatment that can be performed to increase the reactivity of pulp (Chen et al. 2017b; Wang et al. 2018); however, it has not been studied thoroughly, only a couple of methods have been found. There are several reasons why acid treatment can be useful to obtain a high reactivity pulp. Firstly, acids can hydrolyze the cellulose chain and decrease the DP, making it easier for the reagents to react, acidic conditions can also hydrolyze hemicelluloses and increase the reactivity of pulp. Secondly, they can act as a chelating reagent, removing impurities such as inorganic compounds that can hinder the processability of cellulose into viscose.

Combinations of these methods can also be applied to increase the individual effects they can produce on cellulose, or to optimize the conditions of each treatment (Köpcke et al. 2008; Gehmayr et al. 2011; Duan et al. 2016a; Yang et al. 2018; Wang et al. 2020). Most of the combinations used, involve a mechanical step to improve the performance of the chemicals used in the following steps. Another method that is not used individually is the cold caustic extraction (CCE). Alkali conditions solubilize hemicelluloses and other impurities. However, the conditions of the pretreatment need to be controlled because the use of alkali, can reduce the reactivity of pulp by hornification (Li et al. 2018a). Other novel treatments have been found such as ultrasound and electron beam radiation (Chen et al. 2017a; Zhou et al. 2019), these two treatments, as well as the methods mentioned before, focus on disrupting the cellulose intra and inter interactions. While in the ultrasound pretreatment, the increase of reactivity is produced by cavitation, small bubbles formed by the ultrasounds that collapse, electron beam radiation uses the energy of an electron to destroy the uniform cellulose structure by oxidation or chain scission.

A novel alternative for pulp pretreatment was still needed, so after the research perform on pre-treatments, it was decided to use DES. One of the treatments from Table 11 used ionic liquids (IL) coupled with other methods (Yang et al. 2018). Furthermore, it was found that new green solvents have emerged, similar to IL's, called deep eutectic solvents (DES). These systems were proposed by Abbott et al. (2003), who found that mixing amides with quaternary ammonium salts form a low melting point eutectic, with solvent properties. In other words, DES are a mixture of two or more components with high melting points with a resulting melting point much lower than that of the individual components (Kumar et al. 2016), which makes DES liquid at room temperature (Procentese and Rehmann 2018). These solvents are usually composed by quaternary ammonium, phosphonium or sulfonium cation or a metal chloride (Smith et al. 2014), defined as Hydrogen Bond Acceptor (HBA) and a Hydrogen Bond Donor (HBD). Depending on the components employed to form the solvent, DES can be classified in four types (Zdanowicz et al. 2018): (1) Organic salts and metal chlorides; (2) Organic salts and metal hydrates; (3) Organic salts and organic compounds (carboxylic acids, alcohols, or amides); and (4) Metal chlorides and organic compounds (amides, alcohols). Figure 21 shows some examples of type four DES components.

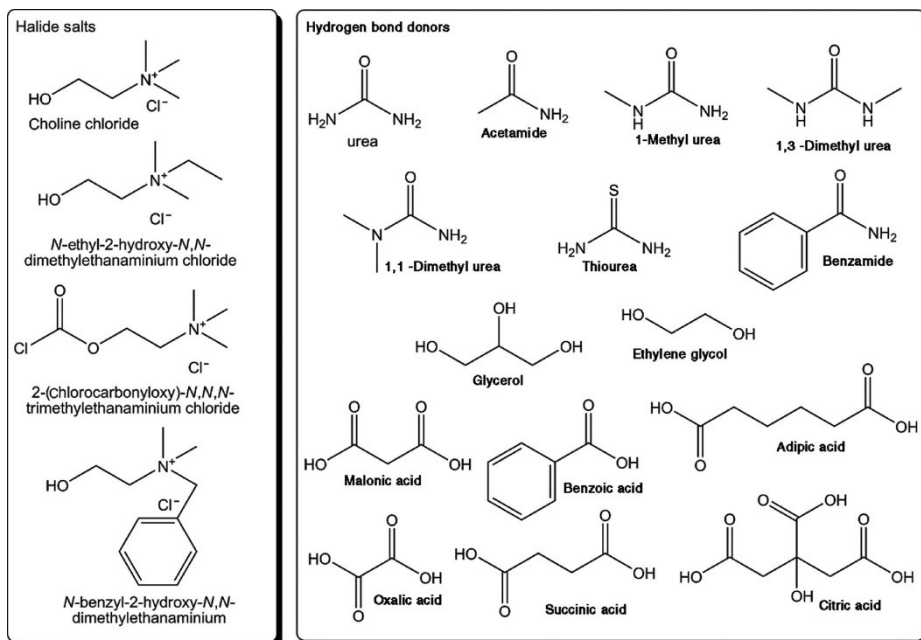


Figure 21 Examples of the compounds of type four DES (Smith et al. 2014)

These solvents have similar properties to Ionic Liquids: low vapor pressure, chemical and thermal stability, non-flammability and can be tailored (Wilpiszewska and Sychaj 2011). However, DES mixtures exhibit some advantages when compared with IL, i.e. easier to prepare, cheaper and have higher biodegradability (Ling et al. 2020). These characteristics make DES to be used in a wide range of research areas, as can be seen in Table 12.

Table 12 Application of DES on different areas

DES	Molar ratio	Highlights	Reference
Metal processing			
ChCl:Ethylene glycol	1:2	Electropolishing of stainless steel	<i>Abbott et al. 2006</i>
ChCl:Ethylene glycol ChCl:Urea	1:2	Electrodeposition of Zinc	<i>Abbott et al. 2011</i>
ChCl:Urea	1:2	Extraction of metals from oxides	<i>Abbott et al. 2005</i>
ChCl:Urea	1:2	Electrodeposition of silver	<i>Sebastián et al. 2013</i>
Biotechnology and Bioengineering			
ChCl:Urea	1:2	DES used as a catalyst for B-hydroxyfunctionalized derivatives	<i>Singh et al. 2012</i>
ChCl:ZnCl ₂	1:2	Reaction media to obtain primary amides from aldehydes and nitriles	<i>Patil et al. 2017</i>
ChCl:Urea	1:2	Substrate for deposition of gold nanoparticles	<i>Raghuwanshi et al. 2014</i>
ChCl:Polyols	1:2	Extraction media to obtain Astaxanthin from Shrimp residues	<i>Zhang et al. 2014</i>
Lignocellulosic biomass processing			
Several ChCl based DES	1:2;1:1:1	Pretreatment of rice straw for butanol fermentation	<i>Xing et al. 2018</i>
ChCl:Glycerol	1:2	Pretreatment of coffee silverskin for fermentable sugars production	<i>Procentese and Rehmann 2018b</i>
ChCl:Urea	1:2	Fractionation of rice straw	<i>Pan et al. 2017a</i>
ChCl:Malic acid	1:1	Used as cosolvent for cellulose dissolution with NMMO	Nguyen et al. 2020
	1.5:1		
	2:1		
	1:1.5		
	1:2		
ChCl:Lactic acid	1:9	Delignification of kraft pulp	<i>Majová et al. 2017</i>
ChCl:Oxalic acid	1:1		
ChCl:Malic acid	1:1		
Alanine:Lactic acid	1:9		

Some examples of the areas of application of DES are shown in Table 12: Metal processing (Abbott et al. 2005, 2006, 2011; Sebastián et al. 2013), Biotechnology and Bioengineering (Singh et al. 2012; Raghuwanshi et al. 2014; Zhang et al. 2014; Patil et al. 2017) and biomass processing (Majová et al. 2017; Pan et al. 2017b; Procentese and Rehmann 2018; Xing et al. 2018). Regarding biomass processing, the use of DES has focused on lignocellulosic materials because of their ability to dissolve lignin with the almost negligible dissolution of cellulose (Francisco et al. 2012), making biomass suitable for further

processing. However, lignin is not the only undesirable component in lignocellulosic materials. Hemicelluloses, in the form of pentosan, can hinder the processability of this kind of materials, in this sense, enzymatic treatment (Kaur et al. 2016) or alkali treatment (Kaur et al. 2017) can be used effectively. The application of DES to lignocellulosic biomass covers a wide range of steps during biomass processing: pre-treatment (Fang et al. 2017; Tommasi et al. 2017; Shen et al. 2019), delignification, (Jablonský et al. 2015; Liu et al. 2017; Chen and Wan 2018), extraction (Huang et al. 2017; Cao et al. 2019; Deng et al. 2019) and reaction media (da Silva Lacerda et al. 2015; Sert et al. 2018; Lou et al. 2019). Researches have tested several DES in biomass: Using different HBD's (Gunny et al. 2015; Ling et al. 2020); different HBA's (Francisco et al. 2012; Abdulmalek et al. 2017) or even a different kind of DES (Biswas et al. 2006; Supeno et al. 2014). For the components of the DES used in this field, Choline Chloride (ChCl) has been extensively used as HBD, due to its availability and biodegradability (Gadilohar and Shankarling 2017). Carboxylic acids such as malic acid (MA), oxalic acid (OxA) and lactic acid (LA) and amides such as urea (Ur) can be used as HBA for treatment of lignocellulosic biomass (Tan et al. 2019).

Even though DES have been used for lignocellulosic materials processing, they have not been used as pre-treatment of dissolving pulp to increase its reactivity. One of the hypotheses of this thesis is that, since DES exhibit similar properties to DES, they might increase the reactivity of pulp towards viscose, so it was decided to use them as pre-treatment with this objective. The results obtained from this treatment will be shown next.

4.3.2. Effect of DES pre-treatment on pulp quality parameters

In this work, the pre-treatment of dissolving pulp with DES to increase reactivity has been assessed. Four DES were tested: ChCl:MA, ChCl:LA, ChCl:OxA and ChCl:Ur at two different S/L ratio, 1/5 and 1/20. Intrinsic viscosity, lignin content (micro-kappa), pentosan content and reactivity of the pulp were analyzed to evaluate the effects of the pre-treatment α -cellulose content.

Table 13 shows the characterization of the samples used as raw materials for the DES treatment.

Table 13 Untreated pulp quality parameters

Pentosan (%)	Fock's reactivity (%)	α -cellulose (%)	Viscosity (mL/g)	Kappa
2.89 \pm 0.169	80.58 \pm 2.437	91.05 \pm 0.045	465.90 \pm 14.46	1.04 \pm 0.179

The parameters α -cellulose and intrinsic viscosity are shown in Figure 22, with both solid to liquid ratios.

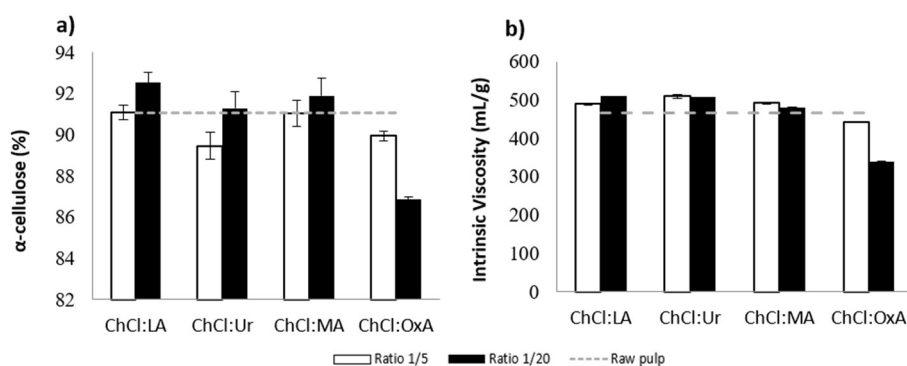


Figure 22 Evolution of a) α -cellulose content and b) intrinsic viscosity after DES treatment

At a 1/20 solid to liquid ratio, cellulose content increases slightly when the system is formed by ChCl:LA (1.65 %), ChCl:MA (0.29 %) and ChCl:Ur (0.94 %), showing that the solubility of cellulose in the DES used in this work is almost negligible as stated by Kumar et al. (2016). It should be noted that the increase in cellulose does not mean that it is a product of a chemical reaction; it means that other compounds are eliminated; thus, cellulose content is concentrated.

Viscosity also increases when using the same DES systems, as long fibers of cellulose are released. Higher viscosity values are obtained when the ChCl:LA and ChCl:Ur systems are used, reaching values of 509.25 and 507 mL/g respectively. The system ChCl:MA nearly did not affect viscosity (479.61 mL/g concerning 465.9 mL/g in the raw pulp). However, using the ChCl:OxA DES mixture both α -cellulose content (86.86 %) and viscosity (338.70 mL/g) decrease. These results are following Škulcová et al. (2016) and Zhang et al. (2020). The later studied the dissolution of cellulose when using many DES systems. It was found that ChCl:OxA lead to the higher dissolution of cellulose,

up to 2.5 % of cellulose was dissolved in OxA. In this study the dissolution of cellulose was 4.57 %; however, the system in this study was formed by 1/3 ChCl:OxA and Zhang et al. (2020) used 1/2 ChCl:OxA, therefore it is possible that increasing OxA in the mixture, might lead to higher cellulose dissolution.

Regarding the S/L ratio, also affects the dissolution of OxA significantly, since increasing the quantity of DES results in the higher dissolution of cellulose. The decrease in cellulose, significantly affects viscose, since α -cellulose includes high molecular weight chains. This effect is probably due to the H-bonds formed when using this system. At 1/5 solid to liquid ratio, cellulose content remains almost constant for all the systems used with values ranging between 91.09 % for ChCl:LA and 89.46 % for ChCl:Ur. Therefore, using a lower S/L ratio softens the effect that DES has on the pulp, in terms of α -cellulose content.

Regarding viscosity changes, the trend is very similar to that shown for a 1/20 ratio. The highest viscosity increase was obtained with ChCl:Ur and the system ChCl:OxA gave the lowest viscosity as well; therefore this system harms pulp viscosity, making it unsuitable for pulp pre-treatment for viscose purposes. Figure 23 shows the influence of DES pre-treatment on lignin content (kappa) and pentosan content.

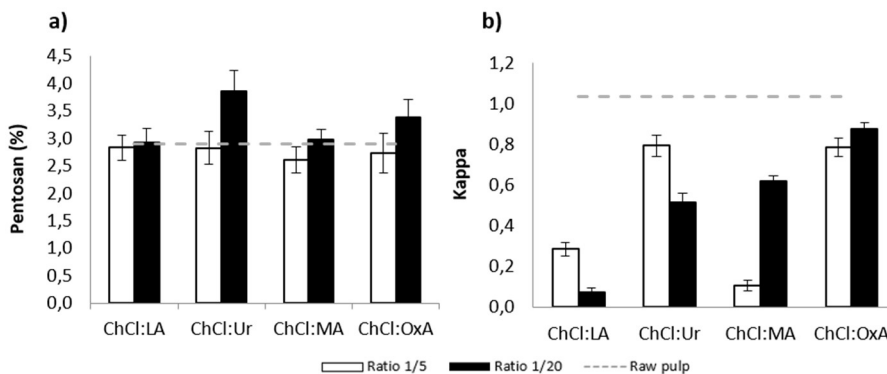


Figure 23 Evolution of a) pentosan content and b) kappa number after DES treatment

As can be seen from Figure 23.b lignin content decreases for all the DES systems and ratios tested. When a 1/20 ratio is used, the higher lignin reduction is achieved with ChCl:LA, reducing kappa number until 0.07 (91.83 % reduction). On the other hand, the lowest lignin reduction is obtained using ChCl:OxA with a final kappa value of 0.87 (3.71 % reduction). Recent studies

obtained the highest delignification with ChCl:OxA showing a kappa reduction of 38.7 % (Majová et al. 2017). However, initial lignin content had a strong influence on delignification, the lower the initial lignin, the lower the delignification. In fact, Majová et al. (2017) had a 0.8 % kappa reduction when initial kappa was 11.8. This trend is also shown in this work, with an initial kappa value of 1.16, the lignin reduction was 32.45 %. Nevertheless, initial kappa of 0.91 results in a 3.71 % lignin reduction. This trend is the same when using ChCl:MA, achieving up to 90.87 % lignin elimination when initial lignin content was higher. Taking into account the fact that the raw material of this work is dissolving pulp, ChCl:OxA is not recommended because it gives low delignifying properties, a reduction of α -cellulose and a decrease of viscosity in relation to the raw pulp. Zhang et al. (2016) used ChCl:LA, ChCl:OxA and ChCl:MA to increase the saccharification rate of corncob, achieving 86.1 %, 98.5 % and 22.4 % of lignin reduction, respectively. Procentese et al. (2015) employed ChCl:Ur in agricultural biomass giving total lignin reduction of 7.1 %. In this work, the reduction of lignin when using ChCl:Ur was in the range of 31.75 % and 43.17 % when the S/L ratio was 1/5 and 1/20, respectively.

Most of the studies focus on delignification of untreated biomass residues with higher lignin content than high-cellulose dissolving pulps such as rice residues (Kandanelli et al. 2018), corn stover (Xu et al. 2016) or potato peels (Procentese et al. 2018). Based on results obtained in this study, and comparing with the literature working with oxalic-based DES mixtures, it can be concluded that ChCl:OxA is more effective when used with high-lignin content samples than with dissolving pulps.

Pentosan content in the pulp showed in Figure 23.a, increases when a higher ratio is used. The highest increase is produced when using ChCl:Ur at a 1/20 S/L ratio, up to 3.9 %. In the bibliography studied, Zhao et al. (2018) achieved a 6 % xylan removal at a 1/5 S/L ratio whereas Tan et al. (2019) obtained 20% xylan removal when using ChCl:Ur at 1/10 S/L ratio in the same study the authors reached a 100 % xylan removal with ChCl:LA at 1/10. As happened with lignin content, pentosan content seems to be affected by the initial content. The studies mentioned before use wheat straw (21.8 % xylan content) and oil palm empty fruit bunch respectively, which have a higher amount of pentosan content than dissolving pulp. Therefore, pentosan elimination reduces as the initial pentosan content decreases. The evolution of pentosan content is not linear, since increasing the quantity of DES in the system, does not always translate on higher pentosan elimination. Morais et al. (2018) studied the effect solubilization of xylans, similar to pentosan, using DES, specifically ChCl:Ur, at different ratios and concentrations, and found out

that increasing DES quantity in the system does not lead to the same increase on xylan dissolution, the maximum extraction was obtained at 50 % DES/water concentration whereas increasing DES content to a 75 %, xylan extraction did not improve. From Table 14, which shows the yields obtained when compared with the raw pulp; negatives values imply the property decreased. , reducing DES quantity leads to a reduction in pentosan. Morais et al. 2018, employed temperatures from 70 to 90 °C, thus reducing the viscosity of DES. In this work, the temperature was kept at 60 °C; therefore, viscosity is higher. This fact might explain why 1/5 S/L ratio can extract more pentosan than 1/20 S/L ratio.

It should be noted that the raw material used in this work, has already been through several processes (cooking and bleaching) which makes pulp more accessible to reactants than the untreated material, by increasing the porosity and thus, the specific surface area (Li et al. 2018a).

The selectivity of the DES treatment towards delignification can be seen comparing Figures 22.a and 23.b. While α -cellulose content remained constant or even increased, lignin content decreased for all the DES employed. Alvarez-Vasco et al. (2016) explained this effect by the ability of DES to cleave ether bonds present in lignin. They also observed no carbohydrates dissolved in the DES. Tang et al. (2017) showed that DES exhibit strong interactions with lignin; in fact, some of the DES precipitated with the lignin extracted. Therefore, the results showed in this work, regarding lignin and cellulose content, agree with the bibliography studied.

Table 14 Yields, in %, obtained referred to the raw pulp

S/L ratio	α -cellulose		Intrinsic Viscosity		Pentosan		Kappa	
	1/20	1/5	1/20	1/5	1/20	1/5	1/20	1/5
ChCl:LA	1.65	0.01	6.95	7.17	5.55	-6.08	-91.83	-75.47
ChCl:Ur	0.29	-1.78	6.47	11.63	38.99	-6.28	-43.17	-31.75
ChCl:MA	0.94	-0.08	0.72	7.81	7.42	-13.56	-31.78	-90.87
ChCl:OxA	-4.57	-1.25	-28.87	-3.14	21.66	-9.38	-3.71	-32.45

From Table 14, some conclusions can be drawn. Regarding α -cellulose content, some DES lead to a low quantity (DES:Ur and DES:OxA), undesirable for viscose purposes. The reference values for pulp quality were obtained from the standard FZ/T 51001-2009. Regarding pentosan content, even though it increases for some systems, pentosan content never reaches 4 %, which is the

maximum value that the standard considers. Kappa is always below 1 %, and viscosity barely changes, except for DES:OxA, which leads to a 28.87 % viscosity reduction and a 4.57 % α -cellulose reduction. These results make DES:OxA unsuitable to be used as pre-treatment for viscose purposes.

Figure 24 represents the changes in reactivity with each DES and at each S/L ratio. DES effect over this parameter has never been studied before and is crucial for improving the viscose process and decrease the use of non-environmentally friendly reagents, i.e. CS_2 and NaOH. Error bars have been added in the Figure. These errors are based on standard deviation and are lower than 10 for every analysis.

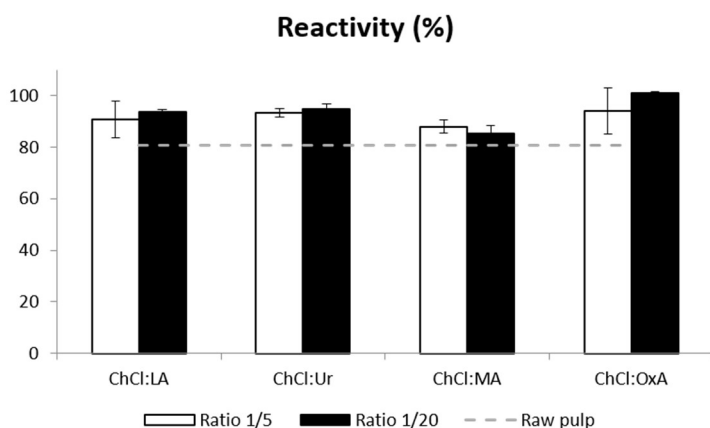


Figure 24 Evolution of reactivity after DES treatment

Reactivity increases for all the DES employed. The best results were obtained using an S/L ratio of 1/20, except for ChCl:MA. The highest increase of reactivity was produced using ChCl:OxA at a 1/20 ratio, however, as stated before, this DES will not be considered as the best, because pulp after the treatment does not have enough quality to be considered suitable for viscose purposes. Tian et al. (2020), stated that the hydrogen bonding abilities of DES could swell cellulose and as a result, increase reactivity, which agrees with this work. No literature has been found about the use of DES to increase reactivity. Previous works have used different lignocellulosic materials to increase their accessibility to chemicals, i.e. several authors used DES for glucose release from cellulose (Nor et al. 2016; Xu et al. 2016; Xing et al. 2018).

Nevertheless, such behavior had not been determined. Regarding reactivity towards viscose, several authors have used different methods to upgrade

cellulose pulp, recently. Duan et al. (2019) used mechanical and chemical treatments simultaneously to increase reactivity up to 83.5 % while reducing viscosity to 411 mL/g. Zhou et al. (2019) performed an ultrasonic pre-treatment to increase Fock's reactivity by breaking H-bonds through cavitation. This treatment leads to a reactivity value of 73.2 % with nearly no changes on viscosity. Similar effects occurred in this study, since DES barely changed viscosity, except for ChCl:OxA. Sango et al. (2018) used an enzymatic treatment and obtained a resulting pulp with a Fock's reactivity of 77.4 % with a small decrease in viscosity. As an alternative, it was proposed to increase Fock's reactivity through bleaching, instead of using pre-treatments. As a result, bleaching operating conditions were adjusted, and Fock's reactivity was improved to 95.3 % with a viscosity of 448 mL/g. In this study, DES pre-treatment was proved to be an exciting alternative, since Fock's reactivity was increased up to 93.7 % when using ChCl:LA with minor changes on viscosity.

4.3.3. XRD spectra and effect on crystallinity index

Since the best results were obtained when using a 1/20 S/L ratio, XRD of the resulting and untreated pulps were performed to explain this modification in cellulose reactivity. Figure 25 shows the XRD for treated and untreated pulp using 1/20 pulp to DES ratio.

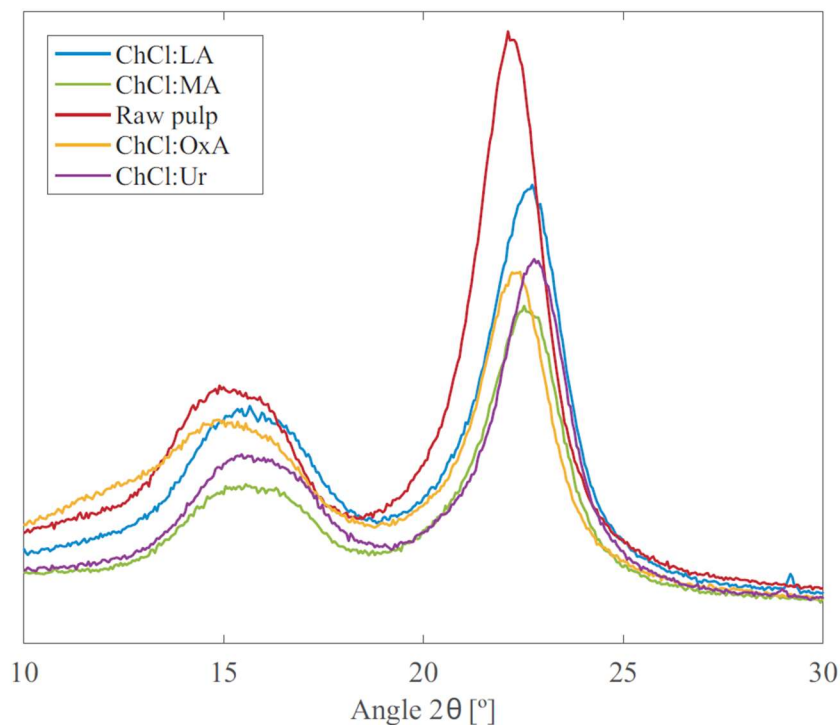


Figure 25 XRD spectra of pulp before and after DES treatment

XRD spectra show the typical shape associated to cellulose I, with a broad peak at 2θ between 12° and 18° and a maximum at around 22° (Li et al. 2012), which correspond to the planes $\bar{1}10$, 110 and 200 (Sirviö et al. 2015). After DES treatment, the structure of cellulose remains intact, and the intensity of both peaks is reduced after the treatment. No cellulose II is formed because there are no peaks at 20° and 22° , which are characteristic of cellulose II (Hori and Wada 2006). To assess the influence of the reduction of the intensity, a crystallinity index (CrI) for each pulp was calculated following the Segal method. This method was chosen because it gave results easily comparable with other samples (Segal et al. 1959; Park et al. 2010). Table 15 shows the results obtained.

Table 15 Crystallinity indexes for untreated and DES-treated pulps

	Raw pulp	ChCl:MA	ChCl:LA	ChCl:OxA	ChCl:Ur
CrI (%)	79.09	71.63	70.23	65.8	70.63

The CrI of the pulps were calculated using Equation 13. As can be seen from Table 15, CrI of pulp decreases after treatment with DES, making pulps more accessible for subsequent reagent or enzymatic attacks and therefore more reactive. The highest decrease in crystallinity is obtained with ChCl:Ox. Interestingly, the treatment with ChCl:Ox also resulted in the lowest viscosity. This decrease was produced by the decrease of the amorphous and crystalline regions, as proposed by Kumar et al. (2016), who found a decrease in the CrI of rice straw when treated by ChCl:LA system. Gondhalekar et al. (2019a), proposed that the reduction of crystallinity is caused by the weakening of the hydrogen bonding (Gondhalekar et al. 2019a). Procentese et al. (2015) found a slight decrease, as well, in the crystallinity index of corncob when treated with ChCl:Urea system (Procentese et al. 2015). Additionally, a linear relationship between CrI and reactivity was found as represented in Figure 26. Looking at Figure 26, for reactivity values ranging between 75 and 100 %, the higher the crystallinity, the lower the reactivity.

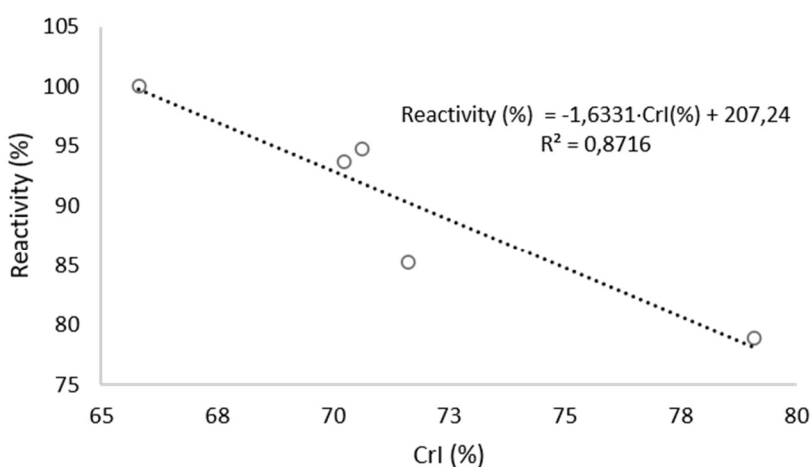


Figure 26 Relationship between reactivity and CrI

4.3.4. CS₂ consumption after DES treatment

Carbon disulfide is a critical compound in the manufacture of viscose fiber and environmental wise, one of the most concerning. CS₂ consumption was calculated, as stated in section 4.2.2. This calculation considers the α -cellulose content and Fock's reactivity, to measure the theoretical quantity of fibers, and the stoichiometric quantity of CS₂, used in the xanthation phase to

calculate the quantity used of this compound, described by Gondhalekar et al. (2019b). Finally, a ratio between the CS₂ usage and the theoretical fibers was obtained. The reduction was assessed using the untreated pulp (raw pulp) as reference. Results are shown in Table 16. DES treatment reduces the usage of CS₂ for every system.

Table 16 CS₂ consumption after DES treatment at a ratio of 1/20

Treatment	α -cellulose	Fock's reactivity(%)	CS ₂ (%)	TF(%)	RCF	CS ₂ reduction (%)
Raw pulp	91.02	78.86	21.4	71.8	0.30	-
ChCl:LA	92.52	93.70	21.7	86.7	0.25	15.83
ChCl:Ur	91.28	94.81	21.5	86.5	0.25	16.82
ChCl:MA	91.88	85.18	21.6	78.3	0.28	7.416
ChCl:OxA	86.86	100.00	20.4	86.9	0.24	21.14

The DES that gave the highest reduction of CS₂ usage was ChCl:OxA, even though α -content was the lowest, meaning that reactivity has a more substantial influence on CS₂ than α -cellulose content.

Modifying the operating conditions of the bleaching stage of dissolving pulp, obtained lower reductions, with a maximum reduction of 13.74 %. So, DES pre-treatment can be an excellent alternative to increase the reactivity of dissolving pulp and decrease the CS₂ in the process of viscose fiber manufacturing.

ChCl:LA at a 1/20 S/L ratio was considered as the best pre-treatment among the experiments performed. The authors would like to remark that the best DES treatment depends significantly on the objective of the research, i.e. Zhang et al. (2016) found that ChCl:OxA was the best for butanol fermentation and saccharification Kumar et al. (2016) chose ChCl:Glycerol. Regarding lignin elimination and mechanical properties of pulp, Škulcová et al. (2016) found ChCl:MA as the best, whereas Xu et al. (2016) selected ChCl:Formic acid as the best for lignin elimination and Abdulmalek et al. (2017) determined that Ethylamonium ethylene glycol as the best for both lignin and hemicellulose removal.

Even though reactivity is not the highest obtained with ChCl:LA, the results obtained using this configuration are following the pulp quality standards of

FZ/T 51001-2009 for viscose purposes. It should be noted that the decrease in crystallinity can affect not only to CS₂ consumption but also to NaOH consumption, since accessibility increases when crystallinity decreases (Gondhalekar et al., 2019b).

Depending on the DES pre-treatment crystallinity is reduced and Fock's reactivity is increased

5. Conclusions

The conclusions obtained from the different studies performed throughout this thesis will be shown. They will be organized in the same order as the results.

A multivariate statistical analysis was carried out to determine the main process variables affecting the quality of the dissolving pulp during EOP-PO bleaching of the Z-EOP-PO bleaching sequence. The second-order response surface models developed from the factorial experiments for each bleaching stage fitted the pulp's bleaching behavior very well with the coefficient of determination (R^2) values between 88.8% and 98.7%.

Dosages of NaOH and H_2O_2 were the most influential variables of EOP stage, whereas reaction time and reaction temperature were the influential variables for PO stage (except for intrinsic pulp viscosity where time and H_2O_2 dosage were the most influential variables).

Three dissolving pulp grades were considered in the cost optimization of EOP-PO partial bleach sequence: one regenerated cellulose product (viscose) which is the most widely commercialized worldwide; and two novel products: nanocrystalline cellulose (NCC) and nanofibrillated cellulose (NFC), which are currently being investigated. A software program (GAMS) was used to obtain an optimization solution to the non-linear problem developed that had equations describing the chemical and energy costs of EOP-PO partial bleach sequence. GAMS optimization of the three pulp grades indicated cost saving to the pulp mill of 62.2%, 73.4%, and 63.3% for producing viscose, NCC, and NFC grades, respectively.

High NaOH dosage leads to low reactivity values. At the recommended operating conditions values, reactivity can increase up to 95.3 % leading to a reduction of CS_2 usage reduction of 11.88 %. The most affecting operating conditions to reactivity in the EOP stage are, NaOH dosage and temperature and in the PO stage are time and temperature. Regarding pentosan content, in the EOP stage, NaOH and H_2O_2 are the most affecting conditions and in the PO stage are H_2O_2 and temperature. From this study, it can be concluded that the two bleaching stages are needed in order to obtain a good pulp quality. However, both of these can be improved according to this paper to the following recommended values: in the EOP stage, NaOH dosage 50 kg/ADT; H_2O_2 15 kg /ADT; 150 min; 150 °C and in the PO stage, NaOH dosage 0 kg /ADT; H_2O_2 30 kg /ADT; 180 min; 90 °C. Pulp obtained at the best conditions had the following characteristics: α -cellulose content, 91.17 %; intrinsic viscosity, 448 mL/g; kappa number, 1.81; reactivity, 95.3 % and pentosan content 2.86 %.

The use of DES as a pre-treatment of dissolving pulp increases its reactivity together with other pulp parameters was assessed in this work. As a result, it was concluded that DES used in this research, increase the reactivity of pulp and reduce the crystallinity index.

Additionally, a relationship between reactivity and this index was obtained. The highest increase of reactivity was obtained with ChCl:OxA, however, other quality parameters of the pulp were not suitable for viscose purposes. Lactic acid with choline chloride at a 1/20 ratio is recommended in this work. At these conditions, reactivity increased up to 93.70 %, reducing the CS₂ usage by 15.83 %. Treated pulp had the following characteristics: 92.50 % of α -cellulose, a kappa number of 0.07, an intrinsic viscosity in mL/g equal to 509.25, pentosan content of 2.93 %, with a crystallinity index of 70.20 %.

A method to calculate the CS₂ reduction for dissolving pulp to be used for viscose production, using α -cellulose content and Fock's reactivity has been developed

As future work and with the knowledge acquired from this research, an optimization of the DES pre-treatment can be performed to find the most suitable operating conditions to obtain the best quality for the pulp. Furthermore, the use of DES pre-treatment on different parts of the bleaching process can also be considered, to observe if it would be possible to replace bleaching stages for DES pre-treatment or reduce the consumption of chemicals during said process.

6. Conclusiones

En este apartado se mostrarán las conclusiones obtenidas a partir del análisis de los resultados de la investigación realiza. Estarán dispuestos de la misma manera que los resultados.

Se llevó a cabo un análisis estadístico multivariable para determinar las variables que más afectan a la calidad de pasta *dissolving* durante las secuencias EOP y PO correspondientes a un blanqueo TFC con secuencia global: Z-EOP-PO. Los modelos de superficie de respuesta de segundo orden desarrollados a partir de un diseño de experimentos factorial para cada etapa de blanqueo se ajustan adecuadamente al comportamiento del blanqueo de la pasta con valores del coeficiente de regresión (R^2) entre 88,8 % y 98,7 %.

Las variables que más afectan a la calidad de pasta en la etapa EOP son la carga tanto de NaOH como de H_2O_2 , mientras que el tiempo de residencia y la temperatura de reacción son las que más incidencia tienen en la calidad de pasta en la etapa PO (con la excepción de la viscosidad que se ve más afectada por el tiempo de residencia y la carga de H_2O_2).

Para la optimización de costes, se consideraron tres escenarios diferentes: Viscosa, celulosa nanocrystalina (NCC) y celulosa nano fibrilada (NFC). El software de optimización GAMS fue empleado para encontrar la solución del sistema de ecuaciones no lineales desarrollado en esta investigación. Estas ecuaciones expresan los costes asociados a los reactivos y la energía empleados. La optimización de estos costes dio como resultado una reducción de costes del 62,2 %, 73,4 % y 63,3 % para la producción de viscosa, NCC y NFC, respectivamente.

Emplear cargas elevadas de NaOH en el proceso de blanqueo da como resultado una reducción de la reactividad de la pasta *dissolving*. Con las condiciones de operación recomendadas, la reactividad puede aumentar hasta alcanzar el 95,3 %, lo que da como resultado una reducción en el uso del CS_2 del 11,88 %. Las variables que más influencia ejercen sobre la reactividad en la etapa EOP del blanqueo son la carga de NaOH y la temperatura, y en la etapa PO son tiempo y temperatura. En cuanto al contenido en pentosanos, en la etapa EOP NaOH y H_2O_2 , son las condiciones de operación que más afectan, y en la etapa PO son H_2O_2 y temperatura. Del estudio realizado se puede concluir que las dos etapas de blanqueo son necesarias para obtener una calidad de pasta aceptable. Sin embargo, ambas etapas pueden mejorar la calidad de la pasta con las recomendaciones siguientes: en la etapa EOP,

carga de sosa 50 kg/ADT; carga de H₂O₂ 15 kg/ADT, 150 min, 150 °C y en la etapa PO, carga de sosa 0 kg/ADT; carga de H₂O₂ 30 kg/ADT; 180 min, 90°C. Los parámetros de calidad de pasta obtenidos con las mejores condiciones de operación fueron los siguientes: contenido en α -celulosa, 91,17 % viscosidad intrínseca, 448 mL/g; número kappa, 1,81; reactividad, 95,3 % and contenido en pentosanos 2,86 %.

El uso de los DES como pretratamiento de la pasta *dissolving* aumenta la reactividad además de las otras propiedades de pasta consideradas. De manera que se puede concluir que el empleo de los DES aumenta la reactividad y disminuye la cristalinidad de la pasta.

Adicionalmente, se encontró una relación entre la reactividad y el índice de cristalinidad. El empleo del sistema ChCl:OXA, dio como resultado el mayor incremento en la reactividad, sin embargo otros parámetros de calidad de pasta no estaban dentro del rango de valores adecuados para el uso de ésta en producción de viscosa. El sistema ChCl:LA, con un ratio de 1/20, es el que se recomienda emplear a la vista de los resultados. A estas condiciones, la reactividad aumenta hasta el 93,7 %, reduciendo el consumo de CS₂ un 15,83 %. La pasta después del tratamiento con el sistema mencionado tenía las siguientes características: contenido en α -celulosa, 92,50 % viscosidad intrínseca, 509,25 mL/g; número kappa, 0,07; and contenido en pentosanos 2,93 %, con un índice de cristalinidad del 70,20 %.

En este trabajo se ha desarrollado un método para el cálculo de la reducción teórica del CS₂ en la producción de viscosa a partir de pasta *dissolving*. Este método emplea el contenido el α -celulosa y la reactividad de Fock.

Como trabajo futuro y con el conocimiento adquirido en esta investigación, se puede obtener una optimización del pretratamiento de pasta *dissolving*, para encontrar las mejores condiciones de operación posibles para la obtención de la mejor calidad de pasta. Además, se podría considerar el empleo de los DES en diferentes partes del blanqueo, para estudiar la sustitución de alguna de las etapas del proceso o la reducción del consumo de reactivos durante el proceso de blanqueo.

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8. Dissemination of results

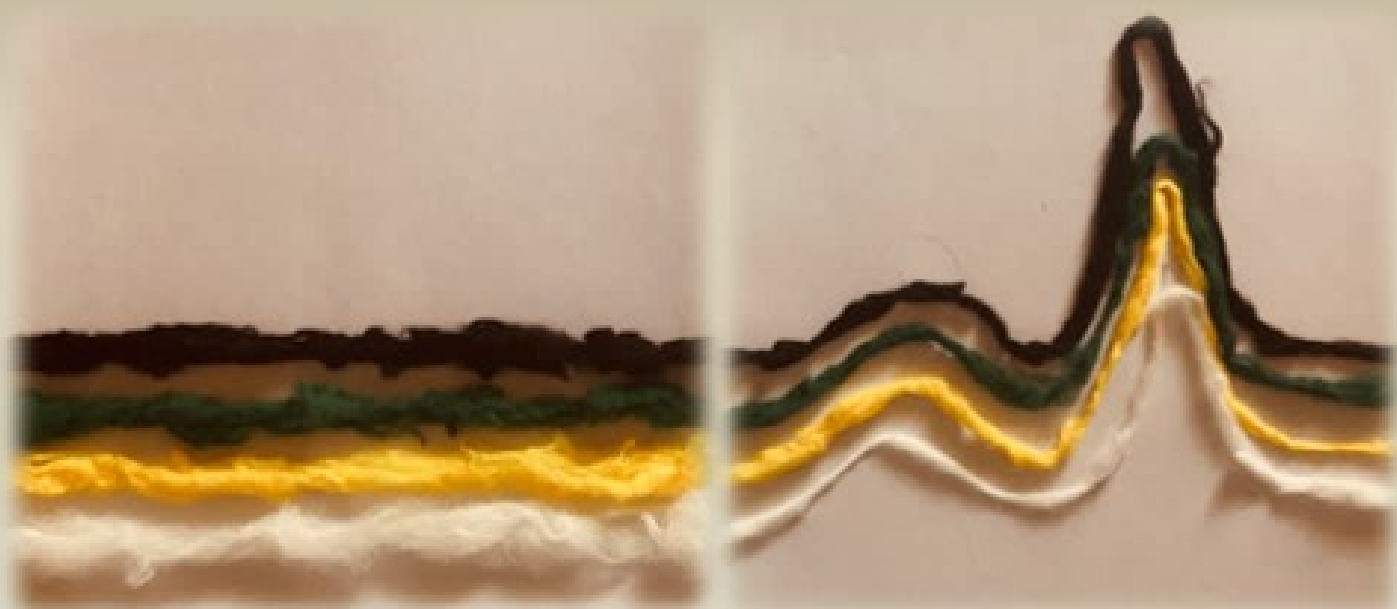
Scientific papers that were published while this thesis was being done and that are directly related to it, are listed next:

- 1 Llano T, Arce C, Ruiz G, et al. (2018) Modelling and optimization of the last two stages of an environmentally compatible TCF bleaching sequence. *BioResources* 13:6642-6662.
- 2 Arce C, Llano T, García P, Coz A (2020) Technical and environmental improvement of the bleaching sequence of dissolving pulp for fibre production. *Cellulose*. <https://doi.org/10.1007/s10570-020-03065-1>
- 3 Arce C, Llano T, González S, Coz A (2020) Use of green solvents as pre-treatment of dissolving pulp to decrease CS₂ consumption from viscose production. *Cellulose*. <https://doi.org/10.1007/s10570-020-03465-3>

Oral presentations and posters sent to International Congresses will be listed next:

- 1 Arce C, Llano T, Dacuba J, Andrés A, Coz A. Characterization of dissolving pulp to assess its use as reinforcement on construction materials. 10th International Conference on the Environmental and Technical Implications of Construction with Alternative Materials. Oral Communication. Tampere, June 2018
- 2 Arce C, Llano T, Ruiz G, Chenna N, Coz A. Optimisation of a dissolving pulp bleaching sequence towards its valorisation. 7th International Conference on Engineering for Waste and Biomass Valorisation. Oral Communication. Prague, July 2018.
- 3 Arce C, Maican E, Llano T, Ferdes M, Coz A. Lignocellulosic waste pre-treatment with Deep eutectic solvents. 4th Iberoamerican Congress on Biorefineries. Oral Communication. Jaén, October 2018.
- 4 Arce C, Llano T, Coz A. Deep Eutectic Solvents Treatment of Industrial Dissolving Pulp for Viscose Production. 1st International Meeting on Deep Eutectic Solvents. Poster Presentation. Lisbon, July 2018.

- 5 Arce C, Llano T, Coz A. Cellulose reactivity enhancement by TCF bleaching and DES treatment for viscose production. 1st International Conference on Cellulose Fibres. Cologne, February 2020.



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