Universidad Pablo de Olavide

Biotecnología, Ingeniería y Tecnología Química

2017

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Cationization of cellulose from conventional and alternative raw materials for papermaking

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Cationization of cellulose from conventional and alternative raw materials for papermaking

Dissertation submitted to the Pablo de Olavide University (Seville) for the degree of Doctor of Philosophy. The thesis was developed under the supervision of Dr. Ana Moral (Pablo de Olavide University), tutor, and Dr. Antonio Tijero (Complutense University of Madrid).

Cationización de celulosa procedente de materias primas convencionales y alternativas para la fabricación de papel

Memoria depositada en la Universidad Pablo de Olavide (Sevilla) para la obtención del grado de doctor, realizada bajo la dirección de la Dra. Ana Moral (Universidad Pablo de Olavide), tutora, y del Dr. Antonio Tijero (Universidad Complutense de Madrid).

ABSTRACT

The environmental performance of the paper industry in Western countries has drastically improved over the past few decades, but manufacturers still depend on wood and on poorly biodegradable polyelectrolytes. In this dissertation, I inquire into the functionalization of cellulose from various sources to produce cationic derivatives that could partially replace those polyelectrolytes. Sources included cellulose powder, cotton linters, softwood, hardwood and different lignocellulosic residues —wheat straw, rapeseed stalks and orange tree trimmings. Commercial cellulose and linters could be cationized straightaway, while wood and waste needed chemical pulping. Specifically, residues were cooked without sulfur compounds, yielding satisfactory results both in terms of lignin removal and paper properties.

The functionalization took place by treating cellulose or a chemical pulp with (3-chloro-2-hydroxypropyl)trimethylammonium chloride and sodium hydroxide in a batch reactor, aiming to produce cationic fibers or water-soluble cationic derivatives. We (the authors of the publications) took samples at different reaction stages to model reaction kinetics. Characterization of the products involved X-ray diffraction, elemental analysis, viscosity measurements, pycnometry, infrared spectroscopy, microscopy, zeta potential measurements, and potentiometric titrations. Then, cationic fibers were added to a suspension of non-modified fibers, fines and fillers to evaluate the effects on retention and optical properties. Also, soluble derivatives were tested in a suspension of mineral fillers to study flocculation kinetics. The fillers we used were precipitated calcium carbonate, ground calcium carbonate, kaolin, and titanium dioxide.

Results from elemental analyses were successfully fitted —with correlation indices above 0.95— to pseudo-second order rate equations with two parameters. We found the values of these parameters to depend strongly on crystallinity. Decrystallization or amorphization of cellulose by an alkaline pretreatment increased the highest degree of substitution that could be reached, especially when working with refined pulps.

Regarding the applications of cationic cellulose in papermaking, our findings contributed to understand what can be improved and what cannot. A water-soluble cationic derivative enhanced the flocculation of kaolin, whose zeta potential is clearly negative, by increasing the median equivalent spherical diameter from 4 μm to 25 μm in 2 min. It surpassed the performance of a conventional cationic polyacrylamide. The addition of cationic fibers before sheet formation improved the retention of fines, lowering the losses from 0.09 to 0.02 grams of fines per gram of pulp. As a consequence, opacity increased. However, neither soluble derivatives nor insoluble fibers improved the retention of precipitated calcium carbonate. Cationic fibers had a positive effect on the

retention of titanium dioxide, which was evidenced by an increase in brightness of an unbleached pulp from 37.8% to 41.9%.

Although the degree of substitution reached for softwood fibers was as high as 0.4, the lignocellulosic residues studied reached values around 0.2, good enough for cationic fibers, under much milder conditions. The procedure with lignocellulosic residues would involve mild chemical pulping with soda or ethanolamine, refining to less than 1000 PFI revolutions, mild peroxide bleaching if desired, 60 min-long alkaline pretreatment, and an even shorter cationization stage at 70 ºC. Even if papermakers keep refusing to replace wood with non-wood materials, these residues could be reused towards value-added products that may reduce the need for hardly biodegradable polyelectrolytes.

KEYWORDS

alkalization; cationization; cellulose; elemental analysis; functionalization; papermaking; pulp; quaternary ammonium; refining; X-ray diffraction.

RESUMEN

Pese a la indudable mejora ambiental que ha experimentado la industria del papel en los países desarrollados, los fabricantes aún dependen de la madera y de polielectrolitos no biodegradables. Mi proyecto de tesis doctoral explora la funcionalización de celulosa procedente de distintas materias primas para producir derivados catiónicos que puedan reemplazar parcialmente esos polielectrolitos. Las materias primas fueron: celulosa comercial en polvo, línter de algodón, madera de pino y de eucalipto, y tres residuos lignocelulósicos: paja de trigo, tallos de colza y poda de naranjo. La madera y los residuos requirieron tratamientos químicos para eliminar la mayor parte de la lignina. La cocción de los residuos, empleando métodos alternativos sin compuestos de azufre, proporcionó resultados satisfactorios, tanto en la eliminación de lignina como en las propiedades físicas del papel.

La funcionalización tuvo lugar tratando celulosa o una pasta química con cloruro de (3-cloro-2-hidroxipropil)trimetilamonio e hidróxido de sodio en un reactor discontinuo, persiguiendo obtener fibras catiónicas o bien derivados solubles con carga positiva. Adquirimos muestras a diferentes tiempos de reacción para establecer un modelo cinético. Las técnicas de caracterización incluyeron difracción de rayos X, análisis elemental, medidas de la viscosidad y de la densidad, espectroscopía de infrarrojo, microscopía, medidas del potencial zeta y valoraciones potenciométricas. Además, realizamos ensayos de floculación, retención y formación de papel con las fibras modificadas. Los derivados solubles sirvieron para evaluar la cinética de la floculación de determinadas cargas minerales. Estas cargas fueron: carbonato de calcio precipitado, carbonato de calcio molido, caolín y dióxido de titanio.

Los resultados de los análisis elementales se ajustaron con éxito (con índices de correlación superiores a 0,95) a ecuaciones de pseudo-segundo orden con dos parámetros. Hallamos que los valores de esos parámetros dependen de la cristalinidad. La amorfización de celulosa mediante una base fuerte, especialmente con pastas refinadas, propició un aumento en el máximo grado de sustitución alcanzado.

En cuanto a las aplicaciones de la celulosa catiónica en la fabricación de papel, nuestros descubrimientos ayudaron a comprender su utilidad y sus limitaciones. Un derivado catiónico soluble mejoró la floculación de caolín, cuyo potencial zeta es negativo, aumentando su diámetro equivalente de 4 µm a 25 µm en 2 min. Este resultado fue mejor que el obtenido con una poliacrilamida catiónica convencional. Por otro lado, añadir fibras catiónicas antes de la formación del papel disminuyó las pérdidas de finos de 0,09 a 0,02 gramos de finos por gramo de pasta. Como consecuencia, la opacidad aumentó. Sin embargo, ni los derivados solubles ni las fibras modificadas aumentaron significativamente la retención de carbonato de calcio precipitado. Las fibras catiónicas

tuvieron, ahora bien, un efecto positivo sobre la retención de dióxido de titanio, evidenciado por un incremento en la blancura de una pasta no blanqueada desde un 37,8% hasta un valor del 41,9%.

Si bien las fibras de pino alcanzaron el mayor grado de sustitución (0,4), los residuos lignocelulósicos llegaron a valores aceptables (0,2) bajo condiciones mucho más suaves. El proceso con residuos lignocelulósicos comprendería: cocción suave con sosa o etanolamina, refino, blanqueo con baja concentración de peróxido si se desea, amorfización durante 60 minutos y cationización aún más breve a 70 ºC. Incluso si los residuos no convencen a los fabricantes de papel, pueden ser revalorizados hacia una alternativa biodegradable a los polielectrolitos convencionales.

PALABRAS CLAVE

alcalización; amonio cuaternario; análisis elemental; cationización; celulosa; difracción de rayos X; fabricación de papel; funcionalización; pasta; refino.

This is the dedication page.

If you are not skipping it, a small part of you probably expected to find your name. And why not? You may have done something quite important for me, like giving birth to me, teaching me how to read, dating me, supervising my work, lending me a book, or even reading something I have written —and still wanting to read more!

Alas, your name is not here.

Well, this has to end.

Unless you are the kind of person who skips the dedication page, writes in passive voice all the time, or thinks that there must be different email domains for professors and students in the same university, this dissertation is dedicated…

To you

A ti

Contents

Acknowledgements

I am deeply thankful to my supervisors, Dr. Ana Moral (Pablo de Olavide) and Dr. Antonio Tijero (Complutense). They set a good framework for my PhD thesis project and created what bookmakers nowadays call a Positive Work Environment. The work environments I enjoyed during my short scientific missions in Portugal were great too, so credit goes to Dr. P.J. Ferreira (Coimbra, 3 months) and to Dr. A.J. Silvestre (Aveiro, 1 month). I also thank all the colleagues who have taken part in my research and taught me something —i.e., I thank all of them. Dr. Julio Tijero was particularly helpful at planning and at interpreting results. It is only fair to name Patricio López, Lourdes Campaña, Dr. Rocío Jarabo, Dr. Menta Ballesteros, Raquel Roldán, María Seara, Dr. M.C. Monte, Dr. J.S. Torrecilla, Elena Cabeza, Dr. M.J. De la Torre, A.F. Lourenço, Dr. J.A. Gamelas, Dr. M.G. Carvalho, Dr. Pere Mutjé, Dr. Marc Delgado, Dr. Patrícia Ramos, and I am so cautious that I am finishing the list with *etc*.

Those wonderful people in the auxiliary research centers have to be acknowledged too. Dr. J.C. Menéndez, M.J. Saucedo, Pilar Cledera, Julián Velázquez, thank you for your collaboration. I must mention Dr. Nuria Gómez and Dr. J.C. Villar, awesome people from INIA-CIFOR, always willing to help.

The lessons provided by Dr. Ángel Delgado on bibliographic research was priceless, and so was the ones taught by Dr. Juan Tena on data treatment with *R*. I thank the committee members, who have kindly answered any question of mine. Another word of gratitude goes for Dr. Carlos Santos, coordinator. I wish I could remember the names of everyone who made me learn and enjoy so much in the seminar on divulgation, in *Canal Sur* facilities, in *Jornadas Doctorales*, and in *Eukaryogenesis Workshop*.

Special thanks to my parents. Mom and Dad have always been so supportive. Perhaps out of naivety, they feel so proud of me. They have to know that pride goes both ways. I would also like to thank Laura Álvarez, for making me so happy during these years. And this cannot end without expressing my appreciation to my friends —all of them, but especially Alex, Sarai, Alba, Lucía, and Míriam. Always interested in what I was doing with my life.

So many names in this page, right! But it is my wish to convey the message that whoever teaches me something gets credit for it. Such is the word of a scientist and the word of a scholar, which is essentially the same.

List of tables and figures

Tables

Figures

List of abbreviations and symbols

AF	Amorphous fraction
APAM	Acrylamide-based polyelectrolyte with negative charge
ATR	Attenuated total reflectance
BEKP	Bleached eucalyptus kraft pulp
BI	Burst index
C *or* CD*	Charge density
CED	Copper(II) ethylenediamine
Cell-I	Cellulose I
Cell-II	Cellulose II
CEPI	Confederation of European Paper Industries
CF	Cationic fibers
CHPTAC	(3-chloro-2-hydroxypropyl)trimethylammonium chloride
CI *or* CrI*	Crystallinity index
CPAM	Acrylamide-based polyelectrolyte with positive charge
CSF	Canadian Standard Freeness
DFR	Drainage, freeness, retention
DNS	Degree of nitrogen substitution
DP	Degree of polymerization
DS	Degree of substitution
EPTAC	2,3-epoxypropylalkyldimethylammonium chloride
FTIR	Fourier transform infrared spectroscopy
G	Grammage or basis weight
GCC	Ground calcium carbonate
HexA	Hexenuronic acids
I	The author of this dissertation
IR	Infrared
K	Constant of the polymer in the Mark-Houwink equation
K_2 or K_2'	Constant in the pseudo-second order equation
KN	Kappa number
LDS	Laser diffraction spectrometry

N	Mass fraction or percentage of nitrogen
%N	Percentage of nitrogen
OCF	Cationic fibers from orange tree trimmings
PCC	Precipitated calcium carbonate
PCF	Cationic fibers from pine wood
PDADMAC	Polydiallyldimethylammonium chloride
PKP	Pine kraft pulp
PVSNa	Sodium polyvinylsulfate
RCF	Cationic fibers from rapeseed stalks
SEM	Scanning electron microscopy
S_N2	Nucleophilic substitution 2
SR	Schopper-Riegler number (magnitude)
ºSR	Schopper-Riegler degrees (unit)
T	Time
TearI	Tear index
TensI	Tensile index
We	The authors of publications included in this dissertation
WCF	Cationic fibers from wheat straw
XRD	X-ray diffraction
η *or* LVN*	Intrinsic viscosity or limiting viscosity number
Θ	Angle of incidence
Λ	Wavelength
ω_N	Mass fraction of nitrogen

*Used in one of more publications, but never in the text before or after the publications.

Note: In Publications I and II, *CI* stood for *cellulose I*, while *CII* stood for *cellulose II*. These abbreviations may be confusing. They are never used along the text placed before or after the publications.

Terminology

This is a general glossary of the technical terms used along the dissertation. Some definitions, such as that of *cellulose*, are universal. They are the least, though, and thus a chapter of definitions was deemed necessary. Terms like *crystallinity* are specifically applied to polymer science. Terms like *wire* or *stock* would not mean the same outside the context of papermaking. Moreover, among papermakers and researchers who deal with cellulose and paper, there is not a consensus regarding the classification of fibers and fines.

Acid sulfite pulping: process by which wood and/or lignocellulosics are cooked with sulfurous acid, producing dissolved cellulose or low-yield cellulosic pulps.

Alkalization: treatment of a cellulosic or lignocellulosic material with a concentrated solution of a strong alkali at 0-25 ºC, aiming to swell fibers, to convert cellulose I into cellulose II and/or to decrease crystallinity.

Amorphization (or **decrystallization**): decrease in the crystallinity of a polymer, be it caused by chemical treatments or mechanical actions.

Anhydroglucose unit: glucose molecule which has lost an –OH and a –H, specifically from carbons 1 and 4, generally forming glycosidic bonds with neighbor units in polysaccharides.

Anhydrohexose unit: hexose (e.g., glucose and mannose) which has lost an –OH and a –H, generally forming glycosidic bonds with neighbor units.

Anhydropentose unit: pentose (e.g., xylan and arabinose) which has lost an –OH and a –H, generally forming glycosidic bonds with neighbor units.

Black liquor: dark liquid that remains after a chemical pulping process, containing lignin and spent cooking chemicals.

Basis weight or **grammage** (used interchangeably): Mass of paper per unit of surface, e.g., 40 g m^{-2} or 60 g m^{-2}.

Bleaching: process involving one or several stages of reaction with oxidizing agents, washing, screening and extraction, which lowers the lignin content of chemical pulps and increases their brightness.

Brightness: measurement of the amount of reflectance of blue light whose wavelength is 457 nm (TAPPI T452).

Canadian Standard Freeness (mL): milliliters of filtrate that are collected in the probe when TAPPI test method T227 is followed.

Cationization: insertion of cationic functional groups in the structure of a polymer, either by modifying the polymer backbone or by grafting.

Cellulose: linear homopolymer consisting of anydroglucose units with β-1-4-glycosidic bonds.

Charge density (meq/g): milliequivalents of a polyelectrolyte of opposite charge that are needed to reach the isoelectric point of 1 gram of a certain polymer or pulp.

Crystallinity (of a polymer): degree in which macromolecules are arranged in a regular order.

Degree of polymerization: number of units (monomers) in a polymer macromolecule.

Degree of substitution: after the functionalization of a polymer, ratio of the number of functional groups inserted to the degree of polymerization.

Dewatering or **drainage**: removal of water by fast filtration in the drainage table of a paper machine.

Drainage aid: substance that is added to the stock prior to sheet formation and increases drainage rate.

Extractives: compounds in lignocellulosic materials that can be removed by extraction with organic solvents, such as ethanol, benzene, toluene and acetone.

Fiber: thin structure whose length is larger than 100 μm and whose length/width ratio is greater than 30.

Filler: particle added to the stock before the paper sheet is formed to reduce costs or to improve optical properties.

Fine: thin structure whose length is smaller than 100 μm and whose length/width ratio is greater than 10.

Functionalization (of a polymer): chemical modification of a polymer by which functional groups of any kind are inserted.

Furnish: dilute suspension (its consistency is lower than 2%) that comprises the stock, the fillers and, if applicable, the additives.

Graphic paper: general term for any kind of paper produced with the purpose of displaying information, e.g., printing paper.

Green liquor: liquid that results after burning the organic matter of the black liquor. It contains sodium carbonate, from which sodium hydroxide can be recovered.

Glycosidic bond: in cellulose and hemicelluloses, covalent bond that links two sugar units via an ether group.

Handsheet: paper sheet made in a laboratory, not in a paper machine, for testing purposes (ISO 5269-1).

Hardwood: wood from angiosperm trees, such as eucalyptus, birch, beech or aspen.

Hemicelluloses: linear or branched heteropolymers with anydrohexose and/or anhydropentose units, found in the vegetable biomass along with cellulose and lignin.

Holocellulose: sum of cellulose and hemicellulose in a material.

Kappa number: milliliters of a 0.1N potassium permanganate solution that are consumed by 1 g of moisture-free pulp at 25 ºC (ISO 302, TAPPI T236).

Kraft pulping: process by which wood and/or lignocellulosics are cooked with aqueous sodium hydroxide and sodium sulfide, producing cellulosic pulps.

Lignin: group of aromatic polymers found in the support tissues of vascular plants, along with cellulose and hemicelluloses.

Limiting viscosity number: measure of the contribution of a polymer to the viscosity of the solution in which it is dissolved, calculated by following the ISO standard 5351. It is more known as **"intrinsic viscosity"**, mistakenly or not, in the literature regarding cellulose and papermaking.

Nucleophile: chemical species that is prone to donate an electron pair to form a covalent bond.

Organosolv pulping: process by which wood and/or lignocellulosics are cooked with an organic solvent, producing sulfur-free lignin and pulps that preserve hemicelluloses.

Package paper or **packaging paper**: general term for any kind of paper manufactured with the purpose of wrapping, carrying or protecting goods.

Polyelectrolyte: polymer whose monomers bear negative charge (polyanion) or positive charge (polycation).

Polysaccharide: polymer consisting of a large number of monosaccharides linked by glycosidic bonds.

Pulping: chemical and/or mechanical process in which cellulosic fibers are separated from lignocellulosic materials.

Quaternization: insertion of a quaternary ammonium functional group in the structure of a polymer.

Refining: mechanical operation during stock preparation in which the fibers are shortened and their surface is roughened, resulting in increased surface area.

Retention aid (or retention agent): substance that is added to the stock prior to sheet formation and promotes fiber-to-filler, fiber-to-fine and/or filler-to-filler flocculation, aiming to increase the total retention of fillers and fines on the wire.

Soda pulping: process by which wood and/or lignocellulosics are cooked with aqueous sodium hydroxide, producing cellulosic pulps and possibly sulfur-free lignin.

Soda-anthraquinone pulping: process by which wood and/or lignocellulosics are cooked with aqueous sodium hydroxide and anthraquinone, producing cellulosic pulps and possibly sulfur-free lignin.

Softwood: wood from gymnosperm trees, such as pine and spruce.

Stock: diluted suspension of fibers, fines and fillers that are used to form the paper sheet.

Wet end: in a paper mill, section in which the stock is mixed with retention aids and/or other additives, lands on the drainage table and starts forming the paper sheet.

White liquor: in chemical pulping, liquid that contains the cooking reagents.

Wire: in a paper machine, the mesh conveyor belt through which the suspension of fibers, fines, fillers and additives is filtered.

Yellowness: degree to which the color of the paper surface is shifted from white to yellow.

All serious empirical inquirers use their imagination to come up with a hypothesis (…) and use their judgement whether to accept the conjecture, modify it, reject it and start again, or figure out how to get more decisive evidence.

Susan Haack (2003). “Defending Science – within Reason.” Prometheus Books, USA.

I am advocating that writers should write naturally and economically, without affectation of a special ‘scientific style’.

John Kirkman (1954). “That pernicious passive voice.” Phys. Technol. 6: 197-200.

1. OUTLINE

The driving force of this dissertation is the firm determination of making scientific efforts towards a cleaner paper industry. But a cleaner industry is not only achieved by decreasing emissions to air, land and water. Papermakers, at least in Europe, have made huge progress in this area, to the point of diminishing emissions of chlorinated compounds and sulfur dioxide by approximately 90% since ca. 1990. Also, the recycling rate lies above 70% [1].

Nonetheless, some environmental issues remain:

- Despite the progress on odor control in the recent past years, many pulp mills still report **odor** problems [2]. In addition, the formation of hydrogen sulfide, although not released unless a leak occurs, always arises safety concerns.
- The **water intake** is still very high: 3506 million m^3 in 2015, and nearly 87% of it came from surface water [1].
- **Refractory pollutants** from lignin and its derivatives.
- In the first section of a paper machine, papermakers depend on polyelectrolytes with low **biodegradability** to achieve acceptable filler retention and fast drainage. These synthetic flocculants cannot pass through biological membranes, and the rate of degradation by extracellular enzymes is slow [3].
- The European pulp and paper industry is missing the opportunity to reuse **agricultural waste**.

My PhD thesis project has dealt with these pending environmental problems of papermaking. Nevertheless, water consumption and refractory pollutants are only tangentially addressed here.

Water consumption could be reduced, for instance, by pulping with organic solvents that can be recovered through distillation [4]. It would only be honest to say that, currently, the bleaching plant and the paper mill consume more water than pulping, though. Anyway, among all the stages preceding sheet formation, this text engages more particularly in pulping, since it is the key to produce cellulosic fibers —the main material along the dissertation. Sulfate mills dominate chemical pulping of virgin fibers, but the combination of soda or organosolv processes and some non-wood materials can result in acceptable paper strength [5,6]. Refusing to use sulfur compounds in pulping implies avoiding many of the odor issues affecting pulp mills, besides the generation of refractory pollutants owing to the reaction between sulfur compounds and lignin.

The focus was more particularly in those synthetic polyelectrolytes that are commonly used in paper mills to aggregate fillers and/or to attach them to fibers. Sheet formation involves filtration, but the aperture size of the wire is larger than that of fines, calcium carbonate, clay and other particles that may be part of the furnish. Their zeta potential is usually negative [7]. In order to retain fillers and fines on the paper web, papermakers purchase cationic flocculation agents, such as polyacrylamides with positive charge (CPAM), poly-diallyldimethylammonium chloride (PDADMAC) and polyethyleneimine (PEI). They can be very effective, but their drawbacks include toxicity to fish and some invertebrates, difficulty or impossibility to be measured in the environment, and lack of biodegradability [3].

Synthetic polyelectrolytes could be partially replaced with **cationic cellulose**, easily biodegradable if water-soluble [8], or not even discharged to water in the form of insoluble fibers [9]. Pulp mills, paper mills and integrated mills already have the raw materials needed to synthetize those products and, therefore, manufacturers could separate a part of the cellulosic pulp to be functionalized. In contrast, polyelectrolytes need to be provided by external suppliers.

Cellulose, a highly available material, can be chemically modified –essentially by oxidation, etherification and esterification [10]. **Functionalization of cellulose**, in any of its forms, is increasingly interesting for researchers, as can be seen from Figure 1. The trend is undoubtedly up. Frequently, cellulose derivatives, which can be broken down by many organisms, are presented as a sustainable alternative to hardly biodegradable polymers. Our publications address one kind of etherification: the insertion of quaternary ammonium groups, positively-charged, into cellulose.

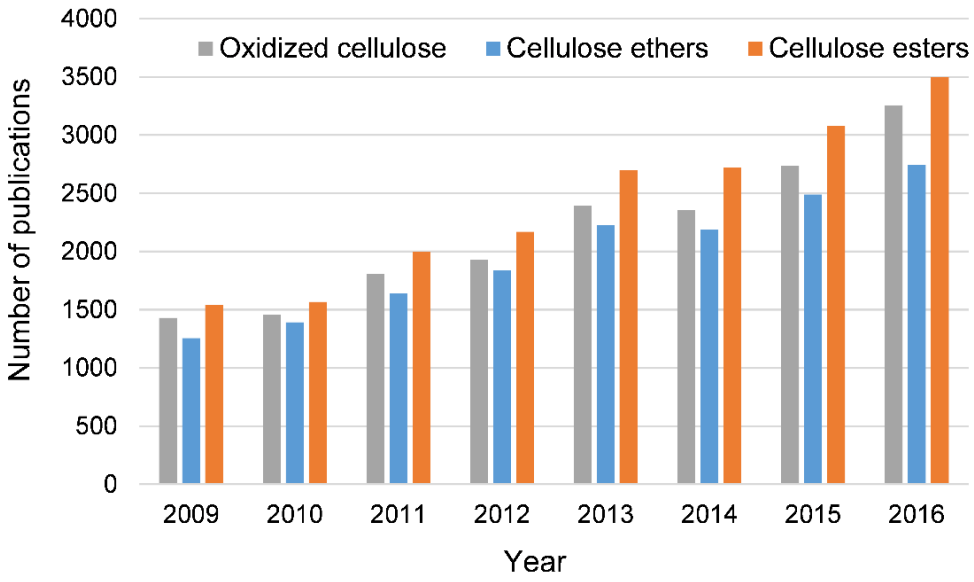

Figure 1. Results of a search in Elsevier's journals and books from 2009 to 2016.

Any reaction which involves the introduction of cationic functional groups into a polymer is called *cationization*.

The cellulosic material to be cationized can come from countless sources. Manufacturers can produce high-purity cellulose from cotton, from microorganisms and from softwood sulfite pulps. Undoubtedly, cotton linters, dissolved pulp, commercial cellulose or any natural material with a high cellulose content can be directly functionalized. Kraft pulps from wood add a new challenge, given the high degree of polymerization and the intermolecular forces between cellulose chains in their fibers. Finally, with the twofold aim of producing biodegradable derivatives and reusing waste, **lignocellulosic residues** from agriculture should be considered. They should not be open-field burnt, as this activity produces air pollutant emissions, hazards to the soil and risk of wildfires. Given their moisture content, when it comes to waste management, incineration with energy recovery or pyrolysis should not have priority over the manufacturing of useful materials.

Most agricultural residues contain less lignin than softwoods, even less lignin than hardwoods. This makes them easier for pulping, not needing the use of sulfur compounds. They require to spend less energy to achieve certain freeness values during refining. Such advantages drove Pande [11], in 1998, to predict an increase in the use of alternative fibers for papermaking in Europe:

- Scenario 1 ("continuation of historical trends"): 658 kt in 2010.
- Scenario 2 ("optimal non-wood fibre use"): 5446 kt in 2010.
- Scenario 3 ("no further advances will be made in non-wood fibre usage"): 878 kt in 2010.

Almost two decades later, the production of pulp from non-wood materials in 2016 was as low as 369 kt [1], accounting for 0.36% of the total production of paper and board (Figure 2). This lies far from the best-case scenario and it is even worse than the worst-case scenario for 2010.

Pande's predictions were not unreasonably optimistic. To the best of my knowledge, nobody predicted that the current production of non-wood pulps would be lower than it was in the nineties (512 kt in 1993) [11]. Surprisingly, non-wood fibers could not overcome some important disadvantages, such as the high amount of silica and fines in wheat straw [12], while wood pulping overcame many environmental problems.

Nevertheless, the advocates of alternative raw materials, including myself, have not run out of reasons to insist. Whilst replacing wood with non-wood materials seems to be unnecessary from the European papermaker's point of view, it is much more appealing from waste management strategies.

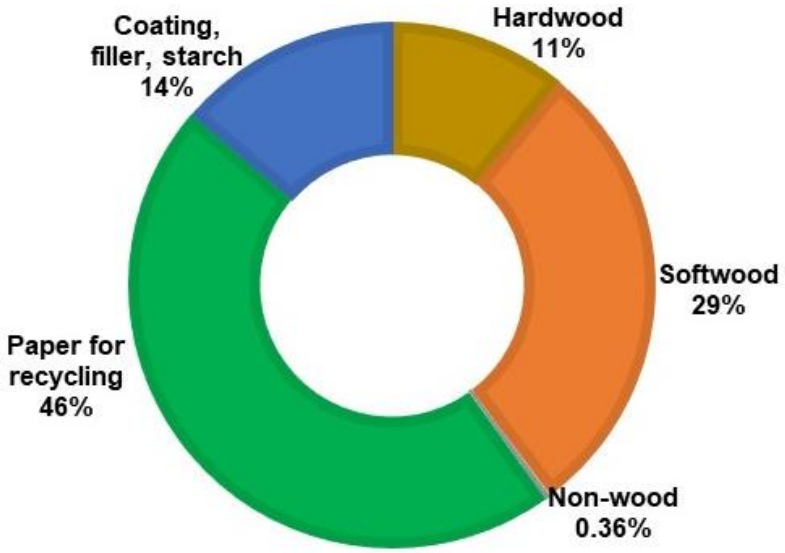

Figure 2. Raw materials used in the manufacturing of paper and board [1].

Also, making things different may be good for an industry whose added value is decreasing year by year, as shown in Figure 3. Innovation has been usually oriented to reduce the environmental impact of pulp and paper mills while using the same raw materials, but alternative materials could boost new product development.

Even if Western manufacturers are not convinced by the papermaking potential of lignocellulosic residues, these can be delignified through sulfur-free processed and converted into useful fibers to be added to conventional pulps. This way, three research questions are raised:

- Which procedure allows us to produce highly-substituted cationic fibers in a feasible way?
- How can the cationization of cellulose, under various conditions and from various sources, be modeled?
- What are the applications of cationic cellulose in papermaking?
- What are the best ways to reuse lignocellulosic residues, such as rapeseed stalks and orange tree trimmings, for papermaking?

And they converge into a single broad objective, which is stated in **Chapter 2**. **Chapter 3** provides the theoretical framework that is needed to understand how the aims of this dissertation were fulfilled, including an overview of the papermaking process. The ways in which the products were characterized are extensively, but not prolixly, explained in **Chapter 4**.

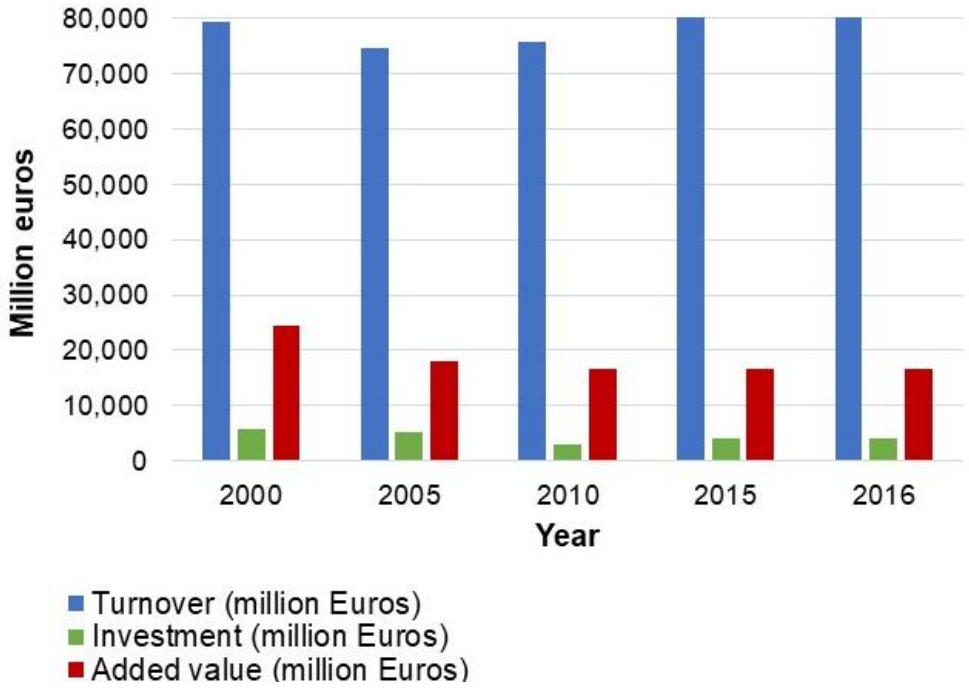

Figure 3. Evolution of financial variables in the European paper industry [1].

All the publications included in **Chapter 5** belong to JCR-indexed journals. Four of these works, eight in total, were accepted and/or published in Q1 journals. Out of courtesy to the reader, a perfunctory reproduction of the results is avoided, and thus **Chapter 6** jumps to the discussion and conclusions drawn from those results. Consistently, I interpret the results by relating them to the hypotheses stated in Chapter 2.

Last, **Chapter 7** indicates publications that are framed in the same category as the whole thesis, since they refer to the properties of pulps from crop residues. They were not included in the dissertation to prevent the cationization of cellulose from becoming unfocused.

2. OBJECTIVES AND HYPOTHESES

All the experiments carried out in laboratories located across the Iberian Peninsula (Seville, Madrid, Coimbra, Girona) were motivated by a broad objective. This **broad objective** can be stated as follows:

To explore the possibilities to alleviate pending environmental problems of papermaking, specifically the dependence on hardly biodegradable flocculants and the dependence on wood, with products obtained by chemical treatments of different raw materials.

Derived from this aim, three key goals arose. Publications could be grouped by the choice of raw material in each case: cellulose (I, II, III), conventional pulps (IV, V) and sulfur-free pulps from lignocellulosic residues (VI, VII, VIII).

2.1. Publications I, II and III

The first goal of this dissertation is to present our (Ecowal's) particular focus on the cationization of cellulose, using cotton linters and commercial alpha-cellulose as materials (as they consist almost entirely of alpha-cellulose). Publications I, II and III are not as ambitious as the rest, but they play the role of setting the stage. Therefore, the statement of this goal could be:

To establish a procedure for the cationization of cellulose, proposing a reaction mechanism and a kinetic model, and evaluating the effects of chemical treatments of cellulose itself.

These works insist on the need of partial amorphization (decrystallization) prior to cationization. The reaction mechanism suggested, applicable to mild conditions, implies that only the –OH group on carbon 6 of anhydroglucose is substituted. As for kinetics, we proposed an original model, a pseudo-second order rate equation. Techniques to analyze the effects on cellulose involved X-ray diffraction, elemental analysis, and viscosity measurements.

2.2. Publications IV and V

Publication IV is the first work in which the material to be cationized is cellulosic pulp: unbleached kraft pulp from pine wood (PKP). In Publication V, we cationized bleached eucalyptus kraft pulp (BEKP). However, those papers are very different in many ways.

As the degree of polymerization is lower in cellulose from hardwoods than in cellulose from softwoods, BEKP was chosen to produce water-soluble derivatives to be used as flocculation agents in papermaking. Thus, these derivatives would be added to the head box, in the wet end of a paper machine, in a similar way to conventional cationic polyelectrolytes. In contrast, cationic fibers from PKP were produced to be added earlier in the process and enhance retention. Hence, the second goal is:

To cationize part of the pulp that is received in a paper mill towards water-soluble aids and insoluble fibers, in order to improve flocculation and retention of fillers and fines.

Both BEKP and PKP are materials conventionally used in the manufacturing of paper and board. If the objective of achieving suitable flocculation agents or useful cationic fibers is fulfilled, papermakers could reduce the use of hardly biodegradable flocculation agents. They could produce their own retention aids from their own materials.

2.3. Publications VI, VII and VIII

There is little novelty in looking for alternatives to wood in lignocellulosic residues, other than: (i) proposing raw materials not studied or scarcely studied before; (ii) addressing the problems that keep almost all Western papermakers away from non-wood materials. Currently, reusing residues to manufacture pulp, paper and board is more appealing from the point of view of waste management than from the point of view of manufacturers, unless newly found properties of them serve to increase the added value of the paper industry. Instead of giving up, this research should continue and explore more possibilities. Below is the third goal of my dissertation:

To evaluate the use of agricultural residues for papermaking purposes, including pulping, bleaching, refining, dewatering, sheet formation, and chemical modifications leading to cationic fibers.

Those agricultural residues are rapeseed stalks (Publications VI and VIII), orange tree trimmings (Publications VII and VIII) and wheat straw. However, since the latter has been thoroughly studied for papermaking, it is only used for the production of cationic fibers (Publication VIII).

2.4. Statement of hypotheses

Hypothesis 1. Soaking a cellulosic material in a concentrated aqueous NaOH solution, at room temperature, makes cellulose prone to cationization (Publications I and II).

Hypothesis 2. Kinetics of cationization can be modelled and the shape of the kinetic curve (percentage of nitrogen vs. time) is nearly the same for any given raw material (Publications I, II and VIII).

Hypothesis 3. The rate of cationization of low-DP cellulose is greater than the rate of cationization of high-DP cellulose (Publications I, II and III).

Hypothesis 4. Cationization of cellulose has a positive impact on intrinsic viscosity (or in the limiting viscosity number) –given that the spatial distribution of the polymer is changed (Publication III).

Hypothesis 5. Refining a pulp before alkalization and cationization increases the reaction rate (Publication IV).

Hypothesis 6. Cationization has a positive effect on bulk (Publications IV and VIII).

Hypothesis 7. Cationic fibers enhance the retention of fines and mineral fillers during sheet formation. This is a conglomeration of three hypotheses that are tested along the publications:

Hypothesis 7.1. Cationic fibers enhance the retention of fines during sheet formation (Publications IV and VIII).

Hypothesis 7.2. Cationic fibers enhance the retention of PCC during sheet formation (Publication IV).

Hypothesis 7.3. Cationic fibers enhance the retention of TiO_2 during sheet formation (Publication VIII).

Hypothesis 8. Cationization of cellulose can produce soluble derivatives to enhance flocculation of mineral fillers in the wet end of the paper machine:

Hypothesis 8.1. Cationization of cellulose can produce soluble derivatives to enhance flocculation of PCC (Publication V).

Hypothesis 8.2. Cationization of cellulose can produce soluble derivatives to enhance flocculation of GCC (Publication V).

Hypothesis 8.3. Cationization of cellulose can produce soluble derivatives to enhance flocculation of kaolin (Publication V).

Hypothesis 9. Since the solubility of cationic cellulose depends on the degree of polymerization (negative influence) and on the degree of substitution (positive influence), hydrolyzing cellulose with orthophosphoric acid is a proper pretreatment to produce water-soluble cationic cellulose (Publication V).

Hypothesis 10. Rapeseed stalks and orange tree trimmings can be cooked through sulfur-free processes to produce pulps of enough strength for papermaking.

Hypothesis 10.1. Rapeseed stalks can be cooked through sulfur-free processes to produce pulps of enough strength for papermaking (Publication VI).

Hypothesis 10.2. Orange tree trimmings can be cooked through sulfur-free processes to produce pulps of enough strength for papermaking (Publication VII).

Hypothesis 11. By refining, pulps from rapeseed stalks and orange tree trimmings need less energy than conventional pulps to reach a given value of CSF or SR

Hypothesis 11.1. By refining, pulps from rapeseed stalks need less energy to reach a given value of CSF or SR (Publication VI).

Hypothesis 11.2. By refining, pulps from orange tree trimmings need less energy to reach a given value of CSF or SR (Publication VII).

Hypothesis 12. One-step bleaching with hydrogen peroxide can achieve a high brightness gain, even though the kappa number is considered too high (Publication VII).

Hypothesis 13. The addition of cationic fibers to the stock favors collapsing, thus slowing dewatering (Publication VIII).

Hypothesis 14. Lignocellulosic residues can be cationized to produce valuable fibers to be added to conventional pulps, with the goal of enhancing the optical properties of the final product (Publication VIII).

3. FRAMEWORK OF THE STUDY

3.1. Cellulose and its possibilities to develop new products

The first of all reasons that should make anyone think about cellulose is its **availability**. Cellulose is the most abundant biopolymer in planet Earth. It can be found, at least, in wood, bark, seeds, leaves, stalks, rhizomes, fruits, algae, oomycetes, bacteria… and even in certain animals, the tunicates [13].

It was discovered in 1838 by French chemist Alselme Payen. Working with different types of wood, he isolated a substance that was the main constituent of all of them and that, like starch, could be broken down into glucose [10].

Cellulose is a linear polysaccharide consisting of anydroglucose units (AGU) with β-1-4-glycosidic bonds. This means that each monomer in the chain, unlike in starch, is rotated 180º with respect to the previous one and the following one. Each AGU has three hydroxyl groups, as shown in Figure 4. One of them, the one outside the cycle (bonded to carbon 6), is more prone to etherification or esterification.

This polymer is used as a food additive (E460), e.g., as an anti-caking agent in shredded cheese. In the pharmaceutical industry, it is a filler, diluent or builder in tablets [14]. It can be used in the manufacturing of composite materials for building or medical purposes. However, out of all the possible applications, this text is focused on papermaking.

In this context, in which cellulose comes from materials that have hemicellulose and lignin as well (vegetable biomass), we often call cellulose **alpha-cellulose**, in order to distinguish it from hemicellulose.

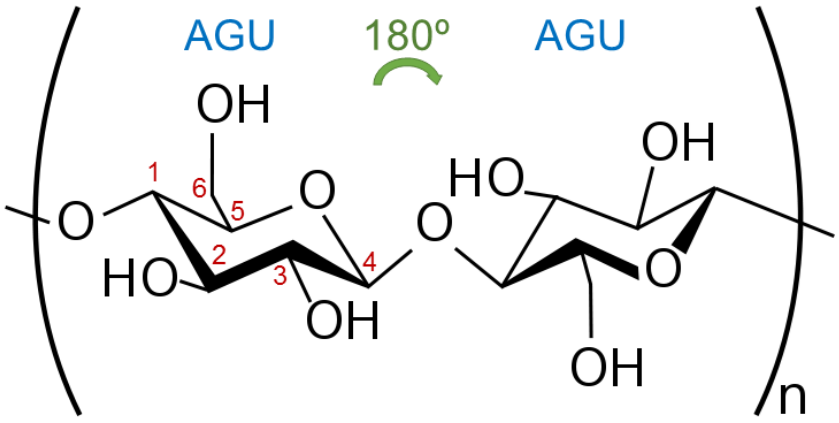

Figure 4. Anhydroglucose units in the structure of cellulose, numbering the carbon atoms.

Hemicelluloses are heterogeneous polysaccharides, usually with ramifications and different glycosidic bonds, whose role is that of a supporting material in wood, stalks, etc. Monomers found in hemicelluloses include anydrohexose units, anydropentose units and anhydrouronic acid units. Depending on the composition, hemicelluloses can be xylans, xyloglucans, mannans and glucomannans, besides other heterogeneous polymers that are specific to certain taxons [15].

It should be noted that when the term *cellulose* is used in any part of the text, including the research articles, it means *alpha-cellulose*. To nominate both alpha-cellulose and hemicelluloses at the same time, I use *ab hinc* the term ***holocellulose***.

3.1.1. Modifications of cellulose in which the product is still cellulose

Many chemical agents can produce key changes in the structure and the properties of cellulose, as a polymer not needing to modify the anydroglucose units. Since cellulose is a linear homopolymer, cellulose chains will not differ in composition, but they can differ in: (i) degree of polymerization; (ii) ionization of hydroxyl groups; (iii) intramolecular and intermolecular forces.

- The **degree of polymerization** (DP) in pulps used in papermaking, and thus the molecular weight, is much lower than that of native cellulose in wood. This is so because pulping processes take place at high temperatures and pH values far from neutrality. It decreases by alkaline hydrolysis (soda pulping, kraft pulping, alkaline sulfite pulping) or acid hydrolysis (acid sulfite pulping). Decrease during bleaching is slight [16]. DP is usually estimated by measuring the intrinsic **viscosity** (Publications III and V).
- **Ionization** can occur by dissociation of one of the hydroxyl groups, especially the one attached to carbon 6. Strongly alkaline conditions are needed for this to happen to a significant extent.
- Cellulose **polymorphism** has to be taken into account to explore further modifications. Native cellulose in wood and lignocellulosics is mostly cellulose Iβ. Bacterial cellulose and cellulose from some algae are mostly cellulose Iα [17]75. If treated with aqueous sodium hydroxide at low temperatures (R.T. or lower), they are converted into cellulose II, which is natively found in some algae [18]. A liquid ammonia treatment of cellulose Iα, cellulose Iβ or cellulose II gives out cellulose III [19]. Cellulose IV is generated by heating cellulose III in glycerol to 260 ºC [13]. All of them are crystalline forms. A scheme is shown in Figure 5.

These changes are of great importance for my PhD thesis. They are repeatedly present in our works. All works involved insoluble fibers in aqueous alkaline media, but only one (Publication V) implied the dissolution of non-cationized cellulose.

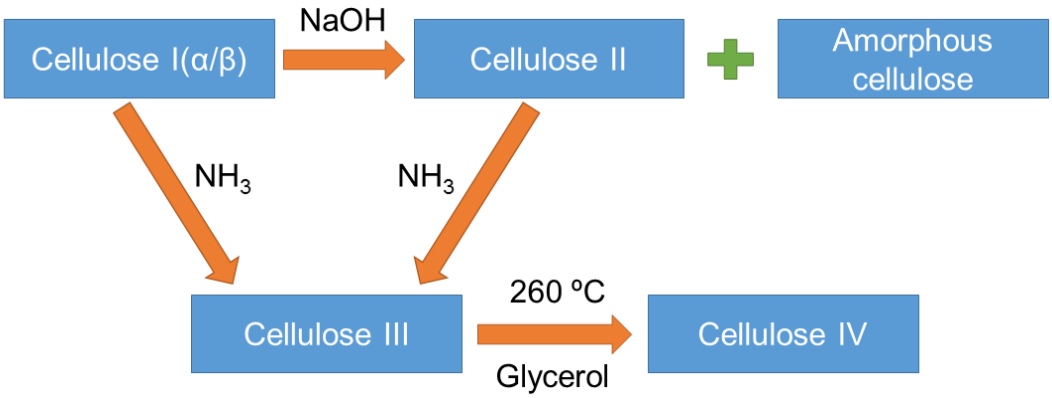

Figure 5. Cellulose: crystalline polymorphs and amorphous cellulose, schematically showing how to convert one into the others.

In Publications I, II, III, IV, V and VII, we treated cellulosic materials with aqueous NaOH (10-30%) at room temperature, but the objective was not to convert cellulose Iβ into cellulose II. That was a side effect. The objective was *decrystallization* or *amorphization*: **converting crystalline cellulose into amorphous cellulose**, by the breakdown of intramolecular and intermolecular hydrogen bonds.

As will be shown in Publication I, amorphous cellulose is much more reactive. It is more prone to ionization, dissolution, hydrolysis and substitutions. Aqueous agents can penetrate easily into its disorganized structure.

3.1.2. Functionalization of cellulose

New **functional groups** can be introduced in anhydroglucose units by the **oxidation** of hydroxyl groups towards carbonyl or carboxyl groups, by **esterification** with acids, or by **etherification** [10]. Table 1 shows the reagents commonly used for these chemical reactions and an example product for each of them. Oxycellulose can be used as an adsorbent in chromatography, carboxymethyl cellulose is the food additive E466 (thickener, stabilizer), and cellulose phosphates inhibits calcium absorption into the blood [20].

Table 1. Common chemical modifications of cellulose.

Reaction	Reagent	Example of product
Oxidation	Cl_2, H_2O_2, NO_2, HClO, $NaIO_4$, peracetic acid	Oxycellulose [20]
Etherification	CH_3Cl, ethylene oxide, chloroacetic acid, epoxides	Carboxymethyl cellulose [21]
Esterification	Acetic acid, HNO_3, H_3PO_4, H_2SO_4	Cellulose phosphate [22]

Carboxymethyl cellulose, besides a food additive, is an anionic wet strength agent in papermaking, a thickening agent in pharmaceuticals, a non-toxic viscosity modifier, an electrode binder in lithium ion batteries, a lubricant in artificial tears, a soil suspension polymer in detergents, and a cation-exchange resin in chromatography [24]. Other successful derivatives are hydroxypropyl cellulose, cellulose acetates and methyl cellulose [10].

There is a vast number of different cellulose derivatives proposed in the literature [23]. They are often synthetized and thoroughly characterized by FTIR, NMR and other analytical techniques, although the potential applications of many of them are unknown.

3.2. Cationization of cellulose

The first work involving the production of cationic cellulose was probably the PhD thesis of Montégudet in 1957 [25]. He reacted the polymer with 2,3-epoxypropyldiethylamine. He even used a **sodium hydroxyde aqueous solution** as the reaction medium. Cellulose was not dissolved (Publication V), and so the reaction was heterogeneous (Publications I, II, IV, VIII). The only difference between this and many of our reactions is the choice of the cationizing agent. 2,3-epoxypropyldiethylamine was rarely used afterwards [24].

3.2.1. Cationizing agents

Undoubtedly, the most common cationizing agent is not 2,3-epoxypropyldiethylamine but another epoxide: 2,3-epoxypropylalkyldimethylammonium chloride (EPTAC) [25], as shown in Figure 6. It is the one we used wherever cationization was involved, although we decided to start from a more stable chlorohydrin which can be stored for a long time: **(3-chloro-2-hydroxypropyl)trimethylammonium chloride (CHPTAC).** In presence of a strong alkali, EPTAC is produced from CHPTAC and chloride ions are released to the medium.

Table 2 shows other possible cationizing agents. Among them, Girard's reagent is truly remarkable, but it does not work with native cellulose. It needs a previous oxidation stage with sodium periodate, in which the ring of anydroglucose units is broken and two carbonyl groups are formed, particularly on carbons 2 and 3 (Figure 4). Then, those groups are prone to nucleophilic additions. The breakdown of the AGU ring allows to insert two cationic functional groups per unit, thus reaching degrees of substitution slightly above 1 [26]. For nearly every other reagent, substitution or addition on consecutive monomers is strongly hindered by repulsive forces (including steric effects), not to mention the insertion of more than one group in the same unit.

Table 2. Examples of cationizing agents used in the literature.

Cationizing agent	Reference
2,3-epoxypropyldiethylamine	[25]
2,3-epoxypropylalkyldimethylammonium chloride	[27]
(3-chloro-2-hydroxypropyl)dimethyldodecylammonium chloride	[28]
(3-aminopropyl)trimethoxysilane	[29]
2,3-epoxypropyltrimethylammonium chloride (EPTAC)	[8]
(3-acrylamidopropyl)-trimethylammonium chloride	[25]
1-(carboxymethyl)pyridinium hydrazide (Girard's reagent)*	[26]
(2-chloro-3-hydroxypropyl)trimethylammonium chloride	This work

*Instead of attacking hydroxyl groups, it attacks carbonyl groups of oxidized cellulose.

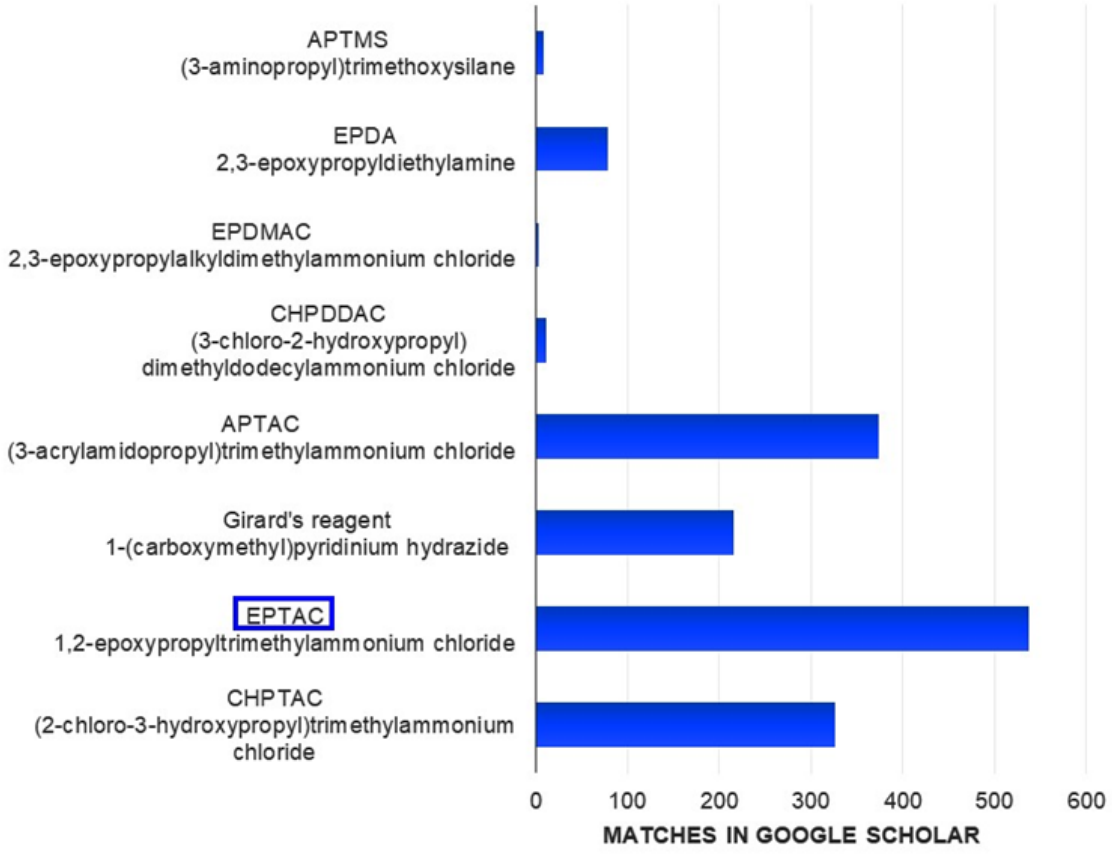

Figure 6. Results of a search in Google Scholar regarding the functionalization of cellulose towards cationic derivatives.

3.2.2. Activation of cellulose

At the moment, no cationizing agent can functionalize cellulose fibers with ease in aqueous suspensions. The main reason is the **crystallinity** of cellulose, i.e., its strong intramolecular and intermolecular hydrogen bonds. Native cellulose, be it from wood,

from lignocellulosic residues or from cotton, is not prone to cationization. There are at least three ways to overcome this problem:

- Starting from **cellulose ethers** which are easier to obtain, preferably hydroxyethyl cellulose. In this case, the cellulose derivative is dissolved in an aqueous NaOH solution and then the cationizing agent is provided [24]. In this case, cationization is a homogeneous reaction.
- Breaking the AGU ring by oxidation with **periodate** [26].
- Using a cellulose **activator**. As aforementioned, NaOH was the first activator used [25]. And even though researchers have tried many different chemicals to make the polymer prone to cationization, NaOH is still the most common one. It has proven better than Na_2CO_3, $NaHCO_3$, methylamine and ethylamine, and as effective as diethylamine [28].

Since a strong alkali is also required to obtain EPTAC from CHPTAC (Publications I, II, II, IV, V, VIII), cellulose activation with NaOH was preferred. This way, the activating solution could simply be diluted with water before adding the cationizing agent and heating to the temperature at which cationization happens.

During my internship in Coimbra, one of the goals was testing different chemical agents as activators for the heterogeneous cationization of cellulose —phosphoric acid and ammonium thyocianate, among others. No one yielded better results than NaOH [31]. However, testing the influence of urea and FeTNa —an iron(III)-tartrate-sodium complex— provided interesting findings, as a lower amount of NaOH was needed to achieve a certain degree of substitution with cationization. This can be appreciated in Figure 7. Urea's actions on hydrophobic interactions justify its use in Publication V.

Moreover, **sodium hydroxide can be used in every chemical stage** from pulping to the production of cationic derivatives.

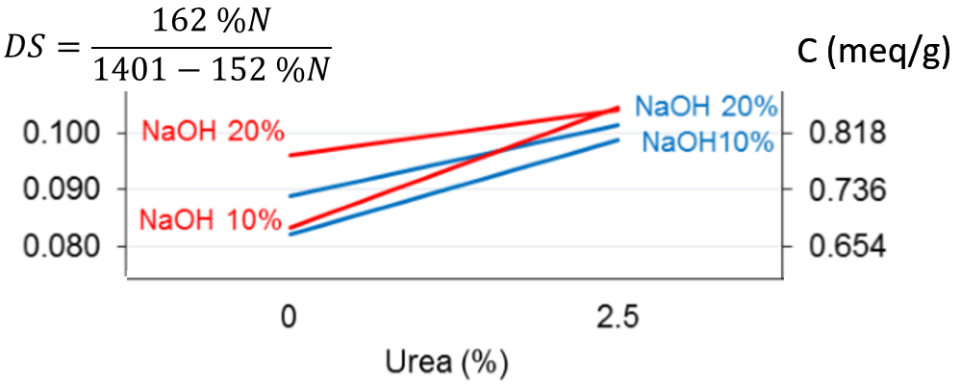

Figure 7. Effect of a small amount (2.5%) of urea on the reactivity of cellulose [31].

NaOH is the main reagent during kraft pulping or soda pulping, it is always involved in bleaching, it decrystallizes cellulose, and very high pH values promote the dissociation of hydroxyl groups. Again, when the reagent chosen is CHPTAC (Publications I, II, II, IV, VIII), cyclization under alkaline conditions is needed to produce EPTAC, the true cationizing agent.

3.2.3. Mechanism and conditions

Figure 8 depicts the most probable mechanism, according to our hypotheses. Substitution can occur on carbons 2, 3 and 6 (Figure 4), but the latter is more prone to etherification with a large functional group, *i.e.*, there is less steric hindrance. Here, this —OH group in AGU acts as a nucleophilic agent upon the epoxide, EPTAC. Under alkaline conditions, substitution occurs in a S_N2 (nucleophilic substitution 2) fashion. The nucleophile is ionized —negative charge— and attacks the least hindered end of the epoxide. In Figure 8, the least hindered end of the epoxide corresponds to the C—O bond on the left side.

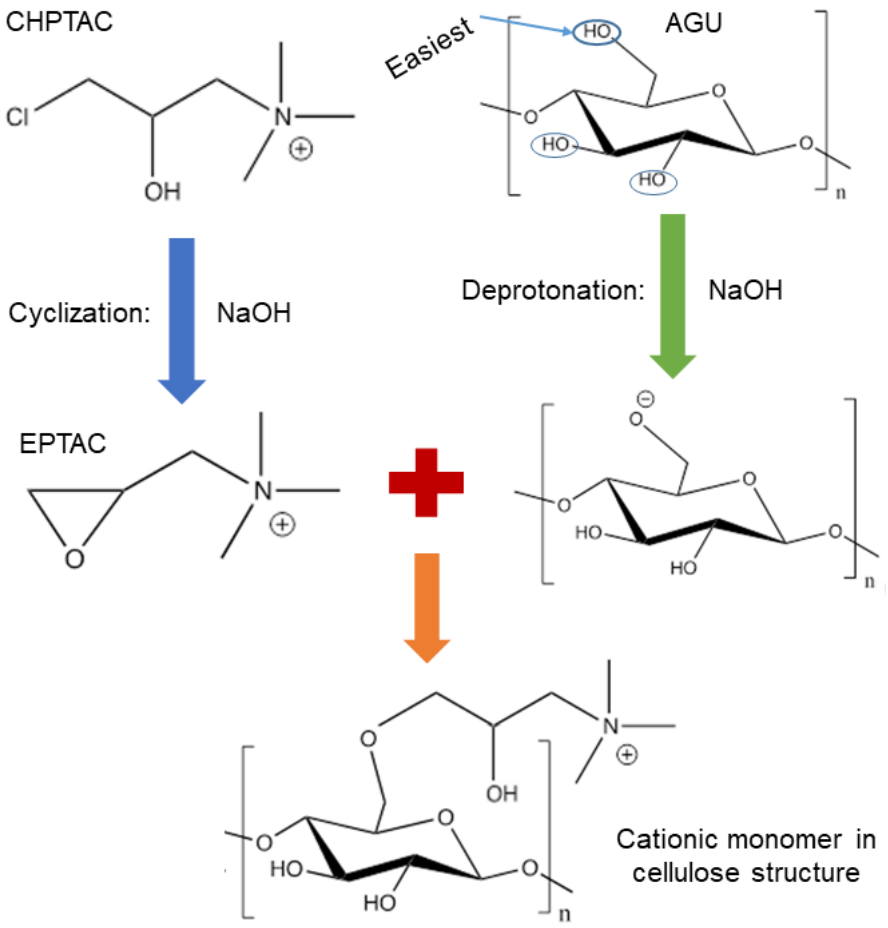

Figure 8. Cationization of cellulose with CHPTAC: proposed mechanism.

Up to a certain point, alkali concentration is expected to have a positive impact in kinetics. However, if pH values are too high, EPTAC is easily broken down towards a non-reactive diol [25]. There does not seem to be any drawbacks for high concentrations of cationizing agent [8], other than the cost of the chemicals. CHPTAC/AGU ratios above 4 are likely cost-ineffective.

Regarding the temperature, it has been suggested that 70 ºC is the optimum value, since lower degrees of substitution may be obtained at higher temperature due to degradation [25]. Yet, the authors failed to see that this degradation was the combined effect of high temperatures and long reaction times (6 h), because samples were not taken for shorter times. Hence, this did not refrain us from cationizing fibers at 120 ºC in Publication IV.

3.2.4. Applications of cationic cellulosic derivatives

Current industrial uses of cationic cellulose are scarce. None of them, as far as I am concerned, involves papermaking, even though cationic starches, structurally similar, are widely used in paper mills [25].

In cosmetics, the substance known as Polyquaternium-10 or Quaternium-19 is a certain kind of cationic or quaternized cellulose [32]. It is produced in a homogeneous reaction, starting from hydroxyethyl cellulose (alkali-soluble) and using EPTAC as the functionalizing agent. Polyquaternium-10 adsorbs easily to proteins in hair and reduces static electricity, enhancing the appearance of hair. The principle is not very different for wet end chemistry (Publications IV, V and VIII): electrostatic interactions.

For instance, soluble cationic derivatives are proposed as **flocculants in papermaking** (Publication V) or wastewater treatment [8]. The use of these derivatives is usually restricted to particles whose zeta potential is clearly negative, such as kaolin.

Regarding insoluble fibers, cationization has been suggested for salt-free dyeing of cotton in the textile industry, avoiding the necessity of polluting electrolyte baths for the sorption of anionic dyes [33]. In a similar way, **cationic fibers could be used in papermaking to improve the retention of negatively-charged particles or additives**. Nevertheless, the most common process to cationize cotton fibers, *i.e*., mercerization followed by functionalization with EPTAC, had not been identically exported to papermaking before this PhD thesis project. The approach of Sain and Boucher [9] to produce cationic fibers for papermaking involved thin film deposition of a precursor, while Sang and Xiao [34] opted for grafting, thus converting cellulose into a branched polymer.

In any case, cationic fibers or cationic cellulosic derivatives should not be intended to replace starch, which is biodegradable and easier to cationize towards a soluble polymer. The purpose is to replace, even if only partially, synthetic polyelectrolytes.

3.3. The papermaking process

There are three key types of production centers dedicated to the manufacturing of paper and board: (i) **pulp mills**, in which the raw material is pulped and usually bleached, resulting in market pulp; (ii) **paper mills**, in which the pulp is refined and filtered in the paper machine to form the sheet; (iii) **integrated paper mills**, in which the pulp is produced and processed to make paper or board.

The raw material is debarked and fractionated to chips. Chips are pre-impregnated with low-pressure steam to remove air and ease pulping. Released air can be vented to atmosphere without treatment. Pulping can be chemical or mechanical, or a combination of thereof (**semichemical**, semithermomechanical). **Mechanical** pulping is grinding the chips between refiner plates. **Thermomechanical** pulping also involves steam and/or hot water to soften lignin and separate fiber bundles. **Chemical** pulping implies *cooking* the chips with, in most cases, an aqueous alkaline liquor known as white liquor [16].

Figure 9 presents a simplified diagram of a pulp mill in which bleached market pulp is produced. Alkaline hydrolysis takes place with an aqueous solution of sodium hydroxide and sodium sulfide, which is the white liquor in kraft pulping processes. NaOH can be recovered from Na_2CO_3 in the green liquor by causticizing.

In small mills (100 kt per year or less), chips can be **cooked** in a batch reactor. Batch digesters are becoming less used. As small mills tend to cease and large mills tend to increase their production, a huge continuous reactor known as *Kamyr digester* or *Richter digester* is commonly used. It was named after engineer Johan Richter, inventor and CEO of Kamyr, currently part of Andritz and Metso.

Outlet streams of a Kamyr digester include the black liquor and the pulp. The black liquor, which contains hydrolyzed and solubilized lignin, is concentrated in a series of evaporators and burnt to produce energy. The pulp is screened to remove knots, large particles which can be recirculated to the reactor, and washed with water. Then, it can be conducted to the bleaching plant. An oxygen delignification stage is increasingly common, especially when cooking softwoods, and its position within the pulp mill may vary [36].

Not only was continuous pulping made possible by Johan Richter. By that time, this engineer had already patented **continuous bleaching**. And, again, it was first used by Kamyr.

Traditional bleaching processes involved selective delignification with chlorine and extraction with sodium hydroxide [16]. Now, bleaching comprises from 4 to 7 stages, reaching brightness values above 110% [37].

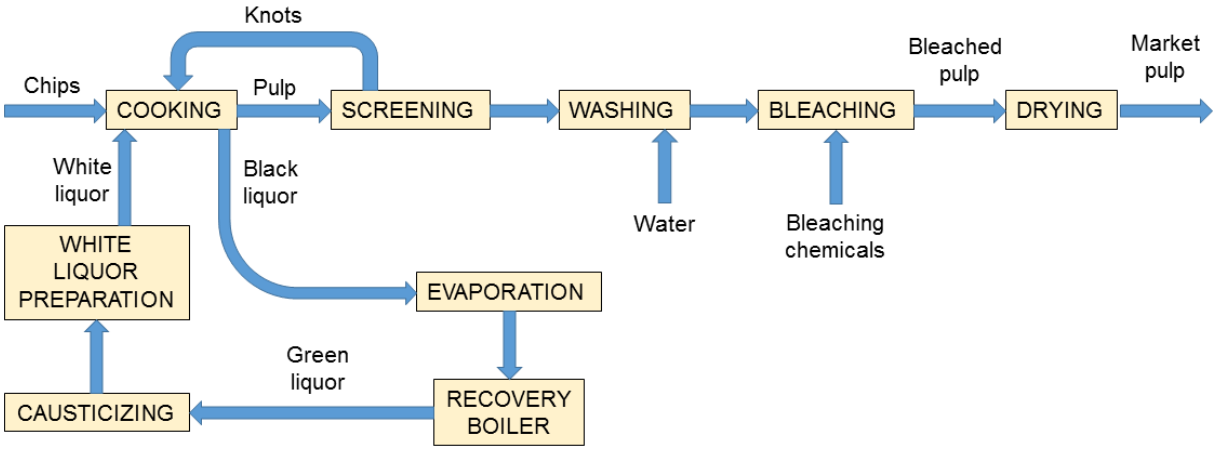

Figure 9. Scheme of the main operations taking place in a kraft pulp mill.

Regardless if the pulp has been bleached or not, it is **air-dried to the desired moisture content**. Even if this pulp has been produced in an integrated paper mill, drying is a necessary step to achieve a strong product: the elastic modulus of fiber walls was found to be doubled [38].

Then, this material is transported to the paper mill or, in the case of an integrated mill, processed *in situ*. It is crushed in the pulper and pumped to a series of chests. In the stock preparation chest, the pulp can be blended with some additives, possibly with alternative fibers (from recycled or mechanical pulps, for example), and diluted to the desired consistency to form the *stock* (2-5%). **It usually needs to be refined to strengthen fiber-to-fiber interactions** by increasing the relative bonding area of fibers. The stock passes between a stationary disc and a rotating disc. Refining is a mechanical operation involving cutting, swelling and fibrillation.

After refining, the stock is pumped towards the **blend chest**, where it is diluted again. Mineral fillers and some additives may be added. From there, the *slurry* goes to the **machine chest**, where consistency is meticulously controlled so that the paper sheet has the desired basis weight.

The **paper machine** is based on a wire or polyester woven mesh conveyor belt in which dewatering, pressing, drying and smoothing take place. Current machines have vastly evolved from the invention of Henry and Sealy Fourdrinier at the beginning of the 18th century [39].

The **head box** receives the slurry, which is stirred and whose air bubbles are removed. It lands of the wire and the sheet starts to be formed. As the web progresses, consistency becomes higher, reaching 25% and the end of the drainage table. This section is called **wet end**. Afterwards, the paper web is **pressed** to consistency values between 35% and 50%. **Dryers** use high-pressure steam to achieve the desired moisture content. Paper is then finished by passing between the **calenders**, becoming smooth

and ready to be wound onto rolls, stored, cutted, shipped and used. These operations are indicated in Figure 10.

This PhD thesis seeks opportunities to alleviate the environmental impact of the manufacturing of pulp and paper in pulping, bleaching, refining and wet end chemistry, by choosing sulfur-free methods, chlorine-free processes, alternative raw materials and cationic cellulose, respectively.

3.3.1. Pulping and sulfur compounds

If the raw material is adequate, packaging paper can be made out of mechanical pulps and thermomechanical pulps, as we showed for rapeseed stalks [5]. In general, these pulps can be used for all types of low-grade paper, such as newsprint [40]. However, non-chemical pulps cannot reach high brightness values, they turn yellow with time, and the large amount of lignin may hinder fiber-fiber interactions, which is translated into lower strength.

Therefore, almost all lignin must be removed for the manufacturing of quality printing paper or any kind of white paper that is meant to stay white with time. **Chemical pulping** involves several chemical reactions, mainly hydrolysis. Most pulp mills use kraft pulping in continuous reactors (Kamyr digesters). The most remarkable exception in Western countries is SAICA, the largest producer of corrugated paper. The SAICA process involves alkaline sulfur-free cooking, causing much less pollution than conventional mills [41].

Despite the complexity of continuous digesters, or more likely due to this complexity, researchers usually perform chemical pulping in batch reactors. And they (we) hope that their (our) experiments could be up-scaled.

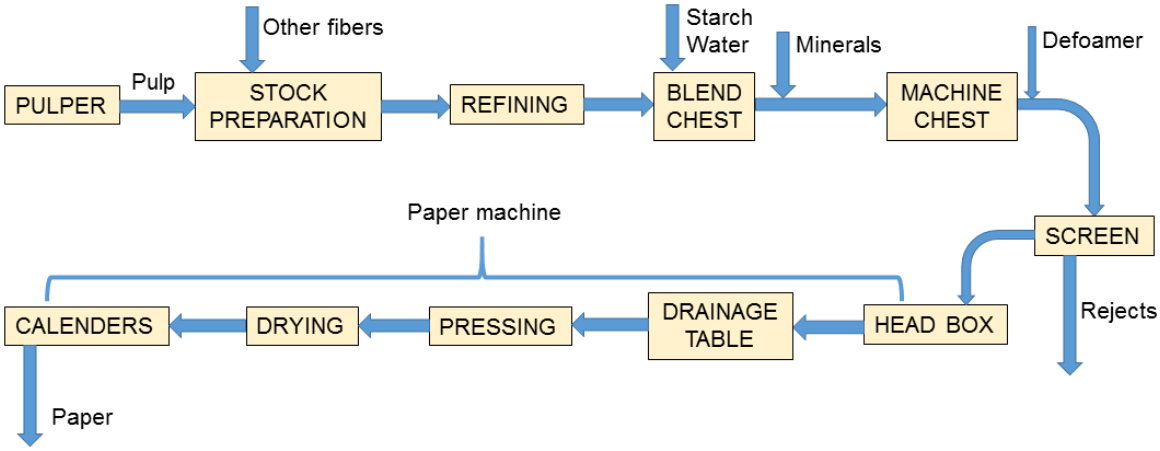

Figure 10. Possible block diagram for a paper mill.

Agarwal and Gustafson [42] modeled the kinetics of kraft pulping in batch reactors, but they stated that their equations could be exported to model the cooking zone of a Kamyr digester. I did it, although it should be taken into account that continuous reactors can achieve the same results with a lower liquid-to-solid ratio. The Matlab script can be found for free at my blog [43], but I suggest papermakers to look for more complex and more expensive models, such as that from the Purdue University [44].

The goal of kraft pulping is the alkaline hydrolysis of lignin with an aqueous solution, but, as opposed to the ancient soda process, it uses **sodium sulfide**.

To explain why most pulp mills use sodium sulfide, it must be clarified that alkaline hydrolysis of wood is not highly selective towards lignin. Most hemicelluloses are solubilized and lost in the black liquor. Even cellulose can be hydrolyzed to a tenth or less of its original degree of polymerization, and this depolymerization is enhanced by high NaOH concentrations and high temperatures. Excessive hydrolysis of cellulose results in weak products (paper or board). However, when papermakers started using the basic salt NaS_2, they were able to achieve the same degree of delignification with less NaOH. The presence of S_2^{2-} and HS^-, which is formed during the process, increases selectivity and the rate of delignification, particularly due to the nucleophilic attack of HS^- on lignin [45].

Acid **sulfite** pulping, which used to be more common than alkaline sulfate pulping (kraft pulping), has also found its place in modern papermaking. Its yield is lower, as it breaks down cellulose to a greater extent and it completely hydrolyzes hemicelluloses. As another consequence of this, paper is weaker, but it is good enough for tissue and glassine.

Sulfur compounds are related to bad odors and other environmental issues of a pulp mill. In an undesired side reaction of kraft pulping, HS^- ions attack methoxyl groups of lignin. This results in **methyl mercaptan**, whose odor threshold is as low as 1 ppb and whose leaks can cause fatal accidents at work. If no malfunction occurs, methyl mercaptan is almost completely converted at high pH values into **dimethyl sulfide**, much less dangerous. Other important gaseous emissions of kraft pulp mills include **hydrogen sulfide** and **dimethyl disulfide**. All of them have unpleasant odors, even at very low concentrations. Toxic emissions also include non-sulfur compounds like **formaldehyde** and **acetaldehyde**, which are rarely found when using caustic soda alone. In sulfite pulp mills, the most important emissions involve **SO_2** and particulate matter [46].

We have tried two different approaches regarding sulfur-free pulping:

- **Soda or soda-anthraquinone** (SAQ) pulping (Publications VI and VIII). The addition of a very small amount of anthraquinone was first proposed by Holton [47], decades later than the addition of sodium sulfide, and it plays a

similar role: increasing selectivity. However, instead of enhancing the delignification rate, it inhibits the hydrolysis of polysaccharides. It works best with non-wood materials, such as cereal straw. Yet, Holton's findings were often used to complement, not replace, sodium sulfide in the kraft process [48]. A diagram of a semichemical SAQ pulping process is shown in Figure 11. Like in kraft pulping, the green liquor, containing Na_2CO_3, can be causticized to recover NaOH.

- **Organosolv** pulping with ethanolamine as a selective solvent for lignin (Publications VI and VII). This started in 1971 with a patent of Kainert [49], but the only industrial application was the Alcell process, between 1989 and 1995, in Canada [4]. The paper industry consumes more water than any other manufacturing industry, but organosolg pulping requires notoriously less water than SAQ pulping or kraft pulping. Also, the yield reached by pulping with organic solvents is much higher, since it preserves hemicelluloses. As drawbacks, it needs higher temperatures and, besides holocellulose, preserves too much lignin. Figure 12 presents a scheme of this process.

3.3.2. Bleaching and chlorine compounds

Pulping processes manage to remove the majority of lignin from the raw material, which is in the range of 11-23% for straw, 19-27% for hardwoods and 24-33% for softwoods [50,51]. But **unbleached kraft pulps still have a notorious amount of remaining lignin**, 2-5%, and its brightness is lower than 50%. White printing paper generally requires brightness values above 93% and a lignin content below 0.6%.

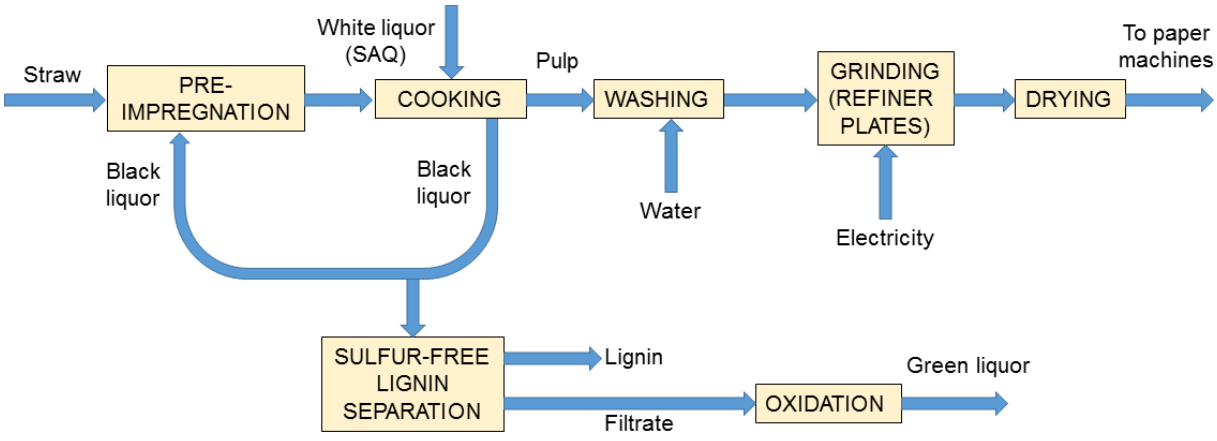

Figure 11. Block diagram of a semichemical pulp mill with soda-anthraquinone pulping, inspired in the sulfur-free SAICA process [41].

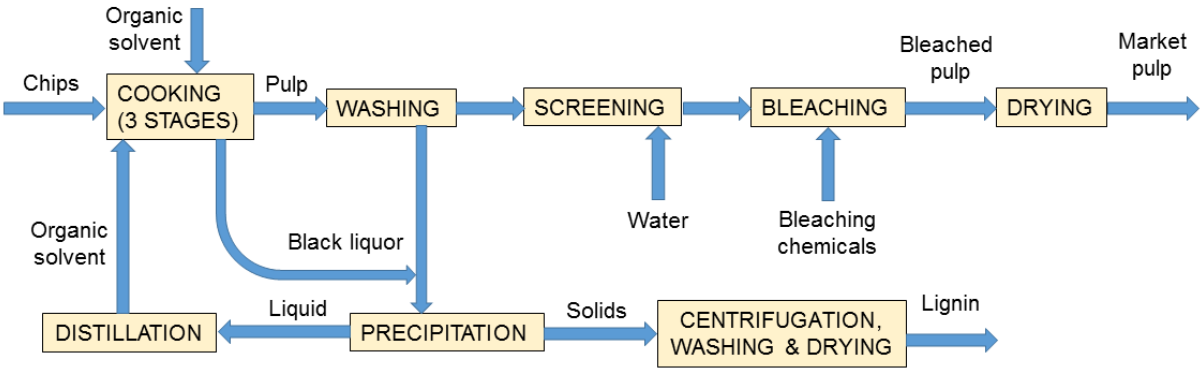

Figure 12. Block diagram of an organosolv pulping process. The Alcell process used ethanol as the organic solvent [4].

Bleaching processes keep reducing the lignin content, but in a more selective way and using more expensive chemicals than pulping. Besides being more expensive per gram of lignin removed, bleaching consumes more water. Also, while the main environmental issues of pulping were related to gaseous emissions, the main issues of bleaching plants are found in their **liquid effluents**.

Bleaching chemicals are oxidizing agents which break bonds inside the structure of lignin and between lignin and holocellulose. Table 3 presents their equivalent chlorine, defined as the mass of Cl_2, in kg, that has the same oxidizing power as 1 kg of the reagent in each case. Efficiency indicates how much of that power is used in selectively breaking lignin. The codes shown are used to describe bleaching lines, which consist of several stages in series. For example, a sequence labelled O(DE)H(DE)P starts with oxygen delignification, has two stages of ClO_2 with caustic extraction and hypochlorite treatment between them, and finishes with hydrogen peroxide.

Most modern bleaching plants are based on *elemental chlorine free* (ECF) processes, avoiding the huge risks of Cl_2. **The key reagent in ECF bleaching is chlorine dioxide**. Unlike Cl_2, ClO_2 does not generate 2,3,7,8-tetrachlorodibenzo-p-dioxin, extremely toxic. It reduces the generation of chlorinated compounds by approximately 90% [52].

Possibly, papermakers did not replace Cl_2 with ClO_2 for safety or environmental concerns, but because ClO_2 allowed them to work with higher pulp consistencies, from 3-4% to 11-12% [16]. While ClO_2 is much less hazardous than Cl_2, chlorine dioxide and sodium hypochlorite still generate small but noticeable amounts of chlorinated organic by-products. These include chloroform and 2,3,7,8-tetrachlorodibenzofuran [52].

Total chlorine free (TCF) bleaching is a step beyond ECF sequences. It implies using no chlorine compounds, neither chlorine dioxide nor sodium hypochlorite. As a consequence, no chlorinated by-products are formed.

Table 3. Codification and characteristics of different chemicals in a bleaching plant [53].

Reagent	Cl_2	ClO_2	O_2	H_2O_2	NaClO	O_3	NaOH
Code	C	D	O	P	H	Z	E
Equivalent chlorine	1.00	2.63	4.44	2.09	0.93	4.44	--
Efficiency	High	High	Low	Low	Medium	High	--
Reactivity	High	Medium	Low	Low	Medium	High	--
Environmental impact	High	Medium	Low	Low	High	Medium	--

A TCF sequence should consist on a combination of these stages:

- **Oxygen** delignification. It is very helpful as the first stage of ECF processes, but mandatory in TFC bleaching. Phenolic groups and arylalkyl groups oficio depolymerized lignin are oxidized to arylcarbonyl groups. These structures are more hydrophilic and can be easily removed [36].
- Selective lignin oxidation with **ozone**. Although more expensive and less environmentally friendly, it gives out higher delignification rates than oxygen. It even attacks double carbon-carbon double bonds in aromatic groups of lignin. Its selectivity is higher [54].
- Oxidation with **hydrogen peroxide** (or sodium peroxide) of chromogenic groups in lignin (Publication VII). While the brightness gain is notorious, lignin removal is slight. Hydrogen peroxide bleaching was originally used to complement chlorine dioxide, as the last step of the bleaching sequence [16]. Figure 13 shows a diagram of a P stage.

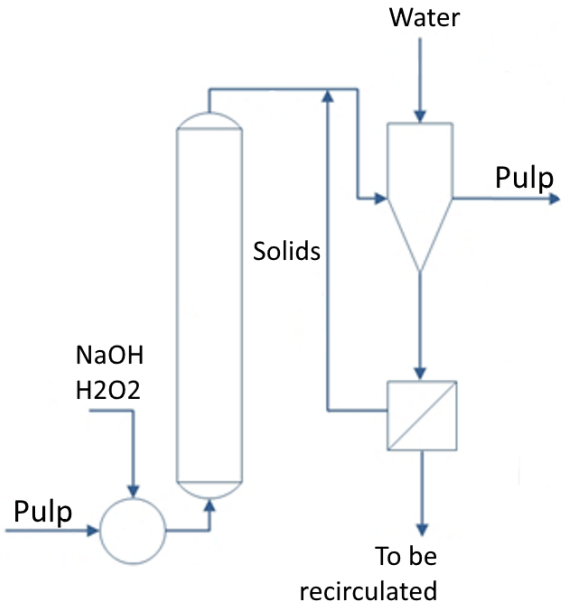

Figure 13. Flowchart of a hydrogen peroxide stage in a bleaching sequence.

- Caustic extraction with **NaOH**. This is common to traditional bleaching with Cl_2, ECF bleaching and TCF bleaching.

From an economic point of view, if high brightness values are desired, ECF processes are more advantageous than TFC bleaching. The first pulp mill which had no chlorine or chlorine compounds in its bleaching line, Metsä Fibre's Rauma mill in 1996, switched from TFC to EFC in 2007 [55]. More research needs to be conducted into TFC bleaching stages to make them capable of reaching high brightness values while staying feasible.

3.3.3. Refining and electricity consumption

Refining accounts for the **highest energy input during stock preparation**. The specific energy consumption for graphical papers in this stage ranges from 1.5 to 3 GJ per tonne of stock, most of which goes to refining [56]. In a mill which produces virgin paper, the most energy-consuming operations are refining and drying.

The Schopper-Riegler number (SR) and the Canadian Standard Freeness (CSF) are the two primary ways to measure and express the effects of refining, at least those effects that are directly related to sheet formation and paper strength. They are rough indications of water retention and dewatering rate, but the latter should not be confused with the former, since there are specific methods or devices to determine and report the water retention value and the drainage rate.

Refining generates fines and causes fiber fibrillation. This strengthens fiber-to-fiber interactions, thus increasing the amount of water that is retained on the wire upon filtration of a diluted pulp suspension.

Regardless of the cooking method, chemical pulps from softwoods require more energy than chemical pulps from hardwoods to achieve the same values of SR or CSF. Cereal straw pulps do not need refining, given their high proportion of fines [12]. Therefore, the most evident way to save energy during stock preparation is **changing the raw material**, if possible.

Figure 14 presents CSF values for chemical pulps from different materials, as a function of the number of PFI revolutions. Data related to softwoods, hardwoods, bagasse and straw belong to the work of Banavath et al. [57]. Mutjé et al. [6] reported the results for olive tree trimmings. As for rapeseed stalks and orange tree trimmings, they are characterized in our contributions (Publications VI and VII).

PFI revolutions are revolutions in a laboratory device that fulfills the ISO standard 5264-2. This device is called *PFI mill*. The standard allows for comparisons to be made between works which involve refining mills from different manufacturers. Also, the number of PFI revolutions is linearly proportional to energy consumption.

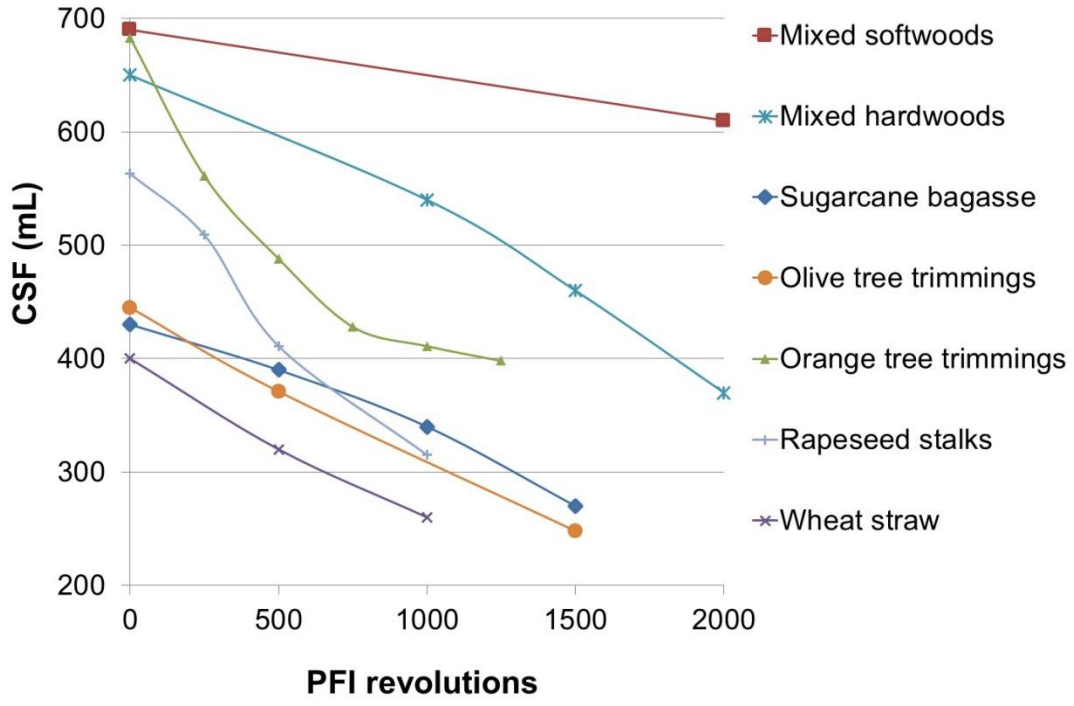

Figure 14. Effect of the number of PFI revolutions on freeness (CSF) for pulps from various raw materials.

The horizontal axis in Figure 10 has been cropped for the sake of easy comparison, but softwoods would require 4000 PFI revolutions to reach a CSF value of 460 mL, which is what hardwoods achieve with 1500 PFI revolutions [57]. In a paper not included in this document, we showed that **CSF is very influential** on the tensile strength, the tear strength and the burst strength of paper sheets [31].

The lower CSF is, the stronger the **interactions** among fibers. However, **dewatering becomes slower** and this may hinder sheet formation. No matter how large the relative bonding area is, if sheet formation goes wrong, the final product will lack dry strength.

Let us figure, for instance, that a CSF value of 460 mL is desired for a certain kind of paper. If 1000 revolutions in a PFI mill correspond to roughly 1 GJ/t in a paper mill, which is a reasonable assumption, then:

- Softwoods (e.g. pine wood) would need 4 GJ/t.
- Hardwoods (e.g. eucalyptus wood) would need 1.5 GJ/t.
- Orange tree trimmings and rapeseed stalks would need 0.7 and 0.4 GJ/t, respectively.
- Olive tree trimmings and bagasse would be in the right range to proceed with blending.
- Some fines would have to be removed from wheat straw by screening.

Almost all works on refining deal with its **influence on mechanical properties, surface charge and fiber morphology** [5]. Fibers are shortened but their surface is roughened, so there is generally an increase in tensile strength and burst strength, and the negative charge of fibers becomes higher [58]. Nonetheless, few works deal with the effect on refining on chemical modifications of fibers. Choi et al. [59] found that pulps are swollen to a greater extent with NaOH if they have been refined before the alkaline treatment. If an alkaline treatment eases cationization and refining enhances the effects of alkaline treatments, evaluating the use of mechanical operations to improve cationization seems appropriate (Publication IV).

3.3.4. Wet end chemistry and the limitations of recirculating water

Since the first papermaking processes appeared in the second century, makers have wished to achieve, at the same time, fast drainage and a strong web of fibers. Currently, they also want abundant retention and homogeneous distribution of mineral fillers.

It is known that “difficult” fiber furnishes —those than run poorly on the paper machine due to the slow filtration— are related to the adverse effects of recycling, which is why we insist in our publications on the need to produce virgin fibers in a cleaner way [5]. But wet end problems may also happen with virgin pulps: too many fines, too much filler, high conductivity, excessive fibrillation, anionic colloids, surfactants, and pitch [7].

Sheet formation is a **filtration and thickening operation**. Water drains from the sheet through paths along the random web of fibers. Fines, fillers and other small particles may block the paths, although they are necessary for a number of reasons —e.g., opacity. Also, when fibers collapse, which is favored by severe chemical pulping, the contact between fibers is so close that water has little space to flow.

However, **fibers are negatively charged**, mainly due to the remaining carboxylic groups from uronic acids (Figure 15). The negative charge density of commercial paper might be as high as 24 μeq/g [60]. With the focus on sheet formation, this is good. Repulsion between fibers prevents them from collapsing. It also helps us achieving good retention of cationic additives, such as cationic starch.

Fines may constitute a large part of the pulp [12], but they are small enough to pass through the wire. In fact, although consensus about the definition of ‘fine’ seems to be impossible, it is reasonable to regard as fines those fibrous elements whose length is smaller than the aperture size of the wire. This aperture size generally lies between 100 and 150 μm. Table 4 contains the dimensions of fibers, fines and fillers that are considered along the text. Note that this classification does not presume to be universal.

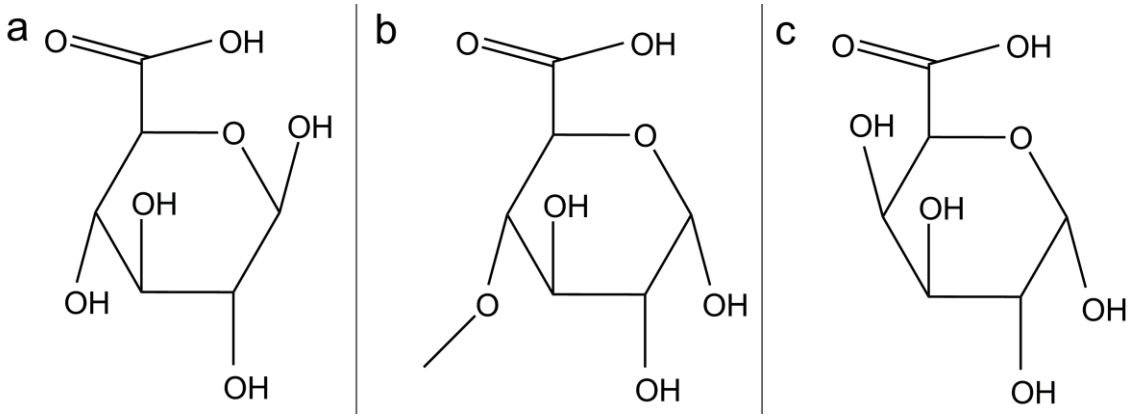

Figure 15. Some uronic acid monomers from hemicellulose: a) β-glucuronic acid; b) α-4-methoxyglucuronic acid; c) galacturonic acid. Author's drawing.

Table 4. Sizes and surface areas of fibers, fines and fillers as considered in this dissertation.

	Fibers	**Fines**	**Fillers**
Length	0.1-4 mm	<100 µm	0.2-4 µm
Length/width	30-60	>10	1-5
Surface area	1-2 m^2/g	3-6 m^2/g	6-15 m^2-g

Three things can happen with fines, but only one of them is good:

- **Fines are retained because they become attached to fibers**. This is the one thing that papermakers want to happen. It rarely occurs spontaneously, since fines are even more negatively-charged than fibers due to their higher surface area. Cationic polyelectrolytes are usually needed to achieve good retention of both fines and fibers.
- **Fines are mechanically retained (sieving mechanism)**. That is, they do not pass simply because the web of fibers below them does not let them pass. Then, they become unevenly distributed and they block the paths for water, slowing drainage.
- **Fines are hardly retained**. Low fines retention is related to severe problems in papermaking. A poor retention of fines slows drainage [7]. And when fines are lost, many wet-end additives are lost too, since fines collect more additives than fibers [61]. Wastewater issues, deposits in chests and instability are consequences of not retaining the fines.

Likewise, filler retention cannot depend on the sieving mechanism. The size of those particles is even smaller than the size of fines, so they must be somehow attached to the surfaces of the fibers and fines. Nonetheless, **many fillers** commonly used in papermaking are, like cellulosic fibers, **negatively charged**. London dispersion forces, although irrespective of the surface charge, are too weak to overcome repulsion [7].

Anionic colloidal substances, which generally come from hemicellulose, slow down drainage, form complexes with cationic starch —which should be bonded to the fiber surface— and stay in recirculating water. The way to deal with fines, fillers and anionic substances is nearly the same: **cationic polyelectrolytes** such as positively-charged copolymers of acrylamide (CPAM), poly-diallyldimethylammonium chloride (PDADMAC), poly-aluminum chloride (PAC) and polyethyleneimine (PEI). In papermaking, these flocculation agents are commonly known as *retention aids*.

As shown in Figure 16, polymeric retention aids usually interact with particles in three different ways:

- **Charge neutralization** (Fig. 16a) makes the net zeta potential of the furnish particles approach zero, speeding drainage and easing the retention of anionic substances [62]. A suitable aid for this purpose is PAC. It must be noted that neutralizing all the negative charges at the surface of the cellulosic fibers is rarely a goal of papermakers [7].
- **Cationic patches** (Fig. 16b) are islands with positive charge on the fiber surface [63]. Electrostatic interactions between these islands and negatively-charged particles enhance retention. Cationic patches are produced when polymers with high charge density and low or medium molecular weight, such as PEI, are used.
- By **bridging flocculation** mechanisms (Fig. 16c), as long as the molecular weight of the polymers is high enough, they attach fillers and fines to fibers. Bridging is especially important in papermaking because it provides fast flocculation [64]. This is why cationic polyacrylamides with high molecular weight and medium charge density are so valuable. They achieve good results with short residence times in the head box, even when the zeta potential of the mineral filler is not negative.

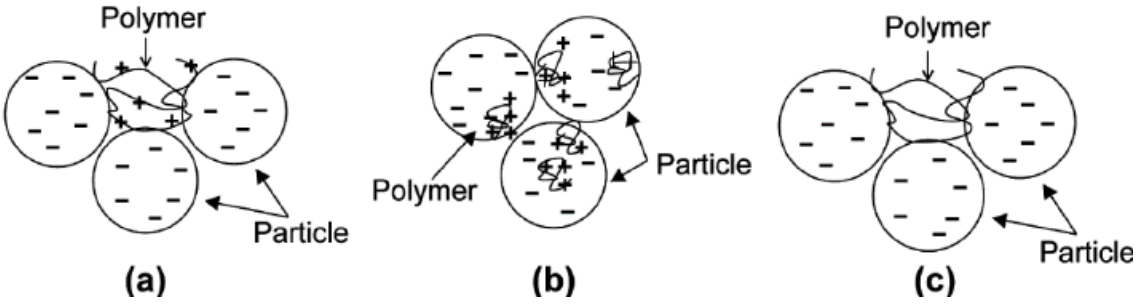

Figure 16. Dominant flocculation mechanisms when dealing with negatively-charged particles and polyelectrolytes [65]: a) charge neutralization; b) cationic patches; c) bridging.

As aforementioned (*vid*. *3.2. Cationization of cellulose*), **cationization of polysaccharides** has been proposed as a way to replace oil-based polyelectrolytes with cost-effective, more biodegradable, less toxic polymers from vegetable biomass [24]. Cationic starches are already implemented in papermaking, but as a sizing agent and a strength agent, not as a replacement of CPAM [7]. Regarding the cationization of cellulose, the main problem is the difficulty to produce a polyelectrolyte which is soluble in water and long-chained at the same time (Publication V).

3.4. State of the European pulp and paper industry

Almost the whole European production of pulp and paper comes from CEPI countries. *CEPI* stands for *Confederation of European Paper Industries*. It comprises all the manufacturers from Austria, Belgium, Czech Republic, Finland, France, Germany, Hungary, Italy, the Netherlands, Norway, Poland, Portugal, Slovak Republic, Slovenia, Spain, Sweden and United Kingdom.

In 2015, CEPI's manufacturing of paper and board accounted for 22.3% of worldwide production, which was as large as 407.6 million tonnes. Asian papermakers constituted the greatest producing region in the world, accounting for 46.1%. Among CEPI countries, Sweden and Finland are the largest pulp producers [1].

The trend in this industry is characterized by **the increasing shutdown of small mills and the increasing company closures**, as shown in Figure 17. Instead, the capacity of large mills is raised. Employment diminished from 411 thousand workers in 1991 to 177 thousand workers in 2016 [1]. Likely due to the high-fixed capital investment that is required, papermaking seems to favor centralized manufacturing, at least in Europe. The total production of market pulp, paper and board remains nearly constant upon time. However, although the annual turnover stays approximately the same, the added value is decreasing (Figure 3).

Fortunately, European manufacturers of pulp and paper have been diligent and innovative in techniques to **decrease hazardous emissions to air and water**. Table 5 shows that in 1991, 433 g of organic chlorinated compounds were discharged. It should be taken into account that, by then, ECF bleaching was already the standard —those high values of AOX were not due to chlorine gas. The implantation of new technologies for wastewater treatment [66] made bleaching with chlorine dioxide much more environmentally-friendly. The specific emissions of AOX to water decreased by 94.7% from 1991 to 2015.

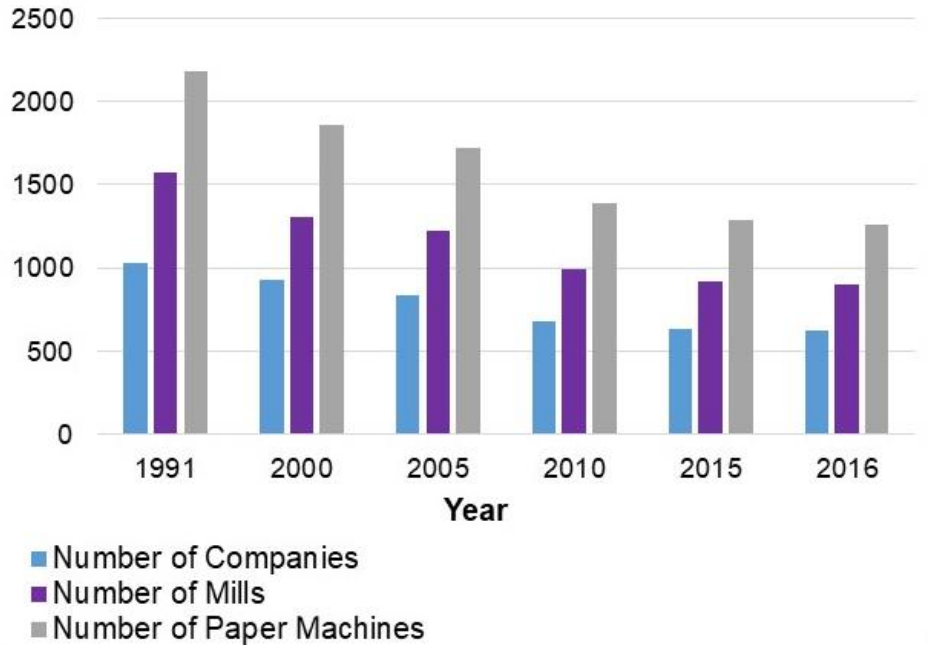

Figure 17. Evolution of the number of facilities dedicated to the manufacturing of pulp, paper and/or board in CEPI countries (CEPI, 2017).

Table 5. Environmental performance of European pulp and paper mills, from 1991 to 2015.

Year	Electricity consumption (MWh/kt)	AOX to water (kg/t product)	SO_2 to air (kg S/t product)
1991	1.2	0.433	1.32
2000	1.12	0.049	0.4
2005	1.04	0.03	0.32
2010	1.07	0.03	0.24
2014	0.98	0.022	0.15
2015	0.98	0.023	0.16

Likewise, the specific emissions of SO_2 to the atmosphere was reduced by 87.9% in less than 25 years (Table 5). SO_2 emissions can be directly produced by acid sulfite pulping or by oxidizing dimethyl sulfide, dimethyl disulfide and hydrogen sulfide in a kraft pulp mill. Nowadays, acid sulfite pulping is scarcely used for the manufacturing of paper and board, and it has been surpassed mechanical and semichemical pulping (Table 6).

Also, as shown in Figure 2, the main raw material for the manufacturing of paper and board is wastepaper. **Recycling** wins over the production of virgin fibers.

This motivated the final hypothesis of this PhD thesis (*vid. 2.4. Statement of hypotheses*). **Lignocellulosic residues** *per se* are not appealing to Western papermakers, while lawmakers are satisfied with the environmental performance of

modern pulp mills. Using the experience gained with cellulose cationization to modify non-wood fibers may result in a more feasible alternative to reuse agricultural waste, improving certain properties and providing a way to increase the added value of the paper industry (Publication VII).

Table 6. Production and consumption of pulp in 2016, differentiating by the pulping method.

	Production (kt)	**Consumption (kt)**
Mechanical and semichemical pulps	10145	10105
Kraft pulp	24993	29411
Sulphite pulp	1820	1639
Total	36958	41155

4. ANALYTICAL TECHNIQUES

4.1. X-ray diffraction

Out of 8 publications that are presented in my dissertation, six involve X-ray diffraction (XRD). Cellulose Iβ, the main structure of cellulose in vascular plants, is arranged in small crystals as a result of the interactions among hydroxyl groups from different chains and from the same chain. In Publications I, II, III, IV, V and VIII, XRD is used to identify polymorphs and to estimate the crystallinity index.

X-rays are emitted by a cathode ray tube, filtered to produce monochromatic rays, collimated and directed towards the sample. The sample and the detector are rotated to record the intensity of the reflected X-rays trough the desired range of angles of incidence (*θ*). The device used in the works mentioned was a X-ray powder diffractometer from PANalytical.

At certain incident angles, scattered X-rays interfere constructively. In Figure 18, where *d* is the distance between planes of the crystal, there will be constructive interference when the travel length difference between paths A-B-C and A'-B'-C' is an integer (*n*) multiple of the wavelength (*λ*). Wavelength values satisfy Bragg's equation [67]:

$$n\,\lambda = 2\,d\,sin\theta \qquad (1)$$

Then, a diffracted ray will leave the sample at the same angle as that of the incident beam. **This is translated into a peak in X-ray diffraction patterns**.

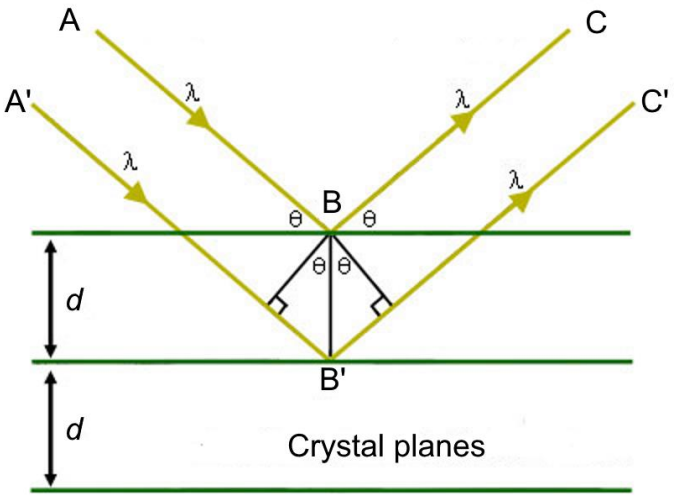

Figure 18. Incident X-rays (A-B, A'B') and diffracted X-rays (B-C and B'-C') over a crystalline sample.

For each crystalline structure, including organic matter, there is a certain XRD pattern. If we submit a cellulosic sample to this technique, we may obtain peaks from different polymorphs (viz. 3.1.1. Modifications of cellulose in which the product is still cellulose). French [17] showed ideal patterns of cellulose Iα, cellulose Iβ, cellulose II and cellulose III. Amorphous cellulose is characterized by the lack of peaks. Moreover, the author advocated for a convention regarding the Miller indices [17].

A **Miller index** is formed by three indices and designates a certain plane or family of planes in a crystal lattice. It defines the orientation of this or these planes in a vector space. For example, according to French [17], a cellulose II pattern shows a characteristic peak at 2θ = 20.1º, corresponding to the (110) plane. But for a given vector space, different researchers can place unitary vectors $\vec{\imath}$, $\vec{\jmath}$ and $\vec{k}$ in different ways. For instance, in publications I and II, the Miller index we assign to this reflection is '(101)'. When I first read French's work, I was convinced of the need of a convention, and thus his notation is followed in Publications IV, V and VIII.

In addition, the way to show negative terms may value. French [17] writes '(1-10)' for the peak of cellulose Iβ at 2θ = 14.9º, but other authors express the same thing by '$(1\bar{1}0)$' [68]. Figure 19 shows an example of X-ray diffraction pattern for cellulose from wood (mainly Iβ), placing Miller indices at the corresponding peaks.

The degree of crystallinity or **crystallinity index (CI)** was estimated in Publication I by our own variation of the height method, consisting on a ratio of intensity values. Most authors use a ratio of intensities to calculate CI, but this results in an overestimation [68].

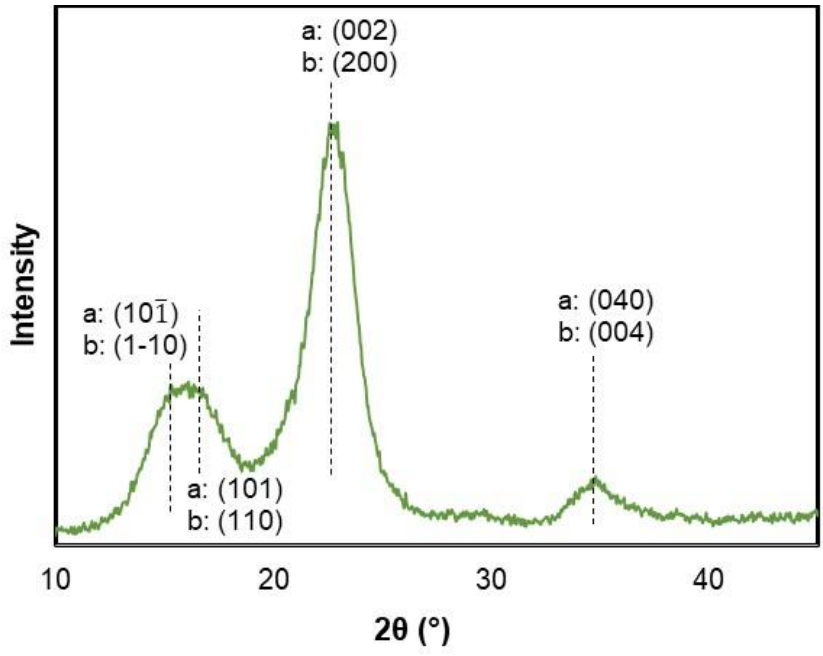

Figure 19. X-ray diffraction pattern of cellulose from pine wood; a: Miller index used in Publications I and II; b: Miller index used in Publications IV, V and VIII.

From Publication II on, we chose the area method. This way, following peak deconvolution by adequate software, crystalline peaks are identified and the sum of their areas is divided by the total area below the pattern [69]. The software we used was Systat's Peakfit.

4.2. Elemental analysis

Publications I, II, III, IV, V and VIII included the determination of the amounts of carbon, hydrogen and nitrogen contained in a cationic cellulose powder. The technique chosen for this measurement was elemental analysis by combustion.

If the aim was to determine the percentage of nitrogen in fibers (Publications I, II, III, IV, VIII), they were vacuum-dried and ground up in a knife mill to a powder as fine as possible. In Publication V, where a water-soluble derivative was obtained, water was removed by evaporation. Either way, 1 mg of sample was enough for the device used, a CNS-2000 analyzer from LECO Corporation.

When the sample was ready, it was burnt in excess of oxygen. Different traps in the elemental analysis instrument collected **CO_2, H_2O and NO**. The masses of these combustion products was used by the device's software to express the percentage of carbon, the percentage of hydrogen and the percentage of nitrogen in the initial sample.

The results from this analysis allowed us to report the degree of substitution (DS), also called degree of nitrogen substitution (DNS) in this case, of cationic cellulose. For that, the sample was always assumed to consist solely of cellulose. The remaining contents of lignin and hemicellulose after alkaline pulping are not negligible, but those compounds are also cationized [70]. From the percentage of nitrogen (%N), DS is given by:

$$DS = \frac{162\ \%N}{1401 - 152\ \%N} \quad (2)$$

In Equation 2, 162 is the molecular mass of AGU, 152 is the molecular mass of a quaternary ammonium group, and 1401 is 100 times the atomic mass of nitrogen. If the sample is suspected to have some moisture, the measurements of carbon and/or nitrogen can be used to correct the result.

Another way to calculate DS was followed in Publication V. By using the carbon/nitrogen ratio, the moisture content is no longer a problem:

$$C/N = \frac{14\ DS}{144\ DS + 72\ (1 - DS)} \quad (3)$$

In Equation 3, 14 is the atomic weight of nitrogen. There is only one nitrogen atom per quaternary ammonium group (Figure 6). 144 is twelve times the atomic weight of

carbon, since a substituted monomer contains 12 carbon atoms. 72 is six times that weight, as a non-substituted monomer in cellulose contains 6 carbon atoms.

4.3. Viscometry

When a polymer is dissolved in a liquid, the viscosity of the new solution is higher than that of the starting liquid. This increment of viscosity depends on the nature of the polymer, on its spatial distribution and on its molecular weight, although the contribution of polymers bearing electric charges, like cationic cellulose, can be difficult to predict. The **Mark- Houwink equation** relates the limiting viscosity number or intrinsic viscosity (η) to the molecular weight of the polymer (M):

$$\eta = K\,M^{a} \quad (4)$$

K and a are positive constant parameters. While a ranges from 0.7 to 0.8 for most polymers, it can be as high as 2 for anionic or cationic polyelectrolytes [71].

η can be determined by using a capillary viscometer, following the TAPPI standard T230 (2008). This determination was carried out in Publications III, IV and V. Figure 20 presents the Cannon-Fenske viscometer, which, like the Ostwald viscometer, is compatible with TAPPI T230.

First, a 0.5M aqueous solution of copper(II) ethylenediamine (CED) was prepared. CED is a well-known solvent for cellulose [72]. We wrote down the time that took the solution to fill each of the bulbs of the viscometer at 40 ºC. The non-modified, alkalized or cationized chemical pulp was added to the aqueous solution so that the consistency was 0.5%. We needed vigorous stirring to dissolve the fibers. Again, the time spent in filling the bulbs was measured.

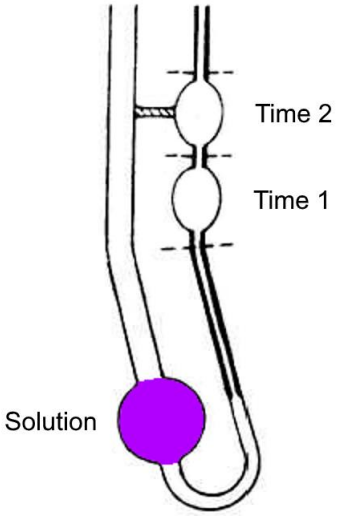

Figure 20. Cannon-Fenske viscometer.

The quotient between the time of the cellulose solution and the time of CED provided the relative viscosity. After each cycle, the viscometer was cleaned in two steps, first with sulfuric acid and then with acetone.

The ISO standard 5351 (2010) contains tables and equations to calculate the **limiting viscosity number** from the relative viscosity. In Publication III, following the terminology of most researchers or journals and not that of the standards, the limiting viscosity number is called **intrinsic viscosity**.

4.4. Gallium pycnometry

In Publication IV, we introduced a novel way to measure the **apparent density** of a test pad of fibers. We proposed gallium pycnometry as a safe and easy alternative to mercury pycnometry. Like liquid mercury, liquid gallium does not enter the pores either, but the method, which resembles that of water pycnometry, does not require any particular device.

For each of the measurements, a suspension of disintegrated pulp was dewatered on a wire screen to obtain a pad of fibers. The pad was left drying at room temperature and at a relative humidity of 50% for 48 h. Then, we weighed it.

Gallium was heated to its melting point at 1 bar, 29.8 ºC, and poured into a glass pycnometer for liquids and solids. The pycnometer was filled until the mark was reached. Once full, it was weighed. In order to empty the pycnometer, viscosity was decreased by heating to 100 ºC or more.

The test pad was placed in the pycnometer for liquids and solids, as described in the TAPPI standard T258 for the determination of the density of pulpwood chips, but then we used gallium instead of water to fill the container. The pycnometer was weighed once more, which allowed us to calculate the **specific gravity** (*SG*):

$$SG = \frac{M_1}{M_1 - (M_2 - M_3)} \quad (5)$$

In Equation 5, M_1 is the mass of the test pad, M_2 is the mass of the pycnometer with pulp and gallium, and M_3 is the mass of the pycnometer with gallium only.

The specific gravity was multiplied by 6.095 g cm^{-3}, the density of gallium at 30ºC [73], although we performed the test at higher temperatures to decrease viscosity —the density of liquids can be assumed to stay constant in a certain range.

At any given temperature, the surface tension of gallium is even higher than that of mercury, and thus this liquid metal could be, besides safer, at least equally suitable to measure the apparent density of materials [74]. The only major drawback seems to be its viscosity, also higher than that of mercury [73].

4.5. Determination of optical properties

Opacity, light scattering coefficient, brightness and color are key optical properties of paper sheets. All of them can be easily determined with a spectrophotometer that conforms to ISO 2471 (2008) for opacity, to ISO 9416 (2009) for light scattering, to ISO 2469 (2014) for brightness and to ISO 5631 (2015) for color. The Elrepho spectrophotometer from Lorentzen & Wettre that was used in Publications IV, VII and VIII fulfills those requirements [75].

The user only has to place the sample or samples on the measurement table and select the appropriate filter on the software. The light source of the Elrepho spectrophotometer is a pulsed xenon lamp.

To measure **opacity**, the device needs to compare the reflectance factor of a handsheet over a black cavity to the reflectance factor of an opaque pad of the same material. We decided to stack five identical sheets to form the opaque pad. The measurement was always carried out at C/2º (illuminant/observer). The report included parameters to calculate the **light scattering** coefficient. For **brightness**, the equipment chose a wavelength of 457 nm (diffuse blue reflectance factor) and a width at half-height of 44 nm. **Color** measurement was performed by quantifying the degree of light to dark (*L**), red to green (*a**) and yellow to blue (*b**). Yellowness was reported in Publication VIII.

4.6. Determination of mechanical properties

Typically, the most common ways to break paper are tearing, pressing and stretching. In Publications VI and VII, and also in Aguado et al. [76][31], we report the performance in those tests with the tear index, the burst index and the tensile index.

Mechanical testers are devices that apply increasing forces on a handsheet until it gets broken. The **burst** test was carried out by using a Metrotec tester that conforms to the ISO standard 2758 (2014). The raw result was the absolute pressure at which the sheet was perforated. Then, the burst index (*BI*) was calculated from this pressure and the basis weight (*G*) as follows:

$$BI\left(kPa\ m^2/g\right) = \frac{P(kPa)}{G(g\ m^{-2})} \quad (6)$$

The Elmendorf **tear** tester, a device from Messmer Instruments which carries a pendulum, determined the work done in tearing the paper by measuring the loss of potential energy from the pendulum, according to the ISO standard 1974 (2012). The force at which paper has been broken is the quotient between this work (*W*) and the

distance over which the tearing force acts (*D*). The tear index (*TearI*) is given by Equation 7:

$$TearI\left(mN\ m^2/g\right) = \frac{W(mJ)}{D(m)\ G(g\ m^{-2})} \quad (7)$$

Finally, **tensile** properties were measured by following the ISO standard 1924 (2008). We used a mechanical tester from HT Hounsfield. The principle is very simple. The device stretches a rectangular handsheet, whose width (*w*) has to be taken into account to calculate the tensile index (*TensI*), and reports the elongation force (*F*) at which breaking occurs.

$$TensI\left(N\ m/g\right) = \frac{F(N)}{w(m)\ G(g\ m^{-2})} \quad (8)$$

4.7. Infrared spectroscopy

Molecular vibrations occur at any temperature above 0 K. When infrared radiation —above 800 nm wavelength— interacts with a molecule, there is a certain value of absorbance or transmittance for any given frequency of wavelength. This generates a characteristic infrared (IR) spectrum. The shape of the spectrum in Figure 21 corresponds to a bleached kraft pulp, essentially alpha-cellulose.

The horizontal axis of Figure 19 is located in the mid-infrared region, i.e., 4000-400 cm^{-1} or 2.5-25 μm. This range is the appropriate one to study the fundamental vibrations of bonds in most polymers, including cellulose.

Currently, the most common way to record infrared spectra is using a **Fourier transform infrared** (FTIR) spectrometer with a dedicated computer, as we did in Publication V. Infrared light passes to an interferometer before reaching the sample and an *interferogram* is recorded. The Fourier transform gives out the IR spectra in an accurate way [77].

For the direct analysis of cellulosic fibers, it is recommended to use a technique called **attenuated total reflection (ATR)**. IR radiation passes through a crystal of high refractive index which is located right before the sample, in contact with it. The crystal has an evanescent effect on the IR beams, allowing them to penetrate into the solid sample [78].

Table 7 relates notorious peaks in a cellulose IR spectrum to the corresponding bending and stretching vibrations of covalent bonds. In the spectrum of Figure 21, we can identify typical peaks for cellulose at 3327 cm^{-1} (f), related to O—H stretching, and at 2882 cm^{-1} (e), assigned to symmetrical stretching of C—H bonds. The most prominent peak of the cellulose spectrum is found at 1020 cm^{-1} (b).

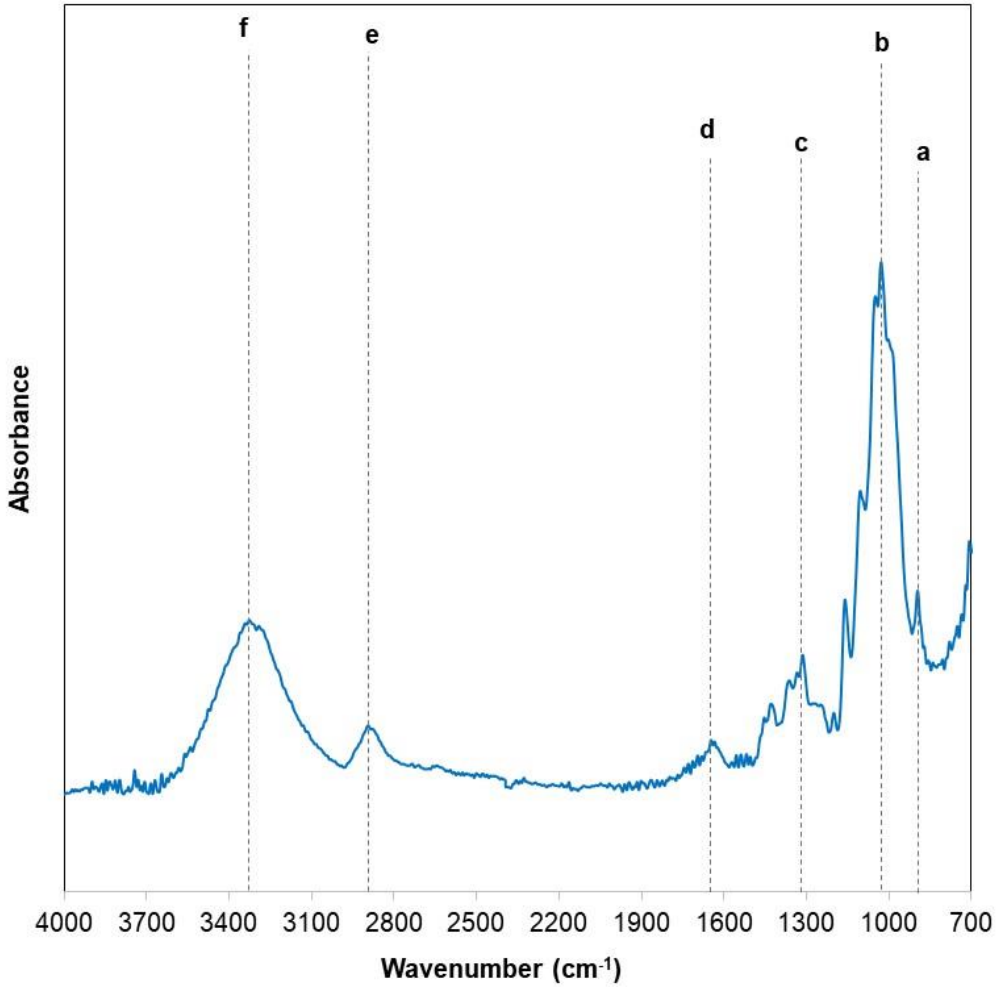

Figure 21. Infrared spectra for fibers from a bleached eucalyptus kraft pulp.

Table 7. Assignment of peaks in the IR spectrum of cellulose to vibrations [77,79].

Peak wavenumber (cm^{-1})	Absorption band
3327	OH stretching
2883	C—H symmetric stretching
1724	C=O stretching
1623	OH bending of water
1368, 1363	C—H bending
1232	C—OH bending at carbon 6 of AGU
1204	C—O—C symmetric stretching
1152	C—O—C asymmetric stretching
1046	C—C, C—OH and C—H ring vibrations
1020	Different vibrations of C—C and C—O bonds
897	C1—H bending, C—O—C vibrations

The peak at 1623 cm^{-1} (d) is due to O—H bending, not in cellulose itself but in water molecules that had been retained. The band at 1368 cm^{-1} (c) is related to C—H bending.

The absorbance at 897 cm^{-1} (a) is particularly sensitive to a rearrangement of intramolecular hydrogen bonds, and thus to decrystallization [79]. In fact, besides XRD patterns (vid. 4.1. X-ray diffraction), spectra of cellulose in the mid-infrared region can be used to estimate the crystallinity index [68].

4.8. Laser diffraction spectrometry

The particle size of mineral fillers used in papermaking is so small that mechanical retention is not enough (vid. 3.3.4. Wet end chemistry and the limitations of recirculating water). Besides fiber-filler and fiber-fine attachments, filler-filler aggregation is also desired. **Fast flocculation** is particularly appreciated, since long residence times in the head box are not feasible. To evaluate flocculation kinetics, Rasteiro et al. [64] proposed the use of laser diffraction spectrometry (LDS).

Through devices such as Malvern's Mastersizer, LDS provides the median equivalent spherical diameter of particles, its size distribution and the mass fractal dimension. But what is more remarkable is **continuous data acquisition**. Those measurements are performed and reported every few seconds. The sample medium, a dilute aqueous suspension with gentle or vigorous stirring, is suitable for flocculation. Hence, LDS can be used to monitor the process, to evaluate the effects of polymer concentration and to compare different polyelectrolytes [80].

Laser beams are diffracted upon the encounter with a particle. Particle size is obtained from the distribution pattern of the intensity of light diffracted by the particle. In order to calculate the former from the latter, researchers usually choose between the Fraunhofer diffraction theory, more simple, and the Mie scattering theory, much more complex. In Publication V, given the small size of the particles [64], the software was set to base the calculations on the Mie theory [81].

4.9. Potentiometric titration

The charge density of a positively-charged solution can be determined by titrating with an anionic polyelectrolyte, whilst measuring the charge density of a negatively-charged solution would require titrating with a cationic polyelectrolyte. Publications IV, V and VIII involved the use of **sodium polyvinylsulfate (PVSNa)** as the anionic polymer and **polydiallyldimethylammonium chloride (PDADMAC)** as the cationic polymer. A potentiometric titration, i.e., a volumetric titration whose endpoint is the neutralization of

charges —0 mV, isoelectric point—, was performed by means of a Charge Analysis System device from AFG.

In Publication V, where cationic derivatives are soluble in water, the sample was dissolved and the titration was performed in a direct way with PVSNa. Measuring the charge of fibers, however, was not a straightforward task. In Publications IV and VIII, we decided to perform a **back titration**. Fibers were weighed (less than 0.3 g) and soaked, with no stirring, in excess polyelectrolyte of opposite charge (10 mL). The titrating agent was the polyelectrolyte whose charge was of the same sign as that of the initial sample.

Publication IV presented an additional challenge. It was not easy to know whether the surface charge of fibers cationized for short reaction times was negative or positive. For some samples, it was necessary to test both polyelectrolytes as the titrating agent.

The charge density (*C*), expressed in milliequivalents per gram of pulp, was calculated as follows:

$$C\left({}^{meq}/_{g}\right) = N_{titrating}\left({}^{meq}/_{mL}\right)\frac{V_{blank}(mL)-V_{analyte}(mL)}{m(g)} \quad (9)$$

In Equation 9, $N_{titrating}$ is the equivalent concentration or normality of the titrating solution, $V_{analyte}$ is the volume of titrating agent spent to neutralize the charge of the solution with the fibers, V_{blank} is the volume of titrating agent used to neutralize 10 mL of the polyelectrolyte of opposite charge, and *m* is the mass of analyte.

4.10. Kappa number of pulps

It is not easy to remove or isolate lignin from carbohydrates in wood or in vegetable biomass, not even for characterization purposes. The method developed by Klason (TAPPI T222, 2002), which is used by most authors to report the lignin content of lignocellulosic materials [82], is time-consuming and provides acid-insoluble lignin only.

The kappa number, which is determined by following the ISO standard 302 (2015) or the TAPPI test method T236 (1999), is an easier and faster way to express the lignin content. However, this determination is restricted to pulps that have been severely delignified by chemical treatments —in other words, bleachable or bleached pulps. It does not yield acceptable results with raw materials or mechanical pulps.

Regardless of the standard chosen, the kappa number is defined as the volume (in milliliters) of a 0.1N potassium permanganate solution that are consumed by 1 g of moisture-free pulp. Potassium permanganate can oxidize, with acceptable selectivity, **double bonds** in compounds that remains after chemical pulping, especially lignin.

When the raw material is not xylan-rich, the kappa number is approximately 6.7 times the lignin content in %. Nonetheless, materials with a high amount of xylan, such

as hardwoods, produce hexenuronic acids (HexA) during chemical pulping. The 4-O-methylglucuronic acid units in xylan suffer an elimination reaction to generate 4-deoxyhex-4-enuronic acids [83]. The double bond in carbon 4 is easily attacked by permanganate, thus giving out an overestimation of the lignin content in hardwood pulps. This is shown in Figure 22. Still, the kappa number is even a better expression for **bleachability** than the lignin content, since the bleaching process is negatively affected by HexA.

We determined kappa numbers in Publications VI, VII and VIII. The pulp was soaked in excess **potassium permanganate** 0.1N and sulfuric acid (catalyst) at approximately 25 ºC, for 10 min. The objective when deciding the amount of oxidant is that permanganate consumption must lie between 30% and 70%. The volume of permanganate spent on lignin oxidation can be estimated by a back titration.

After 10 min, the reaction was stopped with potassium iodide. It was immediately oxidized to iodine by the remaining permanganate. A volumetric titration with **sodium thiosulfate**, using starch as the indicator, was carried out to reduce iodine back to iodide. This allowed us to determine the amount of iodine and, through stoichiometric calculations, the amount of potassium permanganate that reacted. The kappa number (*KN*) is given by:

$$KN = \frac{N_{thiosulfate}\left({}^{eq}/_{L}\right)}{N_{permanganate}\left({}^{eq}/_{L}\right)} \frac{V_{blank}(mL) - V_{analyte}(mL)}{m(g)} f \qquad (10)$$

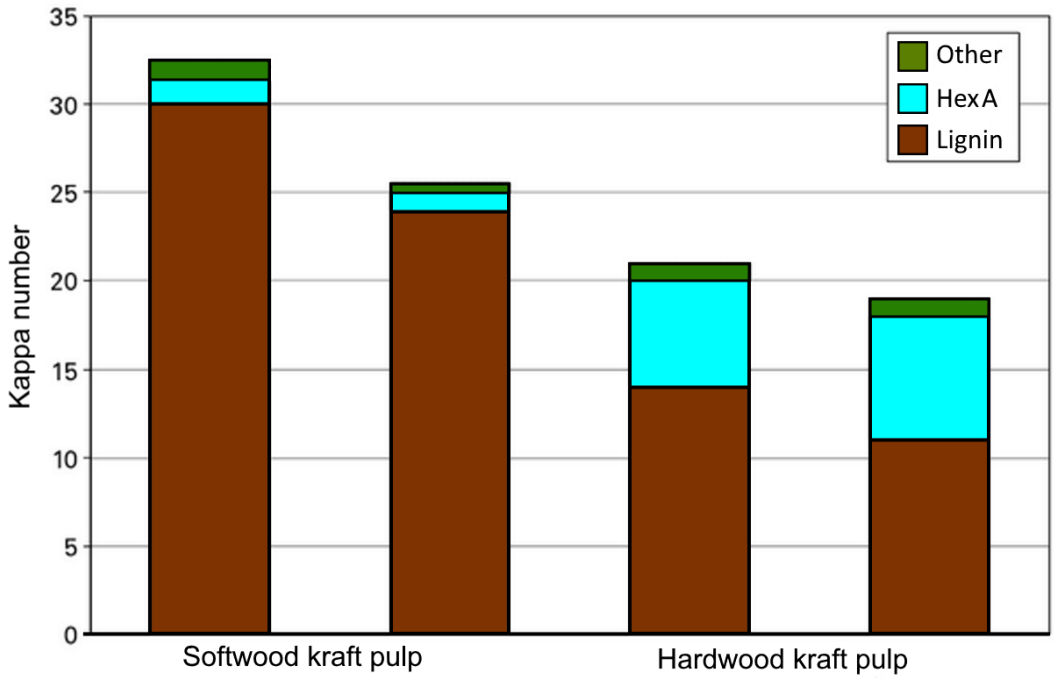

Figure 22. Typical contributions to the kappa number in conventional pulps used for papermaking [83].

In Equation 10, $N_{thiosulfate}$ is the normality of the titrating solution, $N_{permanganate}$ is 0.1 eq/L, $V_{analyte}$ is the volume of thiosulfate consumed by the test specimen, V_{blank} is the volume of thiosulfate consumed in the blank determination, m is the mass of moisture-free pulp, and f is the factor for correction to a 50% permanganate consumption (TAPPI T236, 1999).

4.11. Microscopy

Scanning electron microscopy (SEM) is a non-destructive technique involving a **focused beam of accelerated electrons** to generate different signals at the surface of solid samples. These signals include secondary electrons which the device uses for imaging.

The field emission microscope used in Publications IV and VIII, the model JSM-6335F from JEOL, is so powerful that it can reach a magnification of 500000x [84]. Nonetheless, magnifications of 100x to 2000x were enough to visualize cellulosic fibers with good resolution, as presented in Figure 23 for example purposes. Fig. 23A, with a magnification of 100x, shows entire fibers. Fig. 23B, with a magnification of 1000x, allows us to appreciate the external fibrillation at the surface.

Besides fibers in vacuum-dried pulp pads [5], SEM can produce images of the surface of a paper sheet and even cross-sectional views. This is particularly useful to evaluate the distribution of mineral fillers (Publications IV and VIII). In any case, the cellulose sample has to be coated with gold before the visualization.

Another signal that is produced by the interaction of accelerated electrons with the sample consists on characteristic X-rays that can be used for elemental analysis [85]. For instance, when working with wheat straw pulps (Publication VIII), the SEM device, other than providing images, can estimate the amount of silicon that remains in a paper sheet.

In Publication VI and in Aguado et al. [76], we used a totally different (but also powerful) device to measure the morphological characteristics of fibers –length, width, fibrillation, kinks, etc. The **MorFi analyzer** (Techpap) required to soak a small amount of pulp in water and put the dilute suspension under stirring. It also produced micrographs, but their quality was too low to be displayed in our publications. The spatial resolution was 3 µm, much larger than that of SEM. Instead of imaging for display purposes, Techpap's software processed thousands of images to produce size distributions, population values and useful information about the shape of the fibers [86].

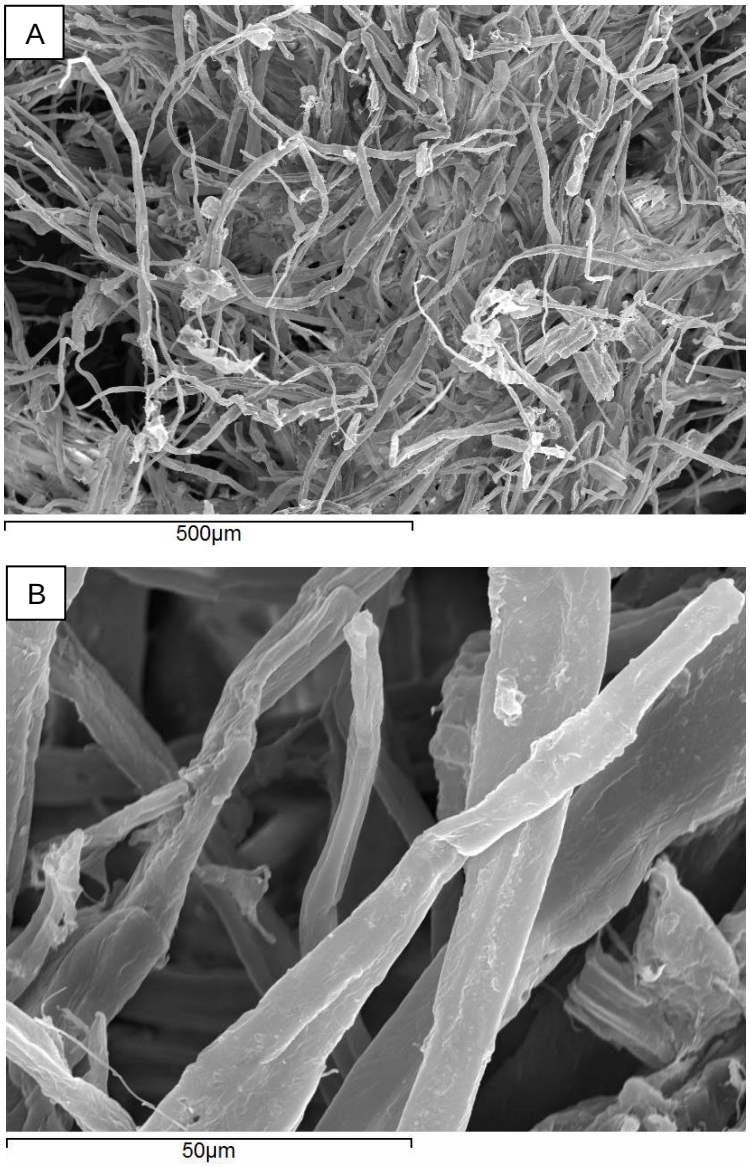

Figure 23. Unpublished and discarded micrographs of an Organosolv pulp from orange tree trimmings, with a magnification of 100x (A) and 1000x (B).

4.12. Drainage, retention and freeness

The laboratory device **Mütek DFR-05** from BTG simulates dewatering of a head box sample at the beginning of a paper machine. In Publications IV, VI and VIII, we placed the test furnish —fibers, fines, fillers and water— in the stirring chamber. The rotational speed and the time at which the chamber opens to begin dewatering, which could be associated with the residence time of the head box in a paper mill, are set in the software. The user can start a measurement after choosing the *Drainage* program, the *Retention* program or the *Freeness* program. Retention and drainage aids can be added at any moment via the dosing module of the device.

The terms *drainage* and *freeness* are frequently used interchangeably. Even the TAPPI test method T227 (2009) states that freeness equals drainage rate. However, the TAPPI methods to determine the drainage time (TAPPI T221, 1999) and the so-called drainage rate (freeness) involve clearly different operations.

In our publications, the drainage rate is considered to be the relationship between the weight of the filtrate and the drainage time. Editors and reviewers have agreed to this. In Table 8, where key magnitudes and their units are shown, drainage and freeness are classified as different categories.

The **drainage** behavior is studied by gravimetric measurements of the filtrate after a stirring period in which flocculation and deflocculation can occur, unlike in freeness determinations. Mütek's software plots a line of filtrate weight (g) vs. time (s).

Retention is expressed as percentage and it should not be confused with filler retention. The device is able to tell the amount of solids that remain after filtration, but not to distinguish between fines and fillers. For instance, to determine calcium carbonate retention, one could perform a complexometric titration with EDTA (Publication VI) or simply burn away the organic matter (ISO 1762, 2015).

These determinations should be performed with the 100-mesh screen (aperture size of 149 µm) or with the 120-mesh screen (aperture size of 125 µm), as they resemble the wire of a paper machine.

In order to determine **freeness**, specifically the Schopper-Riegler number, a 70-mesh screen, whose aperture size is approximately 210 µm, must be used. No stirring should be applied. According to ISO 5267-1 (1999), the pulp must be diluted to 0.2% consistency with distilled water. Temperature should be adjusted to 20 ºC and the sample volume has to be 1 liter.

While the *Freeness* program of the DFR-05 device conforms to ISO 5267-1 (1999) and the Schopper-Riegler number can be related to Canadian Standard Freeness (CSF) for any given raw material, CSF was preferred to express the effects of refining (Publications VI and VII). In this case, the pulp is diluted to 0.3% consistency, according to the ISO standard 5267-2 (2001) and the TAPPI test method T227 (2009).

The apparatus for CSF determinations consisted on a chamber with a screen plate, a funnel with a spreader cone inside and a side orifice besides the normal orifice at the bottom, and a backing plate to support both parts. The furnish was charged into the chamber and left to rest. We opened the chamber and let the sample drain until it stopped going through the side orifice. This part was poured into a measuring cylinder with a sensitivity of ±1 mL, at least. The part of the filtrate which went through the bottom orifice was discarded.

Table 8. Magnitudes associated with drainage, retention and freeness.

	Magnitude	Unit
Drainage	Drainage time	s
Retention	Total retention	%
	Filler retention	%
Freeness	Schopper-Riegler number	ºSR (degrees)
	Canadian Standard Freeness	mL

If the test was carried out at 20 ºC and the consistency was 0.3%, the measured volume equaled CSF. Otherwise, correction factors were applied according to the TAPPI test method T227 (2009).

5. PUBLICATIONS

5.1. Publication I. Cationization of native and alkalized cellulose: mechanism and kinetics

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Journal: Cellulose Chemistry and Technology.

JCR-indexed: Yes.

Category: Materials Science — Paper & Wood.

Reference: Moral, A., Aguado, R., Tijero, A. *Cellulose Chem. Technol.* 50(1): 109-115 (2016).

Status: Published in January 2016.

CATIONIZATION OF NATIVE AND ALKALIZED CELLULOSE: MECHANISM AND KINETICS

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Received November 7, 2014

The insertion of functional groups (particularly cationic groups) in starch and cellulose is especially useful with a view to developing new industrial polysaccharide derivatives. The aim of this work was to develop a standard protocol for the mercerization–cationization of cellulose fibres based on the kinetic equations governing the process. The cationization of NaOH-pretreated cellulose with an alkaline solution of 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) was found to be a pseudo second-order reaction. Under the experimental conditions used, the equilibrium condition for nitrogen as a quaternary ammonium ion in cellulose was dependent on the initial amorphous fraction of cellulose, as determined by X-ray spectroscopy. Also, the kinetic constant increased with an increasing amorphous fraction. However, the nitrogen content or degree of substitution in the carbohydrate reached near-equalibrium values after relatively short reaction times.

Keywords: mechanisms, kinetics, cellulose, mercerization, cationization, X-ray spectroscopy

INTRODUCTION

Cellulose, formed by repeated linkage of D-glucose units, anhydroglucose units (AGU), is the most abundant natural resource. This homopolymer has a rigid, highly functionalized linear chain that is chiral, hydrophilic, biodegradable, and easily modified by chemical means or shaped into versatile semi-crystalline fibres.[1]

Some chemical derivatives of cellulose play prominent roles in industrial production processes. Cellulose xanthate, cellulose acetate, carboxymethyl cellulose and cellulose nitrate are largely used in the manufacturing of plastics, fabrics, packaging, lacquer and explosives. Some recently developed cellulose derivatives are being explored for uses in textile finishing and sizing agents, absorbable surgical fat, protective colloids, adhesives, pharmaceutical creams and paper products, among others.[1]

Developing new cellulose-based products entails subjecting the polymer to various pretreatments. For example, the treatment of textile cotton with concentrated sodium hydroxide patented by John Mercer in 1844 provides brighter, stronger cellulose fibres amenable to dyeing.[2] This treatment, named "mercerization" after its developer, is still widely used, particularly in textile processes.

Native cellulose (e.g., cotton linter) consists essentially of cellulose I, which is formed by parallel chains in a linear structure. In its reaction with an alkali, cellulose I swells and then shrinks when washed to form a new allomorph: cellulose II.[3] The alkali penetrates fibres and causes parallel chains in cellulose I to rearrange into antiparallel chains of cellulose II.[4] This change is irreversible and accompanied by a decrease in crystallinity and a reduction in the degree of polymerization. The new cellulose form has a more open structure and its fibres possess a higher specific surface area; as aresult, the hydroxyl groups in cellulose macromolecules are easier to access.[5] The ordered structure of the crystalline form and the disordered structure of the amorphous form influence the accessibility and reactivity of cellulose fibres.[6]

Under specific conditions, a treatment with sodium hydroxide improves the mechanical properties of cellulose fibres to an extent considerably dependent on the treatment time and alkali concentration.[7] Cellulose is modified more markedly by soda than is lignin.[8] As a result, reacting cellulose with an aqueous solution of sodium hydroxide alters its morphological, molecular and supramolecular properties, thereby also changing its crystallinity, pore structure, accessibility, rigidity, unit cell structure and fibre orientation. Some other properties can be improved, including dimensional stability, fibrillation, tensile strength, dyeability, reactivity, brightness and softness in fabrics.[9]

The structure of cellulose is commonly characterized by wide-angle X-ray spectroscopy. This technique has proven effective to distinguish between amorphous and crystalline cellulose andto assess the influence of crystallinity on the rate of hydrolysis.[6,10]

Another line in the production of new cellulose derivatives involves the insertion of functional groups (e.g., cationic groups) into polysaccharide chains. While cationic starches are widely used by the paper industry to improve retention and draining properties in pulp, the cationization of cellulose is usually performed to improve affinity towards anionic dyes. Cationized cellulosic products are also useful for the removal of toxic heavy metals from wastewater.[11]

These processes involve making the substrate react with an electrophilic reagent contaning a quaternary ammonium salt. The properties of the resulting cationized derivative are different from and often better than those of the starting substrate. Cationization of cellulose shows little negative impact on the mechanical properties of fibres, although brightness may decrease considerably.[12] To date, no standard protocol for the mercerization–cationization of cellulose fibres has been reported, despite the industrial significance of the process.

The primary aim of this work was thus to develop a standard protocol for the mercerization–cationization of cellulose fibres based on the kinetic equations governing the process. The use of modified natural polysaccharides is currently regarded as a sustainable alternative to synthetic polymers and hence as specially desirable with a view to developing new, improved products.

EXPERIMENTAL

Mercerization

The raw material used here was commercial medium-sized cellulose fibre (Aldrich ref. C6288), which was reacted with an alkaline solution of NaOH from Aldrich, in a batch reactor at room temperature. Nine mercerization experiments were carried out for different raction times and NaOH concentrations (Table 1). Afterwards, fibres were separated by passage through a Whatman Glass Microfiber Binder Free Grade GF/D filter (2.7μm) and washed with demineralized water. The alkalized cellulose thus obtained was dried in a vacuum stove at 45 ºC.

Cationization

The cationizing agent was an aqueous solution of 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) at 60wt% from Aldrich. An amount of 20 g of dry alkalized cellulose was mixed with the reagent in a CHPTAC/AGU mole ratio of 4, an identical number of moles of CHPTA and 5% NaOH, and enough isopropyl alcohol to make to 1 L.

The reactor was a 2 L three-mouthed spherical glass furnished with a refluxing condenser, a magnetic stirrer, heating controlled by an electronic PID device and a Pt-100 probe for temperature measurements. Temperature was held at 70 ºC, through the process. After the solution containing mercerized cellulose, sodium hydroxide and isopropyl alcohol was heated to setpoint temperature under stirring, the mixture was supplied with the CHPTAC via a funnel and the reaction timer started.

Table 1
Mercerization conditions: codification

Soda concentration (%) \ Reaction time (min)	60	120	180
10	A1T1	A1T2	A1T3
20	A2T1	A2T2	A2T3
30	A3T1	A3T2	A3T3

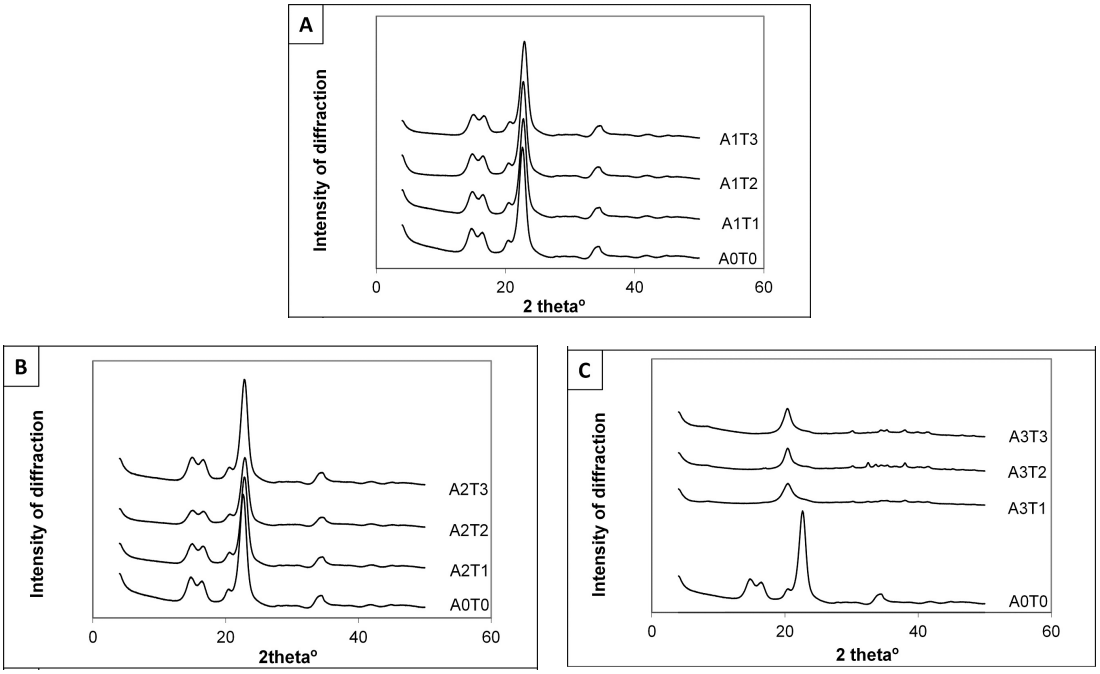

Figure 1: Diffractograms of untreated cellulose (A0T0) and of samples alkalized with different NaOH concentrations and times

Samples from the reaction mixture were withdrawn every 30 minutes by using a 50 mL wide mouth pipette. Immediately, they were diluted ten times with cold water to stop the reaction, passed through a Whatman Glass Microfiber Binder Free Grade GF/D filter (2.7μm), washed with demineralized water and dried in a vacuum stove at 45 ºC. Dried samples were kept sealed at room temperature.

The process developed in two steps: first, formation of epoxypropyltrimethylammonium chloride (EPTMAC) by reaction with hydroxyl ions; second, nucleophilic substitution of the hydroxyl group bonded to C_6 in the anhydroglucose unit (AGU).

Characterization of samples

Cellulose and alkalized cellulose samples were characterized by using a PANalytical powder X-ray diffractometer in combination with X'Pertsoftware.

Carbon and nitrogen contents were determined by combustion on a LECO CNS-2000I elemental macroanalyser.

RESULTS AND DISCUSSION

X-ray diffraction spectroscopy

Figure 1 shows the XRD patterns for the starting cellulose and alkalized cellulose at the preset 2θ° values used. We chose to represent the patterns in a staged manner in order to envisage the changes in the initial fibres under the effect of the alkaline treatmentmore easily. The structural changes undergone by cellulose in the treatments preceding cationization were used to examine their potential relationship to the cationization results.

The changes caused by a NaOH concentration of 10% were minimal, even at the longest operation times used; however, they increased as the alkali concentration was raised and levelled off at 30%.

Although the enzymatic and non-enzymatic reaction are additionally influenced by other factors, we used the crystallinity index (*XRD CrI*), and the fractions of amorphous cellulose (1 – Am), cellulose I (CI) and cellulose II (CII) in the starting alkalized cellulose to compare and interpret the results of the cationization process.

Oh *et al*.[16] previously examined the structure of cellulose treated with sodium hydroxide and carbon dioxide by X-ray difraction and FTIR spectroscopies. The crystallinity index (*CrI*) was calculated from the height ratio of the intensity at 2θ = 22.5° for cellullose I, or the 101 reflection at 2θ = 19.8° for cellulose II (crystalline height, *hcr*), to the height of the amorphous reflection corresponding to 2θ = 18.8° for cellulose I or 2θ = 16.1° for cellulose II (amorphous height, *ham*), respectively.[6]

The intensity of scattered diffracted light was measured in arbitrary units without normalization of the mass sample. Therefore, samples were

compared in terms of peak height ratios rather than absolute intensities.

$$CrI(CI) = 1 - \frac{h_{am}}{h_{cr}} \quad (1)$$

$$\frac{h_{am}}{h_{cr}} = \frac{I_{18.8\,min}}{I_{19.8\,max} + I_{22.5\,max} - I_{18.8\,min}} \quad (2)$$

$$CrI(CII) = \frac{I_{12.1}}{I_{12.1} + 0.5(I_{14.6} + I_{16.1})} \quad (3)$$

As shown in Table 2, structural changes in cellulose under the influence of the treatments preceding cationization had a marked effect under the experimental conditions used. The conversion into cationized cellulose must be governed largely by those of cellulose I into cellulose II and of the latter into hydrated and amorphous cellulose II.

Elemental analysis

The amounts of elemental nitrogen incorporated as quaternary ammonium ions into cellulose under the effect of the cationization treatment after different reaction times are shown in Table 3. The results were processed with various kinetic models and a pseudo-second-order model was found to provide the best fit.

The pseudo-second-order kinetic model originally proposed by Blanchard *et al.*[17] and Ho *et al.*[18] is typically applied to adsorption phenomena occurring in solution. These kinetic expressions have been applied to a variety of systems.[19] The theoretical background of the pseudo-second-order rate equation has been examined by Azizian.[20] The kinetic constants of pseudo-second-order models are combinations of the initial solute concentration and the adsorption and desorption constants.

Table 2
Crystallinity index of cellulose samples

Allomorph	A0T0	A1T1	A1T2	A1T3	A2T1	A2T2	A2T3	A3T1	A3T2	A3T3
Cellulose I	0.52	0.53	0.56	0.45	0.50	0.50	0.53	0.14	0.13	0.05
Cellulose II	0.31	0.32	0.29	0.31	0.33	0.34	0.31	0.50	0.51	0.55
Cellulose amorphous	0.17	0.15	0.15	0.24	0.18	0.17	0.17	0.36	0.36	0.40
XRD crystallinity index	0.83	0.85	0.85	0.76	0.82	0.84	0.83	0.64	0.64	0.60

Table 3
Parameters of pseudo-second order rate equations

Parameters of linearized equation	A1T1	A1T2	A1T3	A2T1	A2T2	A2T3	A3T1	A3T2	A3T3
Intercept: $N_{eq}^{-2} \cdot K^{-1}$, min/%N	19.6	17.2	9.4	31.2	15.5	10.1	7.1	5.3	4.6
Slope: N_{eq}^{-1}, $\%N^{-1}$	9	6.8	5.8	7.7	6.8	5.4	1.5	0.64	0.56
R^2	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.98	0.98
Parameters of original kinetic equation	A1T1	A1T2	A1T3	A2T1	A2T2	A2T3	A3T1	A3T2	A3T3
N_{eq}, %N	0.11	0.15	0.17	0.13	0.15	0.19	0.67	1.56	1.79
NSD_{eq}	0.013	0.018	0.020	0.015	0.018	0.022	0.084	0.217	0.257
$N_{eq}^2 K$, %N/min	0.051	0.058	0.106	0.032	0.065	0.099	0.140	0.189	0.217
K, $(\%N \cdot min)^{-1}$	4.13	2.69	3.54	1.93	2.99	2.87	0.32	0.08	0.07
RMSD/10^{-3}	5.1	6.1	6.6E	3.9	4.7	5.1	33	67	78

The proportion of epoxypropyltrimethylammonium chloride (EPTMAC) bound to cellulose in the cationization reaction was referred to that of elemental nitrogen fixed by cellulose. The driving force was the difference between the proportion of nitrogen fixed by cellulose at time *t* and the maximum (saturation or equilibrium) proportion. The rate equation in terms of the proportion of elemental nitrogen fixed by cellulose was:

$$\frac{dN_t}{dt} = k(N_{eq} - N_t)^2 \quad (4)$$

where N_t is proportional to the number of active sites occupied by the active cationic group on cellulose at time *t* and so is N_{eq} to the number of

sites available on cellulose fibres at equilibrium (both as percentages of elemental nitrogen).

The integration of this differential equation under the boundary conditions t=0to t=t and N_t=0 to N_t=N_t yields:

$$N_t = \frac{N_{eq}^2 kt}{1 + N_{eq} kt} \quad (5)$$

which is the integral form of the equation for a pseudo-second-order reaction. Expressing this equation in terms of the time/fixed nitrogen proportion ratio leads to a linear function of time.

The previous kinetic equation can be written in a linear form as:

$$\frac{t}{N_t} = \frac{t}{N_{eq}} + \frac{1}{kN_{eq}} \quad (6)$$

The concentrations of nitrogen at different reaction times t as determined by elemental analysis of dry cationized samples were used to plot the linearized form of the equation. If the assumption of a pseudo-second-order model is fulfilled, then the intercept of the curve will represent the highest proportion of elemental nitrogen incorporated by effect of the reaction ofepoxypropyltrimethylammonium chloride (EPTMAC), previously formed in the reaction between 3-chloro-2-hydroxypropyl-trimethylammonium chloride (CHPTAC) with NaOH, with alkali-activated sites of the hydroxyl group on C_6 in the anhydroglucose unit (AGU). Likewise, the slope of the curve will coincide with the reciprocalof the percent equilibrium (saturation) concentration.The figures of merit of the linearized equations as obtained by least-squares regression are shown in Figure 2. As can be seen, the coefficients of correlation ranged from 0.98 to 0.99.

The dotted lines in Figure 3 represent the experimental percent nitrogen contents as measured by elemental analysis as a function of the reaction time for cellulose treated with NaOH, whereas the solid lines represent the integrated kinetic equations in terms of parameters N_{eq} and$K$ as calculated from the linearized equation:t/Nt vs. t (see Table 3).

Table 3 also lists the root mean square deviation (RMSD) as a measure of differences between experimental values and predicted values (i.e., those obtained from the pseudo-second-order kinetic equation). The degree of nitrogen substitution (DNS) of the cellulose was calculated from the nitrogen content (%N) and the molecular weight of the anhydroglucose unit (AGU), 162.15, using the following expression:

$$DNS = \frac{162.15 \times \%N}{1400 - 151.64 \times \%N} \quad (7)$$

where %N denotes the percentage of dry elemental nitrogen, 1400 is 100 times the atomic weight of nitrogen and 151.64 the molecular weight of the epoxypropyltrimethylammonium chloride (EPTMAC) group added.

Comparing theresults of this work with the results of De la Motte *et al.*,[21] under the conditions leading to maximal incorporation of nitrogen in cationic form, DNS was greater in this work: 0.404 (i.e., 40.4%) at the maximum %N level.

We used constant CHPTAC/AGU ratio, NaOH concentration and isopropyl alcohol proportion throughout. DNS for cationic starches typically ranges from 0.0075 to 0.1215 and increases with increasing reaction time and proportion of cationizing reagent. Our results are consistent with those of other studies.[22]

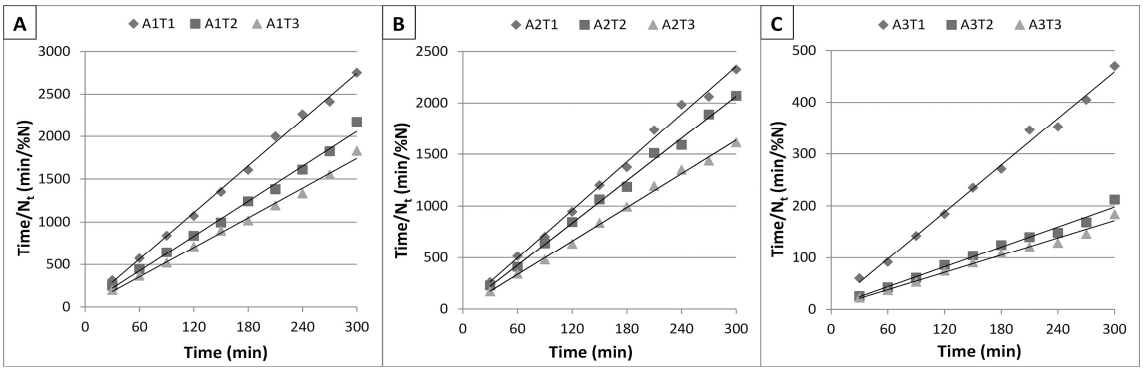

Figure 2: Linearized representation of the pseudo-second-order rate equation: (A) of cellulose alkalized with 10%NaOH; (B) of cellulose alkalized with 20%NaOH; (C) of cellulose alkalized with 30%NaOH

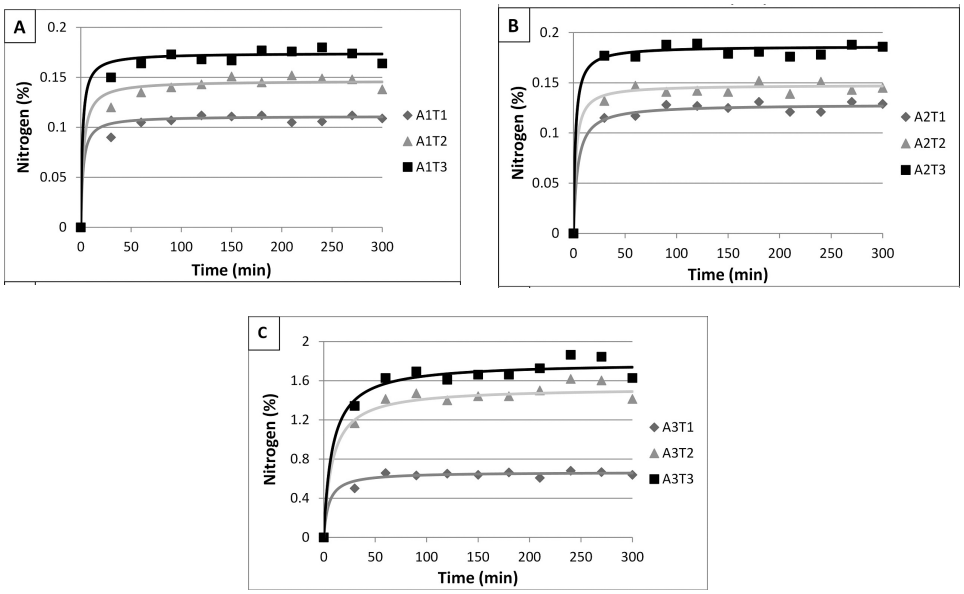

Figure 3: Nitrogen in cellulose vs. reaction time. Isolated points are the experimental data

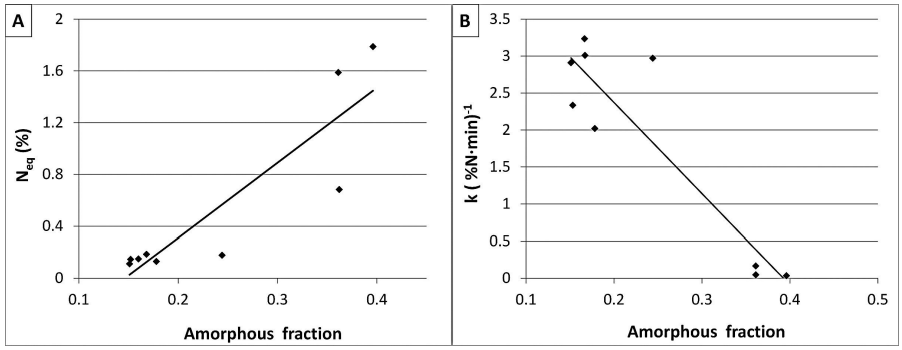

Figure 4: Nitrogen proportion (A) and constant of the pseudo-second-order rate equation (B), versus amorphous fraction of cellulose

Based on available literature, DNS increases with an increase in the CHPTAC concentration; also, using an inadequate amount of NaOH hinders the formation of epoxide and alkoxides from the polysaccharide, whereas excess NaOH causes degradation of the epoxide and decreases the molecular weight of the product.

Figure 4 shows the variation of N_{eq} with the amorphous fraction of cellulose as calculated by XRD analysis of the starting alkalized cellulose. A comparison of the variation of N_{eq}vs. the different cellulose allomorphs revealed that the best results were obtained by linearly fitting this parameter to the amorphous faction (AF):

$$N_{eq} = 5.79AF - 0.85 \quad (8)$$

with R^2= 0.80. Likewise, the best fit with the pseudo-second-order rate constant k was provided by:

$$K = -12.32AF + 4.84 \quad (9)$$

with R^2= 0.83. Despite the reduction in K, the overall rate of nitrogen fixation was greater under the influence of the amorphous fraction, increasing the proportion of fixed nitrogen at equilibrium.

CONCLUSION

Under the experimental conditions used in this work, the overall cationization reaction fits a pseudo-second-order kinetic equation. The reaction rate increases with the square of the difference between the equilibrium and the apparent concentrations of nitrogen. This squared difference decreases –and so does the reaction rate, in an asymptotic manner – as the amount of nitrogen fixed to cellulose approaches its equilibrium level.

As previously found for other chemical and enzymatic reactions, the reactivity of cellulose increases with an increasing proportion of the amorphous fraction (AF) to a greater extent than it does with the proportions of cellulose I (CI) and cellulose II (CII), even though the amorphous fraction (AF) is related to CII.

The proportion of nitrogen at equilibrium in cationized cellulose increases linearly with increasing content of amorphous cellulose in the starting material. Initially, the reaction rate is comparatively high. As a result, the proportion of nitrogen reaches a near-equilibrium level within a short time (about 30 min).

ACKNOWLEDGMENTS: The authors wish to acknowledge the Ministry of Science and Innovation of Spain for the financial support of the Project CTQ2010-21660-C03-01, to which the present study is related.

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5.2. Publication II. Cationization of alpha-cellulose to develop new sustainable products

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Journal: International Journal of Polymer Science.

JCR-indexed: Yes.

Category: Polymer Science.

Reference: Moral, A., Aguado, R., Ballesteros, M., Tijero, A. *Int. J. Polym. Sci*. 2015, 9 pages (2015). DOI: 10.1155/2015/28963.

Status: Published in June 2015.

Hindawi Publishing Corporation
International Journal of Polymer Science
Volume 2015, Article ID 283963, 9 pages
http://dx.doi.org/10.1155/2015/283963

Research Article

Cationization of Alpha-Cellulose to Develop New Sustainable Products

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Received 18 March 2015; Revised 26 May 2015; Accepted 27 May 2015

Academic Editor: Yulin Deng

Papermaking has been using high quantities of retention agents, mainly cationic substances and organic compounds such as polyamines. The addition of these agents is related to economic and environmental issues, increasing contamination of the effluents. The aim of this work is to develop a cationic polymer for papermaking purposes based on the utilization of alpha-cellulose. The cationization of mercerized alpha-cellulose with 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) is governed by a pseudo-second-order reaction. The initial amorphous fraction of cellulose is reacted with CHPTAC until the equilibrium value of nitrogen substitution is reached. Nitrogen is incorporated as a quaternary ammonium group in the polymer. Also, the kinetic constant increased with decreasing crystallinity index, showing the importance of the previous alkalization stage. The use of modified natural polysaccharides is a sustainable alternative to synthetic, nonbiodegradable polyelectrolytes and thus is desirable with a view to developing new products and new processes.

1. Introduction

Paper manufacturing processes require the addition of retention agents for (i) compacting the pulp, formed by anionic-charged biopolymers, and (ii) avoiding industry wastewater effluents containing high amounts of microfibers that are released from the original pulp [1, 2]. Traditionally, papermaking has used high quantities of retention agents, mainly cationic substances such as inorganic aluminium compounds (aluminium sulphate and poly(aluminium chloride)), and/or certain organic compounds, mainly polyamines [3]. The addition of these agents is related to economic and environmental issues, as they induce the apparition of adherent flocs [4] increasing contamination of the effluents. This has awakened the scientific community's interest to explore new alternatives. In the last decades, semisynthetic compounds manufactured from natural polymers (e.g., highly cationic starch) have also been employed in papermaking industries [5–10]. Modification of natural polymers in order to achieve new materials with specific properties can be carried out by cationization. In fact, in many industries, cationic polysaccharides are replacing the traditional consumption of cationic polyacrylamides for their use as colloid flocculants, due to their lower toxicity and less legal restrictions on their consumption [11].

The cationic modification of cellulose commonly goes by the etherification with a 2-hydroxy-3-(trimethylammonium)propyl group, which can be obtained by the reaction of the biopolymer and 2,3-epoxypropyltrimethylammonium chloride (EPTAC). EPTAC, however, is an unstable and toxic reagent that cannot be used in industrial applications [11]. An alternative is the use of 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC). CHPTAC has been successfully used for the cationization of cellulose [12–15], textile fibres [16–20], and other polysaccharides such as agarose or backbone of tamarind kernel polysaccharide (TKP), among others [21, 22]. The flocculation efficiencies achieved for the resulting products are similar to those obtained with classical commercial polyacrylamides [21].

A three-step mechanism was proposed for the reaction of CHPTAC and cellulose. In the first, fast reaction, the chlorohydrin CHPTAC is converted to the epoxide EPTAC.

Then, a hydroxyl group of the cellulose is converted into an alkoxide by reacting with a base (e.g., NaOH). Finally, the alkoxide from cellulose reacts with EPTAC, resulting in cationized cellulose. A secondary reaction could occur between EPTAC and water, which must be avoided as the formed diol is unable to react with cellulose, increasing the cost of the cationic modification [11, 12, 23]. During cationization, the degree of substitution is highly influenced by the quantity of base added. This addition is necessary not only to generate EPTAC from CHPTAC, but also to weaken the hydrogen bonds between molecules, making cellulose more accessible [17]. Therefore, it can be used as a pretreatment, taking into account the fact that an excess of base favours polysaccharide hydrolysis and epoxide degradation towards the aforementioned diol.

Cellulose is a linear homopolymer composed of a-D-glucopyranose units linked by β-1,4-glycosidic bonds ($C_6nH_{10}n + 2O_5n + 1$ (n = degree of polymerization of glucose)). Native cellulose is essentially cellulose I, which has a structure made of parallel chains [24]. When subjected to strong alkaline media during the alkalization-cationization process, cellulose becomes swollen and, upon washing, shrinks back to yield a new allomorph, cellulose II [25, 26], within the crystalline domains [27–29]. X-ray diffraction gives the most direct results for the characterization of the crystalline structure of cellulose [30–32]; however, its interpretation is still under discussion.

The objective of this work is to develop a cationic polymer for papermaking purposes based on the utilization of alpha-cellulose. X-ray measurements were used to study the crystalline structure and the kinetic equations governing the process are discussed to find out the optimal concentrations of reagents. The use of modified natural polysaccharides is currently regarded as a sustainable alternative to synthetic polymers and hence as specially desirable with a view to developing new improved products.

2. Experimental

2.1. Alkalization. The raw material used was commercial α-cellulose (Aldrich C8002). Reactions took place in a 2 L three-mouthed spherical glass reactor with a refluxing condenser, a magnetic stirrer, heating controlled by an electronic PID device, and a Pt-100 probe to measure temperature, which was kept at 25°C. NaOH pellets were purchased from Aldrich. In each experiment, 25 g of cellulose (on the basis of dry pulp weight) was mixed with 500 mL of an aqueous NaOH solution (10–30% w/w). Nine alkalization experiments were carried out for different reaction times and NaOH concentrations (Table 1). Afterwards, fibres were separated by passage through a Whatman Glass Microfiber Binder Free Grade GF/D filter (2.7 μm) and washed with demineralized water. The alkalized cellulose thus obtained was dried in a vacuum stove at 45°C.

2.2. Cationization. The cationizing agent was an aqueous solution of 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) at 60% (w/w) from Aldrich. The process was carried out in two steps: first, formation of epoxypropyltrimethylammonium chloride (EPTAC) by reaction with hydroxide ions, and second, nucleophilic substitution of the hydroxyl group bonded to C_6 in the anhydroglucose unit (AGU).

Table 1: Mercerization conditions: codification.

Soda concentration (%)	Reaction time (min)		
	30	60	90
10	A1T1	A1T2	A1T3
20	A2T1	A2T2	A2T3
30	A3T1	A3T2	A3T3

An amount of 20 g of alkalized cellulose (on the basis of dry pulp) was mixed with the reagent in a CHPTAC/AGU mole ratio of 4, assuming that the material is wholly constituted by anhydroglucose units. A volume of 395 mL of an aqueous NaOH solution at 5% (w/w) was added. Then, the mixture was completed with enough isopropyl alcohol to achieve a final volume of 1 L. The reactor was the one used in the previous alkalization step and the temperature was held at 70°C through the process. The reaction timer started when the setpoint temperature was reached.

Samples from the reaction mixture were withdrawn every 30 minutes by using a 50 mL wide mouth pipette. Immediately, they were diluted ten times with cold water to stop the reaction, passed through a Whatman Glass Microfiber Binder Free Grade GF/D filter (2.7 μm), washed with demineralized water, and dried in a vacuum stove at 45°C. Dried samples were kept sealed at room temperature.

2.3. Characterization of Samples. Cellulose and alkalized cellulose samples were characterized by using a PANalytical powder X-ray diffractometer in combination with the X'Pert software. Adopting the two-phase theory of structure and the amorphous halo correction, the crystallinity index (*CrI*) was obtained from the X-ray diffraction curves [33].

Carbon and nitrogen contents were determined by combustion on a LECO CNS-2000I elemental macroanalyser. Knowing the amounts of nitrogen incorporated as quaternary ammonium into cellulose by effect of the cationization treatment, the degree of substitution was determined. The carbon content was used to apply a correction to systematic errors. The results could be processed to evaluate the kinetics models [32, 34, 35].

3. Results and Discussion

3.1. X-Ray Diffraction Spectroscopy. Figure 1 shows the XRD patterns for the starting cellulose and alkalized cellulose at the preset $2\theta^{\circ}$ values used. We chose to represent the patterns in a staged manner in order to more easily envisage changes in the initial fibres by effect of the alkaline treatment. The structural changes undergone by cellulose in the treatments preceding cationization were used to examine their relation to the cationization results. The changes caused by a NaOH concentration of 10% were minimal, even at the longest

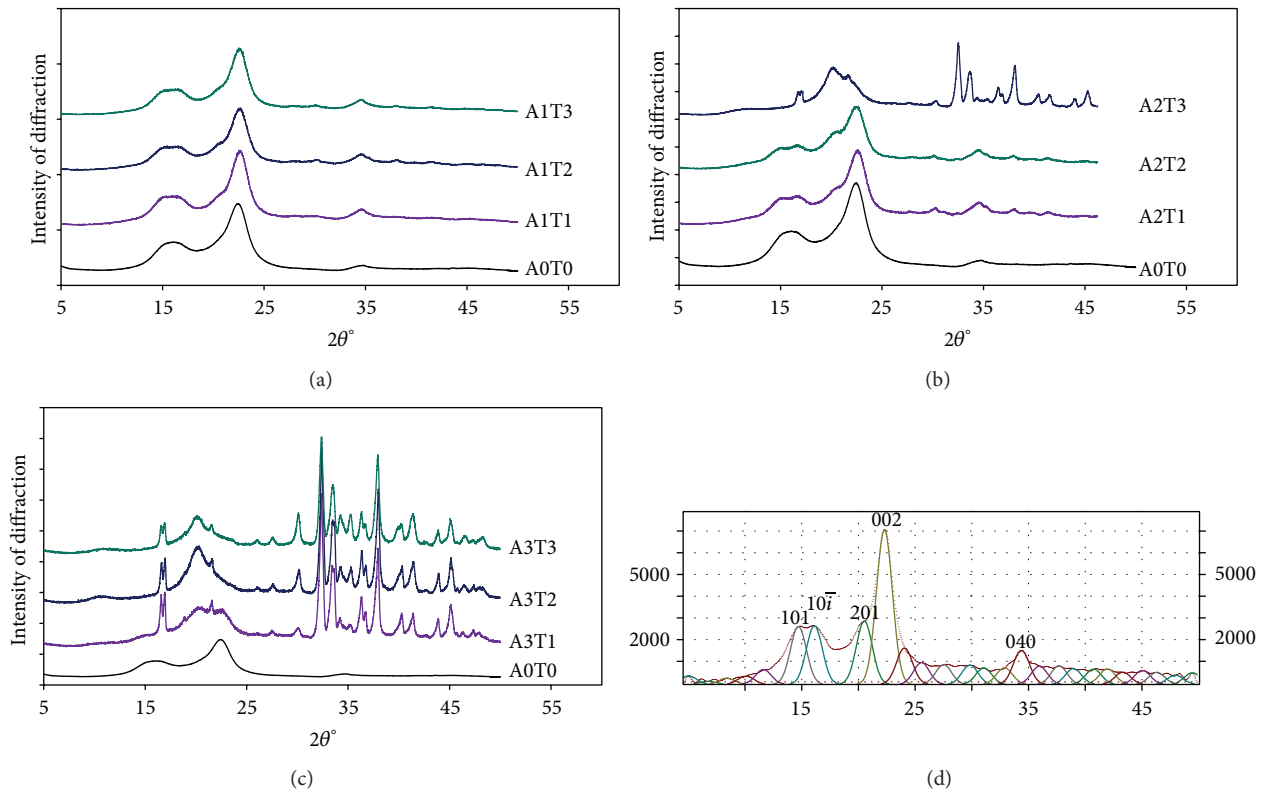

Figure 1: Diffractograms of untreated cellulose and of samples alkalized with different NaOH concentrations and times. (a) NaOH 10%. (b) NaOH 20%. (c) NaOH 30%. (d) A1T1 after deconvolution.

operation times used; however, they increased as the alkali concentration was raised.

Although the enzymatic and nonenzymatic reaction are additionally influenced by other factors, we used the *crystallinity index* (*CrI*) and the fractions of cellulose I and cellulose II in the starting and alkalized cellulose to compare and interpret the results of the cationization process.

Park et al. [36] previously examined the structure of cellulose treated with sodium hydroxide and carbon dioxide by X-ray diffraction and FTIR spectroscopy. The crystallinity index was calculated from the height ratio of the intensity at $2\theta = 22.5^\circ$ for cellulose I, or the 101 reflection at $2\theta = 19.8^\circ$ for cellulose II (crystalline height, *hcr*), to the height of the amorphous reflection corresponding to $2\theta = 18.8^\circ$ for cellulose I or $2\theta = 16.1^\circ$ for cellulose II (amorphous height, *ham*), respectively [6]. While the peak height method is widely used to measure the crystallinity index, due to its simplicity, it produces an overestimation of this index and neglects the influence of peak width [37]. We measured the proportion of cellulose I (CI) and that of cellulose II (CII) by using the peak height (see (1)), but the crystallinity index was determined following the XRD deconvolution method, and thus using the peak area:

$$\mathrm{CI} = 1 - \frac{h_{\mathrm{am}}}{h_{\mathrm{cr}}}$$

$$\frac{h_{\mathrm{am}}}{h_{\mathrm{cr}}} = \frac{I_{18.8\,\mathrm{min}}}{I_{19.8\,\mathrm{max}} + I_{22.5\,\mathrm{max}} - I_{18.8\,\mathrm{min}}}$$

$$\mathrm{CII} = \frac{I_{12.1}}{I_{12.1} + 0.5\left(I_{14.6} + I_{16.1}\right)}. \tag{1}$$

Gaussian deconvolution was performed with Systat's PeakFit software. The crystallinity index was calculated by dividing the sum of the areas of the five crystalline peaks (101, 10$\bar{i}$, 021, 002, and 040) by the total area [37]. Figure 1(d) shows the crystalline peaks of sample A1T1 after deconvolution, as an example.

As is shown in Figure 2, structural changes in cellulose by effect of the treatments preceding cationization were notorious under the experimental conditions used. The conversion into cationized cellulose must be governed largely by that of cellulose I into cellulose II and the latter into hydrated and amorphous cellulose.

For a NaOH concentration of 10% (Figure 2(a)), the CI was still the most frequent allomorph. The crystallinity index decreased very slightly through the alkalization step. When the alkali concentration was 20% (Figure 2(b)), the CI fraction decreased once the alkalization step started, whereas the percentage of CII increased from 0 to 90 min. The conversion of CI into CII was faster for the highest NaOH

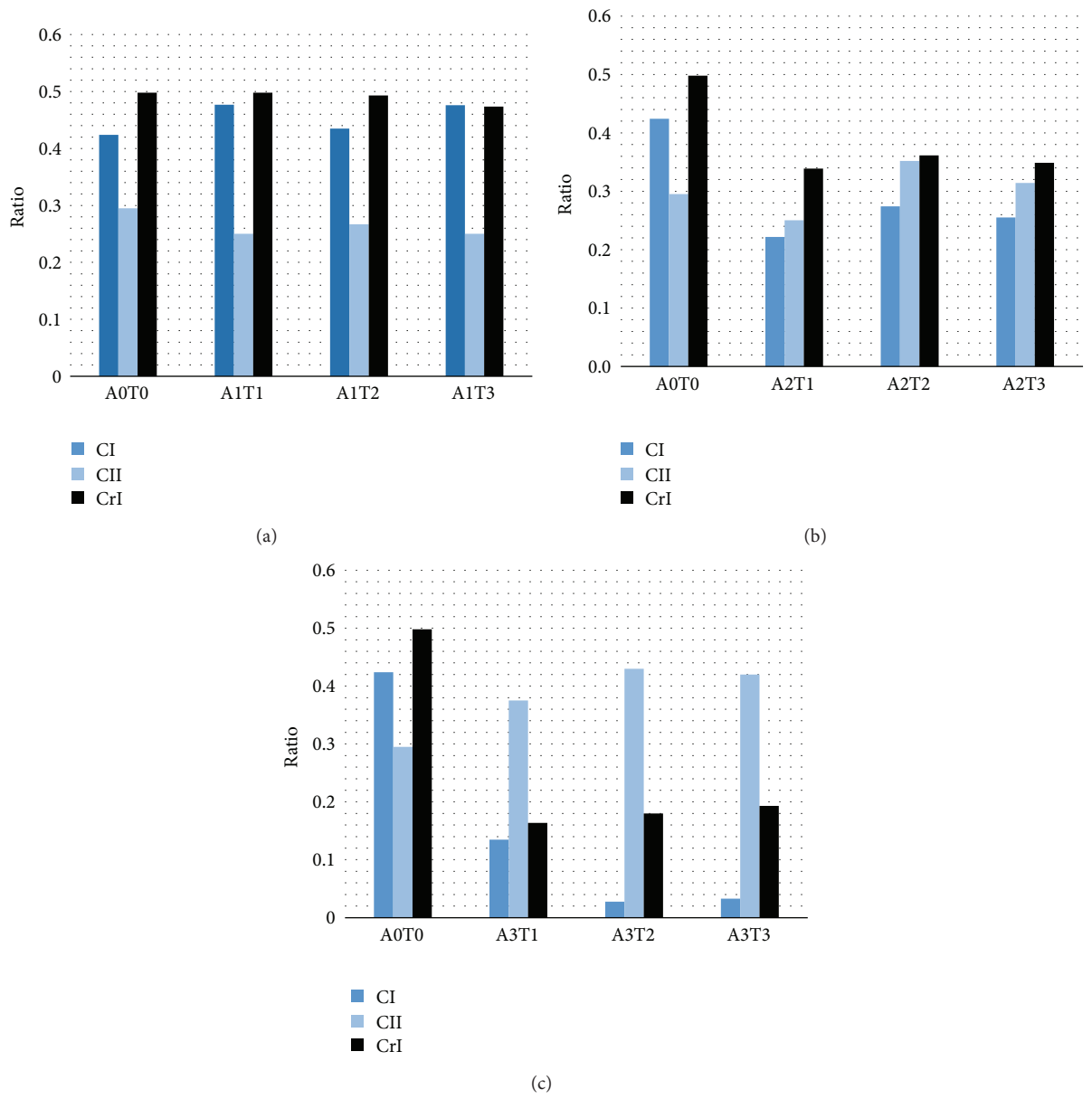

Figure 2: Crystallinity index and ratios of CI and CII for various NaOH concentrations and times. (a) NaOH 10%. (b) NaOH 20%. (c) NaOH 30%.

concentration (Figure 2(c)). The crystallinity index decreased abruptly with NaOH concentration.

3.2. Elemental Analysis. The results were processed with various kinetic models and a pseudo-second-order rate equation was found to provide the best fit. The pseudo-second-order kinetic model proposed by Blanchard et al. [38] is typically applied to adsorption phenomena occurring in solution. These kinetic expressions have been applied to a variety of systems [39]. The theoretical background has been examined by Azizian [40]. The kinetic constants of pseudo-second-order models are combinations of the initial solute concentration and the adsorption and desorption parameters.

The proportion of EPTAC bound to cellulose in the cationization reaction was referred to that of elemental nitrogen fixed by cellulose. The driving force was the difference between the proportion of nitrogen fixed by cellulose at time t and the maximum (saturation or equilibrium) proportion. The rate equation in terms of the proportion of elemental nitrogen fixed by cellulose was

$$\frac{dN_t}{dt} = k\left(N_{\text{eq}} - N_t\right)^2, \tag{2}$$

where N_t is proportional to the number of active sites occupied by the active cationic group on cellulose at time t and so is N_{eq} to the number of sites available on cellulose

fibres at equilibrium (both as percentages of elemental nitrogen).

Integration of this differential equation under the boundary conditions $t = 0$ to $t = t$ and $N_t = 0$ to $N_t = N_t$ yields

$$N_t = \frac{N_{eq}^2 kt}{1 + N_{eq} kt}, \tag{3}$$

which is the integral form of the equation for a pseudo-second-order reaction. Expressing this equation in terms of the time/fixed nitrogen proportion ratio leads to a linear function of time.

The previous kinetic equation can be written in linear form as

$$\frac{t}{N_t} = \frac{t}{N_{eq}} + \frac{1}{kN_{eq}} \tag{4}$$

The concentrations of nitrogen at different reaction times t as determined by elemental analysis of dry cationized samples were used to plot the linearized form of the equation. If the assumption of a pseudo-second-order model is fulfilled, then the intercept of the curve will represent the highest proportion of elemental nitrogen incorporated by effect of the reaction of EPTAC, previously formed in the reaction between CHPTAC and NaOH, with alkali-activated sites of the hydroxyl group on C_6 in the anhydroglucose unit (AGU). Likewise, the slope of the curve will coincide with the reciprocal of the equilibrium (saturation) concentration. The figures of merit of the linearized equations as obtained by least-squares regression are shown in Figure 3. As can be seen, the coefficients of correlation ranged from 0.97 to 0.99.

The dotted lines in Figure 4 represent the experimental percent nitrogen contents as measured by elemental analysis as a function of the reaction time for cellulose treated with NaOH, whereas the solid lines represent the integrated kinetic equations in terms of parameters N_{eq} and K as calculated from the linearized equation: t/Nt versus t (Table 2).

Table 2 also lists the root mean square deviation (RMSD) as a measure of differences between experimental values and predicted values (i.e., those obtained from the pseudo-second-order kinetic equation). The degree of nitrogen substitution (DNS) of the cellulose was calculated from the nitrogen content (%N) and the molecular weight of the anhydroglucose unit (AGU), 162.15, using the following expression:

$$\text{NSD} = \frac{162.15 \times \%\text{N}}{1400 - 151.64 \times \%\text{N}}, \tag{5}$$

where %N denotes the percentage of dry elemental nitrogen, 1400 is 100 times the atomic weight of nitrogen, and 151.64 is the molecular weight of the epoxypropyltrimethylammonium chloride (EPTMAC) group added.

Comparing the results of this work with the results of de la Motte and Westman [41], under the conditions leading to maximal incorporation of nitrogen in cationic form, DNS was greater in this work: 0.404 (i.e., 40.4%) at the maximum %N level.

We used a constant CHPTAC/AGU ratio, NaOH concentration, and isopropyl alcohol proportion throughout. DNS for cationic starches typically ranges from 0.0075 to 0.1215 and increases with increasing reaction time and proportion of cationizing reagent. Our results are consistent with those of other studies [42].

Based on the available literature, DNS increases with increase in the CHPTAC concentration; also, using an inadequate amount of NaOH hinders formation of the epoxide and alkoxides from the polysaccharide, whereas excess NaOH causes degradation of the epoxide and decreases the molecular weight of the product.

Figure 5 shows the variation of N_{eq} and k with the amorphous fraction (AF) of cellulose (see (6)). N_{eq} was linearly fitted to the amorphous faction (see (7)). Hence,

$$\text{AF} = 1 - \text{CI} - \text{CII} \tag{6}$$

$$N_{eq} = 6.94\text{AF} - 0.996 \tag{7}$$

with $R^2 = 0.98$. Likewise, the best fit with the pseudo-second-order rate constant k was provided by

$$k = +\,9.33\text{AF} + 8.27 \tag{8}$$

with $R^2 = 0.78$. Overall, the rate of nitrogen substitution was found to increase with increasing amorphous fraction. The more severe the conditions of the alkalization stage were, the faster the cationization reaction occurred and the higher the equilibrium value was.

4. Conclusion

Under the experimental conditions used in this work, the overall cationization reaction fits a pseudo-second-order kinetic equation. The reaction rate increases with the square of the difference between the equilibrium and the apparent concentrations of nitrogen. This squared difference decreases—and so does the reaction rate, in an asymptotic manner—as the amount of nitrogen fixed to cellulose approaches its equilibrium level.

As previously found for other chemical and enzymatic reactions, the reactivity of cellulose increases with decreasing crystallinity index and increasing amorphous fraction to a greater extent than it does with the proportion of cellulose II (CII), even though the amorphous fraction is related to CII.

The proportion of nitrogen at equilibrium in cationized cellulose increases linearly with increasing content of amorphous cellulose in the starting material. Initially, the reaction rate is comparatively high. As a result, the proportion of nitrogen reaches a near-equilibrium level within a short time (about 30 min). To obtain cationic cellulose with a high substitution degree, it is advisable to have a previously performed alkalization stage under severe conditions.

Table 2: Parameters of pseudo-second-order rate equations.

Parameters of original kinetic equation	A1T1	A1T2	A1T3	A2T1	A2T2	A2T3	A3T1	A3T2	A3T3
N_{eq}, %N	0.11	0.15	0.17	0.13	0.15	0.19	0.67	1.56	1.79
DNS_{eq}	0.013	0.018	0.020	0.015	0.018	0.022	0.084	0.217	0.257
$N_{eq}^2 k$, %N/min	0.051	0.058	0.106	0.032	0.065	0.099	0.140	0.189	0.217
k, (%N·min)$^{-1}$	4.13	2.69	3.54	1.93	2.99	2.87	0.32	0.08	0.07
RMSD/10^{-3}	5.1	6.1	6.6	3.9	4.7	5.1	33	67	78

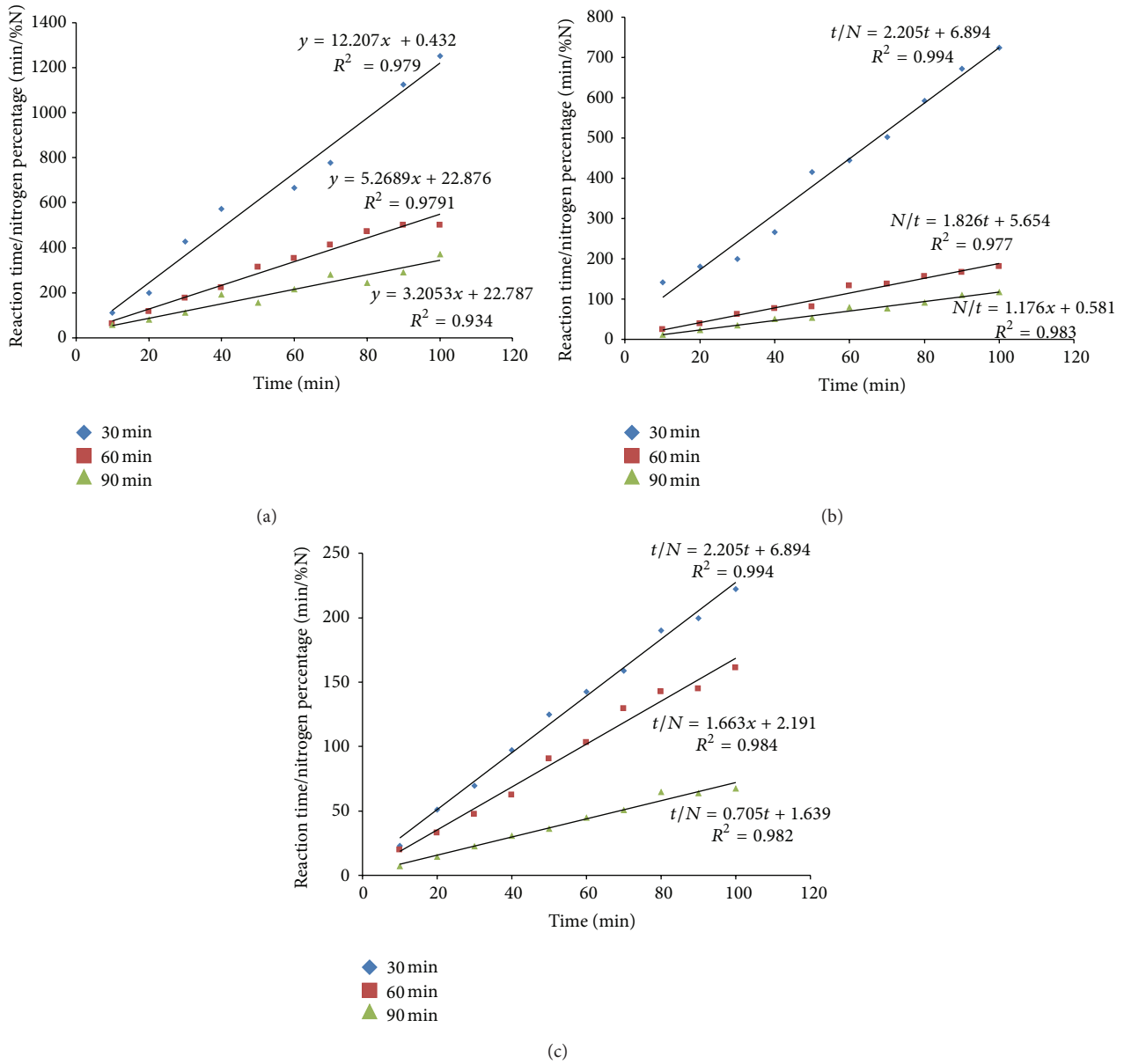

Figure 3: Linearized representation of the pseudo-second-order rate equation for cationized cellulose, previously alkalized with (a) NaOH 10%, (b) NaOH 20%, and (c) NaOH 30%.

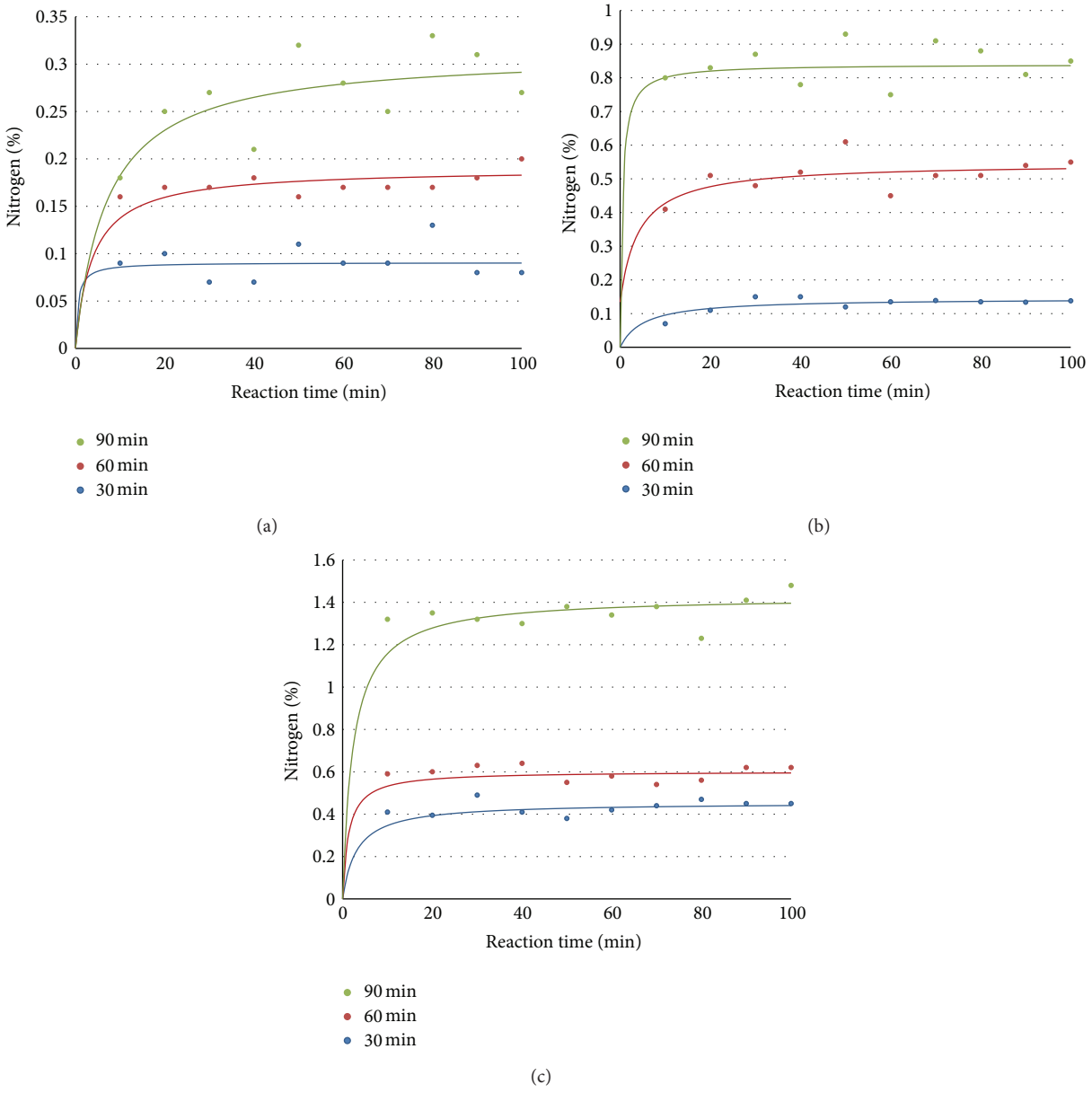

Figure 4: Percentage of nitrogen in cellulose after cationization following alkalization with aqueous solutions of (a) NaOH 10%, (b) NaOH 20%, and (c) NaOH 30%.

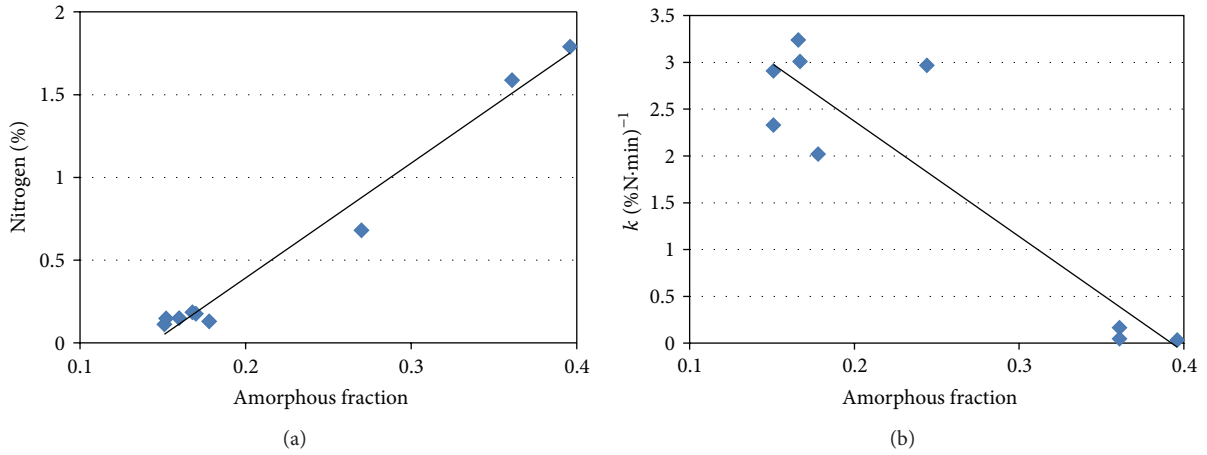

Figure 5: Nitrogen percentage (a) and kinetic constant of the pseudo-second-order model (b) versus amorphous fraction of cellulose.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

The authors wish to acknowledge the Ministry of Science and Innovation of Spain for the financial support of the Project CTQ2010-21660-C03-01, to which the present study is related.

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5.3. Publication III. Alkalization and cationization of cellulose: effects on intrinsic viscosity

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Journal: Fibers and Polymers.

JCR-indexed: Yes.

Category: Materials Science — Textiles.

Reference: Moral, A., Aguado, R., Tijero, A. *Fiber. Polym*. 17(6): 857-861 (2016).

Status: Published in July 2016.

Fibers and Polymers 2016, Vol.17, No.6, 857-861
DOI 10.1007/s12221-016-5819-y

ISSN 1229-9197 (print version)
ISSN 1875-0052 (electronic version)

Alkalization and Cationization of Cellulose: Effects on Intrinsic Viscosity

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(Received November 5, 2015; Revised February 15, 2016; Accepted May 5, 2016)

Abstract: Researchers have studied the cationization of polysaccharides to replace conventional cationic polyelectrolytes, linked to environmental issues. However, cationic celluloses have not achieved the success of cationic starches. The knowledge of the cellulose cationization proccess needs to be improved. In this work, we pretreat (alkalize) and cationize cotton linters and α-cellulose powder, using 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) in an aqueous-alcoholic alkaline solution. The pretreatment took place under different conditions, whereas the cationization itself was always performed at 70 ºC, for a CHPTAC/AGU (anhydro glucose units) mole ratio of 4, and for a total time of 5 h for cotton linters or 100 min for α-cellulose powder. The degree of substitution, the crystallinity index and the temporal evolution of intrinsic viscosity are provided for the 18 experiments performed. The background was uncertain about the effect of cationization on intrinsic viscosity. Here, we report increasing viscosity with increasing degree of substitution and cationization time. Furthermore, intrinsic viscosity increased with increasing cationization time, even when the degree of substitution had leveled off. Seemingly, the incorporation of positive charges into cellulose changed the polymer distribution and the interactions between the polymer and the solvent.

Keywords: Alkalization, Cationization, Cellulose, Viscosity

Introduction

Polysaccharides can be cationized towards sustainable polymers to be used for flocculation processes in wastewater and industrial effluent treatment, or in papermaking and petroleum industries, replacing non-biodegradable synthetic polyelectrolytes [1]. Results are often comparable to those obtained with conventional flocculation agents, such as cationic polyacrylamides, polyethyleneimine, and polyDADMAC. Alternatively, instead of using cationic polysaccharides to replace conventional polyelectrolytes, they can be combined with anionic polyacrylamides to improve their performance [2].

Researchers have studied the use of cationic derivatives from starch, dextran, cellulose, xylan, chitosan, inuline, and other polysaccharides for the aforementioned purposes [3-8]. Among them all, cellulose is the most abundant in nature. However, while cationic starches are already well-known and widely used for industrial applications, the cellulose cationization process still needs to be studied and optimized. Since this polymer is water-insoluble, mixing a cellulose suspension with a cationizing agent is not enough to obtain cationic cellulose. Further research is necessary to find pretreatments, reagents or solvents to solubilize and/or increase the reactivity of cellulose, thus obtaining high degrees of substitution [9,10].

One of the most popular reagents to produce cationic cellulose is 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC), always used with an aqueous NaOH solution. Using this chlorohydrin, the process generally involves three stages. 2,3-epoxypropyltrimethylammonium chloride (EPTAC) is formed by reaction between CHPTAC and hydroxide ions. Also, the hydroxyl group bonded to C_6 in some anhydroglucose units (AGU) undergoes etherification with NaOH, resulting in an alkoxyde group. Then, a substitution occurs, a cationic 3-(trimethylammonium)propyl group being introduced into the AGU structure. Figure 1 shows these steps and a secondary reaction consisting of the loss of EPTAC towards 2,3-dihydroxypropyltrimethylammonium chloride by hydrolysis. The mechanism is described in more detail elsewhere [8,11].

It is unclear how the cationization process affects the intrinsic viscosity of a cellulose solution. According to Song *et al.* [9], intrinsic viscosity increases with increasing degree of substitution and depolymerization of cellulose is negligible, but Yan *et al.* [12] found the opposite, attributing the diminishment of viscosity to depolymerization and hydrophilicity. The conditions were very similar, although the former authors used CHPTAC and the latter ones used EPTAC directly. This difference, however, does not seem enough to explain the discrepancy, given that direct functionalization with EPTAC requires less alkali, and there is no difference in the functional group introduced. Comparing the intrinsic viscosity of cellulose suspensions or solutions, before and after a chemical treatment, is a very valuable way to estimate the changes in molecular weight [13,14], but viscosity is influenced by other factors. As we lack a complete theoretical explanation of the influence of molecular mass and electrostatic interactions on viscosity, experiments are needed to study each case [15].

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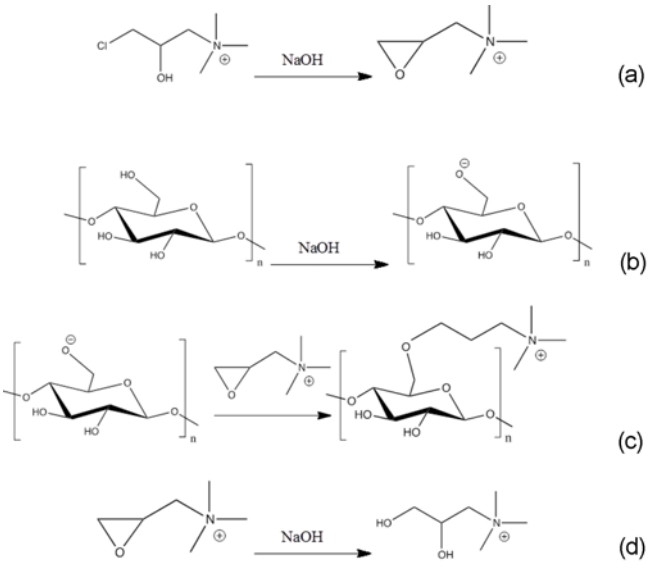

Figure 1. (a) Formation of epoxypropyltrimethylammonium chloride (EPTAC) from 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC), (b) alkalization of cellulose, (c) cationization of cellulose, and (d) hydrolysis of EPTAC.

In this work, we wish to make a contribution to the state of the art of cellulose cationization and, specifically, to something as uncertain as the influence of cationization on viscosity. Cationic cellulose samples obtained after different pretreatments and with different degrees of substitution are analysed. We discuss the influence of process variables on the intrinsic viscosity of cationic cellulose produced from two different materials.

Experimental

Materials

Two commercial cellulose-based materials were used in this study: medium-length fibers from cotton linters (Aldrich C6288), coded as C1, and α-cellulose powder (Aldrich C8002), coded as C2. Their viscosity (η), their fiber length, and their crystallinity index (CI) are presented in Table 1. NaOH pellets and 2-propanol were provided by Panreac.

Alkalization of Cellulose

The alkalization process was carried out at room temperature, in a 2 *l* spherical glass reactor with refluxing condenser and magnetic stirrer. In each run, 25 g of cellulose (on the basis of dry pulp weight) were mixed with 500 m*l* of an aqueous NaOH solution. Two factors were changed at three levels: reaction time (30, 60, and 90 min) and NaOH concentration (10, 20, and 30 % w/w), as Table 2 shows. Taking the two different materials used into account, the number of different experiments performed was 18. After the reaction time was reached, the suspension was cooled down and separated by filtration, aperture size being 2.7 μm. The solid fraction (alkalized cellulose) was washed with demineralized water and then dried in a vacuum stove at 45 ºC and 10 kPa.

Table 1. Key characteristics of the raw materials

Code	Material	Fiber length	CI (%)	η (ml/g)
C1	Cotton linters	1.5-5 mm mainly	68.0	218
C2	α-cellulose powder	75-150 μm mainly	49.9	242

Cationization of Alkalized Cellulose

An aqueous solution of 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) at 60 % (w/w) was purchased from Aldrich. 20 g of alkalized cellulose (on the basis of dry pulp) were put in the spherical reactor. Cellulose was mixed with 134 m*l* of the CHPTAC aqueous solution. This implies a CHPTAC/AGU (anydro glucose units) mole ratio of 4. A volume of 395 m*l* of an aqueous NaOH solution at 5 % (w/w) was added. The mixture was completed with isopropyl alcohol to reach a volume of 1 *l*. This alcohol was used by Kweon *et al.* [10] in starch cationization to minimize starch swelling. The timer started when the temperature of the mixture reached 70 ºC. This temperature was held constant by heating, controlled by an electronic PID device and measured by a Pt-100 probe. It is a suitable temperature, according to Ren *et al*., who performed cationization experiments between 50 ºC and 80 ºC [18].

Reaction time was 300 min for C1 and 100 min for C2. 10 samples were taken in each of the 18 runs, immediately diluting them with cold water to stop the reaction. They were filtered (again, aperture size of 2.7 μm), washed with demineralized water and dried at 45 ºC and 10 kPa.

Characterization of Samples

The content of carbon and nitrogen was measured by using a LECO CNS-2000I elemental macroanalyser. The degree of nitrogen substitution was calculated from the amount of nitrogen, incorporated as quaternary ammonium, in the structure of cellulose [19]:

$$DNS = \frac{162.15 \times \%N}{1401 - 151.64 \times \%N} \quad (1)$$

To compensate random errors, this result was corrected with the deviations in the carbon content. The mass percent of carbon in cellulose is 44 %, and thus the preliminary *DNS* result was multiplied by *%C*/44.

The intrinsic viscosity of all samples was determined according to the ISO 5351-1 standard, using a capillary viscometer and an aqueous cupriethylenediamine solution as the solvent.

In order to measure crystallinity, we obtained XRD patterns with a PANalytical's X-ray diffractometer. Diffraction patterns were deconvoluted by a Gaussian algorithm with Systat's PeakFit software, calculating the area under each of

the peaks. The crystallinity index (CI) was determined by dividing the area under the five crystalline peaks by the total area [20,21].

Results and Discussion

Degree of Substitution

The longer the alkalization pretreatment, whose aim was to decrease crystallinity [16], and the higher the soda concentration, the higher the degree of substitution (DNS) was, as it can be seen in Table 2. The only exception is C1A2T3, but it is likely due to the random error of the measurements. After alkalizing under severe conditions, the degree of substitution is one order of magnitude higher than when using mild conditions. These results were expected, since the amorphous proportion of cellulose is more reactive than the crystalline one [11,17]. DNS is higher for the α-cellulose powder, more accessible, than for fibers from cotton linter, but the difference between them was found to be smaller than expected. Hence, particle size has little influence compared to crystallinity, the index of the α-cellulose powder (49.9 %) being lower than that of cotton linters (68.0 %), as shown in Table 1. It should be noted that crystallinity indices obtained by area-based methods are lower and more accurate than those obtained by height ratios between crystalline and amorphous peaks [11,21].

These degrees of substitution reached are not as high as the highest values obtained by Song *et al.* [9], who used urea to increase accessibility even more, achieving a DNS of up to 0.6. However, these values are in the same order of magnitude, and slightly lower than the DNS values obtained by Ren *et al.* [18] at a temperature of 70 ºC.

Influence of the Alkalization Pretreatment on Viscosity

Clearly, both for C1 and C2, and for each of the sampling times, intrinsic viscosity (η) after cationization was higher when the pretreatments had been severe, as Table 2 shows. Particularly, the influence of concentrarion was larger than that of time. For both cotton linters and α-cellulose powder, the three highest DNS values correspond to the three lowest CI values. The influence of these pretreatments is explained mainly by how they ease cationization, making cellulose more accesible and reactive. Due to the same reason, severe alkalization treatments resulted in a more abrupt increase of viscosity with cationization time. The pretreatments themselves had little effect on viscosity, as can be seen from Figures 2 to 7 at time zero. This agrees with studies on the mercerization of cotton [22]. Nonetheless, η was observed to increase, slightly but significantly, with increasing NaOH concentration, probably due to the ionization of cellulose (-OH in carbon 6 to $-O^-Na^+$), since ionization of polymers is usually related to chain stiffness [23].

It can be concluded that the higher the degree of substitution, the higher the intrinsic viscosity. Pearson's *r*, also provided in Table 2, was calculated from DNS and viscosity values for the two materials studied. There is a good correlation for cationized cotton linters, *r* being over 0.9. Hence, when it is complicated to perform an elemental analysis, intrinsic viscosity

Table 2. Experimental planning for the pretreatment and degrees of substitution reached after cationization

Experiment	NaOH concentration (%)	Time (min)	CI after alkalization (%)	DNS after cationization	η after cationization (ml/g)	Pearson's *r*
C1A1T1	10	30	66.7	0.011	207	
C1A1T2	10	60	66.7	0.016	222	
C1A1T3	10	90	60.5	0.021	243	
C1A2T1	20	30	65.8	0.020	277	
C1A2T2	20	60	66.6	0.022	286	0.915
C1A2T3	20	90	64.0	0.013	314	
C1A3T1	30	30	51.1	0.094	461	
C1A3T2	30	60	50.4	0.189	463	
C1A3T3	30	90	47.8	0.204	517	
C2A1T1	10	30	49.9	0.013	267	
C2A1T2	10	60	49.4	0.018	288	
C2A1T3	10	90	43.5	0.020	301	
C2A2T1	20	30	31.9	0.015	413	
C2A2T2	20	60	33.0	0.018	426	0.806
C2A2T3	20	90	32.3	0.022	433	
C2A3T1	30	30	18.9	0.084	472	
C2A3T2	30	60	18.8	0.217	530	
C2A3T3	30	90	19.5	0.257	568	

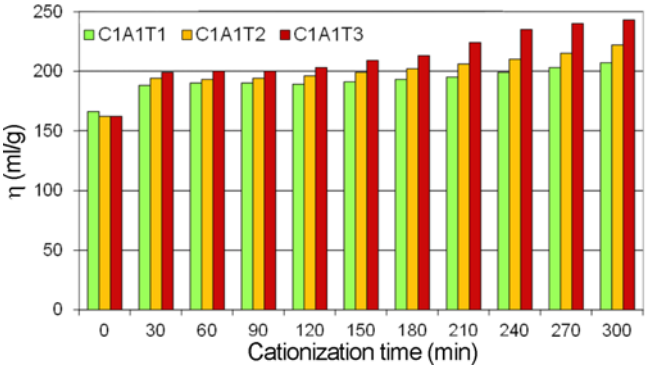

Figure 2. Viscosity of cationized cotton linters after pretreatments performed with NaOH (10 % w/w).

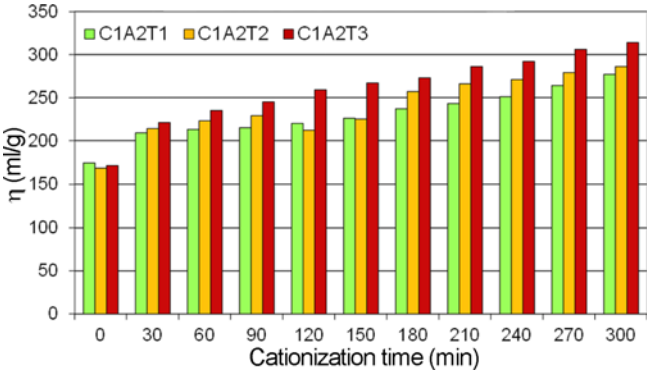

Figure 3. Viscosity of cationized cotton linters after pretreatments performed with NaOH (20 % w/w).

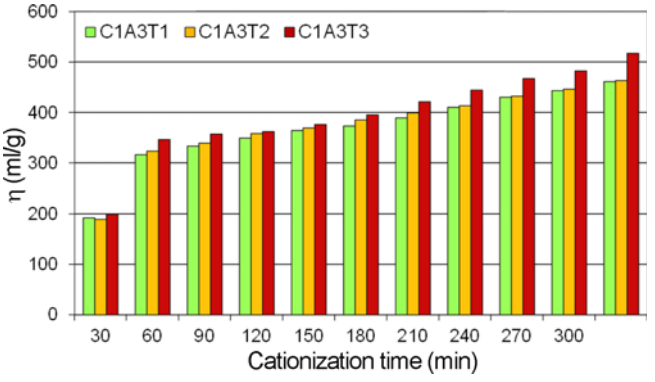

Figure 4. Viscosity of cationized cotton linters after pretreatments performed with NaOH (30 % w/w).

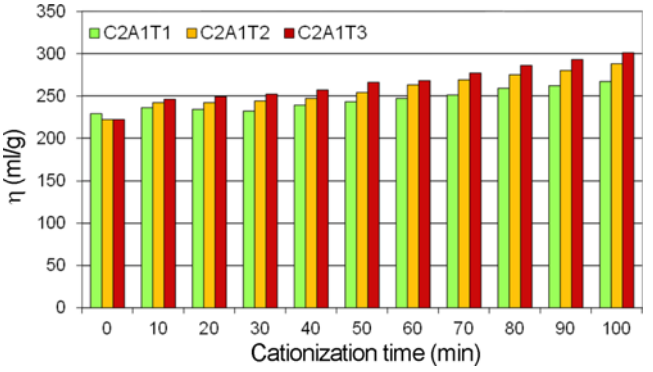

Figure 5. Viscosity of cationized α-cellulose after pretreatments performed with NaOH (10 % w/w).

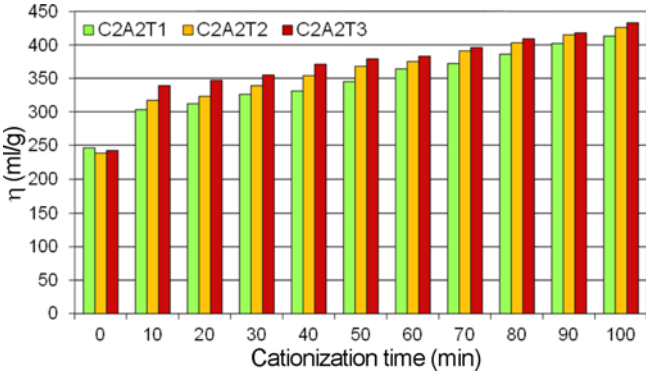

Figure 6. Viscosity of cationized α-cellulose after pretreatments performed with NaOH (20 % w/w).

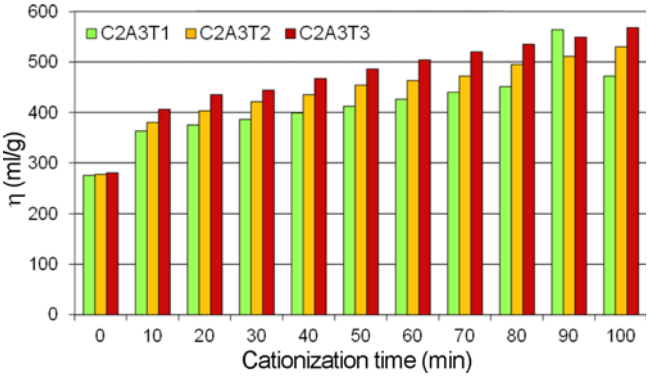

Figure 7. Viscosity of cationized α-cellulose after pretreatments performed with NaOH (30 % w/w).

can be used to roughly estimate the degree of substitution.

These results support the ones obtained by Song *et al.* [9]. They were not completely expected, as viscosity could have decreased due to hydrolysis of cellulose in a strong alkaline medium [12]. While there could have been some degradation of both cellulose and CHPTAC to a certain extent, other factors had a greater effect. Polarity, structure, and all possible interactions between the polymer and the solvent have an effect on intrinsic viscosity. Furthermore, polymers bearing electric charges are more difficult to predict than neutral polymers. Due to the charges, the polymer chains surrounded by solvent may become almost fully extended. This increases friction and thus viscosity. The Mark-Houwink equation is well-known:

$$\eta = KM^a \tag{2}$$

In equation (2), K and a are positive constant parameters,

while M is the average molecular weight of the polymer. The exponent of the molecular weight, a, rarely exceeds 0.8 for neutral polymers. Nonetheless, for polyelectrolytes, a can approach 2 [13]. Since cationic celluloses are interpolyelectrolytes, their a should take an intermediate value.

Influence of Cationization Time on Viscosity

The temporal evolution of intrinsic viscosity of cotton linters during cationization is presented in Figures 2, 3, and 4 for NaOH concentrations of 10 %, 20 %, and 30 % (w/w), respectively. Likewise, Figures 5, 6, and 7 show the results for α-cellulose powder.

Through cationization, for both raw materials and regardless of the pretreatment performed, the intrinsic viscosity of the cellulose suspension increased with time. This can be explained by the changes in the flexibility of the polymer chains, which decreases [22], and by the electrostatic interactions, including hydrogen bonds, that are intensified by the introduction of positive charges in cellulose.

It has been pointed out that Song *et al.* found that cationization causes viscosity to increase [9]. However, those authors stated that viscosity increased with increasing DNS, while we found that viscosity increases with cationization time, even if the degree of substitution stays the same. According to cationization kinetics, DNS reaches its equilibrium value and then it levels off or even decreases due to degradation of CHPTAC [18]. For these conditions, the highest DNS is reached after 60 or 90 min and then the degree of substitution fluctuates around that value [11]. Seemingly, under dillution and stirring, the hydrodynamic behavior of cationic celluloses with a certain DNS keeps changing.

Conclusion

Cotton linters and α-cellulose powder were cationized with CHPTAC in aqueous-alcoholic alkaline solutions to degrees of substitution of 0.204 and 0.257, when the materials had been pretreated with NaOH (30 % w/w) for 90 min.

Intrinsic viscosity of cationic cellulose was found out to increase with the degree of substitution, which is dependent on the severity (i.e., soda concentration and time) of the alkalization pretreatment. The introduction of positive charges changes how the polymer chain is distributed in space, increasing its persistence length, and how it interacts with the solvent and with other chains. Thus, for a given reaction time, viscosity measurements could be used as a quick way to estimate the degree of substitution.

Also, regardless of the degree of substitution, cationization time was found out to cause intrinsic viscosity to increase. For cellulose from severely-pretreated cotton linters, viscosity varied from 218 to 517 ml/g. For severely-pretreated α-cellulose, viscosity increased from 242 to 568 ml/g.

Acknowledgments

The authors wish to acknowledge the Ministry of Science and Innovation of Spain for the financial support of the Project CTQ2010-21660-C03-01, to which the present study is related.

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5.4. Publication IV. Cationized fibers from pine kraft pulp: advantages of refining before functionalization

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Journal: Holzforschung.

JCR-indexed: Yes.

Category: Materials Science — Paper & Wood (Q1).

Reference: Moral, A., Aguado, R., Jarabo, R., Tijero, A. *Holzforschung* 71(11): 843-851 (2017).

Status: Published online in July 2017. Printed version: October 2017.

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Cationized fibers from pine kraft pulp: advantages of refining before functionalization

DOI 10.1515/hf-2017-0023
Received February 8, 2017; accepted June 10, 2017; previously published online xx

Abstract: A partial cationization of cellulosic pulps has been suggested to enhance the retention of fillers and fines in the paper and board manufacturing industry. The challenge is the highly crystalline structure of cellulose and the mass transfer limitations of softwood fibers, which are long and resistant to and hinder the chemical reactions. In the present paper, it was demonstrated that refining (leading to decrystallization) and alkaline treatments facilitate the subsequent cationization process with quaternary ammonium groups. Cationization was performed with 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) at 120°C for 2 h, and degrees of substitution above 0.3 were achieved. Beating to 4000 or 4500 PFI revolutions was found to be an optimum to achieve these high degrees of substitution. Mixing a small percentage (4%) of cationized pulp (with a charge density of approximately 0.8 meq g^{-1}) with the untreated pulp could compensate for the negative surface charge of the original fibers. In this way, the highest charge density and opacity of the paper and the best retention of fines were achieved. If cationization was implemented in a paper mill, it should follow, not precede, the refining stage.

Keywords: amorphization of cellulose, cationization of cellulose, cationization of wood fibers, fines retention, pine kraft pulp, refining

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Introduction

The negative surface charge of cellulosic fibers in water, nearly 20 μeq g^{-1}, causes some trouble in the manufacturing of paper and board, given the repulsive forces between fibers and fines (Sood et al. 2010). Furthermore, in the usual pH range (7.5–8.5) in the fiber suspension of a paper machine, the surface of most mineral fillers is negatively charged. Because their particle size is lower than the aperture size of the wire in a paper machine, the use of flocculation agents is mandatory. It is also the reason why papermakers usually rely on cationic wet strength agents (Dang et al. 2007; Schäfer et al. 2007; Postma et al. 2014; Aguado et al. 2015).

Replacing some hydroxyl groups with positively charged groups, i.e. producing cationic fibers (CF), would reduce the need for synthetic polymeric aids and even enhance the wet strength (Besemer et al. 2005; Moral et al. 2016a). The stock would be prepared by mixing non-treated fibers with a small percentage of positively charged pulp to make the net charge density or the global zeta potential approach zero. Cationization is usually performed via reacting the substrate with an electrophilic reagent containing a quaternary ammonium salt (Šimkovic et al. 1990; Yan et al. 2009). The cationization of cotton for textile applications is well documented, but few studies deal with the production of cationic fibers for papermaking purposes (Fang et al. 2005; Acharya et al. 2014). Sang and Xiao (2009) prepared papermaking-oriented cationic fibers with diallyldimethylammonium chloride (DADMAC) and found that the retention and distribution of a clay filler was improved.

Pulp from pine wood, usually obtained by the kraft process, is the most common raw material for manufacturing paperboard, package paper and, mixed with eucalyptus wood pulp, printing paper (Baptista et al. 2006). However, the large moiety of crystalline cellulose from wood is resistant to chemical modifications, due to intramolecular and intermolecular hydrogen bonds. The crystallinity index is commonly estimated by X-ray diffraction (XRD) (Park et al. 2010). Certain XRD peaks are linked to crystalline conformations, normally cellulose Iβ in native wood cellulose. Alkaline treatments (mercerization at low temperatures) convert the allomorph cellulose I to

cellulose II with different crystalline characteristics (Ioelovich 2016; Moral et al. 2016b). The thermodynamic stability and the packing density of the paracrystalline parts in cellulosic fibers are lower than those of crystalline parts and are more accessible and more reactive, and prone to modifications (Buschle-Diller and Zeronian 1992). As a drawback, their length tends to shrink (Ward 1950), and the extreme processes required to lower the crystallinity negatively affect the strength of the final product.

A higher accessibility of cellulose in fibers can be achieved by refining. This process step is always performed to different degrees in all paper and board mills in order to increase the tensile strength via strengthening the fiber-to-fiber bonding (Laine et al. 2004). After refining, structural changes occur such as fiber shortening and internal and external fibrillation (Carrasco et al. 1996; Bhardwaj et al. 2007). Choi et al. (2016) found that the crystallinity index decrement of cellulosic pulps after swelling with NaOH was more abrupt if the pulps had previously been refined.

Refining also changes the electrokinetic properties of fibers by increasing their negative surface charge (Bhardwaj et al. 2004, 2007; Banavath et al. 2011). In the case of cationized pulps, it is plausible to assume that refining would lead to a higher positive surface charge for a given degree of substitution. To the best of our knowledge, this was not investigated earlier in terms of convenient and effective chemical modifications (cationization) of pulp fibers. The present study aimed to evaluate the properties of cationized *Pinus pinaster* fibers to improve retention of precipitated calcium carbonate (PCC) in the usual pH range during paper and board manufacturing. In focus will be the relationship between refining, fiber morphology, crystallinity index, degree of substitution, charge density, apparent density, and retention.

Materials and methods

An unbleached kraft pulp from pine wood (*Pinus pinaster* Ait.) was obtained from Tolsa S.A (Madrid, Spain). NaOH pellets, 2-propanol, ethylenediaminetetraacetic acid (EDTA), ammonia and ammonium chloride were obtained from Panreac (Barcelona). Sigma-Aldrich (Barcelona) provided the cationizing agent, an aqueous solution of 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC). PCC was applied as a filler, as it is the most usual filler in the paper industry, with a median equivalent spherical diameter (d_{50}) of 5.5 µm.

The experimental procedure and the analyses performed are presented in Figure 1.

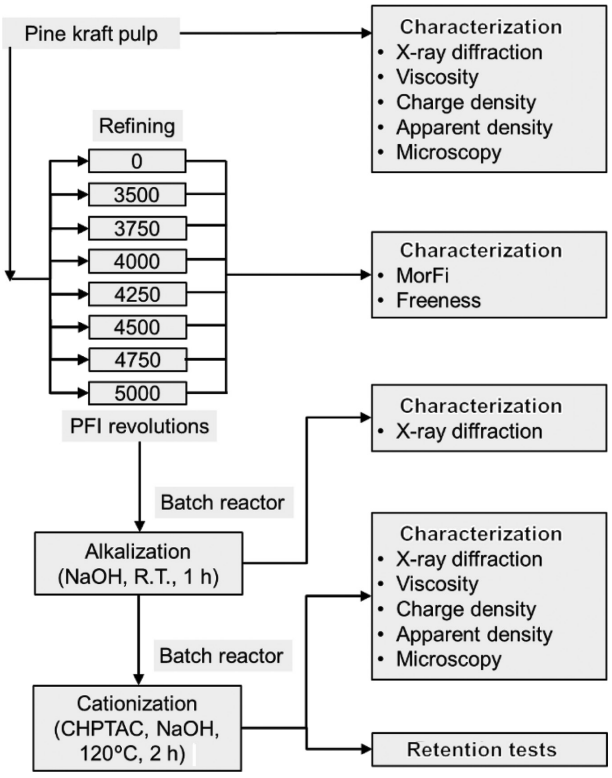

Figure 1: Schematic diagram of the operations and analyses.

Refining and fiber characterization: Pine kraft pulp was diluted to 1.5% consistency and disintegrated at 3000 rpm for 10 min, with a Lorentzen and Wettre (Stockholm, Sweden) device that conforms to ISO 5263 (ISO TC/6 2011). Refining was performed by means of a Maskin's Mark VI PFI mill (Hamar, Norway) (0.37 kW) following ISO 5264/2. Seven refining intensities were chosen at 3500, 3750, 4000, 4250, 4500, 4750 and 5000 PFI revolutions. The drainage capabilities of the unbeaten and beaten pulps were measured with a Canadian Standard Freeness (CSF) tester, in accordance with the Tappi method T 227 (1999). Enough replicates were made so that the relative standard deviation (StD) remained below 2%. The dimensions and populations of fibers were measured by a MorFi fiber analyzer from Techpap (France). Each suspension was prepared by diluting 1 g of pulp in 600 ml of water. The software (V. 7.9.13E) was adjusted to stop imaging after counting 5000 fibers and then the average values were calculated. Each measurement was repeated three times (see Moral et al. 2010).

Alkalization: All reactions were carried out in a 2 l three-neck spherical glass reactor equipped with a refluxing condenser and magnetic stirring. Among the eight pulps (the original one as control pulp and the seven refined ones), the refined pulps at 0, 3500, 4000, 4500 and 5000 PFI revolutions were selected for alkalization and cationization. In each experiment, 20 g of pulp (b.o. dry pulp) was soaked in a 10% NaOH aq. solution. After 1 h of vigorous stirring at room temperature, the fibers were separated by filtration over a Whatman Glass Microfiber GF/D filter (2.7 µm), and washed with demineralized water.

Cationization: Alkalized cellulose was mixed with the reagent in a CHPTAC/AGU mole ratio of 4, adding a 5% NaOH solution dropwise so that the NaOH/CHPTAC mole ratio became 1, and enough isopropyl alcohol was added to have a 1 l suspension. Heating to 120°C for 2 h (heating mantle) was controlled via a Pt-100 probe and an electronic

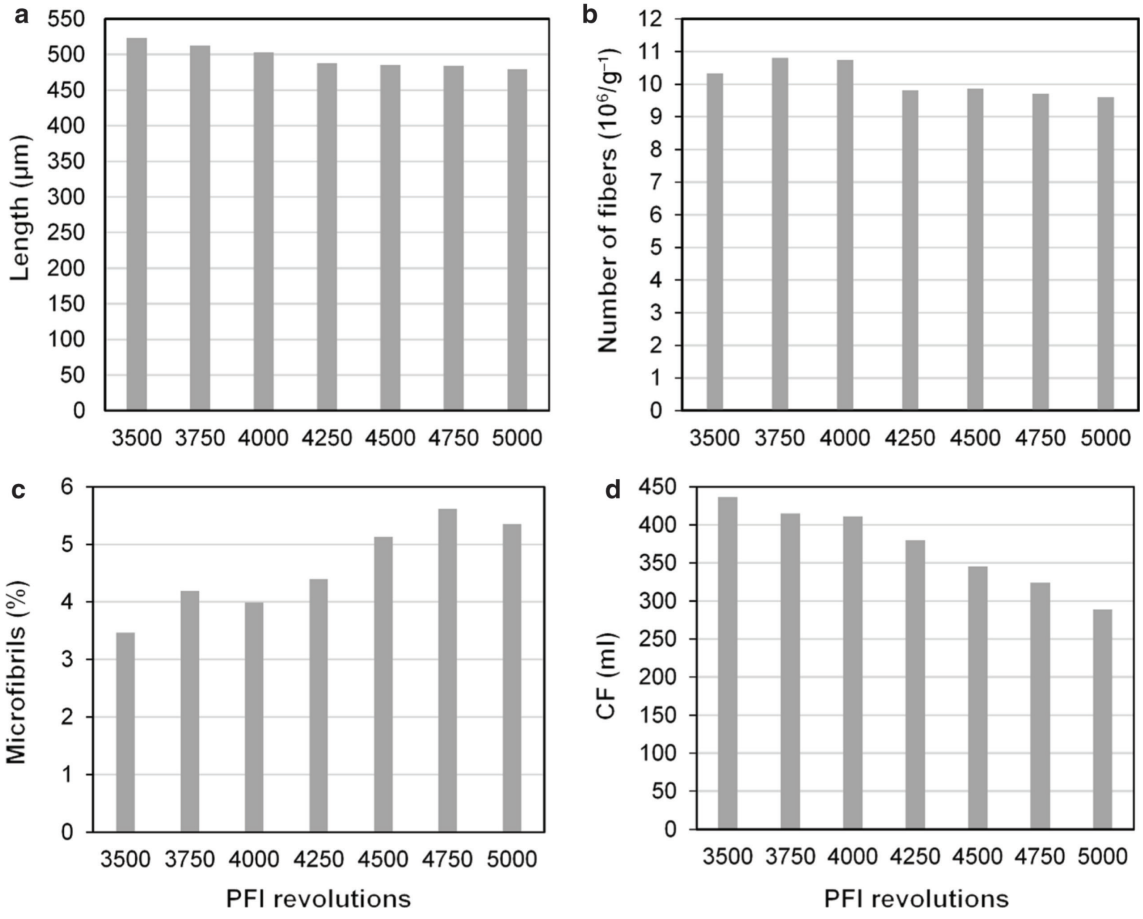

Figure 2: It is shown how fibers are slightly shortened by refining and how freeness is clearly reduced.
Effect of refining on (a) fiber length, (b) fiber population, (c) proportion of microfibrils on the fiber surface, and (d) Canadian Standard Freeness.

PID device. The heating time began from T_{max}. Afterwards, the cationized pulp was diluted to lower the pH, separated from the liquid with the aforementioned filter, carefully washed, and dried in a vacuum furnace at 45°C. Washing ensured that the small portion of cellulose that became water soluble after cationization was removed.

Determination of cationicity: The N-content of the cationized samples was measured by an LECO CNS-2000I elemental analyzer (LECO Instrumentos, Madrid, Spain). The charge density was determined via automatic potentiometric titration [Charge Analysis System (CAS) device from AFG]. The equipment is designed for liquids, and thus a back titration mode was applied instead of the direct approach. A small amount of fibers (less than 0.3 g) were soaked in excess sodium polyvinylsulfate (3 ml of PVSNa, 1.8 meq l^{-1}) as an anionic polyelectrolyte. No stirring was applied, because the surface charge and not the total charge should be neutralized. Water was immediately added to make up to 10 ml and the resulting liquid was titrated with polydiallyldimethyl-ammonium chloride (PDADMAC, 2.2 meq l^{-1}) as a cationic polyelectrolyte. The endpoint of the titration was the isoelectric point (0 mV). Reversely, to measure the charge density of the control pulp (pine kraft pulp before treatments), a sample was soaked in PDADMAC and the titration was carried out against the anionic electrolyte.

Characterization of pulps: The original pulp and the alkalized samples were grinded and submitted to a PANalytical's powder XRD equipped with X'Pert software. The 2θ angle ranged from 10° to 45°. The limiting viscosity number of all cationic samples and of the original pulp was determined according to the ISO 5351-1 standard, in a capillary viscometer and an aqueous copper (II) ethylenediamine (Cuen) solution as solvent.

The bulk density was measured in a novel way. In each case, a suspension of disintegrated pulp was dewatered on a wire screen to obtain a test pad of fibers. After drying at room temperature at a relative humidity (RH) of 50% for 48 h, the density of the test pad was determined with a pycnometer for solids and liquids, as described in T258 om-02 for the basic density determination of pulpwood chips, but gallium at 30–50°C was the agent instead of water. In this temperature range, the surface tension of gallium is even higher than that of mercury at 25°C, and thus this liquid metal does not penetrate into the pores (Poole 2004). The raw density value was multiplied by 6.095 g cm^{-3}, the density of gallium at 30°C (Hardy 1985).

Selected pulps were observed by scanning electron microscopy (SEM) with magnifications of 100× and 1000× (JEOL device, model JM-6400). Fibers were put on a cylindrical slide, which was dried at 45°C and 200 mbar and coated with gold. Another device from JEOL, a model JSM-6335F, was used to study the distribution of PCC on the surface of handsheets, with and without cationic fibers.

Performance in papermaking: The retention of fillers and fines was studied by a laboratory device DFR-05 from Mütek. Four percent

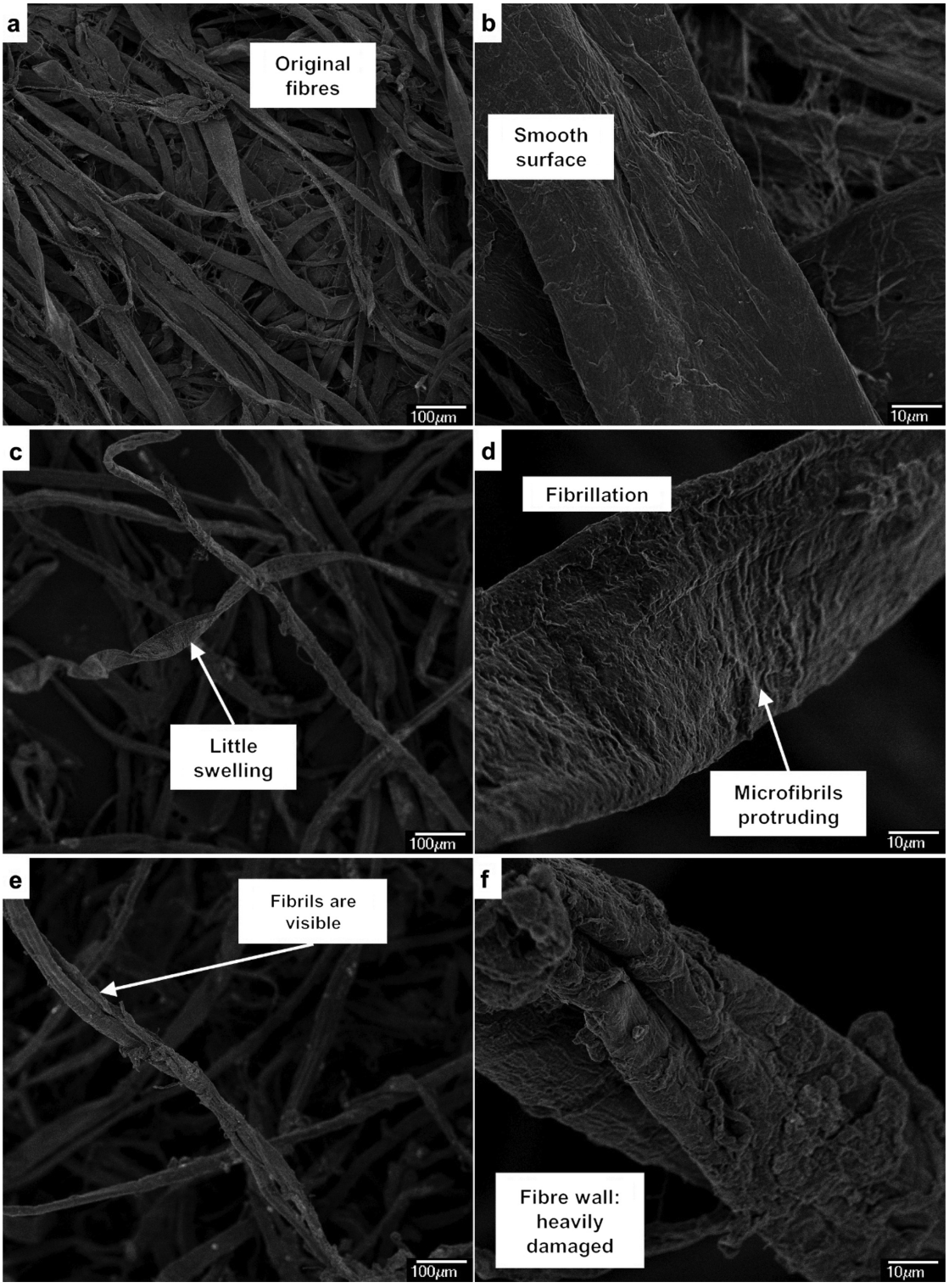

Figure 3: Chemical treatments damaged the surface, especially if the pulp had been refined.
Micrographs for (a) original kraft pulp (100×), (b) original kraft pulp (1000×), (c) pulp after alkalization and cationization (100×), (d) pulp after alkalization and cationization (1000×), (e) pulp after refining to 4500 PFI revolutions, alkalization and cationization (100×), (f) pulp after refining to 4500 PFI revolutions alkalization and cationization (1000×).

cationized pulp was combined with the original pulp refined to 3500 PFI revolutions (96%) and a suspension with a 0.5% consistency was prepared with tap water of conductivity 500 μS cm^{-1}. This suspension was mixed with PCC (0.2 g PCC as filler per gram dry pulp) to obtain a total mass of 800 g. The pH of the suspension was adjusted to 7.5 by adding HCl or NaOH dropwise. The retention program of Mütek's

software was applied to the fiber mixture under stirring (200 rpm for 60 s, and then at 300 rpm for 30 s). The suspension went through a 100-mesh screen, corresponding to a wire size of 0.11 mm.

As the DFR device does not distinguish between fillers and fines, the filtrate was submitted to a complexometric titration with EDTA to determine the amount of PCC with eriochrome black T as the indicator. The pH was kept around 10 by adding a buffer solution of ammonia and ammonium chloride. The amount of PCC retained is the difference between the PCC mass furnished initially and that in the filtrate. Five isotropic sheets were made from each of the following materials: kraft pulp, kraft pulp/PCC (8/2), and kraft pulp/PCC/cationic fibers (77/20/3), while the cationic fibers were beaten to various refining degrees. To this purpose, a laboratory sheet former was applied according to the ISO standard 5269/1 (ISO TC/6 2011). Agitation was carried out by hand, with a standard stirrer. The sheets were left to dry between rings to keep them pressed, at 23°C and 50% RH. The basis weight was 60 g m^{-2}. The opacity was determined by means of an Elrepho spectrophotometer from Lorentzen and Wettre with a C/2° light source, following ISO 2471 (ISO TC/6 2011).

Results and discussion

Influence of refining and chemical treatments on morphology

The dimensions of the native fibers from pine are reported in the literature (Sable et al. 2012). Figure 2 presents the results of average fiber length (weighted in length), number of fibers (length higher than 100 μm) and percentage of microfibrils over the fiber surface (area-based calculations), obtained by means of the morphological analysis. Freeness decrement is visible as a function of refining (Figure 2d). The fiber shortening (Figure 2a) and the increasing protrusion of the microfibrils (Figure 2c) are also presented. Kraft pulps from hardwoods, in contrast, may need only 3000 PFI revolutions to achieve the values obtained for the pine kraft pulp after 5000 PFI revolutions (Bhardwaj et al. 2007). Compared with other fiber sources, softwood pulp needs the most energy for noticeable freeness differences. During refining, fibers undergo shear and compression. The generation of fines (length <100 μm) is evidenced by the cutting of fibers (Figure 2a). These secondary fines increase the water retention of the web, filling the gaps between fibers and lead to lowering CSF data. Refining to 3750 PFI revolutions slightly increased the fiber population because some fibers were cut. After a long beating time, the mechanical damage resulted in a notorious fiber loss from 10.8 M g^{-1} to 9.6 M g^{-1}.

The SEM images in Figure 3 reveal that the control pulp is nearly not curled (Figure 3a) and that their surfaces contain only a few microfibrils (Figure 3b). Alkalization and cationization of this unrefined pulp increased the number of curls, but the fibers were swollen to a lesser extent than expected (Figure 3c). As can be seen from Figure 3d, the fiber surface became much rougher and the fiber wall was clearly peeled due to the chemical damage. When the pulp was refined to 5000 PFI revolutions and then pretreated and cationized, extreme internal and external fibrillation was found (Figure 3e), and at the end, the fiber walls were nearly destroyed (Figure 3f). It is obvious that refining to a certain extent before cationizing increases the specific surface area.

Influence of refining on decrystallization and charge

The XRD patterns displayed in Figure 4 resemble the typical shape of cellulose Iβ, which is the main cellulose polymorph in wood. Miller indices are assigned to the most prominent peaks, based on the suggestions of French (2014). Despite the treatment with NaOH, there was little conversion to cellulose II. The most prevalent peaks of this polymorph, which correspond to the planes (110) and (020), should appear at 20.1° and 21.5°, respectively. At most, the (200) peak of cellulose Iβ became slightly

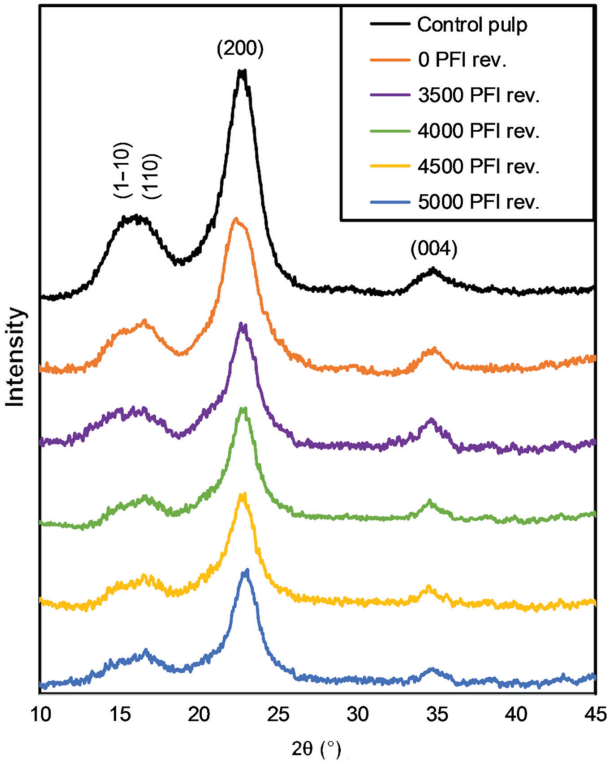

Figure 4: X-ray diffraction patterns for the original pulp and for the alkalized samples after refining.

lopsided. Nonetheless, partial amorphization of fibers is visible after pretreatments. The intensity of the crystalline peaks at 15° and 16.5° decreased after alkalization, and this decrease was found to be more abrupt in the case of a preceding beating at 4000 PFI revolutions or more. There is an evident diminishment in the area under the peaks for the plane (200) of cellulose Iβ (22.5°) and (004) of both cellulose Iβ and cellulose II (34.6°).

The crystallinity index (CI) listed in Table 1 was estimated from the diffraction patterns by performing a Gaussian deconvolution with Systat's Peakfit software, identifying four crystalline peaks, and dividing their area by the total area according to Eq. (1) (Park et al. 2010). Also, as a way to estimate the conversion of cellulose I to cellulose II, the area of the distinguishable crystalline peaks associated with cellulose I after deconvolution was divided by the area of the distinguishable crystalline peaks associated with cellulose II (Eq. 2). Overlapping peaks with those of other polymorphs were omitted. This is only a comparative estimation, and it is not representative of the quantitative conversion of cellulose I to cellulose II.

$$\mathrm{CI} = \frac{\text{Area } (1-10) + \text{Area } (110) + \text{Area } (200) + \text{Area } (004)}{\text{Total Area}} \quad (1)$$

$$\mathrm{A}\frac{\text{Cell}-\text{I}}{\text{Cell}-\text{II}} = \frac{\text{Area } (110)_{\text{I}} + \text{Area } (200)_{\text{I}} + \text{Area } (004)}{\text{Area } (110)_{\text{II}} + \text{Area } (004)} \quad (2)$$

Refining enhanced the interactions between the hydroxide and the fibers during alkalization and led to a crystallinity decrement. Nonetheless, its influence on the conversion of cellulose I into cellulose II is not clear (Table 1). Refining increases the negative surface charge of fibers (Banavath et al. 2011) because of the enlarged area and the higher amount of hemicelluloses in the fiber wall. Alkalization alone produces a higher value, even without refining, because the hydroxyl groups in cellulose are ionized.

Characterization and testing of cationized pulps

Elemental analysis data of CF are presented in Table 2. To calculate the degree of nitrogen substitution (DNS) of the CF, it was assumed that they consist entirely of anhydrohexose units. The amount of anhydropentose units is low because of the alkaline hydrolysis of hemicelluloses during kraft pulping (Deutschle et al. 2014; Postma et al. 2014) and their molecular mass is around 30 Da or lower. Hence, Eq. (3) contains the molecular mass of an anhydrohexose unit (162 Da), together with that of the quaternary ammonium group (152 Da) and 100 times the atomic mass of nitrogen (Moral et al. 2015).

$$\mathrm{DNS} = \frac{162\,\%\mathrm{N}}{1401 - 152\,\%\mathrm{N}} \quad (3)$$

The degree of substitution (DS) was in the high range for insoluble cationic cellulose. According to Besemer et al. (2005), the functionalization of fibers should not reach

Table 1: Key properties of the alkalized pulps before functionalization, compared to the original pulp.

		PFI revolution				
Sample	**Control pulp**	**0**	**3500**	**4000**	**4500**	**5000**
CI	0.81	0.73	0.64	0.62	0.62	0.59
A(Cell-I)/A(Cell-II)	3.01	2.29	2.23	2.60	2.08	2.19
Surface charge (meq g^{-1})	−0.033	−0.044	−0.061	−0.065	−0.065	−0.068

Table 2: Key properties of the cationized pulps, compared to the original pulp.

		Cationic fibers refined to PFI revolutions				
Sample	**Control pulp**	**0**	**3500**	**4000**	**4500**	**5000**
%N	0	2.00	2.36	2.52	2.55	2.24
DNS	0	0.296	0.367	0.401	0.408	0.342
Limiting viscosity number (ml g^{-1})	1232	1637	1773	1759	1803	1720
Surface charge (meq g^{-1})	−0.033	0.442	0.613	0.793	0.854	0.724
Apparent density (g cm^{-3})	0.57	0.45	0.42	0.44	0.40	0.40

more than 30 cationic groups per 100 monomers; otherwise a lot of water-soluble polyelectrolytes may arise. Regardless of the pretreatment, the yield was approximately 95%, as the high DP of cellulose from pine wood and its high crystallinity prevented the polymer from being dissolved. Overall, the DS increased with decreasing crystallinity, because amorphous and paracrystalline cellulose is less stable thermodynamically and more reactive than cellulose I and cellulose II (Poletto et al. 2014). The exception was the pulp with the lowest crystallinity fraction, likely because the part with the highest DS was solubilized. The charge density followed the DS trend. The 4% CF would be sufficient to neutralize the global surface charge when the cationized pulp is refined.

Cationization has a positive effect on the pulp viscosity and a negative effect on the apparent density of the pulp pads. The former is due to the changes in the spatial distribution of the cellulose chains in fibers, which become stiffer (Moral et al. 2016b). The latter is explained by the strong positive charge of the cationic fibers, which are repelled from each other, and by the breakage of intermolecular hydrogen bonds.

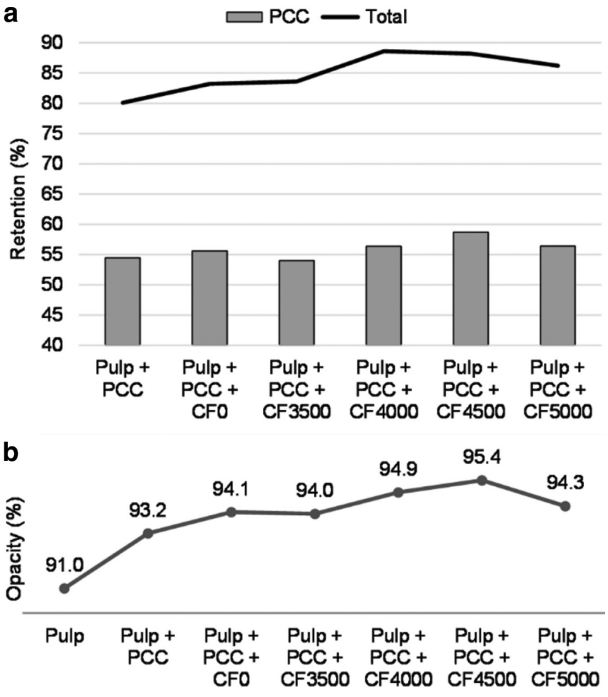

Figure 5: Results for the pine kraft pulp (77%) and PCC (20%), when mixed or not with cationic fibers (3%).
(a) Total retention and retention of PCC; (b) C/2° opacity.

Enhancement of retention

The performance of the CF refined to different levels is illustrated in Figure 5. Mechanical retention of PCC, without aids, did not reach 55% (Figure 5a), as the aperture size of the wire was much larger than the particle size of PCC. There is no appreciable difference in filler retention (Figure 5a). To the best of our knowledge, so far, CF have only been proved to improve kaolin retention (Sang and Xiao 2009). The filler has a strongly negative zeta potential and its retention is favored by charge neutralization. PCC may require a flocculation agent (a soluble polyelectrolyte), regardless of the surface charge of the fibers. Nonetheless, the total retention of solids was clearly improved by the presence of CF. Therefore, the insertion

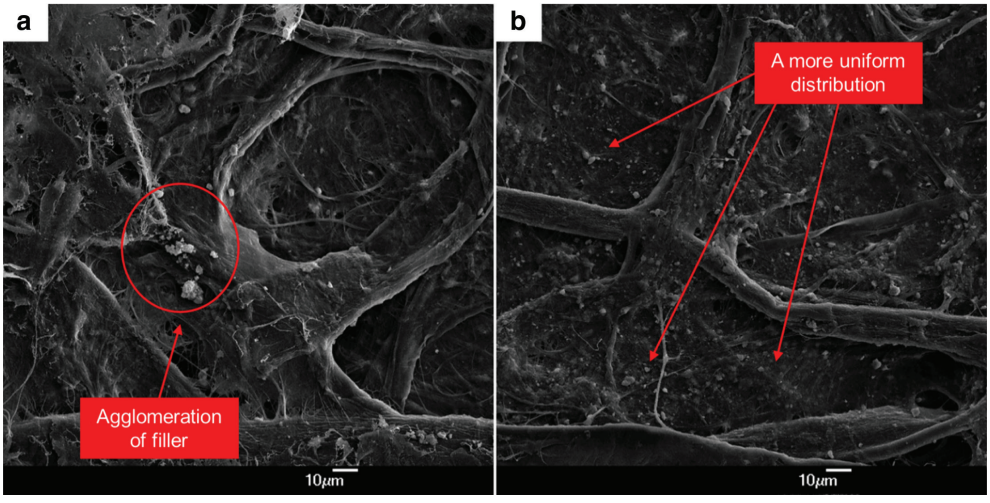

Figure 6: Addition of cationic fibers seemed to improve filler distribution.
Micrographs of the paper surface for (a) pine kraft pulp with PCC, (b) pine kraft pulp with PCC and cationic fibers that had been refined to 4500 PFI revolutions.

of cationic functional groups in some fibers increased the retention of pulp fines. The results were particularly good for the CF refined to 4000 and 4500 PFI revolutions, matching their high surface charge. In these cases, the pulp loss was less than 1%.

Because of the reduced loss of fines, the opacity was increased by the addition of CF, particularly when its DS was high (Figure 5b). Fines fill the gaps between fibers in the paper web, blocking the light in a higher degree for a given basis weight.

As the SEM images demonstrate in Figure 6 (surface of isotropic sheets with PCC without flocculants), cationic fibers modified the filler distribution. Figure 6a shows a very heterogeneous distribution of the calcium carbonate particles, which became aggregated in the area circled. These particles are more evenly distributed in Figure 6b, due to the addition of CF with the highest surface charge, enhancing fiber-filler bonding. A small amount of CF can both increase the bulk and the apparent density and improve the optical properties.

Conclusions

A previous refining stage before alkaline treatment facilitates the insertion of quaternary ammonium groups with a positive charge. Refining enhances the effect of the decrystallization and increases the external area of the fibers and improves mass transfer. In terms of the wet-end chemistry in a paper mill, the heavily refined cationic fibers have a larger contact surface, which likely improves the fiber-fine interactions. Beating to 4000 or 4500 PFI revolutions is advisable to achieve the highest DS possible. With a charge density of ca. 0.8 meq g^{-1}, 4% of CF mixed with the untreated pulp is able to compensate the negative surface charge of the original fibers. As a result, the retention of pulp fines is improved and the opacity is increased. However, cationization does not replace the polyelectrolytes for adsorbing PCC particles.

Acknowledgments: We are thankful to the Ministry of Science and Innovation of Spain for the financial support (project *FIBRALT*); to the auxiliary research centers at Complutense University of Madrid, which helped a lot with some determinations (degree of substitution, crystallinity), and to CIFOR-INIA (Spain), for letting us use their spectrophotometer. Ministerio de Ciencia e Innovación, (Grant/award number: "CTQ2010-21660-C03-01").

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5.5. Publication V. Cationic cellulosic derivatives as flocculants in papermaking

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Journal: Cellulose.

JCR-indexed: Yes.

Category: Materials Science — Paper & Wood (Q1).

Reference: Aguado, R., Lourenço, A.F., Ferreira, P.J., Moral, A., Tijero, A. *Cellulose* 24(7): 3015-3027 (2017).

Status: Published in July 2017.

Supplementary information: Appendix 1.

Cellulose (2017) 24:3015–3027
DOI 10.1007/s10570-017-1313-y

ORIGINAL PAPER

Cationic cellulosic derivatives as flocculants in papermaking

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Received: 22 December 2016 / Accepted: 24 April 2017 / Published online: 28 April 2017

Abstract Water-soluble cationic cellulose derivatives were synthesized by three different procedures, cationizing bleached hardwood kraft pulp with (3-chloro-2-hydroxypropyl) trimethylammonium chloride. The first procedure involved a previous depolymerization step with orthophosphoric acid. The second one consisted on dissolving cellulose in NaOH/urea before cationization. For the third procedure, the reaction medium was heterogeneous since it was carried out with a part of cellulose with high degree of polymerization. Oppositely to the common methods, cationization occurred under mild conditions. Differences among the three derivatives are illustrated by X-ray diffraction patterns of pretreated samples, infrared spectra, and determinations of the degree of substitution, the zeta potential, the charge density and the molecular weight. The performance of these polyelectrolytes for the flocculation of mineral fillers used in papermaking was tested by laser diffraction spectrometry. The flocculant with the highest degree of polymerization and charge originated the best results, particularly when the filler used was kaolin, proving that water-soluble cationic cellulose derivatives can aid in the flocculation of fillers used in papermaking. On the contrary, the shortest-chained derivative was not effective. The results were interpreted in terms of the characteristics of the cellulose derivatives flocculants and of the fillers, and neutralization and patching were proposed as the dominant mechanisms.

Keywords Cationization · Cellulose · Fillers for papermaking · Flocculation · Laser diffraction spectrometry

Electronic supplementary material The online version of this article (doi:10.1007/s10570-017-1313-y) contains supplementary material, which is available to authorized users.

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Introduction

Non-renewable and scarcely biodegradable polymeric aids, such as cationic polyacrylamides (CPAM) or polyethyleneimine (PEI), are often applied in paper mills to achieve good retention of mineral fillers. The particle size of these fillers is generally much smaller than the wire mesh at the forming and drainage section of the paper machine, and thus mechanical retention

alone, if no flocculation agents are used, results in high losses (Allen 1985). Cationic polyelectrolytes, besides enhancing retention, improve the drainage behavior and sheet formation, compensating somehow the disruption of fiber bonding caused by fillers (Antunes et al. 2008a).

Environmental concerns have led to research into alternative flocculation agents to be used in different fields, dedicating efforts to obtain cleaner and/or cheaper polyelectrolytes from natural and renewable sources. Introducing cationic ammonium groups into polysaccharides has been the answer for many researchers, given their availability and biodegradability. Starch, guar gum, cellulose, dextran and chitosan, among others, have been proved useful (Wood and Mora 1963; Prado and Matulewicz 2014). Nonetheless, while cationic starch and cationic guar gum have found good markets in the manufacturing industries (QY Research 2017), the production of cationic derivatives from the most abundant and available of all polysaccharides, cellulose, remains scarce. Although they are sold as cosmetic ingredients (Kozubal et al. 2014), their potential in the paper industry is being missed.

Yan et al. (2009) produced water-soluble cationic cellulose (WSCC) from microcrystalline cellulose to enhance flocculation in wastewater treatments. A similar procedure, i.e., dissolving short-chained cellulose in NaOH/urea and then performing cationization in a homogeneous medium, was followed by Li et al. (2015) aiming at using it as filler modifier. Other authors started from chemically modified cellulose, e.g., cellulose acetate and hydroxyethyl cellulose, as raw materials to obtain WSCC (Liesiene 2010; Liesiene and Kazlauske 2012). Those substrates consisted of alkali-soluble cellulose or modified cellulose with low degrees of polymerization (DP). The resulting cationic derivatives, obtained by means of epoxypropyltrimethylammonium chloride (EPTAC) or (3-chloro-2-hydroxypropyl) trimethylammonium chloride (CHPTAC), were not only soluble in aqueous alkaline solutions but also in water. However, solubilizing wood pulp in aqueous media is much tougher. Actually, total dissolution of high-DP α-cellulose may be simply impossible (Qi et al. 2011).

Short-chained WSCC may be adequate for flocculation by charge neutralization, as long as particles with negative zeta potential at the working pH are involved, but due to its small DP, it is not a good option for flocculation by bridging, which is the primary mechanism of particle aggregation in the first stage of the process. In fact, it was proved that the bridging mechanism dominates when polymers of high molecular weight and medium charge density are used (Rasteiro et al. 2008a).

In order to obtain high molecular weight WSCC, solubility in water must be achieved by the introduction of enough ionic groups into high-DP cellulose, such as that from wood. Previous studies report the production of cationic fibers with a degree of substitution around 0.2, which can be useful for some applications, but is still too low to promote solubility (Moral et al. 2016).

Cellulose-based polyelectrolytes from birch wood pulp were produced by Liimatainen et al. (2011) and Sirviö et al. (2011). Instead of using NaOH and CHPTAC or EPTAC, they performed a previous oxidation step with sodium periodate, and then cationized the substrate with Girard's reagent. They were able to incorporate more than one cationic group per monomer, thus obtaining a very high degree of substitution (and consequently high charge density). In spite of its high DP, this polymer was water-soluble due to its high ionic character. However, to simultaneously improve retention and drainage in papermaking, an agent of medium charge density is more appealing than a highly charged one, as the latter adopts a conformation that favors patching but hinders bridging (Antunes et al. 2008b).

In this paper, the syntheses of three different water-soluble cationic cellulosic derivatives from bleached hardwood kraft pulp are reported. The conditions applied, based on a previous kinetic study (Moral et al. 2016), are not as harsh as those usually reported in literature (Song et al. 2008; Sirviö et al. 2011; Acharya et al. 2014), since the reaction times are smaller, making the process more feasible. Characterization of the derivatives involved elemental analysis, X-ray diffraction patterns and infrared spectra. Their charge density, viscosity and zeta-potential were measured. Their performance was tested by laser diffraction spectrometry (LDS) with three different mineral fillers: precipitated and ground calcium carbonate (PCC and GCC, respectively), and kaolin, all of them frequently used in paper mills. In fact, LDS has proved to be very useful in assessing the performance of polymeric aids in flocculation (Antunes et al. 2008b; Pinheiro et al. 2013; Rasteiro et al. 2008a; Seo et al. 2016).

Materials and methods

Materials

Industrial bleached *Eucalyptus globulus* kraft pulp (BEKP) with a refining degree of 34° SR was used as raw material.

An aqueous solution of the cationizing agent (3-chloro-2-hydroxypropyl) trimethylammonium chloride (60%) (CHPTAC), was purchased from Sigma-Aldrich, and orthophosphoric acid (85%) was bought from Panreac. A cationic polyacrylamide (CPAM) from BASF with MW = 3.7×10^6 g/mol and CD = 1.1 mmol/g (data provided by the supplier), commonly used as retention agent in papermaking, was used for comparison purposes. Two different industrial calcium carbonates and a hydrated aluminum silicate were used as fillers: scalenohedral PCC, rhombohedral GCC and lamellar kaolin, respectively. Their zeta potentials, measured in aqueous suspensions by electrophoretic mobility in a Zetasizer NanoZS (Malvern Instruments) were +9 (pH 10), −28 (pH 10) and −24 mV (pH 6) respectively. The negative values of GCC are due to the presence of anionic polyelectrolytes used to stabilize the GCC dispersions (Vanerek et al. 2000). The fillers also differ in size: their median particle sizes (d_{50}), determined by LDS in a Mastersizer 2000 (Malvern Instruments), were 4.2, 2.0 and 3.5 μm, respectively. NaOH and urea, from Panreac, were also used as solvents.

A representative scheme of the whole experimental procedure, including pretreatments, cationization and separation processes, is depicted in Fig. 1.

Pretreatments

The different polyelectolytes produced are distinguished by the treatment previous to cationization. The cationic celluloses (CC) were labelled by ascending order of degree of polymerization (corresponding to descending order of yield), namely CC1, CC2 and CC3. The materials prior to cationization were named, respectively, C1, C2 and C3.

BEKP was depolymerized with orthophosphoric acid (H_3PO_4): a sample of BEKP, with a moisture content of 66%, was soaked in acid so that H_3PO_4 concentration was 80% and the consistency of the suspension (on a dry basis) was 2%. The acid hydrolysis occurred at room temperature for 2 h, the first hour without stirring and the second one with agitation with a four-blade stirrer at 600 rpm. A gel-like, whitish solution was obtained, similar to a suspension of nanofibrillated cellulose. Apparent dissolution was reverted when the pulp was diluted to 0.5% with distilled water. The suspension was filtered through an 11 μm paper filter, obtaining a powder-like amorphous cellulose (C1). The filtrate was discarded.

A precooled NaOH/urea solution was used to produce C2 and C3. For that, BEKP was diluted to 2% in an aqueous solution containing 6% NaOH and 6% urea, the mole ratio of alkali to anhydroglucose units (AGU) being 12. The suspension was stirred for 1 h at 600 rpm and then filtered through a 11 μm paper filter. The filtrate (lower DP fraction) was named C2, while the fibrous solid retained (higher DP fraction) was labelled as C3.

Cationization

Cationization was performed on the filtration retained fractions (C1 and C3) and on the filtrate (C2) with CHPTAC using a mole ratio to AGU of 3, as shown in Fig. 1. NaOH and urea were also added to C1 and C3 aiming for the same concentration (NaOH 6%, urea 6%, CHPTAC/AGU 3) in all three samples. Cationization lasted only 60 min, by applying gentle mechanical agitation (200 rpm) and maintaining the temperature at 65 °C. The mechanism by which CHPTAC and cellulose are activated with alkali and react is described elsewhere (Moral et al. 2016).

CC1 and CC2 seemed to be completely dissolved in the alkaline media. Since the derivatives are intended to be not only alkali-soluble but also water-soluble, the media were neutralized with hydrochloric acid. While CC2 remained in solution at neutral pH, a part of CC1 (insoluble part) was precipitated, filtered and discarded. Cationization of C3 originated a large amount of undissolved material, which increased even more after the neutralization. In this case, only 20% of the weight of C3 passed through the filter. The three cationic derivatives were soaked in a regenerating medium in which the volume percentage of ethanol was at least 50% (Fig. 1).

The aqueous-alcoholic suspensions were filtered by using a paper filter with an aperture size of 2.5 μm. The filtrates were discarded, although a liquid sample

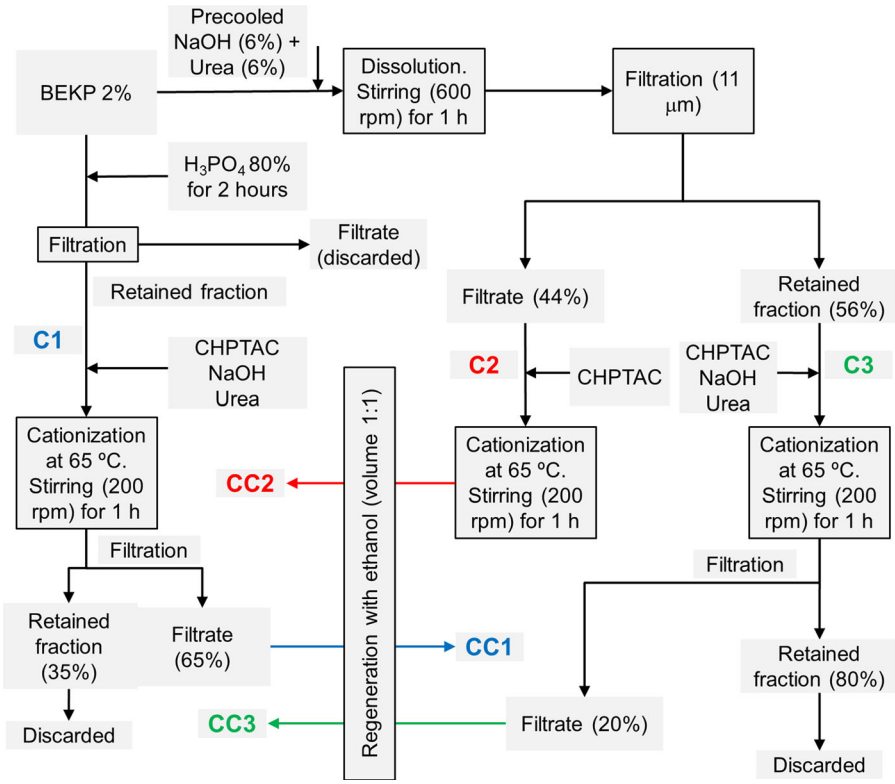

Fig. 1 Simplified diagram of the experimental procedure used to produce three different cationic cellulose derivatives

from the CC2 filtration was submitted to mass spectroscopy-gas chromatography (GCMS) to identify any possible by-products. The retained fractions of the filtrations (wet solids) were dried firstly at room temperature for 24 h, and after at 60 °C for 4 h. The solubility in water was confirmed by centrifugation of 1% solutions at 3000×*g* for 10 min.

Characterization

The samples were characterized for their degree of polymerization (DP), crystallinity, degree of substitution (DS), charge density (CD), zeta potential, yield and also with FTIR-ATR measurements.

The degree of polymerization of the pretreated samples was determined by dividing the corresponding mean molecular weight (M) by the molecular mass of AGU (162). In turn, the mean molecular weight of the C1, C2 and C3 pretreated cellulose chains was estimated from the limiting viscosity number (mL/g) by using the Mark–Houwink equation with the parameters reported by Eckelt et al. (2011) for cellulose solutions in a copper (II) ethylenediamine solution (Cuen):

$$\eta = 0.0653M^{0.735} \quad (1)$$

The limiting viscosity number necessary in Eq. 1 was determined according to the ISO standard 5351-1.

For the crystallinity assessment, aliquots of the pretreated samples C1, C2 and C3 were dialyzed by using a sack from Sigma-Aldrich which ensures retention of compounds whose molecular mass is 12,000 Da or higher, and placed in deionized water for 24 h, in order to remove phosphate salts and other undesired substances. A PANalytical's powder diffractometer with the software X-Pert HighScore provided X-ray diffraction patterns. The original pulp was also analyzed for comparison purposes.

A LECO CNS-2000I elemental analyzer was used to measure the content of carbon, hydrogen and nitrogen. The degree of substitution (DS) was calculated from the ratio of %N to %C (N/C), assuming that only one cationic quaternary ammonium group can be incorporated per anhydroglucose unit (Moral et al. 2016):

$$N/C = \frac{14DS}{144DS + 72 \cdot (1 - DS)} \quad (2)$$

where 14 is the atomic weight of nitrogen, 144 is twelve times the atomic weight of carbon (substituted monomer), and 72 is six times that weight (non-substituted monomer).

The charge density (CD) of the cationic derivatives was determined by potentiometric titration in a Charge Analysis System (CAS) from AFG. For that, a small amount of sample (less than 0.1 g) was dissolved in 10 mL of deionized water and the solution was titrated with an anionic polyelectrolyte, sodium polyvinylsulphate (PVSNa, 0.001 N).

The zeta potential of 1% (w/w) dispersions in distilled water of the dried CC1, CC2 and CC3 was measured with a Zetasizer Nano ZS device from Malvern Instruments.

FT-IR-ATR spectra were recorded by a Bruker Tensor 27 spectrometer with a MKII Golden Gate accessory, setting the resolution to 4 cm^{-1} and the number of scans to 128.

Flocculation tests

The performance of CC1, CC2 and CC3 as polymeric flocculants was evaluated by LDS in a Mastersizer 2000 device from Malvern Instruments, equipped with the Hydro 2000 module. To process the raw scattering patterns, the Mie theory (De Boer et al. 1987), which is rigorous and suitable for small particles (below 10 μm), was used considering the refractive index of the mineral fillers as being 1.57 (Wypych 2016).

Aqueous suspensions [1% (w/w)] of PCC, GCC and kaolin were submitted to magnetic stirring for 20 min and placed in an ultrasound bath (50 kHz) during 15 min in order to disaggregate the particles. For each experiment, 6 mL of the filler suspension were added to the equipment vessel containing 600 mL of distilled water. This was enough to reach an adequate obscuration of the He/Ne laser beam. The pump speed was set to 2000 rpm during the measurement of particle size.

As for the flocculants, solutions of CPAM, CC1, CC2 and CC3 [0.1% (w/w)] were prepared and stirred. A certain amount of the flocculant in each case (1 mg/g for CPAM, 20 mg/g for the cationic cellulosic derivatives) was added after the stabilization of the filler median size (some initial aggregation occurs spontaneously to a certain degree). Then, the evolution of the median particle size of the fillers together with the added polymer was monitored. Smaller amounts of the WSCC were previously tested (see supplementary information).

Results and discussion

Characterization of the pretreated samples

For the necessary calculations, BEKP was assumed to consist entirely of anhydroglucose units (AGU). This assumption is safe, given the negligible amount of lignin after bleaching, the most probable dissolution of the remaining hemicellulose in the preliminar NaOH/urea treatment and the fact that cationic groups are also incorporated into anhydropentose units (Deutschle et al. 2014).

For C1, BEKP was depolymerized with orthophosphoric acid (H_3PO_4), since this compound works both as a hydrolysis agent, as long as its concentration is higher than 30% (w/w), and as a cellulose activator, causing total amorphization if its concentration is superior to 79 wt% (Vinogradov et al. 2002).

For C2 and C3, a precooled NaOH/urea solution was used as solvent due to the influence of urea on hydrophobic interactions of low-DP cellulose (Zhang et al. 2002). As mentioned, the NaOH/AGU mole ratio was 12 in order to ensure a good cellulose solvation, since theoretically at least 4 OH^- ions per monomer are necessary in alkaline dissolution (Myasoedova et al. 1991).

All samples differ in solubility. As visible in Table 1, the DP of C1 was much inferior to that of BEKP. On the contrary, and as intended, C2 produced from the lower-DP part (soluble in NaOH/urea, at least to a degree in which solvated particles, macroscopically undistinguishable from the solvent, passed through the filter) exhibited a higher value than C1 but a smaller value than the original pulp. As for C3, it has the highest mean DP value, superior to that of the original pulp as a result of being obtained from the higher-DP fraction of this pulp.

Table 1 also presents the crystallinity index (CI) as calculated from the diffraction patterns shown in Fig. 2a. A linear baseline correction and a Gaussian deconvolution of peaks were carried out with Systat's Peakfit, as exemplified in Fig. 2b for the non-treated BEKP sample. The assignment of Miller indices to the peaks and the notation of these indices are based on the

Table 1 Characteristics of the bleached kraft pulp (BEKP) and of the pretreated cellulose samples

Sample	η (mL/g)	M × 10^{-4} (Da)	DP	CI	I(Cell-I/Cell-II)
BEKP	494	18.9	1170	0.813	4.30
C1	132	3.1	194	0.518	1.33
C2	380	13.3	820	0.386	0.36
C3	658	28.0	1703	0.540	0.88

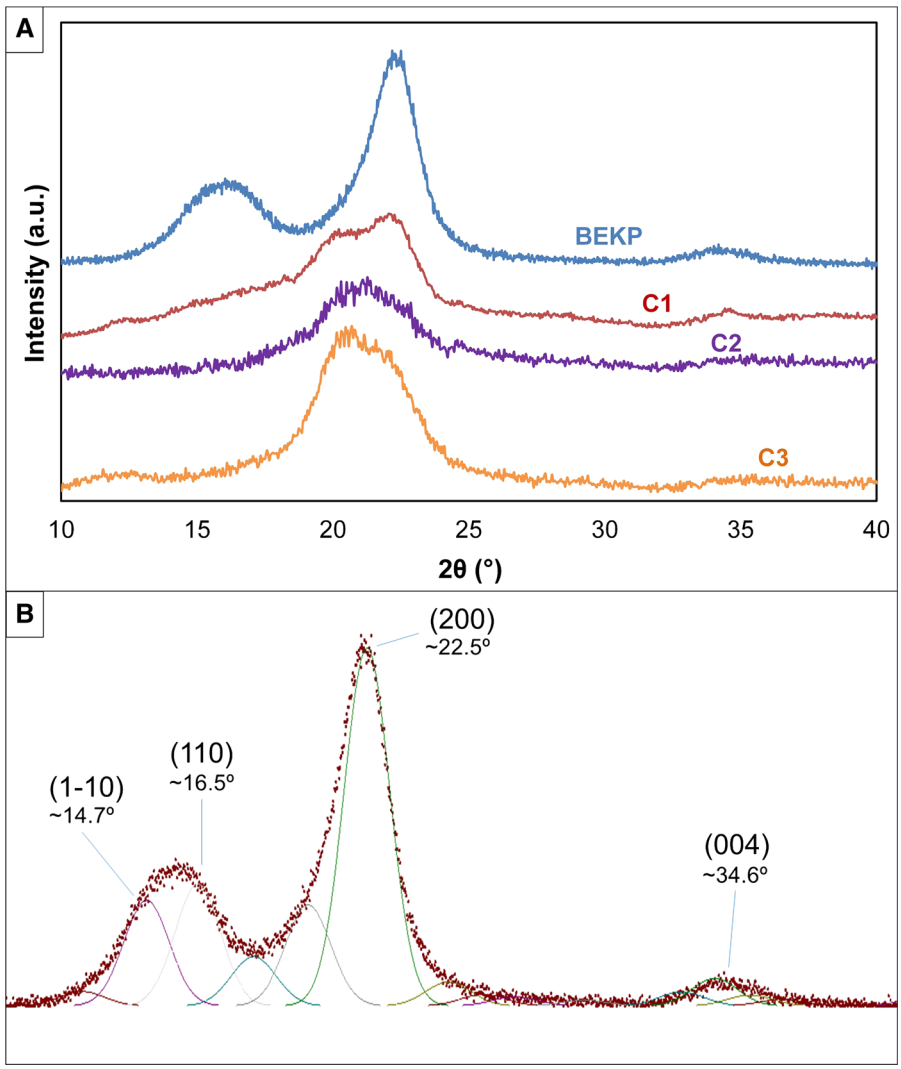

Fig. 2 X-ray diffraction patterns of the bleached kraft pulp (BEKP) and of the pretreated cellulose samples (**a**) deconvolution of the BEKP X-ray diffraction pattern (**b**)

conventions used by French (2014). It is assumed that BEKP, as cellulose from wood, consists fundamentally of cellulose Iβ, while the pretreated samples are mixtures of cellulose Iβ, cellulose II and amorphous cellulose. The crystallinity of the samples was estimated from XRD by identifying the four most prevalent peaks of cellulose I and the cellulose II (110) peak, and dividing their area by the total area (Eq. 3) (Park et al. 2010):

$$CI = \frac{A_{1-10(I\beta)} + A_{110(I\beta)} + A_{200(I\beta)} + A_{110(II)} + A_{004}}{A_{total}} \quad (3)$$

Both orthophosphoric acid and sodium hydroxide caused a diminishment in *CI*. The lowest crystallinity index corresponded to C2, the only pretreated sample which was totally alkali-soluble.

The diffractogram of BEKP displayed the typical shape of cellulose I (Fig. 2a). Likely, some phosphate groups incorporated into the structure of C1 during the pretreatment remained after dilution and regeneration, since the shape of the corresponding pattern before 21° resembles that of cellulose phosphate esters (Olaru et al. 2007). For C2 and C3, partial amorphization was evident: the peak at 22.5° for the (200) plane of cellulose I became much shorter (C3), or simply indiscernible from the (020) reflection of cellulose II, at 22° (C2). The other peaks became broader, which is a consequence of an increase in the amorphous fraction (Park et al. 2010).

Besides phosphoric acid and inorganic ions, the filtrate of C1, analyzed by GCMS, contained soluble products from the hydrolysis, but not necessarily furanic compounds. The temperature of the pretreatment (20–25 °C) was too low for dehydration.

To elucidate to what extent cellulose I is converted into cellulose II by the pretreatment, the intensity ratio (I(Cell − I/Cell − II)) was calculated with Eq. 4. The numerator contains peaks assigned to cellulose I, while the denominator contains peaks assigned to cellulose II (French 2014; Kolpak et al. 1978). The peak assigned to the (020) plane of cellulose II is omitted because it overlaps with the highest peak of cellulose I. The peak (004) is roughly the same for both cellulose Iβ and cellulose II. It must be stressed that this parameter serves as an indication of the ratio of cellulose I to cellulose II for comparison purposes, but never as an accurate and absolute determination of that ratio.

$$\mathrm{I(Cell-I/Cell-II)} = \frac{\mathrm{I_{14.7^\circ} + I_{16.5^\circ} + I_{22.5^\circ} + I_{040}}}{\mathrm{I_{12.4^\circ} + I_{20.3^\circ} + I_{040}}} \quad (4)$$

The value corresponding to C1 is not reliable, since the peak (110) of cellulose II (20.1°) may be confused with the most prominent band of cellulose phosphate. As expected, the proportion of cellulose II, more thermodynamically stable, increases with the alkaline treatments (C2, C3), as it also happens, for instance, in cotton mercerization (Poletto et al. 2014). When this alkaline treatment results in apparent dissolution (C2) and the sample is regenerated with an alcohol, specific peaks of cellulose I cannot be perceived in XRD patterns. C2 may consist completely of cellulose II and amorphous cellulose.

Characterization of the cationic derivatives

The DP values estimated from Eq. 1 for the pre-treated samples were also used for the cationized CC1, CC2 and CC3 samples. In fact, it is legitimate to consider that the DP is not modified with the cationization process, because the temperature is too low for an alkaline hydrolysis to happen at an appreciable extent. For instance, Song et al. (2008) using size exclusion chromatography, showed that the hydrolysis of cellulose during cationization with CHPTAC, NaOH and urea is negligible, even when the reaction took place at 60 °C for 8 h. As can be seen in Table 2, the cellulosic derivative with the highest DP (CC3) was the one presenting, after cationization, the highest degree of substitution, charge density and zeta potential. This is due to the fact that high-DP cellulose needs to have more ionized monomers to become soluble in water, and thus the lowly-substituted parts were rejected. As a drawback, given the mildness of the conditions used in this study, these lowly-substituted parts accounted for the majority of the material. Crystalline and lowly-substituted parts of CC3 could not pass through the filter after neutralizing with HCl.

Table 2 also shows the yield of WSCC from the bleached kraft pulp. It should be noted that CC2 and CC3 share the same pretreatment. 100 g of BEKP could be used to produce 44 g of CC2 and 11 g of CC3 (a total of 55 g of cationic cellulose from one single process), or 60 g of CC1, which is less electrically charged. Sirviö et al. (2011) obtained higher yield values, achieving complete dissolution of high-DP cellulose by producing a polymer with a very high

Table 2 Characteristics of the three cationic cellulosic derivatives

Sample	Yield (%)	DS[a]	CD[a] (mmol/g)	ζ-Potential (mV)
CC1	60	0.33	2.07	+4.5
CC2	44	0.34	2.80	+6.8
CC3	11	0.46	5.01	+16.7

[a] DS and CD mean degree of substitution and charge density, respectively

degree of substitution, but at the cost of a 24 h-long first treatment, a 3 h-long second treatment at 75 °C and then by cationizing with Girard's reagent.

Substitution was in the expected range. Lower degrees of substitution would have implied lack of solubility, while obtaining values close to 1 was impossible under mild conditions. Higher reaction times and higher concentrations of CHPTAC could have improved the yield, but probably not the degree of substitution. Yan et al. (2009) cationizing cellulose with a reagent/AGU molar ratio of 10, achieved DS values of 0.32 and 0.47 by applying reaction times of 6 and 9 h, respectively. These values are in the same range as those presented in Table 2, but their conditions and the use of low-DP cellulose eased solubility and avoided discards of undissolved parts, achieving a yield of 100%.

A gentle process, like the one suggested in this work, can generate samples with degrees of substitution higher than 0.3 at the expense of the yield. If a continuous reactor had been used instead of a batch one, the insoluble fraction could have been recycled, keeping the mild conditions. This would be a feasible alternative to the expensive and time-consuming processes.

The zeta potential of the starting material (fibers from BEKP) in water is slightly negative in a wide pH range and cationization involved a switch towards positive values. As cationic functional groups were incorporated into cellulose, the polymer reached the isoelectric point and then its charge density increased with the degree of substitution. The small difference between the CC1 and CC2 zeta potentials could be deemed not significant. The value found for CC3 suspended in water was much higher. This could be explained by the pretreatments applied in the latter, which decreased the stability of the dissociable groups that have a negative contribution to the surface charge.

All ATR-FTIR spectra, normalized and presented in Fig. 3, showed typical peaks for cellulose in absorption bands at 3330 cm^{-1} (g), related to O–H stretching, and at 2882 cm^{-1} (f), associated with symmetrical stretching of C–H bonds. The intensity of the absorption at 897 cm^{-1} (a), due to C1–H bending and sensitive to a rearrangement of intramolecular hydrogen bonds (Yang et al. 2010), increased with the amorphous fraction of the sample. Particularly for CC2, the derivative with the lowest crystallinity, this peak was almost as high as the one found at 1040 cm^{-1} (b). Bands at 1160 and 1019 cm^{-1} are assigned to C–O–C asymmetric stretching and different vibrations of C–C and C–O bonds, respectively. In the spectra for CC2 and CC3, the decrease in sharpness is evident and these peaks become mere shoulders. The band at 1623 cm^{-1} (e) is due to O–H bending in absorbed water (Granja and Barbosa 2001). Purification after regenerating succeeded to remove urea, since its absorption bands, which would be very prominent between 1700 and 1400 cm^{-1} and between 3500 and 3100 cm^{-1} (Turney et al. 2013), cannot be distinguished.

Spectra of CC1, CC2 and CC3 showed additional peaks at 1427 and 1390 cm^{-1} (d), linked to the quaternary ammonium groups (Sang et al. 2012). Due to the conversion of cellulose I to cellulose II, the spectra of CC2 and CC3 do not possess a peak at 1345 cm^{-1} (Granja and Barbosa 2001). Whether phosphate groups remain in the structure of CC1 is not proved by its spectrum, but their absence is not confirmed either, since the most prominent band of PO_4 is given at 1020 cm^{-1}, thus interfering with one of the most noticeable bands in the spectrum of cellulose (Hallac and Ragauskas 2011).

Performance in flocculation tests

The evolution of the median equivalent spherical diameter (d_{50}) of the three fillers when in contact with the WSCC is plotted in Fig. 4. On the left side (Figs. 4a–c) the influence of the WSCC addition on the different fillers flocculation is shown. The results were normalized considering the particles median size at the moment of the flocculant addition and the corresponding values are shown in Fig. 4d–f, which provide a better perception of the influence of each polyelectrolyte separately. As stated, CPAM was always used for comparison purposes since it is one of the most common flocculants used in papermaking. Table 3 presents the zeta potential of the suspensions used in the flocculation tests at given pH values.

When kaolin was used, it is evident that CPAM and CC3 promoted a high filler flocculation, with a maximum filler particle size increment close to 6.5 and 7.5 times, respectively. As stated in the literature CPAM is able to flocculate the particles by bridging due to its high molecular weight (Neimo 1999). As for CC3, with a molecular weight one order of magnitude off but a much higher charge density

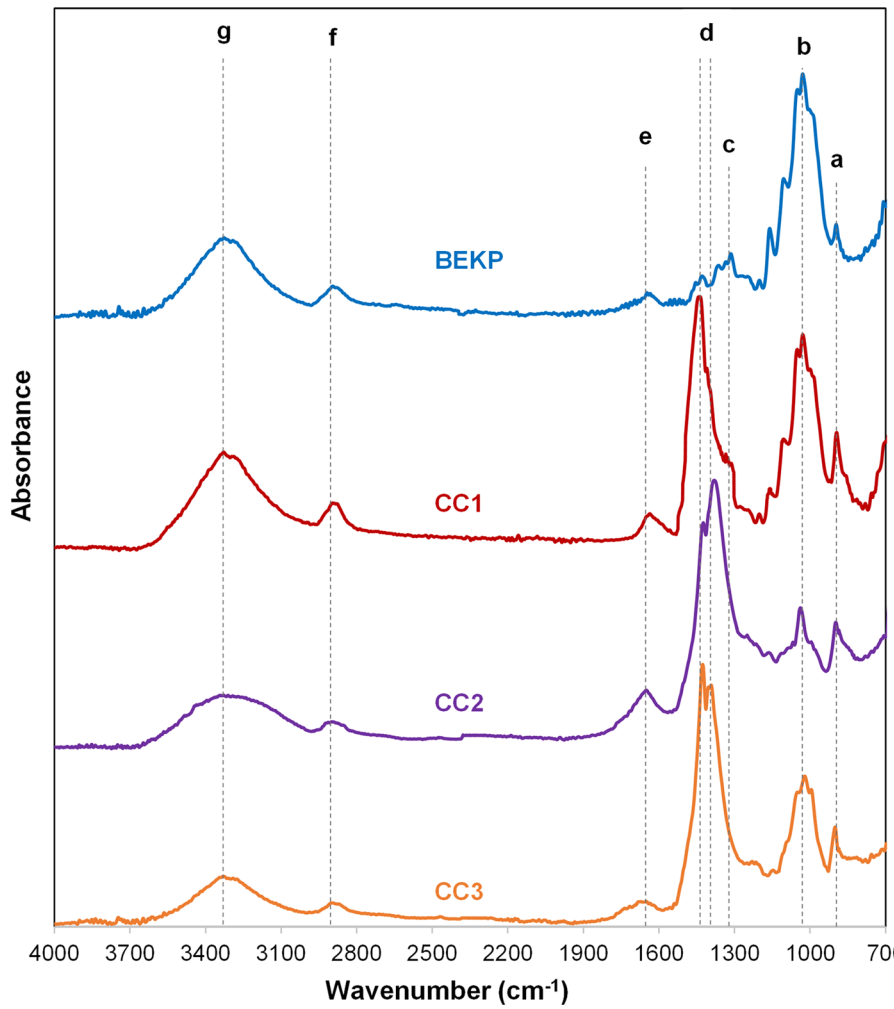

Fig. 3 Infrared spectra of the original bleached kraft pulp (BEKP) and of the cationic cellulosic derivatives

(Tables 1, 2), neutralization was most probably the dominant mechanism (Neimo 1999). However, due to the high charge, patching was also likely to occur, which was proven by the good reflocculation ability of the particles after a step of high shear, shown in Fig. 5. According to Rasteiro et al. (2008b), flocs formed by bridging mechanisms do not reflocculate as easily as those formed by patching. In fact, the electrokinetic potential of the kaolin/CC3 mixture was only slightly negative (−7.3 mV), which increases the probability of particle aggregation. In contrast, with CC2 this value was much higher (−27.2 mV) and the flocculation effects were attenuated, in accordance with the smaller values of the molecular weight and also charge density. CC1 has no influence in filler flocculation, regardless the mineral used, and this is a result of the very small molecular weight, degree of polymerization and also charge density. For this reason, the plot with the normalized values is not presented. This confirms that the pretreatment with ortophosphoric acid was not successful to induce filler flocculation.

For GCC similar results are observed with CC2 and CC3, revealing a negligible increment of the particles size. In spite of having also a negative charge, as kaolin, GCC particles are scalenohedral shaped, and not lamellar, and this fact may have hindered the aforementioned flocculating mechanisms. In this case only CPAM seems to be effective.

Contrary to kaolin and GCC, PCC has positive charge (+9 mV) and therefore the influence of the WSCC on filler flocculation is expectedly different.

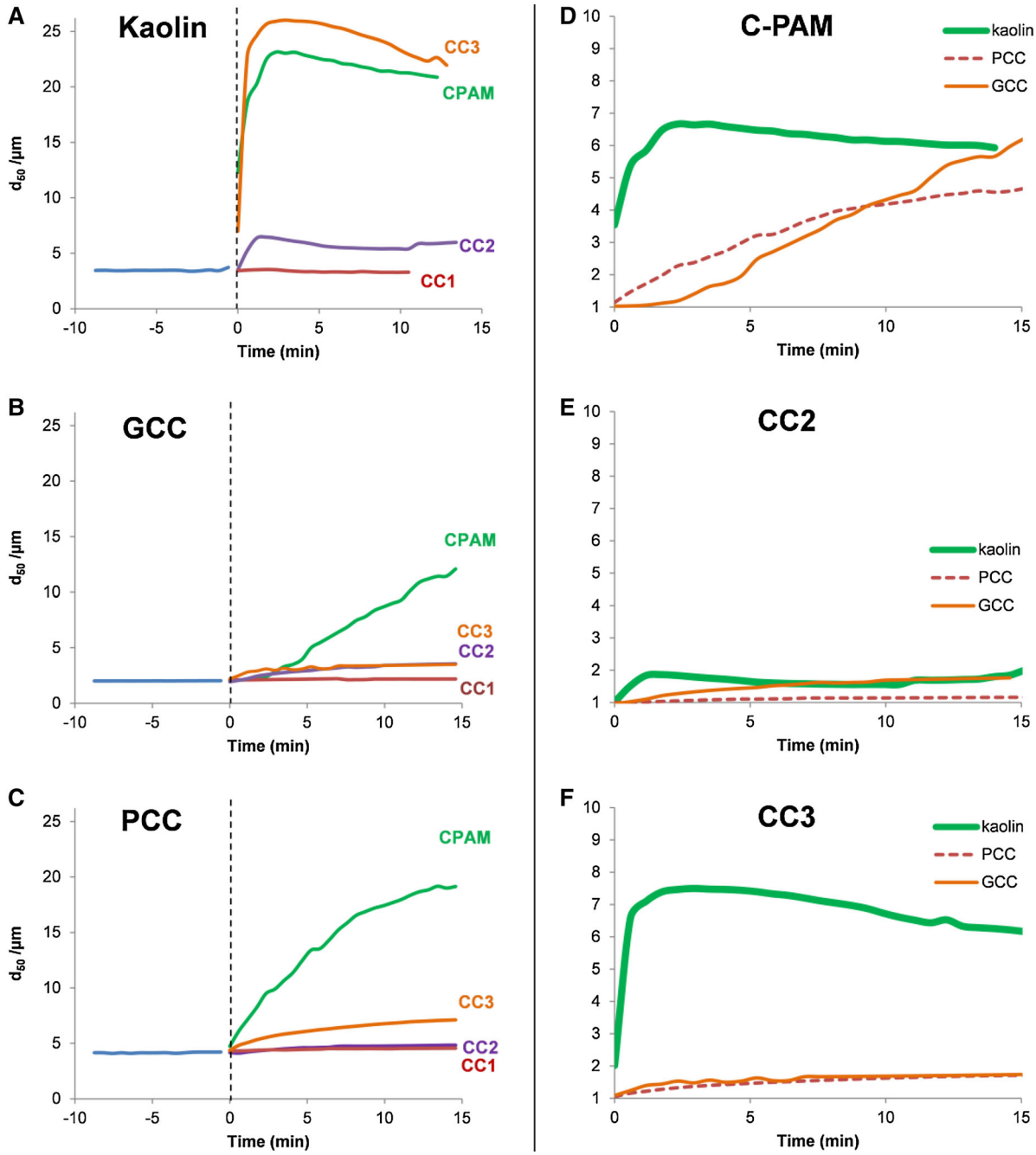

Fig. 4 Flocculation kinetics of three mineral fillers with a cationic polyacrylamide (CPAM) and with the cationic cellulosic derivatives (CC1, CC2 and CC3), depending on the choice of filler (**a–c**) and on the choice of flocculation agent (**d–f**)

However, similarly to GCC, both CC2 and CC3 don't have significant impact on flocculation. By the contrary, CPAM has a positive effect on PCC flocculation, by bridging, in agreement with many studies reported in the literature (Rasteiro et al. 2008a; Lourenço et al. 2017).

The flocculation process with CPAM is however somewhat distinct for the three fillers studied: with

Table 3 Zeta potential of the suspensions used in the flocculation tests

Filler	WSCC	ζ-Potential (mV)	pH
Kaolin	–	−23.7	5.6
	CC1	−29.5	7.1
	CC2	−27.2	7.0
	CC3	−7.3	7.0
	CPAM	−9.7	7.1
GCC	–	−27.8	10.1
	CC2	−2.7	9.9
	CC3	−11.7	9.8
	CPAM	−18.9	9.9
PCC	–	8.7	10.1
	CC2	0.8	9.9
	CC3	15.4	10.0
	CPAM	7.3	10.1

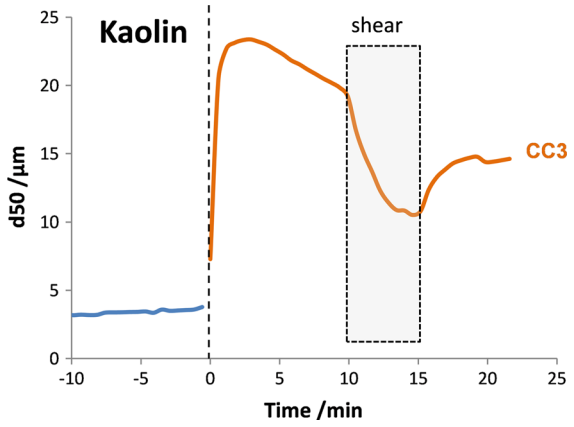

Fig. 5 Reflocculation behavior of kaolin with CC3 after floc rupture

kaolin a fast flocculation occurred, while for GCC it took almost 5 min to double the particle size. It is worth mentioning that CC3 was the polyelectrolyte that promoted the faster kinetics with kaolin. In papermaking a fast flocculation is of utmost importance since the contact time between the stock and the retention agents is as short as possible (usually 30 s or less) (Antunes et al. 2008a) to not disturb the runnability and sheet formation.

It should be noted that a smaller dosage of WSCC (10 mg/g) was tested, and the results showed that flocculation of fillers occurred but in a clearly smaller extent. Those results can be found in the supplementary material of the electronic version of this article.

It is safe to state that by cationizing cellulose it is possible to obtain water soluble derivatives with promising applications as filler flocculant for papermaking. In order to promote an effective flocculation, the WSCC must possess high charge and/or high DP, which in this work was achieved by pretreating cellulose fibers with NaOH and urea, followed by a cationization with CHPTAC, and finally by regenerating the resulting filtrate with ethanol. The obtained dry product, soluble in water, presented a medium degree of polymerization, high charge density and a moderate zeta potential, but the yield of production under mild conditions was quite small (11%). In this work, the best flocculation results were obtained with kaolin due to its higher surface charge and lamellar shape that allowed the WSCC to be adsorbed more easily on its surface.

Conclusions

Three water-soluble cationic derivatives of cellulose (WSCC), containing at least 30 quaternary ammonium groups per 100 anhydroglucose units and a charge density above 2 mmol/g, were produced with NaOH and CHPTAC under mild conditions, following different pretreatments.

The pretreatment with orthophosphoric acid caused the yield to be the highest, easing solubility by acid hydrolysis and amorphization, but the degree of polymerization (DP) of CC1 was too low to promote a suitable flocculation of filler for papermaking. In fact, by comparing the results with those obtained by applying the other alkaline pretreatment (NaOH/urea), it is possible to conclude that the WSCC whose DP was the highest (CC3) originated the best results in flocculation tests, even better than those with a conventional cationic polyacrylamide (CPAM), when the filler used was kaolin. The performance of the derivative with an intermediate DP, CC2, was worse when flocculating PCC and kaolin, but as good with GCC as that of CC3.

When using GCC, the flocculation was faster with CC2 and CC3 than with the CPAM polymer. However, the flocculation tests with PCC only yielded acceptable results with CPAM, most likely due to the high molecular weight of this polyelectrolyte. Further research could be beneficial if a water-soluble cationic polymer with medium charge density from high-DP cellulose could be obtained.

Supplementary information

The evolution of the median particle size of the fillers with smaller dosages (10 mg/g) of WSCC is provided.

Acknowledgments Roberto Aguado is thankful to Asociación Universitaria Iberoamericana de Posgrado for the Grant to fund an internship in Coimbra. Ana F. Lourenço acknowledges Fundação para a Ciência e Tecnologia for the Ph.D. Grant SFRH/BDE/108095/2015.

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5.6. Publication VI. Rapeseed stalks for papermaking: studies on pulping, refining and dewatering

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Journal: Cellulose Chemistry and Technology.

JCR-indexed: Yes.

Category: Materials Science — Paper & Wood.

Reference: Aguado, R., Moral, A., Mutjé, P., Tijero, A. *Cellulose Chem. Technol*. 49(9-10): 833-839 (2015).

Status: Published in November 2015.

RAPESEED STALKS FOR PAPERMAKING: STUDIES ON PULPING, REFINING AND DEWATERING

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Received October 31, 2014

Cereal straw, bamboo and bagasse are the most widely used non-wood raw materials, but work is being done towards other interesting sources of fibres, such as rapeseed stalks and straw. Rapeseed oil production for energetic purposes is increasing, and so are wastes. In this work, pulps from *Brassica napus* (rapeseed) stalks were obtained by soda-anthraquinone and Organosolv cooking. They were refined in a PFI mill. Handsheets made from those pulps were tested. Drainage rate and retention of fillers were also evaluated. We address the capabilities of rapeseed stalks and stems for papermaking and the influence of refining on the mechanical properties, the morphology of fibres and the amount of fines. This material was found to be suitable for papermaking and, as an advantage, a small number of PFI revolutions resulted in a substantial gain in mechanical properties.

Keywords: rapeseed, soda-anthraquinone, organosolv pulping, paper properties, drainage

INTRODUCTION

The manufacturing of paper from non-woody plants works in three ways to diminish the environmental impact. First, by re-using residues their open burning is avoided, a hazardous activity that causes air pollution. Second, the pulping of non-wood materials gives satisfying results using sulphur-free methods, such as SAICA's semichemical process cooking.[1] Finally, their processing may result in energy savings, as many non-wood species need less energy consumption in the refining process, or may not even require refining at all.[2]

The European Union (EU) is the largest rapeseed (*Brassica napus*) producer in the world, as the Union members produce 21.1 million tonnes annually, out of a worldwide production of 60 million tonnes. Still, the EU is also the greatest consumer, as 2.2 million tonnes are imported annually and only 0.1 million tonnes are exported.[3] Rapeseed main products are oil, used as a lubricant in industrial applications and for human consumption, and meal for animal feeding.

Rapeseed oil is being used and studied as an interesting source for biodiesel production,[4] and as a source of polyacids to manufacture biocomposites.[5]

The potential of rapeseed wastes for papermaking has already been studied by Mousavi *et al*.,[6] as they analysed rapeseed straw and its papermaking potential. Soda-anthraquinone pulping showed better results than soda alone. Tofanica *et al*.[7] characterised rapeseed stalk fibres, and found them to be very slender, with length ranging from 0.71 to 1.99 mm, and width from 9.10 to 19.60 μm. Potůček *et al*.[8] found that rapeseed stalks are mainly constituted by holocellulose (76.15%) and lignin (21.35%). According to them, paper from rapeseed straw pulp has a higher breaking length than paper from many other non-wood materials.

The ancient soda pulping method was relegated in benefit of the kraft process, but the addition of anthraquinone as a homogenous catalyst has made it a competitive technique, and

it seems to be especially competitive for annual plants.[9,10,11] Another unconventional method, organosolv pulping, implies the use of organic solvents, such as methanol or ethanolamine. Despite its higher energy consumption, it allows for lignin recovery and higher yield values than the soda-anthraquinoneprocess.[12,13]

A weakness of the pulps made from many non-wood materials to be used for papermaking is their drainage behaviour. Compared to pulps from wood materials, drainage time is notably longer. This could be explained by their high content of parenchyma cells.[14] The use of adequate retention agents is necessary to increase the retention of fillers and the dewatering rate.

In this work, chemical pulps from *Brassica napus* stalks were obtained through minimal environmental impact techniques (soda-anthraquinone cooking and organosolv cooking), refined and tested for their papermaking potential. Tests involved the preparation of paper sheets, their mechanical characterization and the study of their drainage properties. This work aims to evaluate the potential application of rapeseed stalks for papermaking purposes, and to discuss the influence of cooking conditions and refining.

EXPERIMENTAL

Materials

Specimens of rapeseed (*Brassica napus*) were grown in Castilla y León, Spain, and stalks or stems of all diameters were harvested as raw materials for pulping.

Sodium hydroxide pellets and a monoethanolamine commercial solution were provided by Panreac, as were ammonia, solid ammonium chloride and ethylenediaminetetraacetic acid (EDTA). Anthraquinone was purchased in powder form from Sigma Aldrich. As filler, we used precipitated calcium carbonate (PCC) for analysis from Merck, with an approximate particle size (d_{50}) of 14 μm.

Two linear polyelectrolyte-based flocculants (retention agents) were supplied by Nalco Chemical Company. One of them was a co-polymer of acrylamide of high molecular weight with cationic charge, hereinafter referred as "cationic flocculant". The other one was a co-polymer of acrylamide of medium molecular weight with anionic charge, referred from now on as "anionic flocculant". Solutions of polyelectrolytes were prepared by adding 0.3 g of dry flocculant to 300 mL of water. The furnish was kept under gentle stirring (120 rpm) for 90 minutes.

Pulping

Stalks were isolated, crushed, and introduced into a stainless steel batch digester. Cooking took place by using ethanolamine (organosolv pulping) and sodium hydroxide. For the latter, anthraquinone was added to increase the selectivity towards lignin. Conditions are summarized in Table 1. Liquor-to-solid ratio was held at 6. Temperature was kept constant by means of a PID controller. The resulting pulps were washed, screened and stored at 4 ºC. Remaining lignin was analysed following TAPPI Useful Method 246, Micro-Kappa number, given that the amount of sample was limited.

Refining

Prior to refining, the pulps were disintegrated by means of a lab disintegrator ENJO model 692 according to ISO 5263, working at 3000 rpm. Pulp refining was carried out by a Maskin's Mark VI PFI mill at 10% consistency in accordance with ISO 5264/2. The power of the engine was 0.37 kW and the voltage applied was 220 V. Three refining intensities were used: 250, 500 and 1000 PFI revolutions.

The refining degree of the unbeaten and beaten pulps was measured using a Canadian Standard Freeness (CSF) tester, following the TAPPI standard T227 om-94. Up to four replicates were made, and in each case the relative standard deviation was not higher than 3%.

Morphological characterisation

A morphological analyzer (MorFi) from Techpap was used to determine the dimensions of fibers (length and width), the fibre population and the amount of fines in each pulp sample. Both unrefined and refined pulps were subjected to this characterisation, which is based on an image analysis system. Fines were defined as those fibrous particles whose length ranged from 10 μm to 90 μm. The proportion of fines was expressed as the average percentage of the area occupied by fines in the images taken. The suspensions were prepared by dispersing 2 grams of pulp (oven-dry weight) in 1200 mL of water. Three replicates were made for each of the pulp samples.

Handsheet preparation and testing

Ten handsheets, with an oven-dry weight of 60 g/m^2, were obtained from each of the pulps according to the ISO 5269-1:1998 standard. The experimental equipment consisted of a pulp dispersing-disintegrator, conventional sheet former, press (130 kPa), and heating system to remove moisture. Agitation was done by hand, by means of a standard stirrer. Blotters and standard couch weights were used to separate the wet sheet.

Brightness was determined according to ISO 2470-1:2009. The tensile index of the handsheets was measured by means of a mechanical tester from HT Hounsfield following the ISO 1924-2:2009 standard. Tear index was determined by a MESSMER tester according to UNE-EN 21974:1996. To measure burst strength, a METROTEC tester was used and the ISO 2758:2004 standard was followed.

Table 1
Pulping conditions and properties

Pulp code	Reagent	T (ºC)	t (min)	Yield (%)	Kappa no.	ISO brightness (%)
ETN40	40% ethanolamine, 60% water	140	40	77.6	46.4	38.9
ETN60	60% ethanolamine, 40% water	180	60	58.7	30.9	39.7
SAQ10	10% NaOH, 0.1% AQ on o.d. pulp*	140	40	69	48.1	37.5
SAQ20	20% NaOH, 0.1% AQ on o.d. pulp*	180	60	54.5	29	40.8

*On the basis of oven-dried pulp weight
T: cooking temperature; t: cooking time; ETN: ethanolamine; S: soda; AQ: anthraquinone

Drainage testing

In order to test the drainage performance, a lab device DFR-05 from Mütek was used. Only the pulp coded SAQ10 (Table 1) was tested, since the drainage behaviour is more dependent on the nature of the raw material, the size, shape and content of the filler and the refining degree than on the cooking method. A pulp suspension at 0.5% consistency was prepared with tap water of conductivity 500 µS/cm. This suspension was mixed with calcium carbonate (filler). The total mass of the suspension was 500 grams. We used 0.16 grams of filler per gram of dry pulp. The pH of the suspension was adjusted to 7 by adding small amounts of HCl.

The mixture was put into the stirring chamber. The "Drainage" program was selected in Mütek's software. We set the stirring at 200 rpm for 60 seconds. Then a retention agent was added into the suspension, and we ran the stirrer for 30 seconds more at 300 rpm. The suspension went through a 100 mesh screen, wire size being 0.11 mm. The cake was rejected and the filtrate was collected for analysis.

The amount of precipitated calcium carbonate in the filtrate was determined by complexometric titration with EDTA. Eriochrome Black T was used as indicator. A buffer solution of ammonia and ammonium chloride was used to keep the pH around 10. Knowing the amount of filler in the filtrate and in the initial furnish, the amount of filler retained in the fibrous matrix was determined by difference. As tap water was used, we also measured its hardness, following this same method, to apply a correction.

The drainage tests performed on Mütek's device were repeated on the handsheet formation apparatus, in order to confirm the results or point out the differences found. Again, a pulp suspension of 0.5% consistency and tap water were used. The total mass was 4 kg and the pH, slightly above 7, was not adjusted. The nominal aperture size of the wire screen was 0.125 µm (115 mesh). A fourth part of each of the handsheets was disintegrated and dispersed in water. The amount of calcium carbonate in this suspension was determined by titration with EDTA. This was a direct measurement of the amount of PCC retained in the handsheets.

RESULTS AND DISCUSSION

Besides the conditions under which stalks were cooked, Table 1 shows the yield obtained, expressed as the weight of oven dried pulp obtained per weight of oven dried stalks. The Kappa number and ISO brightness are also shown.

Table 2 shows the mechanical properties of the handsheets for the different beating degrees. The deviations are expressed for a confidence level of 90%. Fibre length and coarseness are shown in Table 3, along with the number of fibres per gram of oven-dry pulp and the proportion of fines.

Table 2
Influence of cooking and refining on the mechanical properties

Pulp	PFI revolutions	Tear index (mN m^2/g)	Burst index (kN/g)	Tensile index (N m/g)
ETN40	0	11.1 ± 0.7	0.84 ± 0.04	7.5 ± 0.1
	250	13.3 ± 0.4	0.97 ± 0.06	14.2 ± 0.6
	500	15.0 ± 1.0	1.45 ± 0.05	16.2 ± 0.4
	1000	17.6 ± 0.3	1.87 ± 0.14	18.1 ± 0.9
ETN60	0	11.5 ± 0.3	0.84 ± 0.05	10.2 ± 0.5
	250	13.9 ± 0.5	1.53 ± 0.11	22.9 ± 2.0
	500	14.2 ± 0.4	4.87 ± 0.30	45.8 ± 1.8
	1000	15.2 ± 0.7	5.14 ± 0.26	47.5 ± 3.1

SAQ10	0	4.6 ± 1.0	0.73 ± 0.08	8.2 ± 0.3
	250	12.6 ± 0.9	1.25 ± 0.12	12.9 ± 1.1
	500	17.8 ± 0.5	1.52 ± 0.04	17.2 ± 0.5
	1000	19.9 ± 0.6	2.18 ± 0.11	26.6 ± 1.5
SAQ20	0	14.0 ± 1.2	0.72 ± 0.04	9.5 ± 1.0
	250	20.1 ± 0.8	1.62 ± 0.11	17.1 ± 0.4
	500	21.8 ± 0.9	2.12 ± 0.06	19.8 ± 1.1
	1000	19.5 ± 0.5	3.70 ± 0.19	38.5 ± 1.7

Table 3
Influence of cooking and refining on the characteristics of fibres, their population and the number of fines

Pulp	PFI revolutions	Average length (μm)	Coarseness (mg/m)	Number of fibres (10^6 g^{-1})	Proportion of fines (% in area)
ETN40	0	617	0.201	13.7	7.20
	250	567	0.162	18.0	8.37
	500	582	0.147	19.3	9.60
	1000	554	0.139	21.1	10.06
ETN60	0	574	0.106	27.3	7.74
	250	543	0.116	25.3	8.95
	500	563	0.114	25.4	9.05
	1000	507	0.115	26.2	9.34
SAQ10	0	654	0.166	16.6	4.51
	250	629	0.114	24.0	5.41
	500	628	0.108	25.5	6.00
	1000	617	0.095	28.7	7.01
SAQ20	0	632	0.114	15.9	4.40
	250	632	0.085	31.6	4.56
	500	621	0.082	32.9	4.92
	1000	587	0.083	33.2	7.03

Influence of cooking conditions

Mild treatments, at 140 ºC and after 40 minutes of cooking, resulted in higher yields, more pronounced for the organosolv pulps. However, only severe cooking provided enough removal of lignin to make feasibly bleachable pulps, as it achieved Kappa numbers around 30.

Unbleached pulps from rapeseed stalks showed good values of brightness (around 40%), even when cooked under mild conditions. ISO brightness of rapeseed straw pulps, according to the experiments of Mousavi *et al.*,[6] lies around 16-18%. Unbleached rice straw kraft pulps, Alfa soda pulps and *Eucalyptus citridiora* kraft pulps show brightness values of 45-50%,[15] 47%,[16] and 15-20%,[17] respectively. Hence, the brightness values of the pulps studied are in the high range.

Cooking under severe conditions gave higher burst index and tensile index (Table 2). These values were found to be particularly high for the organosolv pulps. Also, severe conditions caused fibre coarseness to decrease (Table 3), which has a positive effect on fibre bonding.[18] Cooking with ethanolamine resulted in the largest amounts of primary fines (i.e., before refining). This is likely due to the lesser damage to carbohydrates. Therefore, the proportion of fines in organosolv pulps ranges between that of mechanical pulps and that of soda pulps.

Influence of refining

Figure 1 presents the degree of refining, expressed as Canadian Standard Freeness, for the different pulps. For all pulps, 1000 PFI revolutions were enough to achieve freeness values below 350 mL. Hardwood kraft pulps need around 3000 PFI revolutions to get to such a low refining degree, and softwood kraft pulps need more than 5000 PFI revolutions.[19] Therefore, the use of rapeseed stalks implies great energetic savings at this stage, as expected from a non-wood material.[2] Pulp ETN60 showed the lowest freeness values, since the freeness of the pulp was already low prior to refining, meaning that Organosolv pulping alone resulted in good fibre-to-fibre bonding.

The tear index values of the sheets from non-refined pulps were high enough for papermaking, while the tensile index and the burst index were still too low for that purpose (Table 2). Hence, a

refining stage would be necessary to obtain pulps of sufficient quality.

The tear index was slightly improved by refining (Table 2) and was in the high range, similar to that of soda pulps from abaca.[20] The tensile and burst indices were greatly increased from non-refined pulps to 1000 PFI revolutions, the burst index being similar to that of rice straw pulps.[15]

As expected, fibre length decreased with refining (Table 3), but this shortening was not a major drawback considering that 500 PFI revolutions may be enough to produce printing paper. Coarseness was found to decrease notably from 0 to 250 PFI revolutions and hardly changed with further refining, whereas fibre population showed the opposite trend. Refining resulted in a great generation of fines, considering the low numbers of PFI revolutions. This is related to the abrupt decrease in freeness.

Drainage properties

Low freeness is associated with slow dewatering and compels manufacturers to use a longer paper machine or to decrease the production rate.[14,21] In addition, a great amount of energy is consumed by drying. In this work, water removal was not increased, but the use of flocculants could hasten it.

The more retention agent was added to the chamber, in the range that was studied, the faster the drainage was, as shown in Figure 2. This does not imply that the process could be improved by using even higher dosages of retention agent. A small addition of cationic flocculant was enough to achieve a great reduction of the time at which an asymptotic value of the filtrate weight was reached, while further additions gave a slight improvement (Figure 2B). As for the anionic flocculant, a concentration of 6 mg/L was needed to get the drainage time obtained for 3 mg/L of cationic flocculant.

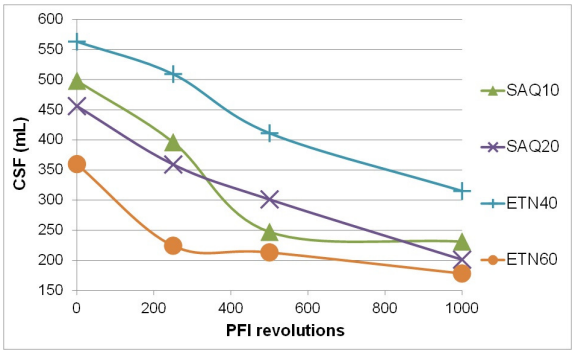

Figure 1: Evolution of Canadian Standard Freeness with the number of PFI revolutions

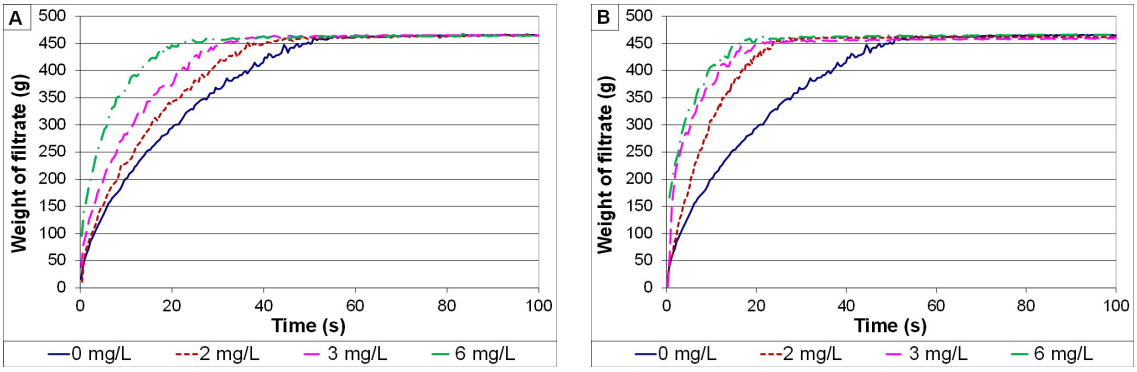

Figure 2: Drainage – weight versus time curves for different amounts of added anionic flocculant (A) and cationic flocculant (B)

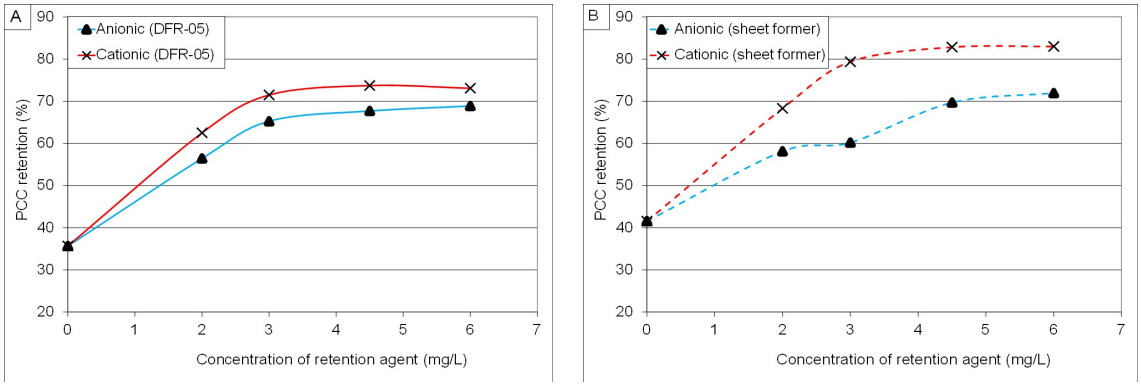

Figure 3: Evolution of filler retention with the concentration of anionic and cationic flocculants, using the DFR-05 (A) or the handsheet formation apparatus (B)

Figure 3A shows the evolution of filler retention in the pulp with the amount of retention agent added, when Mütek's device was used. Both flocculants made calcium carbonate retention reach values around 70%. Concentrations higher than 6 mg/L were not considered, since the curves tend to reach an asymptotic value (anionic flocculant) or a maximum peak (cationic flocculant).

As shown in Figure 3B, when using the handsheet former, the initial retention of PCC (without retention agents) was higher. This was due to the lower aperture size of its wire screen. Upon addition of the cationic flocculant, the retention reached 83%. Nonetheless, the proportional increase was slightly lower since stirring was done by hand. Agitation influences the adsorption of polyelectrolytes on fibres and fines, and thus the kinetics of flocculation. The advantage of the cationic flocculant over the anionic one was confirmed and it became more evident without automatic stirring.

It may be concluded that a cationic polyacrylamide is better for drainage and retention of calcium carbonate, as expected.[22] This is explained by the presence of dissociated carboxyl groups, negatively charged, in pulp fibres.

CONCLUSION

Comparing the brightness and mechanical properties of pulps from rapeseed stalks with those of pulps from rapeseed straw, rice straw and common hardwoods, it can be concluded that rapeseed stalks represent a source of fibres suitable for producing market pulp and/or certain grades of paper. Handsheets prepared from the pulps that were studied showed high tear index and their brightness was found to be in the high range. The mechanical properties were notoriously improved by refining. Even low numbers of PFI revolutions resulted in the generation of large amounts of fines and in a strong decrease in fibre coarseness.

Organosolv pulping under severe conditions is recommended, since low freeness values are achieved with little refining energy consumption. Moreover, it results in the highest mechanical resistance.

The retention of calcium carbonate in a non-refined pulp sample was clearly improved by the addition of polyelectrolyte-based flocculants, the cationic polyacrylamide being the best. The dewatering rate was also increased. When the consistency of the suspension is 0.5%, a dosage of 3 mg of cationic polyacrylamide per liter of water is suggested.

ACKNOWLEDGEMENTS: The authors wish to acknowledge the Ministry of Science and Innovation of Spain for the financial support of the project ctq2010-21660-c03-01, in the framework of which the present study has been carried out.

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5.7. Publication VII. Papermaking potential of *Citrus sinensis* trimmings using organosolv pulping, chlorine-free bleaching and refining

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Journal: Journal of Cleaner Production.

JCR-indexed: Yes.

Category: Environmental Sciences (Q1).

Reference: Moral, A., Aguado, R., Mutjé, P., Tijero, A. *J. Clean. Prod*. 112: 980-986 (2016).

Status: Published in January 2016.

https://doi.org/10.1016/j.jclepro.2015.09.008

Additional information: Appendix 2.

Journal of Cleaner Production 112 (2016) 980–986

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Papermaking potential of *Citrus sinensis* trimmings using organosolv pulping, chlorine-free bleaching and refining

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ARTICLE INFO

Article history:
Received 8 April 2015
Received in revised form
1 September 2015
Accepted 4 September 2015
Available online 12 September 2015

Keywords:
Citrus sinensis
Orange tree
Organosolv
Peroxide bleaching
Pulp and paper
Refining

ABSTRACT

One of the most popular ways to carry out the re-use of wastes from agriculture is the pulping, refining and bleaching of those residues for papermaking. Spain annually produces more than 300 thousand tonnes of *Citrus sinensis* (orange tree) trimmings, crops being concentrated in the East and the South of the country. Their chemical composition is similar to that of common hardwoods.

This work aims to show the suitability of ethanolamine cooking when applied to orange tree trimmings, and to study the effect of peroxide bleaching and refining on some key properties. As for bleaching, we used a design of experiments to discuss the influence of peroxide concentration, time and temperature on the yield, brightness, viscosity, kappa number of pulps and mechanical properties of paper sheets. Refining was studied by analysing the diminishment in freeness and the mechanical properties of paper sheets formed. Results showed that even a mild bleaching process gives out a high relative brightness gain, but a multiple-step process is necessary to achieve enough brightness for printing paper. Mechanical properties of non-refined pulps were found to be too low for paper of any grade, but they were greatly improved by refining.

1. Introduction

With the high prices of wood constituting a major drawback in papermaking, the use of agricultural wastes to manufacture fibre-based products stands as one of the most attractive options for their valorization (Jiménez and Rodríguez, 2010). If no use is found to those residues, field burning is all that awaits them, causing pollution and GHG emissions.

CEPI's production of pulp from wastes accounted for 248 kt in 2013, making it the 0.7% of total pulp production, 17.6% more than the previous year (CEPI, 2014). While the manufacturing of pulp from alternative sources was slightly increased, the production of pulp from conventional sources decreased in Europe. Total pulp production was diminished from 38,127 kt in 2012 to 37,303 kt in 2013. It is since 2005 that the CEPI countries are lowering their pulp and paper production. In a market where the number of companies decreases and there is little product differentiation, the use of new raw materials and the discovery of new properties might be one of the keys of success. Many agricultural wastes have been studied for papermaking purposes, namely rapeseed straw (Mousavi et al., 2013), hemp core (Barberà et al., 2011), olive tree trimmings (Díaz et al., 2005). All of them can be used to obtain printing paper of acceptable quality after being cooked through sulphur-free processes, according to the authors' conclusions.

In Spain, the total production of trimmings implies a large wood potential, over 6.5 million tonnes. This includes trimmings from sweet orange tree (*Citrus sinensis*) with a potential between 300,000 and 400,000 tonnes, mainly located in Eastern and Southern Spain. Fortunately for a potential pulp mill, they are rather concentrated: Comunidad Valenciana, a region comprising 23,255 km^2, accounts for 60% of total harvesting of oranges in Spain (Server et al., 2009). This results in transport and storage savings.

Orange tree trimmings consist mainly of 73% of holocellulose and 20% of lignin (González et al., 2011). Residues from orange tree pruning have been used by González et al. (2013) to make paper and evaluate the influence of cooking conditions and beating. However, to the best of our knowledge, ethanolamine pulping and hydrogen peroxide bleaching of orange tree trimmings have not been studied yet.

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http://dx.doi.org/10.1016/j.jclepro.2015.09.008
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Organosolv pulping processes use an organic solvent that selectively dissolves lignin, such as ethanol and ethanolamine, resulting in less water consumption and less production of wastewater (Jiménez et al., 2002). It allows for higher yield values, since it is less damaging to cellulose and hemicellulose, and recovery of lignin, furfural and hydroxymetylfurfural as by-products. As a major drawback, in the current market enough profit cannot be obtained from value-added products made out of lignin (Ibrahim et al., 2013; Sahoo et al., 2011).

Traditional bleaching processes used to be based on elemental chlorine, related to various pollution problems. This reagent was progressively displaced by chlorine dioxide, less hazardous, since its first use in 1946 (Rapson, 1970). Stages involving ClO_2 are present in the majority of bleaching plants today, but a next step is being taken by trying new bleaching processes with oxygen, ozone and/or hydrogen peroxide (López et al., 2003; Reinstaller, 2008). These reagents do not form chlorinated organic derivatives needing to be removed. Particularly, peroxide stages are claimed to be able to replace chlorine dioxide stages (Bajpai, 2012). Comparing hydrogen peroxide to chlorine dioxide, the latter achieves a greater lignin removal, but they are similar in terms of brightness gain and water consumption. H_2O_2 bleaching does not need to remove large amounts of lignin to increase brightness greatly. Due to this, besides its less environmental impact, H_2O_2 is advised over chlorinated compounds when working with high-yield pulps, whose lignin content is high (Ghose and Chinga-Carrasco, 2013).

Besides the use of alternative raw materials, an alternative way of pulping and a chlorine-free bleaching process, the refining stage should be taken into account. Works have shown that the refining of non-wood materials and some alternative woody materials result in less energy consumption compared to conventional hardwoods and softwoods (Banavath et al., 2011; Stoica et al., 2010).

In this study, residues from orange trees were harvested and pulped under two different sets of conditions, using monoethanolamine as the reagent, and the resulting pulps were characterized. One of the pulps was bleached, both of them were refined, and we measured the change in key properties. This work is related to environment protection in at least three ways: first, by re-using wastes that otherwise would be open-burnt; second, by using environmentally friendly processes of cooking and bleaching, not tested before with this raw material; third, by saving energy in the refining stage. The influence of three variables (temperature, time, reagent concentration) in a one-stage bleaching process with hydrogen peroxide is studied. The convenience of this bleaching process to remove lignin and increase brightness of cellulosic pulp obtained from orange tree trimmings through organosolv pulping, using ethanolamine as the solvent, is discussed, and so is the improving of mechanical properties by refining.

2. Experimental

2.1. Harvesting and pulping

Trimmings were harvested from orange trees grown in the East of Spain. A monoethanolamine commercial solution was purchased from Panreac (Castellar del Vallés, Spain).

First, the wood fraction of orange tree trimmings, i.e., stems whose diameter was greater than 5 mm, was separated from the rest, washed, crushed, and then cooked to obtain the pulp. Cooking was performed in a stainless steel batch reactor. Liquor to solid ratio was held at 6. Cooking liquor consisted of ethanolamine and distilled water. Temperature and inner pressure were held constant thorough the process. The different conditions tested are summarized in Table 1. The resulting pulp was washed, screened, crumbled and stored at temperatures below 10 °C.

Prior to bleaching or refining, the pulp was disintegrated in a lab disintegrator ENJO model 692, working at 3000 rpm. Fig. 1 shows the experimental procedure, from the raw material to the paper sheet.

2.2. Bleaching

Only the severely-treated pulp (OP2) was considered for bleaching, due to its lower kappa number, higher brightness when unbleached and, in short, higher bleachability.

Peroxide bleaching of organosolv pulp was performed following a fractional experimental design. In each essay, a pulp sample was mixed with deionized water, hydrogen peroxide, sodium hydroxide, magnesium sulphate and diethylentriaminepentaacetic acid (DTPA), these last two being used as a cellulose protection agent and lignin oxidation activator, respectively. All reagents were supplied by Panreac. The pulp sample and the bleach liquor were placed in a polyethylene bag, which was sealed and kept at the desired temperature by means of a water bath. Pulp consistency was held at 10% for all the experiments. Amounts of NaOH, $MgSO_4$ and DTPA added per gram of oven-dry pulp were held constant (1.8%, 0.2% and 0.5%, respectively).

Once bleaching was complete, the sample was quenched to room temperature, filtered, washed, air-dried, weighted and stored. Yield was calculated as the weight of oven-dried bleached pulp per weight of oven-dried pulp prior to bleaching.

Remaining hydrogen peroxide in bleaching liquor was determined by iodometric titration (Kolthoff and Belcher, 1957). First, a known amount of potassium iodide was added in excess, being oxidized to iodine by reaction with H_2O_2. Sodium thiosulphate was the titrating agent, allowing for the quantification of iodine. The amount of H_2O_2 was then determined by stoichiometry.

2.3. Experimental design

To study the influence of bleaching conditions, we performed a second-order factorial design of experiments (Montgomery, 1991), consisting of three factors (hydrogen peroxide concentration, temperature and time) and three levels. 15 different runs were considered: a central experiment and several additional points lying at the cube vertices and side centres in a cube-plot.

The hydrogen peroxide concentration was 2%, 6% and 10%, on the basis of oven-dried pulp weight. Bleaching temperature was 55, 70 and 85 °C. Duration of peroxide bleaching was 30, 90 and 150 min. The inputs were normalized, casting them in a range between −1 and +1 (Table 2). The codes for the normalized factors are X_P (peroxide concentration), X_T (temperature) and X_t (time).

2.4. Refining

Unbleached pulps were beaten at 10% consistency in a Maskin's Mark VI PFI mill (ISO 5264/2). The numbers of revolutions applied were 250, 500, 750, 1000 and 1250. The electric power of the engine was 0.37 kW as the voltage applied was 220 V.

The degree of refining, expressed as freeness, was measured using a Canadian Standard Freeness (CSF) tester, following TAPPI standard T227 (Canadian Standard Method). Relative standard deviation was never higher than 3%.

2.5. Analysis of handsheets

We made up to seven handsheets from unbleached pulp and from the bleached pulp obtained through each of the experiments.

Table 1
Cooking conditions of trimmings.

Code		OP1	OP2
Temperature (°C)		140	180
Cooking time (min)		40	60
Composition of cooking liquor	Ethanolamine (%)	40	60
	Water (%)	60	40
Pressure (bar)		4	9

OP1: Organosolv pulp 1. OP2: Organosolv pulp 2.

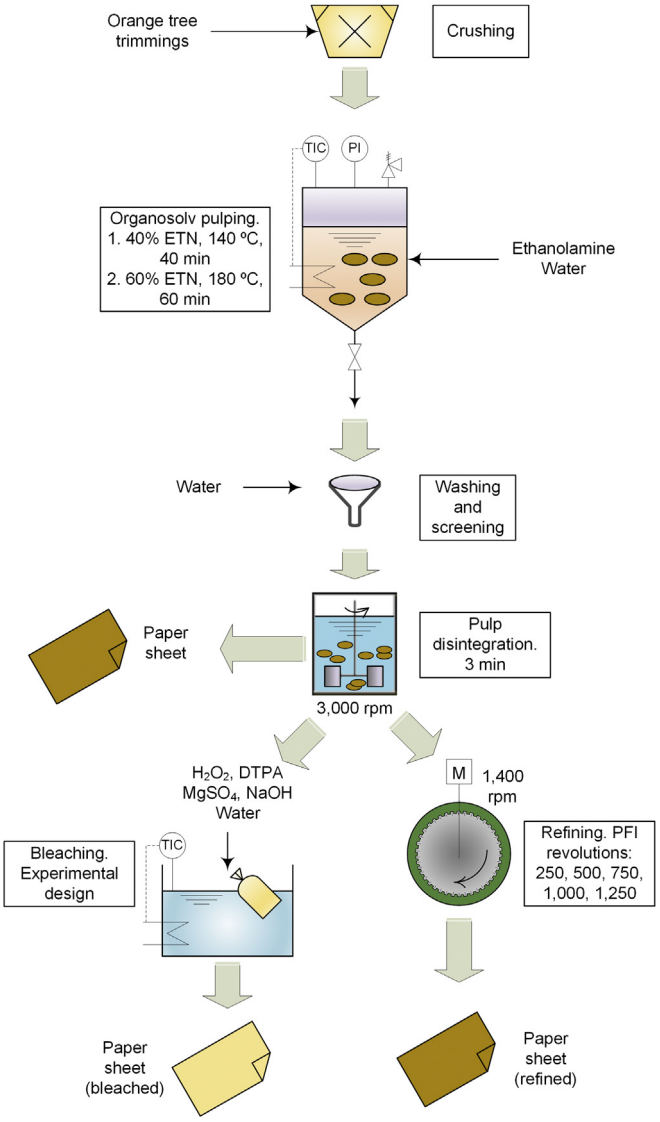

Fig. 1. Chemical and mechanical treatments undergone by *Citrus sinensis* trimmings.

Table 2
Bleaching: independent variables and their coded values.

		Actual values at coded factor levels		
Independent variable	Code	−1	0	1
H_2O_2 (%)	X_P	2	6	10
Temperature (°C)	X_T	55	70	85
Time (min)	X_t	10	85	150

The conventional sheet-former method (ISO 5269-1) was followed. Handsheets were pressed at 130 kPa and dried at 140 °C for 10 min. The grammage of the handsheets was 60 g/m^2. Brightness was determined according to ISO 2470-1 (ISO Brightness). Stretch and tensile index of handsheets were measured by means of a mechanical tester from HT Hounsfield following UNE 57-054 (resistance to folding) and ISO 1924-2 (determination of tensile properties), respectively. Tear index was determined by a MESSMER tester according to ISO 1974. Burst strength was measured by using a METROTEC tester, according to ISO 2758.

Micro kappa number was measured according to TAPPI Useful Method UM 246, for both the unbleached pulp and the one-stage bleached samples. Intrinsic viscosity was determined following TAPPI standard T230. Between 5 and 9 repetitions were carried out for mechanical properties, between 10 and 20 for brightness, and between 3 and 6 for the kappa number and the intrinsic viscosity. Starch, $KMnO_4$ and copper(II)ethylendiamine solutions were provided by Panreac.

3. Results and discussion

3.1. Properties of unbleached, non-refined pulp

Paper sheets from pulps with no further treatment were found to be unacceptably weak, as it is shown in Table 3. Mechanical properties of unrefined pulps are clearly better for other raw materials, such as drunken horse grass, rapeseed straw and rice straw (Li et al., 2015; Mousavi et al., 2013; Rodríguez et al., 2008). Only the tear index is high enough for papermaking purposes. Furthermore, the pulp obtained is rather dark even for an unbleached pulp, indicating that ethanolamine treatment leaves a high amount of lignin remaining in the cooked pulp. In all cases, error is expressed in terms of a 95% confidence interval using Student's t distribution for a p-value of 0.05 or lower (two-tailed tests).

Comparing these results with those of González et al. (2011) using another sulphur-free method, soda-anthraquinone cooking, we found the yield to be higher, as expected, since a large amount of the hemicellulose remains in the pulp, whereas its content is severely diminished when pulping with caustic soda. Also, organosolv pulping grants less water consumption (González-García

Table 3
Properties of unbleached, non-refined pulps.

Pulp	OP1	OP2
YI (%)	81	62
KN	62.5 ± 1.8	51.9 ± 1.2
IV (mL/g)	401 ± 18	286 ± 7.8
BR (%)	32.60 ± 0.05	34.49 ± 0.06
Tear index (mN m^2/g)	3.05 ± 0.15	3.11 ± 0.13
Stretch (%)	0.12 ± 0.06	0.26 ± 0.09
Burst index (kN/g)	0.29 ± 0.07	0.43 ± 0.13
Tensile index (N m/g)	5.6 ± 0.3	7.1 ± 0.9

BR: ISO brightness. KN: Kappa number. IV: Intrinsic viscosity. YI: Yield.

Table 4
Properties of bleached pulp for different conditions. PC: Hydrogen peroxide consumption.

Run	X_P	X_T	X_t	BR (%)	KN	IV (mL/g)	YI (%)	PC (%)
1	1	1	1	72.9 ± 0.4	38.5 ± 0.7	192 ± 8	90	99.6
2	1	1	−1	70.0 ± 0.5	40.6 ± 1.4	184 ± 12	90.1	99.5
3	1	−1	1	68.3 ± 0.2	43.2 ± 1.0	211 ± 11	93.8	99.4
4	1	−1	−1	68.2 ± 0.3	42.3 ± 0.7	215 ± 8	89.6	99.2
5	−1	1	1	67.5 ± 0.1	44.2 ± 0.3	246 ± 6	94.2	99.7
6	−1	1	−1	67.4 ± 0.4	44.8 ± 1.8	234 ± 21	94.3	99.3
7	−1	−1	1	67.6 ± 0.2	44.1 ± 1.4	246 ± 13	95.7	98.1
8	−1	−1	−1	67.3 ± 0.2	44.5 ± 1.2	250 ± 11	95.5	98.2
9	0	0	0	68.3 ± 0.3	42.6 ± 1.8	201 ± 6	92.4	99.4
10	1	0	0	68.8 ± 0.3	41.9 ± 0.1	184 ± 1	93.5	99.0
11	−1	0	0	67.6 ± 0.5	43.7 ± 0.8	219 ± 8	94	99.5
12	0	1	0	68.1 ± 0.1	41.8 ± 1.9	188 ± 11	94.4	99.2
13	0	−1	0	67.9 ± 0.2	42.1 ± 1.7	234 ± 0	94.3	99.5
14	0	0	1	68.4 ± 0.2	41.5 ± 1.8	211 ± 16	93.7	99.3
15	0	0	−1	67.0 ± 0.1	44.6 ± 0.8	223 ± 1	92.8	99.2

Fig. 2. Paper strips corresponding to different bleaching conditions.

et al., 2010). On the other hand, tensile properties were worse than those obtained by soda-anthraquinone pulping.

A mild treatment (OP1) resulted in a dark pulp with a high kappa number, although a high yield was achieved. The treatment at high temperature and high reagent concentration (OP2) gave out a significant diminishment in the kappa number, although intrinsic viscosity was severely lowered, showing that carbohydrates were degraded or destroyed at a higher extent (Isihara, 1992). However, this high degree of depolymerization of carbohydrates was not translated into lower mechanical strength, as values found for both pulps are in the same range. In fact, severely cooked pulp gave out even stronger sheets, due to the stronger fibre bonding that takes place.

Brightness of unbleached pulp is strongly dependant on the raw material. For instance, ISO brightness of unbleached rice straw kraft pulps lies around 45–50% (Rodríguez et al., 2010), while Li et al. (2015) found the brightness of drunken horse grass soda-AQ pulps to range from 40.7 to 43.1, to name other two alternative materials. As for organosolv pulps from orange tree trimmings, the values obtained are slightly lower, likely due to their higher lignin content.

3.2. Bleaching

Table 4 shows the normalized values of independent variables and the four dependent variables, according to the proposed experimental design. 95% confidence intervals are shown for kappa index and viscosity. Nearly all hydrogen peroxide was consumed by the pulp samples during bleaching, as it was found in the spent liquors at very low concentrations. Reaction time and temperature showed little influence on peroxide consumption, which was more dependent on the initial amount of hydrogen peroxide.

Comparing with the unbleached pulp, even a mild bleaching process raises brightness greatly. This brightness gain was higher than that observed by López et al. (2003) for organosolv pulps from olive tree trimmings under similar conditions. Such a high increment in brightness corresponds to a low decrement in kappa number. This is due to the mechanism of peroxide hydrogen bleaching: brightness gain is mainly caused by the oxidation of chromophoric groups in lignin structure, rather than the removal of lignin itself (Zhao et al., 2010).

Even very severe conditions cannot achieve brightness values higher than 72%. Additional bleaching stages should be taken into account if it is aimed to obtain higher values, like the ones required for printing paper. In spite of that, hydrogen peroxide bleaching is a good choice to obtain the so-called kraft colour (in the web version), or even brighter, as can be seen from the photograph shown in Fig. 2, starting from the dark colour that results from mild sulphur-free cooking methods. It can be done in only one step with low energy inputs and small amounts of reagents. More importantly, as no chlorinated compounds are used, AOX emissions are negligible. The only pollution issue to be taken into account is the production of H_2O_2, which requires to spend a large amount of energy and releases some toxic compounds. Overall, it is still clearly cleaner than ClO_2 (González-García et al., 2009).

We fitted the results to a 2nd grade-polynomial model, giving the inapplicability of universal mechanistic models. The aim was to

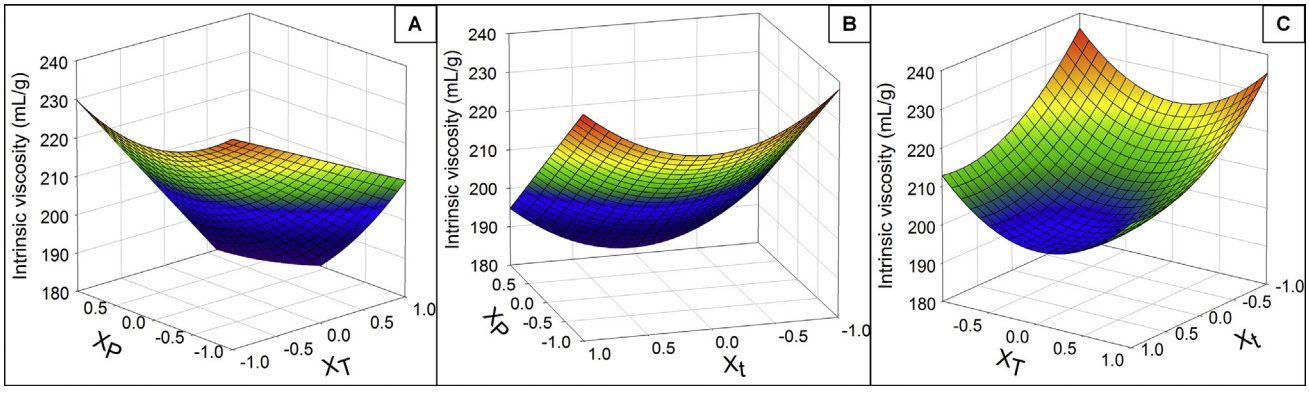

Fig. 3. Response surfaces for bleaching efficiency. A) Bleaching time is 90 min. B) Temperature is 70 °C. C) H_2O_2 concentration is 6%.

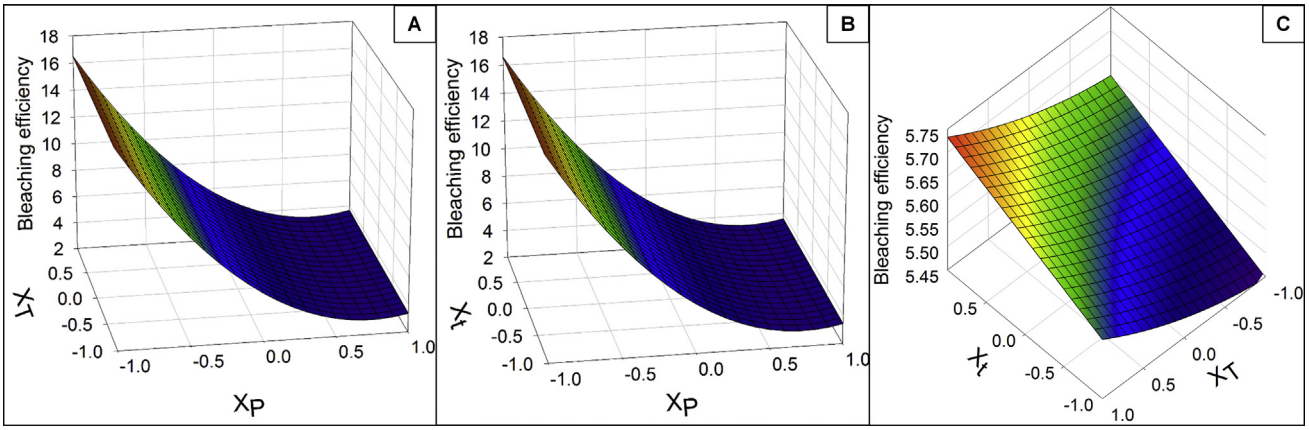

Fig. 4. Response surfaces for intrinsic viscosity. A) Bleaching time is 90 min. B) Temperature is 70 °C. C) H_2O_2 concentration is 6%.

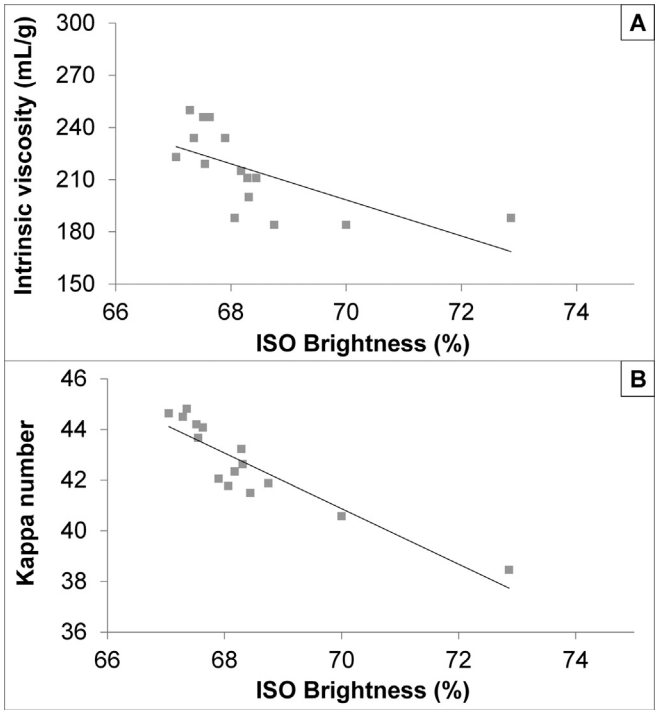

Fig. 5. Change of intrinsic viscosity (A) and Kappa number (B) with brightness.

Table 5
Effect of bleaching conditions on mechanical properties.

Run	Tear index (mN m^2/g)	Burst index (kN/g)	Tensile index (N m/g)
1	3.20 ± 0.10	0.38 ± 0.02	3.90 ± 0.34
2	3.26 ± 0.16	0.52 ± 0.09	4.08 ± 0.21
3	3.15 ± 0.15	0.40 ± 0.05	4.10 ± 0.26
4	3.18 ± 0.24	0.34 ± 0.02	3.96 ± 0.25
5	3.11 ± 0.15	0.38 ± 0.05	4.46 ± 0.38
6	3.35 ± 0.29	0.42 ± 0.08	4.15 ± 0.32
7	3.26 ± 0.22	0.36 ± 0.09	4.90 ± 0.23
8	3.16 ± 0.10	0.40 ± 0.03	5.16 ± 0.18
9	2.95 ± 0.19	0.48 ± 0.07	4.85 ± 0.35
10	3.15 ± 0.10	0.35 ± 0.07	4.56 ± 0.53
11	3.28 ± 0.18	0.39 ± 0.08	4.33 ± 0.23
12	3.40 ± 0.38	0.38 ± 0.06	5.11 ± 0.44
13	3.01 ± 0.16	0.50 ± 0.05	3.88 ± 0.36
14	3.34 ± 0.28	0.46 ± 0.00	4.45 ± 0.19
15	3.26 ± 0.08	0.52 ± 0.08	4.67 ± 0.29

evaluate the influence of the input variables on the outputs. We used the software BMDP for this purpose. The terms possessing a Snedecor F-value greater than 6 and a Student t-value greater than 2.5 were deemed statistically significant. Equations found are the next:

$$BR = 67.8 + 1.073X_P + 0.652X_T + 0.487X_t + 0.455X_P^2 + 0.805X_PX_T + 0.308X_PX_t + 0.287X_T^2 + 0.321X_t^2 \quad (1)$$

$$KN = 42.5 - 1.479X_P - 0.638X_T - 0.540X_t - 0.873X_PX_T - 0.400X_tX_T \quad (2)$$

$$IV = 203 - 21.3X_P - 11.6X_T - 0.4X_t - 4.75X_PX_T + 13.56X_PX_t + 7.56X_T^2 \quad (3)$$

$$YI = 93.7 - 1.67X_P - 0.59X_T + 0.51X_t - 0.08X_PX_T + 0.5X_T^2 - 0.58X_tX_T \quad (4)$$

The correlation coefficient R^2 was 0.84 for brightness, 0.66 for kappa number, 0.82 for viscosity, and 0.42 for yield. No response

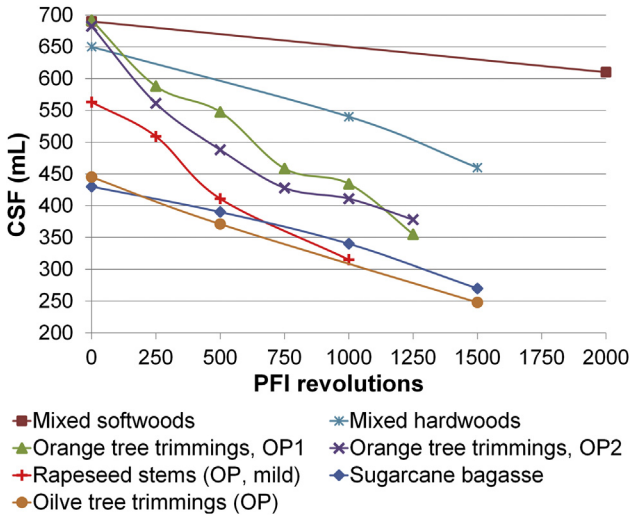

Fig. 6. Effect of the number of PFI revolutions on freeness (CSF) for various pulps.

Table 6
Mechanical properties of pulps for various degrees of refining.

Pulp	CSF (mL)	Tear index (mN m^2/g)	Stretch (%)	Burst index (kN/g)	Tensile index (N m/g)
OP1	588	5.57 ± 0.26	1.07 ± 0.20	1.72 ± 0.22	19.3 ± 3.0
	548	4.94 ± 0.29	1.12 ± 0.19	1.73 ± 0.25	19.6 ± 2.4
	459	5.57 ± 0.22	1.34 ± 0.20	2.49 ± 0.35	25.0 ± 3.8
	435	5.43 ± 0.11	1.14 ± 0.22	2.07 ± 0.28	19.8 ± 3.5
	355	5.78 ± 0.41	1.30 ± 0.22	2.90 ± 0.31	28.0 ± 4.0
OP2	561	5.17 ± 0.18	1.09 ± 0.15	2.00 ± 0.26	18.8 ± 2.2
	488	5.43 ± 0.21	1.19 ± 0.18	2.10 ± 0.34	22.9 ± 3.1
	428	5.70 ± 0.44	1.21 ± 0.10	2.37 ± 0.23	23.8 ± 2.5
	411	5.74 ± 0.23	1.34 ± 0.13	2.42 ± 0.18	28.2 ± 3.6
	378	5.88 ± 0.29	1.40 ± 0.19	3.26 ± 0.35	29.2 ± 1.8

surfaces were drawn for kappa number and yield polynomial models, considering their weak correlation.

Bleaching efficiency is defined as (Zhao et al., 2010):

$$BE = \text{Brightness gain } (\%)/\text{Amount of hydrogen peroxide in relation to mass of o.d. pulp } (\%) \quad (5)$$

Where the brightness gain is the difference between the ISO brightness of a certain bleached sample and that of the unbleached pulp. Note this magnitude is dimensionless. Bleaching efficiency is an objective function. We preferred this function to be shown in response surfaces, since minimizing the inputs is as important as maximizing the outputs. An additional correlation was proposed:

$$BE = 5.577 - 6.488X_P + 0.065X_T + 0.078X_t + 4.416X_P^2 + 0.020X_T^2 + 0.082X_PX_T \quad (6)$$

Fig. 3 shows response surfaces relating brightness effectivity to normalized values of temperature and peroxide concentration, to normalized values of peroxide concentration and time, and to normalized values of temperature and time. Bleaching effectivity decreases with peroxide concentration in the same way that it was found by Zhao et al. (2010).

Response surfaces for intrinsic viscosity are presented in Fig. 4. As expected, severe conditions resulted in a decrease of viscosity, indicating depolymerisation of carbohydrates. Nonetheless, viscosity of the most severely-treated sample was not the lowest, as a minimum is reached between the limits considered. This might be explained by the removal of hemicelluloses (López et al., 2003). Fig. 5 shows that higher brightness values are associated with lower kappa number and lower pulp viscosity, because of the removal of lignin and the degradation of cellulose, respectively. As it is shown in Table 5, bleaching was observed to affect tensile strength (expressed by the tensile index) negatively. Stretch percentage was too low to obtain reliable values, always below 0.2%. Tear index was slightly increased and burst index remained similar. These results are not distant from what Shatalov and Pereira (2005) found with organosolv pulps of giant reed. The great diminishment of the tensile strength is due to the degradation of carbohydrates.

3.3. Refined pulps

The decrease in freeness for a given number of PFI revolutions was similar for both pulps, as Fig. 6 shows. A comparison with pulps from other commonly studied raw materials is presented as well. This diminishment of freeness is greater than the one achieved with conventional hardwoods, much greater than when softwoods are used, and in the same range of organosolv pulp from olive tree trimmings (Jiménez et al., 2008; Mutjé et al., 2005). This finding allows for energy savings when using orange tree trimmings, since less energy is required to achieve a certain degree of refining.

Burst index, tensile index and stretch were drastically improved by refining, while the tear index increased too (Table 6). Even a little energy input, as is the one corresponding to only 250 PFI revolutions, is translated into a huge improvement. 1000 PFI revolutions seemed to be enough for paper of certain grades. A refining process turns out to be necessary to manufacture paper of enough mechanical strength.

4. Conclusions

One-step alkaline bleaching with hydrogen peroxide, using DTPA as activator, achieved a high brightness gain in organosolv pulps from orange tree trimmings, although delignification was poor. For brightness values above 71%, a multi-stage bleaching process is necessary.

Tensile index, stretch and burst index of non-refined pulps, be them bleached or unbleached, were found to be too low. However, they were greatly improved by refining. Hence, a refining stage is necessary when manufacturing paper from orange tree trimmings. Fortunately, acceptable mechanical strength is achieved with little energy consumption.

Temperature, peroxide concentration and duration of the bleaching process affected brightness positively. Temperature and concentration showed negative influences over kappa number and yield. Viscosity could increase with those factors due to the removal of hemicellulose, or decrease due to the partial degradation of carbohydrates.

Given the results of mechanical properties and brightness, the authors recommend to cook orange tree trimmings under severe conditions with ethanolamine. For feasibility reasons, it is advisable to give the pulp a mild bleaching treatment, since a 5% peroxide concentration, 30 min and 83.5 °C are, according to our models, enough to increase ISO brightness from 34.5% to 68%. If brightness values over 70% are desired, we suggest to increase the hydrogen peroxide concentration to 8%, the reaction time to 90 min and the temperature to 85 °C. In addition, pulps should be refined to a CSF of 350 mL at most, which can be achieved at a low energy spending (1000 PFI revolutions were found to be enough).

Acknowledgement

The authors wish to acknowledge the Ministry of Science and Innovation of Spain for the financial support of the Project CTQ2010-21660-C03-01 in which the present study is framed.

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5.8. Publication VIII. Cationic fibers from crop residues: making waste more appealing for papermaking

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Journal: Journal of Cleaner Production.

JCR-indexed: Yes.

Category: Environmental Sciences (Q1).

Reference: Aguado, R., Moral, A., Tijero, A. *J. Clean. Prod*. 174, 1503-1512 (2018).

Status: Accepted in November 2017. To be published in January 2018.

https://doi.org/10.1016/j.jclepro.2017.11.053

Journal of Cleaner Production 174 (2018) 1503–1512

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Cationic fibers from crop residues: Making waste more appealing for papermaking

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ARTICLE INFO

Article history:
Received 8 July 2017
Received in revised form
6 November 2017
Accepted 8 November 2017
Available online 11 November 2017

Keywords:
Cationization
Orange tree trimmings
Pulp and paper
Rapeseed stalks
Titanium dioxide
Wheat straw

ABSTRACT

Although the environmental performance of the paper industry has drastically improved since the nineties, Western manufacturers still refuse to reuse agricultural waste. Moreover, papermakers make extensive use of poorly biodegradable polyelectrolytes which are toxic to fish. With this in mind, we suggest pulping lignocellulosic residues by sulfur-free processes, decrystallizing cellulose, and introducing positively charged functional groups with the goal of partially replacing conventional cationic polymers. Functionalization of pulps from orange tree trimmings, rapeseed stalks and wheat straw was carried out with different concentrations of (3-chloro-2-hydroxypropyl)trimethylammonium chloride (CHPTAC). When the mole ratio of CHPTAC to anhydroglucose units was 4, cationic fibers reached charge density values over 0.2 meq/g after 40 or 60 min of reaction. Then, we tested the performance of these fibers in papermaking, using titanium dioxide, whose zeta potential is negative, as filler. Opacity of lightweight paper was raised to 90%, surpassing a conventional cationic polyacrylamide (CPAM), while the increase in brightness (from 37.8% to 41.9%) was not as good as that achieved with CPAM. Even if residues cannot replace wood, chemical modifications of them can result in valuable cationic fibers, making synthetic polyelectrolytes less necessary.

1. Introduction

Over the past few decades, researchers have been proposing countless potential sources of fibers for papermaking to replace or complement wood, frequently for environmental purposes (Hurter, 1990; Gonzalo et al., 2017). However, predictions were perhaps too optimistic about the future use of alternative materials in Europe and America. Pande (1998) projected three scenarios in which the annual production of non-wood pulp in European countries would account for 658 kt, 878 kt and 5446 kt by 2010. Actual production of non-wood pulp in 2010 was 588 kt (CEPI, 2011), even worse than the worst-case scenario. More recently, in 2016, the production of non-wood pulp was much lower, 273 kt (CEPI, 2017).

Despite the advantages of using non-wood fibers (González-García et al., 2010), manufacturers could not overcome key problems affecting dewatering and thickening in the paper machine. Cereal straw pulps, as promising as they were (Harris et al., 2008; Thykesson et al., 1998), contain large amounts of fines and silica, which hinders sheet formation (Guo et al., 2009; Shao et al., 2017). Furthermore, while keeping with wood, European papermakers have managed to reduce hazardous emissions to air and water by approximately 90% (CEPI, 2017).

We do not suggest giving up on the effort to replace wood, whose prices are still high (Wood Resources International, 2017), with agricultural residues. Reusing waste to produce paper and board is, undoubtedly, better than burning. Considering this, our suggestion is to pulp lignocellulosic residues by sulfur-free methods to remove as much lignin as possible, and then functionalizing cellulosic fibers. For instance, cationic fibers could be added to the furnish, along with conventional fibers from wood, to reduce the need of cationic polyelectrolytes.

Cationic polyacrylamides with medium or high charge density are extensively used in paper mills to improve the retention of

Abbreviations: AGU, Anhydroglucose unit; APAM, Anionic copolymer of acrylamide; AQ, Anthraquinone; CHPTAC, (3-chloro-2-hydroxypropyl)trimethylammonium chloride; CI, Crystallinity index; CPAM, Cationic copolymer of acrylamide; DS, Degree of substitution; EPTAC, Epoxypropyltrimethylammonium chloride; OCF, Cationic fibers from orange tree trimmings; PDADMAC, Polydiallyldimethylammonium chloride; PKP, Pine kraft pulp; PVSNa, Sodium polyvinylsulphate; RCF, Cationic fibers from rapeseed stalks; SEM, Scanning electron microscopy; WCF, Cationic fibers from wheat straw.

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https://doi.org/10.1016/j.jclepro.2017.11.053
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fillers and fines, and also to treat wastewater. Although only a residual amount is discharged, their poor biodegradability (Guezennec et al., 2015) and their toxicity to aquatic organisms explain why they are considered pollutants to water (Umwelt Bundesambt, 2017). Cationic polyelectrolytes are particularly toxic to fish, since those polymers bind to the surface of gills, which carry negative charge, and hinder breathing (Murgatroyd et al., 1996). Taking this into account, cationization of agricultural waste can be useful both for waste management and for natural water protection.

A mechanism for cationization is proposed in Fig. 1. Not many authors insist on the importance of a pretreatment before chemical modifications, but partial amorphization with NaOH can make cellulose much more accessible and reactive (Moral et al., 2015). The alkali is also involved in the ionization of cellulose itself and in the conversion of (3-chloro-2-hydroxypropyl)trimethylammonium chloride (CHPTAC), more stable, to epoxypropyl-trimethylammonium chloride (EPTAC). If the conditions are mild, only the substitution on carbon 6 is expected.

The surface charge of unmodified cellulosic fibers is negative (Sood et al., 2010). Most applications of cationized fibers lie in the textile industry, with the goal of reducing or removing the need of polluting electrolyte baths when using anionic dyes (Arivithamani and Giri Dev, 2017). Nonetheless, similar reasons could drive papermakers to perform these chemical modifications. It has been stated that paper sheets are strengthened if fibers contain cationic functional groups (Montplaisir et al., 2006). Sang and Xiao (2009) produced cationic fibers by grafting, resulting in improved

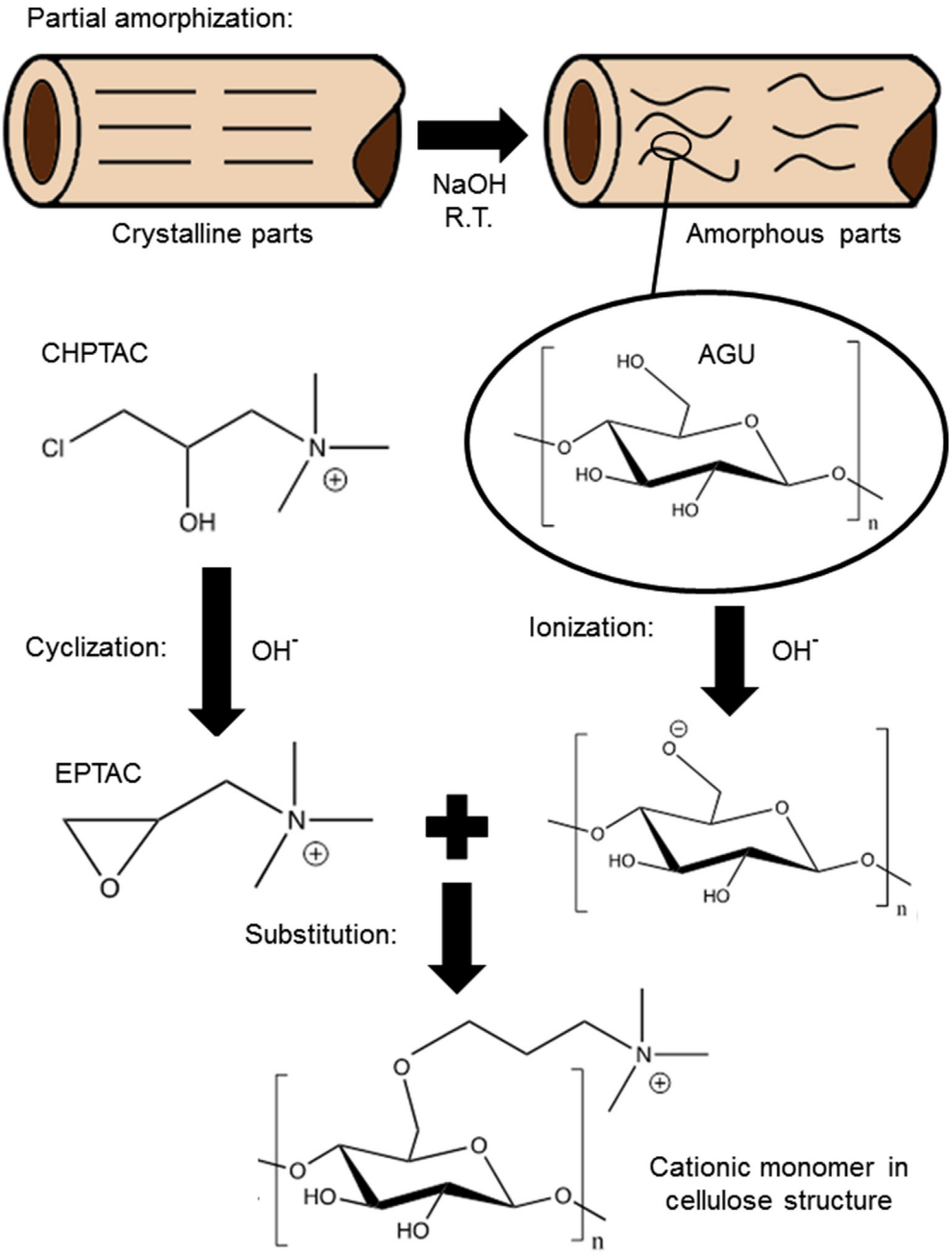

Fig. 1. Mechanism of the heterogeneous cationization of cellulose in fibers.

retention of china clay, a filler whose surface charge is negative. Sain and Boucher (2002), using amino trimethoxy silane to produce cationic fibers, clearly enhanced the retention of fines.

In this paper, we report the functionalization of alkaline pulps from rapeseed stalks, orange tree trimmings and wheat straw, whose capability as raw materials for papermaking has been already studied (Aguado et al., 2015; Moral et al., 2016). We hypothesize that cationic fibers enhance the effects of titanium dioxide (TiO_2) on brightness and opacity, since the surfaces of rutile and anatase are negatively charged (Sood et al., 2010), and thus a cationic polyacrylamide is not needed to bind the filler particles to the fibers. The kinetics of the chemical process was studied under the hypothesis that long reaction times are not needed. The performance of cationic fibers was evaluated for the drainage behavior, for the apparent density and for the improvement of key optical properties.

2. Materials and methods

2.1. Pulping

Rapeseed (*Brassica napus* L.) stalks, orange tree (*Citrus sinensis*) and wheat (*Triticum aestivum*) straw were harvested in different parts of Spain. In each case, the raw material was fractionated to a size below 5 mm and cooked in a stainless steel batch reactor for 60 min. The white liquor, an aqueous alkaline suspension consisting of 0.2–0.3 g of NaOH and 0.01 g of anthraquinone (AQ) per gram of pulp, was heated to 180 °C before supplying the lignocellulosic material. The water-to-solid ratio was 6. The temperature was kept constant with a proportional-integral-derivative controller. Soda-AQ pulps were filtered, washed with cold water and stored at 4 °C. The kappa numbers (ISO 302) of the pulps from rapeseed stalks, orange tree trimmings and wheat straw were 27, 37 and 23, respectively.

2.2. Pretreatment

Pulps were diluted to a consistency of 1.5% and disintegrated, at 3000 revolutions per minute (rpm) for 10 min, in accordance to ISO 5263 (ISO, 2011). Afterwards, the suspensions were filtered to increase consistency to 10%. 20 g of each pulp, on the basis of dry pulp weight, were soaked in 150 mL of a strongly alkaline solution, in which NaOH concentration was 30% (w/w). After stirring for 1 h at room temperature, fibers were separated from the liquid by filtration over glass microfiber (2.7 μm) and washed with cold water. We took small samples (approximately 1 g) to evaluate the effects of alkalization. The rest was cationized.

2.3. Cationization

Functionalization of cellulosic pulps took place in a 2 L three-mouthed spherical glass reactor with refluxing condenser, magnetic stirring and heating mantle. Alkalized pulps to be cationized were mixed with distilled water and NaOH. When a temperature of 70 °C was reached, an aqueous solution of CHPTAC (60% w/w), purchased from Sigma-Aldrich, was poured into the reactor. Pulp consistency was 2%. Temperature was kept at 70 °C for 90 min by a controller with an on/off action. The NaOH-to-CHPTAC mole ratio was always 1.5, while the mole ratio of CHPTAC to cellulose, in terms of anhydroglucose units (AGU), was varied from 1 to 4. Once cationized, pulps were filtered and thoroughly washed with 2-propanol and water.

2.4. Characterization of pulps

The untreated pulps and the alkalized samples were submitted to a powder X-ray diffractometer from PANalytical. X-ray diffraction patterns were obtained with X'pert software. The peaks of the crystalline polymorphs were identified and integrated, thus determining the height and area of each of them, by choosing a Gaussian deconvolution in Systat's software Peakfit.

After cationization, the percentage of nitrogen in all pulps was determined by combustion with an elemental analyzer from LECO. To measure the surface charge of cationic fibers, we chose a Charge Analysis System device from AFG, performing a potentiometric titration whose endpoint was 0 mV (isoelectric point). We opted for a back titration, since the system was not designed to measure the charge density of solids. Approximately 0.1 g of fibers were soaked in excess sodium polyvinylsulphate (PVSNa), an anionic polyelectrolyte. The mixture was not stirred. The liquid was titrated with polydiallyldimethylammonium chloride (PDADMAC), a cationic polyelectrolyte. When the number of equivalents of PDADMAC surpassed the amount of PVSNa, the surface charge was deemed negative and the measurement was discarded. Then, another sample of pulp was soaked in excess PDADMAC and titrated with PVSNa.

Some pulps were observed by scanning electron microscopy (SEM) with a device from JEOL. Untreated and cationized fibers were placed on a cylindrical slide. The slide was left to dry in a vacuum oven, then coated with gold and visualized.

2.5. Sheets with cationic fibers

Five handsheets with a basis weight of 40 g/m^2, in the range of lightweight offset paper, were made from pine kraft pulp (PKP) provided by TOLSA (Madrid, Spain) and refined to 4000 PFI revolutions. Its Canadian Standard Freeness was 420 mL (TAPPI, 2017).

Five other sheets were made from the same pulp (94%) with paper-grade TiO_2 (6%), Tiona RCL-722, kindly provided by Cristal, with a particle size comprised between 0.3 and 0.4 μm. Three sets of five sheets each had 0.06 g of cationic pulp per gram of untreated pulp, plus TiO_2 (6%): one of those sets was prepared with cationic fibers from rapeseed stalks (RCF), another one with cationic fibers from orange tree trimmings (OCF), and the last one with cationic fibers from wheat straw (WCF). In each case, we selected the experiment that resulted in the highest degree of substitution (DS).

To compare the use of cationic fibers to that of cationic polyacrylamides, the sixth set was prepared with TiO_2 (6%) and 5 mg/g of a cationic copolymer of acrylamide (CPAM) with medium charge density and high molecular weight, supplied by NALCO. The seventh one involved TiO_2 (6%), cationic fibers of high DS (6%) and 5 mg/g of an anionic copolymer of acrylamide (APAM) from the same provider. To make all the isotropic sheets, we used a laboratory sheet former that conforms to the ISO standard 5269/1 (ISO, 2011).

2.6. Characterization of sheets

The thickness of all sheets from PKP, with and without cationic fibers (RCF, OCF, WCF), was measured by means of a motor-driven micrometer from IDM Instruments. Bulk was calculated and expressed according to the TAPPI test method T220 (TAPPI, 2017).

Opacity of all sheets was determined with an Elrepho spectrophotometer from Lorentzen & Wettre, using a C/2° light source and stacking five sheets over a black cavity in each case. The device conforms to ISO 2471 (ISO, 2011). Besides opacity, it provided R457 brightness (ISO 2469) and yellowness (ASTM method E313).

Analogously to the production of micrographs from pulps, two

paper sheets with TiO_2, with and without cationic fibers, were observed by SEM.

To evaluate the effect of this addition of cationic fibers on dewatering, we used a laboratory device DFR-05 from Mütek. The furnish consisted in 1 kg of a water suspension containing PKP and TiO_2, with and without cationic fibers (6%). Consistency was 0.25%. The "Drainage" program was chosen in Mütek's software. The stirring was set at 600 rpm for 60 s, and then the suspension went through a screen with an aperture size of 0.11 mm. Conductivity was approximately 500 mS/cm and the pH was adjusted to 7.5.

Fig. 2 shows a schematic diagram of the experimental procedure.

3. Results and discussion

3.1. Effects on fibers

3.1.1. Effect of the pretreatment

The alkaline pretreatment produced notorious changes in intramolecular and intermolecular bonds of cellulosic fibers, as can be appreciated in X-ray diffraction patterns (Fig. 3). Miller indices were assigned to the key refraction bands of crystalline polymorphs of cellulose in accordance with the conventions followed by French (2014). Unless the subscript *II* (cellulose II) is indicated, those bands are related to cellulose Iβ. Peak (004) belongs to both cellulose I and cellulose II.

Peaks (1–10) and (110) of cellulose Iβ were flattened, becoming nearly indistinguishable after the treatment with NaOH for pulps from rapeseed stalks (Fig. 3a) and orange tree trimmings (Fig. 3b). Decrystallization was evident: the intensity (expressed as arbitrary units) of all crystalline peaks in the original pulps, including (004), decreased. Conveniently, some crystalline parts were kept in the fibers, as some crystalline peaks remain appreciable. Amorphous cellulose is more reactive, but also linked to worse mechanical properties (Nakai et al., 1977). If these fibers are meant to be used in papermaking, their diffraction pattern should look more like the one for wheat straw pulp (Fig. 3c), in which decrystallization is clear but not excessive.

Table 1 presents the crystallinity indices (CI) of untreated and treated pulps. The area of the peaks ideally found in crystalline cellulose (French, 2014) was divided by the total area (Park et al., 2010):

$$CI = \frac{A_{1-10(I\beta)} + A_{110(I\beta)} + A_{200(I\beta)} + A_{110(II)} + A_{020(II)} + A_{004}}{A_{TOTAL}} \quad (1)$$

In Eq. (1), *A* is the area under each of the Gaussian peaks resulting from the deconvolution with Xpeak. Indices *1–10(Iβ)*, *110(Iβ)*, *200(Iβ)*, *110(II)*, *020(II)* and *004* correspond to the peaks found at 15°, 16.5°, 22.5°, 20.1° and 34.6°, respectively, in Fig. 3.

After alkalization, the most prominent peak in X-ray diffraction patterns became not only shorter, but also lopsided to the left (Fig. 3). This is due to the conversion of cellulose Iβ, whose most

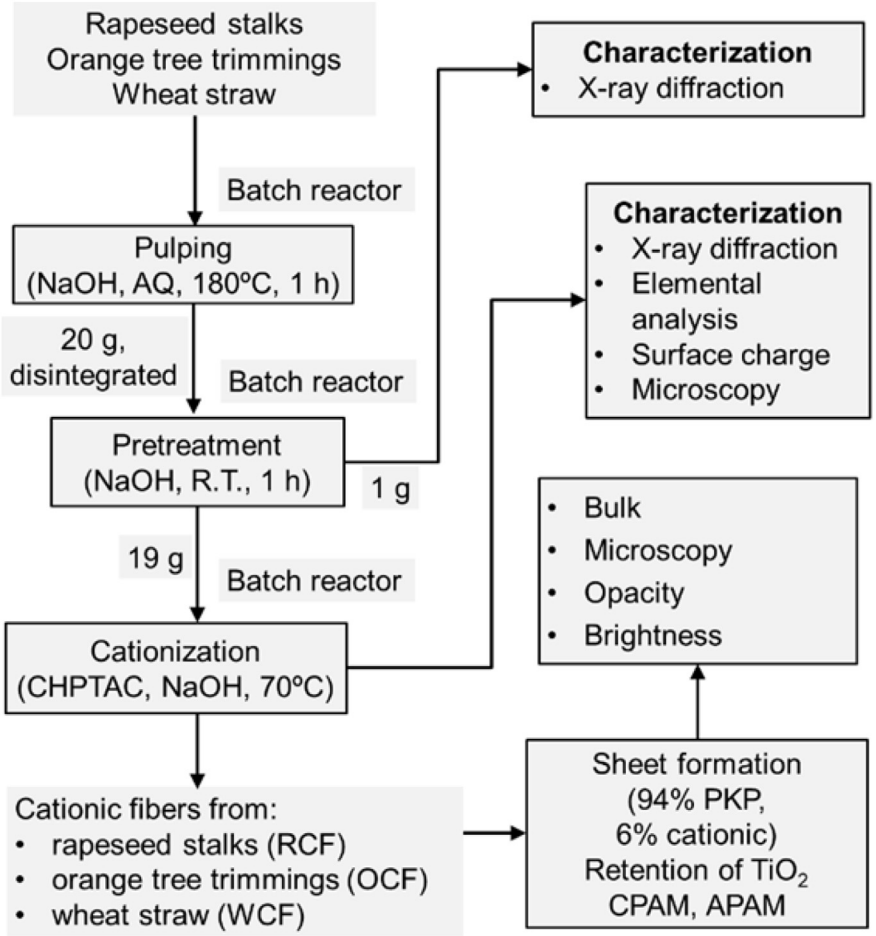

Fig. 2. Scheme of the experimental procedure.

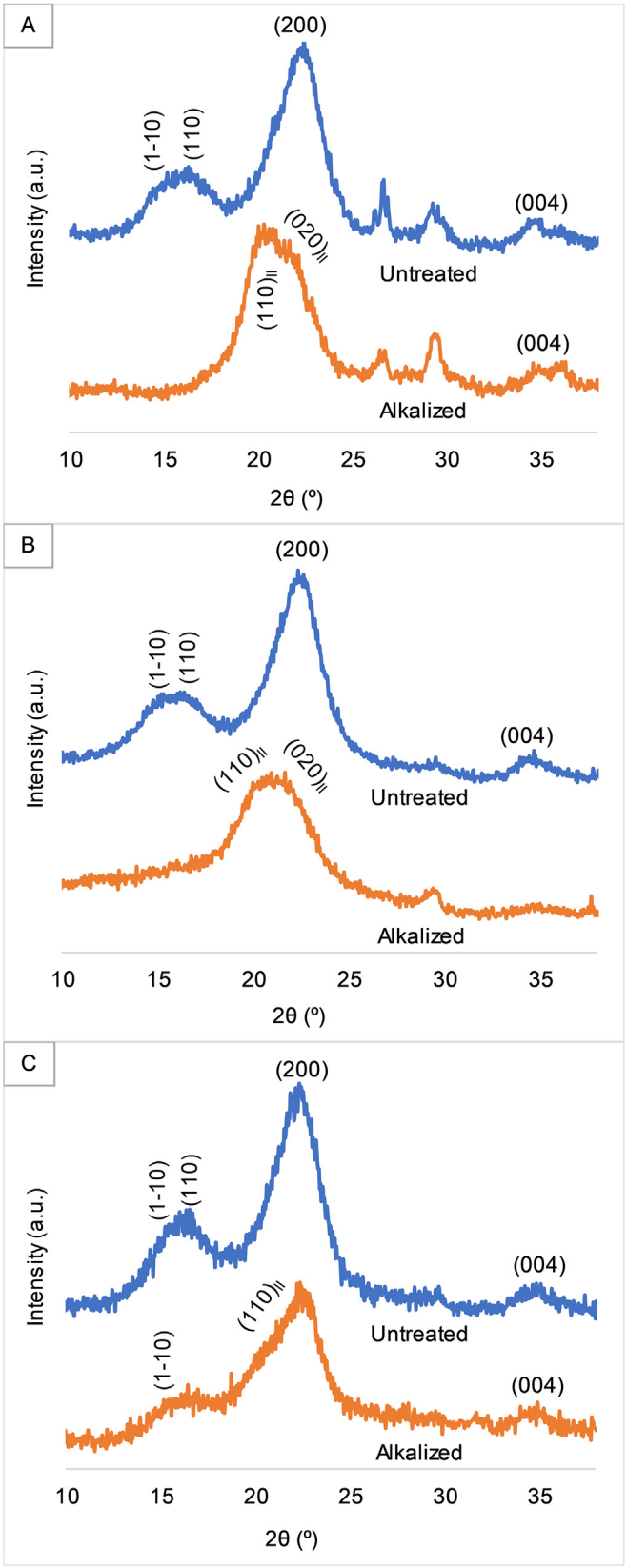

Fig. 3. X-ray diffraction patterns of untreated and pretreated soda-AQ pulps of rapeseed stalks (A), orange tree trimmings (B), and wheat straw (C).

prominent peak is found at $2\theta = 22.5°$, to cellulose II, whose most characteristic peak is located at $2\theta = 20.1°$. Determining the ratio of

Table 1
Crystallinity and indication of the conversion to cellulose II before and after the alkaline treatment of soda-AQ pulps.

Pulp	Kappa number	CI	A(I/II)
Rapeseed, untreated	27	0.75	2.0
Rapeseed, alkalized		0.61	0.8
Orange tree, untreated	37	0.77	2.1
Orange tree, alkalized		0.58	0.9
Wheat, untreated	23	0.81	2.1
Wheat, alkalized		0.68	1.4

cellulose Iβ to cellulose II is a complicated task involving very selective cellulases, but the quotient of the two aforementioned peaks (after deconvolution) is useful for comparison purposes:

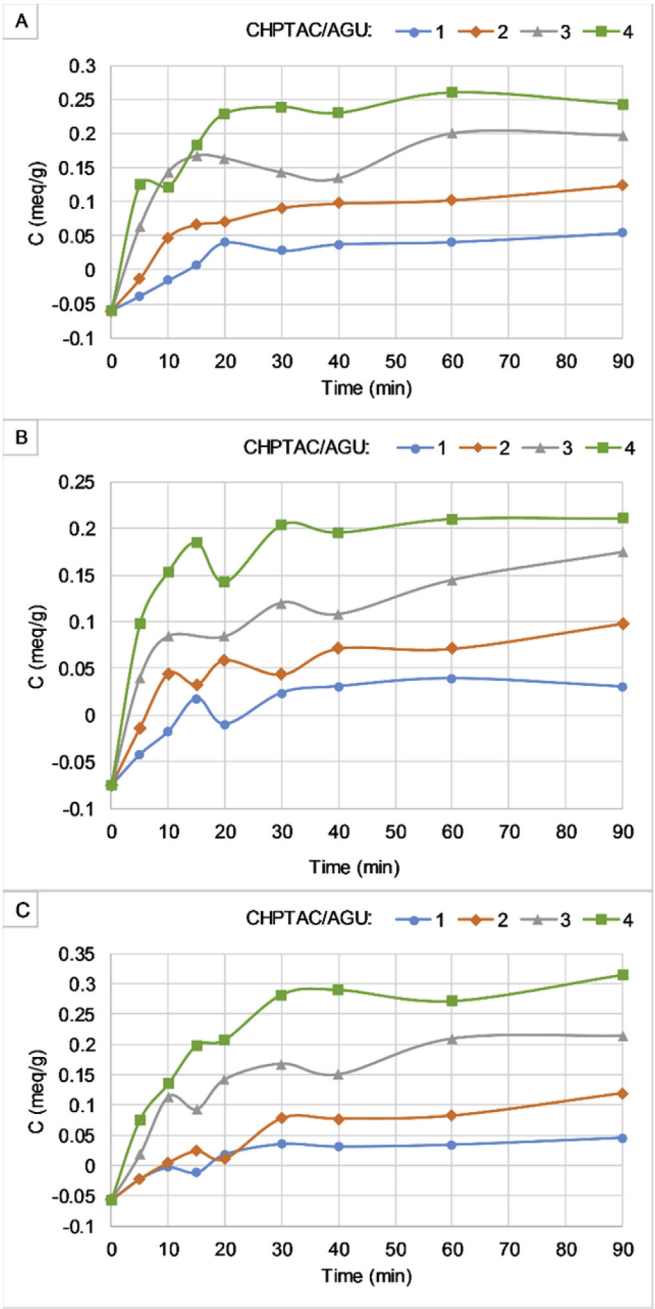

Fig. 4. Evolution of the surface charge with time in pulps of rapeseed stalks (A), orange tree trimmings (B), and wheat straw (C), for CHPTAC/AGU mole ratios ranging from 1 to 4.

$$A(I/II) = A_{200(I\beta)} \Big/ A_{110(II)} \quad (2)$$

The ratio calculated by Eq. (2) is shown in Table 1 for all materials. Like decrystallization, conversion to cellulose II was very notorious for pulps from rapeseed stalks (Fig. 3a) and orange tree trimmings (Fig. 3b). In contrast, the pattern of the pulp from wheat straw (Fig. 3c) still resembles the ideal shape of cellulose Iβ.

3.1.2. Effect of cationization

Fig. 4 presents the results from the charge analysis system, expressed as milliequivalents of the counter polymer needed to reach the isoelectric point when 1 g of pulp has been soaked. The most negatively-charged pulp before the functionalization was the one from orange tree trimmings, corresponding to the largest content of remaining lignin and uronic acids, since its kappa number was 37 (Table 1). Consistently, for any given values of time and CHPTAC/AGU ratio, cationizing the pulp from orange tree trimmings resulted in the least positively-charged fibers.

The surface charge of fibers was rapidly switched from negative to positive. Charge measurements are subject to errors due to the heterogeneity of the samples, and thus the values after 20 min are fluctuating. Nevertheless, the influence of the CHPTAC/AGU ratio on charge is evident for all pulps, and apparently linear. When only the stoichiometric amount of cationizing agent was supplied to the reactor, cationicity lied around 0.05 meq/g. When the ratio was 4, the charge density reached 0.25 meq/g for RCF, 0.22 meq/g for OCF, and 0.33 meq/g for WCF. The maximum values are in the same range as those reported by Sain and Boucher (2002) with amino trimethoxy silane (0.25 and 0.31 meq/g). We could not expect them to be as high as the charge density of water-soluble cationic cellulose, which is one order of magnitude greater (Aguado et al., 2017). Insoluble fibers, as an advantage, do not pass through the wire to the recirculating water. Anyway, both ways of producing

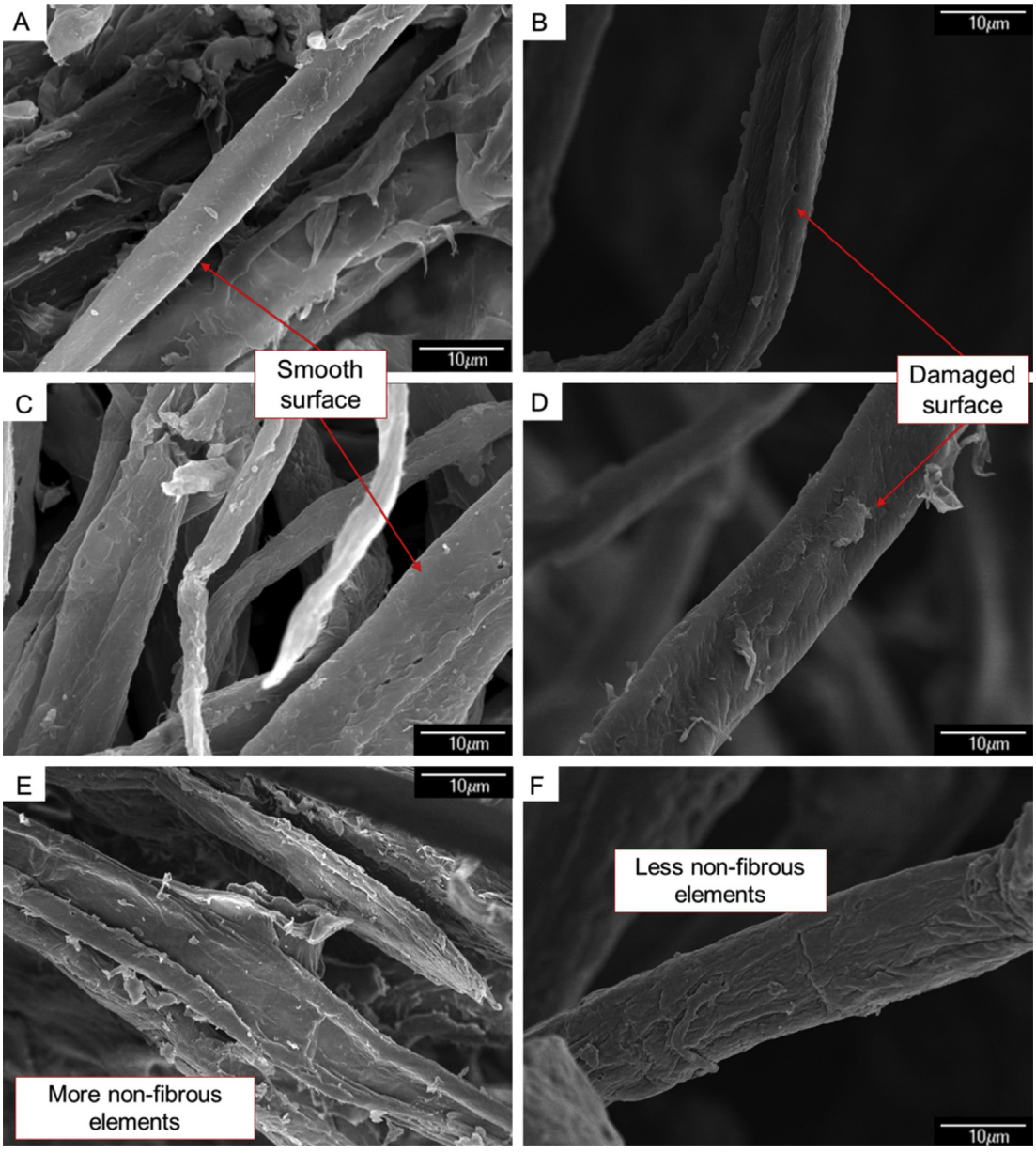

Fig. 5. SEM images of pulps: rapeseed stalks, original (A) and cationized (B); orange tree trimmings, original (C) and cationized (D); wheat straw, original (E) and cationized (F).

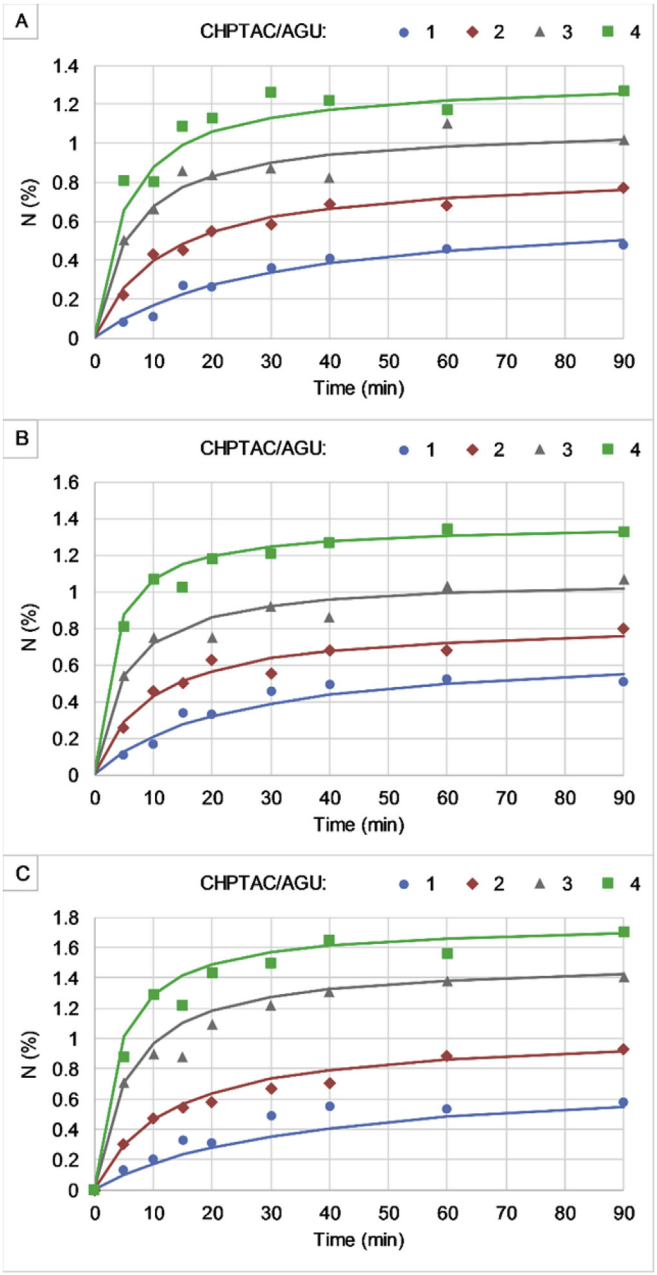

Fig. 6. Reaction kinetics for various concentrations of cationizing agent: (A) rapeseed stalks; (B) orange tree trimmings; (C) wheat straw, for CHPTAC/AGU mole ratios ranging from 1 to 4.

cationic cellulose, soluble and insoluble, can be complementary.

Taking as example a market pulp whose surface charge is 0.02 meq/g, in order to achieve global charge neutralization, the percentage of cationic fibers obtained with a CHPTAC/AGU molar ratio of 4 would range from 5.5% (wheat straw) to 8.5% (orange tree trimmings). Total neutralization might not be desirable Hubbe, 1999), but even smaller amounts could improve key paper properties and retention of anionic additives Montplaisir et al., 2006).

Micrographs obtained with a magnification of 2000 times are shown in Fig. 4. The surface of the original fibers in soda-AQ pulps from rapeseed stalks (Fig. 5a) and orange tree trimmings (Fig. 5b) was smoother, with an almost intact cell wall and with few microfibrils protruding from it. Alkalization and cationization resulted in evident damage on the wall and in the swelling and shrinking of fibers (Fig. 4d and e). With exposed fibrils, the relative bonding area clearly increased, somehow compensating the loss of strength. It also eased chemical modifications of cellulose, overcoming mass transfer limitations, and allowed the material to reach a higher surface charge for a given DS value.

The fiber wall of fibers from wheat straw was also damaged (Fig. 4f), although their surface was not as smooth in the beginning (Fig. 4c). What is remarkable of the original pulp from wheat straw is the large number of fines and non-fibrous elements. Many of them, however, were lost upon cationization because they became water-soluble. This overcomes one of the main problems of using wheat straw fibers, as Guo et al. (2009) proposed the removal of wheat straw fines to achieve good sheet formation.

3.2. Kinetics of cationization

Kinetic curves (Fig. 6) achieved an abrupt increase after the first few minutes of cationization, leveling off at the end of the treatment. It must be taken into account, then, that an equilibrium value is reached during functionalization, and this value seems to depend on the concentrations of CHPTAC and NaOH. Even homogeneous reactions, aiming to produce water-soluble cationic cellulose, have displayed a very similar shape of the kinetic curves (Liesiene and Kazlauske, 2013).

In previous studies, Moral et al. (2015) proposed an approach similar to the modeling of many adsorption processes. The mass fraction of nitrogen can be successfully fitted to Eq. (4), a pseudo-second order rate equation with two parameters: K' and N_{eq}.

$$\frac{d\omega_N}{dt} = K'\left(N_{eq} - \omega_N\right)^2 \tag{3}$$

where ω_N is the mass fraction of nitrogen as provided by an elemental analysis.

This model provided good results for a given amount of NaOH,

Table 2
Cationization: varying experimental conditions and kinetic parameters.

Experiment	Raw material	CHPTAC/AGU	[NaOH] (mol/L)	DS_{max}	K (L mol^{-1} min^{-1})	N_{eq} (%)	R^2
1	Rapeseed stalks	1	0.185	0.059	27.1	0.670	0.964
2		2	0.371	0.098		0.857	0.984
3		3	0.556	0.145		1.086	0.952
4		4	0.742	0.171		1.322	0.963
5	Orange tree trimmings	1	0.185	0.064	34.8	0.684	0.956
6		2	0.371	0.102		0.832	0.960
7		3	0.556	0.141		1.071	0.964
8		4	0.742	0.182		1.367	0.988
9	Wheat straw	1	0.185	0.072	21.0	0.754	0.952
10		2	0.371	0.120		1.038	0.980
11		3	0.556	0.193		1.514	0.977
12		4	0.742	0.242		1.759	0.980

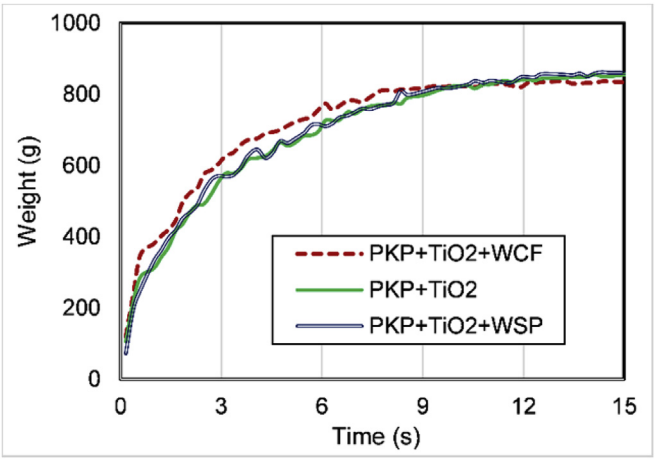

Fig. 7. Drainage rate, presented as increasing weight of the filtrate, normalized to 900 g, with dewatering time, for pine kraft pulp (PKP) with TiO_2, wheat straw pulp (WSP) and cationic fibers from wheat straw (WCF).

which would affect both K' and N_{eq}. It is not clear how the maximum amount of fixated nitrogen is affected (Hashem et al., 2003). De Vries et al. (2014) found, for the cationization of cotton, first-order dependence on NaOH concentration. While cyclization is fast, cellulose ionization with OH^- is surely a controlling stage. Eq. (4) results from including the alkali concentration into the differential equation:

$$\frac{d\omega_N}{dt} = K[NaOH]\left(N_{eq} - \omega_N\right)^2 \tag{4}$$

This way, K is a rate constant which should not depend on the concentration of any reagent. Eq. (4) can be easily integrated if the concentration of NaOH is assumed to stay constant through the process. Although OH^- ions are first consumed in cellulose ionization, they are then released by the reaction between ionized cellulose and the epoxide.

$$\omega_N = \frac{K[NaOH]tN_{eq}^2}{1 + K[NaOH]tN_{eq}} \tag{5}$$

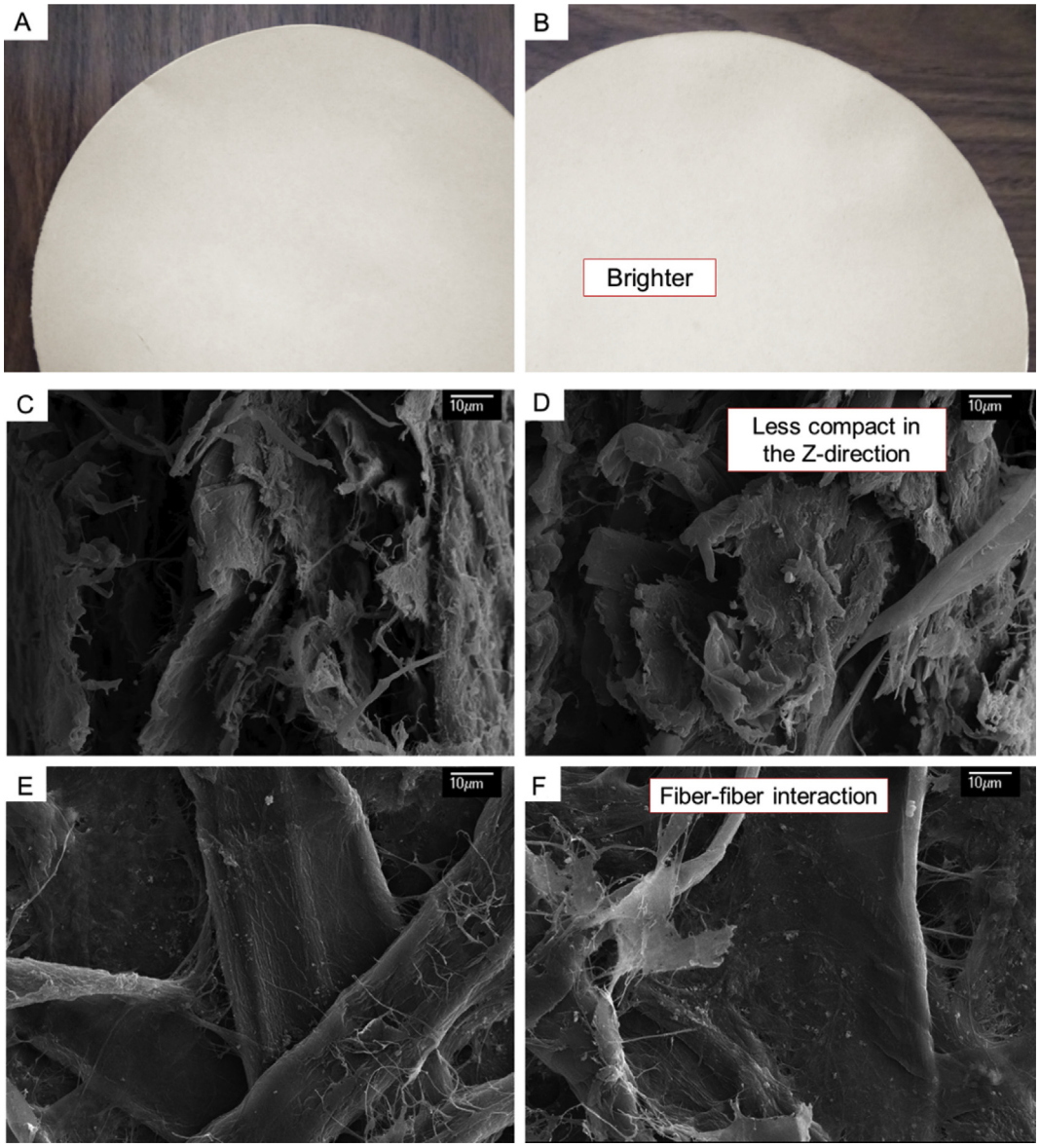

Fig. 8. Paper with TiO_2: photograph, without WCF (A) and with WCF (B); micrograph of the surface, without WCF (C) and with WCF (D); micrograph of the cross-section, without WCF (E) and with WCF (F).

Eq. (5) presents the integrated form of the rate equation. For the 12 experiments (Table 2), the mass fraction of nitrogen was fitted to this model by using Origin 8.5. The fittings are shown in Fig. 6 as continuous lines, while dots represent experimental data. Residues are more notorious between 10 and 40 min of reaction time. Anyway, as can be read from Table 2, all regressions presented R^2 values above 0.95.

Table 2 also shows the maximum DS reached in each of the 90 min long reactions. DS was calculated under the assumption that fibers solely consisted of cellulose. Actually, the remaining contents of lignin and hemicellulose after chemical pulping are not negligible, but those compounds are modified by CHPTAC too (Šimkovic et al., 1990). Given that the molecular mass of anhydropentose units (132 Da) is only slightly lower than that of anhydrohexose units (162 Da), Eq. (6) should provide a satisfactory estimation:

$$DS = \frac{162\ \%N}{1401 - 152\ \%N} \quad (6)$$

Here, 162 is the molecular mass of AGU, 152 is the molecular mass of a quaternary ammonium group, and 1401 is 100 times the atomic mass of nitrogen (Moral et al., 2015). Some DS values were above 0.15, which is in the high range for insoluble fibers. When DS is higher than 0.3, cationic fibers may be so ionized that they get dissolved in water.

As expected, the percentage of nitrogen and the surface charge are correlated. Pearson's coefficient was found to be as high as 0.97 for WCF and OCF, and 0.98 for RCF. Remarkably, the cationic pulp from orange tree reached a higher DS value than the cationic pulp from rapeseed, but the charge density was lower. This is explained by the fact that, before cationization, the former was more negatively charged than the latter.

3.3. Performance in papermaking

3.3.1. Influence on sheet formation

The use of cationic fibers did not hinder sheet formation in terms of dewatering. For a furnish with WCF, drainage was slightly faster, as can be seen from Fig. 7. The improvement of dewatering can be explained by the improvement of retention of fillers and fines Hubbe, 1999). It may be argued that this effect could come from mixing a heavily refined pulp with a non-refined pulp, regardless the surface charge, but the combination of PKP and the original soda-AQ pulp was also tested. No effect of untreated fibers could be appreciated. In fact, unrefined pulps from wheat straw contain as many fines, if not more, as heavily refined softwood pulps (Guo et al., 2009).

Fig. 8 presents two handsheets: a sheet made with PKP and TiO_2 and a sheet made with PKP, TiO_2 and WCF. To ease comparisons, these handsheets were produced with a higher basis weight than those whose opacity was measured. Photographs (Fig. 8a and b) were taken during daylight and at the same hour and place. The sheet with cationic fibers is slightly but appreciably brighter.

Micrographs of the cross-section of paper seemed to indicate that the presence of decrystallized fibers (Fig. 9d) results in more void space, while the layers of fibers are more compact in Fig. 9c. As for the surface (Fig. 9e and f), the distribution of TiO_2 was found to be uniform enough and very similar for both sheets, proving that the addition of cationic fibers does not produce undesirable big aggregations of fillers.

3.3.2. Enhancement of paper properties

The opacity and the light scattering coefficient for the different sets of handsheets are shown in Fig. 9. Bulk, brightness and yellowness are presented in Table 3. Cationic fibers from wheat straw

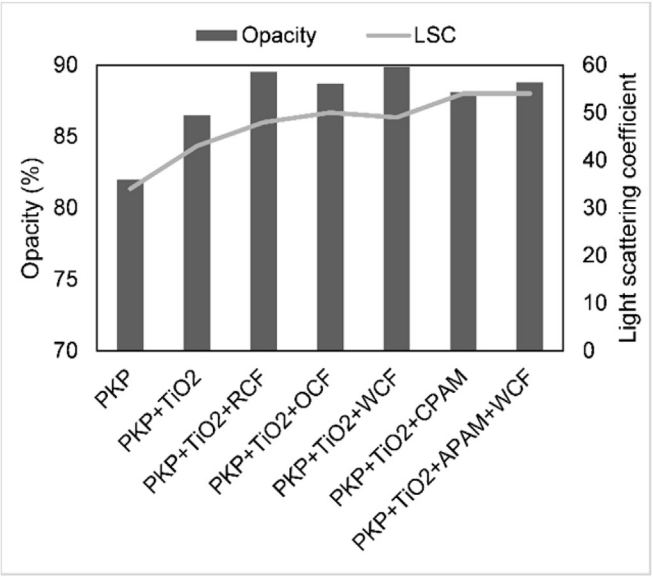

Fig. 9. Opacity and light scattering coefficient of sheets from wheat straw pulp and TiO_2, cationized pulps, CPAM and APAM.

Table 3
Codification and key optical properties of sheets from wheat straw pulp (WSP) with and without titanium dioxide, cationic fibers and polyelectrolytes.

Composition	Bulk (cm^3/g)	Brightness	Yellowness
PKP	0.115	31.5	47.8
PKP + TiO_2	0.110	37.8	43.0
PKP + RCF + TiO_2	0.120	41.5	40.0
PKP + OCF + TiO_2	0.119	41.6	39.8
PKP + WCF + TiO_2	0.114	41.9	41.1
PKP + CPAM + TiO_2	0.116	43.3	38.4
PKP + APAM + WCF + TiO_2	0.124	42.2	38.5

with the highest DS value, obtained under a CHPTAC/AGU mole ratio of 4, clearly improved opacity and brightness, due to the enhanced retention of TiO_2 and fines, even without polyelectrolytes. Moreover, opacity reached its highest value when the original pulp was mixed with WCF.

Adding a small amount of CPAM resulted in the brightest sheets (Table 3) and in the highest light scattering coefficient (Fig. 9). As the brightness gain is provided by TiO_2 and not by fines, this indicates that cationic fibers are better for the retention of fines but, still, cationic flocculants are better for filler retention. Combining APAM with cationic fibers, unfortunately, did not achieve better results than using a cationic polyelectrolyte alone (Fig. 9).

It is noteworthy that the apparent density of paper sheets decreased with the addition of cationic fibers (Table 3). Likely, this was not as due to cationization itself as to the reduction of the packed density of pulp pads by the partial amorphization (Vinogradov et al., 2002). With the breakage of many intermolecular and intramolecular hydrogen bonds, the less crystalline structure tends to swell, occupying a larger volume for the same basis weight.

The increase of bulk is desired for any paper grade. This way, a sheet can be produced with a certain thickness while using less raw material. However, amorphization also implies drawbacks. Although it has been stated that cationic fibers can improve the strength of the paper web Montplaisir et al., 2006), further research is needed to address the effect of using cationic fibers with low CI.

4. Conclusions

We successfully produced cationic fibers under different concentrations of CHPTAC, by chemically modifying soda-anthraquinone pulps from lignocellulosic residues. First, cellulose Iβ was partially converted (wheat straw) or almost completely converted (rapeseed and orange tree) to cellulose II and amorphous cellulose. This pretreatment, together with high concentrations of CHPTAC and NaOH, allowed the material to reach DS values above 0.15, after only 40 or 60 min of cationization at 70 °C. We adjusted cationization kinetics to a pseudo-second order rate equation with a first-order dependence of NaOH concentration.

The process is mild enough to be regarded as feasible. The addition of only a small amount of cationic fibers (5.5–8.5%) should be enough to neutralize market pulps, and we did not even need total charge neutralization to enhance optical properties that were provided by fines and TiO_2. While the choice of TiO_2 in the paper industry will remain hindered by its price, the addition of cationic fibers can alleviate the unaffordable losses of these particles, whose zeta potential is strongly negative at a wide pH range. Hence, as long as the surface charge of a filler in a papermaking process is clearly negative, agricultural residues could be reused towards cationic fibers, which would reduce the need of toxic and non-biodegradable polyelectrolytes.

Acknowledgements

The authors are grateful to the Ministry of Science and Innovation of Spain for the financial support (project FIBRALT: CTQ2010-21660-C03-01); to the auxiliary research centers at the Complutense University of Madrid, regarding some measurements (degree of substitution, crystallinity); to CIFOR-INIA (Spain), for their spectrophotometer; to the research group LEPAMAP at the University of Girona, for providing pulps.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jclepro.2017.11.053

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6. DISCUSSION AND CONCLUSSIONS

6.1. Interpreting results: for or against hypotheses

6.1.1. Effects of the pretreatments on further modifications

Evidence **supports** Hypothesis 1: *Soaking a cellulosic material in a concentrated aqueous NaOH solution, at room temperature, makes cellulose prone to cationization*. Both the reaction rate and the maximum nitrogen percentage that could be reached increased with decreasing crystallinity. Decrystallization or amorphization occurred by treating cotton linters (Publication I) and alpha-cellulose powder (Publication II) with caustic soda, as indicated by X-ray diffraction (XRD) patterns. Table 9 shows the highest degree of nitrogen substitution (DNS) reached for cotton linters and cellulose powder and the crystallinity indices (CI) after 90 min-long treatments with NaOH 10%, NaOH 20% and NaOH 30%. It should be noted that the two sets of data cannot be interpreted jointly, since the crystallinity of cotton linters was estimated by the height method, while the area method was followed to measure the crystallinity of alpha-cellulose.

Due to the lack of a baseline correction of XRD patterns, the area method probably resulted in an underestimation of crystallinity [68]. Evidence from later works [76] suggested me that, if the amorphous fraction of the alpha-cellulose powder were as high as 50%, this material could have been cationized to high DNS values without the need of severe pretreatments. Still, CI calculations in Publication II are suitable for comparison purposes, which is the objective stated in the paper.

Table 9. Crystallinity indices (CI) after 90 min-long alkaline treatments and maximum degrees of nitrogen substitution (DNS) reached.

Material	CI*	DNS	Source
Cotton linters	Initial CI*: 0.83		Publication I
	0.76	0.021	
	0.83	0.013	
	0.60	0.204	
Commercial alpha-cellulose	Initial CI*: 0.50		Publication II
	0.44	0.020	
	0.33	0.022	
	0.19	0.257	

*Abbreviated as CrI in Publications I and II.

Results in Publication IV **support** Hypothesis 5: *Refining a pulp before alkalization and cationization increases the reaction rate*. Refining itself had no visible impact on crystallinity, but this mechanical treatment caused fibers to become easily swollen in aqueous alkaline suspensions, thus weakening hydrogen bonds between cellulose chains. XRD patterns corroborated the enhancing of alkalization by refining: the crystallinity index of the unrefined pulp after alkalization was 0.75, but refining to 4500 PFI revolutions (vid. 3.3.3. Refining and electricity consumption) and then alkalizing was translated into a CI of 0.66. As a consequence, the degree of substitution of the pulps refined and cationized was always above 0.34, while its value was 0.296 for the unrefined pulp.

Even more notorious was the impact on the surface charge of fibers. This was 0.442 meq g^{-1} for the unrefined, alkalized and cationized pulp, but as high as 0.854 meq g^{-1} when the pulp had been refined to 4500 PFI revolutions. Swelling and decrystallization are not enough to explain such difference. External fibrillation by surface roughening during refining was key. The surface had more positive charges per unit of mass because there was more surface per unit of mass.

Hypothesis 9 is **not supported** by Publication V. That hypothesis was formulated as follows: *Since the solubility of cationic cellulose depends on the degree of polymerization (negative influence) and on the degree of substitution (positive influence), hydrolyzing cellulose with orthophosphoric acid is a proper pretreatment to produce water-soluble cationic cellulose*. However, the use of H_3PO_4 served to produce the flocculation agent with the worst performance. Incapable of working by bridging mechanisms, due to its low molecular weight, this derivative did not boost aggregation of any of the fillers tested in Publication V (precipitated calcium carbonate, ground calcium carbonate and kaolin).

What we achieved with H_3PO_4 and not with NaOH, however, was increasing the proportion of amorphous cellulose —CI: from 0.813 to 0.518— while most crystalline cellulose remained as cellulose I. But this does not seem to be relevant for the purpose of cationization.

Table 10 lists the treatments that precede functionalization in our publications. By the time we started hypothesizing, it was already known that cellulose chains whose molecular weight is low can be dissolved in an aqueous solution of NaOH and urea [87]. This treatment, followed by cationization, was used in Publication V to separate medium-DP (820) cellulose from high-DP (1703) cellulose. It was also known that the solubility of charged cellulose derivatives would decrease with the length of the polymer chain and increase with the amount of charged units along this chain. This is why the high-DP part needed to reach a higher degree of substitution (0.46) than that of the medium-DP part (0.34) to become soluble in water.

Table 10. Pretreatments used in our publications and their effects.

Pretreatment	Tested in	Usefulness
NaOH	Publications I, II, III, IV, VIII	Decreasing crystallinity of cellulose without dissolving it
Refining	Publication IV	Enhancing the NaOH treatment to be carried out afterwards
NaOH + urea	Publication V	Decreasing crystallinity of cellulose and solubilizing the low-DP part
H_3PO_4	Publication V	Depolymerizing cellulose while amorphizing it
NaOH + FeTNa	[31]	Decreasing crystallinity of cellulose and solubilizing the low-DP part
NH_4SCN	[31]	Slightly activating cellulose without dissolving it

6.1.2. Kinetics of cationization

Observations **support** Hypothesis 2: *Kinetics of cationization can be modelled and the shape of the kinetic curve (percentage of nitrogen vs. time) is nearly the same for any given raw material*. This curve always looked like the one depicted in Figure 25. There is a region in which the reaction is fast, at the beginning, and then the percentage of nitrogen slowly levels off towards an asymptotic value —and so does the degree of substitution. There is an easy explanation for this. The first region corresponds to less crystalline, reactive parts, which are quickly modified, while the second region corresponds to more crystalline, stable parts in fibers.

The general shape of cationization kinetics (Figure 24) is similar to that of other reactions involving cellulose etherification. For the production of carboxymethylcellulose, Hedlund and Gemgard [88] proposed a model comprising two first order rate equations:

$$t < t_c,\ \frac{dX}{dt} = k_1\, X \qquad (11)$$

$$t < t_c,\ \frac{dX}{dt} = k_2\, X \qquad (12)$$

In Equations 11 and 12, t_c is the time at which nearly all reactive parts are modified, X is the fraction of functional groups inserted, and the rate constant k_1 is much higher than the rate constant k_2. Nevertheless, there is not an abrupt discontinuity (Figure 24) and, according to this model, X would not tend towards an asymptotic value.

Again for carboxymethylcellulose, we found the model of Li et al. [89] more appealing. It is a pseudo-first order rate equation:

$$\frac{dX}{dt} = k\,(C - X) \qquad (13)$$

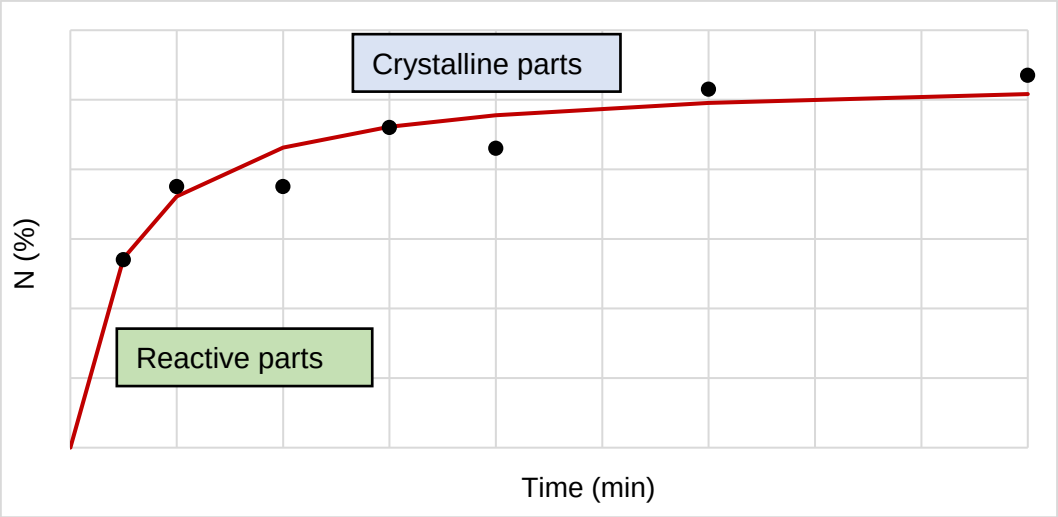

Figure 24. General shape of the kinetic curve for cationization.

Here, *C* is the asymptotic or equilibrium value.

As for cationization, regardless of the raw material used, we got better results by fitting the variation of the mass percentage or mass fraction of nitrogen (*N*) per unit of time (*t*) to a pseudo-second order equation:

$$N = \frac{K_2{}' \, t \, N_{eq}{}^2}{1 + K_2{}' \, t \, N_{eq}} \tag{14}$$

In Publications I and II, the lowest correlation index reached by fitting the results to the linearized form of Equation 14 was 0.979 (Publication II). At the same time, Equation 14 is the integrated form of:

$$\frac{dN}{dt} = K_2{}' \left(N_{eq} - N\right)^2 \tag{15}$$

In Eqs. 14 and 15, K_2' resembles the constant of common chemisorption models. According to Plazinski et al. [90], pseudo-second order equations are useful for a very broad spectrum of sorbates and sorbents, as long as the *surface reaction* controls the overall kinetics. In this case, in which the thermodynamic stability of cellulose polymorphs is even more important than mass transfer limitations, what is called the *surface reaction* would involve all reactive parts. Because of the alkaline pretreatment, they are more abundant on the surface.

However, K_2' depends on the concentration of reagents, or at least on the concentration of homogeneous catalyst (caustic soda). Later, in Publication VIII, we got acceptable results ($R^2 > 0.95$) by defining a concentration-independent constant, K_2, and assuming first-order dependence of the reaction rate on NaOH concentration:

$$\frac{dN}{dt} = K_2 \, [NaOH] \left(N_{eq} - N\right)^2 \tag{16}$$

In Equation 16, N is expressed as mass fraction of nitrogen (ωN), while K_2 is to be expressed in L mol^{-1} min^{-1}.

However, Equation 16 was tested for a constant NaOH/CHPTAC mole ratio (Publication VIII). The high correlation indices obtained do not mean that K_2' does not depend on CHPTAC concentration, as the influence of CHPTAC may be contained in that of NaOH. Various NaOH/CHPTAC ratios should be tried to determine the impact of the cationizing agent on the reaction rate.

Results do **not support** Hypothesis 3: *The rate of cationization of low-DP cellulose is greater than the rate of cationization of high-DP cellulose*. Crystallinity seemed to hinder cationization much more than the degree of polymerization (DP), whose influence, if any, was very slight. The intrinsic viscosity of commercial alpha-cellulose, 242 mL/g, was higher than that of cotton linters, 218 mL/g (Publication III). This meant that the first material had a higher molecular weight, according to the Mark-Houwink equation (*vid. 4.3. Viscometry*). But the crystallinity of cotton linters was higher too, and this alone can explain their lower degrees of substitution (Publication III). This does not imply that the hypothesis should be rejected or refuted, but specific research would be needed to address the influence of DP on the cationization rate.

6.1.3. Effects of cationization on cellulosic materials

Hypothesis 4 is **supported** by Publication III and Publication IV. *Cationization of cellulose has a positive impact on intrinsic viscosity (or in the limiting viscosity number)*. Figure 25 displays the Pearson's coefficient for the relationships between the limiting viscosity number (η) and DNS. Cationized cotton linters, cellulose powder and softwood fibers are considered.

While the results do not allow us to conclude that the intrinsic viscosity is linearly proportional to the degree of substitution —R^2 would be as low as 0.65 for alpha-cellulose powder—, it goes without a doubt that the former increases with the latter. Yet, Yan et al. [8] found the opposite, associating the decreasing viscosity to alkaline hydrolysis of cellulose during cationization with NaOH and EPTAC, even though the conditions were mild. But experiments with size-exclusion chromatography showed that depolymerization during cationization is negligible [91]. Our observations support those of Song et al. [91], which drive us to propose:

- *Conjecture 1*: At 70 ºC or less, NaOH concentration being below 5% (w/w), alkaline hydrolysis can be neglected.
- *Conjecture 2*: Cationization changes how the polymer chain is distributed in space, becoming more extended. Therefore, it interacts with the solvent and with other chains in a different way.

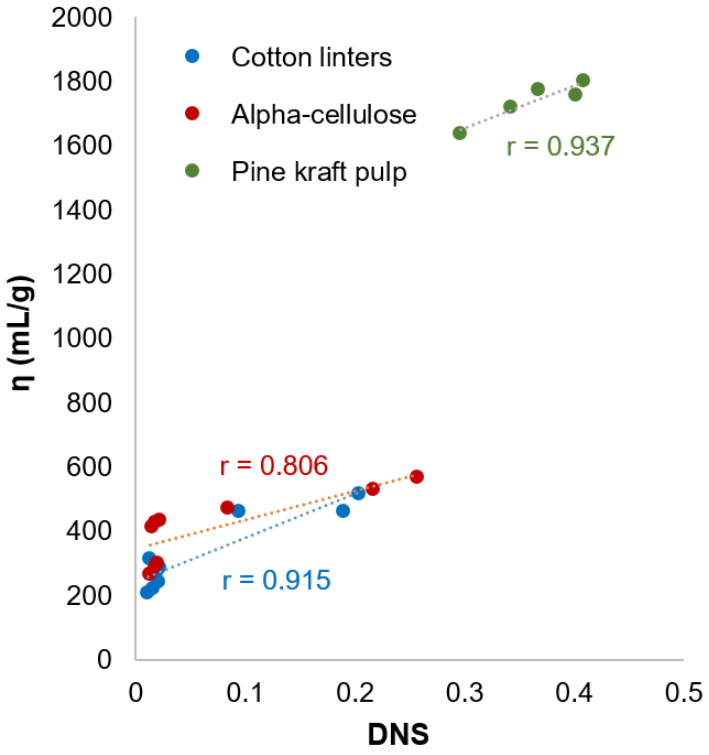

Figure 25. Correlations between the intrinsic viscosity or limiting viscosity number and the degree of nitrogen substitution (Publication III, Publication IV).

In Publication V, viscosity measurements were used to estimate the molecular weight, and thus the degree of polymerization, of cationic cellulose derivatives, but the values taken by *K* and *a* in the Mark-Houwink equation (Eq. 4) correspond to unmodified alpha-cellulose [92]. What we did was measuring the viscosity right before cationization, since it was assumed that cationization involved no significant impact on molecular weight (*Conjecture 1*).

Further experimentation is needed to **test** Hypothesis 6: *Cationization has a positive effect on bulk*. Certainly, the apparent density of pulp pads (Publication IV) and sheets (Publication VIII) decreased, and thus the bulk increased. The apparent density of softwood pulp samples went from 0.57 g cm^{-3} to 0.40 g cm^{-3} (Publication IV). By adding cationic fibers with very low CI to the same pine kraft pulp, the bulk of sheets with TiO_2 increased slightly but significantly, from 0.11 cm^3 g^{-1} to 0.12 cm^3 g^{-1}. However, we could not distinguish whether this increment of bulk was due to decrystallization or to cationization. Decrystallization weakens attractive interactions among hydroxyl groups, while cationic functional groups act as spacers between cellulose chains [93]. In order to test it the effects of each process separately, it would be necessary to cationize pulps by following a non-amorphizing procedure.

6.1.4. Applications of cationic cellulose in papermaking

Cationic cellulose was tested as an additive to the stock in two ways: (i) as insoluble fibers and (ii) as water-soluble derivatives. Both in Publication IV and in Publication VIII, cationic fibers (CF) increased the retention of fines, thus **supporting** Hypothesis 7.1: *Cationic fibers enhance the retention of fines during sheet formation*. However, retention of precipitated calcium carbonate (PCC) was not enhanced by the use of CF from a pine kraft pulp (Publication IV). This tells **against** Hypothesis 7.2: *Cationic fibers enhance the retention of PCC during sheet formation*.

Adding CF to the furnish in Publication IV made the total retention go from 80% to 89%. Out of the 0.11 g of solids lost per gram of pulp in this experiment with CF, 0.09 g corresponded to PCC. This meant that only 0.02 g of fines per gram of pulp were lost, as exposed in Table 11. We conjectured that fines were retained to a great extent because their surface is negatively-charged in aqueous suspensions, so they tend to collapse over cationic fibers during stirring. Now, I wish to suggest another reason, a reason related to the morphology of the particles. Their surface is far from being totally smooth. Indeed, fibers and fines have hollow centers that make them able to drape over each other, especially after refining [7]. Fiber-to-fiber collapsing is not desired before sheet formation —papermakers do not want fiber bundles to be formed in the head box. But attachment of fines to fibers is desirable and what prevents it from happening at a greater rate is repulsion. Cationizing a part of the pulp, then, promoted attraction and collapsing.

Depending on the source and on the pH, the zeta potential of PCC may be slightly positive or slightly negative (Publication V). Anyway, PCC autoflocculation occurs, without aids, and once the particle size stops increasing, cationic patches or neutralization will not result in a noticeable change. In papermaking, PCC's primary flocculation mechanism is bridging [64], while electrostatic interactions play a minor role. This is why PCC retention was not enhanced (Table 11). It is clear that cationic cellulose could only work by bridging mechanisms if dissolved, and only if its chains are long enough (*vid. 3.3.4. Wet end chemistry and the limitations of recirculating water*).

ECOWAL did not give up on the idea of improving filler retention with CF, but a different mineral compound had to be chosen. The choice was titanium dioxide, which is expensive and is usually relegated to be used as coating of specialty papers, but its strongly negative zeta potential drove us to ask for a sample. The zeta potential of TiO_2 powder suspensions at pH 6 lies around -65 mV [94]. This implies that TiO_2 particles are highly stable, not prone to aggregation. Instead, they tend to stay dispersed. The addition of positively-charged fibers can decrease the stability of mineral particles with highly negative zeta potential.

Table 11. Performance of cationic cellulose, in the form of insoluble fibers or soluble derivatives, in retention and flocculation essays.

Agent	Tested with	Performance	Source
Cationic fibers	Fines	Losses reduced to 0.02 g per gram of pulp	Publication IV
	PCC	No significant effect	
	TiO_2	Higher brightness gain when CF are used	Publication VIII
Water-soluble cationic cellulose derivatives	PCC	Poor. Slow flocculation	Publication V
	GCC	Fast flocculation, but floc size levels off too soon	
	Kaolin	Even better than CPAM	

Results **supported** Hypothesis 7.3: *Cationic fibers enhance the retention of TiO_2 during sheet formation*. Hence, cationic fibers can enhance filler retention, as long as the filler particles are stable by virtue of their negative electrokinetic potential.

It should be noted that the particle size of TiO_2 —300-400 nm, not prone to autoflocculation— was much lower than that of PCC —around 5.5 μm after autoflocculation. Further experimentation is required to address the effects of particle size and particle shape on the performance of cationic fibers.

Like cationic fibers, soluble cationic derivatives from cellulose showed their worst performance as flocculation agents when the filler was PCC (Table 11). The medium-DP derivative and the low-DP derivative did not boost PCC flocculation at all, while the high-DP derivative promoted a slow increment of floc size. Still, its molecular weight was at least one order of magnitude below that of the cationic polyacrylamide (CPAM) used, which was able to duplicate the median particle size of PCC —from 4 μm to 8 μm— in 3 min (Publication V). Producing polymers for PCC flocculation requires them to be long-chained and soluble at the same time, which is particularly challenging when the raw material is cellulose. Therefore, evidence **does not support** Hypothesis 8.1: *Cationization of cellulose can produce soluble derivatives to enhance flocculation of PCC*.

The best of the soluble derivatives, the one whose DP and DS were the highest, promoted fast flocculation of GCC, even faster than when CPAM was used. To reach a median particle size of 3.5 μm, starting from 2.2 μm, cationic cellulose needed 1.5 min under stirring, while CPAM required 3 min. As a drawback, large flocs could not be achieved (Publication V). While the surface charge of GCC is negative, its scalenohedral shape may have hindered flocculation. Producing cationic derivatives by different ways

is advised to **test** Hypothesis 8.2: *Cationization of cellulose can produce soluble derivatives to enhance flocculation of GCC*.

When the filler was kaolin, flocculation was faster and achieved more aggregation with cationic cellulose than with CPAM. Median particle size went from 4 µm to 25 µm in only 2 min (Publication V). This can be explained by the fact that the charge density of the best cationic cellulose derivative was much higher than that of CPAM, and thus its performance in flocculation by neutralization and patching mechanisms is better. The zeta potential of a 1% suspension of kaolin and CPAM at pH 7.1 was -9.7 mV, more stable than a 1% suspension of kaolin and cationic cellulose, whose zeta potential was -7.3 mV. This **supports** Hypothesis 8.3: *Cationization of cellulose can produce soluble derivatives to enhance flocculation of kaolin*.

Fortunately for the applications of cationic fibers in papermaking, results in Publication VIII told **against** Hypothesis 13: *The addition of cationic fibers to the stock favors collapsing, thus slowing dewatering*. Starting from 1 kg of furnish, a filtrate weight of 800 g was reached after 9 s with CF and after 8 s without them. Apparently, formation of fiber bundles during stirring was negligible. The increase in drainage rate was likely due to the higher retention of fines [7]. This does not mean that CF could be used as drainage aids –the improvement was very slight. But they do not hinder sheet formation.

6.1.5. The use of lignocellulosic materials

Unlike semichemical pulps from wheat straw [41], pulps from rapeseed stalks and pulps from orange tree trimmings needed to be refined to show acceptable paper strength. The tensile index was 10.2 N m g^{-1} in the best case, for rapeseed stalks cooked with ethanolamine-water at 180 ºC. The burst index was always lower than 1 kN g^{-1}. Only the tear index was in the high range, always above 3 mN m^2 g^{-1} (cf. [12]). However, the strength of these sulfur-free pulps from lignocellulosic residues was drastically improved by refining to less than 1000 PFI revolutions. Figure 26 shows the tear index, the tensile index and the burst index for the pulps cooked and refined under optimal conditions in each case:

- For rapeseed stalks, ethanolamine (60%) and water (40%) as the cooking liquor, 180 ºC, 60 min, refined to 500 PFI revolutions.
- For orange tree trimmings, ethanolamine (60%) and water (40%) as the cooking liquor, 180 ºC, 60 min, refined to 1000 PFI revolutions.

Hypothesis 10.1 is **supported**: *Rapeseed stalks can be cooked through sulfur-free processes to produce pulps of enough strength for papermaking*. Nonetheless, Hypothesis 10.2 is **partially supported**: *Orange tree trimmings can be cooked through sulfur-free processes to produce pulps of enough strength for papermaking*. It is only

partially supported because the tensile index of pulps from orange tree trimmings was never high enough for paper bags [5]. The use of orange tree trimmings, whose fibers are short and thick (Appendix 2) should be restricted to graphic paper.

Freeness measurements of pulps from both rapeseed stalks and orange tree trimmings **support** Hypothesis 11: *By refining, pulps from rapeseed stalks and orange tree trimmings need less energy than conventional pulps to reach a given value of CSF or SR*. This is common to many non-wood materials (Figure 14), which is why we hypothesized this, but for different reasons.

The freeness of unrefined pulps from wheat straw is similar to that of heavily refined conventional pulps (i.e., kraft pulps from hardwoods and softwoods) because of its high content of fines. Rapeseed stalks are rich in fines too, with much more fines than wood and less than cereal straw, but orange tree trimmings are not. CSF values of pulps from trimmings decreased abruptly because the surface of their fibers was less resistant than that of wood fibers. It was easily roughened by refining. Anyway, spending less energy to achieve a certain freeness value is an advantage, both for rapeseed stalks and for orange tree trimmings. For instance, to get CSF below 400 mL, rapeseed stalks would suffice with 1000 PFI revolutions (Publication VI) and orange tree trimmings would need 1250 PFI revolutions, while common hardwoods may require 2000 PFI revolutions [57].

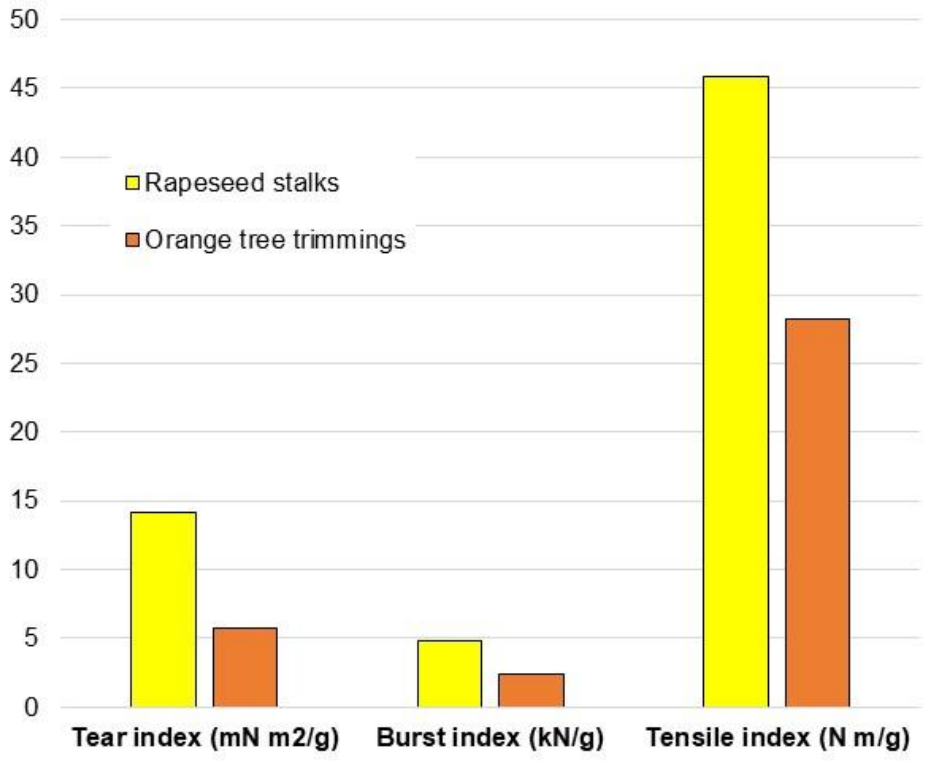

Figure 26. Strength indices for an organosolv pulp from rapeseed stalks (Publication VI) and for an organosolv pulp from orange tree trimmings (Publication VII).

Evidence in Publication VII **supported** Hypothesis 12: *One-step bleaching with hydrogen peroxide can achieve a high brightness gain*. By bleaching an organosolv pulp from orange tree trimmings at 85 ºC for 150 min, spending 0.1 g of H_2O_2 per gram of pulp, brightness went from 34.5% to 72.9%.

Hydrogen peroxide is not a cheap reagent and a residence time of 150 min would be unacceptable, but we found severe conditions unnecessary. Bleaching at 70 ºC for 90 min, spending 0.06 g of H_2O_2 per gram of pulp, raised brightness from 34.5% to 68.3% (Publication VII).

What is more remarkable of Publication VII is that the pulp was, in principle, hardly bleachable. Its kappa number, instead of lying below 30, was 52. Its lignin content was too high for conventional bleaching. But, unlike other bleaching reagents, hydrogen peroxide bleaching is not based on lignin removal. It is based on the oxidation of chromogenic groups [97]. This conjecture was corroborated by the very slight decrease in the kappa number by H_2O_2 bleaching (Publication VII).

As aforementioned, titanium dioxide is expensive, but its characteristics made it a good choice to test the potential of cationized pulps from lignocellulosic residues. Besides its negative zeta potential, a small amount of TiO_2 has a strong positive impact on brightness and opacity, but it is easily lost upon filtration. In Publication VIII, cationic fibers from wheat straw, rapeseed stalks and orange tree trimmings enhanced this impact on brightness and opacity by reducing TiO_2 losses. This **supports** Hypothesis 14: *Lignocellulosic residues can be cationized to produce valuable fibers to be added to conventional pulps, with the goal of enhancing the optical properties of the final product*. Due to electrostatic interactions, many mineral particles became attached to cationic fibers but, fortunately, micrographs of handsheets did not show excessive agglomeration of TiO_2 (Publication VIII).

Figure 27 displays the opacity gain in Publications IV and VIII, defined as follows:

$$Opacity\ gain(\%) = \frac{Opacity\ with\ fillers - Opacity\ without\ fillers}{Opacity\ without\ fillers} 100 \quad (17)$$

The improvement caused by cationic fibers from pine wood (PCF) in Publication IV was due to the impact on the retention of fines, not to PCC retention. Cationic fibers from wheat straw (WCF), from orange tree trimmings (OCF) and from rapeseed stalks (RCF) increased the opacity gain achieved by TiO_2 and fines to a greater extent than 5 mg/g of CPAM.

However, whilst the opacity gain was higher when using CF, the brightness gain was higher when using CPAM. With CF from lignocellulosic residues, brightness went from 37.8% —unbleached pulp and TiO_2 alone— to 41.5-41.9%.

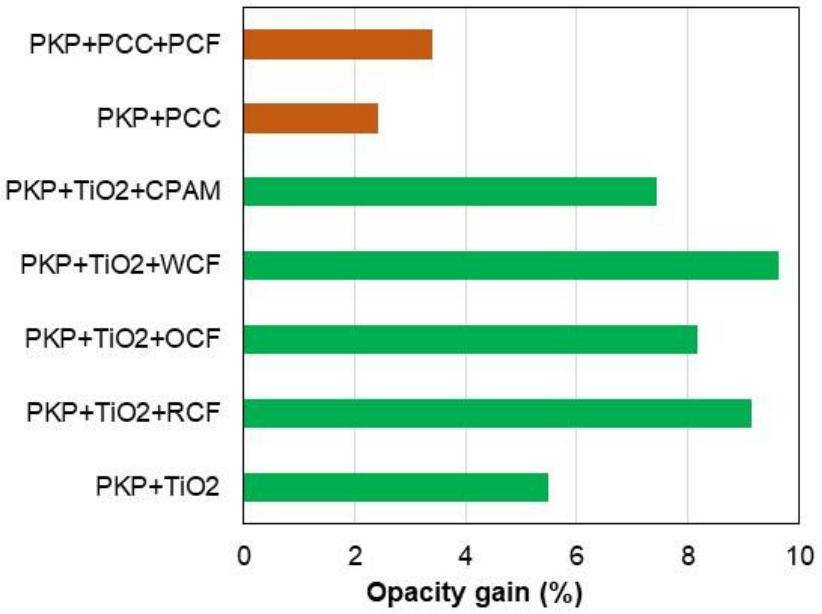

Figure 27. Opacity gain with PCC and cationic fibers from pine (Publication IV), and with TiO_2 and cationic fibers from wheat straw, orange tree and rapeseed stalks (Publication VIII).

With the addition of CPAM, brightness reached 43.3% (Publication VIII). We conjecture that the latter is probably the best choice to enhance TiO_2 retention, while CF are better when it comes to enhance the retention of fines.

6.2. Concluding remarks

The contribution made by this research involves answers to several questions related to the functionalization —specifically, cationization— of cellulose with CHPTAC, from studies on different raw materials to the applications in papermaking. Native cellulose is not prone to cationization, but decrystallization with NaOH (20-30%) at room temperature activated the polymer. Between the degree of substitution of cationic fibers from highly-crystalline cellulose and that of cationic fibers from severely amorphized cellulose, there was a difference of one order of magnitude, as shown for cotton linters and commercial cellulose. The role of NaOH also involved the conversion of CHPTAC into EPTAC, the true cationizing agent, and deprotonating at least one hydroxyl group in AGU to promote cellulose etherification.

We successfully fitted reaction kinetics to a pseudo-second order rate equation with first order dependence on NaOH concentration. Correlation indices above 0.95 were obtained. The maximum degree of substitution reached was strongly dependent on the crystallinity index, whose influence was negative, and on the CHPTAC/AGU mole ratio, whose influence was positive.

Out of all the materials used in our works, the fibers with the highest degrees of substitution were produced from pine kraft pulp. The high degree of polymerization of cellulose in this material allowed the polymer to stay insoluble even after reaching DS values of approximately 0.4. These cationic fibers, when added to the original pulp to form a paper sheet, clearly improved the retention of fines, whose surface is negatively charged, but not PCC retention. Likewise, cationic fibers from rapeseed stalks, orange tree trimmings and wheat straw increased the opacity of sheets to a greater extent than CPAM, a conventional cationic polyelectrolyte. We conjectured that fines tend to collapse over cationic fibers during stirring of the furnish and/or during sheet formation.

Cotton linters and commercial cellulose, for instance, could be used right away, while wood and lignocellulosic residues needed to be delignified. This delignification of wheat straw, rapeseed stalks and orange tree trimmings was successfully performed by soda-anthraquinone pulping. While cereal straw had been widely studied long before the writing of this dissertation, I presented two publications of ours dealing with rapeseed stalks and orange tree trimmings. We found out that cooking them with ethanolamine (60%) / water (40%), at 180 ºC and for 60 min, yielded even better results than soda-anthraquinone pulping, reaching tensile indices of 46 N m g^{-1} for rapeseed stalks and 28 N m g^{-1} for orange tree trimmings. Cationic fibers from these materials improved the retention of TiO_2, whose highly negative zeta potential —around 60 mV— prevents particle aggregation, but not as much as CPAM did.

Besides cationic fibers, water-soluble cationic derivatives were also tested. For performance reasons, I remark a derivative with a degree of substitution of 0.46 and a degree of polymerization of approximately 1700. Its enhancement of kaolin flocculation surpassed even the addition of CPAM. However, due to the inability of cationic cellulose to work by bridging mechanisms, the trials with PCC yielded very modest results.

Although further research is required to address the feasibility of using cationic cellulose in papermaking, these findings show what can and cannot be improved by its addition. We suggest a mild process, insisting on the importance of the pretreatment and, if possible, reusing waste from agriculture.

6.3. Future research

In the publications and all along this dissertation, some **research limitations** hindered the testing of certain hypotheses. For instance, when functionalizing cellulose, the focus was only on one procedure to cationize the polysaccharide –a procedure involving decrystallization. This prevented us from telling whether certain effects, such as the increase in bulk, were due to the insertion of charged functional groups in cellulose

or to the fact that cationized fibers had been amorphized before. Moreover, we have noted the lack of a convention regarding the estimation of crystallinity. As a consequence, the crystallinity index is reported only for comparison purposes. And while we presented gallium pycnometry as a novel way to measure the apparent density of pulp pads, this novelty was due to the impossibility of using mercury pycnometry.

To address unanswered questions, further research involves an **alternative approach to cationize cellulose**. When the aim is to produce cationic fibers, the method should have little effect on crystallinity. When water-soluble derivatives are produced, the reaction should reach very high degrees of substitution (above 0.5) for cellulose of high degree of polymerization.

The finding that adding cationic fibers to the stock increases the retention of fines, with no detrimental effect on dewatering and sheet formation, leads us to consider the **cationization of fines**. Would adding cationic fines to the stock result in good retention of all fines? Would only the cationic fines be affected? Continuous imaging of the stirring suspension could throw some light on how cationic fines are attached to fines and fibers, or on how cationic fibers are attached to negatively-charged fines.

Other than wheat straw, rapeseed stalks and orange tree trimmings, we have been considering **different raw materials**. We got some work done that is patiently waiting to be published. Also, we are testing a new hypothesis related to the activation of cellulose before cationization, using various reagents.

Working with papermakers could be very fruitful. Scientific findings cannot be subject to market mechanisms but, as long as they can allow manufacturers to address environmental issues, collaboration is key to transfer results to society.

And to finish this dissertation with what could be a little flash of genius, I would like to try **ammonia fiber expansion**. It would be performed with lignocellulosic residues, with the raw materials, with a twofold aim of delignifying and decrystallizing. According to my hypothesis, the cellulosic material resulting from this treatment would be ready for many sorts of functionalization, including cationization.

7. OTHER WORKS (related to the PhD thesis)

7.1. Publications in JCR-indexed journals

The four papers referenced in this section deal with lignocellulosic residues. They can be consulted for more information regarding cereal straw, rapeseed stalks and orange tree trimmings. The works published in *J. Spectrosc*., *Ind. Crops. Prod*. and *Measurement* suggest timesaving and non-destructive ways to predict key properties of pulps. The article published in *BioResources* presents the convenience of using mechanical and thermomechanical pulps from rapeseed stalks.

- **NIRS characterization of paper pulps to predict kappa number**

Authors: Ana Moral (corresponding author), Elena Cabeza, Roberto Aguado, Antonio Tijero.

Reference: Moral, A., Cabeza, E., Aguado, R., Tijero, A. *J. Spectrosc*. 2015: 6 pages (2015). DOI: 10.1155/2015/104609.

Abstract: Rice is one of the most abundant food crops in the world and its straw stands as an important source of fibres both from an economic and an environmental point of view. Pulp characterization is of special relevance in works involving alternative raw materials, since pulp properties are closely linked to the quality of the final product. One of the analytical techniques that can be used in pulp characterization is near-infrared spectroscopy (NIRS). The use of NIRS has economic and technical advantages over conventional techniques. This paper aims to discuss the convenience of using NIRS to predict Kappa number in rice straw pulps produced under different conditions. We found that the resulting Kappa number can be acceptably estimated by NIRS, as the errors obtained with that method are similar to those found for other techniques.

- **Morphological analysis of pulps from orange tree trimmings and its relation to mechanical properties**

Authors: Roberto Aguado, Ana Moral (corresponding author), Patricio López, Pere Mutjé, Antonio Tijero.

Reference: Aguado, R., Moral, A., López, P., Mutjé, P., Tijero, A. *Measurement* 93: 319-326 (2016).

Abstract: To optimize the pulping and refining processes of new alternative raw materials for papermaking, researchers generally perform tests that consume

considerable time and large amounts of sample. We propose measuring the morphological properties of pulps from orange tree trimmings by image analysis systems, which are fast and user-friendly, to develop models relating key mechanical properties to the dimensions, the deformation and the population of fibers. Data modeling involves multiple linear regression, as used in other studies, and support vector regression, not used before for this purpose, achieving higher R^2 values (up to 0.90). Although tensile, tear and burst tests are still required to obtain accurate values, a quick morphological characterization allows for a rough but satisfactory prediction of paper strength. In this case, chemical pulping and moderate refining are shown to be necessary to obtain pulps of acceptable quality from orange tree trimmings.

Graphical abstract: Figure 28.

- **Relating near infrared spectra of *Oryza sativa* pulps to paper mechanical strength and brightness**

Authors: Ana Moral (corresponding author), Elena Cabeza, Roberto Aguado, Antonio Tijero.

Reference: Moral, A., Cabeza, E., Aguado, R., Tijero, A. *Ind. Crops Prod*. 89: 493-497 (2016).

Abstract: Rice straw pulps produced under different conditions were subject to near infrared (NIR) spectroscopy. At the same time, samples from those pulps were used to make handsheets, whose mechanical properties were measured. These values and those of brightness were successfully fitted to the pulping variables. Relating them to the NIR spectra, we found valid correlations for all parameters except the burst index, concluding that NIR spectroscopy could be used as an economical, timesaving and non-intrusive way to predict the mechanical strength of pulps before the paper sheet is made.

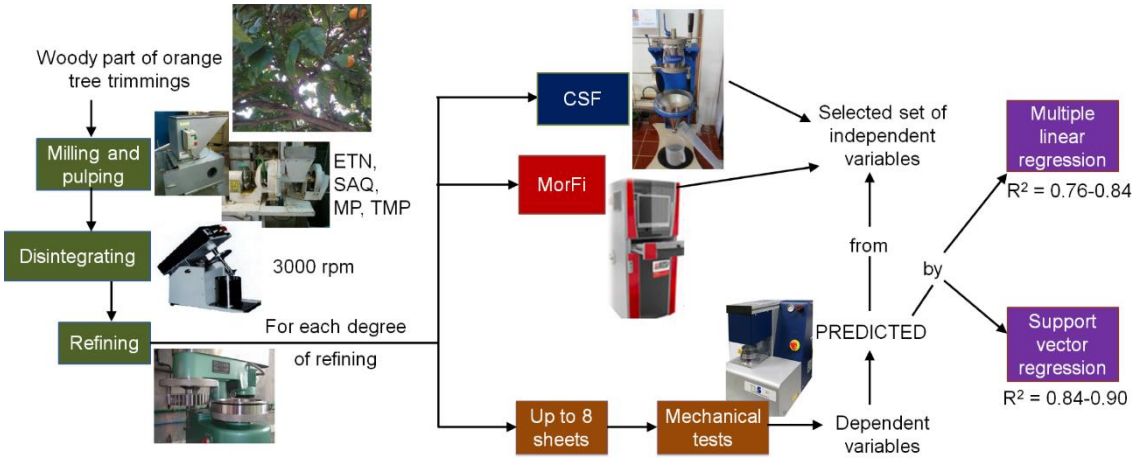

Figure 28. Graphical abstract included in Aguado et al. [76].

- **High-yield pulp from Brassica napus to manufacture packaging paper**

Authors: Ana Moral (corresponding author), Roberto Aguado, Antonio Tijero, Quim Tarrés, Marc Delgado-Aguilar, Pere Mutjé, 2017.

Reference: Moral, A., Aguado, R., Tijero, A., Tarrés, Q., et al. *BioResources* 12(2): 2792-2804 (2017).

Abstract: The stalks that are left on the field after harvesting rapeseed crops could be used to make packaging grade paper. This work evaluates the suitability of mechanical and thermomechanical pulps from rapeseed stalks for papermaking, with a view to alleviating the limitations of recycled fluting. Their performance was compared to that of commercial fluting (recycled fluting) of the same basis weight, 100 g/m^2, and to that of virgin pulps from pine wood. The thermomechanical pulp was refined to improve key mechanical properties. Its drainability was found to be very low, even before refining, and its breaking length after beating to 1200 PFI revolutions, 4 km, surpassed that of sheets of recycled fluting that were obtained under similar conditions. These findings support the hypothesis that high-yield pulps from rapeseed stalks are a strong choice of virgin fibres to produce fluting and, generally speaking, packaging paper.

7.2. Conference papers, posters and oral communications

All contributions listed below deal with cationization of cellulose, pretreatments suggested to activate cellulose before functionalization, and/or lignocellulosic residues. For more detail, the reader is invited to visit my ResearchGate profile (Roberto_Aguado2).

Moral, A., Aguado, R., Cabeza, E., Ballesteros, M., Tijero, A. “TCF bleaching of Organosolv pulp from orange tree trimmings.” EWLP: 13th European Workshop on Lignocellulosics and Pulps, Seville, Spain (2014).

Aguado, R., Moral, A., Pérez, A., Monte, M.C., Tijero, A. “Potential of rapeseed stems as an alternative raw material for papermaking purposes.” EWLP: 13th European Workshop on Lignocellulosics and Pulps, Seville, Spain (2014).

Moral, A., López, M.M., Aguado, R., Torrecilla, J.S., Tijero, A. “Cellulose from Ulva sp. as a reinforcing fibre for the pulp and paper industry.” EWLP: 13th European Workshop on Lignocellulosics and Pulps, Seville, Spain (2014).

López, M.M., Moral, A., Aguado, R., Campaña, M.L, Tijero, A. “Evaluation of Bloom algae as raw material for papermaking.” EWLP: 13th European Workshop on Lignocellulosics and Pulps, Seville, Spain (2014).

Tijero, A., Hernández, M.D., Moral, A., Aguado, R., De la Torre, M.J. “Relationship among cationization degree, crystalline structure and viscosity of cationized cellulose.” EWLP: 13th European Workshop on Lignocellulosics and Pulps, Seville, Spain (2014).

Tijero, A., Hernández, M.D., Moral, A., Aguado, R., De la Torre, M.J. “Electrokinetic properties (cationic demand) of cellulose suspensions.” EWLP: 13th European Workshop on Lignocellulosics and Pulps, Seville, Spain (2014).

Monte, M.C., Aguado, R., Tijero, A., Moral, A. “Use of orange tree prunings as an alternative source of fibres for papermaking.” VIII International Congress of ANQUE: Science and Technology of Materials, Madrid, Spain 2014.

Ballesteros, M.M., Moral, A., Lorenzo, A., Aguado, R., Tijero, A. “Zoostera noltii como materia prima alternativa en la extracción de celulosa.” CONAMA, Madrid (2014).

Moral, A., Cabeza, E., Aguado, R., Tijero, A. “NIRS en la determinación de las propiedades de la pasta de papel.” CONAMA, Madrid, Spain (2014).

Moral, A., Aguado, R., Espinosa, E., Tijero, A., Jiménez, L., Rodríguez, A. “Influence of mercerization-cationization process in the structure of cellulose.” 2nd International Conference on Natural Fibers, São Miguel, Portugal (2015).

Moral, A., Aguado, R., Rodríguez, A., Espinosa, E., Tijero, A. “Cationization of soda-AQ pulps and its influence on retention effectiveness.” 18th ISWFPC, Vienna, Austria (2015).

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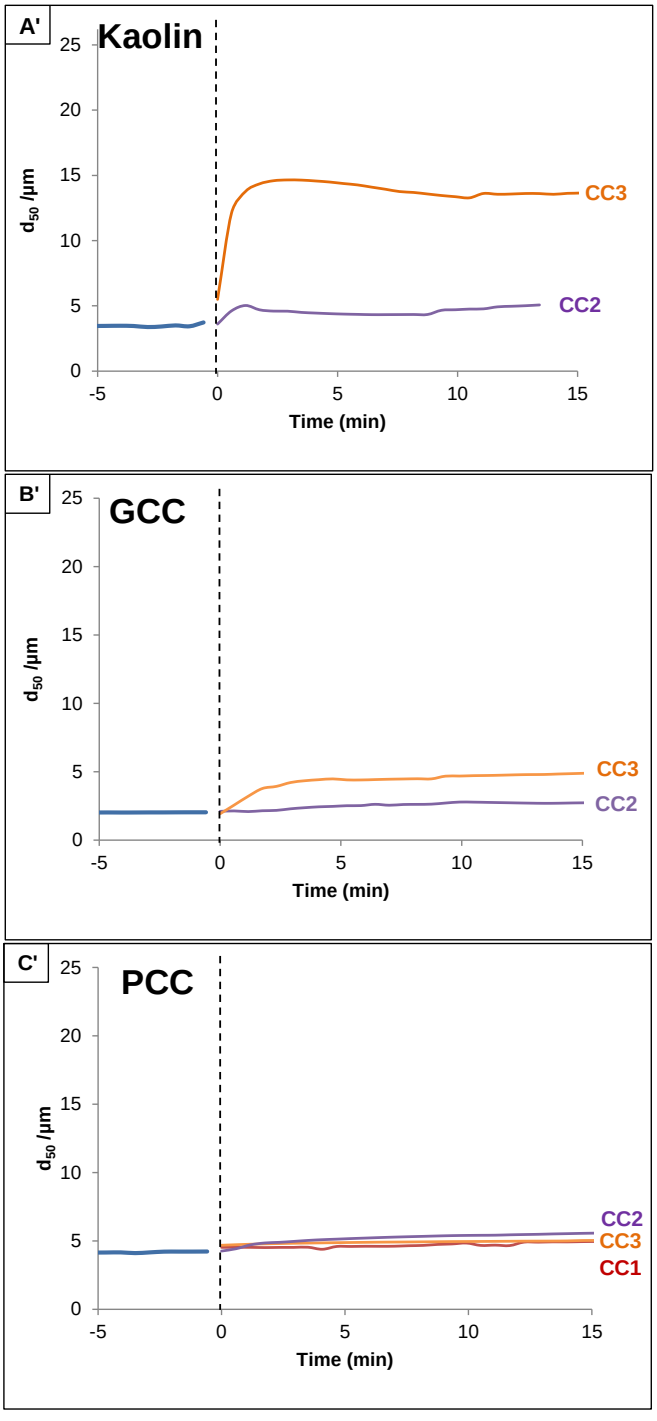
APPENDIX 1

Supplementary information for **Publication V**: *Cationic cellulosic derivatives as flocculants in papermaking*.

Flocculation kinetics of the three mineral fillers with the cationic cellulosic derivatives (CC1, CC2 and CC3), measured by laser diffraction spectrometry (Mastersizer 2000, Malvern Instruments). The dosage of cationic cellulose is 10 mg per g of filler.



APPENDIX 2

Additional information for **Publication VII**: *Papermaking potential of Citrus sinensis trimmings using organosolv pulping, chlorine-free bleaching and refining*. Not included in the submission.

While Publication VI shows morphological data for chemical pulps from rapeseed stalks, the focus of Publication VII is more particularly in bleaching. This appendix presents the results from the morphological characterization of soda-anthraquinone, organosolv, mechanical and thermomechanical pulps from orange tree trimmings.

The different levels of refining are expressed by the Canadian Standard Freeness (CSF).

Pulp 1-6: Organosolv pulp, ethanolamine 60%, 180 ºC, 60 min.

Pulp 6-12: Organosolv pulp, ethanolamine 40%, 140 ºC, 40 min.

Pulp 13-18: soda-anthraquinone pulp, NaOH 15%, anthraquinone 0.1%, 140 ºC, 40 min.

Pulp 19-24: soda-anthraquinone pulp, NaOH 15%, anthraquinone 0.1%, 140 ºC, 40 min.

Pulp 25-30: mechanical pulp.

Pulp 31-36: thermomechanical pulp, water 100%, 180 ºC, 60 min.

NF: number of fibres per gram. *L*: fibre length (weighted in length). *W*: fibre width. *CN*: coarseness. *KF*: percentage of kinked fibres. *CI*: curl index. *MF*: percentage of microfibrils (in area). *BE*: percentage of broken ends. *FI*: percentage of fines (in area).

Pulp code	CSF (mL)	NF (10^6 g^{-1})	L (μm)	W (μm)	CN (mg/m)	KF (%)	CI (%)	MF (%)	BE (%)	FI (%)
1	692	20.8	543	20.7	0.134	22.2	6.87	29.5	1.3	4.7
2	588	27.3	538	19.5	0.099	20.2	7.13	30.2	1.5	5.3
3	548	27.4	518	19.3	0.092	19.2	7.13	30.9	1.5	6.7
4	459	29.6	502	19.3	0.083	16.9	6.38	32.0	1.7	6.9
5	435	27.1	483	19.1	0.089	16.7	6.85	32.6	1.5	6.2
6	355	32.6	483	19.5	0.081	15.7	6.26	33.9	1.7	7.3
7	683	16.2	541	22.6	0.159	24.1	7.80	35.7	1.3	7.7
8	561	19.4	507	22.0	0.135	24.1	8.27	36.5	1.3	9.0
9	488	19.5	489	21.3	0.130	22.9	8.28	35.9	1.5	9.4
10	428	20.1	464	21.0	0.131	22.7	8.07	35.5	1.4	9.9
11	411	23.3	452	20.9	0.122	21.7	8.08	36.9	1.7	10.6
12	398	23.5	438	20.8	0.111	20.5	7.97	36.9	1.6	9.8
13	606	23.4	575	19.2	0.099	20.6	6.79	28.4	1.2	7.5
14	389	30.0	582	19.4	0.087	22.3	8.10	27.9	1.4	10.4
15	365	28.7	565	19.3	0.082	22.0	8.06	30.5	1.5	10.9
16	315	30.3	559	18.9	0.078	20.7	7.67	29.0	1.5	11.3
17	295	30.0	543	19.9	0.083	20.1	7.84	33.4	1.6	12.1
18	289	37.3	532	19.8	0.068	19.8	7.77	34.1	1.8	12.7
19	645	18.6	510	21.2	0.116	23.9	7.28	34.8	1.7	4.3
20	391	25.2	513	21.7	0.110	22.3	7.78	37.4	1.7	5.3
21	354	25.2	510	21.2	0.104	21.8	8.14	34.8	1.7	5.1
22	333	26.6	496	20.8	0.102	22.2	8.21	35.9	1.7	5.7
23	280	28.3	489	20.8	0.098	22.6	8.63	36.4	1.8	5.7
24	276	26.5	485	20.8	0.090	22.4	8.95	36.6	1.8	5.8
25	729	12.8	445	21.1	0.226	14.3	4.19	32.8	1.1	23.3
26	693	13.0	441	21.3	0.236	14.1	4.30	33.5	1.2	21.5
27	661	14.1	422	21.2	0.219	14.2	3.91	33.8	1.2	21.4
28	625	14.0	411	21.0	0.221	13.9	3.98	32.9	1.2	22.4
29	597	13.9	385	20.8	0.230	14.4	4.14	33.4	1.3	23.4
30	584	15.7	406	21.0	0.202	14.2	4.09	34.7	1.3	22.9
31	712	8.4	467	25.0	0.421	13.9	5.02	37.9	1.2	16.9
32	648	8.6	371	21.4	0.314	14.0	5.12	40.3	1.6	18.0
33	645	9.3	356	24.4	0.386	13.8	4.88	39.1	1.5	19.4
34	593	9.8	342	24.5	0.376	13.8	4.90	41.4	1.5	19.0
35	591	11.9	333	24.5	0.315	14.4	5.09	41.9	1.7	19.0
36	532	10.9	322	24.2	0.351	15.0	5.18	41.4	1.6	18.9

ABOUT THE AUTHOR

Aguado graduated from Complutense University of Madrid in February 2013 with a 5-year Chemical Engineering degree, Environmental Specialization. In February 2015 he completed a 2-year master's degree on Process Engineering. He has been a PhD student in Pablo de Olavide University (Seville) since November 2014. This three-year period has resulted in 12 JCR publications and 25 contributions to congresses. More importantly, a lot of know-how on R&D, science and technology has been acquired. Aguado likes to write and he is fairly good at it, even considering that he is clumsily describing himself in the third person right now. Anyway, research articles are not the only thing his keyboard produces. One could —should— pay a visit to his blog, *Herencia Sostenible*, in which Aguado talks humbly of the things he knows and arrogantly of the things he utterly ignores. The book series "El mundo del interior de la tostadora" is authored by him.

SOBRE EL AUTOR

Aguado se tituló en la Universidad Complutense de Madrid en febrero de 2013 como Ingeniero Químico con especialidad medioambiental. En febrero de 2015, finalizó un máster de dos años en Ingeniería de Procesos. Ha sido doctorando en la Universidad Pablo de Olavide (Sevilla) desde noviembre de 2014. Este período de tres años ha resultado en 12 publicaciones JCR y 25 contribuciones a congresos, pero lo más importante es el conocimiento adquirido sobre I+D, ciencia y tecnología. Aguado disfruta escribiendo y se le da bastante bien, incluso teniendo en cuenta su perniciosa tendencia a hablar de sí mismo en tercera persona. De todas formas, los artículos científicos no son lo único que produce su teclado. El lector puede y debe visitar su blog, *Herencia Sostenible*, donde Aguado habla humildemente de las cosas que conoce y arrogantemente de las cosas que ignora. La serie literaria «El mundo del interior de la tostadora» lleva su firma.

http://herenciasostenible.com

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