Universidade de Aveiro
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Dissertação à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Doutor em Engenharia Química – Especialização em Engenharia de Materiais e Produtos Macromoleculares, realizada sob a orientação científica do Doutor Dmitry Evtyugin, Professor Associado com agregação do Departamento de Química da Universidade de Aveiro e Engenheira Sofia Reis Jorge, Diretora Executiva de Sustentabilidade do Grupo Altri.

Para o João e Miguel

o júri

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palavras-chave

Propriedades de absorção, agentes desligantes, *Eucalyptus globulus*, pasta *fluff*, pressão hiperbárica, hornificação, isotermas de sorção, estabilidade de rede da fibra

resumo

A maior parte de pasta *fluff* produzida mundialmente é utilizada na produção de absorventes, fraldas descartáveis, produtos íntimos e não-tecidos. Os pré-requisitos para pasta *fluff* são bem diferentes das pastas para produção de pasta de papel. As propriedades mais importantes da pasta *fluff* são a capacidade e velocidade de absorção, elevado volume específico, comprimento de fibra, índice de encaracolamento e resistência de rede. Geralmente, a pasta *fluff* é produzida com pasta branqueada de madeira resinosa (BSKP) e pasta quimiotermomecânica (CTMP). No entanto, o potencial da madeira de *Eucalyptus globulus* para a produção deste tipo de pasta é incerto. Neste estudo, a pasta kraft branqueada de madeira de *E. globulus* (BEKP) foi avaliada para produção de pasta *fluff* e a pasta obtida foi comparada com as propriedades da pasta *fluff* (BSKP) comercial.
Uma série de seis pastas industriais branqueadas predominantemente de eucalipto (BEKPs), produzidas sob condições extremas foram desfibradas, a seco, num moinho de martelos, em escala piloto, avaliadas as suas características básicas de pasta *fluff*, nomeadamente o seu volume específico, capacidade de absorção e velocidade de absorção e a estabilidade de rede. Foi avaliado o efeito de aglomerados de fibras não desfibrados (knots) presentes nas pastas. As variações processuais do cozimento e branqueamento revelaram uma variabilidade de 15% na capacidade de absorção das pastas *fluff* e cerca de 25% na estabilidade de rede. Estas variações são atribuídas às alterações na composição química e morfologia de fibras de BEKPs. Foi evidenciada a importância da sequência de branqueamento das pastas BEKPs para aplicações *fluff*. As BEKPs com elevado teor de xilana residual, maior quantidade de frações urónicas/hexenurónicas e fibras encaracoladas/deformadas revelaram uma melhor performance para aplicações *fluff*. O parâmetro coarseness foi considerado um parâmetro morfológico crítico das fibras, afetando fortemente a porosidade das formulações *fluff*, determinante para a capacidade de absorção e estabilidade de rede. A capacidade de absorção da pasta *fluff* BEKP, em comparação com a pasta comercial branqueada de fibra longa (BSKP), foi quase o dobro, embora a pasta comercial tenha apresentado cerca do triplo do resultado de estabilidade de rede determinado na formulação ao ar de pasta *fluff*. As pastas BSKP são mais vulneráveis às condições de desfibramento a seco em comparação com as pastas BEKP e as suas fibras sofreram um pronunciado corte, produzindo uma elevada quantidade de finos (*dust*) e um indesejável *peeling* e endireitamento de fibras. As mesmas pastas industriais kraft branqueadas de eucalipto (pastas *fluff*) foram estudadas para as propriedades de absorção aplicando a sorção dinâmica de vapor e medição de ângulos de contacto. Os resultados mostraram que a acessibilidade da superfície da fibra está relacionada com a redução de ângulos de contacto, mas simultaneamente ao maior tempo de absorção e menor capacidade de absorção da rede de fibra. Portanto, as propriedades de absorção das pastas não estão necessariamente relacionadas com as propriedades da superfície. De facto, a absortividade está relacionada com a composição química da superfície, morfologia da fibra e estrutura da rede de fibra. Deste modo, os grupos carboxílicos de superfície promovem a absorção total de água, resultando numa melhor capacidade de absorção. O maior *coarseness* e deformações da fibra (*curl* e *kink*) promovem uma superfície menos molhável, mas uma rede mais porosa, com maior volume específico, resultando em formulações mais absorventes.

Tendo em consideração que as múltiplas variáveis do processo industrial não permitiram traçar de modo inequívoco as relações entre as condições processuais e as propriedades da pasta *fluff*, foram realizados diversos ensaios laboratoriais, em condições controladas, de forma a compreender estas relações. Deste modo, uma série de aparas de madeira ibérica *E. globulus* foram digeridas sob as mesmas condições (160°C, 2h), mas com diferentes cargas álcali ativo (AA) de 13%, 15%, 17% e 18%. As pastas cruas foram, posteriormente, deslenhificadas com oxigénio (100°C, 1h) e branqueadas com uma sequência de *elemental chlorine free* (ECF) e *totally chlorine free* (TCF). As folhas laboratoriais (com uma gramagem aprox. 600 g/m^2) foram preparadas a partir da pasta branqueada, desfibradas a seco num moinho de martelos, a diferentes velocidades de rotação (rpm) e analisadas no teor em knots, capacidade de absorção e estabilidade de rede. Após desfibração a seco, as pastas digeridas com maior carga AA evidenciaram a redução de knots e as pastas ECF demonstraram melhor performance de desfibração em comparação com as pastas TCF. A estabilidade de rede de fibra é sensível às condições de cozimento e branqueamento e aumentam sempre com o aumento de AA. A estabilidade de rede das pastas TCF é superior em cerca de 20 a 70% em comparação com as pastas *fluff* ECF. As propriedades de absorção das pastas foram significativamente melhoradas pela presença dos ácidos carboxílicos e remoção de hemiceluloses. Com o objetivo de promover as propriedades de absorção, estabilidade de rede e energia de desfibração das pastas *fluff* foram estudadas modificações químicas e físicas. Para a modificação química foram aplicados dois surfactantes desligantes comerciais e um agente antimicrobiano (PHMB). O uso de aditivos químicos melhorou, ligeiramente, a capacidade de absorção de água das pastas,sendo mais acentuada com a aplicação do PHMB. Os surfactantes comerciais não influenciaram significativamente a capacidade de absorção, mas reduziram significativamente o teor de *knots* nas pastas *fluff*, atuando, essencialmente, como agentes desligantes no processo de desfibração a seco. Estes aditivos promoveram a estabilidade de rede e não afetaram a morfologia das fibras celulósicas. As modificações físicas avaliadas para a promoção das propriedades de absorção consistiram na pressão hiperbárica e o processo de hornificação acelerada. A pressão hiperbárica melhorou não apenas a velocidade e a capacidade de absorção das pastas, mas também o volume específico e a estabilidade de rede da fibra. A pasta hornificada laboratorialmente apresentou um maior grau de hornificação em comparação com a pasta acabada industrial, e uma redução na capacidade de absorção, contudo a pasta hornificada industrialmente (pasta acabada) apresentou melhor capacidade de absorção em comparação com a pasta de controlo (ensaio em branco). As modificações físicas a que as pastas foram submetidas facilitaram a desfibração a seco, diminuindo o teor em feixes de fibras (*knots*). Esta redução é mais acentuada nas pastas hornificadas do que nas pastas modificadas por pressão hiperbárica, uma vez que a remoção de água fortemente ligada provoca o colapso das fibras e tenham menor capacidade de ligação entre elas. As pastas de eucalipto BEKPs podem ser consideradas uma promissora matéria-prima para aplicações *fluff*, cujas propriedades básicas podem ser ajustadas de acordo com as necessidades, variando as condições dos estágios de cozimento, branqueamento e tratamentos posteriores através de modificações físicas e com aditivos químicos. Estas modificações aproximam as pastas BEKP das propriedades principais das pastas BSKP.

keywords

Absorption properties, Debonders, *Eucalyptus globulus*, Fluff pulp, Hyperbaric pressure, Hornification, Sorption isotherms, Fibre network strength

abstract

Most of the fluff pulp produced worldwide is used in the manufacture of absorbents, disposable diaper, intimate and non-woven products. Prerequisites for fluff pulp are quite different from pulps produced for papermaking. Absorption capacity, absorbency rate, high specific volume (bulk), fibre length, curl and network strength are the most important properties of fluff pulp. Generally, fluff pulp is made from Bleached Softwood Kraft Pulp (BSKP) and Chemi-Thermo Mechanical Pulp (CTMP). However, the potential of *Eucalyptus globulus* bleached kraft pulp for such kind of applications is still uncertain. In this study, Bleached Eucalypt Kraft Pulp (BEKP) from *E. globulus* wood was evaluated for the fluff pulp applications and compared with properties of commercial fluff BSKP.

A series of six industrial BEKPs produced from predominantly *Eucalyptus globulus* under variable process conditions were dry-defibrated on a pilot scale hammermill at 3500 rpm and the nonwoven air-laid fabrics evaluated for their specific volume, absorption capacity/absorption rate and the fibre network strength. The effect of non-defibrated fibre agglomerates (knots) on the former properties was evaluated. Processual variations in pulping and bleaching conditions revealed variability within 15% in the absorption capacity of fluff pulps and within 25% in the network strength of the air-laid formulations. These variations were attributed to changes in the chemical composition of BEKPs and fibre morphology. The importance of pulp bleaching sequence on the quality of BEKPs for fluff applications was highlighted. BEKPs having a high residual xylan content with a greater amount of uronic/hexenuronic moieties and coarser/deformed fibres revealed the best performance in fluff applications. The coarseness was considered a critical morphological parameter of the fibres, strongly affecting the porosity of air-laid formulations, which determined the absorption capacity and the network strength. The absorption capacity of fluffed BEKP was comparable to that of commercial softwood bleached softwood kraft pulp (BSKP), although the latter showed almost triple the network strength of air-laid formulations produced with BEKP. BSKP proved to be much more vulnerable to dry-defibration conditions than BEKP and suffered a pronounced cut of fibres, producing larger amounts of fines (dust) and stronger undesirable peeling and straightening of fibres. The same industrial *Eucalyptus* bleached kraft pulps (fluff pulps) were studied for the absorption properties employing dynamic water vapour sorption and contact angles measurements. The results showed that the accessibility of the fibre surface is related to the reduction of the contact angles, but, simultaneously, to the longer absorption time and less absorption capacity of the fibre network. Therefore, the absorption properties of the pulps are not necessarily directly related to their surface properties. Indeed, absorptivity is related to the surface chemical composition, fibre morphology, and fibre network structure. Thus, surface carboxylic groups promote total water uptake, resulting in better absorption capacity. Greater fibre coarseness and deformations (curl and kink) provide a less wettable surface, but a more porous network with higher specific volume, resulting in more absorbent air-laid formulations.

Since multiple variables of the industrial process did not allow to unequivocally trace the relationships between the procedural conditions and the properties of the fluff cellulose, laboratory tests under controlled conditions were carried out to be better understand such relationships. Accordingly, a series of *Eucalyptus globulus* wood chips were cooked under the same conditions (160°C, 2h) using different active alkali charges (AA) of 13%, 15%, 17% and 18%. All pulps were further oxygen delignified (100°C, 1h) and bleached using the elemental chlorine free (ECF) and the totally chlorine free (TCF) sequences. Lab handsheets (approx. 600 g/m^2) were prepared from the never dried bleached pulp and dry-defibrated in a pilot scale hammermill at different intensities (rpm) and analysed for the knots content, absorption capacity and the air-laid fibre network strength. Being dry-defibrated, pulps cooked at an increased AA revealed the reduction in knots and ECF pulps showed better defibration ability than TCF pulps. The fibre network strength was sensible to the conditions of pulping and bleaching and always increased with the increase in cooking AA. The network strength of TCF fluff pulps was from 20 to 70% greater than ECF fluff pulps. Regarding the absorption properties, BEKP fluff pulps showed good absorption capacity improved by the presence of carboxylic acid groups and the hemicelluloses removal. To enhance the absorption properties, network strength and defibration energy in fluff pulps, several chemical and physical modification were performed. For pulp modification, two commercial surfactant debonders and an antimicrobial agent (PHMB) were applied. The use of chemical additives slightly improved the water absorption capacity of pulps, being more pronounced with the application of PHMB, which increased the absorption capacity. Commercial surfactants did not promote much absorption capacity, but significantly reduced the knots contents in fluff pulps, acting essentially as debonders. These additives promoted an increase in the resistance of the fibre network and didn't affect the morphology of cellulosic fibres. The physical modifications to promote the absorption properties were hyperbaric pressure and accelerated hornification process. Hyperbaric pressure improved not only the rate and absorption capacity of pulps, but also its specific volume and the fibre network strength. The laboratory hornified pulp showed a higher degree of hornification and a reduction in the absorption capacity than the industrially dried pulp, but the industrial hornified pulp (paper-grade) showed improvements in the absorption capacity when compared to the control pulp. The physical modifications to which the cellulose pulp was subjected improved dry defibrillation, decreasing its knot content. This reduction is more accentuated in hornified pulps than in pulps modified by hyperbaric pressure, since the removal of tightly bound water causes the fibres collapse and have less bonding capacity between the fibres. BEKPs can be considered a promising raw material for fluff applications, whose basic properties can be adjusted according to the needs by varying conditions in the pulping, bleaching and posterior treatments employing physical treatments and auxiliary chemical additives. This brings the BEKPs closer to the main properties of BSKPs.

CONTRIBUTIONS

Published articles

Azevedo CA, Rebola SM, Domingues EM, Figueiredo FML, Evtuguin DV. Relationship between Surface Properties and Fibre Network Parameters of Eucalyptus Kraft Pulps and their Absorption Capacity. *Surfaces* (3): 265-281 (2020). Doi:10.3390/surfaces3030020.

Contribution: Participation in the development of the experimental methodology, execution of the laboratory work and in the writing of draft manuscript.

Rebola SM, Ferreira J, Evtuguin DV. Potential of Bleached Eucalyptus Kraft Pulp for Applications in Nonwoven Fibrous Fabrics. *Journal of Engineered Fibers and Fabrics* (15): 1-13 (2020). Doi:10.1177/1558925020980146.

Contribution: Execution of the laboratory work, writing of the draft manuscript and participation in the development of the experimental methodology.

Articles in press

Rebola SM, Azevedo C, Evtuguin DV (2021) Effect of Cooking and Bleaching Conditions on the Properties of Eucalyptus Kraft Fluff Pulps. Cellulose. Submitted article.

Contribution: Execution of the laboratory work, writing of the draft manuscript and participation in the development of the experimental methodology.

Conferences

Rebola, S.M., Ferreira, J., Margalho, L., Jorge S.R., Evtuguin, D.V. Potential of bleached eucalypt kraft pulp for non-papermaking applications. *Abstracts XXIV TECNICELPA "International Forest, Pulp and Paper Conference",* October 11-12, Aveiro, Portugal, p. 39 (2018).

Azevedo, Catarina, Rebola, S.M., Evtuguin, D.V. Relationship between surface properties of eucalyptus kraft pulps and their absorption capacity. *Conference RICI8 – 8th Iberian Meeting on Colloids and Interfaces* July 17-19, Aveiro, Portugal *(2019).*

Rebola, S.M. Potential of Bleached Eucalypt Kraft Pulp for New Non-Papermaking Applications, Summer School, University of Aalto, 16-18 June, Teams Conference (2020).

Rebola, S.M., Azevedo, Catarina, Evtuguin, D.V. Effect of kraft pulping conditions on the properties of *eucalyptus globulus* fluff pulps*. International Conference EWLP 2020 – 16th European Workshop on Lignocellulosics and Pulp*, Gothenburg, Sweden (postponed to August 2021).

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1 INTRODUTION

In a global world where Portugal is economically highly integrated, the Paper and Pulp business sectors are amongst the biggest contributors to Portuguese exports, the highest investors in production infrastructures and highly internationalized. Portugal is the 4th largest European producer of pulp and the 3rd of chemical pulps. With a total area of about 210,000 ha managed by pulp companies, 75% of eucalyptus wood and 73% of pine wood for this industry is sourced in Portugal. The Portuguese sector is the 11th largest European producer of paper and cardboard, the 1st largest of uncoated fine paper (UWF) and the 6th worldwide producer, where the recovery rate of recycling paper is 63%. Since 2000, the industry has invested over 5.000 Million € in projects for environmental improvement. In the Pulp segment, Portugal is strong in producing and exporting chemical wood pulp. In the paper segment, main export products are paper and cardboard for graphic purposes, packaging paper, household and sanitary papers, as illustrated in Figure 1 [1]. The prospects for 2019 and 2020 are considered similar to the ones observed in previous years as no significant investments on industrial capacity are projected [2].

The pulp market to produce printing and writing papers is in declining territory, and this reduction is related to the increasing use and resource of electronic and digital media of modern societies. Thus, the current situation demands a change of strategy in a way of maintaining the sector's sustainability, and novel approaches to the production of non-paper products, i.e. non-paper applications are mandatory. The success of a commercial product in today’s marketplace is often since it is a convenience item. Such items include disposable diapers, feminine care products, hospital pads, and several types of disposable tissues and towels [3]. Therefore, the market for fluff pulp for a wide range of hygiene and comfort products, as growing sectors, is an opportunity for pulp and paper production companies.

Due to strong competition, the absorbent-product industry is quite research intensive. Global demand for fluff pulp is growing rapidly, driven by increasing sales of absorbent hygiene products. New markets, new potential sources for pulp, and new owners of major producing assets are shifting the competitive balance throughout the industry. The aim of the present study is to evaluate the *E. globulus* potential to produce fluff pulps, according to current kraft cooking and bleaching TCF and ECF technologies. So far, the potential of *E. globulus* bleached kraft pulp for such kind of applications is almost unknown. Accordingly, the major objectives of this work were as follows:

1. To evaluate the potential of industrial eucalypt kraft pulps for fluff applications.
2. To verify how the conditions of kraft pulping and pulp bleaching affect the quality parameters of fluff pulps.
3. To assess the surface properties of fluff pulps and relate them to the absorption capacity.
4. To evaluate the effect of common debonding agents and some physical treatments on the quality parameters of fluff pulps.

The thesis is organized in four tasks and its main body is presented in the form of research papers, whether already published or are still in reviewing process:

- In the first part of this study, paper-grade industrial Bleached Eucalypt Kraft Pulps (BEKPs) from *E. globulus* wood, produced by conventional kraft cooking and TCF/ECF bleaching technologies, were evaluated for the fluff pulp applications and compared with those properties of commercial BSKP. The basic characteristics of eucalypt fluff pulps, such as knots content, absorption capacity, absorption time, soak and drip capacity, network strength, fibre morphology and chemical properties were analysed. Simultaneously, the structural, mechanical and optical properties were determined in the examined kraft pulps. Additionally, sorption isotherms and contact angles were assessed for the TCF and ECF kraft pulps to relate their absorption properties in air-laid formulations with the surface properties of the fibres.
- In the next step, a sample of Iberian *Eucalyptus globulus* wood chips was cooked by the kraft process at different active alkali charges. Afterwards, the brownstock pulp were delignified with oxygen and chemically bleached using both ECF and TCF sequences. The basic characteristics of hardwood bleached pulps, such as chemical composition, fibre morphology, absorption properties, network strength and knots content were evaluated. The crystalline and non-crystalline cellulose of the studied pulps were also analysed by CP-MAS ^{13}C NMR spectroscopy. Simultaneously, two commercial bleached softwood kraft pulp, with enhanced fluff characteristics, were compared with the eucalypt bleached kraft pulp.
- In the third part of this thesis, *Eucalyptus* kraft pulps provided by a pulp mill operating with an ECF bleaching sequence were examined. A meticulously selected amount of $O/OD_{hot}(P_o)D_1P$ never-dried bleached pulp was collected and treated, at a laboratory scale, by the introduction of different commercial additives, under preselected conditions. Simultaneously, this pulp was hornified

at increased temperatures using the contact drying or submitted to ultra-high-pressure hydraulic treatment.

- In the last goal of this thesis, a prototype of fluff pulp for non-paper application was produced on the laboratory scale and characterized.

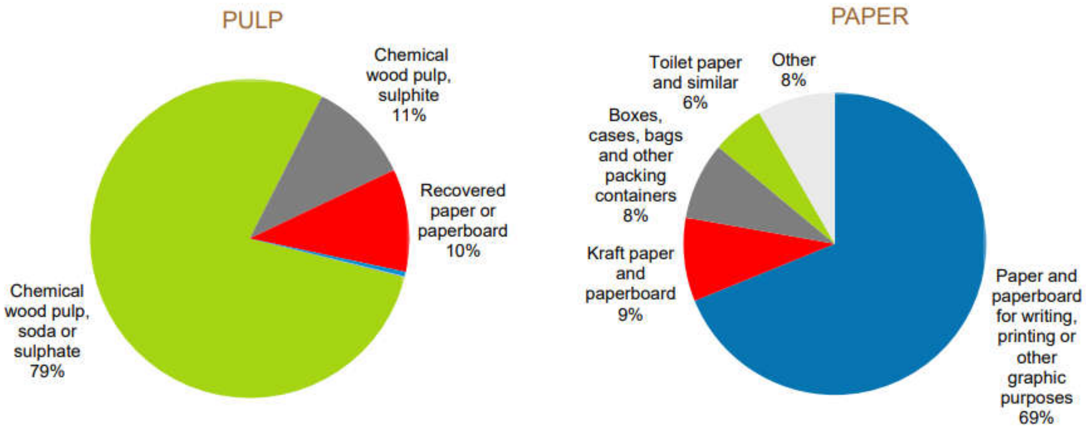


Figure 1- Pulp and paper production in Portugal [1].

2 STATE OF THE ART OF FLUFF PULPS

Most pulp and paper production companies play a key role in national economic development, and in Portugal most of them are specialized in the production of bleached eucalyptus kraft pulp for fine printing and uncoated papers (UWF). However, forecasts for the UWF market are not exciting, with a 1% decline per year, and this fall will be related to the increasing use of electronic and digital media in daily use [4,5]. Regarding this scenario, a change of strategy is necessary to maintain the sustainability of the sector, and innovative approaches to the production of new kind of papers and new non-paper products. For these reasons the market for tissue pulp (papers for domestic use, industrial, hygiene, etc.) and fluff pulp (mainly hygiene products), are growing sectors and great opportunities to the Portuguese paper industries.

The global fluff pulp market accounts for only about a tenth of total market pulp, yet us a growing share of the overall business. Nowadays, most of the fluff pulp produced worldwide is used in the manufacture of absorbents, disposable diapers, intimate and non-woven products. Volume growth in the disposable absorbent hygiene products market continues to be driven primarily by expansion in emerging markets where health standards, disposable incomes and urbanization is on the rise. The global fluff pulp market is expected to post a compound annual growth rate (CAGR) of over 4% during the period 2019-2023, with an incremental growth of 1537 thousand tons. The year-over-year growth rate for 2019 was estimated at 3.74% [6]. The competitive scenario of fluff pulp is dominated by large pulp and paper companies located in North America. However, in 2018 the Asia-Pacific countries (APAC) region led the market, followed by Europe, North America, South America, and MEA respectively. During the forecast period, the APAC region is expected to continue dominating as well as register the highest incremental growth due to the high demand mainly because of the growing per capita income, rising living standards of the people, high birth rate, and growing geriatric population. The mature markets in North America, Western Europe and South America will see tepid demand over the forecast period as these markets are nearly saturated, although adult incontinence markets represent a potential growth segment as elderly population continue to expand in these regions. Growth of global fluff pulp market is likely to be driven by increasing air-laid production volume, rising demand for personal hygiene care products and increasing population of incontinence patients and old people [7]. Over 90% of total fluff pulp capacity is in the US South, where the largest fluff pulp producer in the world today is Georgia-Pacific (GP). Key trends of this market include favourable price trends and development of fluff pulp from hardwood. So far, the production in Portugal of this kind of specific pulp does not exist [8].

The major functional component of most of disposables products is a cellulosic fibre obtained from wood pulp. In its functional state, the fibre has the inherent characteristics of bulk, softness and high absorbency. The intrinsic absorbency of fluff, aside from its hydrophilic nature, is due largely to the length, diameter, stiffness of its fibres [9]. Thus, the best conventional fluffs are derived from long-fibred, coniferous species wood. Southern Bleached Softwood Kraft pulps (SBSK), such as those from southern yellow pine, are often used in fluff pulp applications. Coarser fibres, with greater weight/ unit length, namely pine and Douglas fir, usually provide greater absorbency because their use leads to high levels of fluff bulk, resiliency and void volume [3,9]. The global fluff market has become increasingly concentrated around BSK fluff pulp over time due to the grade's superior performance in absorbent hygiene applications and relatively low production costs. However, other raw materials and processes, such as softwood CTMP (chemi-thermomechanical pulps) and hardwood kraft pulps have and are being used. When mechanical pulps are used, a major goal of the pulp producer is to maintain fibre length. This is extremely important, because mechanical pulps contain less long fibre and this kind of fibres have the advantage of imparting bulk and resiliency to the sheet [10]. Alternatively fluff pulps in some embodiments may also use hardwood as the source of wood for the pulp, or a combination of softwood and hardwoods. More than 90% of the pulps are fully bleached chemical pulps, of which more than 90% are sulphate pulps [11,12]. The proportion of CTMP is less than 10%. The cooking and bleaching of the chemical fluff pulps do not significantly differ from the production of paper pulps. Production of sulphite fluff pulp ceased in 2011 as suppliers of the grade closed operations due to competitive pressures from BSK fluff pulp or swung production to different grades, primarily dissolving pulp (DP). There may be little amounts of sulphite fluff being produced, however these volumes are miniscule overall [13].

The dry defibration of fluff pulp is an important process step in the manufacture of disposable diapers, incontinence products and feminine hygiene products. The web formation, wet pressing, and drying of fluff pulps differ greatly from the production of paper pulp [11]. Moreover, these process steps are more critical for the quality and processability of the final product. The process of defibration is conducted either in hammermill or in refiners. Despite the common use of hammermill, the most commonly used defibration equipment nowadays, there is only a limited understanding of the relation between the defibration conditions and the mechanical properties of the final dry-formed fibre networks [14]. More than 95% of fluff pulps are dried in a continuous sheet form and wound onto rolls in which the moisture content of the pulp varies between 5 and 10% [15].

At the customer´s plant, the rolls are continuous fed into a hammermill, to reduce as much as reasonable possible to individual fibres. Fluff pulp sheets may contain significant numbers of fibre bundles which are bonded together during the sheeting process [11,15]. The unwanted fibre bundles, often referred as knots, present a problem during defibration. It is desirable to have a fluff pulp that is easy to defibrate, with low knot content and low energy inputs [15]. The fibre network formed in a subsequent air-laid process should have good network strength and be resilient in the wet state. The resistance towards dry defibration of a pulp fluff sheet is to a substantial extent dependent on the strength of the bonding between the fibres [16]. For application in fluff pulp, cellulose fibre should have a longer length and high strength, and the fluff pulp sheet requires suitable burst strength. Although other properties such as flexibility and curl may also influence network strength [12,17]. The high bonding strength means that fluff pulp sheet requires relatively high energy to disperse into single fibre under dry conditions [12,18] To offset this problem, the pulp mill needs to add chemical debonders prior to sheet formation. The main purpose of debonders is to reduce the amount of fibre-fibre bonding that take place during drying.

Prerequisites for fluff pulp are quite different from pulps produced for papermaking [19]. Mechanical strength properties and optical properties of paper pulps are not as important as for fluff pulps, while specific properties such as the absorption capacity, water retention in the fibres and the pulp stability agglomerate network to humidification are of immense importance. There are several specific fibre characteristics that are directly related to the quality of the absorbent product, namely high specific volume, which depends on the length and width of the fibres, the porosity and the interfibrillar spaces that should not compact and collapse, to promote penetration and water retention by capillarity [20]. The absorption capacity, expressed as the amount of liquid that can be trapped in the empty spaces of the fibre network, depends significantly on the stiffness, porosity and fibre length. The liquid diffusion, consisting of water absorption rate, depends on the capillary force exerted by the pores and the contact angle between the liquid and the surface layer of the fibre [21]. The pulp network stability to humidification depends on the forces between the fibres in the agglomerate network formed by the dry method [19]. This parameter is related to the fibre length, its flexibility and index curl, as well as the entanglement of the fibres [14]. In order to simultaneously obtain these properties, it is necessary to improve the fibre quality obtained from wood, expressed in chemical composition (extractive content, hemicelluloses and alphacellulose, cellulose crystallinity degree, residual lignin, etc.), anatomical elements (proportion of parenchyma cells, cell porosity, lumen width and cell wall thickness, coarseness of fibres, curl and kink parameters, among others). Within the same wood species and the applied cooking method, the process parameters during the cooking, bleaching and drying of the fibres are predetermining factors for all these characteristics already mentioned [19]. Considering that there is no previous study about *Eucalyptus globulus* fluff pulp with this kind of properties, one of the main objectives of the present work will be an extensive analyses of process variables about pulp quality.

Properties of fluff pulps such as absorbency and pulp network stability to humidification may be improved by modifying the cellulosic fibres or by adding Super Absorbent Polymers (SAP) [22]. Technological change will counter some demand pressures, specifically product innovation in absorbent hygiene development has pushed for thinner, more discrete units, which sacrifice little in terms of performance. The use of superabsorbent polymers has been primarily responsible for this movement toward thinner products [22,23]. Superabsorbent is a synthetic substance made from acrylic acid and is an important constituent in personal care products including baby diapers, feminine care products and adult incontinence products. The absorbent core of these products typically consists of a mixture of SAP and fluff pulp that is formed into pad on a conveyor belt [24,25]. The way the SAP and fluff pulp are dispersed determines the characteristics of the absorbent core. SAP can retain a substantial quantity of liquid, significantly more than what can be retained in a conventional fluff pulp. Because of the unique network structure and a large number absorbing groups, the weight of liquid absorbed by SAP is several times heavier than its dry weight and the liquid will not diffuse easily [26]. Furthermore, SAPs have a much greater ability to absorb fluids in comparison to cellulosic fibres alone. Cellulose, in its various forms, may contribute with many positive attributes to absorbent products, including enhancement of SAP performance. Fluff pulp is bulkier, expands more during absorption and releases liquid under less pressure than SAP [27]. Overall, fluff pulp provides integrity, cushioning, absorbs liquid faster than SAP and is made from a renewable natural source. Today, petroleum-based superabsorbents are widely used, but interest in renewable alternatives is on the rise [25]. Figure 2 illustrates different applications of cellulose fibres from eucalyptus and birch wood, such as disposable nappies, insulation and moulded products. [26].

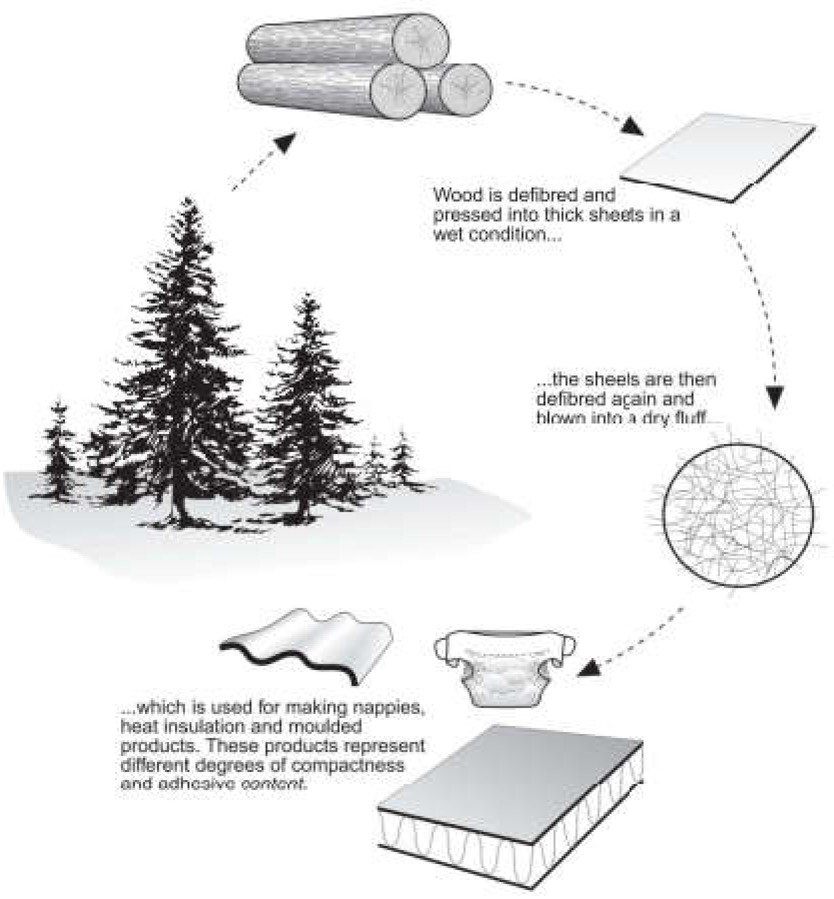


Figure 2 - Dry-shaped cellulose fibre fluff is made from wood and is used for several applications. [28]

3 LITERATURE OVERVIEW

3.1 Structure and ultrastructure of wood

Wood has a complex hierarchic structure that is responsible in part for determining the mechanical and physical properties of all its products including pulp (kraft and mechanical) and sawn wood. These properties are governed by the wood structure namely its anatomical organization and cell wall ultrastructure. Wood is classified into hardwood (gymnosperms) and softwood (angiosperms) [29]. Angiosperms and gymnosperms are the two major groups of vascular seed plants. Angiosperms, which are flowering plants, are the largest and most diverse group within the kingdom Plantae. With around 300 000 species, they represent approximately 80 percent of all the known green plants now living [30]. Gymnosperms are a smaller, more ancient group, and it consists of plants that produce “naked seeds” (seeds that are not protected by a fruit). There are more than 1,000 species of gymnosperms still found on Earth [30]. In Portugal the most common species used for pulping are eucalyptus (e.g. *E. globulus* and *E. nitens*) and pine (e.g. *Pinus radiate* and *Pinus sylvestris*) [31].

3.1.1 The macroscopic structure of wood

Wood is composed of elongated cells, most of which is oriented in the longitudinal direction of the stem. They relate to each other through openings, referred to as pits. The run and the arrangement of the cells may be recognized on the sections cut in the three main planes used for the anatomical characterization of wood: the cross section, the tangential section and the radial section [32]. The cells, varying in their shape according to their functions, provide the necessary mechanical strength to the tree and perform the function of liquid transport as well as the storage of reserve food supplies [33].

Figure 3 exemplifies a transverse view, i.e., when the tree is cut across the stem [30]. The phloem is situated directly under the bark and transports the nutrients from the leaves or root through the branches and the stem. In the cambium, under the phloem, the growth of the tree takes place. The cell dividing tissue is called meristem, and except in the cambium it exists in tips of branches, stem and roots [34]. The xylem is organised in concentric growth rings. When a tree stem is cut transversely, a portion of heartwood may be seen frequently as a dark coloured zone near the centre of the stem. This portion is surrounded by a light-coloured peripheral zone called sapwood. This dark-coloured zone is mainly due to the heartwood is impregnated with various extractives that work as a natural protection against microbial attack. The sapwood or at least the outer part of the stem conducts water through the tissue where the water is transpired, and mineral nutrients are also carried with water from the roots into the wood [35]. The sapwood is considered an active living parenchyma tissue due to its physiological role namely as storage of starch and fat. On the other hand, the heartwood is dead xylem. The dying parenchyma cells produce organic deposits such as resin, phenolic substances and pigments [36].

The pitch represents the tissues formed during the first year of growth. It may be a dark stripe in the middle of the stem and branches (Figure 3). The juvenile wood, closed to the pitch, is created during the first years (10-15) of growth [30].

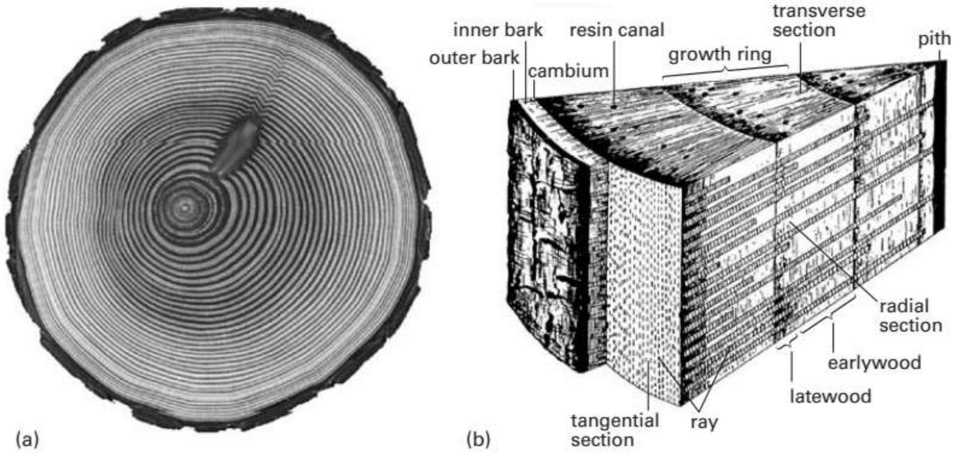


Figure 3 – (a) Transverse section of pine trunk showing the bark, sapwood and heartwood regions, and the annual rings composed of early and latewood. (b) Detailed view of a young pine stem showing its axial and radial organization and location of the major tissue types [30].

3.1.1.1 Softwood and Hardwood Cells

The wood substance in softwoods is composed of two different cells: tracheids (90-95%) and ray cells (5-10%) [37]. Tracheids are long and slender cells with flattened or tapered closed edges, which are arranged in radial files and their longitudinal extension is oriented in the direction of the stem axes. Tracheids give softwoods the mechanical strength required and provide water transport, which occurs through the thin-walled early wood tracheids with their large cavities. Cell wall thickness is related directly to the strength of tracheids [34]. The early tracheids seem to be well adapted to the conducting function whereas the latewood tracheids are loaded with the mechanical property, judging from their shapes (Figure 4). The storage and the transport of assimilates take place within the parenchyma cells, which in softwoods are predominantly arranged in radially running rays [30].

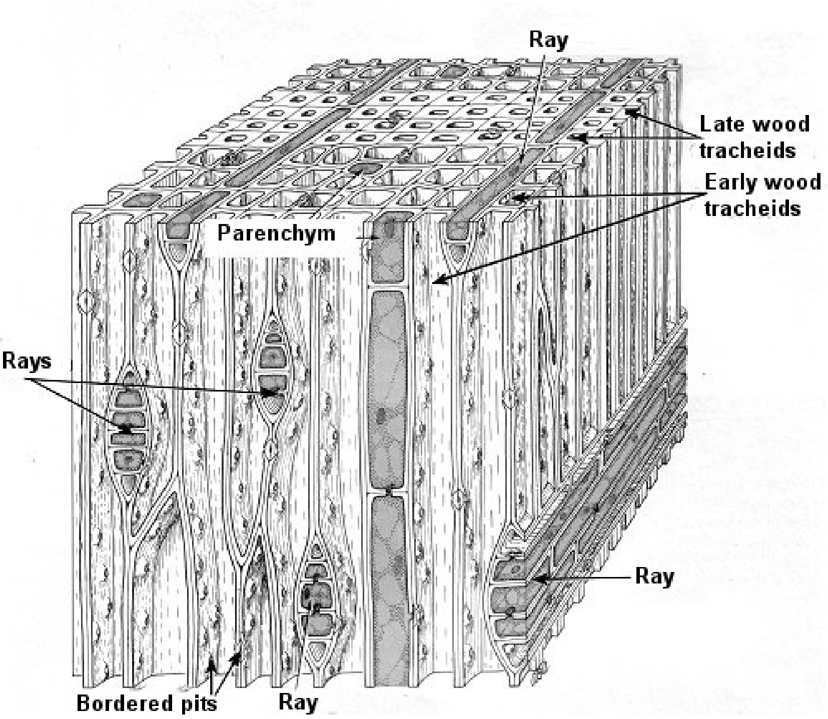


Figure 4 - Schematic drawing of a block of *Sequoia* wood (*Sequoia sempervivens*, Redwood) as an example of the structure of conifer wood. Top = transverse section; Side = radial section; Front = tangential section [30].

Cells of softwood species differ in appearance from cells of hardwood species. Hardwoods are more complex than softwoods. All hardwoods contain several cells types in varying amounts, vessel elements, fibres, longitudinal parenchyma and ray parenchyma, as illustrated in Figure 5 [35]. The supporting tissue consists mainly of libriform cells (often called just “fibres”), the conducting tissue of vessels with large cavities, and the storage tissue of ray parenchyma cells. Furthermore, hardwood contains hybrids which are classified as fibre tracheids [38]. Within this strengthening tissue are distributed conducting vessels, often with large lumina. Vessels are composed of thin-walled and rather short (0.3-0.6 mm) and wide (30-130 μm) elements, which are on the top of one another to form a long tube. These vessels are long pipes ranging from a few centimetres up to some meters in length and consisting of single elements with open or perforated ends. Hardwood rays consist exclusively of parenchyma cells. These cells are short compact cells with stubby ends. The number of parenchyma cells in hardwood is higher than in softwoods, which reveal large rays and longitudinal parenchyma [34]. The wall thickness of the fibres or tracheids, the number and diameter of the vessels, as well as the number of parenchyma cells determine the density of woods [33,35].

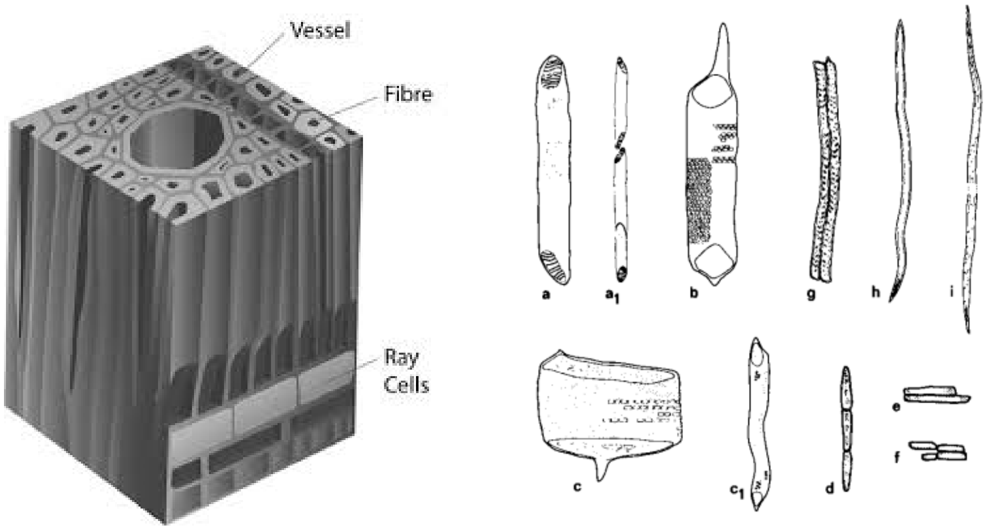


Figure 5 - Hardwood cells. Vessel elements of birch (a), of aspen (b), and of oak in earlywood (c) and in latewood (c1), as well as a birch vessel (a1). Longitudinal parenchyma of oak (d) and ray parenchyma of aspen (e) and of birch (f). Tracheids of oak (g) and birch (h) and a birch libriform (i) [35].

3.1.2 Wood ultrastructure

Wood is a natural composite material and a chemical complex of cellulose, lignin, hemicellulose and extractives. In simplified terms the cellulose forms a skeletal matrix that is surrounded and encrusted by the hemicelluloses and lignin [34]. Cellulose is the framework substance, comprising 40 – 50% of wood in the form of cellulose microfibrils. These microfibrils (aggregated fibrils 10-20 nm in diameter) are visible using electron microscopy and may be aggregated further into macrofibrils and lamellae, the later organized into a concentric arrangement around the wood cell wall layers [32,37]. Lignin, on the other hand, is the encrusting substance solidifying the cell well associated with the matrix substances [39]. Hemicelluloses and lignin located in the spaces between the microfibrils. The hemicelluloses are amorphous although they apparently are oriented in the same direction as the cellulose microfibrils. Lignin is amorphous and isotropic and encrusts both the hemicelluloses and cellulose [30,36,37].

As illustrated in Figure 6, the cell wall is built up by several layers, such as middle lamella (ML), primary wall (P), outer layer of the secondary wall (S1), middle layer of the secondary wall (S2), inner layer of the secondary wall (S3) and warty layer (W) [33]. The concentric arrangement of the cell wall layers is caused by the differences in the chemical composition and by different orientations of the structural elements. The middle lamella is located between the cells and has the function of binding the cells together [30,37]. The lignin content of the middle lamella is high, but since this layer is thin, only 20-25% of the total lignin present in this layer. The primary wall (P) forms the outer layer of the cell and is comprised of randomly orientated cellulose microfibrils. The secondary wall consists of three layers: S1, S2 and S3 layers, the S1 and S3 layers being comparatively thin, and the central S2 middle layer forming the major part of the cell wall in both softwood and hardwoods. The characteristics of the S2 layer (thickness, microfibrillar angle) have a decisive influence on the fibre stiffness as well as on the papermaking properties [40]. The warty layer (W) is a thin amorphous membrane located in the inner surface of the cell wall in all conifers and in some hardwoods [34,36].

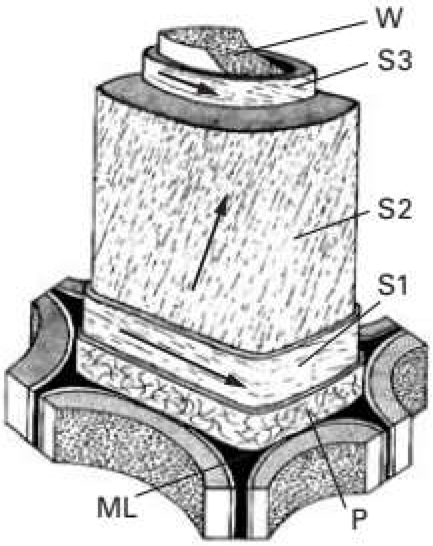


Figure 6 - Simplified structure of a woody cell, showing the middle lamella (ML), the primary wall (P), the outer (S1), middle (S2), and inner (S3) layers of the secondary wall and the warty layer (W) (Côte, 1967). Arrows indicate the orientation of the cellulose microfibrils (MFA) in the individual secondary cell wall layers [33].

3.2 Chemical composition of wood

The chemical composition of wood cannot be defined precisely for a given tree species or even for a given tree. In order to understand the behaviour of wood during pulping, as well as the resulting pulp quality, it is indispensable to have a basic knowledge on the chemical composition and structure of its natural raw material. Chemical composition varies with tree part (root, stem, or branch), type of wood (i.e., normal, tension, or compression) geographic location, climate, and soil conditions [41]. There are two major chemical components in wood: lignin (18– 35%) and carbohydrate (65– 75%) [42]. Minor amounts of extraneous materials, mostly in the form of organic extractives and inorganic minerals (ash), are also present in wood, usually between 4 and 10%. A brief introduction to the chemical wood components follows the general scheme illustrated in Figure 7 Overall, wood has an elemental composition of about 50% carbon, 6% hydrogen, 44% oxygen, and trace amounts of several metal ions [41,42]. The final cellulose and lignin content and its variation, as well as fibre strength properties are typical essential characteristics of the pulp which depend significantly on the chemical composition as well as the structure of the various components of the wood [43].

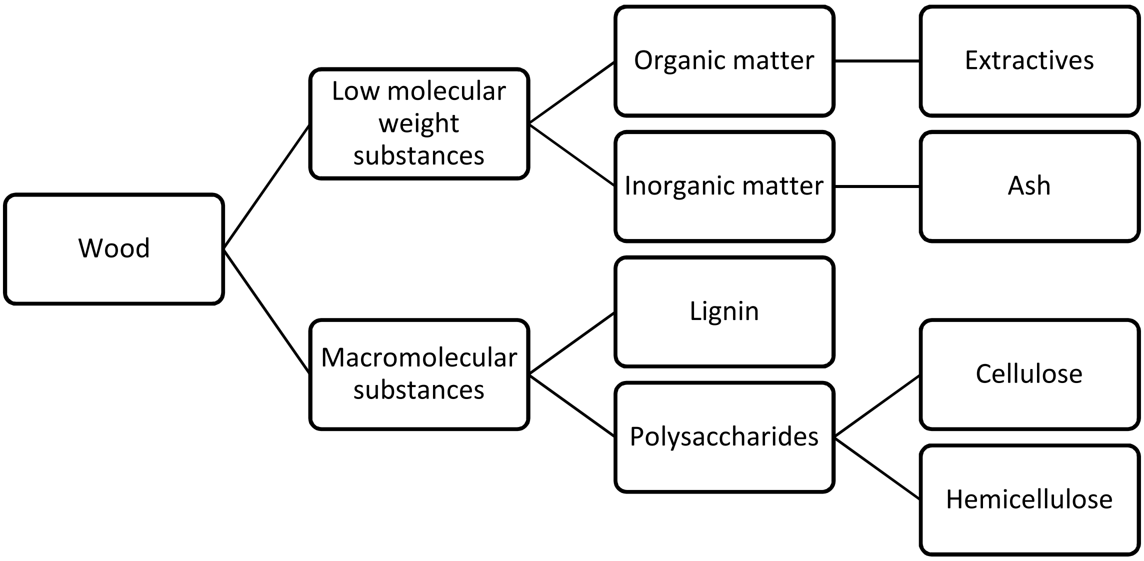


Figure 7 - General scheme of the chemical wood components [35].

3.2.1 Wood carbohydrates

The name carbohydrate was originally applied to the large group of biomolecules which formula may be expressed as $C_n(H_2O)_n$. Carbohydrates are polyhydroxy carbon chains with at least one aldehyde- or keto group [35]. The major carbohydrate portion of wood is composed of cellulose and hemicellulose with minor amounts of other sugar polymers such as starch and pectin. The carbohydrates may be classified into following three large groups: monosaccharides are simple sugars, mainly D-glucose, D-mannose, D-galactose, D-xylose, L-arabinose, D-glucuronic acid and much lesser amounts of other sugars such as L-rhamnose and D-fucose [44]. The monosaccharides have excellent possibilities to link each other by the semiacetal hydroxyl groups. The oligosaccharides consist of several monosaccharide residues, containing from 3 up to approximately 10 monosaccharide units. Polysaccharides are complex molecules composed of many monosaccharide units bonded by glycosidic linkages. Carbohydrates differentiate from each other by rather small structural differences that however can be very important from a biological and mechanical perspective [41,42,44].

3.2.2 Cellulose

Cellulose is the main constituent of wood, approximately 40 – 45% of the dry substance in most wood species is cellulose, located predominantly in the secondary cell wall [45]. On the molecular level, cellulose is a linear polymer of anhydro-D-glucose connected by β-(1→ 4) linkages as shown in Figure 8 [32]. The degree of polymerization is often very high, values of 15 000 residues in one chain are reported making cellulose to one of the longest of known polysaccharides. The cellulose chain is not totally strait, theoretical calculations indicate that a cellulose chain forms a very extended helix [44,46] Cellulose has a strong tendency to form intra and intermolecular bonds. Bundles of cellulose molecules are aggregated together in the form of microfibrils, in which highly ordered crystalline regions alternate with less ordered (amorphous) regions [42]. Microfibrils are aggregations of cellulose molecules into threadlike structures approximately 3.5 nm in diameter, containing both crystalline and amorphous regions. They occur in the secondary cell wall [42,44].

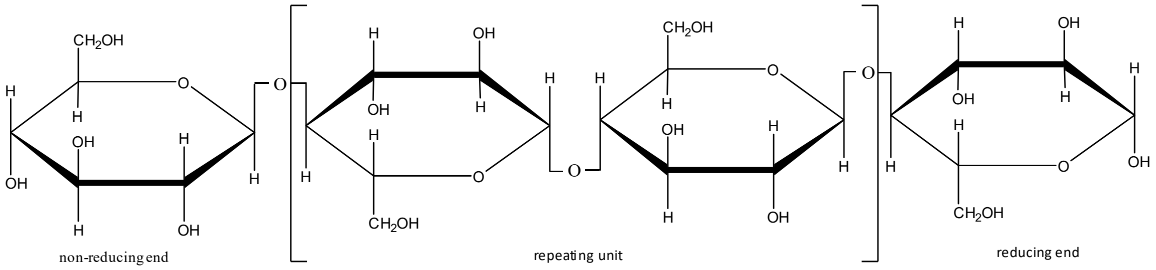


Figure 8 – Primary structure of cellulose. The glucose residues are 180° towards each other, making the repeated unit to a cellobiose residue rather than a glucose residue [32].

The primary structure of cellulose is relatively simple and the properties of cellulose that have made it to such a biological and technical interesting polysaccharide, are dependent on the secondary structure. The secondary structure with parallel chains is called cellulose I allomorph. There exist several other secondary structures that can be formed by various chemical treatments, cellulose II, III and IV. [44] Of these, cellulose II is the most important. There are two hydrogen bonds between the C6 hydroxyl and the C2 hydroxyl and between the C5 oxygen and C3 hydroxyl, which stabilize the glycosidic bond and make the structure stiff. The chains form a layer in the crystallographic plane, where they are held together by hydrogen bonds. There are no hydrogen bonds in cellulose I between these layers, only weak Van der Waal's forces in the direction of the *b*-axis. Cellulose II can be formed from cellulose I principally by two methods: mercerization and regeneration [42,47].

3.2.3 Hemicelluloses

Hemicelluloses belong to a group of heterogenous polysaccharides which are formed through biosynthetic routes different from that of cellulose. Briefly, all cell structural polysaccharides of non-cellulosic origin called hemicelluloses or polyoses. The predominant wood hemicelluloses have a common structural feature of a linear β-(1→4)-linked backbone of conformationally related sugar residues in the pyranose ring form. In contrast to cellulose that is a homopolysaccharide, hemicelluloses are mostly heteropolysaccharides [45]. Hemicelluloses chemically are a class of polymers of sugars, including the six carbon sugars mannose, galactose, glucose, and 4-*O*-methyl-D-glucuronic acid or the five carbon sugars as xylose and arabinose [47]. All the monosaccharides that make up the hemicelluloses have the *D* configuration and occur in the six-member pyranose forms, except arabinose, which has the *L* configuration and occurs as a five-member furanose. The number average DP is about 100-200 unhydrosugar units per hemicellulose molecule [48].

The amount in hemicelluloses of the dry weight of wood is usually varies between 20 and 30%. The composition and structure of the hemicelluloses differ in a characteristic way from those in the hardwoods. [42,43]. The predominant hardwood hemicellulose is a partly acetylated, glucuronoxylan (*O*-acetyl-4-*O*-methylglucuronoxylan), accounting for 20-35%, whereas softwoods contain glucuronoarabinoxylan (arabino-4-*O*-methylglucuronoxylan) in the range of 8-14%. Hardwoods contain only a small quantity of glucomannan (2-5%). In softwoods a partly acetylated galactoglucomannan (*O*-acetylgalactoglucomannan) can reach up to 18%. In addition to these major cell wall components, pectic materials and starch are included in much smaller quantities in both softwoods and hardwoods (typically1-3%). Ash usually makes up between 0,1% and 0,5% of wood, but tropical species often exceed this range [41]. Table 1 summarizes the main structural features of the hemicelluloses appearing in both softwoods and hardwoods [43].

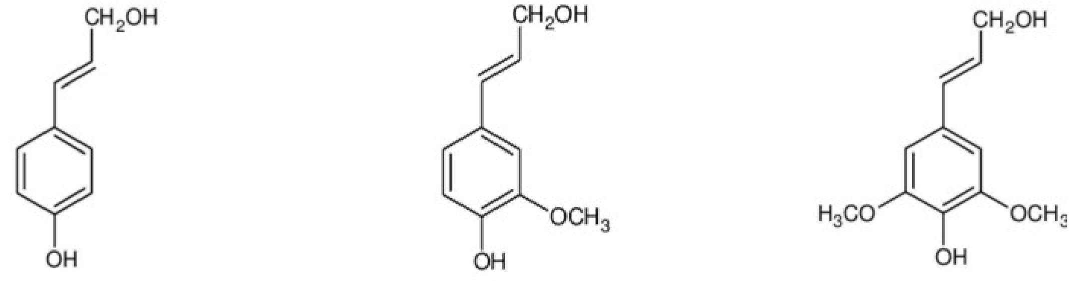
Table 1 - The major hemicellulose components of softwood and hardwood [43].

			Composition		
Hemicellulose type	Ocurrence	Amount (% of wood)	Units	Linkage	DP_n
Galactoglucomannan	Softwood	5 - 8	β-D-Man*p*	1→4	100
			β-D-Glc*p*	1→4	
			α-D-Gal*p*	1→6	
			Acetyl		
(Galacto)glucomannan	Softwood	10 - 15	β-D-Man*p*	1→4	100
			β-D-Glc*p*	1→4	
			α-D-Gal*p*	1→6	
			Acetyl		
Arabinoglucuronoxylan	Softwood	7 - 10	β-D-Xyl*p*	1→4	100
			4-O-Me-α-D-Glc*p*A	1→2	
			α-L-Ara*f*	1→3	
Glucuronoxylan	Hardwood	15 - 30	β-D-Xyl*p*	1→4	200
			4-O-Me-α-D-Glc*p*A	1→2	
			Acetyl		
Glucomannan	Hardwood	2 -5	β-D-Man*p*	1→4	200
			β-D-Glc*p*	1→4	

3.2.4 Lignin

Lignin is a complex polymer consisting of phenylpropane units and has an amorphous, three-dimensional structure [36]. Lignin is not restricted to woody plants and occurs in all vascular plants, including herbs in various systematic groups. The lignin content in non-woody plants are much lower, around 1-20% than in woody plant tissues [40]. Many aspects in the chemistry of lignin remain unclear, such as the specific structural features of lignin located in various morphological regions of the woody xylem. Lignin has an important biological role in plants, provides stiffness to the cell walls, working as a cementing and fixating polymer in the woody plant cell wall in close with polysaccharides [49]. Lignin is the adhesive or binder in wood that holds the fibres together and is highly concentrated in the middle lamella; makes the cell wall hydrophobic, inhibits swelling of the cell walls in water and therefore that water leaks from a woody cell wall [49,50]. In addition, lignin promotes a protection against microbial degradation of wood, a lignified woody tissue is so compact that the polysaccharide degrading proteins excreted by microorganisms cannot penetrate into the cell wall [42], [43]. Although cellulose content is almost the same (43 ± 2%) for softwood and hardwood, the hardwoods contain less lignin. The lignin content of hardwoods is usually in the range of 18-25%, whereas lignin of softwood varies between 25% and 35%. The structure of lignin is different between these two groups: softwood lignin's are composed mostly of guaiacyl units, whereas hardwood lignin's consist of syringyl and guaiacyl moieties [41].

Lignin molecules are derived in the majority of vascular plants from three phenylpropane monomers, designated as ρ-coumaryl alcohol (H units), coniferyl alcohol (G units) and synapyl alcohol (S units), which as all issued from a phenylpropanoid biosynthetic pathway common to all vascular plants [51]. These are propylphenol derivatives, with the differences in the number of methoxy groups attached to the ring [39]. Three main types of lignin are recognized according to their content of monolignols, as shown in Figure 9.



ρ-coumaryl alcohol Coniferyl alcohol Sinapyl alcohol

Figure 9 - Molecular structure of the basic lignin precursors [51].

Lignin heterogeneity may be related to enzyme diversity and specificity substrates, thereby affecting the metabolite flux into diverse branches of biosynthetic pathway. A clear example is the difference in lignin type between softwoods and hardwoods: softwood lignin or guaiacyl (G) lignin consist almost exclusively of coniferyl alcohol and may contain small amounts of ρ-coumaryl alcohol, whereas hardwood lignin or syringyl (S) lignin contain both coniferyl and sinapyl alcohols with proportions from equal amounts, to three/four times higher levels of sinapyl alcohol [52]. Some hardwood lignin may also contain small amounts of ρ-coumaryl alcohol. Grass lignin or HGS-lignin contains all three monolignols and has a higher content of ρ-coumaryl alcohol than other types of lignin. This kind of lignin is present in grass and also other types of monocotyledonous angiosperms [36,47].

The theory underlying lignification was presented by Freudenberg and Neish [51] based o chemical processes involving the oxidative coupling of phenols and addition of the available phenolic substrates to the polymer. The oxidation produces a phenolic radical with unpaired electron density delocalized at the C_1, C_3, C_5 and *O*-4 positions of the aromatic ring and the propanolic $C_β$ forming resonance structures. The lignin polymerization starts with the coupling of monomer radicals with phenoxy radicals formed on the growing polymer. The most reactive positions are the phenoxy oxygen and the $C_β$ that readily couple into aryl-ether linkages; the β-*O*-4’ linkage is predominant in lignin, e.g., almost 50% of all intermonomeric linkages in softwood and 60% in hardwoods. Overall, the coupling of the lignin monomers may be by ether bonds (β-*O*-4’, 4-*O*-5’, 1-*O*-4’) and by carbon-carbon bonds (5-5’, β-5’, β-β’, β-1’) is often called condensed bonds. Table 2 shows the main linkages present in softwood lignin and hardwood lignin [51, 52].

Table 2 - Main linkages (mol. %) of different types of linkages present in softwood and hardwood lignin [52].

Linkage	**Softwood (mol. %)**	**Hardwood (mol. %)**
β-*O*-4’	40-48	50-60
α-*O*-4’	4-8	4-8
β-5’	8-12	2-4
5-5’	9-18	2-5
β-1’	2-5	2-3
4-*O*-5’	3-4	3-6
β-β’ (pine/syringaresinol)	8-14	6-10
β-β’ (THF)	1-2	-
α-6’ + β-6’ + 5-6’	2-3	0,5-1
1-*O*-4’ + 1-5’	1-4	< 1

3.3 Wood fibre anatomy

A comprehensive knowledge of the characteristics of wood, in terms of its fibre anatomy and properties, is essential for its best utilization for pulp and paper production.

Pulp and paper's characteristics greatly depend on the fibre properties and the method of fibre preparation, during pulping, bleaching and fibre processing [53].

The principal raw material for producing paper is cellulose fibres that is the basic building block of plant matter. Pulp fibres can be extracted from almost any vascular plant found in nature, but a high yield of fibres is necessary to give an economic profit [36]. There are four main sources of cellulose fibre used in the manufacture of paper; softwood trees, hardwood trees, recycled fibre, and rag (usually composed of textile cuttings and cotton). As a fifth option, synthetic fibres are sometimes used for specialty papers. Other plants, such as sugar cane or bamboo, are also used as fibre sources. Nowadays, pulp from virgin fibres is produced mostly from wood fibres (more than 90%) and the rest is produced from non-wood fibres [34,54,55].

3.3.1 Hardwood and softwood fibres

Softwood and hardwood trees are the most commonly used sources of fibre for sheet fed offset papers. Each source produces fibre with slightly distinct characteristics, as reported in Table 3. Cellulose fibres have a very high tensile strength and a great affinity for water, meaning that the fibres can be bonded together strongly in a network to form paper [54]. The size and shape of fibres, which vary with type of tree and even within a given tree, have an important influence on paper properties. The void system of wood is different in softwoods and hardwoods, sapwood and heartwood, springwood and summerwood and additionally is also dependent on the individual wood species [38], [43]. Moreover, wood pulp produced from hardwood and softwood trees has different attributes. In Europe, hardwoods account for 29% and softwoods 71% of wood consumption. In Europe it is mostly birches (found in Sweden, Norway, UK and Spain) and eucalyptus (Portugal and Spain) that are used for papermaking [56]. Hardwood fibres are made up of several cell types, differentiated according to their special functions [34,37,53]. The fibre type is short, with an average length of 1 mm, giving properties such as bulk, smoothness and opacity. The fibres of hardwoods are interconnected by pit pairs, but they are smaller and fewer in number as compared to the softwood tracheids. They are less effective for liquid transport [30,43]. Electron microscopic studies have not provided any evidence of pores through the membranes of hardwoods thus indicating that hardwood fibres are ineffective for liquor flow. Springwood is more easily penetrated than summerwood due to its wider lumina and its thinner and more fissured cell walls. Reaction wood and wood knots are very dense and thus more difficult to penetrate. Mass transfer occurs predominantly through the lumina of the vessel elements, which are connected vertically to form long tubes. The channels thus formed contribute very efficiently to the water transport [37,42].

Table 3 - Chemical composition and dimensions of wood fibres [57].

Fibre type	Cell dimensions		Chemical composition		
	Average length, mm	Average diameter, µm	Cellulose %	Hemicellulose %	Lignin %
Softwood	3,3	33	40-44	25-29	26-31
Hardwood	1,0	20	45-50	25-35	18-24

Softwood trees may be found in Sweden, Finland and Norway and are mainly pine and spruce. Softwoods consist mostly of longitudinal fibres, tracheids, with a tubular structure of an average length of approximately 3.5 mm and a diameter of 30–35 µm (Figure 10) [44]. The tapered ends overlap longitudinally by about one-fourth of their length. Penetration occurs through their lumina and pits, which are covered by a membrane. The pit membrane, which consists of primary wall and middle lamella, contains pores with dimensions in the range below of approximately 4 nm [38]. Within the heartwood of softwoods, mass transport is very limited, because the pores in the pit membrane are often sealed by lignification or resignification. Softwood fibres are mainly used in the sulphate process but also in the production of mechanical pulp. The high content of resin makes it difficult to use fibres from pine in the sulphite process [54].

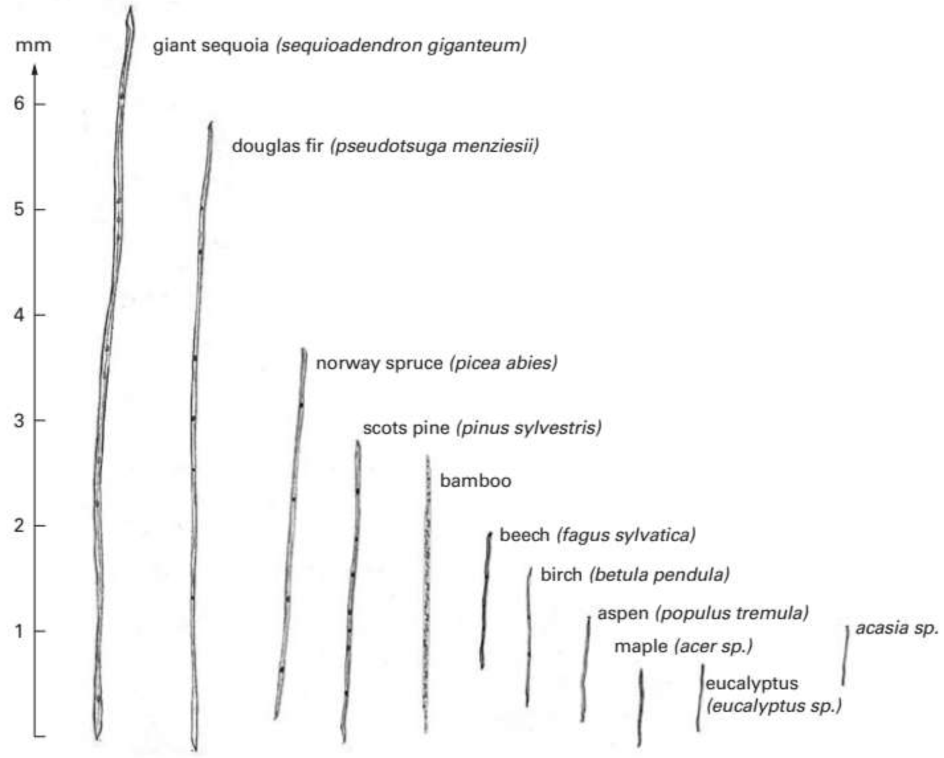


Figure 10 - Fibre lengths of different trees and may vary with different growing place [44].

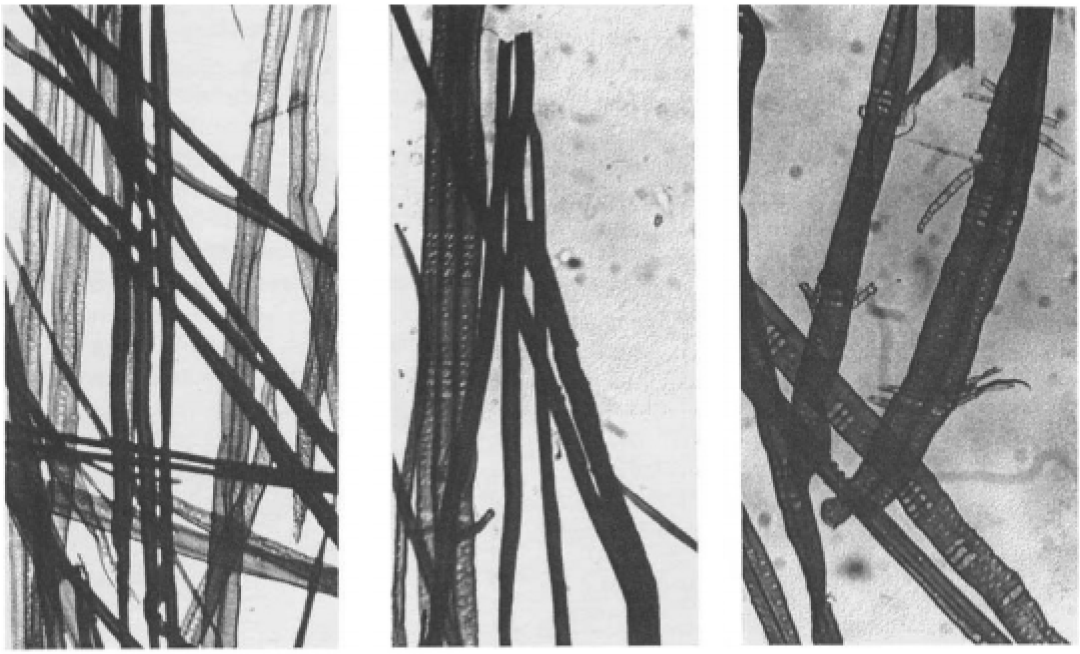
As already mentioned, fibre length is one of the most important papermaking characteristics of fibres. A long fibre can establish many bonds to other fibres and as such will be anchored more strongly in a fibre network compared with a short fibre. Hardwood and softwood fibres can be blended into a single paper, to achieve a desired combination of strength, whiteness, writing surface or other required characteristics. Figure 11 and Figure 12 show several images of softwood and hardwood fibres [36,54].

When fibres are submitted to mechanical forces, they are sensitive to changes in their form. Deformations in good quality fibres are interesting for a several pulp and paper applications. The deformations in the fibres are measured as curl index, fibre kinks, fibre latency, and fibre micro fractures in the cell wall. They affect the individual fibre strengths, but they provide substantial improvements in the paper sheet porosity, bulk, softness and water absorption. Generally, cellulosic fibres become curled when subjected to mechanical shear field at high consistency (15-30%), for example during screw pressing, plug-screw feeding, high consistency pumping and mixing, operations which are commonly used in a pulp mill. A fibre curl is defined as the amount of curvature over a specified length of uncoated fibre, according to expression (3.1):

$$\text{Curl index} = \left(\frac{\text{L(c)}}{\text{L(p)}} - 1\right) \qquad 3.1$$

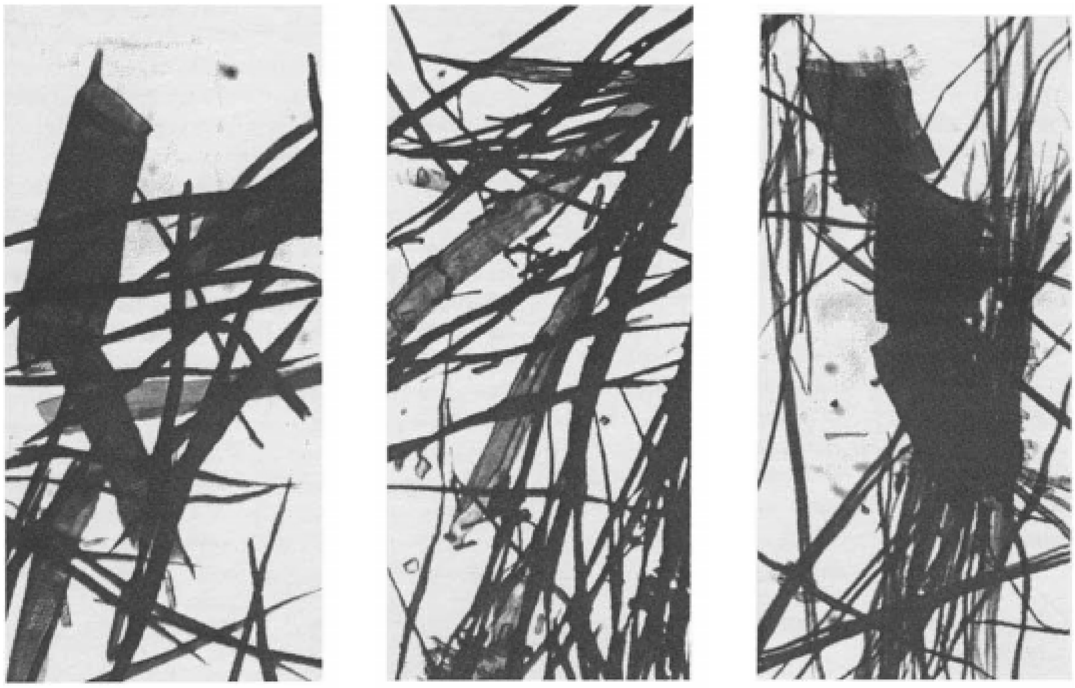
Where $L(c)$ = center line length (mm) and $L(p)$ = projected length (mm) [58].

Local deformations of the fibres such as knees and wrinkles in the fibres are called kinks. A kink can be a weak point of the fibre. Deformed fibres give a more elastic paper (a good property when manufacturing sack paper) if the paper is freely dried. Local deformations are measured in the form of kinks/mm, kinks/fibre, kinks < 60° per fibre, average segment length and kink angle. Detailed measurements of deformations in pulp can be used to optimize pulping, bleaching and the mechanical and chemical treatment of pulp [59].



Douglas-fir Southern Pine Eastern white pine

Figure 11 - Various softwood fibres isolated in a laboratory (amplified 60x) [54].



Black cottonwood Swamp tupelo *Eucalyptus grandis*

Figure 12 - Various hardwood fibres isolated in a laboratory (amplified 60x) [54].

3.4 Chemical pulping processes

Cellulose fibres are in general obtained by defibration of wood, by either chemical, mechanical or combined chemical-mechanical processing [46]. Wood, which is a composite structure where most cellulosic fibres are held together with hemicellulose and lignin, is broken down during the pulping process so that individual fibres are obtained [29,35,43]. Mechanical pulping uses several types of grinding to accomplish this task and most of the hemicelluloses and lignin are retained. On the other hand, chemical pulping uses chemicals reagents to break the linkages holding the composite wood structure together and most of the lignin is dissolved and removed. Foremost among the chemical processes are the well-known kraft and sulphite pulping processes [60]. In the kraft pulping process, a cellulosic source such as wood chips is digested with alkaline pulping liquor containing sodium hydroxide and sodium sulphide; while the sulphite process, as the name implies, employs a sulphurous acid solution of an alkali or alkaline earth metal sulphite to effect lignin removal [61].

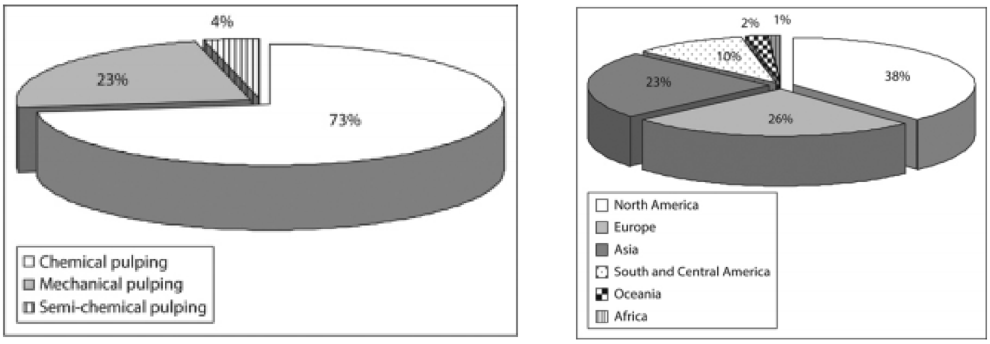
To produce a pulp product with appropriate whiteness and brightness for making non-woven mats, the lignin content of the pulp generally is reduced below about 10 weight percent. A major part of the pulp is used for making paper, which is manufactured by forming the wet fibres into sheets, another important part product made from pulp is dry-shaped cellulose fibre fluff. Fluff pulp is the wood fibre type used in absorption applications. The fluff pulp function is mainly to distribute liquid and hold the absorption core together. There is an industrial interest in improving fluff pulp properties and large attention is focused on modification of this kind of pulp [62].

3.4.1 Conventional pulping methods

Pulping represents the process in which wood or either lignocellulosic material is reduced to a fibrous mass, designated as pulp. Pulping processes range from physical separation of fibres to chemical degradation and removal of lignin [60,63,64]. The different processes to produce pulp are classified as mechanical, chemical and semi-chemical. On a global scale, pulps are predominantly produced by chemical pulping processes [60]. The main commercial chemical pulping techniques comprise the sulphate or kraft, soda and the acid sulphite [61]. Cellulose is largely preserved in sulphite pulps, whereas xylan is most stabilized in kraft pulps. The dominant chemical pulping process is the kraft process, while in comparison only 5,3% of the world chemical pulp production is obtained by the sulphite process [60]. A few mills worldwide use soda pulping of hardwoods and caustic soda (NaOH) is often used for pulping nonwood plants.

In such cases the addition of anthraquinone (sodium anthraquinone-2-sulfonate) is used to increase yield and pulp quality [65].

Figure 13 illustrates chemical, mechanical and semi-chemical pulping and the contribution of different world regions [57].



(a) (b)

Figure 13 - Discrimination of pulps by production methods (a) and contribution of different world regions (b) [57].

3.4.1.1 Kraft pulping process

The name kraft, which means strength in German, characterizes the stronger pulp produced when sodium sulphide is included in the pulping liquor compared with the pulp obtained if sodium hydroxide alone is used as in the original soda process. The term sulphate is derived from the use of sodium sulphate as a makeup chemical in the chemical recovery system [66,67]. The kraft process uses a combination of sodium sulfide and sodium hydroxide. Therefore, the main active chemical agents in the kraft process are hydroxide and hydrosulfide anions, which are present in the kraft cooking liquor, an aqueous solution of caustic sodium hydroxide and sodium sulphide, designated as white liquor. Although sodium sulfide (Na_2S) is often mentioned as a key reagent in the kraft pulping, it exists in water essentially as NaSH. The role of NaSH in chemical pulping is to facilitate a rapid breakdown of the lignin [68]. Without such pulping additives, long cooking times would be required to remove substantial amount of lignin, simultaneously considerable breakdown would occur, leading to a low pulp yield and strength [69].

In order to obtain desired pulp properties, to maximize yield, to minimize chemical and liquor consumption and thus to ensure a most economical production it is required the uniformity of wood chips, as raw material before pulping temperatures are reached

[70,71]. This is done by cutting and screening chips to a uniform thickness, pre-steaming chips at or above atmospheric pressure, applying hydrostatic pressure to chips submerged in pulping liquors, and allowing enough time to reach the process temperature [72,73]. The transport of chemicals into the chips is a combined effect of diffusion and penetration. While penetration is confined to the heating-up period, diffusion occurs during the whole cooking process. Under the conditions of alkaline cooking, the rate of diffusion of chemicals into the chips is almost the same in all the three of its structural directions. It is generally agreed that chip thickness is the most critical dimension for delignification, pulp yield and the amount of screening rejects. Chip thickness determines heterogeneity in delignification, with Backman reporting the maximum yields were generally obtained by using 3 mm-thick chips [71]. Chip thickness is more critical for hardwood than for softwood, the hardwood chips results in significantly more rejects than with softwood chips of the same thickness. The reason for this difference might be related with more heterogeneous hardwood fibre morphology, namely oak or ash, where the vessels are closed by tyloses that enter the vessel from the neighbouring ray cells. Wood density and morphology are factors which influence the rate of diffusion and thereby a critical chip thickness [73].

Wood chips are impregnated with the pulping liquor at liquor-to-wood ratios around 4:1. During impregnation, the cooking chemicals become distributed inside the chips. Impregnation starts as soon as the chips are subjected to digester pressure in the chip feeding system [72,74]. The soaked chips are heated from 150 to 180 °C for 2 hours in batch or continuous systems. Once the chips are in the digester, diffusion takes control over the mass transfer as the chips and liquor move currently through what is commonly referred as the impregnation zone [74]. The impregnation stage passes into the cooking phase as the free liquor is displaced from the chip column by hot cooking liquor. As the chip column moves down, the alkali, temperature and solids levels in the digester may be adjusted by introducing white liquor or wash filtrate into circulation loops [60]. The hydrosulfide ion plays a key role in kraft pulping by accelerating delignification. The NaSH functions primarily as a nucleophile in beneficial lignin degradation reactions, without causing carbohydrate degradation [75]. In standard pulping processes, the levels of NaSH and NaOH drop substantially as the cook proceeds. In general, large quantities of NaOH and NaSH are introduced in the pulping digester at the start so that reasonable levels are still present at the end of the cook [76].

Pulping kinetics have been the subject of numerous investigations. The course of delignification in relation to the content of carbohydrates reveals three distinct phases throughout the whole cooking process, as shown in Table 4 [77]. These phases are the initial phase, the bulk phase and the residual phase. The initial stage is characterized by a substantial loss of carbohydrates, small but rapid delignification and high alkali consumption. In the initial phase, delignification is caused by the cleavage of α-aryl and β-aryl ether bonds in the phenolic units of lignin, which accounts for around 15 to 25 % of native lignin. In this period of the cooking, approximately 20% of the lignin is dissolved as fragments of rather low apparent molecular weight [63]. The dissolution of lignin is accompanied by a substantial degradation and dissolution of carbohydrates, especially hemicelluloses, predominantly through a peeling reaction [78]. In the bulk delignification phase the main part of the lignin is removed whereas simultaneously only minor carbohydrate losses occur and the alkali concentration in the cooking liquor decrease only slightly [60]. Both NaOH and NaHS concentrations affect the rate, the activation energy is varying in a range of 140-150 kJ/mol. At a degree of delignification of around 90-92%, the selectivity in a kraft cook again changes rather dramatically; prolonged cooking results in very slow delignification, accompanied by the degradation and dissolution of amounts of increasing amounts of carbohydrates [69]. Thus, a high sulphidity is quite importance when the cook is about to reach the bulk phase. This transition point may also change if the charge of alkali is changed. Therefore, a high alkali charge in the cook, or alternatively an addition of alkali late in the cook, will affect the amount of residual lignin in the final delignification stage [79]. In the residual delignification step, only approximately 10 to 15% of the native lignin is removed. The low selectivity in the final phase of a conventional kraft cook is a limiting factor, as both the yield loss and the molecular weight degradation of cellulose are unacceptable. To maintain high yields and to preserve an adequate high quality of the pulp, delignification is limited to a certain degree, targeting kappa numbers around 15-20 for hardwood and 30-40 for softwood kraft pulps [79,80]. The kinetics described above are based on work using traditional differential rate equations, all known characteristics of the kraft process may be conveniently by using such an approach. Several difficulties arise in the theoretical treatment, since the chemical structure of lignin still is not accurately known and, consequently, assumptions have to be made [81].

Table 4 - Main reactions of polysaccharides and lignin during kraft pulping [77]

Cooking stage	Polysaccharides reactions	Lignin reactions
Initial	Deacetylation and dissolution of hemicellulose Peeling and stopping reaction at side chains	β- and α-*O*-4 ether cleavage of phenolic units
Bulk	Formation of hexenuronic acids (HexA) Cleavage of side chains Peeling, stopping Alkaline hydrolysis	β-*O*-4 ether cleavage (phenolic and non-phenolic units Major part of lignin removed Condensation
Residual	Reprecipitation Chromophore formation Increased DP loss by alkaline hydrolyses	Condensation Chromophore formation

At the end of the cook, the pulp in the digester still exhibits the physical structure of the wood chips. After cooking the chips are soft and may be fiberized with little mechanical action. At the high temperature levels applied for washing, a considerable number of reactions continue in the washing zone [60]. The significant cooking reactions are stopped when the cool wash filtrate from the first stage of brownstock washing brings the temperature of the digester contents down to 85-95°C. After removing the knots from the pulp through screening on knotter screens, the black liquor, consisting of white liquor enriched with degraded wood components, is removed after counter current washing of the pulp and further processed within the recovery line [75,79,82]. The extraction liquor contains fibres which are undesirable in the evaporation plant. For that reason, the liquor must be subjected to fibre removal before being transferred to evaporation. Efficient washing is crucial to the economics and pollution control of the subsequent bleaching. Unbleached kraft pulps have the brown colour of grocery bags or corrugated containers. Wood containing easily removed lignin can result in less harsh process conditions, which leads to carbohydrate preservation. None of the commercial pulping processes can complete delignify wood without unfavourable affecting the strength properties of the fibres [83]. Furthermore, disadvantages are also present with the loss in pulp yield caused by carbohydrate instability (peeling) and degradation during the alkaline reaction being the major ones. To minimize these losses, it is important to have a reliable understanding of both the chemical process and the raw material employed in the cook

[66,82,84]. Generally, about 2-3% of lignin is left in unbleached hardwood pulps and about 4-5% in softwood pulps. The final delignification is performed with the bleaching agents under much milder conditions than those used in pulping [60].

A fundamental factor that should be considered in process control of kraft pulping is the difference in delignification rate among softwood and hardwood species, which can in turn be related to the specific structural building blocks of lignin [79,80]. Softwood lignins are referred to as guaiacyl lignin, whereas hardwood lignins are composed of both guaiacyl and syringyl units in varying ratios [79,85,86]. The kinetics of the bulk and residual delignification in kraft pulping of birch (*Betula pubescens*) and spruce (*Picea abies*) were compared, with the delignification pattern being described with the same model for both wood species [80]. The amount of residual phase lignins in cooking of both birch and spruce are affected by the reaction conditions in an analogous manner. The only difference is the less pronounced influence of hydrogen sulfide ion concentration on the amount of residual phase lignin in the case of birch. This explains the well-known experience in industrial pulping that, in kraft pulping, sulphidity is less important for hardwood than for softwood. This different behaviour may be traced back to the fact that native lignin in birch wood exhibits fewer cross-linked structures compared to spruce, due to the presence of syringylpropane units. The bulk delignification of birch is 2,2-fold more rapid than that of spruce [60].

Figure 14 shows a simple flowsheet of the kraft chemical recovery process. The process has three main functions: minimizing the environmental impact of black liquor from the pulping process, co-generate steam and power and recycle pulping chemicals, such as NaOH and Na_2S [66].

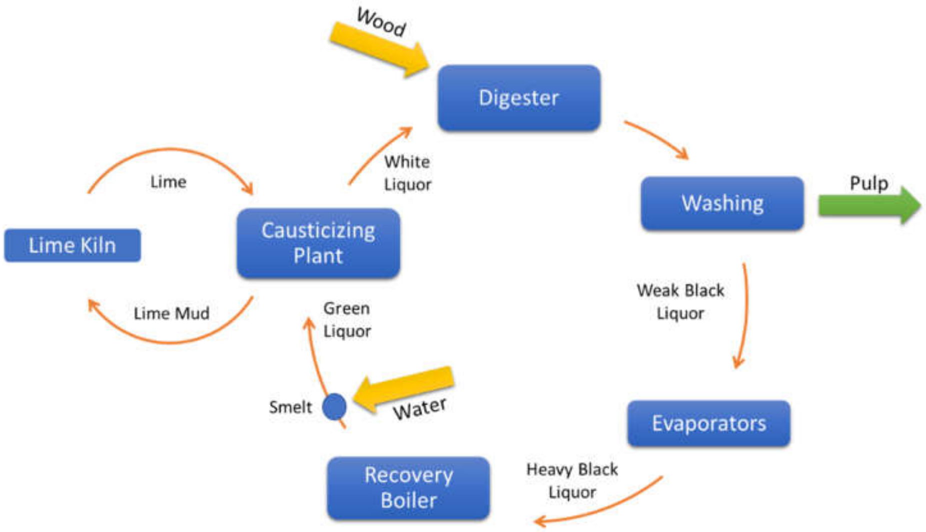


Figure 14 - Kraft recovery process. [66]

3.4.2 Pulping chemistry

The main goal of chemical pulping is to degrade the lignin into small fragments that are water soluble and then separate the aqueous liquor from the fibrous carbohydrate materials. Rapid lignin fragmentation reactions are the key for the successful pulping. However, there are competing reactions that interfere with efficient delignification [87].

The most important fragmentation reaction in alkaline pulping is the cleavage of the β-aryl ether linkage in β-*O*-4 structures, by a nucleophilic attack of the hydrogen sulphide ion on a quinone methide formed under alkaline conditions. This reaction fragments the lignin polymer, along with simultaneous liberation of a new phenolic hydroxyl group. In the alkaline cooking liquor, phenolic groups are ionized and contribute to the solubility of the lignin fragments [64]. Chemical reactions in the kraft process can be divided into two groups; those that involve lignin and those that involve carbohydrates [79,82]. The lignin reactions can be classified under two different headings: degradation and counteracting reactions. Structural differences in lignin, between hardwood and softwood as well as the difference in type of hemicellulose, affect greatly the pulping conditions and delignification and carbohydrate reactions during cooking [88]. Hardwood with its lower lignin content, less condensed lignin structure and with more β-*O*-4' bonds will be cleaved faster compared to softwood [77].

The cleavage of an alkyl-aryl ether (β-*O*-4, α-*O*-4 or β-5) linkage in lignin leads to the formation of a new phenolic hydroxyl end group that is ionized under the alkaline conditions prevailing in the digester. In the alkaline cooking liquor, phenolic groups are ionized and contribute to the solubility of the lignin fragments [88,89]. Figure 15 illustrates the two main β-*O*-4' delignification reaction in which hydrogen or RO^- group are lost thus forming an intermediate quinone methide structure [69]. In the first reaction, non-phenolic β-*O*-4' structures react due to the high pH and a nucleophilic attack occurs giving an epoxide which is not stable and reacts further with nucleophiles present. In the second reaction, that is the most efficient, the quinone methide is formed from a phenolic structure to which hydrogen sulphide is added to give an episulphide. In further reaction steps, the episulphide is first degraded with formation of elemental sulphur and coniferyl alcohol structure. Elemental sulphur is rapidly converted into polysulfide by reaction with the hydrogen sulphide ions present in the cooking liquor and, subsequently, the polysulfide disproportionate to form hydrogen sulphide and thiosulfate. The coniferyl alcohol structure may be found in the cooking liquor, as coniferyl alcohol [90], but is rapidly degraded to structures such as vanillin, vinylguaiacol and others [91].

As aforementioned, in the kraft process, the lignocellulosic feedstock is treated in alkaline media containing hydroxide, sulphide, and bisulfide ions (“white liquor”), causing the dissolution of lignin and part of the hemicelluloses. The sulphidity and active alkali charge are two important ad effective parameters that influence significantly the pulp properties. From the delignification in kraft pulping, sulphide and hydrosulphide ions facilitate the reaction of lignin removal and sulphur works mainly as a catalyst which is not consumed or transformed much. It has been found that the efficiency of lignin removal increases with increasing sulphidity. In practice, sulphidity is most often determined by chemical balance of the mill higher in closed cycle and lower in open mills. The optimum sulphidity also depends on several factors, such as wood species, alkali charge, cooking temperature and properties desired in the final product. The upper limit is typically determined by odour release from the plant. Thus, both alkali charge and sulphidity play an important role in the kraft pulping [75,86].

During the kraft process, wood delignification is accompanied by simultaneous and undesirable dissolution of carbohydrates mainly by alkaline hydrolysis and sequential elimination of the terminal reducing end groups. While the hemicelluloses are susceptible to alkaline glycosidic bond cleavage, the alkaline hydrolysis of cellulose is relatively slow even in the temperature range of 150–190 °C, partially due to the crystalline nature of cellulose. Therefore, the loss of hemicelluloses is responsible for a significant part of the total yield loss observed during Kraft pulping [44]. Solutions of sodium hydroxide cause much greater swelling of wood materials compared to acidic solutions and the caustic conditions do not result in the extensive condensation reactions of lignin found in acid sulphite pulping of wood. The cleavage of glycosidic bonds of polysaccharides in alkali is usually extremely slow in comparison to acid-catalyzed hydrolysis. The mechanism appears to be by nucleophilic displacement to form an epoxide between C-1 and C-2 via the ionized C-2 hydroxyl in basic solutions. The relative rate of sugar glycosidic bond hydrolysis in homogeneous solutions would be expected to increase in the order: galactose (1) < mannose (1.1) < glucose (2.5) < xylose (5.8) < arabinose (32) < glucuronic acid (280) [86, 92]. There is also a second mechanism of alkaline degradation that can cause extensive losses of polysaccharides. This reaction is termed end-wise degradation or the ‘‘peeling’’ reaction and proceeds at a rate of about 10^7 times faster than the alkaline glycosidic bond cleavage reaction. The reaction proceeds by sequential removal of the terminal sugars at the reducing end of the polysaccharide, and thus the sugars are sequentially peeled from the chain. The reaction is initiated by enolization of the reducing end groups followed by beta-elimination via enolate ion intermediates. The peeled sugars then go through a benzilic acid rearrangement to form various saccharinic acids dependent on the nature of the sugar and position of the glycosidic linkage. However, there are factors that inhibit the endwise degradation of polysaccharides in alkaline solutions. For example, the crystalline structure of cellulose inhibits the peeling reaction therefore, losses of cellulose in alkaline pulping are very limited.

During kraft pulping, hexenuronic acids (HexA) are formed under alkaline and temperature conditions, when 4-*O*-methylglucuronic acid from xylan is converted into hexenuronic acid. This conversion occurs through the elimination of the 4-*O*-methoxyl group after the loss of the hydrogen atom attached to the 5th position of the glucuronic acid residue. Such reaction rapidly takes place during the heating phase at early stages of pulping, between temperature of 110 and 150 °C, at pH 12 - 13. HexA rapidly reacts with permanganate, thus affecting the kappa number determination. Indeed, about 3-7 kappa units are reported to be accounted for by the presence of HexA in hardwood pulps [93]. Hexenuronic acids form covalent bonds with the lignin and consume electrophilic chemical reagents during bleaching (chlorine, chlorine dioxide, ozone and peracids). They also bond to ions and cause the brightness reversion of the bleached pulps. Hexenuronic acids have functional enol-ether and unsaturated carboxyl groups, which provide their stability and reactivity [93, 94]. These composites are relatively stable under alkaline conditions, and, for this reason, hexenuronic acid protects xylan against terminal depolymerization reactions, thus, preserving the yield of the pulping process. However, in drastic conditions of temperature and alkali dosage, these composites, as well as other polysaccharides, suffer alkaline hydrolysis and are degraded. Hexenuronic acid also suffers hydrolysis under acid conditions, being prone to the attack of electrophilic oxidants. Therefore, since the discovery of hexenuronic acid structures in kraft pulps, some technologies have been proposed for removing the composites from the pulp during the bleaching phase, which are basically based on the use of a stage with an acid hydrolysis at a temperature of about 80 to 100°C and a pH of about 3 [95,96,97].

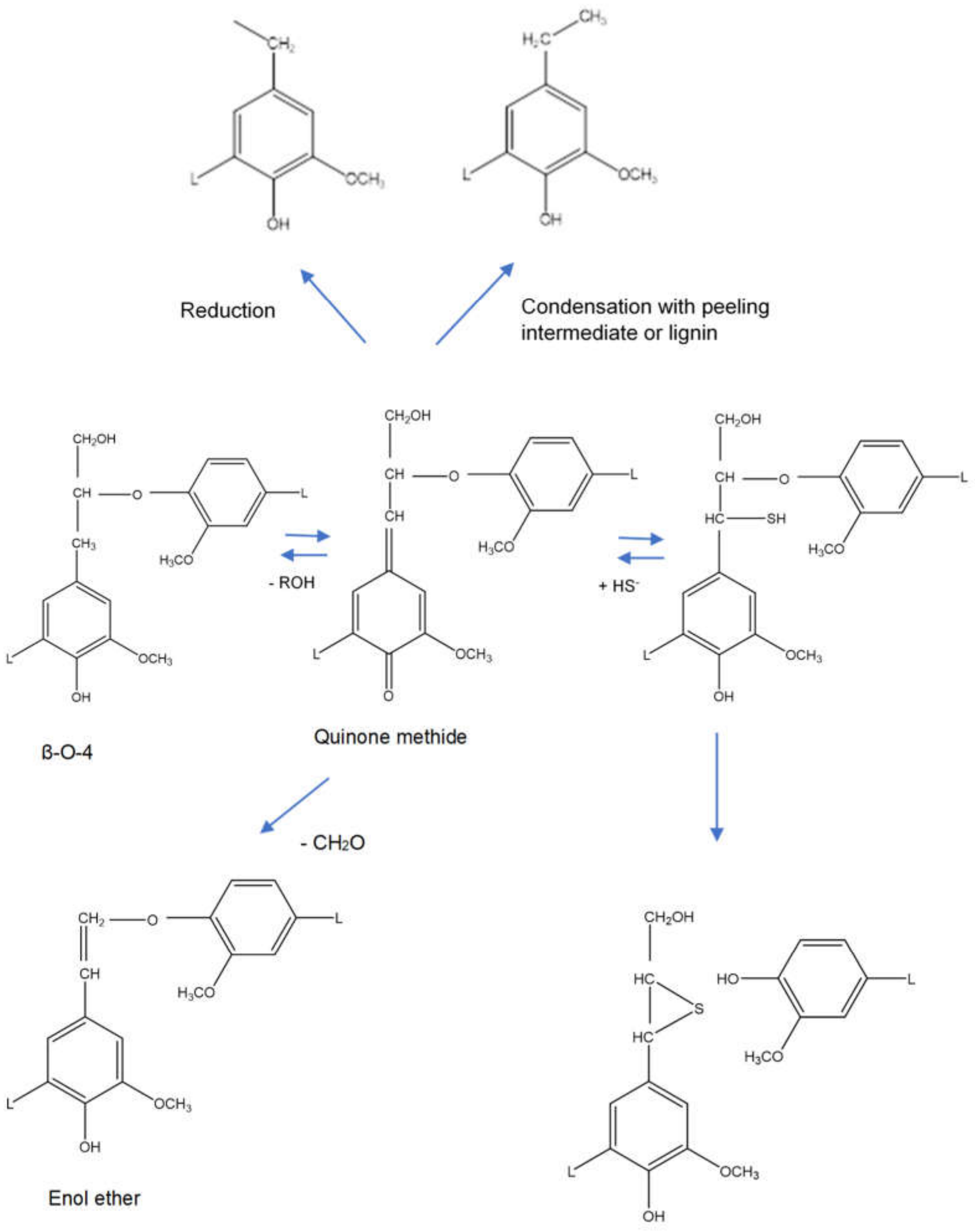


Figure 15 - Reaction scheme for the cleavage of phenolic β-*O*-4' structures in lignin during kraft cooking conditions. Competing reactions are also indicated: R = H, OCH_3, or linkage to another lignin unit; L = linkage to a lignin side chain unit [69].

3.4.3 Sulphite chemical processes

The sulphite process was developed around the acid calcium bisulphite process, wherein wood was pulped with an aqueous solution of sulfur dioxide and lime. Subsequently, calcium bisulphite was used with additional dissolved sulfur dioxide. During the first 50 years of chemical pulp production, the sulphite process was the dominant technology, due mainly to the high initial brightness and the easy bleachability of the sulphite pulps. However, when the need to recover waste liquor and pulping chemicals emerged, due to environmental concerns, the sulphite chemical pulping started to decrease [61,98].

The basic pulping reagent used in sulphite pulping is sulphur dioxide (SO_2) produced by burning molten sulphur or by roasting sulphur-based materials:

$$S + O_2 \rightarrow SO_2 \qquad 3.2$$

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2 \qquad 3.3$$

SO_2 is readily dissolved in water, thus forming sulphurous acid (H_2SO_3) and may be present in aqueous solution in the form of hydrosulphite (HSO_3^-) or sulphite (SO_3^{2-}) depending the pH:

$$SO_2 + H_2O \leftrightarrow H_2SO_3\ (SO_2.H_2O) \leftrightarrow H^+ + HSO_3^- \qquad 3.4$$

$$pKa1 = 1{,}8\ (25\ °C)\ or\ 3{,}0\ (120\ °C)$$

$$HSO_3^- \leftrightarrow H^+ + SO_3^{2-} \qquad 3.5$$

$$pKa1 = 6{,}8\ (25\ °C)$$

At pH < 1 practically all SO_2 is present in solution as non-dissociated H_2SO_3, at pH 4 – 5 as hydrosulphite and at pH > 8 as sulphite (Figure 16) [57,98].

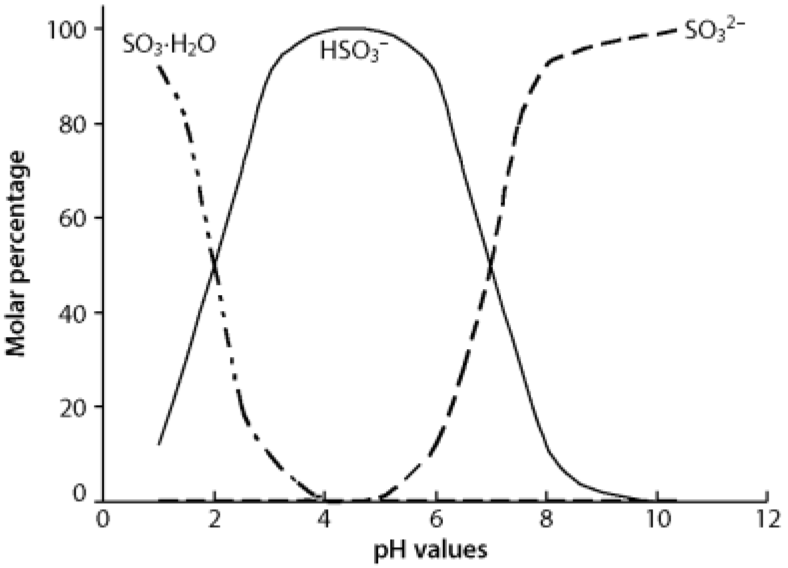


Figure 16 - Relative molar percentage of SO_2H_2O (-..-), HSO_3^- (-----) and SO_3^{2-} (- - -) in aqueous solutions as function of pH at 25 °C [57].

The restrictions for use pulping bases (Me) are related to the solubility of their sulphite salts. Since calcium sulphite has very limited solubility above pH 2, an excess of sulfur dioxide gas was maintained in the digester to keep the pH below this level. At cooking temperature, the calcium hydrogen sulphite decomposes to calcium sulphite and hydrated SO_2. As alternatives to calcium, magnesium, sodium and ammonium cations are also used is sulphite pulping [98, 99]. Since both monovalent cations are soluble over the entire pH range, they may be used in acid, bisulphite (magnefite), neutral and alkaline sulphite processes. Magnesium sulphite has decreasing solubility above pH 5, but sodium and ammonium sulphites are soluble over the entire pH range, as shown in Table 5 [57]. Sulphite pulping at low pH therefore must be carried out a relatively low temperature, around 135°C to avoid excessive polysaccharide depolymerization. Despite some clear advantages of the monovalent over the bivalent bases with respect to flexibility (entire pH range available) and pulping operations (more homogeneous impregnation and higher rate of delignification), their use in sulphite cooking processes has been limited to a few applications, mostly due to deficiencies in recovery of the cooking chemicals [60,98,99]. Moreover, the accessibility and the influence of hemicelluloses, are involved in determining the weight-average degree of the polymerization (DP) of cellulose in acid sulphite pulps is usually higher than that in comparable kraft pulps. In the kraft pulping is obtained higher yields of fibres with great plasticity, lower crystallinity, and more extensively altered cellulose. Due to these properties, the kraft fibre is usually less susceptible to damage by mechanical stress. On the other hand, sulphite fibres are relatively stiff, with high crystallinity and less degraded cellulose. Furthermore, these fibres are more easily damaged by physical treatments than kraft fibres [60].

Table 5 - Summary of wood sulphite pulping process (adapted from [57]).

Nomenclature	Initial pH range at 25°C	Base alternatives	Active reagents	Pulp properties	End use	Pulp yield (%)
Acid bisulphite	1-2	Ca^{2+}, Mg^{2+}, Na^{+}, NH_4^{+}	H^{+}, HSO_3^{-}	Easily bleachable pulp, weaker than kraft pulp, but higher yield (softwood)	Fine paper, tissue, glassine, newsprint, viscose production	48-53
Bisulphite (Magnefite)	3-5	Mg^{2+}, Na^{+}, NH_4^{+}	(H^{+}), HSO_3^{-}	Easily bleachable pulp, stronger than acid sulphite pulp	Newsprint, fine papers	50-55
Neutral sulphite	6-9	Na^{+}, NH_4^{+}	HSO_3^{-}, SO_3^{2-}	Good stiffness and moldability	Corrugating paper	70-80

Full chemical pulp production by the sulphite process has almost disappeared in the United States but is still used in Europe. Sulphite pulps have properties that are desirable for high quality fine paper and tissue paper and for producing dissolving pulps. The dissolving pulp production is a solid established market with a predicted annual growth rate about 5% in the next few years [60].

3.4.4 Mechanical and chemi-mechanical pulping

Mechanical pulping uses mechanical energy to weaken and separate fibres from wood via a grinding action. The advantage to mechanical pulping is that produces much higher yields than chemical pulping processes, up to 97%. However, because this process does not dissolve lignin and due mechanical grinding produces shorter fibres, the fibre strength and age resistance of the resulting pulp are low [68]. Consequently, most mechanical pulp is used for lower paper grades, namely newspapers, magazines and catalogues. Mechanical pulping also requires more screening of the raw materials, in order to remove contaminants such as dirt and knots, than chemical pulping processes. There are four main types of mechanical pulping: stone ground wood (SGW) pulping, refiner mechanical pulping (RMP), thermomechanical pulping (TMP) and chemi-thermomechanical pulping (CTMP). The chemi-mechanical pulping methods involves some chemical treatment before or during mechanical pulping. The chemical pre-treatment of wood chips promotes less destructive separation of fibres from the feedstock, resulting in longer fibres, higher fibre content, and less shives. The CTMP process also produces more flexible fibres, which provide higher sheet density, burst strength, and tensile strength, and higher pulp brightness than the TMP process [60,99].

Special technology is required to manufacture mechanical pulps suitable for fluffing, such as SGW, RMP, TMP and CTMP. Problems to overcome with these include low brightness and brightness reversion, shives or fibre bundles, drastic fibre-length reduction and the influence of wood extractives on fibre wettability [3].

3.5 Pulp bleaching

The bleachability of kraft pulps may be defined as the consumption of chemicals required to achieve a given target brightness using a specific bleaching sequence, either ECF or TCF. Bleaching is a chemical process applied to cellulosic materials to increase their brightness, which is the reflectance of visible light from cellulosic cloth or pulp fibres formed into sheets, using a defined spectral band of light having an effective wavelength of 457 nm [83,100]. Bleaching enhances pulp properties, increases its stability and it means purifying pulp. Furthermore, bleaching is also effective in removing unwanted particles that contaminate pulp fibres [101].

Unbleached chemical pulps still contain lignin in an amount of 1.5 to 4% in the case of hardwood kraft and 3 to 6% in the case of softwood kraft pulps. Lignin in native wood is slightly colored and the residual lignin, after chemical pulping, is highly colored. Bleaching, which consists of a chemical process applied to cellulosic pulps, increases their brightness by removing lignin and/or by its discoloration [101]. Moreover, lignin-removing bleaching promotes brightness stability, pulp cleanliness, freedom from colored particle, and a high cellulose content. These objectives should be achieved without compromising the strength of the pulp, that is cellulose degradation during bleaching may lead to significant loss of strength in the final product [100,101].

Globally, there are several bleaching sequences shown in different pulp mills to achieve the bleaching action [101,102]. Bleaching chemicals are frequently applied sequentially with intermediate washing between stages, because it is not possible to achieve enough removal or discoloration of lignin by the action of any one chemical in a single stage. Multi-stage sequences take advantage of the different action of each chemical and provide synergy in bleaching or delignification. The preference of bleaching sequences depends on many things such as pulp categories, environment issue, operating cost and product quality of final bleached pulp. Bleaching is most efficient when the bleaching sequence contains at least one oxidant from each category. From a process point of view, it is not advantageous to change between electrophilic and nucleophilic stages, due this relates to a change in pH [102].

The bleaching of pulp with chlorine has become a most important universal environmental problem. They produce many hazardous organic compounds (such as organic halides, dioxins, etc.) during bleaching process [103]. Therefore, many leading pulp mills modify their bleaching sequences so that it can be decreased the impact on environment. Following the abandonment of chlorine as bleaching agent two technologies have been developed: Elemental Chlorine Free (ECF) and Total Chlorine Free (TCF). The distinguishing factor between the two processes is the use of chlorine dioxide among bleaching reagents (ECF) or the absence of chlorine dioxide among used reagents (TCF). To compensate for the lack of chlorine dioxide, TCF will either add higher dosages of peroxide, or supplement the process with ozone [102,103,104]. ECF sequences, in which chlorine dioxide is used only in the final bleaching steps, are also called ECF "light" sequences.

Table 6 summarizes the chemicals used in pulp bleaching, their function, formula, stage designation, advantages and disadvantages.

Table 6 - Description of bleaching chemicals [83].

Oxidant	Function	Formula	Stage designation	Advantages	Disadvantages
Chlorine	Oxidize and chlorinate lignin	Cl_2	C	Effective, economical delignification, good particle removal	Organochlorine formation, highly corrosive, hazardous to environment
Chlorine dioxide	Oxidize, decolorize, and solubilize lignin	ClO_2	D	Achieves high brightness without loss of pulp strength, good particle bleaching	Must be produce on site, cost, some organochlorine formation, highly corrosive
Oxygen	Oxidize and solubilize lignin	O_2	O	Low chemical cost, provides chlorine free effluent to recovery	Requires significantly capital equipment, potential loss of pulp strength
Hydrogen Peroxide	Oxidize and decolorize lignin	H_2O_2	P	Easy to use, low capital cost	High chemical cost, poor particle bleaching, may cause loss of pulp strength
Ozone	Oxidize, decolorize and solubilize lignin	O_3	Z	Effective, provides chloride-free effluent for recovery	Must be made on site, cost, poor particle bleaching and pulp strength
Enzymes (xylanase)	Catalyse xylan hydrolysis and aid in lignin removal	-	X	Easy to use, low capital cost	Limited effectiveness
Sodium hydroxide	Hydrolyze chlorolignin and solubilize lignin	NaOH	E	Effective and economical	Cost
Chelants	Remove metal ions	EDTA or DTPA	Q	Improves peroxide selectivity and efficiency	Cost Hazardous to environment

Today most fluff is derived from fully bleached chemical pulps produced by the conventional bleaching technology. Regarding any differences between fluff pulp made from kraft or sulphite, it may have generalized that the behaviour of the final fluff is commonly related more to the physical properties of the fibres. A fluff pulp with satisfactory properties can be manufactured by both methods.

3.6 Fluff pulp production

Pulps are generally classified in the industry as paper-grade pulps or fluff pulps (nor speaking to dissolving pulps that are assigned to special applications). Paper grade pulps, derived from either hardwoods or softwoods, are used in the manufacturing of printing, tissue and packaging papers. Paper-grade pulps are usually sold in a heavy weight sheet form like cardboard, with densities greater than 0.900 g/cm^3. High densities of paper-grade pulp do not set a problem as the aggressive mechanical agitation easily disperses the fibres into a slurry prior to be involved in papermaking [99]. Chemically, fluff quality is essentially equivalent to paper-grade pulp, but there are significant physical differences between fluff pulp and paper pulp in the finished state, that is, as they come off the dry end of the forming machine [3,105]. Fluff pulps are typically employed in the manufacture of non-wovens. Non-wovens are fibrous webs or fabrics in which the fibres are neither woven nor knitted [106]. Fluffed pulp is often marketed in the form of roll pulp, but also may be sold in sheet form as bales (hereinafter both referred to a dried fluff pulp sheets), as shown in Figure 17. The product is rewound into continuous rolls for shipment to the customer. Since the roll product is intended to be later reprocessed into individual fibres, low sheet strength is desirable and typically little, or no refining is used prior to roll manufacturing. The requirements for surface uniformity and formation are similarly moderate [11,12,107].

(a) (b)

Figure 17 - (a) Fluff pulp rolls; (b) Fluff pulp after defibration.

The most preferred wood fibres for producing the fluffy pulp sheet are generally derived from long-fibre coniferous wood species, such as pine, spruce or hemlock. Softwood chemical pulp can be augmented with hardwood chemical pulp fibres, from example from aspen, oak, eucalyptus and with wood pulp fibres obtained from mechanical pulping processes, such as ground wood, thermomechanical, chemi-mechanical, chemi-thermomechanical pulp processes [3,108,110]. Additional fibres may also be added from any of a variety of other natural or synthetic fibres sources, namely silk fibres, bagasse, hemp, jute, rice, corn, cotton, acrylic, nylon and polyester. According with U.S. Patent No. 6.059.924 mechanical pulp fibres and non-wood fibres will constitute less than about 40% by weight of the dry pulp fibre weight, and most often less than about 10% by weight [11]. Conventional fluff pulp sheet is manufactured, following the chemical pulping operation, by forming the pulp into a sheet or non-woven mat by one of several well-known wet-forming processes typified by the Fourdrinier process. In general, this process involves adjusting the pulp furnish to the noted consistency; in a first step, bleached chemical pulp is deposited upon a screen or wire to form a web of pulp fibre [107]. In its initial formation stage, it is usually carried out by passing an aqueous dispersion of low pulp concentration, around 0.5 to 1.0% by weight solids over the screen. This screen assisted by vacuum or suction increases the consistency of the web to approximately 20 to 35 weight percent of solids. Then the web is compressed in a press section to remove additional water and to optimize moisture reduction without excessive wet mat compaction or densification. This step results in an increase in consistency of the web about 30 to 60 weight percent. Other mat forming equipment such as the cylinder and twin-wire machines may alternatively be employed [11,110]. In the production of fluff pulp sheets, less pressure is applied in the pressing step than would normally be found in the conventional drying machine when producing pulp for papermaking. The lightly pressed coherent fibrous web is then dried by any convenient means such as drying tunnel or rotating drum dryer, which more moisture content should be removed from the sheet than generally is necessary in papermaking. The pulp dryer section of the fluff pulp manufacturing process usually includes a series of steam-heat cylinders. Alternate sites of the wet pulp web are exposed to the hot surfaces as the sheet passes from cylinder to cylinder [11,111]. In most cases, the sheet is held closely against the surface of the dryers by a fabric having carefully permeability to steam and air. Heat is transferred from the hot cylinder to the wet sheet and water evaporates. The dried sheet of fluff pulp fibres typically has a calliper of 0.5 to 2.0 mm, a basis weight of 200 to 900 g/m^2 and a burst index of 0.5 to 3.0 kPa.m^2/g. The dried pulp sheets have a density of 0.4 to 0.7 g/cm^3 and a typically moisture range between 6 to 10 weight percent [11,12].

During the manufacturing of fluff pulp sheets, a problem emerges in controlling cross-machine directional basis weight of the formed web. Manufacturers must control the basis weight of the formed web without compromising fibre orientation profile. Excessive rush or drag in the forming wire may cause more orientation of the fibres of the web in the machine and cross directions [107]. Furthermore, wood fibres have tendency to attract to one another, forming clumps, the effect called flocculation. Defloccullation becomes quite difficult at much above 0.5% consistency, minimizing the degree of flocculation is crucial to the physical properties of the fluff pulp. It is desirable to provide processes for forming fluff pulp sheets with improved bulk, softness and reduced inter-fibre bonding without compromising the absorbent properties of the pulp [3,112]. Additionally, the fluff pulp sheet should have low content of fibre bundles (knots) or hard spots, reduced variability in weight, moisture, Mullen strength and low shred energy while possessing high shred quality which results in significantly reduced defibration energy when the sheets are ultimately processed [12,111].

At the customer's plant the fluff pulp is formed by unwinding a rolled-up sheet of substantially dry fibre that is continuously fed into a hammermill (Figure 18). Generally, the hammermill has rapidly moving metals bars that repeatedly impact, tear, and break the free end of the sheet into individual fibres or fibres aggregates [11,107]. This defibration is the process of freeing the fibres from each other before the fluff pulp enters the product forming machinery. The individual fibres are then introduced into a stream of air that is directed to a moving wire, an air-laid process. The air passes through the wire, but most of the fibres and fibre aggregates are retained at the surface of the wire to form a fibrous web. This fibrous web is then incorporated into the disposable absorbent product [12,109]. As already mentioned, the hammermills used for fluff production are very large energy consumers and fibre bundles present in the fluff pulp sheets will increase the amount of energy expended during defibration. The object is to keep the knot´s level as low as possible with the lowest possible energy consumption while maintaining the fibres undamaged [17,110]. Excessive consumption of energy does not only result in economic losses, but also in order drawbacks such as decreasing fibre lengths, dust formation, and static charging of fibres, which in turn hampers the formation of an even web. To alleviate this problem, the pulp mill may need to add chemical peels before sheet formation [110].

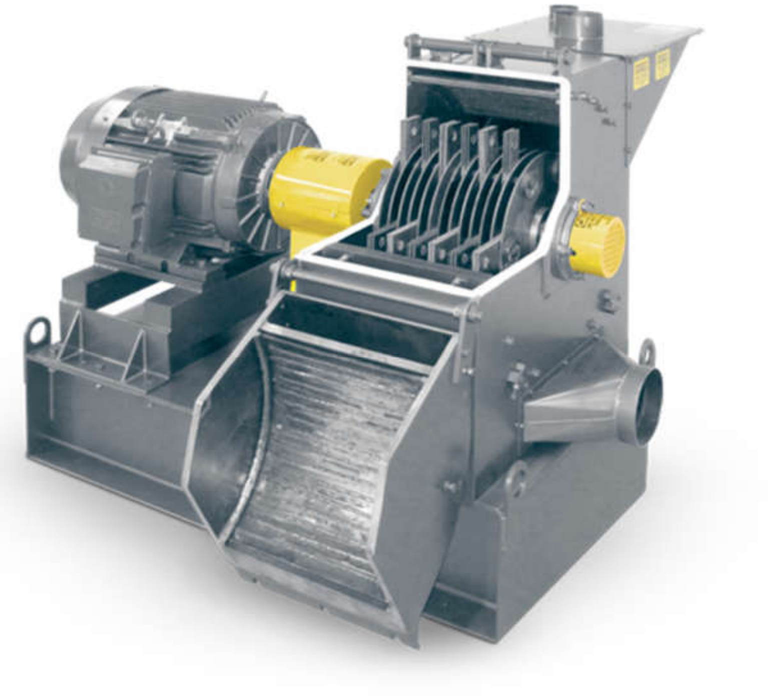


Figure 18 - Pilot scale hammermill.

3.6.1 Modification of fluff pulp

Fluff pulp should have technical properties such as high absorption capacity and low time of absorption, high values of specific volume wet, bulk after wetting, compression, rate of absorption, strength and brightness [3,108]. In order to meet these requirements, various processes and approaches to produce stiffer fibres to be used in fluff have been developed.

3.6.1.1 Crosslinking agents

The many ways to improve fibre properties are based on additives from various chemicals that act as a crosslinking agent for cellulose molecules within cellulose fibres or the use of synthetic resins. One of the properties improved when fluff pulp fibres are cross-linked is wet resilience. High wet resilience yields a fibre network that maintains its porosity even when put under pressure [62].

Commonly, cellulose fibres are crosslinked to impart advantageous properties such as increased absorbent capacity, bulk, and resilience to products containing such crosslinked fibres. Crosslinked cellulose fibres and methods for their preparation are widely known. Crosslinked cellulose fibres are prepared by treating fibres with a crosslinking agent. Lund et al. [62] reported the results of crosslinked softwood kraft pulp fibres with 1,2,3,4– butanetetracarboxylic acid (BTCA). Besides polycarboxylic acids, BTCA and citric acid, reagents such as formaldehyde, dialdehydes and diepoxides may be applied to improve intra-fibre crosslinking of cellulose. However, the use of formaldehyde as a cross linking agent is today questioned due to the health aspects. Dialdehydes act in analogous way as formaldehyde, irritating to skin and mucous membranes. Therefore, these reagents are less suited in cellulose products which can be used in close vicinity of the skin [113].

Crosslinking agents are generally bifunctional compounds that, in the context of cellulose crosslinking, covalently couple a hydroxyl group of one cellulose chain to another hydroxyl group on a neighbouring cellulose chain [105]. These polycarboxylic acids form ester bonds with the hydroxyl groups in the fibre wall and the reaction is thought to proceed via a cyclic anhydride intermediate. One BTCA molecule can form one, two, three ester linkages with the fibre wall polysaccharides. The modification introduced carboxylic acid groups into the fibres, but most of these groups were protonated during the water retention value (WRV) test. It was found that the WRV decreased because of the introduced cross-linker [62,111]. Determining the WRV is a common method in the pulp and paper industry, for example for investigating the effect of beating on fibre swelling and the influence of drying on the ability of pulp fibres to swell when re-slushed [114]. The trend is that higher relative reaction intensity or higher addition of BTCA gives high absorption capacity (measured as Free Swelling Capacity) and high wet resilience in both dry and wet states [62]. Despite washing the fibre after the crosslinking process, residual amounts of these often-expensive crosslinking agents remain in fibre. Furthermore, excessive crosslinking may produce brittle fibres of excessive stiffness, thereby making them difficult to form into densified sheets for transport and to subsequently fluff without fibre damage [111].

US Patent 6821383 B2 describes an easy process for obtaining a modified cellulose fluffed pulp without the use of any crosslinking agents. The method comprises oxidizing cellulose pulp in the presence of a nitroxide radical mediator and fluffing treated cellulose pulp [105]. The modified pulp prepared via this process is characterized by an aldehyde content of between about 1 to 50 mmol/100 g cellulose. The aldehyde functionality generated on the cellulose, by their reactivity with hydroxyl groups on neighbouring cellulose chains, in effect enable self-crosslinking interactions with (intra-fibre) the cellulose fibre or between neighbouring (inter-fibre) cellulose fibres. The modified fluffed pulp prepared according to this method is characterized by highly absorbent properties including absorption capacity, structural integrity, wicking rate and wicking capacity [105].

Conventional cellulosic fluff pulp may be densified by mechanical compression, such as calendaring and subsequently embossing. The embossing process selectively compacts the densified cellulosic pulp fluff material imparting a fibre density profile of alternating high and low fibre density zones, improving flexibility, absorption capacity and wicking properties [109,112]. The high fibre density zones have the ability to disperse fluid throughout the entire surface of the absorbent sheet by virtue of excellent wicking properties, establishing a network of capillary-action channels interconnecting the low fibre density zones which have the task of permanently absorbing and retaining the fluid [17,112]. When a fluid mass is released on a certain point of the absorbent sheet, the fluid will rapidly penetrate the low fibre density zones immediately underneath the fluid impact point. Local overflow is avoided by the wicking power of the high fibre density zones, which transfer fluid from saturated to non-saturated low fibre density zones, thus spreading the fluid throughout as larger absorbent volume [115,116].

3.6.1.2 Hydrolytic enzymes (xylanase and cellulase)

Fluff pulp with improved defibration properties is produced by exposing the pulp to an enzyme treatment at any stage during the pulp production process. Interest in hemicellulolytic enzymes has increased remarkably during recent years. This is mainly due to the new areas of application of these enzymes within the pulp and paper industry [117]. Novel enzyme technologies can reduce environmental problems and modify fibre properties. Because the pulp and paper industry are capital intensive with facilities specific to the tasks, new technology must either reduce expenses or fit easily in into existing process design.

Xylanases and cellulases are glycoproteins that contain the specific prosthetic group capable to catalysis, i.e. increase the rates of chemical reactions. Both enzymes act with great specificity and often catalyse only one specific reaction. Specificity is conferred by the three-dimensional structure of the glycoprotein complex. [117,118]. Xylanases are hydrolytic enzymes, which cleave the β-1,4 backbone of the complex plant cell polysaccharide xylan. They are a widespread group of enzymes, involved in the production of xylose, a primary carbon source for cell metabolism and in plant cell infection by plant pathogens, and are produced by a plethora of organisms including bacteria, algae, fungi, protozoa, gastropods and anthropoids [119,120]. Their official name is endo-1,4-β-xylanase, but commonly used synonymous terms include xylanase, endoxylanase, 1,4-β-D-xylanxylanohydrolase, endo-1,4-β-D-xylanase, β-1,4-xylanase and β-xylanase [102]. A large variety of xylanases produced by microorganisms become a major group of industrial enzymes that are capable to degrade xylan to renewable fuels and chemicals, in addition to their use in food, paper and pulp industries [121]. Cellulase is one such enzymes, which earns consecutively increasing demand. It is produced by fungi, bacteria, actinomycetes, protozoans, plants and animals. All cellulases cleave β-1,4-glucosidic bonds. However, they display a variety of topologies ranging from all β-sheet proteins to β/α-barrels to all α-helical protein [122]. The cellulases can be classified based on their mode of action: endoglucanases, cellobiohydrolases and β-D-glucosidases. Endoglucanases randomly attack the amorphous regions of the cellulose substrate, yielding longer chain oligomers. Cellobiohydrolases are exoenzymes, which degrade the crystalline cellulose, releasing cellobiose. Both types of enzymes act on cellulose chains and cleave β-1,4-linkages between the anhydroglucose units. The β-D-glucosidase also called cellobiase converts cellooligosaccharides and cellobiose to glucose [123,124]. Although cellulose is relatively simple in terms of composition (anhydro-glucopyranose units only) and morphology (mainly amorphous and monoclinic Iβ or triclinic Iα crystalline), there is a vast natural diversity of cellulases that act on the cellulose chain either alone or in concert. Usually, kraft pulp has been treated with cellulases and xylanases, and both enzymes have reduced the energy required for further refining [125]. Cellulase and hemicellulase enzymes modify the surface properties of fibres and possible fines so that bonding is reduced, and the shredding properties of the pulp are improved. However, the cellulases must be used carefully so they do not reduce the strength of the fibres. Xylanase treatments are more effective on unbleached pulps than they are on bleached kraft pulps [126]. Because enzymatic hydrolysis is a heterogeneous reaction and requires direct physical contact between enzyme and substrate, the diffusion of these enzymes towards the cellulosic substrate may be limited by physical barriers, such as lignin, until they adsorb on the substrate surface and then catalyse the hydrolysis [127]. The pulp may be treated with enzyme prior, during and after bleaching and carried out in the drying machine. The enzyme treatment provides the increase of drying capacity of fluff pulps because the wet pressing of pulp can be increased without deteriorating the shredding properties. Additionally, the dry matter content of the pulp prior to drying increases due to the wet pressing and the shredding properties may be substantially improved while maintaining the wet pressing and density level without compromising the absorbency [15].

3.6.1.3 Surfactant debonders

In some embodiments, during the fluff pulp manufacturing process, debonders or debonding agents may be used. Debonders are surface active chemicals that are added prior to, or during, the forming and drying operation of the fluff pulp manufacturing process [18,128]. The purpose of the debonders is to reduce the amount of fibre-fibre bonding that occurs during drying. Debonders are generally surfactants that bare extensively used in the chemical industry to modify different phases [129]. Due to their different structures, surfactants have different applications in industrial processes and product manufacturing. The chemical variety of surfactants available is enormous and growing rapidly [130]. Typically, surfactant debonders contain a large amount of positive functional groups on one side (such as protonated amine/amide ions) and hydrophobic groups (tail) on the other side (such as long alkyl chain) [105]. The function of the hydrophobic side is to interact with non-polar compounds, while the hydrophilic side interacts with the aqueous environment. Currently, cationic, anionic, nonionic and amphoteric surfactants are used worldwide [131]. Cationic debonders consist of two parts: cationic groups ($-N^+$, $-S^+$, $-P^+$) and hydrophobic groups. The positively charged part of the debonding agent is easily absorbed on the fibre surface containing hydroxyl groups. This is due to the negatively charged surfaces of the fibres. The debonding agent can weaken the inter-fibre forces by reducing the formation of hydrogen bonds between fibres. The hydrophobic groups also rearrange on the fibre surface. This results in an increase in the overall bulk of the fibre matrix, creates pockets for fluid accumulation, improve the smoothness of the fibre and consequently reduce the friction between fibres. However, the hydrophobic groups of the debonders exhibit detrimental effects on the water absorption of the pulp [132]. Cationic surfactants are still popular, because of their affinity to adhere and modify the surface properties of solid surfaces. They are also frequently used in combination with non-ionic surfactants. The anionic surfactants are materials in which the dissolved surfactant bears a negative charge. The anions of alkali metal salts of fatty acids (soaps) are typical, as are the anions of long chain sulfonates, sulphates and phosphates [131]. Sulphate-based surfactants are generally more hydrophilic than sulfonated ones due to the presence of an additional oxygen atom in the surfactant structure [133]. The non-ionic surfactants generally refer to polyoxyethylene compounds, but includes also other materials such as sugar esters, fatty alkanolamides and amine oxides. These surfactants are used mainly in the textile processing and are commonly used along with other surfactants. The amphoteric surfactants contain oppositely charged functional groups, usually carboxyl, ($-COOH$), and amino ($-NH_2$) groups, which ionize in accordance to the solution pH. Amphoteric surfactants are usually used in combination with other surfactants (as co-surfactants) as a means to modify and improve the performance of a primary surfactant, because of their ability to associate with both positively and negatively charged molecules, as well as their affinity to alter the structure of micelles. At low pH values, amphoteric surfactants are cationic while at high pH values these are anionic [131,134]. The amphoteric surfactants remain soluble, and hence effective, when they are mixed with high concentration of acids, alkalis or salts. Accordingly, they are found to have applications in personal care products, detergent formulations and strong acid cleaners [130].

Surfactants influence absorbency in several different ways, but all are traceable to the fact that these molecules adsorb strongly at one or more the interfaces in the system. The mentioned surfactants are simple because their hydrophobics were all straight chain alkyl or alkylbenzene radicals, and the classification for type was based only on hydrophilic groups. Many surfactants, both ionic and non-ionic, contain multiple hydrophilic groups, the multiplicity itself imparting special properties [129,131,134].

Debonders can be introduced at several points in the wet end: headbox, stuff box or machine chest. They should be incorporated into the furnish at the point in the wet-end which maximizes contact time with fibres, thus allowing complete and uniform exhaustion of the debonder [18,135]. The debonder surfactants can be suitably sprayed onto the web, using a formation shower or spray boom over the table, coated onto the web or immersing the web with the debonder [18]. This process will promote lubrification effect, which reduces degradation of individual fibres and decreases the number of fines produced during defibration of the pulp. Furthermore, debonded fluff pulp requires lower energy consumption and affords reduced knot formation during hammermill defibration [106].

3.6.1.4 Antimicrobial agents

Materials produced from cellulosic pulps are more susceptible to the development of microorganisms, since they are composed of natural fibres. The function of antimicrobial agents is to destroy these microorganisms or to inhibit their growth. Microorganisms, for example bacteria and fungi, have an external cell wall, composed of polysaccharides, which protects the cell from the outside environment. Underneath the cell wall is a semipermeable membrane, where are the enzymes and nucleic acids, which are responsible for cellular reactions and the storage of genetic information, respectively. Antimicrobial agents damage this cell wall or alter the membrane's permeability, inhibiting enzymatic activity and denaturing proteins, which are essential for its survival. At the same time, antimicrobial agents must be able to remain active for a long period of time and have low toxicity to humans, i.e., they cannot cause irritation or allergies to users [136,137].

Polyhexamethylene biguanide (PHMB) is a polymer used as a disinfectant and antiseptic (Figure 19). The PHMB structure has an average of 12 biguanides per molecule, however, the longer the molecule of PHMB, the greater is the antimicrobial activity. This agent is a biocide that suppresses microorganisms, has a low environmental impact and toxicity, is soluble in water and is chemically stable. PHMB molecules have a positive charge that interacts with the negative charge of phospholipids on the membrane of microorganisms. This interaction causes the non-polar segments of the molecules to go inside the membrane, which makes it more permeable, leading to its rupture and, consequently, to the death of microorganisms [137,138].

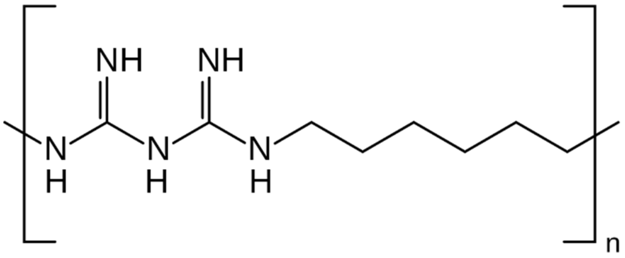


Figure 19 - Molecular structure of PHMB monomer. Chemical formula: $(C_8H_{17}N_5)_n$ [137].

The cationic nature of PHMB allows it to interact with cellulosic fibres, through hydrogen bonds and ionic interactions, due to the carboxylic groups present in the fibre that causes a negative charge. When PHMB concentrations are low, electrostatic interactions between the fibre and PHMB predominate. On the other hand, with increasing concentration, hydrogen bonds dominate [139].

3.6.1.5 Sizing agents

In the previously published study [140], it was proposed to use the calcium carbonate/cellulose fibre composites combining natural polymers and inorganic particles to enhance fluff pulp properties, such as reducing bonds and bonding between fibres. The use of such in-situ modified fibres in fluff pulp is expected to address the issue of limited fibre absorbability by eliminating the need for the hydrophobic debonders. The fluff pulp made from cellulose/$CaCO_3$ modified fibres exhibited high effectiveness in the dry defibration process and high adsorption capacity due to the weak hydrogen bonding

[140]. Embodiments of sized fluff pulp, or fluff pulp treated with a sizing agent, have desirable characteristics for one or more intended applications. The sized fluff pulp can be debonded or non-debonded. Sizing agents are chemicals that are prior to, during, or after the sheet forming process. The purpose of the sizing agent is to increase water resistance of the fibre or fibres, which includes a reduction in fluff pulp absorption characteristics (the pulp is less hydrophilic). Some characteristics improved by the sized fluff pulp include soak, drip capacity and wicking rate. The sizing agent adheres to substrate fibres and tends to form a film, with the hydrophilic tail facing outwards, allowing a smooth finish that tend to be water-repellent. Examples of sizing agents include alkyl succinic anhydrides (ASAs), polysiloxanes, resin, starch and alkyl ketene dimers (AKDs). In general, the sized fluff pulp is less hydrophilic but retain or exhibit several characteristics for producing non-wovens, including low defibration energy and fibreized knot percentage [106].

3.6.1.6 Alkali swelling treatment

As already mentioned, one of most important properties for fluff pulps used in dry forming applications is its behaviour during dry defibration. The fibres need to be sufficiently liberated and the content of fibre bundles (knots) should be low. It has been reported that is likely that fibre-fibre bonding potential would decrease when a large part of the hemicelluloses (mainly xylans) is removed from fibre walls [19]. The total charge of the fibres decreased because of alkali extraction, due to the removal of xylan, which contains uronic acids as substituents. Alkali treatment changes the structure of the fibre wall and its pore via ballooning phenomenon, which have a positive effect on bulk property. The alkali swelling treatment may modify fibre properties, such as dimension and the hydration degree, to potentially reduce the loss of fibre strength while improving bulk. Low concentration alkali treatment NaOH (2%) increases the tensile strength index, possibly due to an increase in the flexibility of the fibres [19,111]. On the other hand, higher concentrations of NaOH promotes water retention value (VWR), improves morphological characteristics, including fibre width, curl and kink index, decreases the crystalline index and reduces the tensile strength index, most likely due to a decrease in the specific bond strength between fibres [19]. This alkali swelling process are more dramatic in the morphological and chemicals of softwood bleached kraft pulp (SBKP) then hardwood bleached kraft pulp (HBKP) [141].

3.6.1.7 Hornification

The hornification phenomena is a technical term used in wood pulp and paper research literature that refers to the stiffening of the fibre structure that takes place in lignocellulosic materials upon drying or water removal [142]. Hornification and internal fibrillation are related to the change in fibre pore structure; involve closing or opening the pores in the fibre wall. This phenomenon occurs when water is removed from the fibre wall, so drying and pressing of pulps can be used to induce hornification. When the fibres are dried, they lose their conformability and swelling capacity, which can be observed as inferior strength properties and bulkier sheet. One of the basic changes in the fibre structure caused by drying is the irreversible closure of pores. Generally, the hornification induced by pressing is designated as wet hornification. Pressing may causes lumens to collapse and fibres to flatten, providing more surface contact for bonding and, consequently, increasing density and tensile strength [143,144].

When water is removed from the fibre wall, adjacent microfibrils come into close contact and hydrogen bonds are formed within the cell wall, that are not completely broken upon rewetting, mainly because some fibrils remain bonded, which leads to a loss of fibre swelling and pore volume [145,146]. Figure 20 illustrates the hydrogen bonding mechanisms between microfibrils induced by wet-pressing [146].

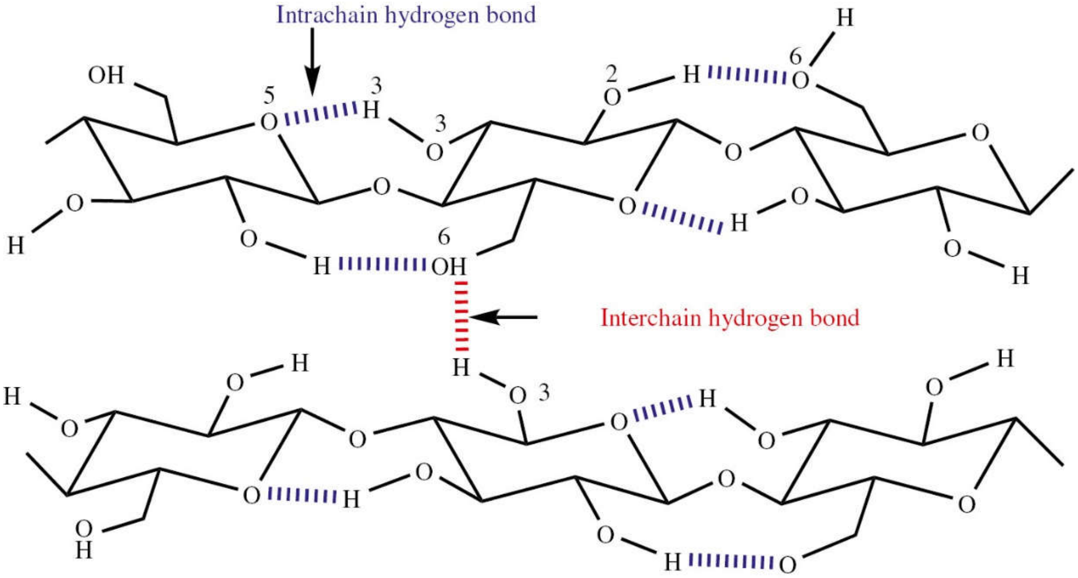


Figure 20 - Effects of wet-pressing induced fibre hornification on hydrogen bonds [146].

The almost irreversible character of hornification was a feature of the original description by G. Jayme [144,147]. Cellulose fibres alter their properties during of repeated morphologic and chemical changes, occurring on drying and wetting (Figure 21). The changes are almost irreversible, especially as to the water retention value (WRV). Jayme introduced the water retention value measurement by centrifugation and defined irreversible hornification as a decrease in WRV, expressed in percentage of the original value [147]. The WRV was originally used to observe the delamination of cell walls. Some authors compared the WRV results with the ones existing at the point of saturation of the fibres and found a good correlation under modest centrifugal forces and time [148]. Later experimentation showed that the swelling capacity of hornified fibres may be partially restored, and hornification reduced by beating, by the addition of bulking agents or by insertion of spacer groups through derivatisation [144,149].

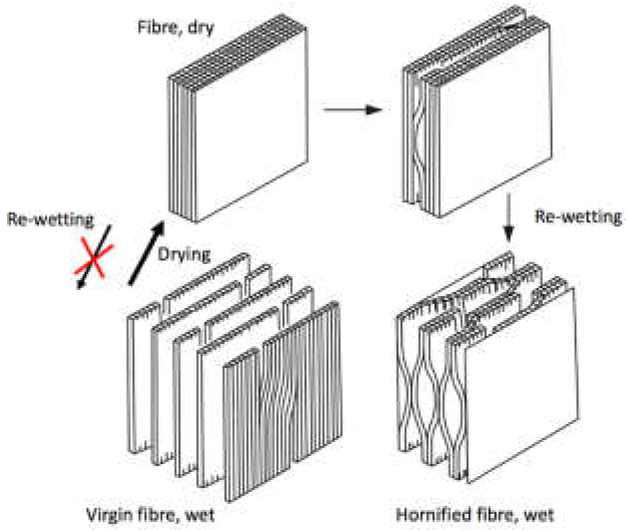


Figure 21 - Model of the fibre re-wetting from Cato and Cameron (1999) [150].

3.6.1.8 Ultra-high-pressure treatment

High pressure (HP) technology was applied for many years in the production of ceramics, composite materials, plastics and artificial diamonds. However, in last decades the use of high pressure for food processing and preservation has been proposed as an alternative to the traditional thermal pre-treatment, mainly due to the advantages that it offers in comparison to thermal processing [151,152]. The HP technology (100 – 1000 MPa) permits microbial inactivation at low or moderate temperatures, leading to food pasteurization, while keeping their nutritional value and organoleptic properties [153,154]. Recently, it was reported that HP treatments of cellulosic pulps are a promising tool for non-degradative modification of cellulose fibres properties [152,155].

As a thermodynamic parameter, pressure has far-reaching effects in the conformation of macromolecules, the transition temperature of lipids and water and a number of chemical reactions [156]. The HP treatment is usually carried out with water as a hydraulic fluid to facilitate the operation and compatibility with materials. Under equilibrium conditions, according to the Le Chatelier Principle, processes associated with volume decrease and encouraged by pressure, whereas processes involving volume increase are inhibited by pressure [153,156]. Pressure in HP treatment acts instantly and it is independent from the size and shape of the substrate. HP breaks the secondary and tertiary structures, which are maintained chiefly by hydrophobic and ionic interactions, and leave the covalent bonds intact [157].

The modification of cellulosic pulps through HP treatment offers numerous potential for pulp and paper industry and, furthermore, for industries that use cellulose as raw material in modification reactions in order to get new cellulose-based products, such as microcrystalline cellulose [158,159]. The HP treatment of pulps promotes the cellulose crystallinity, through the co-crystallization and partial recrystallizations of the paracrystalline domains on the surface of elementary fibrils. This phenomenon promotes the increase the average width of the crystallite [155,160]. The reordering of paracrystalline segments on the surface of elementary fibrils causes an increase in the crystallinity of the cellulose chains. Simultaneously, HP causes a forced hydration of pulps, favouring the incorporation of water molecules that are strongly linked to the amorphous and inaccessible regions of the cellulose, which are only removed at temperatures above 300 °C [152,158,160]. Thus, the hydration of pulps promoted by HP causes the dried fibre to recover some of their ability to swelling, and consequently, decreases the hornification phenomenon in the dried pulps and provides higher flexibility and elasticity to the fibres [149,160]. Furthermore, the HP extends the application areas of cellulosic pulps that have been dried (including recycled pulps) and changes the properties of the never-dried pulps. The pulps modified with HP have higher bulk and improved mechanical properties, such as tensile index, stiffness and burst, compared with pulps with no treatment [152,155,160]. Additionally, after hydration the reactivity of the cellulosic pulps increases due to the increase in its accessibility for interaction with chemical reagents, enabling improved reactivity in enzymatic and chemical reactions. These structural and hydration changes may be used for the chemical modification of cellulose to several applications [160,161].

3.6.1.9 Superabsorbents (SAP)

Fluff pulp is one of the components central to most absorbent product cores for sanitary pad applications. The key requirement for absorbent products core is the ability to absorb and hold substantial amounts of fluid under pressure [162,163]. The fluff pulp fibres used in the absorbent core of an absorbent product allows mechanical strength and integrity to the core. The fluff pulp provides the necessary surface energy to distribute the insulting exudates within the absorbent product [163]. In recent years, an increased use of synthetic, petroleum based Super Absorbent Polymers (SAPs) has result in that amount of cellulose fluff used in certain hygiene products has been radically reduced. A superabsorbent can retain a substantial quantity of liquid, significantly more than what can be retained in a conventional fluff pulp [26]. These SAPs do not contribute to the integrity in the absorption pad and therefore it has become extremely important that the included cellulose fibres can contribute to the strength in the absorption cores in the hygiene products. Moreover, fluff pulps with a reliable network structure and strength of fibres should carry a large amount of the super absorbing polymers, thus allowing a higher moisture adsorption capacity [23,25]. This is accomplished by dry defibration of subsequent air-laying of the fibres in the absorption core. SAP takes some time to absorb liquid, and so is often distributed within fluffed wood pulp to produce a core that absorbs liquid rapidly. Mixing SAP with fluffed pulp promotes the particles apart and overcome the problem of gel blocking. If the SAP particles are too close, they will swell and create a barrier to further entry of more liquid [164]. The retention capacity of SAPs is dependent on the degree of cross linking and degree of protonization [165].

The first superabsorbents were made from renewable resources, such as cellulose and starch, but currently more than 95% of superabsorbents come from synthetic SAP, mainly consisting of cross-linked polyacrylates [25,26]. Since the absorption core in a modern diaper often consists of more than of these petroleum-based absorbents, there have been recent efforts to develop new materials based on resources that can fulfil the functions necessary in the absorption core of a disposable diaper. Microfibrillated Cellulose (MFC) is an example of a renewable material that may be used as a highly absorbent and retentive material [26].

3.7 Absorption properties

Pulps used in absorbent materials are capable of absorbing large amounts of water, which represent about ten times their own weight. For absorption to occur, the main driving force must come from the intrinsic liquid attraction capacity of the material itself, while an externally imposed force, such as gravity or pressure, may play a secondary role in affecting the absorption capacity [165,166]. Pulps should have intrinsic and extrinsic properties that provide good water affinity, rapid absorption and high liquid holding capacity. Furthermore, it is essential that they have affinity for water molecules and a structure that allows rapid transfer of fluid into the material by capillary condensation and has a high specific volume to retain high amounts of water [26,167]. However, there are many other factors, which have a significant influence on the absorbency phenomena. Vapour sorption is an indication of the affinity between the molecules of the absorbent and of the absorbed and this characterized by the equilibrium adsorption isotherms [167].

3.7.1 Moisture sorption

The absorption phenomenon is characterized as the way and extent of transport of a liquid in an absorbent material for absorption to occur and begins at the interface between the fluid and the absorbent material [165]. This phenomenon depends on the nature of the material, the properties of the liquid and the properties between the absorbent surface and the liquid. The main driving force of this process comes from the intrinsic attractiveness of the material to the liquid. When fluid wets the surface of the absorbent material it is physically transported along the porous medium by a moving front of liquid. If fluid intake ceases before saturation is reached, the liquid front will continue to move into the capillary structure for a certain period. The outer pores will have no free water, but the water will be trapped by adsorption. Thus, in addition to intrinsic attraction, the surface of the material must have good affinity for the molecules of the liquid for adsorption to occur [168,169]. Even before an absorbent structure is in contact with the absorbed liquid, it is in contact with vapour. The adsorption phenomena are the capacity of a solid substance to attract to their surface molecules of gases or solutions with which there are in contact. Solids that are used to adsorb gases or dissolved substances are called adsorbents; the adsorbed molecules are usually referred to collectively as the adsorbate. Adsorption of water molecules takes place below a critical temperature, due to Van der Waal's forces between the vapour molecules and the solid surface of the structure [167]. There is no chemical specificity in physical adsorption, any gas tending to be adsorbed on any solid if the temperature is sufficiently low or the pressure of the gas sufficiently high. In chemical adsorption, gases are held to a solid surface by chemical forces that are specific for each surface and each gas. Chemical adsorption occurs usually at higher temperatures than those at which physical adsorption occurs; furthermore, chemical adsorption is ordinarily a slower process than physical adsorption and, like most chemical reactions, frequently involves an energy of activation [170]. Commonly the designation sorption is used to indicate the process of the taking up of a gas or liquid by a solid without specifying whether the process is adsorption or absorption.

In the case of absorbent fibres such as pulp, the moisture sorption is complex due to the interaction of water molecules and the material. All-natural animal and vegetal fibres have chemical groups in their molecules which attract water [169,171]. In the case of hydrophilic fibres, the water is adsorbed onto both acid and hydroxyl groups due to the donor-acceptor interactions. Since the largest proportion of hydrophilic sites in pulp fibres are hydroxyl groups, most of the water is adsorbed there. Other studies also indicate that the amount of water is directly related to the number of accessible hydroxyl groups, whose value is related to the crystallinity of the cellulose. For a pulp, which has undergone purely physical processing, changes in water uptake may indicate changes in the crystallinity of the pulp, while in cases where the fibre chemistry has been altered, changes in other possible adsorption sites should also be considered [172]. In the crystallinity regions, the fibre molecules are closely packed together in a regular pattern and therefore water molecules do not penetrate this region easily. However, if the basic molecule gets hydrated, the crystalline region will open allowing water molecules to penetrate in [173]. The site adsorption theory is rather simplistic as it does not consider such factors as the orientation of the hydroxyl groups which are known to affect hydration [172].

3.7.2 Sorption isotherms

The amount of moisture adsorbed by a given solid substrate depends on the vapour pressure and the temperature, the higher the vapour pressure, or the lower the temperature the higher the amount adsorbed [26,167].

A plot of the amount of fluid adsorbed against vapour pressure at a constant temperature generates a sorption isotherm. The sorption isotherms describe the equilibrium relationship between absorbate content in the solid material as a function of adsorbate concentration in the gas or liquid phase at constant pressure and temperature [174]. The uniqueness of this relation requires several conditions to be met: the various reaction equilibria of retention/release must have been reached and all other physic-chemical parameters are constant. The word “isotherm” was specifically chosen because of the influence of the temperature on sorption reactions, temperature must be kept and specified [168,174,175]. The knowledge and understanding of sorption isotherms is highly important in food science and technology for the design and optimization of drying equipment, design of packages, predictions of quality, stability, shelf-life and for calculating moisture changes that may occur during storage [176]. In material science, sorption isotherms are usually measured with nitrogen at 77 K, whereas in food and cellulose sciences, water sorption isotherms are preferred. The shape of the isotherm depends on the type of adsorbate and adsorbent but also on the molecular interaction between the two phases [177]. The IUPAC classification based on the work of Brunauer et al. [178] includes six general types of isotherms as shown in Figure 22 [179].

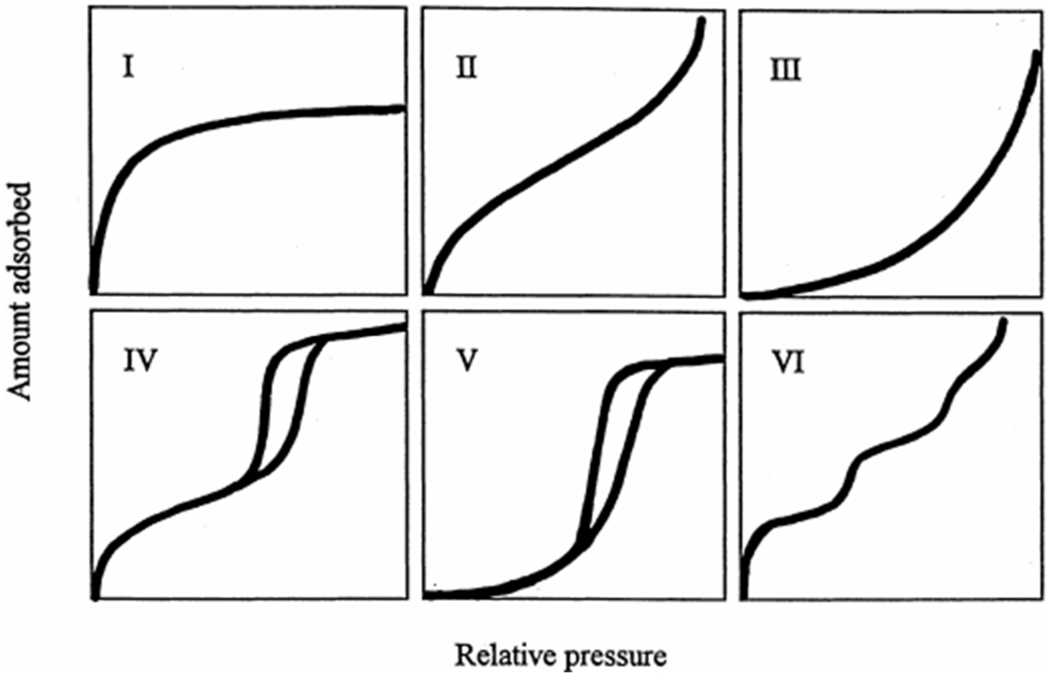


Figure 22 – Types of physisorption isotherms according to IUPAC classification [179].

The sorption isotherm type I is the Langmuir type, characterized by the amount adsorbed approaching a limit value, which corresponds to complete monolayer coverage, typical of microporous solids (hyperbolic type). Type II isotherms are typical of finely divided nonporous or microporous solids and hydrophilic polymers such as natural fibres (cellulosic fibres), is most common and reflects the occurrence of multilayer formation. The adsorbed amount slowly increases to intermediate moisture and faster to relative moisture above 70%. Type III isotherms are typical of water vapour adsorption on hydrophobic materials, such as plastics, rubbers and synthetic fibres (parabolic type) [177]. Type IV isotherms are similar to type II at low relative pressure and are typical of activated charcoal and inorganic materials such as aluminium oxide and type V isotherms (similar to type III at low relative pressure) are representative of some mesoporous materials with particularly strong intermolecular interactions. The levelling off in types IV and V indicates saturation of fine capillary through condensation [167].

The experimental determination of the sorption isotherms is always associated with the use of mathematical models to correlate these data. According to literature, more than 200 different equations have been proposed to fit the moisture sorption isotherms [180]. Some of these models have theoretical basis while others are semi-empirical or fully empirical [181]. The most common equations that are used for describing sorption isotherms are the Langmuir equation, the BET (Brunauer-Emmett-Teller) equation, the Oswin model, the Smith model, the Halsey model, the Henderson model, the Iglesias-Chirife equation, the GAB (Guggenheim-Andersen-de Boer) model and the PEG model [182].

The simplest and still the most useful isotherm, for both physical and chemical sorption, is the Langmuir isotherm. This model assumes that sorption is limited to a monolayer: only a single layer of molecules on the adsorbent surface are absorbed, adsorbent surface is homogeneous and sorption energy is uniform for all sites and there is no transmigration of adsorbate in the plane of surface [183]. Once a pollutant occupies a site, no further sorption may take place in that site, the intermolecular attractive forces rapidly decrease as distance rises. There is no interaction between molecules adsorbed on neighboring sites, sorption on surface is localized, which means that adsorbed atoms or molecules are adsorbed at definite and localized sites [184]. Langmuir proposed the following physical sorption model on the basis of unimolecular layers with identical and independent sortion sites, and which is expressed as it shown in equation 3.6.

$$X_{eq} = \frac{X_m \, C \, a_w}{1 + C \, a_w} \qquad 3.6$$

Where the X_{eq} is the equilibrium moisture content (g water / g dry matter), a_w is the water activity (or generally, the adsorbate relative pressure), C is the interaction constant between adsorbate and adsorbent, and X_m indicates the capacity of the monolayer [177]. The value of the monolayer X_m is extremely important because it represents the amount of water that is strongly adsorbed in specific sites, and it is considered the value at which the product is the most stable. Langmuir´s isotherm is the most crucial equation among the theorical models, which is based on the forces acting between the product surface and the water condensed from the vapour as a monomolecular layer [176]. Based on previous research studies [185] the Langmuir model has the best fitness quality with experimental data among two parameter monolayer sorption isotherm models [183]. The extensions of the Langmuir's underpinning idea on multi-molecular layers result in the

BET and GAB isotherms, which are able to describe sigmoidal shaped isotherms commonly observed in the case of food and other materials of biological origin [176].

The Brunauer-Emmet-Teller (BET) isotherm is a theoretical model most extensively used in gas-solid equilibrium systems. BET is a special form of Langmuir isotherm extended to derive multilayer sorption systems [183]. The model represents a fundamental milestone in the interpretation of multilayer sorption isotherms, mainly type II isotherms, but the model is generally restricted to adsorbate low relative pressures ($\mathrm{P}/\mathrm{P}_0 \leq 0.45$, where P_0 represents the saturation pressure) due to the assumptions used in the derivation of the equation [186]. The BET equation represents a basis in the interpretation of isothermal sorption multilayers and it has been applied in gas adsorption and porous steam in surfaces and solids, as well in water, especially in steam absorption, by homogeneous polymers and other materials [176]. The BET isotherm uses the same assumptions applied in Langmuir isotherm: surface and distribution of sites is uniform, and surface is energetically homogeneous (sorption energy does not change with the progress of sorption in the same layer), and there is no interaction among adsorbed molecules. Besides, the rate of sorption on any layer is equal to the rate of desorption from that layer. This model can be described by the equation 3.7, designated as the n-layer BET isotherm [187]:

$$X_{eq} = \frac{X_m C\, a_w[(1-(n+1)(a_w)^n + n\,(a_w)^{n+1}]}{(1-\ a_w)[1+(C-1)a_w - C\,(a_w)^{n+1}]} \qquad 3.7$$

Where n is the number of the molecular layers of water. This model assumes that there is a maximum number of n layers that can be adsorbed onto the surface of the adsorbent material. According to multilayer sorption of the BET model, other simplifying assumptions were added to this model: the second, third, and higher layers have the same energy of sorption which equals heat of fusion and are not influenced directly by adsorbent-adsorbate interactions. However, the energy for the first layer is different from that for the second or other layers When n = 1, the equation is identical to Langmuir's isotherm (considers only one monolayer) and when n tends to infinity as the concentration reaches saturation, the BET equation is reduced, according to the expression 3.8 [178,183]:

$$X_{eq} = \frac{a_w \; X_m \; C}{(1 - \; a_w)(a_w(C-1)+1)} \qquad 3.8$$

where X_{eq} is the amount of water and X_m is the monolayer moisture content, both generally expressed in dry basis, and C is an energetic constant, which may be estimated for each temperature. In the literature, the BET equation is usually applied without temperature dependency. In this case, different values of X_m and C are used to fit each isotherm. However, the monolayer content is related to the number of sorption sites available on the material surface. Therefore, the value of X_m may be expected to be independent of the temperature, since for the processes and ranges of temperature of interest this variable is expected not to affect the structural surface characteristics [181].

Nevertheless, the considerable success of the isotherm is rather qualitative that quantitative. If we considered the linearized forms of the equations of isotherms as the estimation of the applicability rank that they own in its linear sections, it can be observed that, in almost all cases, BET graphs are linear only in a limited range of water activity from 0.05 to 0.45. This limitation in the process of fitting the experimental data in total range of relative pressure application determined that the main application of the BET equation is the one related to the estimation of the surface areas [188].

The BET and the GAB (Guggenheim-Anderson-de-Boer) isotherms are closely related as they follow from the same statistical model. The term GAB model comes from the names Guggenheim, Anderson and De Boer, who independently derived the equation in 1966, 1946 and 1953, respectively [176]. The GAB model represents an extension of the BET model valid for higher relative pressures ($\mathrm{P/P_0} \leq 0.90$) [186]. This model postulates that the state of sorbate molecules in the second layer is identical to the one in the superior layers, but different from those of the liquid state [174]. In this model, a third constant (K) is introduced to describe the modified properties of the sorbate in the multilayer region in relation to the sorbate in the monolayer and in the bulk liquid. This constant is just the measure of the difference of free enthalpy (standard chemical potential) of the sorbate molecules in these two states, the pure liquid and this second sorption stage, the layers above the monolayer [186]. This parameter is usually between 0 and 1, which means that the sorption heat in the second layer is identical to the upper layers but less than the heat of fusion. [177]. The GAB equation may be presented by the equation 3.9:

$$X_{eq} = \frac{X_m\, C\, K\, a_w}{(1 - \ K a_w)(K\, a_w(C-1)+1)} \qquad 3.9$$

Finally, with K = 1 the GAB isotherm (expression 3.9) reduces to the original BET equation 3.8.

Unlike the BET model that assumes complete surface coverage, the GAB model predicts incomplete coverage due to compression of adsorbate molecules at the surface. The fraction of occupied sites in the first layer (ξ^{l_1}) is a function of water activity and the C and K parameters, as expressed in equation 3.10 [177]:

$$\xi^{l_1} = \frac{C\, K\, a_w}{1 + (C-1)\, K a_w} \qquad 3.10$$

The expression 3.10 shows that even at saturation ($\mathrm{a_w}$ = 1) the local fraction occupied in the first layer is less than 1, since $\mathrm{K} \leq 1$.

The specific surface area of a solid ($\mathrm{S} = \frac{\mathrm{m^2}}{\mathrm{g_{sol}}}$) is related to the monolayer capacity, $\mathrm{X_m}$ by expression 3.11:

$$S = \ X_m \frac{N_A A_m}{M} \qquad 3.11$$

M is the adsorbate molecular weight, N_A the Avogadro number and A_m the effective cross-sectional area of the water molecule (0.125 nm^2 for water at 298 K) [177].

Sorption isotherms depend on temperature due changing temperature leads to different states of excitation of molecules. The influence of temperature on sorption isotherms may be incorporated into parameters C and K for both models (BET and GAB), and is described by Arrhenius equations (3.12 and 3.13) [177,187]:

$$C = \ C_0\, exp\left(\frac{\Delta H_C}{RT}\right) \qquad 3.12$$

$$K = \ K_0\, exp\left(\frac{\Delta H_K}{RT}\right) \qquad 3.13$$

where C_0 and K_0 are entropic factors between the monolayer and the multilayer and between the bulk and the multilayer, respectively; ΔH_C is the difference between monolayer adsorption enthalpy (H_1) and multilayer adsorption enthalpy H_n. ΔH_K is the difference between pure water condensation heat (H_L) and multilayer adsorption enthalpy (H_L). In the BET model K = 1 and therefore ΔH_K = 0 , this model assumes the same properties for the multilayer and bulk adsorbed molecules, i.e. H_n = H_L, thus $\Delta H_C = H_1 - H_L$ [186,189].

Furthermore, to these parameters sorption isotherms allow to determine the net isosteric heat of sorption. This property measures the energy of the binding forces between the adsorbate molecules and the adsorbent and is estimated for a given equilibrium moisture content at different temperatures, by rewriting the Clausius-Clapeyron equation (3.14) to obtain water activity, as a temperature function for constant $\mathrm{X_{eq}}$:

$$\frac{d(\ln a_w)}{d\left(\frac{1}{T}\right)} = \left[-\frac{Q_{st}^{net}}{R}\right]_{X_{eq}} \qquad 3.14$$

The net isosteric heat of sorption ($\mathrm{Q_{st}^{net}}$) value by equation 3.14, is only suitable for qualitative considerations of thermodynamic properties, since the Clausius-Clapeyron equation considers that this parameter does not modify with temperature. This assumption is valid for systems with pure compounds at low temperatures. However, increasing the temperature leads to changes in the properties of the links, changing the value of $\mathrm{Q_{st}^{net}}$. Considering isotherms at different temperatures, it is possible to obtain good adjustments of the Clausius-Clapeyron equation, which means that this parameter does not oscillate with temperature, regarding it as an average value for the considered temperature range [189]. This is an important thermodynamic parameter to understand the sorption mechanism, which enables to determine the total energy required to remove the adsorbed water on the adsorbent surface (Qst), from the expression 3.15:

$$Q_{st} = Q_{st}^{net} + Q_{vap} \qquad 3.15$$

The total energy required to remove water adsorbed on the adsorbent surface ($\mathrm{Q_{st}}$) is the sum of the latent heat of vaporization of pure water ($\mathrm{Q_{vap}}$) defined by equation 3.16 [177]:

$$Q_{vap} = 6887 \times R - 5{,}31 \times RT \qquad 3.16$$

3.7.3 Absorption in porous networks

In surface physics, the term adsorption usually means accumulation at the solid-vapour interface of atoms or molecules coming from the vapour. The most important quantity for the description of this phenomenon is the binding or adsorption energy of the adsorbate i.e., the energy released when an atom of the vapour, at rest, sticks onto the surface. Adsorption phenomena are commonly classified according to the value of this binding energy [190]. Absorption, with which adsorption is often confused, is a phenomena where a liquid is transported into porous medium by immiscible displacement of air from pores [191]. Absorbency depends upon the bulk properties of the solid, namely resistance to compression-expansion, shear, torsional and distortion, the structure of the solid matrix (pore size, size distribution, shape, texture, roughness of the solid surfaces) and the bulk properties of the liquid, such as viscosity. It also extremely depends upon the specific chemical makeup of the three interfaces involved in the absorption process: liquid-gas, solid-gas and solid-liquid [192].

The absorption of a liquid by porous solid may occur through different spontaneous processes, such as the condensation of liquid into the pores of a solid matrix from the vapour phase (capillary absorption) [167,169]. The penetration of liquid into a solid matrix, when one side of the porous solid is in contact with a large liquid reservoir (penetration absorption), the movement of small liquid masses into the interior of a porous matrix, the uptake of liquid into a porous solid totally immersed in a large liquid reservoir (immersion absorption involving the expulsion of air bubbles), the movement of either large or small liquid masses along the macroscopically rough surface of a porous matrix. These different processes are schematically illustrated in Figure 23 [192].

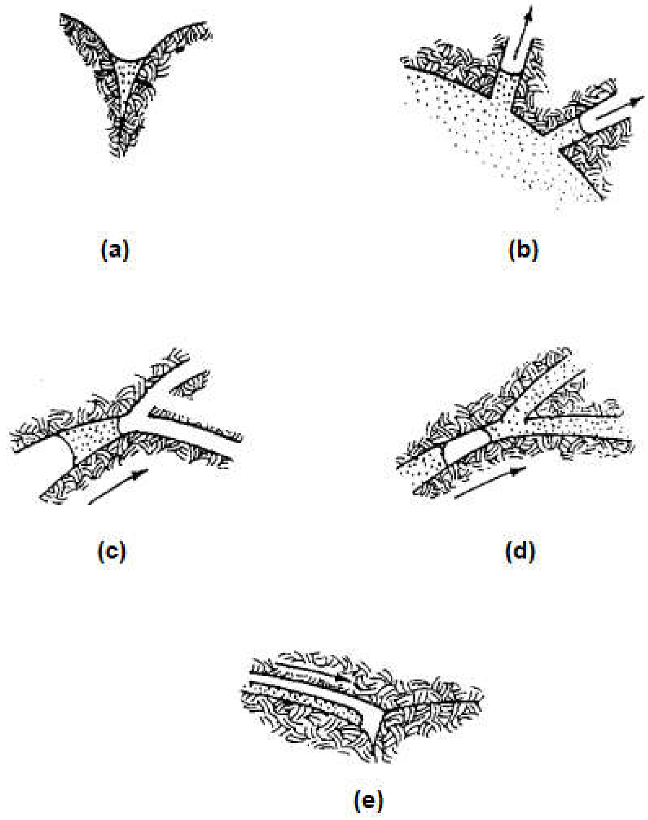


Figure 23 - Processes involved in absorbency. (a) Capillary condensation; (b) Penetration absorption; (c) Motion of liquid thread; (d) Expulsion of air bubble; (e) Surface wicking [192].

Fluid penetration into a porous media is a process of capillary-driven flow. When idealizing porous media as many vertical parallel cylindrical pores randomly distributed in the media the capillary pressure that drives fluid forward in the pore is expressed by the Young-Laplace equation 3.17 as [169]:

$$\Delta P = \frac{2\,\gamma\ \cos\theta}{R} \qquad 3.17$$

Where ΔP is the capillary pressure, γ is the fluid surface tension, R is pore radius and θ is the contact angle established between the fluid and the inner wall of the pore. The capillary condensation corresponds to the condensation of vapour into small pores on or within a porous solid at partial pressures of condensing vapour above the vapour pressure of the condensate and occurs according the Kelvin equation 3.18:

$$a_w = exp\,\frac{2\,v_L\,\sigma\,\cos\theta}{r\,R\,T} \qquad 3.18$$

Where $\mathrm{v_L}$ is the molar volume of the condensate liquid, σ is the surface tension, θ is the contact angle of the condensate against the solid, r is the radius of circular pore, R is the gas constant and T is the absolute temperature [192]. According to Kelvin equation (3.18), capillary condensation occurs only when $\cos\theta > 0$ and is maximum when $\cos\theta = 1\ (\theta = 0^0)$, when the solid is wet out condensate [192]. Moisture uptake by capillary condensation is an important aspect in the wearing comfort of textile fabrics. Cotton, fluff and other cellulosic fabrics are hydrophilic and produce a low contact angle with water, whereas silk, wool and other synthetic fabrics are hydrophobic and produce a large contact angle. The contact angle reflects the reaction of affinity between liquid and solid surface, the stronger affinity, the smaller contact angle. If contact angle is less than 90°, fabric surface is hydrophilic solid. If contact angle is higher than 90°, fabric surface is hygrophilous, so liquid is difficult to wet fabric surface [131,193].

The importance of changes in the affinity of the fibre surface with water for the absorption capacity in relation to structural changes in the fibre network is not entirely clear. The penetration rate of water into porous fibre network via such important absorption mechanism as capillary suction may be described by the modified Washburn equation 3.19 [194]:

$$\frac{dl}{dt} = \frac{\gamma_{lv}\,r\,\cos\theta}{4\eta l} \qquad 3.19$$

where l is the distance penetrated capillarity of radius r in time t by a liquid of surface tension γ_{lv} and viscosity η. The contact angle θ between the drop of liquid and the fibre surface reflects the affinity of this liquid to the capillary surface formed by fibre's mesh. According to equation 3.19, an increase in wettability at the fibre-water interface (low θ) causes faster water penetration in the inner layers of the web. Simultaneously, the larger the average pore size in each pulp network, the greater is the fluid flux inside the web. The maximum absorption capacity (C_{am}) of a sample with porosity ε and density ρ, for liquid with density ρ_l, per unit mass of dry solid medium, and assuming that there is no change in dimension under wetting and the entire pore space is filled up, can be expressed as equation 3.20 [167]:

$$C_{am} = \frac{\rho_l}{\rho} \frac{\varepsilon}{1-\varepsilon} \tag{3.20}$$

In order to evaluate the ability of a material to be processed into final products, such as wipes, towels, sanitary pads, tampons and diapers, it is fundamental to analyse the surface wetting force, adhesion and energy. Additionally, surface contact angle and energy values settle the behaviour of fibres in capillary absorption and transport of fluids, which may provide an insight about the affinity of the fibre for the fluid [195]. Contact angle is one of the common ways to measure the wettability of a surface or a material. Wetting refers to the study of how a liquid deposited in a solid or liquid substrate spreads out or the ability of liquid to form boundary surface with solid states [196]. The most widely used procedure for assessing its value is to place a drop of fluid in a flat surface and measure the angle by some optically enhanced means (Figure 24) [195].

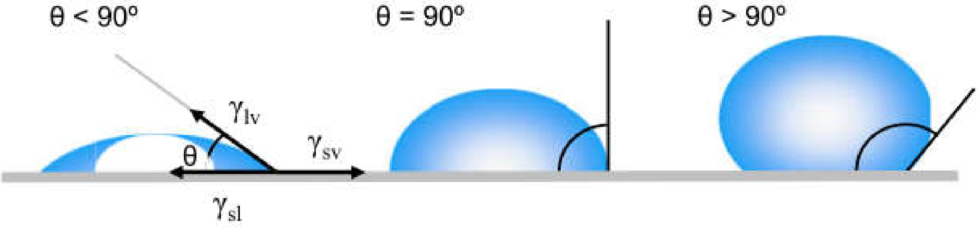


Figure 24 - Illustration of contact angles formed by sessile liquid drops on a smooth homogeneous [196]. γ_{lv} – interfacial tension liquid-vapour; γ_{sv} – interfacial tension solid-vapor and γ_{sl} – interfacial tension solid-liquid.

As already mentioned, the wetting is determined by measuring the contact angle, which is formed when liquid is in contact with the solids or liquids [196]. If the angle is less than 90°, the surface is considered wettable since the solid-liquid attraction is more than the liquid-liquid attraction. A value equal or higher than 90° indicates that the drop resists spreading and hence, the surface is not wettable. The traditional definition of a contact angle corresponds to the angle that a liquid creates with the solid or liquid when it is deposited on it. Additionally, complete wetting occurs when the contact angle is 0°, as the droplet turns into a flat puddle. For super hydrophobic surfaces, water contact angles are usually greater than 150°, showing almost no contact between the liquid drop and the surface. Moreover, contact angles are not limited to the liquid vapour interface on a solid [196,197].

The surfaces of solids are often characterized for their interaction with liquids in terms of parameter designed work of adhesion ($\mathrm{W_A}$). This parameter is the sum of two quantities, a property of the liquid ($\mathrm{\gamma_{lv}}$) and a property of the interaction between the liquid and the solid ($\mathrm{\gamma_{lv}} \cos \theta$), expressed by the equation 3.21. The property ($\mathrm{\gamma_{lv}} \cos \theta$) may also be used to define a parameter designed as Wettability Index, given by the expression 3.22.

$$W_A = \gamma_{lv}\,(1 + \cos\theta) \qquad 3.21$$

$$W_{Al} = \frac{F_W}{P}\,\gamma_{lv}\,\cos\theta \qquad 3.22$$

Where F_W is the wetting force and P the perimeter of the solid (cm). The wettability index expresses the normalized attractive force applied by the solid in the fluid and is directly proportional to the cosine of the contact angle. Fibres with a lower contact angle shows greater attraction force to the fluid, resulting in a higher wettability index, which means that the material has good affinity for the liquid [195,198].

4 MATERIALS AND METHODS

This chapter describes the raw material and experimental methods applied in this thesis. A series of bleached kraft pulps and *E. globulus* chips were used as materials in this thesis: industrial ECF and TCF paper-grade BEKP produced on the same pulp mill (CELBI SA) using varying cooking and bleaching conditions and covering all the quality range of pulps (H1-H6 pulps), one dried commercial ECF paper-grade BEKP and one ECF never-dried pulp from the same mill. The Iberian *Eucalyptus globulus* wood chips of known were used for the cooking experiments. Among industrial kraft-cooked pulps, H3, H5 and H6 were cooked under relatively severe conditions (temperature and active alkali) and ECF bleached after the oxygen delignification ($D_{hot}P_OD_1P$); the H2 pulp was cooked at relatively mild conditions and ECF bleached; the H1, H2 and H4 pulps were cooked at the "typical" cooking conditions of the mill and H1 and H2 were ECF bleached and H4 pulp was TCF bleached (QP_OPP).

4.1 Paper-grade BEKP properties

In order to evaluate several pulp parameters, such as structural, optical and mechanical properties, laboratory handsheets for physical testing were prepared according to ISO 5269-1. The principle consists in a circular sheet formed from a pulp suspension on a wire screen under suction. The sheet was subjected twice to a pressure of 355 kPa. Afterwards it was dried in conditioned air and in contact with a drying plate, to which it adheres so that it does not shrink. The dried laboratory handsheets were separated readily from the drying plates. Any sheets which have separated from the drying plate during drying or are not fully and uniformly glazed on one side or leave some fibres on the surface of the drying plate, were rejected.

Laboratory handsheets were conditioned in a standard atmosphere of 23°C ± 1°C and 50°C ± 2°C relative humidity (RH) before and during the tests.

Drainability is related to the surface conditions and swelling of the fibres and it is an extremely useful index of the amount of mechanical treatment to which the pulp has been subjected. Schöpper-Riegler (SR) method, according to ISO 5267-1:1999, is designed to provide a measure of the rate at which a dilute suspension of pulp may be dewatered. The thickness, density and specific volume were determined following ISO 534:2011. The air resistance was determined according with ISO 5635-5:2013.

The optical properties, such as opacity and light scattering and absorption coefficients were determined according ISO 2471:2008 and ISO 9416:2009, respectively. Opacity was calculated as the ratio of the luminance factor of a single sheet of the paper over a black cavity and the intrinsic luminance factor of the paper. The light absorption and light scattering coefficients were calculated from these data using the Kubelka-Munk theory. Both parameters were measured in a reflectometer equipped with a radiation source having an adequate UV control adjusted to a UV condition corresponding to the C illuminant using a reference standard (ISO 2470-1) and having geometric, spectral and photometric characteristics described in ISO 2469.

The determination of tearing resistance of pulps were performed based on Elmendorf method (ISO 1974:2012). The test is performed using an Elmendorf tear tester, with stationary frame, pendulum (capacity of 2000 mN), a catch, two campling jaws and a cutting knife. Tensile strength index tests were conducted with a L&W Tensile Tester, designed to extend a test piece of given dimensions at an appropriate constant ratio of elongation (20 mm/min), to measure the tensile force and the elongation produced, as described in ISO 1924-2:2008. The bursting strength property was determined according with ISO 2758:2001.

Viscosity (or dynamic viscosity) was calculated according to a method, which yields a number that is an estimate of the limiting viscosity number of pulps in a dilute cupri-ethylenediamine (CED) solution. The principle is the measurement of the times of efflux of the diluted solvent and the pulp solution through a capillary-tube viscometer at a specified mass concentration at 25 °C, as described in ISO 5351:2010. The viscosity of a pulp in cupri-ethylenediamine (CED) solution gives an indication of the average degree of polymerization (DP) of the cellulose. Such a measurement gives a relative indication of the degree of degradation (decrease in cellulose molecular mass) resulting from the pulping and/or bleaching process.

The organically bound chlorine of the pulps was determined according ISO 11480:1997. The air-dry wet pulp samples were placed in an oven at a temperature not exceeding 40°C. Using a separate pulp sample, it was determined the dry matter content, as described in ISO 638:2008. The chlorine content of the pulp was determined by combustion under controlled conditions in a quartz tube at high temperature. The combustion gases are fed through an electrolyte solution where all chlorine, now transformed to hydrogen chloride, is absorbed and determined by microcoulometry. For determination of the organically bound chlorine content, the inorganic chlorine compounds were extracted with dilute nitric acid before combustion.

4.1.1 Sorption isotherms

The surface affinity of the absorbent material was studied by sorption isotherms and contact angles. Water sorption isotherms of defibrated kraft pulps without knots (pulps H1-H6) and pulp H2 (with knots) were obtained at 25, 30 and 35 °C and at relative pressure in the range between 0.05 and 0.95, while using the Dynamic Vapor Sorption

(DVS Adventure, Surface Measurements Systems Ltd. UK (Figure 25) [199]. The experimental sorption data, i.e., equilibrium moisture content, X_{eq}, and water activity (or relative pressure), a_w, were fitted into the Guggenheim-Anderson-de Boer (GAB) model, since it is valid for high relative pressures ($P/P_0 \leq$ 0.90, where P_0 represents the saturation pressure) and proves adequate for surface affinity studies of cellulosic pulps [177,186].

Figure 25 - Dynamic Vapor Sorption Resolution Instrument (DVS).

DVS equipment is a water vapor sorption analyser measuring sorption and desorption isotherms over a broad range of moistures and temperatures (5-85 °C 0-98 %RH). The DVS equipment can precisely control and measure temperature and relative moisture while recording the highest resolution changes in mass. It uses a dry carrier gas typically nitrogen or compressed air for its operation. Digital mass flow controllers regulate flows of dry and saturated gases. Relative moisture is generated by precisely mixing dry and saturated gas flows in desired flow ratios which produce expected relative humidity. In a typical experiment a known concentration of water vapour is delivered over a sample placed inside the sample pan connected to the Surface Measurement Systems Ultrabalance™ measuring real time mass changes caused by sorption or desorption of water molecules. Prior to sorption measurements, the sample can be *in-situ* preheated/dried at temperatures of up to 300 °C. Additionally, the sample chamber and water vapour generation are at thermal equilibrium in a single temperature enclosure allowing for operation over the entire temperature range (5-85 °C) without risk of condensation [200].

This equipment has an incubator in which the constant temperature is accurately maintained, which ensures a highly stable baseline of the instrument and accurate control where steam generation occurs at experimental temperature. Within it has a microbalance with two suspended plates with capacity to measure changes in sample mass of less than 0.001%. One sample is placed on one plate while the other is empty has a reference. The gas carrying the test vapour circulates over the sample at a well-defined flow rate and temperature. Next to the sample is an in-line capacitance probe that checks and controls the system's moisture generation performance [199]. Each lab trial is preheated to the experimental temperature (25°C, 30°C or 35°C). For each relative pressure value (5, 10, 20, 30, 40, 60, 80 and 95%) the corresponding equilibrium moisture content value (Xeq) is determined when the system stabilizes, i.e. when the change in sample mass is less than 0.001% or after 8 hours of testing for the same relative pressure value [175,201].

4.1.2 Contact angles

The contact angles were measured on laboratory sheets, with grammage 65 g/m^2 ± 2 g/m^2, previously prepared from pulps H1 to H6 [175,201]. Using a semi-automatic Rapid-Köthen sheet former, according to ISO 5269-1 standard procedure. The measurements were carried out a Contact Angle System OCA20 goniometer (Data Physics) equipped with a CCD camera and SCA20 software, illustrated in Figure 26.

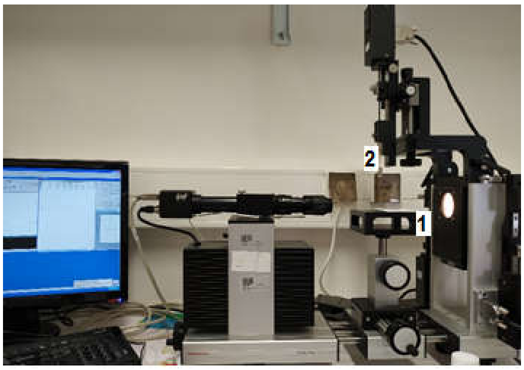


Figure 26 - Optical Contact Measuring and Contour Analysis System (OCA) [199].

In each trial, the smooth surface of the lab handsheet was placed on the platform (1) positioned underneath the pure water syringe (2) and then a micro-drop of distilled water was dropped onto the surface of the sheet and determined the contact angle with drop shape adjustment by the ellipse adjustment method. Since there were some irregularities in the lab handsheet surface the contact angles were determined across the entire surface to calculate a representative average value of the complete sheet. At least 20 determinations were done per each sample and the obtained results were averaged.

The laboratory handsheets for physical testing and measure of contact angles were prepared according to ISO 5269-1.

4.2 Conventional kraft cooking and ECF/TCF bleaching

The chips used in the lab cooking experiments were prepared from freshly cut logs supplied from controlled plantations of Iberian *Eucalyptus globulus*. The chips were fully characterized and chemically analysed. A conventional kraft cooking was carried out in a MK laboratory digester with a capacity of approx. 1.0 kg of dry chips. The industrial white liquor (cooking liquor) was adjusted with addition of NaOH or Na_2S to reach the desirable active alkali of 13-18% (as Na_2O) and the sulphidity of 30%. All pulps were centrifuged to 20-25% dry content (ISO 638) and evaluated with respect to yield, kappa number (ISO 302) and intrinsic viscosity (ISO 5351). The hexenuronic acids content was determined according to the dual wavelength method proposed by Chai et al. (2001), which was adapted by Pedroso and Carvalho (2003) to *E. globulus* samples. The carboxyl content of pulps was determined following the method TAPPI T 237 cm 08. The unbeaten pulp samples were also characterized with respect to total lignin (TAPPI T222 om-88 for Klason lignin and TAPPI UM T250 for soluble lignin). ISO brightness was determined for unbeaten screened pulp according to ISO 2470. The oxygen delignification of kraft pulps was carried out in 1L stainless steel pressurized reactor PARR (Model 4842) at 100 ºC, alkali load of 2.5% and oxygen pressure of 5.0 bar for 60 min. The unbleached kraft pulp consistency was approx. 6%. The oxygen delignified pulps were subjected to the final bleaching trials. The bleaching experiments at pulp consistency of 10% were carried out in a sealed polyethylene bags placed in a constant temperature water bath at programmed temperature, under periodical shaking. Two bleaching sequences were applied in the delignified pulps: Elemental Chlorine Free (ECF) $D_{hot}E_PD_1P_1$ and Totally Chlorine Free (TCF) $D_{hot}E_PP_1P_2$, where D denote the bleaching stage of chlorine dioxide, E_P the alkaline extraction with hydrogen peroxide and P the hydrogen peroxide stage.

The bleached wet pulp was disintegrated according to ISO 5263-1. A suspension of ca. 5.0% pulp consistency was transferred to a conventional sheet former (Rapid–Köthen sheet former) to prepare the low-density laboratory sheets of pulp for the subsequent dry defibration. The density of pulp sheets varied between 0.6 and 0.7 g/cm^3.

4.3 Chemical and physical analysis of pulp

The carbohydrate composition refers to the amounts of the five principals, neutral monosaccharides: arabinose, galactose, glucose, mannose, xylose as they appear in the polysaccharides in wood pulp. The procedure is based on the sulphuric acid hydrolysis of the samples. The monomeric sugar content was determined by injecting 1.0 µl into a high-performance anion-exchange chromatography column with pulsed amperometric detection (HPAEC-PAD) on a chromatography system Varian 3350. The sugars were separated using an analytical column DB-225 J&W (30 m x 0.25 mm i.d., with 0.15 µm of film thickness) on a GC chromatograph (Thermo Fisher Scientific Focus GC series) equipped with an FID detector, using a nitrogen carrier gas, with an injector temperature of 225 °C, column temperature of 220 °C and detector temperature of 250 °C.

The carboxyl content of pulp was determined following the method TAPPI T 237 cm 08. The pulp was deashed with hydrochloric acid for 12h, washed, soaked in sodium chloride-sodium bicarbonate solution, filtered, and an aliquot of the filtrate titrated with 0.01N hydrochloric acid to a methyl red end point. The difference between the concentration of the filtrate and the chloride-sodium bicarbonate solution is a measure of the ion-exchange capacity of the pulp (cellulose).

Solid-state Cross Polarization – Magic Angle Spinning ^{13}C Nuclear Magnetic Resonance (CP-MAS ^{13}C NMR) spectra were registered on a Bruker Advance 400 spectrometer. The CP-MAS ^{13}C NMR spectroscopy can be used to study cellulose crystallinity index (C1) which describes the relative amounts of crystalline and amorphous cellulose. The method is based on the fact that the peak from position 4 (C4) in cellulose appear as two well resolved peaks in a CP-MAS spectrum, one for crystalline cellulose located at 86 ppm – 92 ppm and one for amorphous cellulose located at 79 ppm – 86 ppm. [201,203].

4.4 Production and analysis of fluff pulp

The paper-grade bleached hardwood kraft pulps (BHKP) sheets were tear in small pieces (width = 10 cm) and dry defibrated in a pilot-scale hammermill (Schuttle Buffalo, Model W6H) operated at 3500 rpm. The bleached kraft pulp handsheets produced in laboratory were also tear in small pieces and dry defibrated in a pilot scale hammermill (adapted Schuttle Buffalo) at different intensities (2500 rpm, 3000 rpm and 3500 rpm). The rate of the inlet feed of the sheets was constant and the disintegrated fibres had to first pass in a mesh with 5 mm openings and afterwards in a mesh of 2 mm openings before leaving the hammermill.

The fibre morphology of the dried fibres after air dry defibration were analysed in L&W Pulp Tester Fibre Morphology Test, according to ISO 16065-2. The fluff pulp was soaked according to the relevant part of ISO 5263.

Fluff generated by the test hammermill, during the defibration process described above, was tested for knots content with a RETSCH® sieve shaker. Knots content was evaluated adapting to the norm SCAN-CM 37:85. This device uses a series of standard ASTM mesh screens to separate fluff into knots and accepts. In this test procedure, knots are the fraction that is retained on an ASTM 12 mesh screen.

4.4.1 Dry forming pads

The equipment for the formation of pads, a test piece former, is described in detail in SCAN-C 33:80. Deviations in the present study from the SCAN method were the fluff pulp pad removal and the sample vacuum system. The formed pulp pads had a diameter of 50 mm.

4.4.2 Network strength

Network strength is the force needed to produce rupture in a dry-formed test pad. This can be measured in several ways. Brill et al. [204] developed a burst tester suitable for evaluating the web strength of a standardized test piece. In principle, a burst body is forced through a weight 3.0 g test piece at a specified speed. The force needed to penetrate it is called the network strength [204].

4.4.3 Specific volume and absorption properties

The specific volume, absorption time and absorption capacity were determined accordingly with SCAN-C 33:80. This SCAN-test method describes the preparation of test pieces of fluff and a procedure for their use in determining the specific volume and the absorption properties with respect to water of the fluff.

4.5 Modification of pulp and fluff pulp

Never-dried *Eucalyptus globulus* kraft pulps were provided by a pulp mill with an ECF bleaching sequence. A representative amount of $OOD_{hot}(P_O)D_1P$ bleached pulp was collected in order to investigate the introduction of different commercial additives and chemical and physical modification of pulp to improve fluff pulp properties.

All industrial pulps were thoroughly washed with demineralized water in the laboratory and then conditionate in a dark and cold room.

After pulp modification the lab handsheets were prepared in a conventional sheet former (Rapid Kötthen sheet former), with a density around 0.6 and 0.7 g/cm^3, for subsequent air dry defibrated in a pilot scale hammermill at an intensity of 3500 rpm.

4.5.1 Application of xylanase and cellulase enzymes

Commercial enzymes xylanase and cellulase were kindly donated by Novozymes A/S (Denmark): xylanases NS 51251, NS 51260 and cellulases NS 51257, NS 51246, NS 51259 and NS 51239. The enzymatic treatments were performed in plastic bags in a water bath with a temperature regulator. The aliquot of pulp, with a consistency around 11% was pre-heated in the sealed plastic bag. The effects of the enzyme's dosage, temperature and incubation time were investigated. Different enzyme dosages (50 ml/ton and 100 ml/ton) and incubation time (30 min, 60 min, 90 min and 120 min) were tested. After each treatment, the enzymes were denatured by filtration on a Büchner funnel and mixed with demineralized water at 90ºC. As a control, pulps were treated under identical conditions without enzymes.

4.5.2 Impregnation of cellulosic fibres with surfactants and PHMB

Two commercial fluff pulp debonders were added to the never-dried bleached *E. globulus* kraft pulp at different dosages (1.0; 2.5 and 4.0 kg/tpsa) and constant consistency (11%), temperature (75°C ± 2°C) and retention time (60 min ± 5 min). The products, a blend of nonionic and cationic surfactants, based on imidazolium derivates ($C_3H_5N_2^+$), are highly substantive to fibres and exhibit effective debonding at low application rates. They are easy to handle and readily dispersible in cold water. Additionally, it is VOC-free (measured by EPA Method 24) and non-corrosive to equipment. The modified pulp samples, with the commercial fluff debonders, were filtered and stored at a temperature of 4.0°C.

Never-dried bleached *E. globulus* kraft pulps were impregnated with an antimicrobial agent poly (hexamethylene biguanide) hydrochloride, mostly known as PHMB (20% w/w solution, M_w ca 2000 Da, Arch UK Biocides) [205]. Accordingly, pulp was dispersed in PHMB solution (0.1; 0.3 and 0.5% (w/w)), with 11% of pulp consistency. The suspension, in a sealed plastic bag, was placed in a water bath with temperature regulator at 75°C ± 2°C, and a retention time of 60 min ± 5 min. Afterwards, the samples were filtered, air dried and stored on a desiccator under P_2O_5. Simultaneous, a control sample was performed at same conditions of consistency, temperature and retention time.

The antimicrobial activity was assessed by a quantitative test towards Gram-negative bacteria E. coli (ATCC 25922) and Gram-positive bacteria *L. innocua* (ATCC 33090). The analyses were performed using the transfer method according to NP EN ISO 20743:2007 norm. This consists of an evaluation method in which each microorganism is placed on an agar plate and transferred onto paper samples of 38 mm diameter. The antimicrobial activity for each treated pulp sample in the form of handsheet was assessed in the working pulp series and in control pulp analyses. All samples were analysed in triplicate. In order to transfer the microorganisms to the target paper samples, 1.0 ml of a suspension at 1×10^6–3×10^6 CFU/ml was spread on the surface of a TSA plate (the excess was removed), being the samples set forth the inoculum over 1 min. After that period, one sample was microbiologically evaluated (0 h of incubation) while another one was closed in a Petri plate (without any agar) and remained for 24 h at 37°C being further analysed. The microbiological analysis consisted of the paper sample washing inside a stomacher bag with a neutralizing solution over 2 min being used for that a Stomacher 80 (Seward, UK). Consequently, a series decimal dilution (with 0.1% peptone salt solution) of the resulting washing residue was performed, being plated 1.0 ml on PCA. Afterwards, the plates were incubated at 37 ± 1°C over 36 - 48 and 24 h for *L. innocua* and *E. coli*, respectively

4.5.3 Laboratorial hornification

For the drying and pressing studies, 100 g ± 5 g of never-dried *E. globulus* bleached kraft pulp were air-dried in a conditioned room (temperature of 23°C ± 1°C and 50% ± 2% relative humidity) and oven-dried at a temperature of 140°C ± 5°C in the laboratory under restrained (using a metal frame to hold the fibres between two metal wires) during a retention time of 120 min. After this procedure the pulps were stored in the conditioned room.

In parallel, a sample of hardwood bleached kraft pulp was collect in the finishing line (after the industrial drying pulp machine) in order to evaluate the effect of the processual drying and pressing in the fibres.

4.5.4 Ultra-high-pressure treatment

Never-dried *E. globulus* bleached kraft pulp was disintegrated in demineralized water and diluted in a weight ratio of 1:35 (i.e. 1 g of pulp to 35 ml of water). The pulp suspensions were placed into a flexible screw-cap polypropylene flask of ca. 1000 ml capacity. The samples were processed at 400 MPa and 600 MPa for 15 and 10 min, respectively at ca. 20 °C (thermostatic control). Hyperbaric pre-treatment was carried out in a High Pressure U55 device (Figure 27), using water as a pressure transmitting medium [152].

Figure 27 - Ultra-high pressure U55 device – Department of Chemistry, University of Aveiro.

5 RESULTS AND DISCUSSION

In this section will be analysed and interpreted the results and findings of the laboratory experiment and research of this work.

5.1 Paper-grade ECF and TCF eucalypt bleached pulps

In the first study, a series of six industrial paper-grade BHKPs (H1-H6) produced under varied cooking and bleaching conditions were pre-selected to cover the gamma of typically applied technological parameters. A commercial bleached loblolly pine softwood fluff pulp C1 was used for the comparative reasons. Pulps H1, H2, H3, H5 and H6 were bleached by Elemental Chlorine Free (ECF) sequence $O/OD_{hot}(P_O)D_1P$, whereas H4 pulp was bleached by Total Chlorine Free (TCF) bleaching sequence $O/OE/Q(P_O)PP$.

Figure 28 illustrates the pulp line production of the six industrial BHKPs pulps analysed.

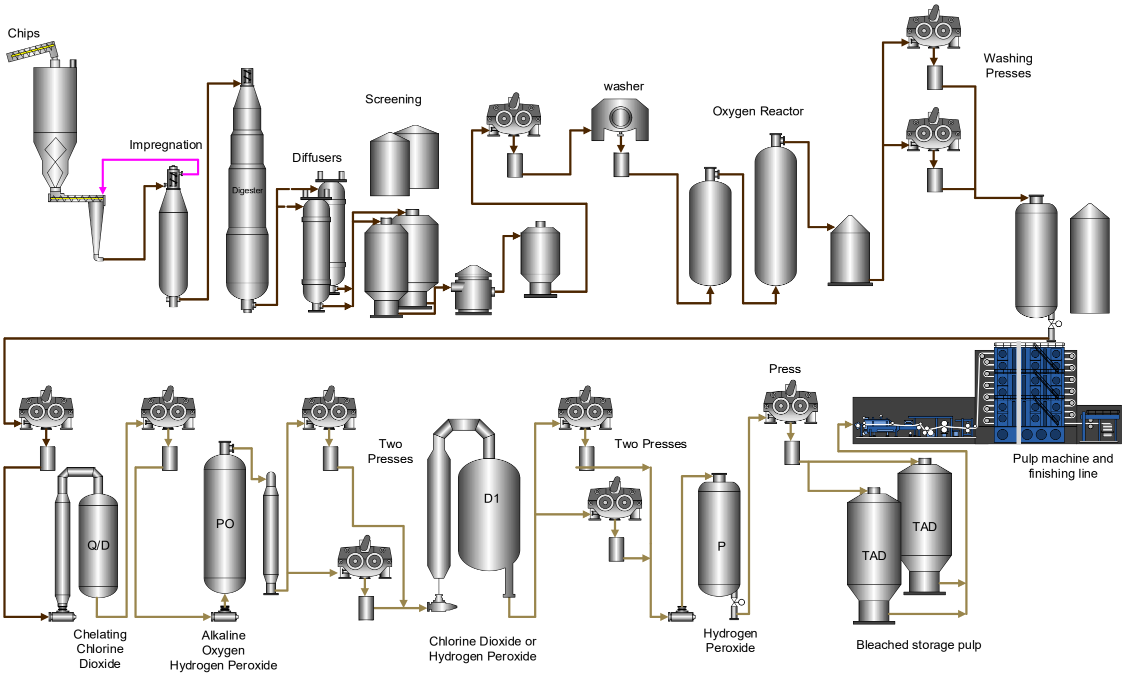


Figure 28 - Pulp Line Production of Portuguese Pulp mill [206].

5.1.1 Pulping and bleaching conditions

Table 7 and Table 8 show the processual conditions of cooking, oxygen delignification and bleaching. These results were collected from the graphical user interface WinMops. H1, H2, H3, H5 and H6 pulps were industrial ECF bleached whereas the H4 pulp was TCF bleached. In this work, a commercial bleached loblolly pine softwood fluff pulp C1 was evaluated for the comparison reasons and related to eucalypt kraft pulps for fluff application. The C1 pulp was selected as an industrial pulp possessing enhanced properties for the fluff pulp production.

Table 7 - Pulping conditions of the kraft eucalypt pulps (values from WinMops).

Pulp samples	**Pulping**							
	Cooking temp., °C	Factor H	EA white liquor, g NaOH/l	IS white liquor %	[Na_2S], g NaOH/l	[NaOH], g NaOH/l	AA white liquor, g NaOH/L	Kappa number
H1	153.1	372	113.0	29.9	39.8	93.1	132.9	14.5
H2	152.0	339	114.8	33.0	45.3	92.1	137.4	14.3
H3	157.1	556	117.1	28.3	38.7	97.7	136.5	16.8
H4*	151.9	367	115.7	31.2	42.7	94.3	137.0	12.9
H5	159.2	543	113.8	31.3	42.2	92.6	134.9	15.6
H6	157.7	603	120.3	29.1	40.9	99.9	140.8	15.1

* TCF bleaching sequence

Table 8 - Oxygen delignification and bleaching conditions of the kraft eucalypt pulps (values from WinMops).

Pulp samples	**O_2 Delignification**		**Bleaching**				
	[O_2] kg/tpsa	[NaOH] kg/tpsa	[ClO_2] kg/tpsa	[H_2SO_4] kg/tpsa	Chelate kg/tpsa	[H_2O_2] kg/tpsa	[NaOH] kg/tpsa
H1	23.1	20.6	20.6	9.3	0	3.6	3.2
H2	20.5	17.1	20.3	8.9	0	4.4	4.5
H3	19.3	13.5	20.1	5.0	0	3.6	-
H4*	22.1	15.7	0	12.7	1.5	17.0	4.0
H5	21.9	17.5	23.0	7.6	0	9.9	-
H6	21.4	16.2	20.1	5.2	0	3.7	-

* TCF bleaching sequence

5.1.2 Properties of industrial kraft pulps

The basic properties of examined industrial eucalypt kraft pulps are depicted in Table 9. Differences in the production conditions reflected noticeably the intrinsic viscosity and the physical properties of pulps. Thus, despite similar origins of unbeaten eucalypt pulps, they still showed about 20-35% variations in their basic strength properties. As shown in Table 9, H2 pulp reveals the highest tensile index of 30.4 N.m/g, while pulp H3 has the lowest value (23.3 N.m/g), being similar to H1 pulp. The H4-H6 pulps showed medium tensile index values. This is in tune with the severity of cooking conditions applied, which indicated the advantage of mild cooking and bleaching on the mechanical properties of obtained pulps (Table 7 and Table 8). Among eucalypt kraft pulps the general tendencies of tensile resistance were coherent with burst resistance (Table 9). Despite the high burst index of the softwood C1 pulp, the tensile index value is one of the lowest (20.6 N.m/g). This behaviour was explained by the morphologic characteristics of the pulp. Softwood fibres are larger and thicker than hardwood fibres and form limited bonding areas between the fibres in the web. Bursting strength is mainly affected by the way, in which fibres are bonded together in paper sheet. Softwood fibres are much longer than the fibres in hardwood and form a greater number of contacts between the fibres, thus demonstrating a reasonable burst resistance, even of unbeaten pulps. At the same time, softwood long-fibre pulp demonstrated a predictably higher tear strength (14.4 mN.m^2/g for pulp C1 and around 3.0 to 5.0 mN.m^2/g for H1-H6 pulps), due to the higher number of fibre-fibre contacts in the mesh than in short-fibre hardwood pulps [207,208].

Table 9 - Properties of industrial eucalypt kraft pulps (H1-H6) and softwood kraft pulp (C1).

Parameters	**Units**	**H1**	**H2**	**H3**	**H4**	**H5**	**H6**	**C1**
Schopper	°SR	21	23	20	21	22	23	13
Density	kg/m^3	561	585	559	558	571	573	550
Bulk	cm^3/g	1.78	1.71	1.79	1.79	1.75	1.74	1.82
Tensile Index	N.m/g	23.9	30.4	23.3	26.3	27.8	27.9	20.6
Stretch	%	1.8	2.4	2.0	2.4	2.1	2.0	2.2
Stiffness index	kN.m/g	3.5	4.1	3.5	3.6	3.9	4.0	2.9
Burst strength	kPa.m^2/g	1.04	1.61	1.07	1.45	1.46	1.44	1.61
Tear index	mN.m^2/g	3.57	4.31	3.44	4.37	5.41	4.27	14.37
CEDL	m^2/kg	40.8	37.4	40.5	39.4	38.9	39.2	-
Opacity	%	76.8	75.3	77.1	77.0	76.2	76.7	71.3
Air resistance, Gurley	s	1.2	1.6	1.0	1.0	1.3	1.6	0.8
Bending stiff.	mN	43.0	46.0	51.9	46.2	50.9	51.5	-
Intrinsic viscosity	dm^3/kg	807	907	787	739	865	841	-
Brightness	% ISO	88.5	88.8	89.8	85.0	88.7	88.8	88.6
OCI content	mg Cl/kg	114	102	74	< 20Lq	108	132	117

The density (kg/m^3) or weight/unit volume of the pulp sheet reflects the interaction of several manufacturing variables. It is an important parameter since it determines, for a given sheet moisture, how easily the sheet can be fluffed. The analysed hardwood and softwood pulps have a moisture content of 10%. Hardwood pulp sheets have a density of 1.300 g/cm^3 whereas softwood pulp has a density of 0.650 g/cm^3. Optimum fluff sheet densities values are around 0.550 to 0.800 g/cm^3 [11]. Sheet density and burst factor can indicate how hard a sheet is and thus raise the energy required for fluffing. It can also imply other potentially undesirable properties, such as increased fibre damage, equipment overheating and excess vibration [115]. However, burst index and internal bond strength can be used as two indirect indices to guide the behaviour of pulp during dry defibration process. The burst index reflects the relative difficulty of dispersing the fluff pulp sheet into individual fibres in a dry state. Burst strength results of H2 and C1 pulps are similar, around 1.61 kPa.m^2/g, H1 to H3 showed the less values of 1.04 kPa.m^2/g and 1.07 kPa.m^2/g, respectively. Despite the high burst index of the softwood C1 pulp, the tensile index value is one of the lowest. This behaviour may be explained by the morphologic characteristics of the pulp. The last are reported to be dependent on lumen width, fibre diameter, specific gravity, Runkel ratio, percentage of fines and coarseness [209]. Softwood fibres are larger and thicker than hardwood fibres and form limited bonding areas between the fibres in the web. Bursting strength is mainly affected by the way, in which fibres are bonded together in paper sheet, where fibre length and fine elements accounted for 99.9% and 98.9% variations in the burst index respectively [59]. Softwood fibres are much longer than hardwood fibres and form a greater number of contacts between the fibres thus demonstrating a reasonable burst resistance even of unbeaten pulps. Nevertheless, a sheet that is too soft allows pull-out of large pieces of pulp promoting poor fluff uniformity and reduced absorbency [15,109]. High bonding strength within the sheet means that more energy is needed during defibration to liberate fibres and excessive energy input during defibration leads to fibre cutting. In this step of the study, it was not possible to simulate different defibration energy, in the pilot-scale hammermill, to evaluate the required power to fluff hardwood and softwood pulps. This gap has been filled in further study, where different energy inputs to defibrate pulp into fluff and analyse the obtained fluff pulp properties.

The air permeation is obtained by measuring the airflow through a defined area, under a known pressure drop, expressed in µm/Pa.s. In this study this unit was converted by calculation into instrument-specific units Gurley seconds. Pulp C1 has the lowest value of 0.8 s and pulps H2 and H6 the highest values of 1.6 s (Table 9). Pulp additives influence this parameter, sheet forming and pressing. The air permeance has a close relationship to the porosity of the sheet and is crucial for the paper machine runnability [210]. The pores in paper form a complicated system of interlocking, crooked and crisscrossing channels which range in size from large diameters to capillary dimensions [59,208]. Low air resistance values are desirable to fluff pulp production.

Figure 29 illustrates a good correlation (R^2 = 0.9206) between air resistance and bulk in both eucalypt and softwood pulps. Probably, fibres from softwood pulp (C1) are not only longer, but also less conformable and/or more collapsed when compared to fibres of H2 and H6 pulps, because the former pulp has a lower tensile strength. Collapsed fibres arisen under hornification are less flexible and have a lower bonding area, therefore they will create a network with much lower density and higher bulk [207]. Wood fibres have circular or rectangular cross sections but may flatten or collapse during the web forming. Under lateral pressure, such as wet pressing, drying or calendaring, the pulp fibres collapse and change the tube structure into a double-layered strip [54]. In addition, softwood pulp has coarser fibres that should create a web with higher porosity and bulk compared with the collapsed ones. The paper made of collapsed fibres usually have higher bending stiffness and are easier to dewater [208].

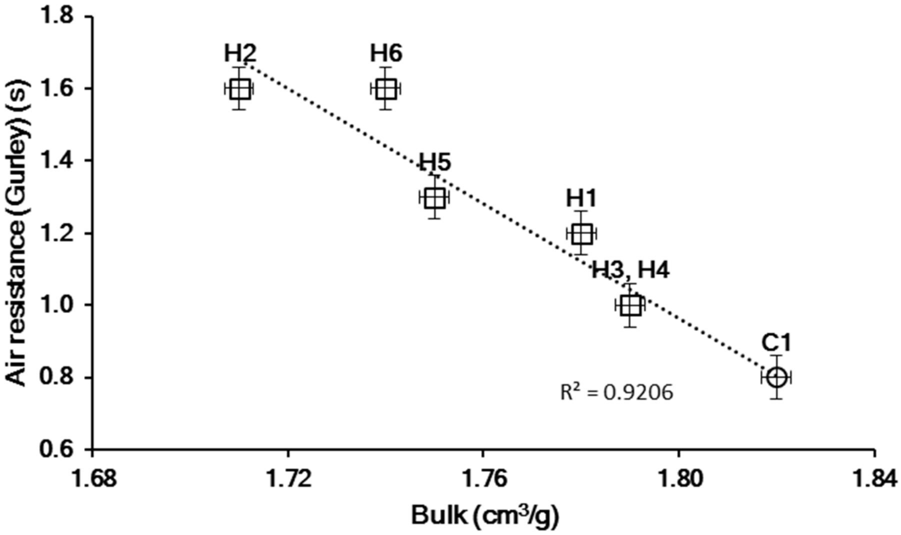


Figure 29 - Correlation between air resistance (Gurley test) and the bulk of eucalypt kraft H1 - H6 pulps and softwood kraft C1 pulp.

Most of the strength properties are affected by the degree of polysaccharide degradation during pulping and bleaching operations. A clear dependency of tensile strength and tear resistance from the intrinsic viscosity of ECF bleached eucalypt pulps is demonstrated in Figure 30. It is noteworthy that TCF-bleached eucalypt pulp (H4) undergoes, apparently, the excessive oxidative depolymerization of polysaccharides and was out of this trend.

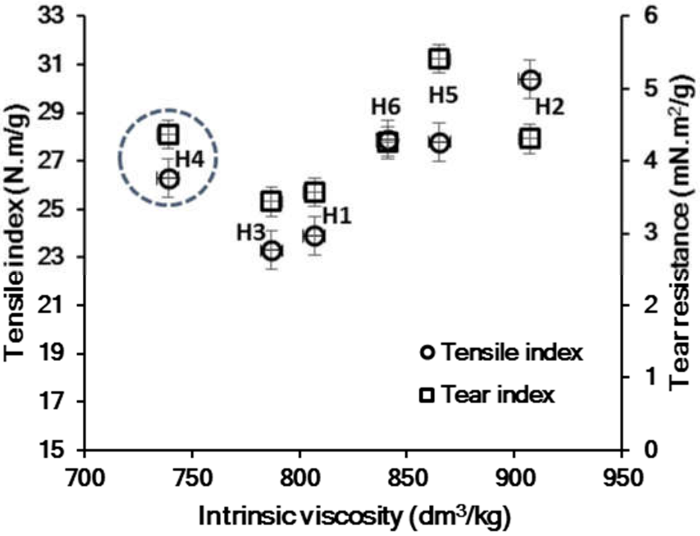


Figure 30 - Dependence of tensile strength (○) and tear resistance (□) on the intrinsic viscosity of eucalypt pulps. The TCF H4 pulp was out of the general trend of other ECF pulps and marked with a circle.

5.1.3 Chemical composition of industrial kraft pulps

5.1.3.1 Pulp polysaccharides

It is natural to assume that variable industrial pulping and bleaching conditions affected the chemical composition of obtained pulps that, in turn, affects their physical properties. The differences in the chemical composition of pulp polysaccharides are reflected from the sugar's analysis and the content of structural units containing carboxylic moieties (Table 10). It was assumed that the major carbohydrates of pulps are cellulose and xylan as follows from the content of glucose and xylose in the analytes. Most of the carboxylic groups in hardwood pulps belongs to 4-O-methyl-D-glucuronic acids (MeGlcA) in xylan, which part is converted to hexenuronic acids (HexA), depending the applied cooking conditions [93,211]. The carboxyl groups in pulps can also arise from polysaccharide reactions during the cooking under alkaline conditions (e.g. by stopping reaction with formation of metasaccharinic acid or other alkali stable carboxyl groups [33,35,60]) and during the bleaching [212,213]. Both MeGlcA and HexA are responsible for the charge of fibres surface and the swelling of pulp in water thus affecting the papermaking process [214,215].

Table 10 – Monosaccharide composition and the carboxyl groups content in BEKPs and BSKP.

Pulp samples	Ramnose %	Arabinose %	Xylose %	Mannose %	Galactose %	Glucose %	HexA mmol/100g	COOH mmol/100g
H1	0.5	0.2	24.6	0.2	0.3	74.2	0.66	9.2
H2	0.5	0.2	26.4	0.2	0.3	72.4	2.00	12.8
H3	0.3	0.1	22.9	0.2	0.3	76.3	0.33	8.4
H4	0.5	0.2	26.8	0.2	0.3	71.9	3.40	9.8
H5	0.6	0.2	27.5	0.2	0.3	71.1	1.21	11.6
H6	0.4	0.4	26.3	0.4	0.5	69.4	0.59	12.0
C1	0.5	0.8	11.2	6.9	0.1	80.4	0.26	6.0

* The relative error in sugars analysis does not exceed 3%.

The amount of the MeGlcA and HexA moieties in hardwood pulps is strongly dependent of the severity of cooking and the bleaching conditions [96,211]. In fact, the cooking conditions that promote the depolymerization of polysaccharides (increase in temperature and in alkali charge) also favours the cleavage of glycoside bond in MeGlcA and HexA and the conversion of MeGlcA to HexA. Consequently, the positive relationship between the viscosity and the amount of carboxyl groups in the pulps is explained by different pulping conditions applied, when the more drastic degradation of xylan with cleavage of the uronic moieties coincided with the stronger degradation of the cellulosic chains (Figure 31). In addition, the positive dependence of the carboxyl group content on the amount of xylan in the pulps, assessed by the sugars analysis (Table 10), confirms the uronic moieties from xylan as the major source of carboxylic groups in bleached pulps. Again, H4 pulp bleached by TFC sequence was distant from other ECF-bleached pulps. This fact suggests that the excessive degradation of the pulp polysaccharides in the oxidative bleaching stages (O, P_O and P) is also harmful for xylan that loses part of the uronic moieties. The lowest content of carboxylic groups in C1 pulp is explained by the low content of xylan in softwoods (Table 10).

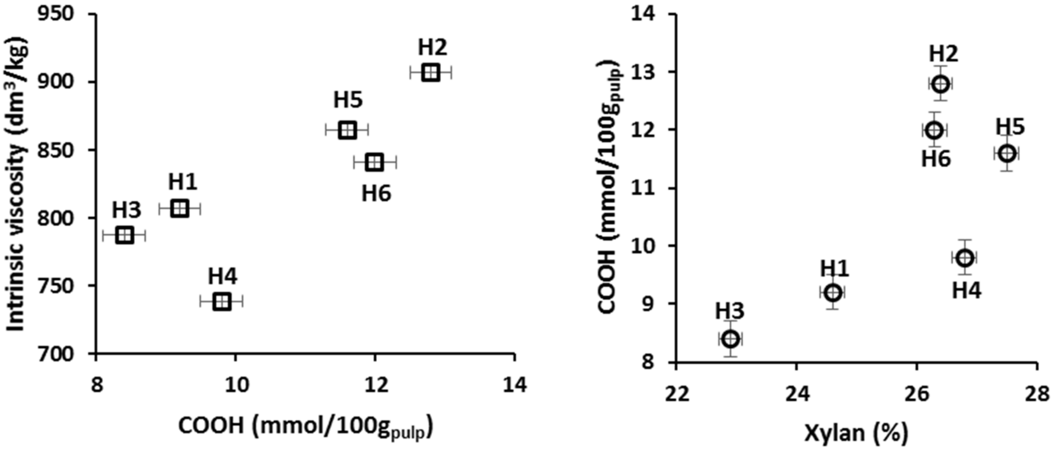


Figure 31 - Relationship between carboxyl group content in eucalypt pulps and their intrinsic viscosities (left figure) and the xylan content (right figure).

Among eucalypt pulps, the highest content of HexA in H4 pulp (Table 10) is due to their poor reactivity with oxygen and hydrogen peroxide used in TCF bleaching, unlike to chlorine dioxide used in ECF bleaching that disproportionate into Cl_2 and HClO, which readily reacts with HexA [239]. Although there is no information about the bleaching sequence of C1 pulp, the low content of HexA (Table 10) allows the proposition that this pulp was ECF bleached.

5.1.3.2 Pulp residual lignin

The residual lignin in pulps was assessed by the analysis of kappa number, which measures the total amount of oxidable material in the pulp. Pulp kappa number depends on different chemical components with unsaturated carbon-carbon bonds [216] and predetermines the consumption of bleaching chemicals [217]. The kappa number of eucalypt H1-H6 pulps leaving the digester were ca. 13-17 being decreasing gradually along the bleaching stages (Figure 32). As higher is the effective alkali the lower is the kappa number of pulp (Table 7). This is also due to the prevention of lignin and hemicelluloses re-precipitation at the end of the cooking [218].

The major part of the residual lignin from unbleached pulp was removed after the oxygen delignification, D_{hot}/Q and P_O bleaching stages (Figure 32). The kappa number of pulps after the P_O stage was ca. 4-6 being further decreased in the final bleaching stages and reaching ca. 2 units in fully bleached pulps. Since a kappa number does not distinguish between the oxidizable material in the residual lignin and other structures susceptible to oxidation, such as HexA groups in the pulp [241], the latter should be considered in the analysis of residual pulp lignin [94,219]. In average, 11.6 mmol/kg of HexA corresponds to 1 kappa unit [220,221] and the contribution of lignin and HexA to the kappa number can be expressed as follows: $K_{total}= K_L+0.086[HexA]$, where K_L is the contribution of lignin to the kappa number and [HexA] is the content of HexA in pulp (mmol/kg). Going from these considerations, the contribution of HexA to the kappa of TCF pulp H4 is much significant that to the kappa of ECF pulps after the PO stage (Figure 33). At the same time, the content of the residual lignin in all pulps, expressed as a corrected kappa number, was very similar for all pulps. As regarding the fully bleached pulps, they showed quite low content of HexA (Table 10) that contributes negligibly to the kappa number. As a result, the residual lignin content in all fully bleached pulps was very similar and is ca. 0.2% ([L]=0.15*Kappa number).

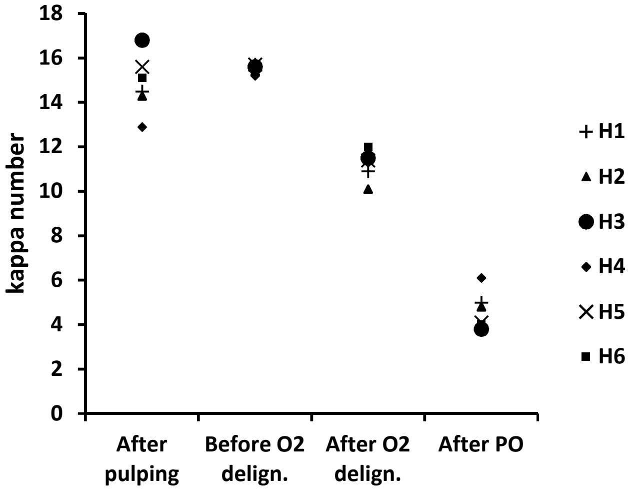


Figure 32 - Kappa number of hardwood pulps after pulping, before and after oxygen delignification and the P_O bleaching stage. (values from WinMops).

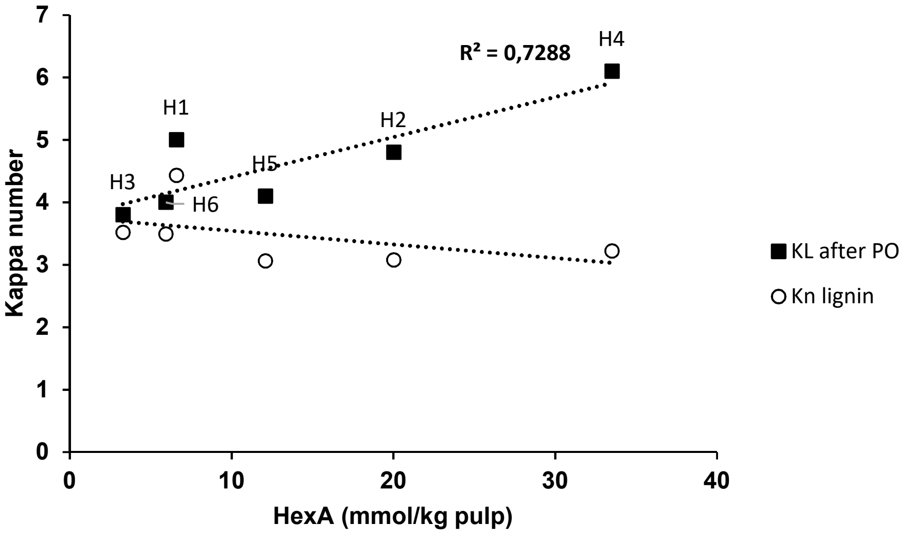


Figure 33 - Relationship between total kappa number, hexenuronic acids content and kappa number related to lignin (K_L).

5.1.3.3 OCl content

Bleaching with chlorine containing chemicals not only result in water soluble halogenated organic compounds (AOX), there is also a residual of halogenated compounds present in fully bleached pulps, so-called OCl [222,223]. In ECF bleaching the acceptable level of OCl is adjusted by using less amounts of chlorine dioxide, more severe extraction stages and by partial substitution of ClO_2 by H_2O_2 [224,225]. The chlorinated organics derived from lignin are more likely stick to the pulp and appear as OCl values in the bleached pulps. It is well stablished that hypochlorous acid (HOCl) and chlorine (Cl_2) are responsible for the chlorination products found in chlorine dioxide-bleached pulps. Table 9 shows the negligible amount of OCl only in the H4 pulp bleached by the TCF sequence. The comparable OCl content in eucalypt and softwood pulps confirmed the application of chlorine dioxide in the bleaching of C1 pulp.

5.2 Dry defibration and properties of eucalypt kraft pulps

5.2.1 Knots content and fibre morphology

All eucalypt bleached kraft pulps (H1-H6) were dry-defibrated from conventional pulp sheets of ca. 1.3 g/cm^3 to obtain fluffed pulps using a pilot hammermill operated at 3500 rpm. The fluffing conditions were selected from the previous work done on the dry defibration of birch kraft pulp, showing the best development of fluff network strength at defibration intensity as higher as 3000 rpm [19].

Considering that the fibre morphology is an important parameter for the fluff pulp, due its direct relation to the structure of air-laid formed network and the absorption properties of corresponding formulations, this was studied in more details (Table 11). According to practical considerations, the fibre length of fluff pulps should be as higher as 2 mm and the fines content should be lowest as possible, because of the dusting problems [226]. Long fibres have more fibre-fibre contacts and the continuity in the structure and therefore forms a stronger network when compared to short fibres [19,227,228].

Unlike to softwood C1 pulp, that suffered a notable fibre cuts upon fluffing, all eucalypt kraft pulps demonstrated less than 10% loss in fibre length being finally comparable with the length of softwood fluff pulp (Table 11). Simultaneously, the percentage of fines in H1-H6 pulps increased up to ca. 30% in contrast to ca. 70% in C1 pulp. Apparently, the applied defibration intensity was excessive for the C1 pulp. In fact, the optimum defibration intensity of hardwood and softwood pulps is not coincident and is lower for softwoods [19]. Softwood pulp (C1) has fibres with larger diameters than eucalypt hardwood pulps (Table 11). It is desired long fibres that naturally stack in such a way that larger capillaries are developed than for short fibres. Long fibres provide greater structural strength than short fibres because of the greater number of fibre contacts and the continuity in the structure. Fibre diameter and fibre wall thickness are quite important because these factors govern the resiliency behaviour of the fibres, especially in the wet state. Thence, the large and thicker fibres tend to resist compression both in the dry and wet states, providing both resiliency and better holding capacity [227]. In addition, the coarseness of softwood fibres was more than twice to hardwood fibres. The fibres with larger fibre diameters and thicker walls are stiffer in networks than fibres with small diameters and thin walls and demonstrate usually an improved compression resistance both in the dry and wet states, providing both resiliency and better holding capacity [19].

The deformation of pulp fibres was evaluated through changes in curl and kink defects (Table 11). Fibre deformations occurs during pulp production (pulping and bleaching procedures) and due to the strong mechanical action in dry defibration. The noticeable diminishing of fibre curl (from *ca.* 20 to 35%) upon defibration can be tentatively explained either by partial straightening or by strong kink of fibres occurred (up to 280% increase). These fibre deformations could have been created by the mechanical stress caused by the hammermill, which can confirm the high defibration intensity. The number of local deformations of the fibre may, on average, be one per fibre, meaning that the fibres in general have weak points, which negatively affect the fibre strength. This straightening of fibres play a negative role on the critical strain of air-laid product while analysing the network strength, because the network starts to deform when curled fibres begin to straighten before any slippage between them takes place [12,17].

The kinks are local deformations, such as knees and wrinkles in the fibres. They are detected as changes in the direction of the main axis of the fibres within a limited distance of the fibre. The number of local deformations of the fibre may, on average, be one per fibre, meaning that the fibres in general have weak points, which negatively affect the fibre strength. On the other hand, kinks favour the bulk of pulp and the porosity that is important for the absorption of water.

As expected, the fines content increased after dry defibration of both hardwood and softwood pulps (Table 11). In chemical pulps, fines include ray cells and parenchyma cells in addition to cell wall shivers. During dry defibration, the cell wall was peeled out to some extent leading to shivers formation thus explaining the notable increase in fines content of fluffed pulps [228]. Another source of fines could be the short cuts of fibres arisen under mechanical degradation. According to obtained results, the formation of fines was more critical for softwood than for hardwood pulp.

Table 11 - Fibre morphology of hardwood and softwood pulp samples before and after dry defibration with a pilot scale hammermill at 3500 rpm.

Pulp Sample		H1	H2	H3	H4	H5	H6	C1
Fibre length, (mm) (± 0.002)	Sheet	0.847	0.863	0.849	0.852	0.852	0.867	2.510
	Fluffed	0.781	0.771	0.775	0.773	0.766	0.758	0.731
Fibre width, (µm) (± 0.1)	Sheet	17.3	17.7	17.5	17.5	17.5	17.6	30.1
	Fluffed	18.2	17.7	18.0	17.9	17.9	17.8	27.0
Curl, (%) (± 0.1)	Sheet	16.1	15.1	14.9	16.3	15.2	16.1	17.4
	Fluffed	9.9	11.0	11.5	12.0	11.6	12.8	9.2
Coarseness, (mg/m) (± 0.0003)	Sheet	0.100	0.105	0.103	0.103	0.104	0.104	0.294
	Fluffed	0.070	0.071	0.071	0.073	0.071	0.072	0.178
Kink angle, (°) (± 1)	Sheet	57	56	56	58	56	57	44
	Fluffed	129	128	128	128	128	126	124
Fines, (%) (± 0.2)	Sheet	19.5	20.4	20.2	20.0	20.0	20.2	42.8
	Fluffed	30.7	29.6	30.8	30.5	29.9	30.5	73.3

Under dry defibration, complete separation of fibres cannot be achieved and a certain amount of agglomerated fibre bundles (knots) is still present in fluffed pulp. Hardwood fluff pulps showed a knot content range of 20-27% while softwood fluff pulp (C1) had a knot content less than 2%. These results can be explained by different intensity of interfibre bonds in two type of pulps, predetermined by their pulp sheets density. Hardwood paper-grade pulp sheets (H1- H6) had a density of about 1.300 g/cm^3 while the commercial C1 softwood fluff pulp sheet for the fluff needs possessed a density of less than 0.650 g/cm^3. In addition, the industrial C1 pulp was doped with debonding agents facilitating the defibration. Pulp sheets with lower density are easier defibrated and have less amounts of knots. For example, in H1-H6 series, H4 pulp showed the lowest knots content being more bulky than other pulps (Figure 34). However, the dependence of knot contents and the pulp bulk was not straightforward. It can be noted that the knots in the hardwood pulps were larger and denser than those of the softwood pulp. This difference in knots morphology can affect the absorption properties of fluffed pulps, because the knots affect negatively the porosity and the wettability of air-laid fibre networks [19].

5.2.2 Absorption properties of industrial kraft fluff pulps

The absorptive qualities of fluff are mainly based on the uptake and retention of fluid by the fluff's void volume. Since the fibres themselves are hydrophilic some fluid is also held within the fibres. However, it is the architecture, stability and surface properties of an interfibre capillary system that have the highest effect on fluff absorbency [17]. The absorption capacity of the fluffed pulp corresponds to the ratio between the mass of water absorbed by a standard air-laid test piece (pad) to the initial mass of the pad, while the absorption time is the time required for a standard pad is completely saturated by absorbed water when tested under specified conditions [166,229].

Noteworthy that during water uptake the fibres swell and thus leads to narrowing of capillaries in the network and decrease in the fluid uptake. In fibrous materials, majority of the fluid is absorbed in spaces between fibres and only a small fraction is absorbed in internal structure. Any fluid diffusing into the internal structure will do so by the fibres swelling and expanding into the air spaces within the web and replacing the free volume. Furthermore, the process of absorption involves breakage of cross-links between the fibres, which causes a loss in modulus and bending rigidity of fibres and, consequently in the ability of the fibrous network to maintain its pore structure under pressure [195]. Although absorption velocity and capacity are not independent of each other, the rate of absorption is controlled by the effective radius of the pores or capillaries between the fibres and the contact angle formed between the fibre surface and the liquid. The absorption capacity depends also of the fibre morphology affecting strongly the network porosity [19,230].

The absorption capacity of H1-H6 pulps varied within *ca.* 15% variance and, in most cases, was negatively affected by elimination of knots (Figure 34). At the same time, the specific volume of the air-laid pads was ca. 25% higher after the elimination of knots. The latter fact is explained by the less dense air-laid network constituted by well-separated fibres. The apparent controversy between the increase of fibre network porosity and the decrease in absorption capacity of pads prepared with knotless pulps can be explained by the collapse of pad pores upon wetting. The contraction of the volume of the pad occurs essentially under the gravity of the absorbed liquid, due to the low mechanical resistance of the wet mesh [167]. Hence, a certain positive effect of knots on the absorption capacity can be explained by the inclusion of rigid fibre bundles in the network that preserve it from collapse under moistening.

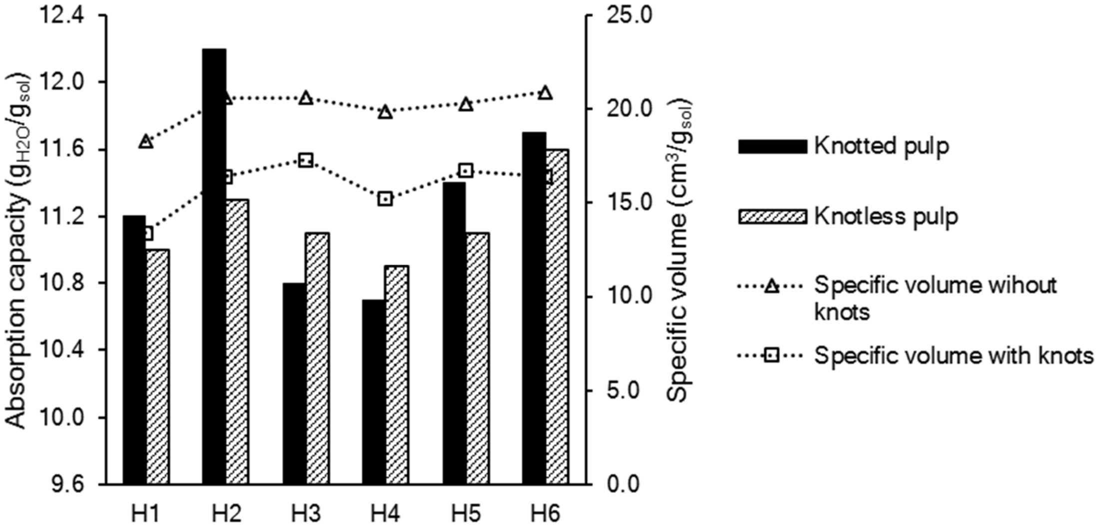


Figure 34 - Absorption capacity and specific volume in fluff pulps (H1 - H6) with and without knots.

By a set of properties, such as absorption capacity and velocity, H2 and H6 pulps show the best results, possessing also the most porous network structure (the highest specific volume). The H1 and H4 pulps showed the lowest absorption capacity and the longest absorption time (Figure 35). Since the absorption of fluffed pulp is positively affected by the specific volume/porosity of the fibre network, the greater absorptivity of pulps H2 and H6 is quite understandable [195,231].

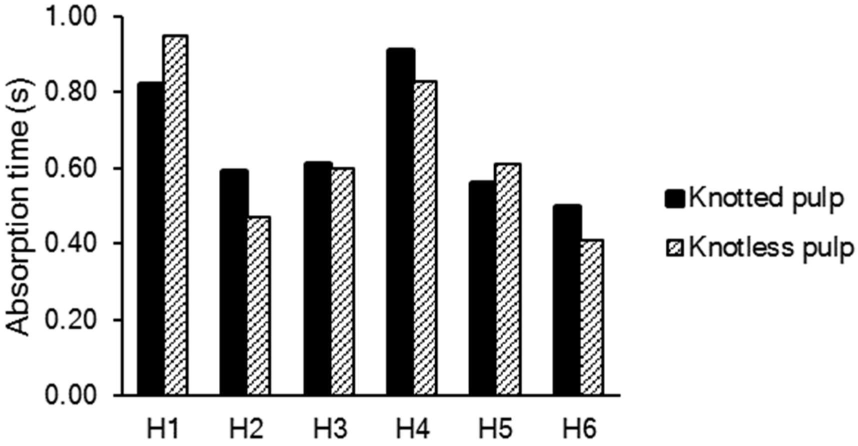


Figure 35 – Absorption time revealed by hardwood fluff pulps (H1-H6).

These pulps showed also the shortest absorption time due to the large capillary in the corresponding pads, as predicted by the modified Washburn equation [195] that describes the penetration rate of capillary suction (5.1):

$$\frac{dl}{dt} = \frac{\gamma_{lv}\, r\, cos\theta}{4\eta l} \qquad 5.1$$

where l is the distance penetrated into capillary of radius r in time t by a liquid of surface tension γ_{lv} and viscosity η; θ is the contact angle between the drop of liquid and the fibre surface.

The high porosity of air-laid pads constituted of deknoted H2 and H6 pulps can be explained, at least partially, by the coarsest, longest and highly deformed fibres (Table 11). However, within the narrow range of variations in fibre morphology, it was difficult to establish reliable relationships between them and the absorption capacity of the corresponding pulps. The highest absorption capacity of H2 and H6 pulps coincides with the highest content of carboxylic groups belonging mostly to the glucuronoxylan (Figure 36). The hemicelluloses containing carboxylic groups contribute largely to the swelling of the pulp [214,232]. The swelling of the polymeric network is one of the basic mechanisms in the absorption by porous materials [167,169]. The importance of the chemical composition of fluff pulp on its absorption can be demonstrated by the correlation between water retention and carboxyl group content in hardwood pulps (Figure 36). Carboxyl groups present in the glucuronoxylan confer hydrophilicity to the fibres and, consequently, contribute to the water absorbing properties of the fluff pads.

The water retention of the softwood C1 pulp was out of the trend revealed for the hardwood H1-H6 pulps and showed higher values (2.7 g/g) with lower content of carboxyl groups (6.0 mmol/100g) in the pulp. This behaviour can be explained by a high proportion of fines (>70%) in defibrated softwood pulp that improve water retention due to their high specific surface.

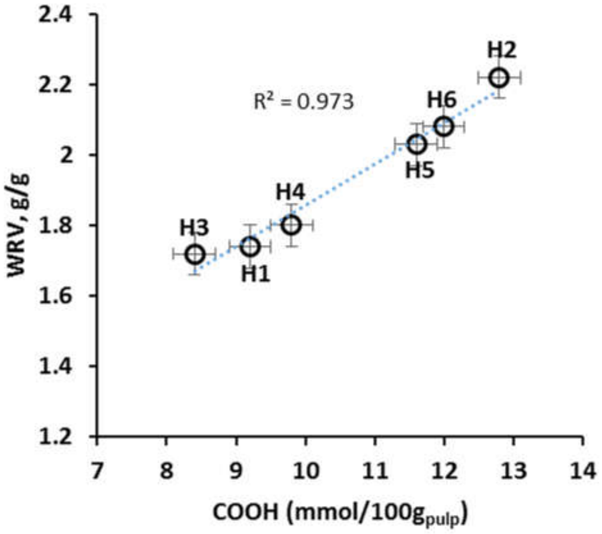


Figure 36 - Correlation between the content of carboxyl groups in H1-H6 pulps and the water retention values (WRV) of corresponding fluff pulps.

The smallest specific volume (i.e. the smallest porosity) was apparently the main factor of less absorption of the pads produced from the pulps H1, H3 and H4. This also explains, to some extent, the longest absorption time with these pulps, due to the smaller diameter of capillary. The shortest length and the smallest coarseness of fibres in H1 and H3 pulps (Table 11) could be one of factors that contributed negatively to the network porosity. On the other hand, pulps H1, H3 and H4 contained also a low amount of carboxyl groups, thus less contributing to the intrinsic water retention of the fibre mesh.

It seems that the effect of chemical composition of fluff pulps on its absorption is not limited to the amounts of hemicelluloses only (e.g. glucuronoxylan in hardwood pulps), but also their chemical structure and the localization in the fibre cell wall. When the variation in xylan did not exceed 10% in H1-H6 pulps, the variation in uronic moieties was as higher as 25%. Hence, the variation in pulping and bleaching conditions induced structural differences in xylan in terms of its substitution with uronic moieties (both the original 4-*O*-methyl-α-D-glucuronic acid (4*O*MeGlcA) and its hexenuronic acid (HexA) derivative). The bleaching sequences affected not only the amounts of uronic moieties (detected through the amount of carboxyl groups) in pulps, but also the proportion between 4*O*MeGlcA and HexA (Table 10). Thus, if ECF-bleached pulps (H1-H3, H5 and H6) possessed a relatively small amount of HexA (0.3-2.0 mmol/100g), the TCF-bleached H4 pulp contained 3.4 mmol/100g of HexA (about 35% of total uronic moieties). Since the pKa of HexA and 4*O*MeGlcA are similar (3.0 and 3.1, respectively), the contribution of these uronic moieties to ion-exchange capacity and pulp swelling must be comparable [231]. In addition to the amount, the allocation of xylan in the fibres plays an equally important role in the swelling and mechanical properties of eucalypt kraft pulp [233]. In turn, the location of the residual xylan depends on the pulping severity, mainly the alkali load and the cooking temperature [233]. Thus, the absence of clear dependency, either on the water retention in the pulp (WRV) or the absorptivity of air-laid pads from the xylan content in eucalypt kraft pulps, could be explained by other associated factors, such as the structure and the location of the residual xylan in pulps.

5.2.3 Network strength

All eucalypt (H1-H6) and the reference softwood (C1) fluffed kraft pulps were evaluated for the network strength (NS) of air-laid pads assessed by measuring the maximum force which the network could withstand and the work of deformation to break in the shear mode with a standard designed equipment. In all essays the knotless fluffed pulps showed the greatest network strength than corresponding knotted pulps (Figure 37). This trend is usually explained by the decrease in the misshapen and inhomogeneous spaces in pads, which resulted in undefined break points [204,234]. Another important factor affected the network strength is the fibre length, which explains much stronger NS of C1 (18.5 N) than that of hardwood pulps (H1-H6). Despite strong detrimental effect of dry-defibration on the fibre´s length (Table 11), still considerable fibre fraction in C1 possessed much longer fibres than H1-H6 pulps. Long fibres provide more fibre-fibre contact points per fibre, which enhances network strength. Similar features were reported previously while comparing birch and softwood fluff pulps [19].

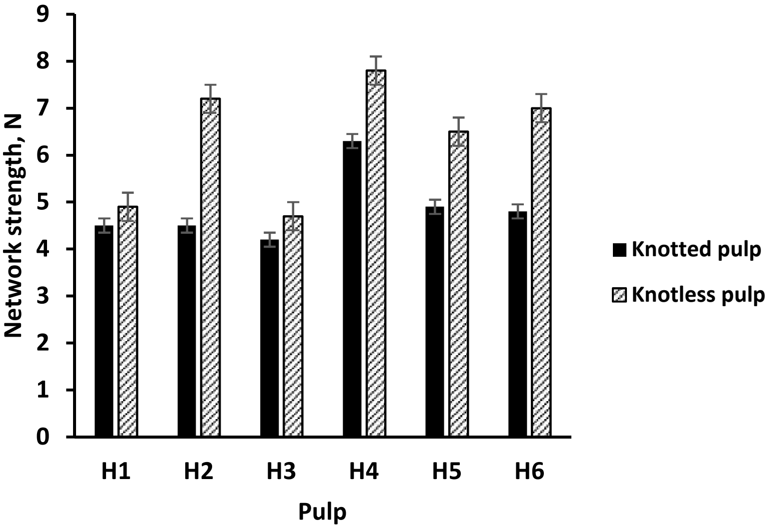


Figure 37 - Network strength of air-laid pads produced from eucalypt kraft pulps (H1-H6).

Among H1-H6 pulps the largest NS values (≥ 7 N) were obtained with H2, H4 and H6 pulps. There was no clear impact of fibre length and its deformation parameters (curl and kink) on NS, though some positive correlation was traced between NS and fibre coarseness (r^2=0.60). In fact, the highest NS detected for the H4 pulp, possessed the highest coarseness and one of the highest fibre deformations (Table 11). Thus, the coarseness of the fibre seems to be one of the most relevant factors that strongly affected the NS of the hardwood pulps under study. Additionally, it explains the aforementioned NS superiority of the softwood fluff pulp having more than twice the fibre coarseness (Table 11). The NS of the air-laid fibre network is positively correlated (Figure 38) with the tensile strength and burst resistance of the wet-formed webs discussed previously (Figure 30). Hence, previous discussions concerning the factors that affect the mechanical properties of wet-formed handsheets are valid to some extent for the air-laid formulations and can be used to predict the network strength of the air-laid formulations. Noteworthy that the pulp showing the largest NS is not necessary demonstrate the largest absorptivity. Thus, H4 pulp showed the highest NS value, but the lowest absorption capacity. At the same time, H2, H5 and H6 pulps revealed a relatively large both network strength and the absorption capacity. Abnormal behaviour of H4 pulp could be assigned to the relatively low porosity of the air-laid pad. The porosity is the major factor determining the absorptivity of the hardwood fluffed pulps, being even more important that the hydrophilicity of the fibres [14,168]. Other factors affecting the absorptivity are related to the collapsibility of wetted network and its water retention ability.

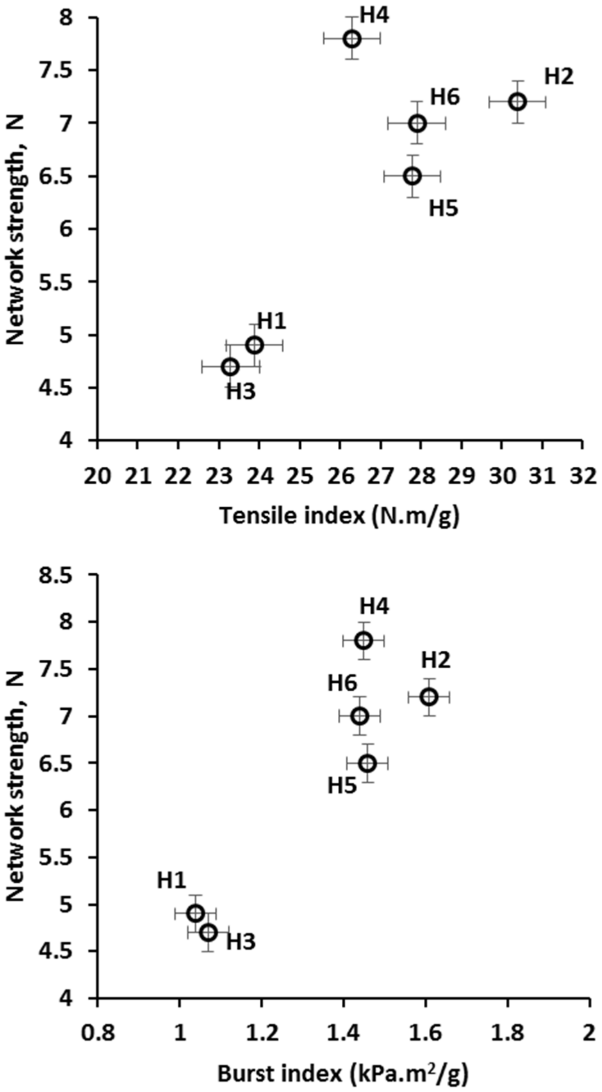


Figure 38 - The relationships between the network strength of air-laid pads and the tensile (upper image) and burst (lower image) resistance of the corresponding wet-formed webs of eucalypt kraft pulps (H1-H6).

The last parameters are also affected by the xylan content in pulp and this dependency is fairly ambiguous [19,168]. It has been found that the removal of moderate amounts of xylan from a hardwood fluff pulp (up to 50% of the initial) leads to an increase in the collapsibility of an air-laid fibre network when wet, while the removal of large amounts of xylan (up to 80% of the initial) decreases the network's ability to collapse under wetting [19]. This fact was explained by the hornification of the pulp fibres with the elimination of xylan and improvement of the network stiffness. Speculating these findings and taken into account a similar amount of xylan in H4 and in H2, H5 and H6 pulps (Table 10), it can be proposed that the lowest absorptivity of H4 pulp, when compared to H2, H5 and H6 pulps, is due to the weaker water retention of the former pulp, rather than due to the increased collapsibility of the network under wetting. This argument is also relevant when explaining the low absorptivity of H1 and H3 pulps, which shows the lowest water retention capacity.

Among ECF-bleached eucalypt kraft pulps, the pulping conditions used to produce H1 and H3 pulps can be considered the least suitable to produce fibrous material for fluff applications. These pulps demonstrated the lowest basic mechanical properties, the lowest intrinsic viscosity, the content of residual xylan and carboxylic groups. In terms of fibre morphology, H1 and H3 pulps showed the shortest average fibre length and the lowest coarseness (Table 11).

5.2.3.1 Sorption isotherms relationships between the surface properties of pulps and their absorption capacity and network structure

The phenomenon absorption begins at the surface of the absorbent material, which is the formation of monolayer and multilayer of water molecules until the absorption takes place in the capillary material [195]. Since the conditions for the manufacture of kraft pulp (wood pulping and pulp bleaching) affect the chemical composition of pulp and the morphology of the fibres, these conditions can cause changes in the absorption capacity in the air-laid fibre network. This subchapter focuses on the characterization of fibre surface of a set of industrial bleached eucalyptus kraft fluff pulps (H1- H6), its affinity towards water in relationship to absorption capacity of pulps using sorption isotherms and inferring the thermodynamics interaction with water. The detailed discussion on this matter can be found in the recent publication [168,199].

The sorption isotherms were assessed for the six industrial fluffed pulps (H1-H6), as discussed above, at temperatures 25 °C, 30 °C and 35 °C and the water relative pressure between 0.05 to 0.95, using the instrument DVS (Dynamic Vapour Sorption Analyser). For each relative pressure value (5, 10, 20, 30, 40, 60, 80 and 95%), the corresponding equilibrium moisture ($\mathrm{X_{eq}}$) content value is determined when the system stabilizes, i.e. when the change in sample mass is less than 0.001% or after 8 hours of testing for the same relative pressure value. From the mathematical models mentioned in the chapter 4.1.1, it was choose the Guggenheim-Anderson-de Boer (GAB) model to fit the experimental points, since this model is the most suitable to the extent that is valid for a higher range of relative pressure.

The sorption isotherms allowed the evaluation of the monolayer capacity (X_m) in knotted and knotless pulps, while adjusting the GAB model to the experimental data and infer the effective parameters. Only free hydroxyl groups not involved in intramolecular and intermolecular hydrogen bonding bind water molecules, thus forming a monolayer at low water activities ($a_w \leq 0.40$) [33,235]. This monolayer is discontinuous, due of randomly distributed free hydroxyl groups and for their differences in accessibility. Bleached eucalyptus kraft pulps contain significant amounts of glucuronoxylan, which is located essentially in the outer layers of the fibres [236]. Accordingly, the content of xylan and its chemical structure (mainly the quantity of uronic moieties) contribute to the absorption of water by the fluff pulps and must be considered in the interpretation of the results of the isothermal sorption.

The monolayer capacity measures the availability of active sites on the material for water sorption to occur [177,183] and was thus used to estimate the specific surface area of the absorbent material, S, according to equation 3.11. The main finding was that knots content did not affect significantly the equilibrium moisture content (Table 12). This means that fibres in bundles maintained the accessibility to water comparable with that of well-separated fibres [168,175]. Hence, the agglomeration of fibres is not a problem for their accessibility inside the knots. However, throughout the analysis of the maximum net isosteric heat of sorption ($Q_{st,max}^{net} = \Delta H_C + |\Delta H_k|$), calculated based on the energetic parameters associated with the adsorption enthalpy of the monolayer and multilayer (constants C and K of the GAB model, respectively), it was concluded that the binding energy of the forces between the water vapour molecules and the pulp surface was much higher in knotless than in knotted pulps. Primary, this was due to the higher monolayer sorption enthalpy (ΔHc) rather than due to the multilayer sorption enthalpy (ΔHk) of corresponding pulps (Table 13).

Table 12 - Monolayer capacity values and specific surface areas at 25, 30, and 35 °C

Pulp	$X_m \pm dX_m \left({g_{H_2O}}/{g_{sol}}\right)$			$S \pm dS \left({\mathrm{m}^2}/{g_{sol}}\right)$		
	T = 25 °C	**T = 30 °C**	**T = 35 °C**	**T = 25 °C**	**T = 30 °C**	**T = 35 °C**
1	0.048 ± 0.002	0.046 ± 0.003	0.046 ± 0.003	201 ± 8	194 ± 15	191 ± 12
2	0.047 ± 0.003	0.046 ± 0.003	0.046 ± 0.003	196 ± 12	193 ± 15	191 ± 12
3	0.047 ± 0.003	0.047 ± 0.003	0.047 ± 0.003	198 ± 12	195 ± 15	195 ± 12
4	0.048 ± 0.004	0.047 ± 0.003	0.046 ± 0.003	200 ± 16	196 ± 15	193 ± 13
5	0.048 ± 0.003	0.046 ± 0.003	0.046 ± 0.003	199 ± 14	194 ± 15	191 ± 13
6	0.047 ± 0.003	0.046 ± 0.003	0.045 ± 0.003	195 ± 11	192 ± 15	189 ± 11
2K*	0.047 ± 0.002	0.046 ± 0.002	0.045 ± 0.003	197 ± 7	194 ± 14	190 ± 12

K* means the knotted pulp

Table 13 - Enthalpy differences and entropic accommodation factors between the monolayer and multilayer (ΔH_C, C_0) and between the bulk liquid and the multilayer (ΔH_K, K_0).

Pulp	$\boldsymbol{\Delta H_C} \pm \boldsymbol{d\Delta H_C}$ **(kJ/mol)**	$\boldsymbol{C_0} \pm \boldsymbol{dC_0}$ **(adm)**	$\boldsymbol{\Delta H_K} \pm \boldsymbol{d\Delta H_K}$ **(kJ/mol)**	$\boldsymbol{K_0} \pm \boldsymbol{dK_0}$ **(adm)**
1	7 ± 1	0.5 ± 0.2	-3.3 ± 0.2	2.9 ± 0.2
2	12 ± 3	0.2 ± 0.01	-2.1 ± 0.6	1.7 ± 0.4
3	16 ± 4	0.02 ± 0.01	-2.4 ± 0.6	2.0 ± 0.5
4	13 ± 3	0.2 ± 0.01	-3.0 ± 0.4	2.6 ± 0.4
5	13 ± 5	0.2 ± 0.01	-2.7 ± 0.2	2.3 ± 0.2
6	16 ± 5	0.02 ± 0.01	-2.9 ± 0.4	2.4 ± 0.4
2K*	7 ± 1	0.7 ± 0.03	-2.0 ± 0.9	2.0 ± 1.0

K* means the knotted pulp

Accordingly, the binding energy between aggregated fibres in knots and water molecules is weaker when compared to well-separated fibre-water binding forces. Simultaneously, the entropy of interaction between water molecules and the binding sites in fibres of knotted pulp is remarkably higher than in knotless pulp. In practical terms, this indicates that knotless pulp will absorb more readily water than the knotted pulp. According to the obtained results the biggest difference between the monolayer and multilayer enthalpies (ΔHc), i.e. the highest adsorption enthalpy in the monolayer, corresponds to the highest value of $\mathrm{Q_{st}^{net}}$, where the bonding force for the pulps are positioned as follows: H3 > H6 > H5 > H4 > H2 > H1 [173]. This difference among pulps is due to different processual conditions used in the mill and is gathering several factors affecting the surface properties, such as variation in the chemical composition and the physical structure of the fibres, fibres morphology, among others. Due to the simultaneous changes in cooking and bleaching conditions, it was difficult to design some clear relationships between them and the $\mathrm{Q_{st}^{net}}$. However, some positive trend was noticed (r^2=0.56) between the $\mathrm{Q_{st}^{net}}$. and the H factor (Table 7).

5.2.3.2 Contact angles of pulps

The affinity of the fibre surface to water is an important factor influencing the rate of water sorption by the fibre network via capillary suction (Eq. 3.19). This kind of interaction can be assessed by contact angle measurements. The contact angles θ were measured on laboratory pulp handsheets with smooth surface to minimize the effect of surface roughness. All the pulps (in lab handsheets) are wettable, since all the contact angle values are much less than 90° (Figure 39). The better the surface wettability (the lower contact angle), the higher is the absorption rate at other variables being equal (Eq. 3.21).

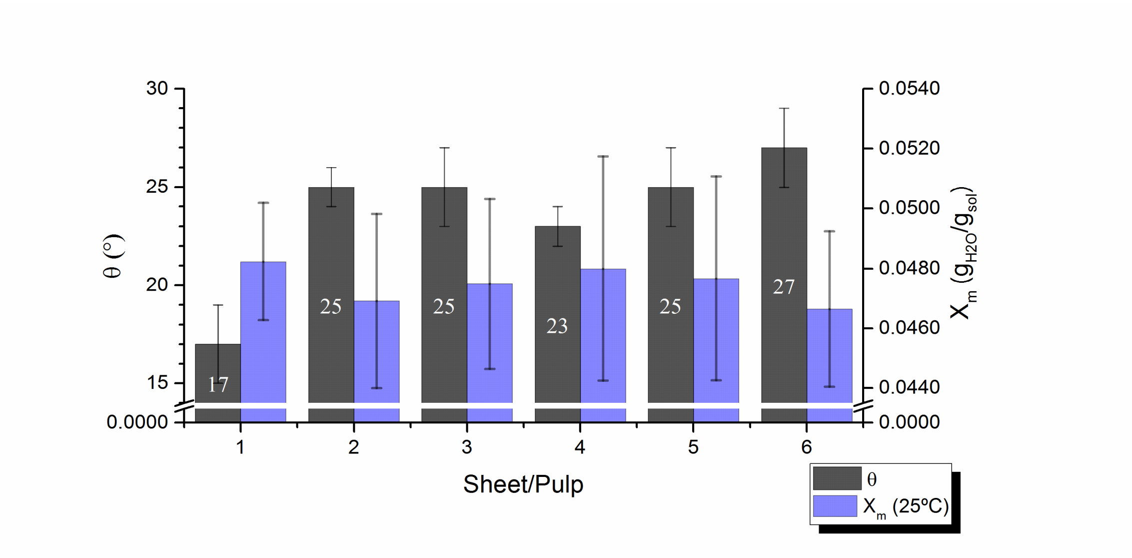


Figure 39 - Monolayer capacity (X_m) of 1–6 pulps at 25 °C and the average contact angles of corresponding handsheets.

The experimental results unambiguously confirm that the wettability of the pulp handsheets and the affinity of the fibre surface with water are inextricably related (Figure 39). Pulps with the lowest contact angles values have highest affinity for the water molecules. The reverse is true for high contact angles [3]. Pulps with extreme contact angles, such as pulp H1 with θ = 17° and pulp H6 with θ = 27° did not correlate univocally with their chemical composition (amount of hemicelluloses or carboxylic moieties, Table 10), or with their basic fibre morphology (average fibre length/width or coarseness, Table 11). On the other hand, a tendency of pulp's contact angle to increase deformation of fibres (curl, kink, Table 11) was clearly traceable (r^2 = 0.7-0.8), as illustrated in Figure 40.

The deformations of the pulp fibres, such as curl and kink, are mostly irreversible being caused by distortion and microcompression of the fibril layers [237]. The misalignment of the fibril lamellas lead to crimps and creases, where some adjacent surfaces in the creases approach each other, forming intrafibre cross-links by hydrogen bonding of free hydroxyl groups [195]. Consequently, the accessible area of the damaged fibres can be slightly reduced, which caused in decrease of the monolayer capacity and the wettability of the fibre mesh, resulting in the increase of θ. On the other hand, the accessible surfaces of deformed fibres, which contain partially disordered cellulose fibrils, are more wettable when compared to surfaces of non-deformed fibres [238]. This behaviour may explains the experimentally observed larger $\Delta\mathrm{H_c}$ and $\mathrm{Q_{st}^{net}}$ of more curled and kinked pulp fibres (Table 11 and Table 13). These accessible surfaces of deformed fibres can also readily form the intensive hydrogen bonds between the fibres in the handsheets, hence contributing to the reduction in paper surface wettability (increases in θ). Therefore, the contact angle of the fibre web reflects the apparent wettability of the surface and not necessarily only the intrinsic contribution of the constituent fibres [239]. Nevertheless, the contact angle is one of the most common and reliable analyses for assessing the wettability of cellulosic materials.

As too many factors can affect the absorption capacity of fluff pulp (chemical composition, surface properties, fibre morphology and physical structure of fibres) their relative contributions are not very easy to trace. This evaluation was carried out using principal component analysis (PCA). The PCA reflects the correlation between the variables, expressing their contribution to the two principal components (PC), in terms of relative variation. In the case study, component 1 (PC1) explains 69.9%, while the component 2 (PC2) explains only 14.9% of variations (Figure 41). Therefore, the correlations between the different variables were analysed, especially in relation to their contribution to PC1 describing mainly the fibre network properties.

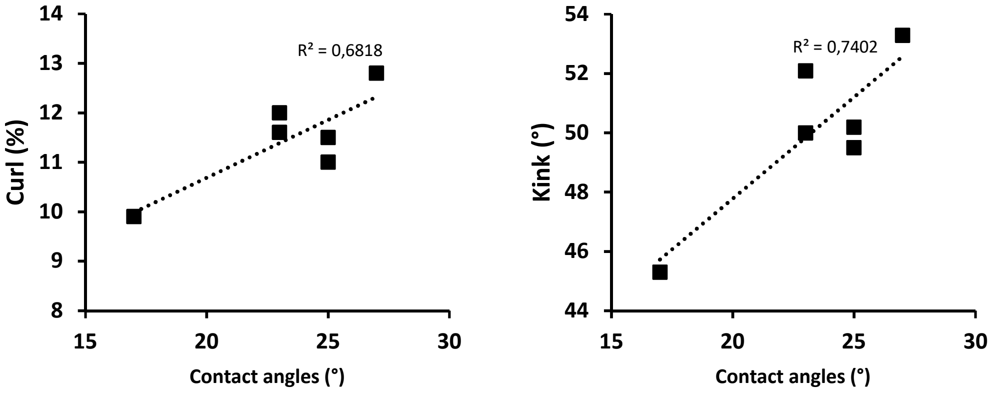


Figure 40 - Correlation between contact angles and fibre deformations: curl (left figure) and kink angle (right figure).

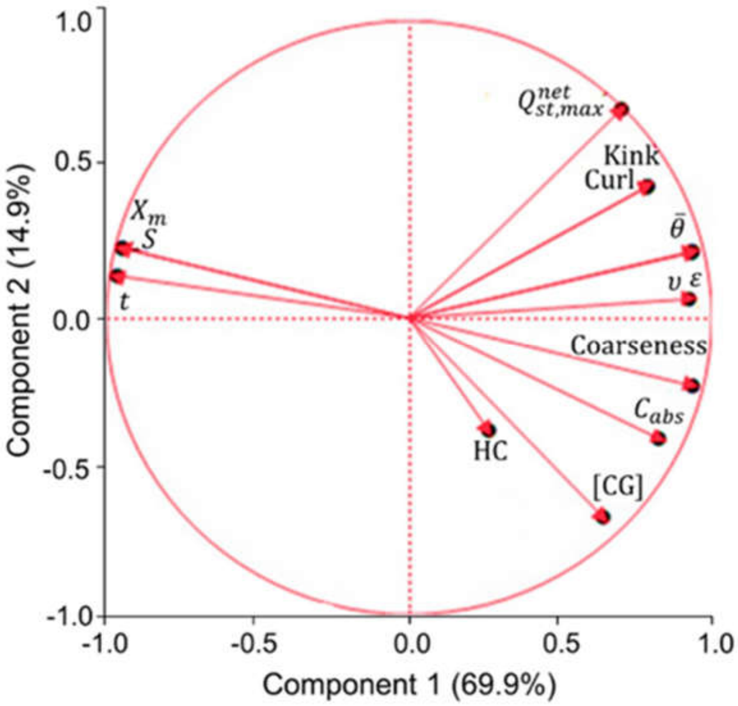


Figure 41 - Principal component analysis (PCA) diagram elucidating the structure-property relationships of H1–H6 kraft fluff pulps.

In general, the PCA supports previous conclusions that the affinity of the fibre surface with water, expressed by X_m and S and the surface wettability (measured by the contact angle, θ), are not necessarily directly related to the improved capillarity absorption properties (C_{abs} and t). In fact, statistically, X_m and S have positive correlation with absorption time (t) and negative correlation with absorption capacity (C_{abs}). The opposite effect is verified in relation to the correlations between the average contact angle (θ) and these absorption properties. The PCA also shows that higher coarseness correlated with the lower accessible surface area (S), the monolayer capacity (X_m) and the increased fibre deformations (kink and curl) to the lesser wettability of handsheet's surface, i.e., larger contact angles (Figure 41). The reasons for such correlations have been previously discussed when analyzing the affinity of the pulp surface with water and the relationship between the absorption capacity and the structure of the fibre network in air-laid pads.

The expectable positive correlation was found regarding the presence of highly hydrophilic components in pulps (hemicelluloses and other polysaccharides containing carboxylic groups) and their absorption capacity (Figure 41). The absorptivity of pulps also positively correlated with fibre coarseness and, to a lesser extent, with curled and kinked fibres. In fact, the network with a higher coarseness of fibres usually exhibits better absorption properties, because these bulky fibres possess less interfibre bonding areas, resulting in a network with high specific volume, high porosity, and, therefore, improved absorbency. The positive contribution of deformed fibres to improve the specific volume (ν) and the porosity (ε) of air-laid pads has also been discussed previously and favored the pulp's absorption capacity. It is worth mentioning that the deformations of the fibres provided the greatest contribution to ν and ε of the pads.

Although the content of hemicelluloses (*HC*) in pulps is expectedly related to the carboxyl groups content (*CG*) (Figure 41), a much weaker relationship exists between the *HC* content and the absorption capacity (C_{abs}). Consequently, the effect of *HC* on C_{abs} is not straightforward. On the one hand, *HC* favors the network swelling and water retention and, on the other hand, *HC* deteriorate the air-laid fibre network structure and strength making it less robust under moistening.

HC contributed negatively to the wettability of the fibres in pads (negative contribution to PC2), according to the PCA data. Thus, the X_m and *HC* located, even in the opposite quadrants, indicating a negative correlation with each other (Figure 41). This feature is in line with the known fact that *HC* can negatively affect the wettability of the fibre web, resulting in an increase in θ with the extent of *HC* present in the pulp [239, 240,241]. The plausible explanation deals with intensive formation of hydrogen bonds between free hydroxyl groups on the surface of cellulose fibrils and amorphous hemicelluloses. As a result, the amount of free hydroxyl groups in the cellulose fibrils is decreasing and the interfibrillar space is reduced being filled with *HC*, thus diminishing the monolayer capacity of fibrils. However, with a very low *HC* content, when the fibres are dried intensively, their surface is collapsed due to the intensive aggregation of fibrils within cell wall and the wettability of the fibres decreases [239,242]. Therefore, hemicelluloses can have both positive and negative effects on fibre wettability. Among the studied pulps, the variations in *HC* content did not exceed 20% and the eventual direct relationship between the decrease in *HC* content (Table 10) and the increase in θ of pulp fibres (Figure 41) was not clearly detectable. It was recently reported that the capacity of pulp fibre to swell depends not only on the amount of hemicelluloses in eucalypt kraft pulp, but also on their location within the cell wall [168,233]. The last feature depended on the pulping severity, mainly the alkali load and the cooking temperature. Hence, it is reasonable to propose that the wettability and absorption capacity of kraft pulps in study also depended not only on the *HC* content, but also on the *HC* distribution in the cell wall of fibres.

5.3 Effect of cooking and bleaching conditions on the properties of fluff pulp

According to the results on industrial pulps, both pulping and bleaching conditions play an important role in the performance of eucalyptus kraft pulps in fluff applications. However, multiple variables of industrial process did not allow to trace unambiguously the relationships between the processual conditions and fluff pulp properties. To avoid such an ambiguity, in this study, eucalyptus chips were laboratory cooked under controlled conditions and with variable alkali load and eucalyptus kraft pulps were laboratory ECF and TCF bleached to similar brightness and dry-defibrated, applying varying defibration intensities. The fluff pulps were evaluated for their fibre morphology and analysed for general chemical composition and the supramolecular cellulose structure employing solid-state ^{13}C NMR. The absorption capacity/absorption rate and the air-laid fibre network strength of eucalyptus fluff pulps were assessed and related to the morphology, chemical composition and physical structure of fibres regarding the cooking and bleaching conditions applied. The chips used in the lab cooking experiments were prepared from freshly cut logs supplied from controlled plantations of Iberian *Eucalyptus globulus*. The cooking experiences were done with variable active alkali (13, 15, 17 and 18% as Na_2O) maintaining the same sulphidity (30%) and H factor (ca. 800). All pulps, after the oxygen delignification, were ECF ($D_{hot}E_PD_1P$) and TCF ($A/QE_PP_1P_2$) bleached to similar brightness.

5.3.1 Cooking, oxygen delignification and bleaching

The results of cooking revealed progressive delignification of the pulps obtained with an increase in the load of active alkali (AA), showing the kappa number from 19.2 for AA13 pulp to 13.3 for AA18 pulp (Table 14). The total cooking yield fell in the same order and the screened yield reached the maximum at AA of 15-17%. The intrinsic viscosity ([η]) of the pulps gradually decreased with the increase in AA due to the enhanced alkaline hydrolysis and cellulose peeling reactions [33,35,60]. In the unbleached pulps, the content of HexA increased with the increase in AA from 13 to 15%, being further decreased with AA of the liquor of 17 and 18% (Table 14). Similar features were observed previously for kraft cooking of eucalyptus wood with variable alkalinity and explained by the simultaneous formation/degradation of HexA and the xylan dissolution in spent liquor [96].

Oxygen delignification allowed *ca.* 40-50% delignification of kraft pulps (Table 14), thus accounting for significant savings of bleaching reagents in subsequent bleaching

[102]. Due to the greater brightness gain for pulps cooked with 17 and 18% AA in delignification with oxygen, the final brightness of these pulps was higher in ECF and TCF bleaching with the same load of bleaching reagents (Table 14). Due to the poor reactivity of (HexA) residues in the residual xylan of pulps during oxygen delignification [94,97], its contents were quite similar before and after the oxygen stage. The content of HexA residues was decreased drastically upon bleaching, being more accentuated for the ECF bleached pulps. The last fact is explained by readily degraded HexA residues by ClO_2 in D stages [96,97,243]. TCF pulps still contained considerable amounts of HexA even applying the A/Q stage at the beginning of the sequence. In general, ECF pulps showed higher brightness and the intrinsic viscosity that corresponding TCF pulps.

Table 14 - Results on the laboratorial kraft cooking of *E.globulus* chips, oxygen delignification and bleaching of the resulted pulps.*

	Parameters	**AA 13%**	**AA 15%**	**AA 17%**	**AA 18%**
After Cooking	Total yield, %	57.5	55.5	55.0	53.1
	Pulp yield, %	51.2	54.0	54.2	52.6
	Rejects, %	6.3	1.5	0.8	0.5
	Kappa	19.2	15.6	14.5	13.3
	IK lignin, %	16.5	12.3	11.4	10.4
	Total lignin, %	3.1	2.3	2.1	1.9
	HexA, mmol/kg pulp	32.2	38.9	36.3	34.2
	Brightness, %	31.0	35.7	36.1	38.3
After O_2 delignification	Kappa	12.5	9.8	8.5	7.4
	IK lignin, %	9.5	6.5	5.5	4.8
	Total lignin, %	1.8	< 1.0	1.0	< 1.0
	HexA, mmol/kg pulp	31.3	34.1	36.9	33.0
	Brightness, %	43.5	47.2	53.9	57.2
After ECF Bleaching	Kappa	1.1	1.2	< 1.0	< 1.0
	HexA, mmol/kg pulp	< 5 Lq.	< 5 Lq.	< 5 Lq.	< 5 Lq.
	Brightness, %	89	89	91	91
After TCF Bleaching	Kappa	5.0	5.0	3.7	3.4
	HexA, mmol/kg pulp	9.6	16.8	13.8	15.3
	Brightness, %	80	82	84	85

*Cooking conditions: T = 160°C ± 2°C, t = 120 min ± 5 min; O_2 delignification: T = 100°C, t= 60 min, PO_2 = 5 bar, NaOH = 25 kg/tpsa; ECF bleaching sequence was $D_{hot}E_PDP$ and TCF bleaching sequence was A/QE_PPP.

5.3.2 Chemical composition of pulps

All bleached pulps revealed a relatively low content of extractives (<0.1%). The content of the residual lignin was substantially higher (3-5 times) in TCF pulps that in the ECF pulps (Table 14) reflecting much less effective delignification in bleaching stages with hydrogen peroxide than with chlorine dioxide. Sugar analysis showed that glucuronoxylan, the main hemicellulose in eucalyptus wood, was largely retained in bleached pulps, although its content in ECF pulps is higher than that of TCF pulps (Table 15). This fact could be explained by predominance of alkaline bleaching stages in TCF sequence. In addition to the backbone degradation, the oxidative alkaline bleaching stages induce the xylan migration and its partial removal from the cellulosic fibre surface [243]. Accordingly, the changes in the severity of cooking conditions, expressed as a variable alkali charge, negatively affected the xylan retention in ECF and TCF pulps. In general, a higher hydroxide ion concentration results in a more extensive removal of hemicelluloses, mainly xylan (Table 15). Therefore, the observed coincidence in simultaneous reduction of pulps viscosity and the content of carboxyl groups (Table 14 and Table 15) are due to the increased alkali load in cooking, when the more drastic degradation of xylan with cleavage of the uronic moieties coincided with the stronger degradation of the cellulosic chains.

Noteworthy that the amount of carboxyl groups was higher in TCF than in ECF bleached pulps (Table 15). Since carboxyl groups belong mostly to the MeGlcA and HexA residues in the residual xylan of pulps, the former fact is attributed, at least partially, to better preservation of HexA residues in TCF bleaching (Table 14). However, the oxidation of polysaccharides in oxidation bleaching stages with formation of carboxyl groups cannot be completely excluded. Carboxylic moieties are the main functional groups responsible for bulk and surface fibre charge of kraft pulps, which can influence ion-exchange properties and fibre swelling ability. These effects influence fibre flexibility, inter-fibre bonding during pressing and drying stages and mechanical properties of the pulp sheets [212,244].

Table 15 - Monosaccharide composition and the carboxyl groups content in ECF and TCF kraft pulps. *

Pulp samples	Ramnose %	Arabinose %	Xylose %	Mannose %	Galactose %	Glucose %	COOH mmol/100g
ECF13	tr.	0.2	14.9	0.2	0.3	84.4	8.9
ECF15	tr.	0.2	14.4	0.2	0.3	84.9	6.7
ECF17	tr.	0.1	13.9	0.2	0.3	85.5	5.1
ECF18	tr.	0.1	13.3	0.2	0.3	86.1	4.8
TCF13	tr.	0.1	13.4	0.2	0.3	86.0	9.3
TCF15	tr.	0.1	13.0	0.2	0.3	86.4	9.5
TCF17	tr.	0.1	12.4	0.2	0.2	87.1	8.1
TCF18	tr.	0.1	11.3	0.2	0.2	88.2	8.0

*The relative error in sugars analysis not exceeded of 3%. The pulp designations include the bleaching sequence (ECF or TCF) and the active alkali (AA=13-17) employed for their production.

5.3.3 Dry defibration of laboratory kraft pulps

The dry-defibration of fluff pulp is an important process step in the manufacture of absorbent products. There is still a limited understanding in the relation between the defibration conditions and the mechanical properties of the final dry-formed fibre networks. This can be explained by the lack of suitable test equipment for characterizing the mechanical properties of these dry-formed networks [14,245]. During dry-defibration process the fibres need to be sufficiently separated and the knots content should be low [246]. The dry-defibration of ECF and TCF bleached pulps was carried out under the same conditions using laboratory hammermill with variable intensities (2500, 3000 and 3500 rpm). The increase in milling intensity revealed clearly the reducing of the knots content in dry-defibrated fluff pulps (Figure 42).

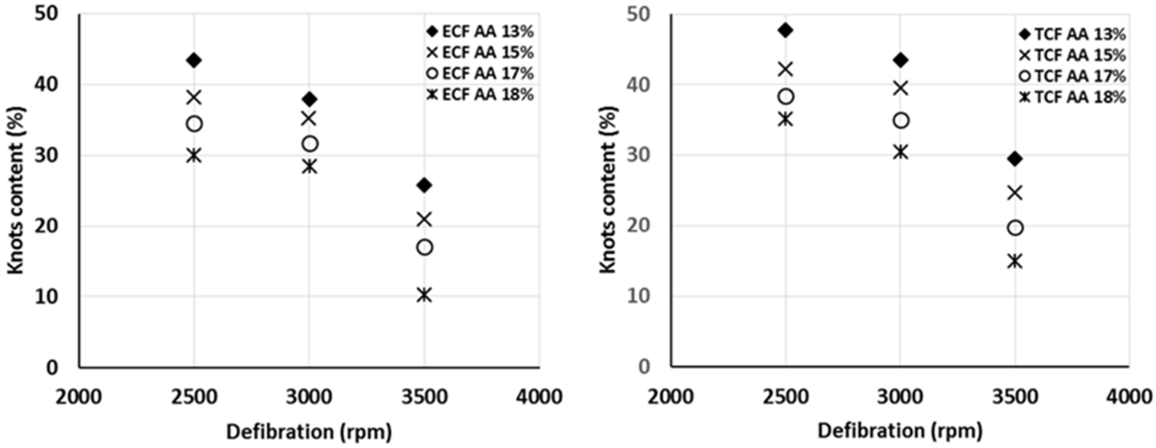


Figure 42 - Effect of defibration intensity on knots content in dry-defibrated ECF and TCF fluff pulps. The standard deviation for the knots content was ca. 4.0%.

A particularly accentual decrease in knots content was registered when the milling intensity increased from 3000 to 3500 rpm. ECF bleached pulps cooked at different AA showed better defibration ability than corresponding TCF bleached pulps. The pulps cooked at an increased AA always show the reduction in knots. This fact can be associated with more delignified pulps containing less amount of the residual lignin and hemicelluloses (Table 14 and Table 15) and that are more susceptible to hornification under drying and possess less flexible fibres with less bonding capacity in pulp sheets [19]. The TCF pulps were harder to defibrate than the ECF pulps. The plausible explanation consists in differences of fibre morphology detected between ECF and TCF bleached pulps (Table 16). Thus, TCF pulps have coarser fibres than ECF pulps, which can be important for dry defibration. The fact is that longer and coarser fibres need more energy for defibration [3,19]. In addition, the fibres of TCF pulps were more kinked during dry defibration that the fibres of ECF pulps, which could deteriorate their effective separation and enhance the already pronounced for the eucalyptus fibres tendency to flocculation in air-laid processes [234].

Table 16 - Fibre morphology of eucalypt kraft pulps before and after dry defibration using a pilot scale hammermill.*

Pulp Sample		**ECF13**	**ECF15**	**ECF17**	**ECF18**	**TCF13**	**TCF15**	**TCF17**	**TCF18**
Fiber length, mm (± 0.003)	Sheet	0.765	0.768	0.766	0.764	0.796	0.785	0.787	0.784
	Fluffed	0.761	0.757	0.758	0.758	0.754	0.752	0.746	0.746
Fiber width, µm (± 0.1)	Sheet	19.4	19.1	19.0	19.1	19.0	18.9	18.7	18.7
	Fluffed	19.5	19.1	19.1	19.1	18.5	18.2	17.9	18.0
Curl, % (± 0.1)	Sheet	8.8	8.7	7.9	7.9	8.8	8.8	8.8	8.8
	Fluffed	9.3	9.9	9.0	8.7	8.7	9.8	9.0	8.8
Coarseness, mg/m (± 0.0003)	Sheet	0.0659	0.0649	0.0641	0.0639	0.0751	0.0720	0.0753	0.0785
	Fluffed	0.0653	0.0645	0.0625	0.0627	0.0714	0.0718	0.0685	0.0686
Kink, % (± 0.2)	Sheet	38.1	38.4	35.0	34.3	27.8	28.7	29.7	29.9
	Fluffed	37.9	40.5	38.0	36.9	42.0	42.4	40.1	39.2
Fines, % in length (± 0.3)	Sheet	33.8	32.9	31.9	32.8	36.2	34.1	34.1	34.8
	Fluffed	42.6	34.2	33.4	34.4	38.3	35.0	35.0	36.2

* pulp designations denote the employed bleaching sequence (ECF or TCF) and the active alkali used in the kraft cooking (13, 15, 17 and 18%).

Since ECF and TCF bleached pulps have the same delignification history, including oxygen pre-delignification, the major changes in fibre morphology took place during the final bleaching and further drying. Alkaline stages in TCF bleaching led to the more extensive removal of xylan from fibres than in ECF bleaching stages (Table 15). Accordingly, such TCF pulps are more susceptible to hornification than ECF pulps [234]. The hornification of eucalypt bleached kraft pulps increase exponentially with the decrease of xylan content [242]. The hornification deals with the collapse of the fibre surface and the fibre stiffening and shrinkage [39,142]. Consequently, the fibres become more consolidated and contracted. This could explain the slightly higher coarseness of TCF than ECF pulps. Furthermore, the increased hornification of pulp makes fibres stiffer [145,242] and this fact affects the dry defibration [19]. Evidently, the more flexible fibres of the ECF pulps were more difficult to kink than the relatively rigid fibres of the TCF pulps. In addition, the less flexible fibres from TCF pulps were harder to curl during dry defibration than the more flexible fibres from ECF pulps. This difference in the deformation of fibres from ECF and TCF pulps under dry defibration should affect the physical properties of air-laid formulations constituted thereof.

The drop-in fibre length after dry defibration was relatively small for all bleached eucalypt pulps (within 5%). Previously, similar trend was noticed for the dry defibration of ECF and TCF eucalypt industrial pulps. It should be noted that the decrease in fibre length and the increase in fibre deformations were observed in all steps of fluff pulp production after cooking (i.e. after oxygen delignification, bleaching and dry defibration). However, the most pronounced aforementioned morphological changes occurred during the pulp bleaching. Noteworthy is the tendency of fibres to deform after the ECF bleaching, showing more pronounced kink and curl when compared to fibres of TCF bleached pulps (Table 16).

5.3.4 Absorption properties of laboratory kraft fluff pulps

The absorption capacity of fluff pulps is largely dependent on the uptake and retention of fluid by the void volume of the fibre web. Accordingly, an air-laid fibre network should have high enough specific volume with enhanced mechanical properties and reduced inter-fibre bonding without compromising the absorbent properties. Furthermore, the architecture, stability and surface properties of an interfibre capillary system have a major effect on fluff absorbency. Therefore, the absorbent capacity is related directly to individual fibre characteristics, such as coarseness, stiffness and length, which control fluff pad resilience.

Pads with a higher specific volume possess a good resiliency and should have higher water absorption capacity. However, the air-laid fibre formulations made of TCF pulps showed slightly higher specific volume (higher porosity), but somewhat lower absorption capacity than pads made of ECF pulps. Among ECF pulps, those cooked with increased AA tended to increase absorption. The opposite tendency was observed with TCF fluff pulps (Figure 43). The absorption time always followed a declining trend with an increase of cooking AA for both ECF and TCF pulps. However, TCF pulps showed slightly shorter absorption times than ECF pulps. In general, variations in absorption capacity were smaller than would be expected from variations in pads porosity.

The porosity of the air-laid fibre network is commonly affected by the fibre morphology, being promoted by the fibre length, coarseness and deformations [14,19,245]. Therefore, the higher specific volume of pads made from TCF pulps (Figure 43), which have greater coarseness and kink (Table 16) than ECF pulps, is not surprising. The resistance of the wet web depends largely not only on the flexibility of individual fibres under moistening [167], but also the amount of knots in the formulation [230]. Knots not only negatively affect the specific volume of the air-laid formulations; they also have less absorption ability than disaggregated fibres [168,199]. In addition, the water retention capacity of the pulp also contributes substantially to the absorption capacity, which in turn is related to the swelling of the fibres.

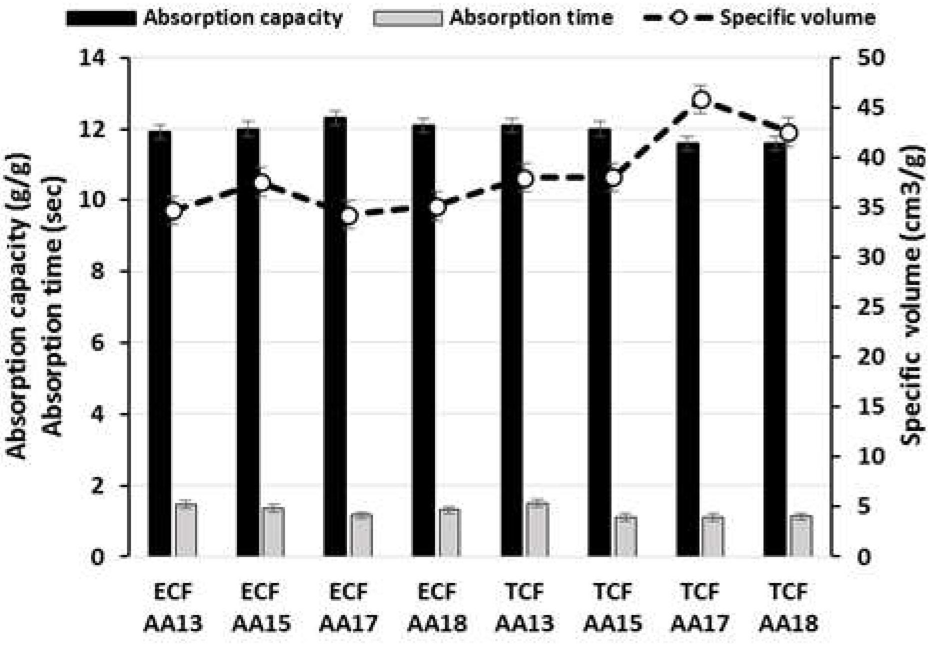


Figure 43 - Absorption capacity and absorption time of ECF and TCF fluff pulps cooked at variable active alkali (AA) from 13 to 18%.The specific volumes of air-laid pads were measured at the compression load of 2.5 kPa.

In knotless industrial eucalypt fluff pulps, the water retention was directly related to the content of carboxyl groups in pulps and positively correlated with the absorption capacity of fluff pulps [230]. However, this was not the case in the present study, where no clear relationship was found between the amounts of carboxyl groups in the ECF or TCF knotted pulps and their absorption capacity (Table 10, Figure 43). Apparently, in the pulps cooked with increased AA, the decrease in hemicelluloses and in the content of the carboxyl groups did not lead to the expected decline in the absorption capacity mostly due to the simultaneous decrease in the knots content of fluffed pulps (Figure 42). Even though there can be other contributing factors such as, for example, some increase in the fibre surface hydrophilicity with removal of moderate amount of hemicelluloses [240, 241]. The contact angles of the pulp handsheets were always smaller with the increase in cooking AA, in both ECF and TCF bleached pulps. For example, the contact angle of handsheets dropped from 38 and 43° in ECF13 and TCF13 pulps, to 31 and 33° in ECF18 and TCF18 pulps, respectively. The increase in fibre hydrophilicity positively contributes to the absorption capacity of fluff pulps, occurring predominantly via the capillary suction mechanism [167]. In this sense, more hydrophilic ECF pulps promote better capillary suction than TCF pulps.

Another factor that affects the absorption capacity of the pads is the change in the physical structure of the cellulose, expressed in the rearrangement of the fibrils, leading to their aggregation after drying (hornification), which results in more collapsed and rigid cellulosic fibres [242]. The changes in supramolecular structure of cellulose in pulps cooked at different AA and bleached by ECF/TCF sequences have been studied employing solid-state ^{13}C NMR (Figure 44).

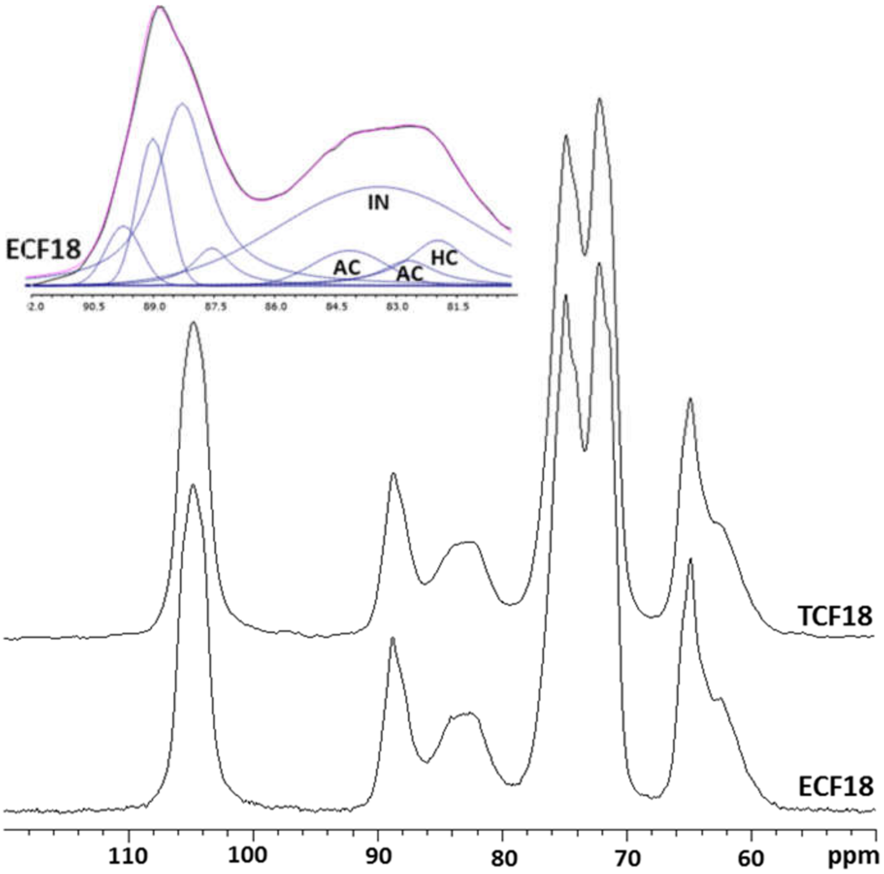


Figure 44 - Typical CP-MAS ^{13}C NMR spectra of ECF and TCF bleached kraft pulps cooked at active alkali 18% (ECF18 and TCF18, respectively). The expanded spectrum region of ECF18 pulp at 80.0-92.0 ppm depicts the deconvolution peaks assigned to hemicelluloses (HC) and accessible (AC) and inaccessible (IN) cellulose surfaces used for the calculations for the lateral dimensions of fibrils and fibril aggregates.

Practically no significant changes were detected in cellulose crystallinity among studied pulps and the *CrI* varied between 0.46 and 0.48 (Table 17). However, the CP-MAS ^{13}C NMR spectra of kraft pulps showed some differences regarding the lateral fibril (D_L) and, especially, fibril aggregate dimensions (D_A). Thus, the increase in cooking AA led to a small increase in the D_L and to a noticeable growth in D_A. This fact indicates the progressive coalescence of cellulose fibrils in the fibre cell wall with increasing severity of processing conditions, also known as a part of hornification mechanism. As known, under conditions of kraft pulping, the cellulose fibrils in the fibre cell wall tend to coalesce due to the purification of its surface from lignin and hemicelluloses and a plasticizing effect of the reaction medium [247,248]. Some neighbouring co-oriented cellulose fibrils may even join surfaces showing a small increase in crystallite width due to cocrystallization. This fibril coalescence is promoted by the cooking alkalinity and increases the aggregation of fibrils during pulp drying, i.e. enhances the hornification

[242,249]. Hence, the severity of the pulping conditions affected the supramolecular structure of the cellulose, which in turn altered the physical properties of the fibres.

Table 17 - Crystallinity index (*CrI*) and average transversal fibril (D_L) and aggregate dimensions (D_A) of ECF and TCF pulps cooked at different active alkali (AA).*

Pulp	Crystallinity index (*CrI*) (±0.1)**	Lateral fibril dimension (D_L) (±0.1 nm)**	Lateral aggregate dimension (D_A) (±0.3 nm)**
ECF13	0.47	4.9	7.2
ECF15	0.47	4.9	7.2
ECF17	0.46	5.2	7.5
ECF18	0.46	5.2	7.5
TCF13	0.47	5.4	8.0
TCF15	0.47	5.4	8.0
TCF17	0.47	5.6	8.2
TCF18	0.48	5.7	8.6

*-pulp designations are the same as in Table 4; **- data obtained by CP-MAS ^{13}C NMR

The pulp hornification is greater in TCF than in ECF pulps due to the more severe alkaline peroxide bleaching stages involved in the former sequence (Table 14). This follows from the more pronounced fibril aggregation in fully bleached TCF than ECF bleached pulps (Table 17) and the lower detected water retention value (WRV) (Figure 45). Apparently, the pulp hornification is one of the explanations for the absence of clear correlation between the amount of carboxyl groups in pulps (Table 15) and their water retention capacity (Figure 45). Hornification decreases the fibre surface and the WRV of the pulp and contributes negatively to the absorption capacity of the fluff pulp. Accordingly, it can be concluded that the observed absorption capacity of the ECF and TCF fluff pulps (Figure 43) is the result of multiple factors that occurred simultaneously (knots content, fibre's hydrophilicity and morphology and physical structure of the cellulose), whose contributions are not always unambiguous.

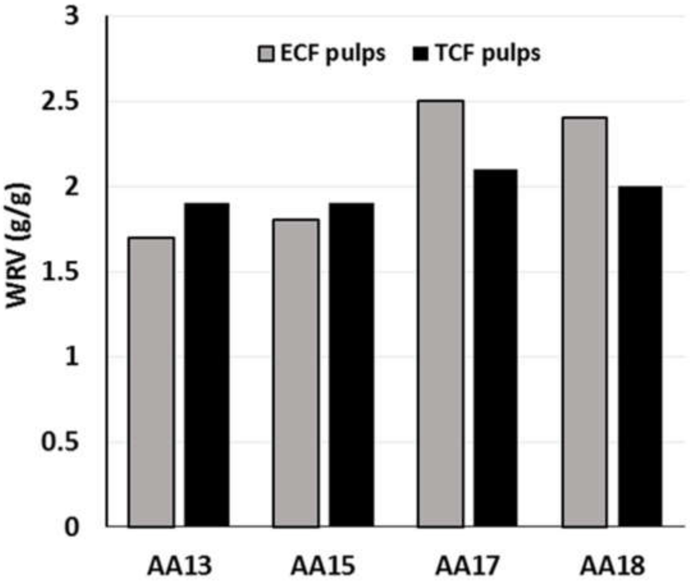


Figure 45 - Water retention volume of ECF and TCF fluff pulps cooked at variable active alkali (AA) from 13 to 18%.

5.3.5 Network strength of laboratory kraft pulps

The network strength (NS) analysis of air-laid fluff pulp formulations were carried out after their dry defibration at 3500 rpm. A similar trend was observed for ECF and TCF pulps regarding the increase in NS with higher cooking AA (Figure 46). For the kraft pulps cooked at the same AA, NS values were greater for the pulps bleached by TCF than by ECF bleaching sequences. These differences were especially noticeable for the high cooking AA.

Taking into consideration that the fibre morphology (fibre length, coarseness and deformations) has a decisive influence on the strength properties of air-laid pulp formulations [14,19], it can be proposed that the coarser and more kinked fibres of the TCF than ECF pulps (Table 16) contributed substantially to the higher NS values of the former. This was also the main argument to explain the higher NS values of the industrial TCF than of the ECF fluff pulps [230]. However, the discussed above dependencies on the physical properties of the eucalypt pulp fibres from the kraft cooking and bleaching conditions show that these factors must also be considered. Thus, the increase in the cooking AA can be associated with stiffer and less conformable fibres in fully bleached pulps, especially those bleached by TCF sequence. Such fibres provide more porous and rigid fibre network.

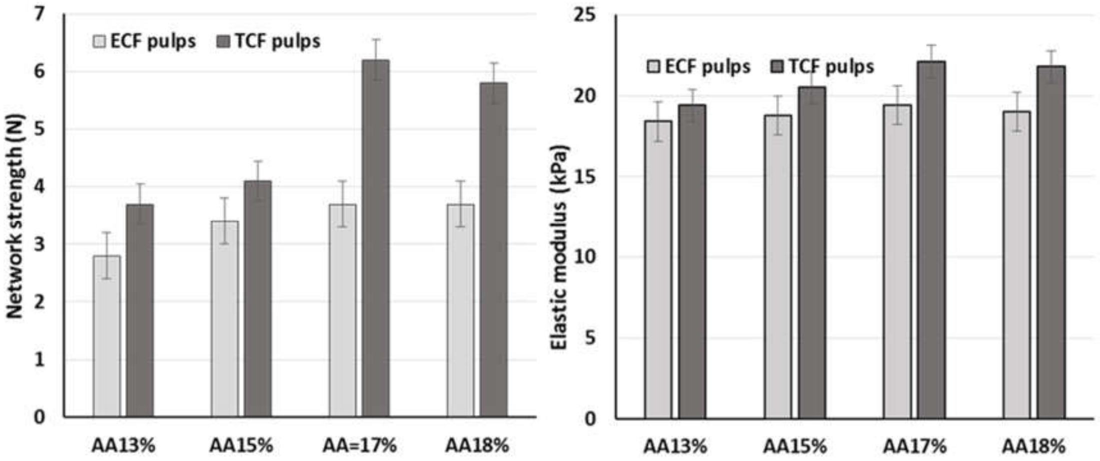


Figure 46 - Network strength of ECF and TCF fluff pulps cooked at variable active alkali (AA) from 13 to 18%.

Thus, the elastic modulus (*E*) was increased for both ECF and TCF fluff pulps with the increase of the cooking AA. Apparently, more rigid and deformed fibres (curled and kinked) are arranged in a network so that the slippage of the fibres under load is less pronounced. In general, the proportional compression deformation of air-laid pads (ε) under load (2.5 kPa) was smaller for TCF than for ECF fluff pulps (Figure 47). However, the dependence of the ε from the cooking AA was not univocal and tended to decrease for TCF fluff pulps and to increase for ECF fluff pulps.

Noteworthy that the absorption capacity and the network strength of fluff pulps are not clearly interrelated (Figure 43 and Figure 46). Indeed, the absorption capacity was not significantly affected by either the cooking or bleaching conditions. However, a clear trend was observed for ECF fluff pulps to increase absorption capacity with increased cooking AA, while the opposite trend was observed for TCF fluff pulps (Figure 43). At the same time, the network strength was sensible both to the pulping and bleaching conditions and always increased with increased cooking AA (Figure 46). The network strength of TCF fluff pulps was 20 to 70% greater than that of ECF fluff pulps.

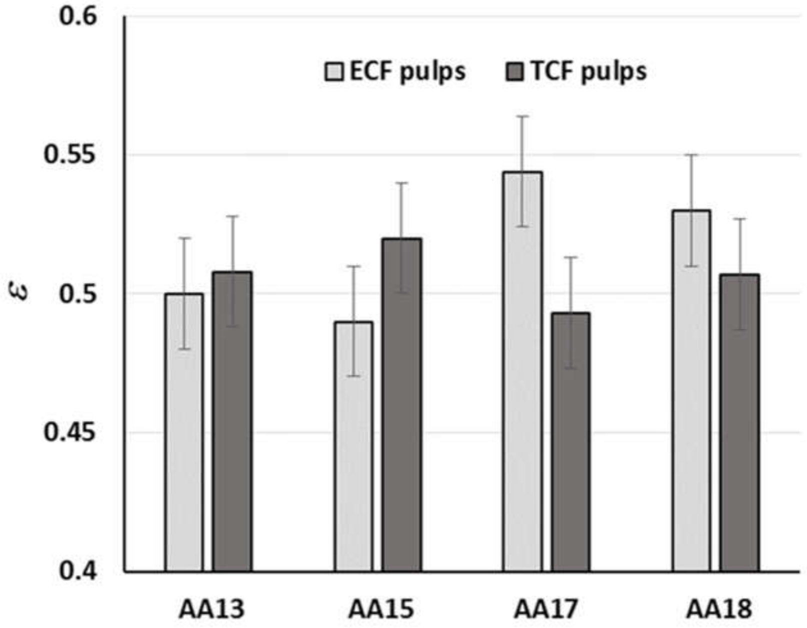


Figure 47 - The proportional compression deformation of air-laid pads (ε) made of ECF and TCF fluff pulps cooked at variable active alkali (AA) from 13 to 18%.

5.4 Modification of eucalyptus kraft pulp for fluff application

In the last chapter of this thesis, the *E. globulus* kraft pulp, supplied by a Portuguese Pulp mill operating with an ECF O/OD$_{hot}$(P$_O$)D$_1$P bleaching sequence, was subjected to a series of treatments, at a laboratory scale, aiming to modify the pulp fibres to improve their performance in fluff applications. Among the modification trials, pulp treatment with hydrolytic enzymes (xylanase and cellulase), with different debonding agents and using physical modification (forced hornification and hyperbaric treatment) have been applied. The results of these treatments were evaluated in terms of performance in water absorption and resistance of the air-laid fibre network.

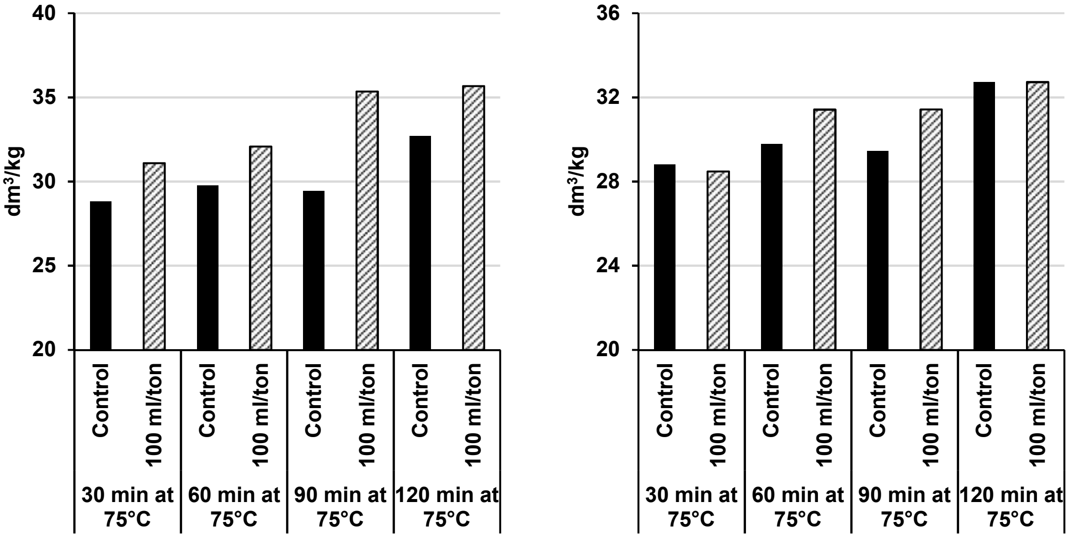
5.4.1 Enzymatic modification by xylanase and cellulase

The pulp and paper industry have been scanning for novel biotechnology methods used for the replacement of a certain part of chemicals used in the papermaking. Thus xylanase applied in the bleaching process is an environment friendly, economical innovation and can diminish the amount of bleached chemicals required to achieve high brightness values [119]. Beyond the utilization in bleaching through aiding in lignin removal, the application of xylanases additionally help in improving pulp fibrillation, decrease of beating energy and expanded freeness in reused fibres [117]. Xylanase can modify the surface of a cellulosic fibre in a targeted manner while changing the accessibility of cellulosic fibrils in the outer layer of the cell wall.

Cellulases are a series of enzymes produced by different microorganisms and have a tremendous potential application in the pulp and paper industry. Most commonly, cellulases are used to improve fibre accessibility [118]. Thus, cellulases can increase fibre flexibility and thereby improve kraft pulp properties. Moreover, cellulase action may promote handsheet density, refining energy reduction, fibre substitution due to the pulp strengthening effects and smoothness while increasing freeness and reducing coarseness [250].

Six different industrially produced enzymes from Novozymes – mono-component endo-xylanases (NS 51251 and NS 51260), mono-component endo-cellulases (NS 51239, NS 51257, NS 51259) and multi-component endo-glucanases (NS 51246) were examined in a never dried ECF bleached kraft pulp under distinct conditions of dosage and retention time. In each lab trial the pH range was constant, around pH 5,5 to 6,5, which did not affect the enzyme activity, since it fitted the activity range of all the tested enzymes. In the first approach the effect of high temperature (75°C) on the catalytic activity and binding abilities of the xylanases and cellulases enzymes were studied. Above temperature of 50°C, the catalytic activity of the enzymes has not decreased, and the binding behaviour has not been adversely affected. It was also investigated the effect of the enzyme dosage. Below the dosage of 100 ml/ton of xylanase and 100 ml/ton of cellulase no differences were found in the specific volume, absorption capacity, absorption time and network strength of the fluff pulp compared to the blank control fluff pulp (no enzymes added).

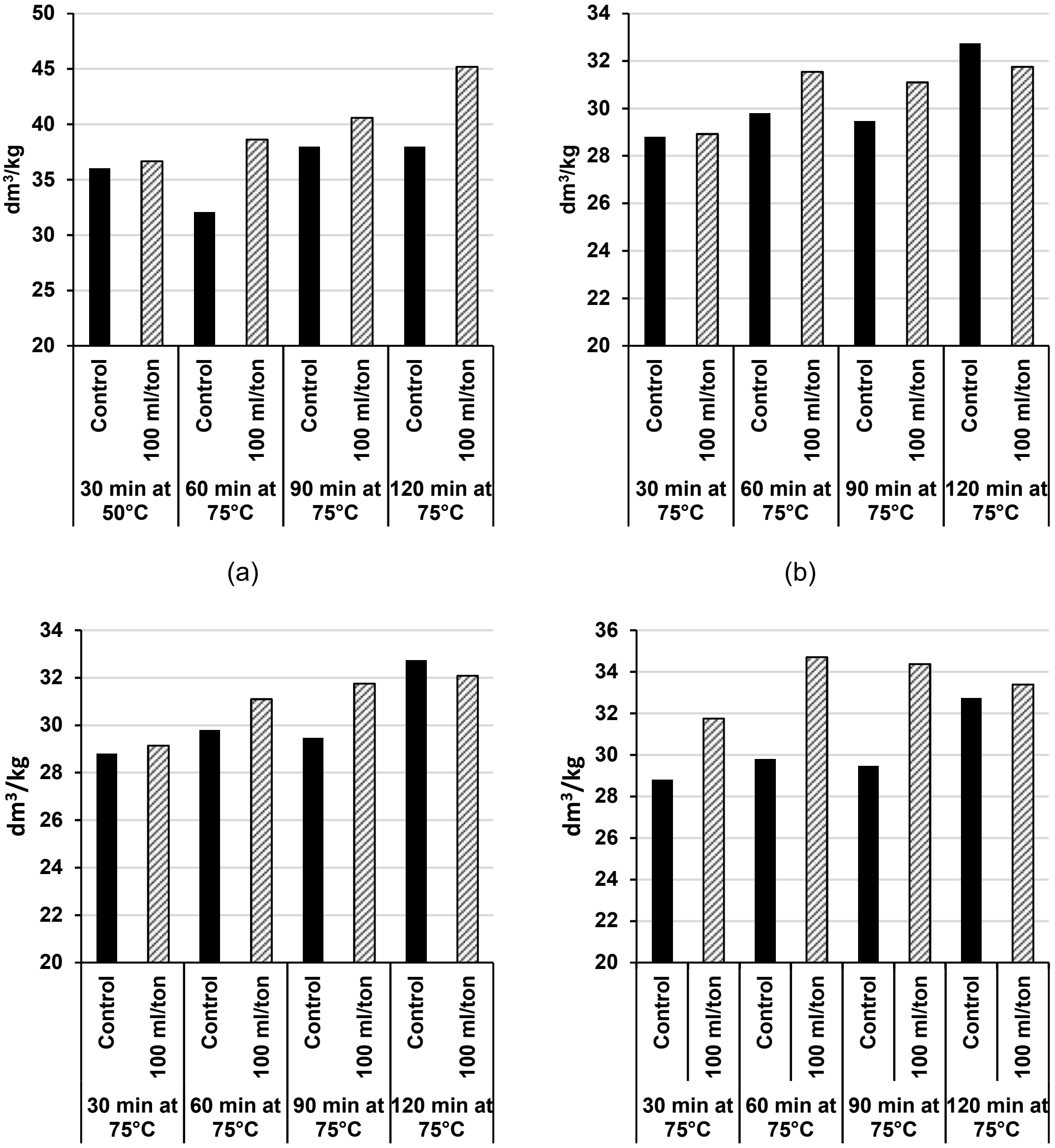
According to data in Figure 48 and Figure 49, xylanase and cellulase treatments improved the specific volume of the resulting fluff pads prepared from bleached kraft pulps. Apparently, xylanase modified the surface properties of the fibres and possibly the fines so that the interfibre bonding was reduced and the pulp shredding properties improved. The most effective way of promoting shredding properties is to reduce the density of the pulp web, i.e. to prevent the formation of hydrogen bonds between fibres [15]. The beneficial effect of cellulases and xylanases on pulp properties appears to result from a collapsing of the coarse fibre and a resulting increase in the surface smoothness [250,251]. The application of xylanase NS 51251 clearly increases the specific volume of the fluff pulp. The effect of xylanase NS 51260 was much more moderate (Figure 48). During all the lab experiments, the use of xylanase enzymes originated a bulkier, softer and smoother fluff pulp. This can be explained by some removal of xylan by the xylanase, which results in loosened fibril structures in the outer layer of the fibres and, consequently, increased porosity. As the enzyme dosage and the retention time are increased, the removal of hemicellulose increases, which favoured the defibration of final pulps. The data presented in Table 18, Table 19, Table 20 and Table 21 demonstrate that the pre-treatment of the bleached kraft pulp with xylanases caused only a slight decrease in xylose content while the amount of lignin, extractives and ash content were maintained almost unchanged. The content of xylan was decreased from 22.2% in the original pulp to around 17.1% after digestion with xylanase 51251, at a retention time of 60 minutes and an enzyme dosage of 100 ml/ton. The comparison of sugar profiles of enzymatic hydrolysates of the pulp samples pre-treated by cellulases with the profile of hydrolysate of the blank control sample, showed that the pre-treatment caused a partial xylan removal, which was reflected by the slightly decrease in xylose concentration in the hydrolysates. This reduction is more effective with the application of enzyme NS 51246 because it is a multi-component cellulolytic product, including cellulases and xylanases. However, excessive enzyme treatment may promote the eroding of the fibre surface and reducing the pulp strength. This degradation is usually more significant in the short fibres than for long fibres. Refining is least effective with the long and coarse fibres so if the pulps are fractionated into various lengths prior to enzyme treatment, the results are more satisfactory [126,252].



(a) (b)

Figure 48 - Effect of the treatment time by xylanase NS 51251 (a) and xylanase NS 51260 (b) on the specific volume of kraft fluff pulp.

The application of xylanase and cellulase promotes clearly the bulk and softness of the fluff pulp. Furthermore, the shredding properties are substantially improved while maintaining the density level, decreasing the knot content and without deteriorating significantly the absorbency of obtained fluff pulps (Figure 50 and Figure 51).



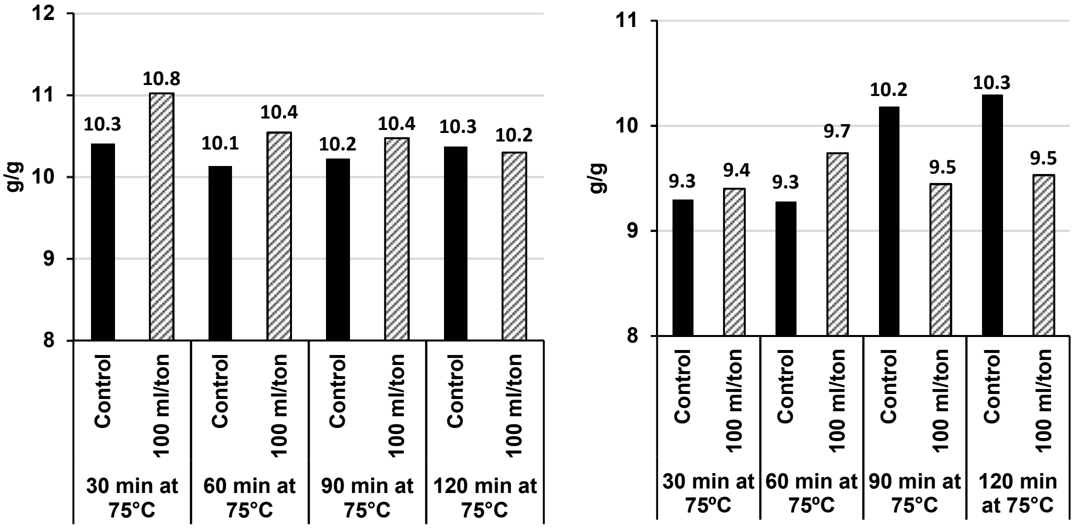
(a) (b)

(c) (d)

Figure 49 - Effect of the treatment time by cellulases NS 51239 (a), NS 51246 (b), NS 51257 (c) and NS 51259 (d) on the specific volume of fluff pulps

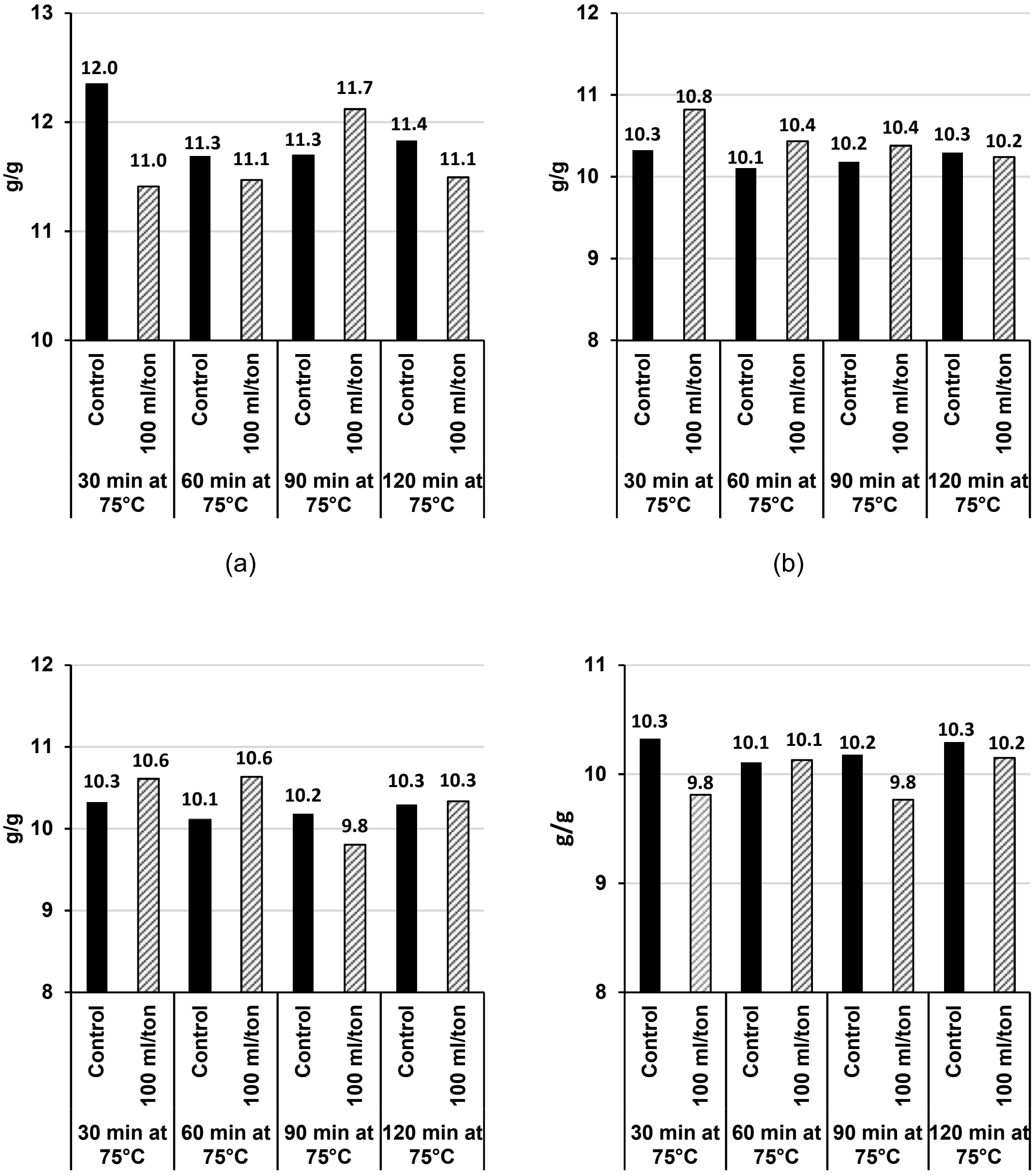
Xylans are amorphous by nature with greater affinity to water than the crystalline cellulose microfibrils. Therefore, xylan can slow down the water flow by capillarity within the paper matrix. Consequently, xylans impair pulp drainability significantly, a result attributable to xylans high water retention capacity. The pulp water retention capacity by capillary soaking increased with reducing xylan content due to increased water penetration by capillarity forces [253]. Figure 50 and Figure 51 illustrate that xylanase slightly promoted the absorption capacity at a retention time of 30 min and 60 min. After that period the absorption capacity is negatively affected by xylanase treatment, probably due to excessive xylan removal. In wet pulp processing, when chemical and mechanical refining are increased, the pulp water absorption capacity decreases significantly, and the effect of xylan content becomes less significant [254,255]. Hence, it is crucial a well optimized dosage/time of the xylanase stage.

The absorption time of the fluff pulp was not affected by the enzymatic treatment demonstrating no improvements were registered with the application of commercial xylanases and cellulases. In the best trials, the gains in absorption capacity of air-laid formulations did not exceed 3-5% affecting certainly the yield of the final fluff pulps (estimated yield loss of 2-5%).



(a) (b)

Figure 50 - Absorption capacity of the fluff pulps treated by xylanase NS 51251 (a) and NS 51260 (b) at different retention times.



(a) (b)

(c) (d)

Figure 51 - Absorption capacity of the fluff pulps pre-treated by cellulases NS 51239 (a), NS 51246 (b), NS 51257 (c) and NS 51259 at different retention time.

Table 18 - The effect of enzymatic pre-treatment on sugar profile of enzymatic pulp hydrolysates, extractives content and ash content.*

RETENTION TIME 30 min	Glucose (%)	Xylose (%)	Galactose (%)	Arabinose (%)	Extractives content (%) (± 0.01)	Ash content (%)
Control	78.8	22.2	< 0.5	< 0.5	0.07	0.48
Cellulase 50 ml/ton						
51239	78.0	22.0	< 0.5	< 0.5	0.09	0.43
51246	79.1	20.4	< 0.5	< 0.5	0.09	0.52
51257	78.0	21.9	< 0.5	< 0.5	0.08	0.50
51259	77.8	22.0	< 0.5	< 0.5	0.06	0.44
Xylanase 50 ml/ton						
51251	80.9	18.9	< 0.5	< 0.5	0.09	0.41
51260	79.7	20.0	< 0.5	< 0.5	0.07	0.50

* Xylanase and cellulase dosage of 50 ml/ton at 75°C and 30 min retention time. The relative error in sugars analysis not exceeded of 3%.

Table 19 - The effect of enzymatic pre-treatment on sugar profile of enzymatic pulp hydrolysates, extractives content and ash content.*

RETENTION TIME 30 min	Glucose (%)	Xylose (%)	Galactose (%)	Arabinose (%)	Extractives content (%) (± 0.01)	Ash content (%)
Control	77.7	22.2	< 0.5	< 0.5	0.07	0.48
Cellulase 100ml/ton						
51239	78.2	21.5	< 0.5	< 0.5	0.08	0.51
51246	80.2	19.5	< 0.5	< 0.5	0.08	0.50
51257	78.3	21.5	< 0.5	< 0.5	0.09	0.52
51259	78.0	21.7	< 0.5	< 0.5	0.06	0.48
Xylanase 100 ml/ton						
51251	82.0	17.6	< 0.5	< 0.5	0.07	0.48
51260	80.0	19.7	< 0.5	< 0.5	0.07	0.53

* Xylanase and cellulase dosage of 100 ml/ton at 75°C and 30 min retention time. The relative error in sugars analysis not exceeded of 3%.

Table 20 - The effect of enzymatic pre-treatment on sugar profile of enzymatic pulp hydrolysates, extractives content and ash content.*

RETENTION TIME 60 min	**Glucose (%)**	**Xylose (%)**	**Galactose (%)**	**Arabinose (%)**	**Extractives content (%)**	**Ash content (%)**
Control	77.7	22.2	< 0.5	< 0.5	0.08	0.45
Cellulase 50 ml/ton						
51239	78.0	22.0	< 0.5	< 0.5	0.06	0.50
51246	77.9	21.8	< 0.5	< 0.5	0.07	0.52
51257	77.7	22.0	< 0.5	< 0.5	0.09	0.49
51259	78.0	21.9	< 0.5	< 0.5	0.08	0.48
Xylanase 50 ml/ton						
51251	79.8	19.9	< 0.5	< 0.5	0.06	0.44
51260	79.8	20.0	< 0.5	< 0.5	0.08	0.52

* Xylanase and cellulase dosage of 50 ml/ton at 75ºC and 60 min retention time. The relative error in sugars analysis not exceeded of 3%.

Table 21 - The effect of enzymatic pre-treatment on sugar profile of enzymatic pulp hydrolysates, extractives content and ash content. *

RETENTION TIME 60 min	**Glucose (%)**	**Xylose (%)**	**Galactose (%)**	**Arabinose (%)**	**Extractives content (%)**	**Ash content (%)**
Control	77.7	22.2	< 0.5	< 0.5	0.08	0,45
Cellulase 100ml/ton						
51239	78.2	21.5	< 0.5	< 0.5	0.09	0.44
51246	80.2	19.5	< 0.5	< 0.5	0.07	0.50
51257	78.2	21.4	< 0.5	< 0.5	0.07	0.51
51259	78.0	21.7	< 0.5	< 0.5	0.08	0.52
Xylanase 100 ml/ton						
51251	82.6	17.1	< 0.5	< 0.5	0.06	0.48
51260	80.0	19.7	< 0.5	< 0.5	0.06	0.42

* Xylanase and cellulase dosage of 100 ml/ton at 75°C and 60 min retention time. The relative error in sugars analysis not exceeded of 3%.

The structural characteristics of the fibre also influence the determination of the specific volume. Stiffer fibres contribute to the collapse with the increase in specific volume of the pulp because they are less able to form a conformable structure. In order to evaluate the effect of enzymatic pre-treatment in the fibre structure, the fibre morphology was also evaluated. According to Table 22 the length of fibres is slightly straighten when the pulp was pre-treated with xylanases while neither the diameter of fibres nor fines content were significantly affected. The mean fibre arithmetic length and fibre coarseness were therefore somewhat greater for the enzymatically treated pulp, which should contribute to improve fluff pulp properties. It could be proposed that the xylanase and cellulase pre-treatments resulted in higher surface porosity and peeling of fibres thus contributing to their accessibility and flexibility. As shown in Table 22, the fines content slightly decreased with enzymatic pre-treatment. Since fines had much higher specific surfaces than fibres, they are easier hydrolysable being partially disappeared.

Table 22 - The effect of the enzymatic pre-treatment on fibres morphology.*

Sample	**Mean weighted fibre length (mm)** (± 0.003)	**Mean fibre width (μm)** (± 0.1)	**Coarseness (μg/m)** (± 0.5)	**Curl index (%)** (± 0.1)	**Mean kink angle (°)** (± 0.2)	**No. of kinks per fibre** (± 0.02)	**Mean kink index (%)** (± 0.05)	**Mean fines (%)** (± 0.2)
Ret. time 30 min								
Control	**0.700**	**17.4**	**77.5**	**8.94**	**51.5**	**0.583**	**1.952**	**16.9**
Cellulase								
51239	0.702	17.4	78.0	8.84	51.8	0.612	2.064	16.5
51246	0.704	17.5	78.9	8.84	51.7	0.611	2.052	16.4
51257	0.703	17.4	79.1	8.89	51.9	0.613	2.055	16.5
51259	0.701	17.4	78.3	8.81	51.8	0.610	2.061	16.3
Xylanase								
51251	0.702	17.2	78.0	8.83	52.2	0.673	2.260	16.6
51260	0.704	17.5	78.9	8.92	52.1	0.663	2.224	16.4
Ret. time 60 min								
Control	**0.696**	**17.5**	**78.3**	**8.91**	**51.6**	**0.600**	**2.013**	**16.2**
Cellulase								
51239	0.698	17.4	79.0	8.88	52.7	0.655	2.200	16.9
51246	0.700	17.5	79.2	8.87	52.3	0.653	2.197	16.6
51257	0.697	17.3	79.1	8.85	52.5	0.654	2.198	16.7
51259	0.698	17.3	79.0	8.86	52.4	0.653	2.196	16.6
Xylanase								
51251	0.699	17.2	79.9	8.80	52.2	0.687	2.307	16.2
51260	0.704	17.5	79.6	8.91	52.1	0.663	2.224	16.7

* The enzyme dosage was 100 ml/ton. The pre-treatment was carried out at 75°C for 30 min and 60 min.

It was reported that xylanase treatment softened and loosened the fibre structure, which could reduce the fibre cutting in the wet defibration process [255,256]. The peeling of the fibre surface layer was also observed by other researchers who used a xylanase treatment for bleaching eucalyptus kraft pulp [257]. Regarding the dry defibration, it can be proposed that the partial removal of the xylan from fibre surface decreases their conformability due to the enhanced collapse of the outer cell wall layers (hornification). In this case, the fibres are less bonded and easier dry-defibrated. The less conformable fibres form also more rigid fibre network.

Regarding the fibre network strength in air-laid formulations, the enzymatic pre-treatment by xylanase significantly improved to 20-50% the network strength of fluffed pulps (Table 23). This fact was assigned to the changes in the physical structure of the fibres dealing with rearrangement of fibrils and their enhanced aggregation upon drying. As it was previously shown, the moderate hornification of pulp fibres favours the network strength properties. However, the fluff pads with cellulase enzyme didn't break during the lab trials and, after several experiments, the behaviour of the fluff pad was quite different compared to the control sample and the pulps pre-treated with xylanase. This can be explained by noticeable decrease in burst resistance for all cellulase-treated pulps, probably due to fibre fibrillation and loosening of intrinsic fibre strength [258].

Table 23 - The effect of enzymatic pre-treatment on the fibre network strength.

Enzyme dosage 100 ml/ton	**Network strength (N)**	
	30 min	60 min
Control	10.8	10.1
Cellulase		
51239	(*)	(*)
51246	7.8	(*)
51257	(*)	(*)
51259	(*)	(*)
Xylanase		
51251	12.9	14.5
51260	13.8	15.0

(*) No clearly defined rupture of the pads has been registered. The enzymatic charge was 100 ml/ton at a temperature of 75°C.

5.4.2 Treatment with surface debonders

The commercial surfactant/debonders added to the never-dried bleached pulp are cationic/non-ionic proprietary blend, based on vegetable and synthetic raw materials. All the commercial fluff pulp debonders used in this study are conform to FDA requirements for aqueous and fatty food contact (specifically under 21 CFR 176.170) as well as for dry food contact (21 CFR 176.180) [259]. Commercial surfactant debonder SD1, used in this study, is commonly industrially applied in absorbent cellulosic pulps and acts as a debonder and softener, without compromising water absorption, while SD2 is a commercial debonder agent and promotes also the absorption capacity of pulps due to its lower cationic content. Additionally, SD1 and SD2 additives are VOC-free (measured by EPA Method 24) and non-corrosive to equipment.

Two commercial surfactant debonders SD1 and SD2 were applied in never-dried bleached eucalypt kraft pulp, at different loads, constant temperature (75 °C ± 2°C) and retention time (60 min ± 5min). According to data in Table 24, the surfactants didn't affect noticeably most of the measured pulp parameters. Nevertheless, the chemical oxygen demand increased around 45% to 142% with the addition of the surfactants, which means that the sorption of the surfactants into the fibres was just partial. It was also found that upload of commercial surfactants increased in proportion to the applied charge. Therefore, an increase in SD1 charge (from 1 kg/tpsa to 2.5 kg/tpsa) showed an increase in COD only twice, while an increase in the charge of the same surfactant four and a half times (from 1 kg/tpsa to 4.0 kg/tpsa) showed an increase of COD only 2.2, times. Consequently, a sorption of SD1 on the surface of the fibres took place, which reaches a value of approximately 50% at a load of 4.0 kg/tpsa. Simultaneously, and following the same considerations, the SD2 surfactant did not show high absorption capacity during the lab trials, reaching a maximum of 5% at the SD2 charge of 4.0 kg/tpsa (Figure 52 (a)). Hence, the application of SD2 at a high load becomes practically impossible.

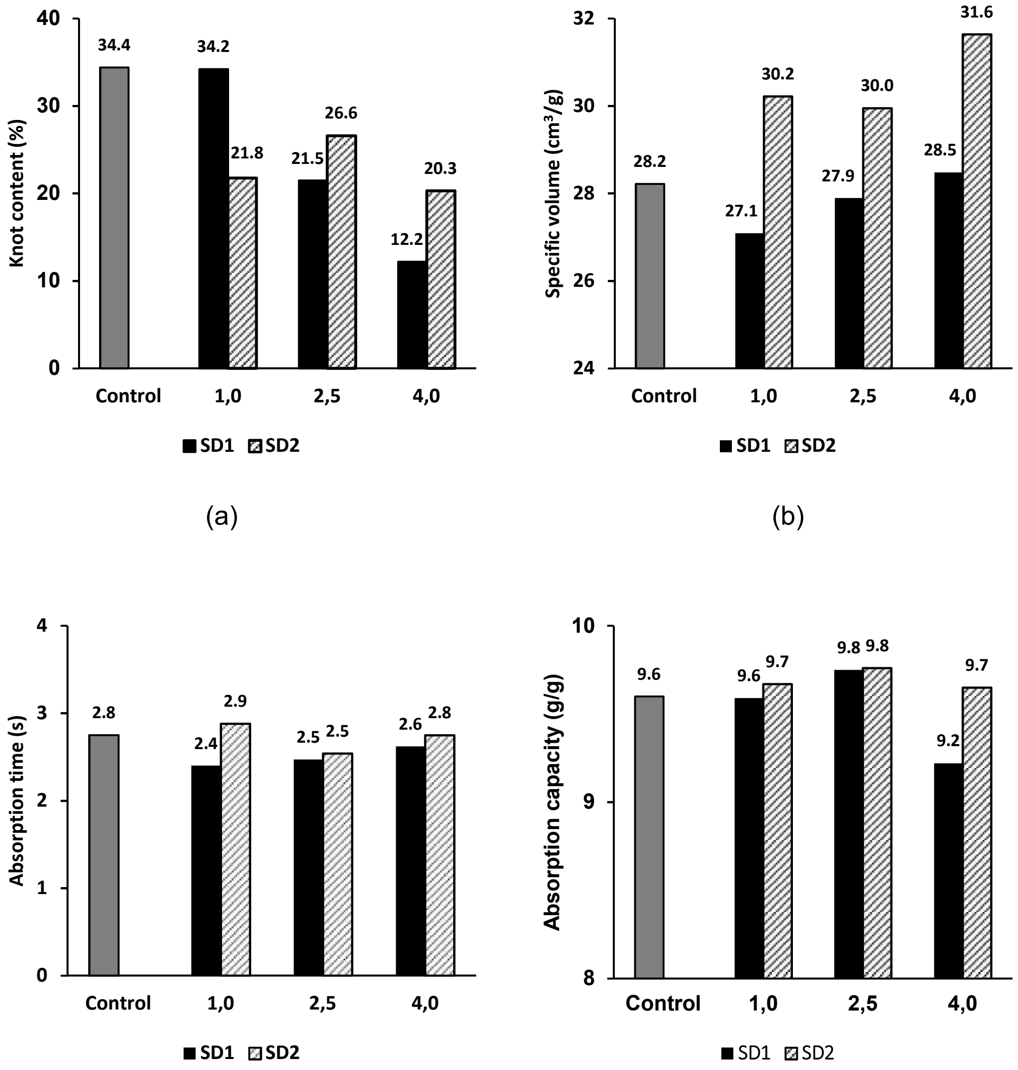
Furthermore, the increase of COD in filtrates is natural considering that surfactants are as an organic matter among the most widely disseminated xenobiotics that may enter in waste streams and in the aquatic environment. They are responsible to cause foams in rivers and effluent treatment plants and to reduce the quality of water [260]. It is a disadvantage the application of high dosages of surfactants in the pulps because it will require several removal operations in the wastewater treatment plant. Additionally, the presence of surfactants in wastewaters treatment by biological processes, such as activated sludge, is problematic due to the low kinetics of degradation and foam production. The coagulation-precipitation process may be an efficient alternative for the treatment of industrial wastewaters with high surfactant content, especially in terms of organic matter and surfactant removals [261,262].

Table 24 - Results on pH, conductivity and chemical oxygen demand (COD) measured in the pulp filtrates and results on kappa number, carboxylic acids, viscosity and brightness measured in pulps after the introduction of the commercial debonders SD1 and SD2.

	Dosage kg/tpsa	pH	Conductivity µS/cm	COD mgO$_2$/l	Kappa	COOH meq/g	Viscosity dm^3/kg	Brightness % ISO
Control	-	8.3	85.2	834	2.3	9.7	921	91.1
SD1	1.0	8.0	87.6	1028	2.3	11.1	915	91.2
	2.5	7.9	91.1	1205	2.7	9.5	905	91.1
	4.0	8.1	93.3	1225	2.7	9.6	918	91.2
SD2	1.0	8.3	84.3	1123	2.3	10.7	939	91.3
	2.5	7.8	93.8	1670	2.3	10.3	933	91.3
	4.0	8.1	86.6	2025	2.3	9.1	905	91.2

Figure 52 illustrates the results of the knot content, specific volume, absorption time and absorption capacity measured in the bleached pulps after dry-defibration in the hammermill. According to the results (Figure 52 (a)), it is clear that the wet end debonders SD1 and SD2 allow the lowing of energy consumption and the reduction in knot during defibration of kraft pulp in the hammermill, while the water absorbency rate and the absorption capacity of the treated fluff is maintained at a high level. The results confirm that the surface-active agents, present in the surfactants, change the interactions on the interface even being applied in low concentrations. The surfactant SD1 was much more efficient debonding agent to decrease the knots content in pulp compared to SD2. This may be explained, at least partially, for better fixation of SD1 in the pulps than SD2 due to the higher content of quaternary ammonium moieties in the former. Moreover, modified pulps with surfactants require less dry defibration energy, which is a significant advantage. Regarding the specific volume it was not noticed any positive or negative impact with the use of SD1. However, the surfactant SD2 slightly improved the specific volume of the fluff pulp in the air-laid formulations (Figure 52). It is well known that the adsorption of cationic compounds on cellulosic fibres totally changed their surface chemistry. This adsorption on a cellulose surface goes through complex mechanisms that are not yet clearly understood. Generally, the adsorption of different non-ionic surfactants is described as a two-step process. The first step is diffusion of surfactant from the bulk solution to a subsurface. The second stage is transport from the subsurface to the surface and subsequent adsorption [263,264]. The increase in the specific volume of pulps modified with commercial surfactants proves the improvement of pulp's porosity and bulk. It is clear that although SD1 was more effective in promoting pulp defibration (Figure 52) the addition of SD2 in pulps showed better specific volume results compared to pulps modified with SD1. However, without significant effect on the absorptivity of pulps.

According to the results (Figure 52 (c), Figure 52 (d)), it was found that commercial surfactants have slightly improved the absorption capacities of pulps only to a small extent. However, increasing the charge of surfactants does not necessarily causes a proportional increase in the absorption capacity. In fact, the highest absorption capacity was achieved with a charge of 2.5 kg/tpsa of surfactant.



(a) (b)

(c) (d)

Figure 52 - Results on the knot content (a), specific volume, (b) absorption time (c) and absorption capacity (d) of fluff pulps measured with the control and modified pulps with surfactants SD1 and SD2, after air dry defibration in the hammermill at 3500 rpm.

Stana-Kleinischeck et al. investigated the reactivity and electro kinetic properties of different types of regenerated cellulose fibres [265,266]. They modified the surface of the fibres by cationic surfactant. The zeta potential of fibres increases from negative to positive charge with increasing surfactant concentration [266]. Cellulose fibres are negatively charged in a neutral aqueous medium. According to Figure 53 the surfactant adsorption onto fibre surface leads to changes in cationic demand, and consequently in the specific charge density of pulp fibres. The cationic demand was determined according to SCAN-W 12:04 using a polyelectrolyte (PolyDADMAC solution, Dially Dimethyl Ammonium Chloride 1 meq^1/l) titration with a streaming current detector [267].

As illustrated in Figure 53 the surface charge of fibres changes from a negative to a positive value with an increasing amount of added surfactant SD1 and SD2. The addition of cationic surfactant causes an increase of positive surface charge in pulps. Some studies reported that the deposition of cationic surfactant on cellulose fibres is a quite fast process [268]. This behaviour confirms the results shown in Figure 52 where a small amount of surfactant SD1 and SD2 (1 kg/tpsa) changed significantly the pulp properties. Although the increasing amount of surfactant does not result in reaching the surface maximal adsorption. It is well established that the surface of cellulose fibres contains two types of functional groups, hydrophilic and hydrophobic groups [192]. Surfactant adsorption onto hydrophilic surfaces is highly cooperative and is in the form of surface aggregates, which are related to the associated solution aggregate structure. The hydrophilic groups furnish the surface negative charge and the cationic surfactant is attracted and adsorbed to such sites (mostly carboxyl and semiacetal hydroxyl groups). The addition of cationic surfactant to the suspension of cellulose fibres leads to the immediate interaction of the fibre surface with surfactant molecules. In the opposite, at the hydrophobic surface, the adsorption is in the form of a monolayer and is similar to that observed at the air-solution interface [265,268].

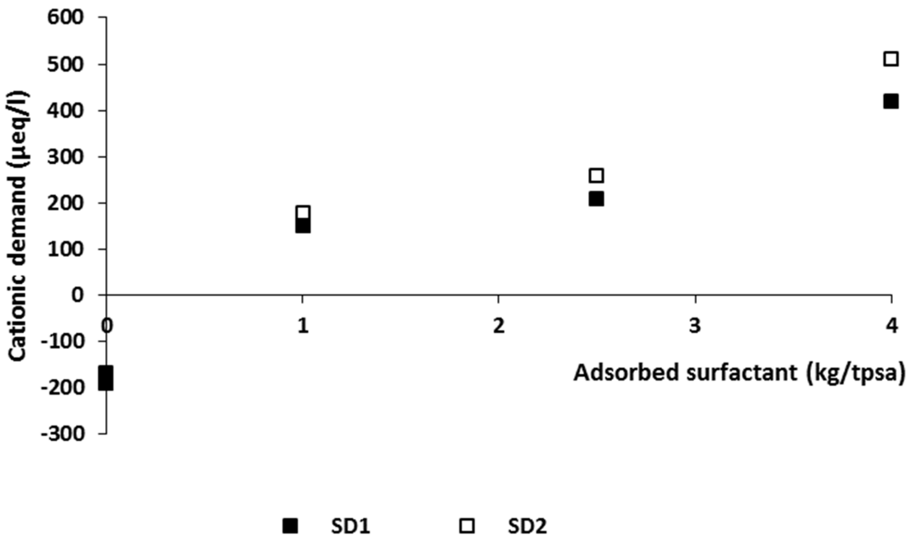
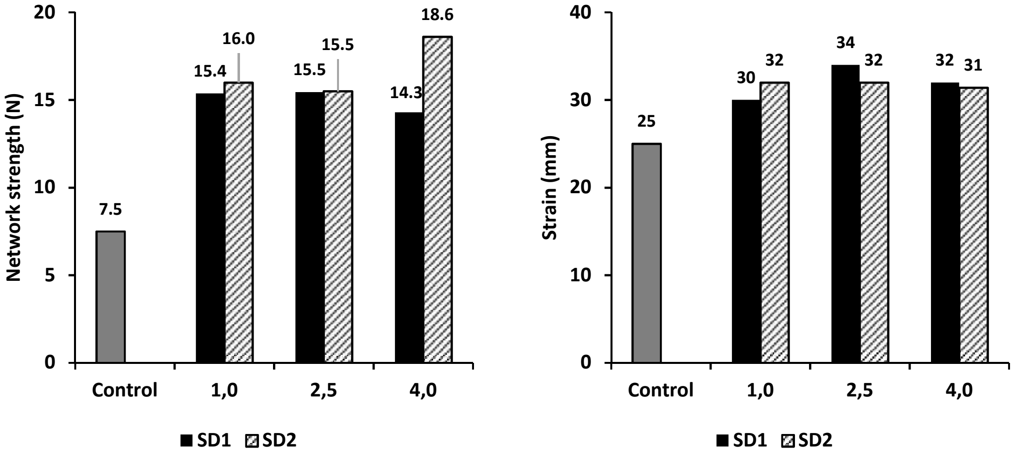


Figure 53 – Cationic demand of fibres as a function of adsorbed cationic surface-active agents SD1 and SD2.

The adsorption kinetics of anionic, cationic and non-ionic surfactants on cellulosic fibres is regulated by the first order non differential equation [192]. The surfactant molecules may be fixed on the fibre surface depending on their size, but the diffusion into the pores of the cell wall could also occur. In previous studies, Kabanov et al. suggested that cationic/non-anionic surfactants can penetrate into the porous wall of anionic cellulosic fibres [269]. The structure of the adsorbed surfactant layer and the way in which it modifies the surface properties depend on the nature of the surfactant and its interaction with the surface (whether due to electrostatic attractions, hydrogen or covalent bonding, or hydrophobic forces) [269,270]. This may explain the great increase of network strength of fluff pulps with the surfactants SD1 and SD2, as shown in Figure 54. The surfactants SD1 and SD2 are substantive to fibres, enhanced the effective debonding between the cellulosic fibres thus favouring their disaggregation and improved the network strength due to the less conformable fibres, even at low application loads. The fluff fibres added with debonding agents showed more resilient air-laid network than that composed of non-doped fibres, as follows from the greater proportional deformation (strain) of corresponding pads (Figure 54). Furthermore, the application of surfactants debonders SD1 and SD2 promoted the bulk softness and the surface softness of the fluff pulps. Bulk softness relates to how easily the paper product flexes, crumples, or otherwise yields to even delicate counterforces while surface softness consists to how smooth or with how much lubricity the paper product can be slid against another surface [135]. The surfactants act simultaneously as a debonder agent and a softening agent that interferes with the natural fibre-to-fibre bonding that occurs during sheet formation in papermaking processes. This reduction of bonding leads to a softer and bulkier sheet of paper.



(a) (b)

Figure 54 - Results on the network strength (a) and strain (b) of air-laid pads produced from fluffed pulp without (control) and with application of debonding agents SD1 and SD2. Dry defibration was carried out in a hammermill at 3500 rpm.

Table 25 and Table 26 show the fibre morphology of the control pulp and the pulps modified with surfactants SD1 and SD2 before and after dry defibration, using the pilot-scale hammermill operated at 3500 rpm. It was not found any significant impact of the debonding agents on the fluffed pulp fibre morphology though some inexplicable fluctuations in coarseness have been registered.

The effect of surfactants/debonding agents on the absorption capacity of fluff pulp with respect to the fibre coarseness is quite controversial (Figure 55). Thus, the increase in load of surfactants does not increase the fibre coarseness, but on the contrary, it decreases though within experimental error. The absorptivity varies almost within the limit of determination error and showed a minimum value with the maximum charge of surfactant SD1 (4.0 kg / tpsa). It is reported that this minimum of absorptivity corresponds to the maximum absorption of this product suggested internally through COD analysis (Table 24). It is possible that the excessive sorption of the surfactant SD1 decreases the hydrophilicity of the fibres and caused a decrease in absorptivity due to less capillary pressure in the pores of the pad. This result is not according to expectations, since the increase in specific volume usually increases the porosity and absorption of pulps [231].

Table 25 - Fibre morphology of the control pulp and pulps added with surfactant SD1, before and after dry-defibration in the hammermill at 3500 rpm.

Before dry defibration	Dosage	Lc(w) ISO	Fibre width (W)	Curl	Mean fines	Coarseness	Fibre wall thickness	No. of kinks per fibre	Mean kink index
	kg/tpsa	mm	µm	%	-	µg/m	µm	-	-
		(± 0.003)	(± 0.1)	(± 0.1)	(± 0.2)	(± 0.5)	(± 0.1)	(± 0.02)	(± 0.05)
Control	-	0.671	19.3	8.5	14.9	84	2.8	0.92	3.36
SD1	1.0	0.698	18.9	8.7	13.9	83	2.9	0.78	2.73
	2.5	0.686	19.2	8.6	14.9	84	2.9	0.84	3.01
	4.0	0.685	19.1	8.6	15.1	87	3.0	0.84	3.00
After dry defibration @ 3500 rpm	Dosage	Lc(w) ISO	Fibre width (W)	Curl	Mean fines	Coarseness	Fibre wall thickness	No. of kinks per fibre	Mean kink index
	kg/tpsa	mm	µm	%	-	µg/m	µm	-	-
Control	-	0.685	18.0	8.9	16.9	81	2.9	0.69	2.32
SD1	1.0	0.683	18.2	8.9	18.9	83	3.0	0.66	2.26
	2.5	0.679	18.1	8.9	17.0	72	2.5	0.67	2.30
	4.0	0.685	18.1	8.9	17.5	76	2.8	0.66	2.34

Table 26 - Fibre morphology of the control pulp and modified pulps with surfactant SD2, before and after dry-defibration, in the hammermill at 3500 rpm.

Before dry defibration	Dosage	Lc(w) ISO	Fibre width (W)	Curl	Mean fines	Coarseness	Fibre wall thickness	No. of kinks per fibre	Mean kink index
	kg/tpsa	mm	µm	%	-	µg/m	µm	-	-
		(± 0.003)	(± 0.1)	(± 0.1)	(± 0.2)	(± 0.5)	(± 0.1)	(± 0.02)	(± 0.05
Control	-	0.671	19.3	8.5	14.9	84	2.8	0.92	3.36
SD2	1.0	0.698	18.9	8.7	13.9	83	2.9	0.78	2.73
	2.5	0.686	19.2	8.6	14.9	84	2.9	0.84	3.01
	4.0	0.697	18.6	8.8	12.4	77	2.7	0.78	2.72
After dry defibration @ 3500 rpm	Dosage	Lc(w) ISO	Fibre width (W)	Curl	Mean fines	Coarseness	Fibre wall thickness	No. of kinks per fibre	Mean kink index
	kg/tpsa	mm	µm	%	-	µg/m	µm	-	-
Control	-	0.685	18.0	8.9	16.9	81	2.9	0.69	2.32
SD2	1.0	0.696	18.2	8.9	17.4	80	2.9	0.70	2.37
	2.5	0.676	18.0	8.9	16.3	72	2.6	0.67	2.32
	4.0	0.693	18.1	8.9	16.8	80	2.9	0.67	2.27

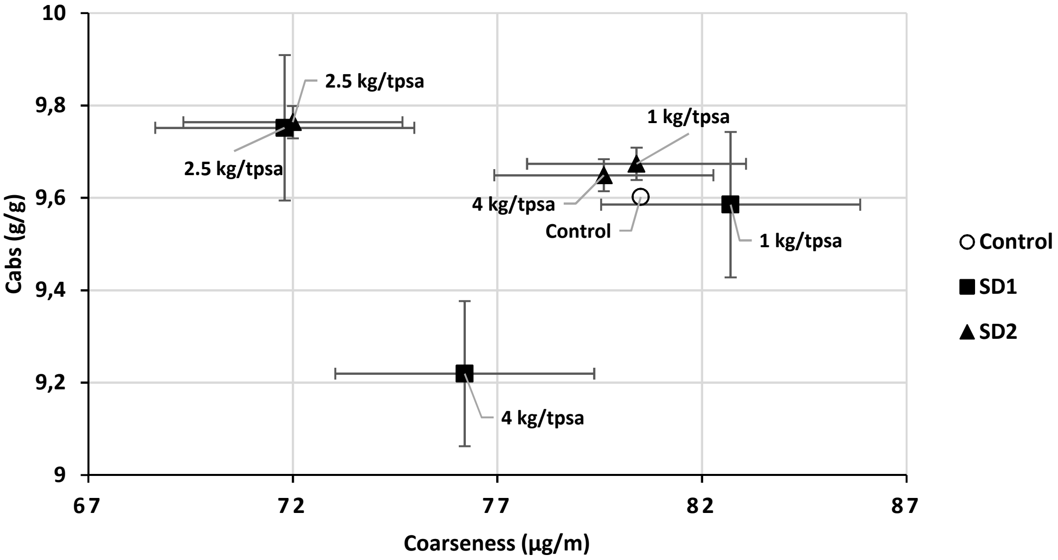


Figure 55 - Correlation between the absorption capacity (C_{abs}) of modified pulps with commercial surfactants SD1 and SD2 and fibre coarseness.

Modified pulps with debonding agent SD2 showed slightly higher specific volume than pulps modified with SD1, but also a higher knots content (Figure 52 (a)), with quite similar absorptivity values. Bearing in mind that the interaction between fibres take place due to the formation of hydrogen bonds between OH groups, this means that SD1 must bond with free OH groups more effectively than SD2. In other words, the agent with the highest positive charge was more effective. A slight increase in the specific volume of modified pulps with SD2 compared with SD1 is not related to the significant change in fibre deformations (kink and coarseness), according to Figure 56. In fact, no trendline was found between SD1 and SD2 charges and results of specific volume.

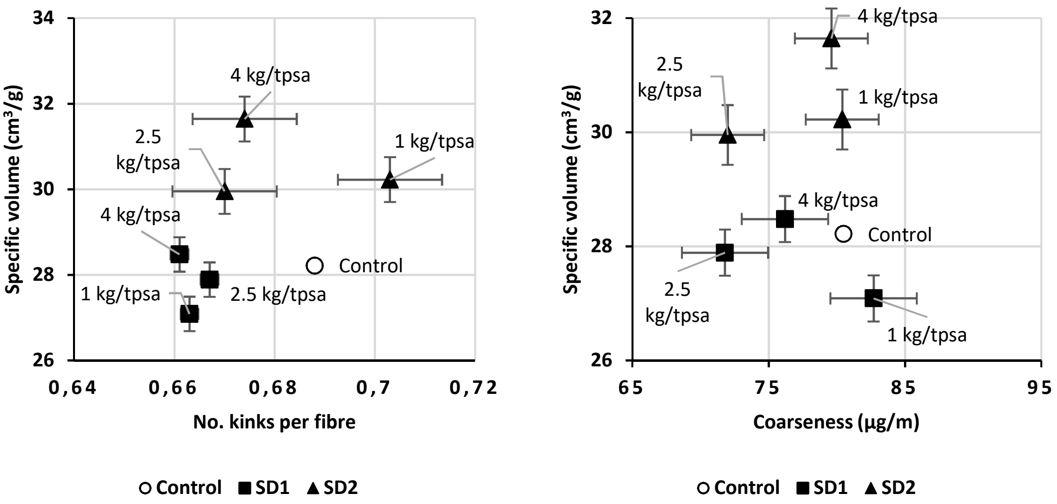


Figure 56 - Correlation between specific volumes of pads made of pulps modified with commercial debonders SD1 and SD2, and number of kinks per fibre (left figure) and coarseness (right figure).

As already mentioned, the application of the debonders SD1 and SD2 improved the absorption time of pulps compared to control pulp (Figure 57). The decrease of the absorption time (t_{abs}) is not related with fines content: in the case of both commercial debonders, it was within the margin of error. Nevertheless, the increase in the absorption velocity (decrease of the absorption time) of modified pulps with commercial debonders is positively related with the reduction of the knots content (Figure 52 (a)). In general, it may be concluded that the addition of SD1 and SD2 caused a decrease in knots content and absorption time of pulps.

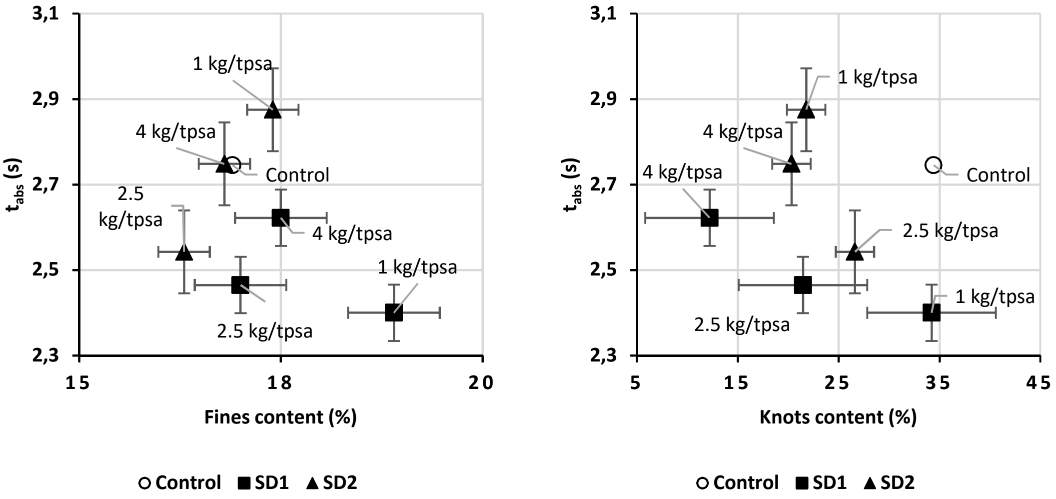


Figure 57 - Correlation between absorption time (t_{abs}) of modified pulps, with commercial surfactants SD1 and SD2, and the fines (left figure) and knots (right figure) content.

5.4.3 Modified with polyhexamethylene biguanide (PHMB)

Antimicrobial agents act by either inhibiting the growth (bacteriostatic) or killing (bactericidal) microorganisms. Examples of antimicrobial agents used in commercial textiles include silver nanoparticles, triclosan, quaternary ammonium compounds, natural polymer derivatives, synthetic polymers, among others [139,273]. Polyhexamethylene biguanide (PHMB), also known as polyhexanide and polyaminopropyl biguanide $(C_8H_{17}N_5)_n$, is a commonly used antiseptic. It is used in a variety of products including wound care dressings, contact lens cleaning solutions, perioperative cleansing products, and swimming pool cleaners. PHMB is a strong and broad-spectrum antimicrobial agent with low toxicity, which has attracted the attention for antimicrobial finishing in textile industry, mainly for the protection of cellulosic fibres, [136,274].

In this study, a commercially available polyhexamethylene biguanide (PHMB), at different dosages and conditions, were applied to a never-dried bleached kraft pulp in order to acquire antimicrobial properties and enhance fluff pulp characteristics. The pulps impregnated with PHMB showed a significant reduction of chemical oxygen demand values in relation with the increase of the PHMB dosage (Table 27). The lethal action of PHMB is an irreversible loss of essential cellular components as a direct consequence of cytoplasmatic membrane damage [273]. The death of the bacteria cell from the action of PHMB may have contributed for the reduction of the COD level. The molecular interaction between PHMB and bacterial membranes has been deduced by over laying this lethal sequence with the findings of experiments modelling the possible interactions of polymeric biguanides and membrane components - particularly phospholipids [273, 274]. Other possible explanation for the reduction of COD is the reaction between PHMB with the components of pulps, first with the carboxylic groups of xylans and oxidized cellulose, forming strong adducts [136]. PHMB is able to charge positively the surface of the fibres and adsorb some components with negatively charge.

The intrinsic viscosity of pulps slightly increased with the PHMB, as reported in Table 27. This behaviour may be interpreted of the presence of PHMB in fibres, which is a biocide polymer. Reports about molecular weight of PHMB cite determinations made by gel permeation chromatography, which results in values of weight-averaged molecular weight, $\overline{\mathrm{M}}\mathrm{w}$, around 2.400 g mol^{-1} and average degree of polymerization $\overline{\mathrm{X}} = 12$ [275]. PHMB equilibrium of polymerization/depolymerization occurs during the impregnation of pulp, with depolymerization happening by biguanide break resulting in one cyanamide chain end and one guanidine chain end. Longer chains (>40 mers) will break up into smaller chains that can undergo interchange reactions promoting the increase of intrinsic viscosity in pulps [276].

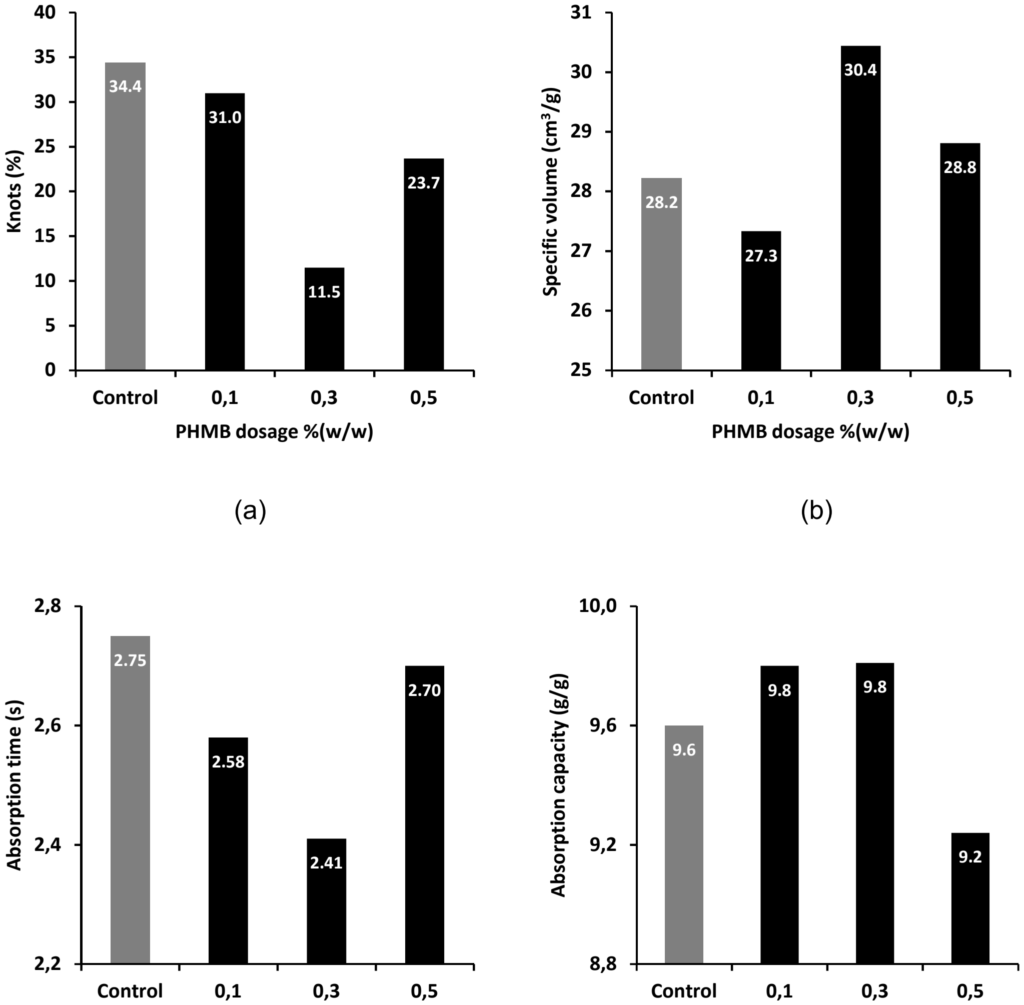
Electrical conductivity also increased with the uptake of PHMB into pulps. These results can be assigned since PHMB is a polycationic amine on which the cationic biguanide groups are interspersed between hydrophobic hexamethylene groups. Electrostatic and Van der Waals interactions occur with microbial cell membrane disruption and lethal leakage of cytoplasmic materials [278,279].

Table 27 - Results of conductivity and chemical oxygen demand (COD) measured in the filtrates of pulp and results of kappa number, carboxylic acids, intrinsic viscosity and brightness measured in pulps after the introduction of polyhexamethylene biguanide.

	Dosage % (w/w)	**Conductivity µS/cm**	**COD mgO$_2$/l**	**kappa**	**COOH meq/g**	**Viscosity dm^3/kg**	**Brightness %ISO**
Control	-	85.2	834	2.3	9.6	921	91.1
PHMB	0,1	92.6	890	2.3	10.2	994	91.1
	0,3	93.7	780	2.3	9.4	957	91.2
	0,5	93.0	540	2.3	8.9	913	90.4

All samples impregnated with PHMB revealed a loss in mechanical properties. A possible explanation is PHMB being a cationic polymer that strongly interacts with negatively charged cellulose fibres through ionic interactions and hydrogen bonding [139]. Therefore, PHMB is likely weakening the fibres network by diminishing their bonding capacity and, consequently, affecting the pulp's strength properties. This explains the low knots content with increment of PHMB uptake, namely in dosage 0.3 % (w/w), according to Figure 58 (a).

In water solutions, PHMB behaves as a low-foaming surfactant, with a critical micellar concentration near 5 x 10^{-2} mol.dm^3 in water at 20°C [276]. The small size of PHMB chains, in fact an oligomeric material, leads to a solution behaviour which is atypical when compared with heavier polymers. The alternating structure of hydrophilic-hydrophobic segments in PHMB chain indicates a potentially conformation in water solution, where the hydrophobic methylene segments points toward the centre of a sphere, and the hydrophilic, mono protonated biguanide groups point outward. PHMB binds to the negatively charged phosphate head groups of phospholipids at bacteria cell wall, causing increased rigidity, sinking non-polar segments into hydrophobic domains, disrupting the membrane with subsequent cytoplasmic shedding culminating in cell death [276,278]. It is assumed that the positively charged PHMB interacts strongly with negatively charged cellulosic fibres [139]. In the case of eucalypt kraft pulp a significant contribution to the negative charge of fibres is done by presenting xylan [136,280]. Since with increasing PHMB concentration in solution the interactions by hydrogen bonding start playing a major role in sorption mechanism, this could lead to multilayer sorption on cellulosic fibres surface. This fact may be assigned to the higher absorption capacity (Figure 58 (c)) and absorption time (Figure 58 (d)) of pulps impregnated with PHMB, compared to control pulp. Since PHMB concentration in solution affects the amount of its uptake in pulp and the debonding properties of fibres simultaneously, some compromise is necessary between the variables.



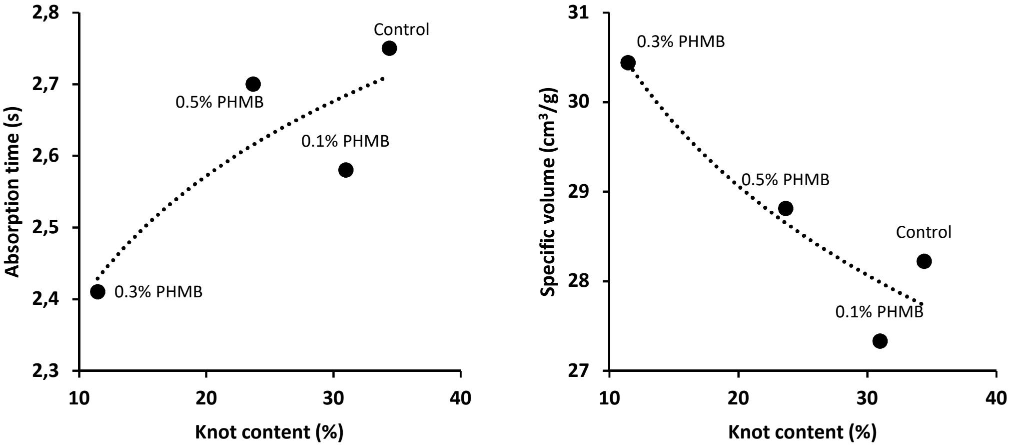
(a) (b)

(c) (d)

Figure 58 - Results on the knot content (a), specific volume, (b) absorption time (c) and absorption capacity (d) of pads made of the untreated (control) and impregnated with PHMB pulps, after dry-defibration in the hammermill at 3500 rpm.

According to the results presented in Figure 58 it may be concluded that at 0.3% (w/w) concentration of impregnation PHMB solution the knot content decreases significantly, and at the same time the specific volume and absorption capacity of fluff pulps increase. The absorption time of fluff pulp suffered a slightly decrease face to the control pulp (Figure 58 (c)).

Correlation between knot content and absorption time (Figure 59 (a)) and between knot content and specific volume (Figure 59 (b)) of pads revealed that the capillarity absorption time increased with the decrease of knots in fluff pulps, since the higher amount of fibre bundle compromises the penetration of liquids into cellulosic fibres. The structure of the absorption core is impaired by the presence of knots, becoming less porous and causing the decrease of the specific volume, as shown in Figure 59 (b).



(a) (b)

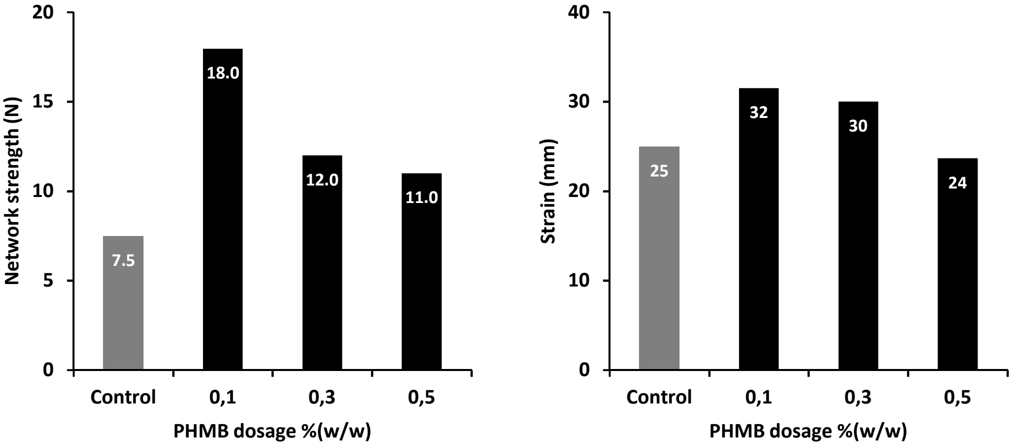
Figure 59 - Correlation between absorption time and knot content (a), between specific volume and knot content (b) of the fluff pulps modified with PHMB at different loads.

The pulps modified with PHMB exhibited less knots, a bulkier and softer structure compared to the control fluff pulp, according to results depicted in Figure 59 and visualised in Figure 60.


(a) (b) (c) (d)

Figure 60 - Fluff pulps treated with PHMB solution: (a) control fluff pulp; (b) Fluff pulp with PHMB 0.1%(w/w), c) Fluff pulp with PHMB 0.3%(w/w); d) Fluff pulp with PHMB 0.5%(w/w);

As shown in Figure 61, the application of PHMB solution improves the network strength. This may be explained from one side by the decrease in knots of PHMB-treated fluff pulps and, from other side, changes in physical properties of fibres regarding the eventual resistance of the network under moistening. PHMB reacts with carboxyl moieties of pulp thus diminishing the hydrophilicity of treated fibrils and their conformability. Finally, more resilient fibre network in air laid pads can be assumed after the treatment with PHMB as follows from greater strain under rupture (Figure 61).



(a) (b)

Figure 61 - Results on the network strength (a) and strain (b) of air-laid pads produced from fluffed pulp without (control) and after treatment with different loads of PHMB. Dry-defibration was carried out in the hammermill at 3500 rpm.

Apparently, such fibres must be less conformable also under moistening thus improving the absorption capacity (Figure 58). However, too high load of PHMB decreases both absorption and strength properties of air-laid formulations made of fluff pulps treated with PHMB (Figure 58 and Figure 61). This must deal with formation of multilayer deposition of PHMB, which change the surface properties of fibres making them too hydrophobic and deteriorating the fibre-fibre interactions due to the less intensive hydrogen bonding [136,139].

No significant changes were found in the morphology of the pulps treated with PHMB solution, as shown in Table 28. As expected, the fines content was increased during dry defibration using pilot-scale hammermill. Surprisingly, the mean kink index and curl did not increase in the dry defibration as well. The dosage of 0.5%(w/w) PHMB caused an increment in the number of kinks per fibre and the mean kink index of pulps.

Table 28 - Fibre morphology of the control pulp and impregnated pulps with PHMB solution, before and after dry-defibration, in the hammermill at 3500 rpm.

Before dry defibration	**Dosage**	**Lc(w) ISO**	**Fibre width (W)**	**Curl**	**Mean fines**	**Coarseness**	**Fibre wall thickness**	**No. of kinks per fibre**	**Mean kink index**
	% (w/w)	mm	µm	%	-	µg/m	µm	-	-
		(± 0.003)	(± 0.1)	(± 0.1)	(± 0.2)	(± 0.5)	(± 0.1)	(± 0.02)	(± 0.05)
Control	-	0.699	18.9	8.8	12.0	82	3.0	0.76	2.64
PHMB	0.1	0.701	19.0	8.8	12.9	77	2.6	0.69	2.38
	0.3	0.693	19.0	8.7	13.3	89	3.2	0.79	2.79
	0.5	0.687	19.0	8.7	13.5	77	2.6	0.81	3.31
After dry defibration @ 3500 rpm	**Dosage**	**Lc(w) ISO**	**Fibre width (W)**	**Curl**	**Mean fines**	**Coarseness**	**Fibre wall thickness**	**No. of kinks per fibre**	**Mean kink index**
	% (w/w)	mm	µm	%	-	µg/m	µm	-	-
Control	-	0.692	18.3	8.9	17.5	80	2.9	0.70	2.37
PHMB	0.1	0.696	18.4	8.9	16.6	81	2.9	0.68	2.29
	0.3	0.678	18.1	8.9	16.9	75	2.7	0.68	2.33
	0.5	0.692	18.3	8.8	16.2	82	3.0	0.74	2.51

The antimicrobial capability of pulp samples treated with different PHMB loadings were evaluated based on the NP EN ISO 20743 norm using the gram-negative *E. coli* (ATCC 25922), and gram-positive *L. innocua* (ATCC 33090) bacteria. Regarding *E. coli* it was noticeable that control samples did not hold any antimicrobial activity, as confirmed by the increase from 3.92 ± 0.11 to 7.64 ± 0.07 Log CFU/specimen, after a 24h incubation period (Table 29). Samples treated with the highest PHMB concentrations (0.3 % w/w and 0.5 % w/w) exhibited strong antimicrobial activity. This fact was evidenced by the values $\leq$ 1.00 Log CFU/specimen (below the detection limit) already on zero time (0 h).

Moreover, the same samples did not exhibit any microorganism's growth during incubation (24h). When the same analyses were carried out for *L. innocua*, the results achieved were quite similar to those of *E. coli*.

Table 29 - PHMB incubated with *E. coli* and *L. innocua*.

Load of PHMB, **% (w/w)**	**Activity *E. coli*** **Log CFU**		**Activity *L. innocua*** **Log CFU**	
	0 h	24h	0h	24h
0.0	3.92 ± 0.11	7.64 ± 0.07	7.64 ± 0.07	7.64 ± 0.07
0.1	≤ 1.00	1.37±0.29	≤ 1.00	≤ 1.00
0.3	≤ 1.00	≤ 1.00	≤ 1.00	≤ 1.00
0.5	≤ 1.00	≤ 1.00	≤ 1.00	≤ 1.00

Detection limit is 1,00 (Log CFU/specimen)

The results of this study confirmed that PHMB cationic moieties allows it to interact with cellulose, not only through hydrogen bonding, but also through ionic interactions [136,139]. Therefore, positively charged PHMB can bind to cellulose fibrils possessing a negative charge [137,139,279]. As mentioned before, besides promoting a higher antimicrobial activity, increased polymer length also provides more cationic sites, for stronger binding with cellulose, improving debonding properties and absorption characteristics in fluff pulp.

5.4.4 Hornification of pulp

The hornification is understood as a process of changes in physical structure of cellulosic fibres under drying and was introduced for the first time by Jayme in 1944 [142]. Hornification consists in aggregation of cellulose fibrils in the fibre cell wall leading to the changes in cellulose supramolecular structure and resulting in drastic collapse of the fibre surface. Among the observed hornification consequences are the reduction in strength properties and water retention ability, the increase in drainability, bulk, opacity, deterioration in flexibility and conformability of fibres [280]. This phenomenon plays a strong negative role in papermaking, but it can be advantageous to some extent in fluff materials [111,281]. As was discussed previously, some physical changes in fibre structure could be advantageous regarding the dry defibration and the fibre network structure of air-laid formulations.

In this study, never-dried bleached kraft pulp was submitted to oven-drying at a temperature of 140°C ± 5°C under contact mode (between two metal wires) for 120 min. Simultaneously, a sample of paper-grade BEKP was collected in the pulp line (at the airborne pulp drying machine) in order to evaluate the impact of the industrial drying and pressing on the cellulosic fibres.

Table 30 summarizes the parameters evaluated in the control (never dried) and hornified pulps. The laboratory-hornified pulp shows small decrease in the amount of carboxylic groups and intrinsic viscosity. This decrease in carboxyls was observed essentially in the laboratory-hornified pulp and to much less extent in the industrially dried paper-grade pulp, as shown in Table 30. Apparently, some labile carboxyl-containing structures were degraded under drying at 140 ºC and some cellulosic chains were cleaved. Carboxyl moieties promote the hornification while presenting in their hydrogen form (no contra cations) [282,283]. The high temperature in the drying process usually promotes hornification, but also promotes a drop in carboxylic acid content in pulps [284]. The increase of the carboxylic acid groups in the paper grade industrially dried pulp (Table 30) is due to the eventual oxidation of the aldehyde groups of cellulose or just a fluctuation of the pulp composition in the pulp line.

There are many factors that influence hornification during pulp drying, including pressing, drying temperature and the chemical environment (type of the contra cations, amount of carboxylic groups, etc.). It has been accepted that hornification is largely due to the formation of irreversible hydrogen bonds when water is removed from wood pulp or paper [285]. Increasing hydrogen bonding is proposed to be possible due to the collapse of pores or tighter packing of cellulose chains during the water removal. Also, other mechanisms of hornification are suggested such as closure of capillaries [286]. For instance, Diniz et al. (2004) strongly believed that hornification couldn't be explained by hydrogen bonding only since these bonds are broken by water. They proposed a theory that covalent lactone bridges are responsible for hornification [144]. It was explained that when water is removed, carboxylic acid groups are interacting with hydroxyl groups and form covalent lactone bridges.

The degree of hornification is greatly related to the accessibility of the hydroxyl groups in cellulose and can be assessed by the water retention capacity of the pulp. Figure 62 shows the water retention value (WRV) and the hornification degree of the hornified pulps. WRV is useful for evaluating the performance of pulps in dewatering on a paper machine and some paper applications. It also provides a relative indication of the swelling capability of the pulps, which is related to pore volume and pore structure of the fibre. WRV describes the amount of water that stays in the pulp after centrifugal forces have been applied [287]. The greater the amount of retained water, the more accessible hydroxyl groups are in the cellulose and the less the pulp is hornified. According to Figure 62, laboratorial hornified pulp revealed the higher hornification degree (24.8%) compared to the paper-grade pulp (21.4%), which indicates that laboratorial hornified pulps have less accessible hydroxyl groups. These results may be interpreted for the forced drying process, which influences the supramolecular arrangement of cellulose. Although it does not alter so much the degree of the crystallinity or crystalline structure, it does influence the size of microfibril bundles, and subsequently the accessibility of cellulose. Irreversible microfibril aggregation upon drying is widely believed to be the underlying reason behind the reduced accessibility of chemical pulps [248,288]. The drop in the brightness of pulps after hornification is due to the heat-induced aging process during the drying treatment [289]. It is clearly that the laboratorial hornification had a particular negative impact in the brightness. Still, these brightness values are perfectly acceptable for fluff pulps.

Table 30 - Results of kappa number, carboxylic acids, intrinsic viscosity, brightness index, brightness reversion measured in the filtrates and hornified pulps.

	Kappa ±0.1 unit	**COOH ±0.3 meq/g**	**Viscosity dm^3/kg**	**Brightness %ISO**	**Brightness Reversion %ISO**
Control	2.3	9.5	932	91.1	-
Laboratory hornified pulp	2.1	8.3	888	89.6	1.54
Industrially dried pulp	2.2	11.0	918	90.0	1.10

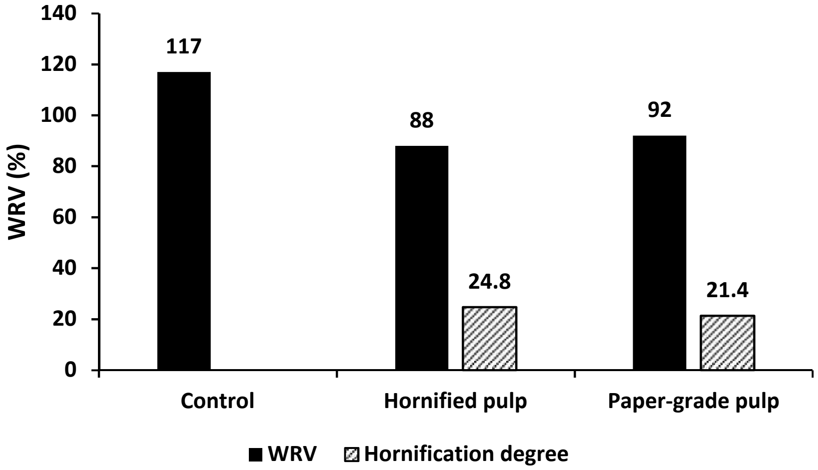
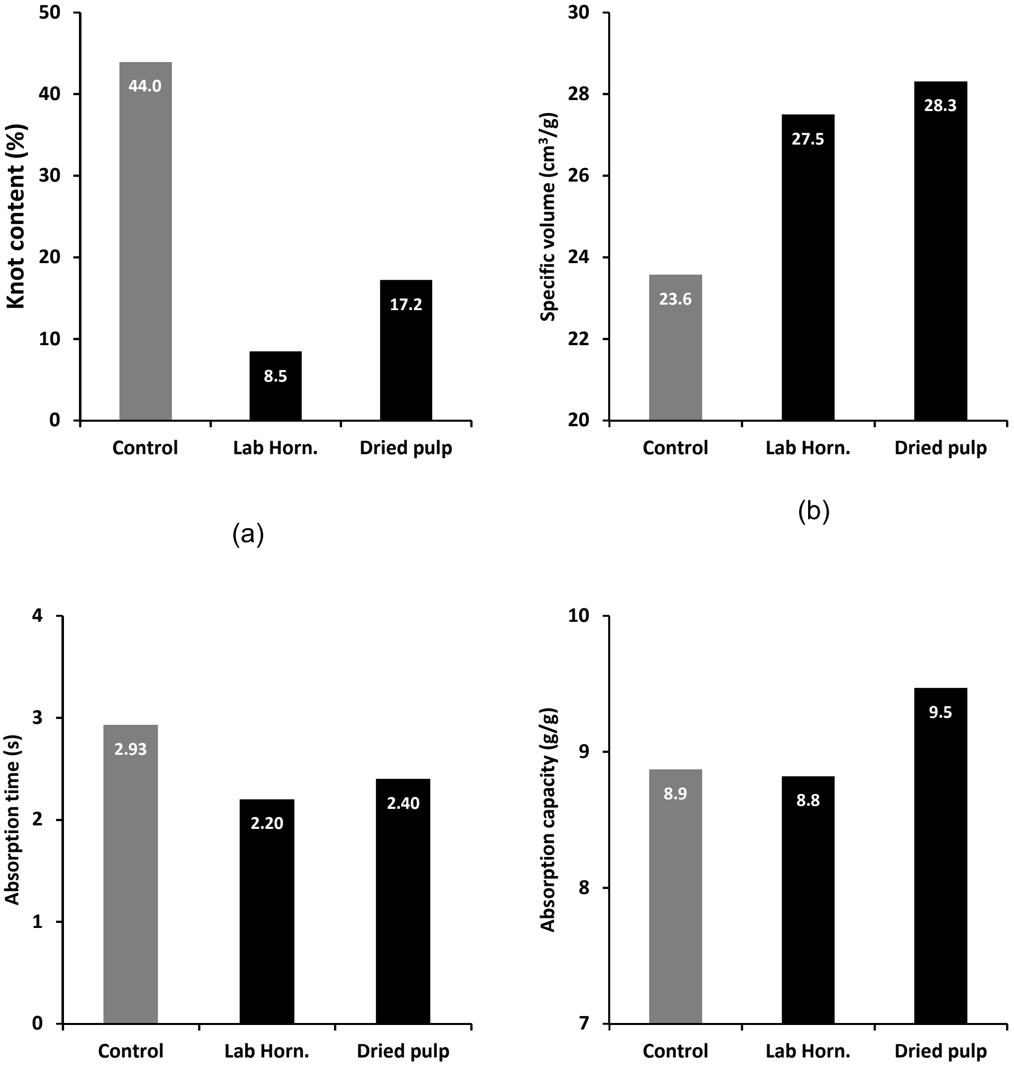


Figure 62 - Results of the water retention value (WRV) and hornification degree of the control pulp and hornified pulps.

The effect of forced hornification on the dry defibration revealed a significant decrease in the knots (Figure 63 (a)). The reduction in the fibre bonding upon hornification might be the primary reason for the decrease in knot contents after dry defibration. Regarding the reduction of knots content, it should be noted that hornification treatment was even more effective than the treatment with surfactant debonders. The results presented in Table 31 confirm that the hornified fibres were more curled and had higher values of kink index and number of kinks per fibre than the never-dried pulp (control pulp). The increase in coarseness after hornification is explained by some shrinkage of fibres under intensive drying [285,290,291]. As could expected, specific



(a) (b)

(c) (d)

Figure 63 - Results on the knot content (a), specific volume (b), absorption time (c) and absorption capacity (d) of the control fluff pulp, laboratorial hornified fluff pulp and ECF paper-grade fluff pulp, after dry-defibration in a pilot scale hammermill, at 3500 rpm.

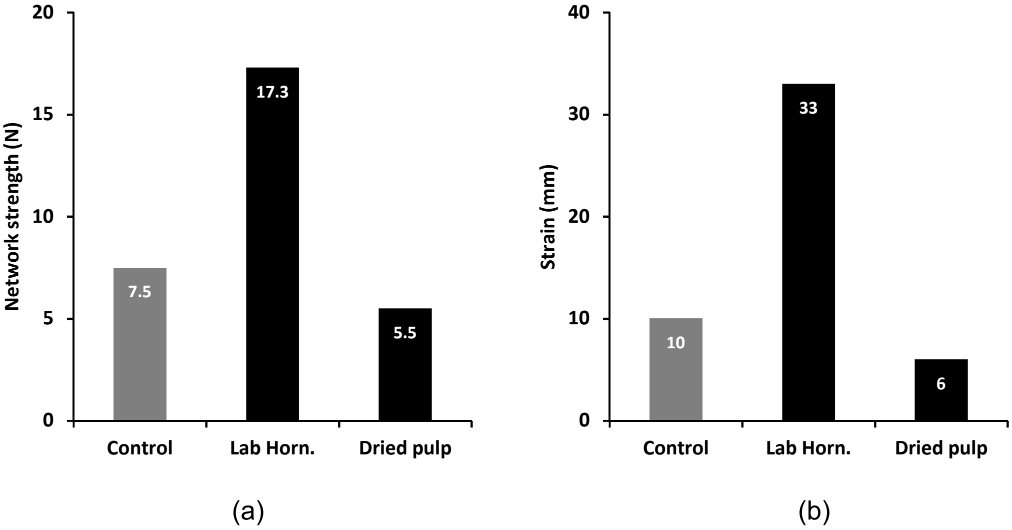
volume of air-laid pads were lower for never-dried pulps compared to dried ones, according to Figure 63 (b). The main explanation for the change in specific volume has been related to hornification and loss of conformability of the fibres, but also may be explained based on the delamination mechanism due to loosening of the cell wall structure upon processing and drying [280,290,292].

In the laboratory-hornified pulps the absorption time (Figure 63 (c)) of fluff pulps decreased when compared to control pulp and the absorption capacity remains similar (Figure 63 (d)).

Table 31 - Fibre morphology of the control and hornified pulps before and after dry-defibration in the pilot-scale hammermill at 3500 rpm.

Before dry defibration	**Lc(w) ISO**	**Fibre width (W)**	**Curl**	**Mean fines**	**Coarseness**	**Fibre wall thickness**	**No. of kinks per fibre**	**Mean kink index**
	mm	µm	%	-	µg/m	µm	-	-
	(± 0.003)	(± 0.1)	(± 0.1)	(± 0.2)	(± 0.5)	(± 0.1)	(± 0.02)	(± 0.05)
Control	0.699	18.9	8.6	12.0	81	3.0	0.76	2.64
Lab. Horn.	0.679	18.6	9.0	8.1	83	3.0	0.86	3.66
Dried pulp	0.691	18.7	8.9	17.0	72	2.5	0.85	3.61
After air dry defibration @ 3500 rpm	**Lc(w) ISO**	**Fibre width (W)**	**Curl**	**Mean fines**	**Coarseness**	**Fibre wall thickness**	**No. of kinks per fibre**	**Mean kink index**
	mm	µm	%	-	µg/m	µm	-	-
Control	0.671	19.3	8.6	14.9	73	2.8	0.92	3.36
Lab. Horn.	0.687	18.1	9.1	14.1	86	3.2	0.92	3.32
Dried pulp	0.698	18.1	8.9	16.2	83	3.1	0.96	3.25

Figure 64 illustrates the changes in the network strength (a) and in the strain (b) required to rupture the air-laid pad produced from reference and hornified pulps. Once more, the laboratory-hornified pulps behaves differently from the ECF paper grade pulp dried in conventional airborne dryer. It might be noted that laboratorial hornified pulps were oven-dried and restrained between two metal wires for 120 min (mimicking the contact drying), while ECF paper grade was pressed and airborne in the industrial pulp dryer (convection drying). Although the specific volume of the laboratory-hornified pulp is lower than for the paper grade pulp (Figure 63 (b)), it shows a higher network strength and strain, while the paper grade fluff pad breaks at much lower applied force and showed low strain (Figure 64). Hence, the pad made of laboratory-hornified fluff pulp is stronger and more elastic than those made of pulps without modification. As can be seen from the results obtained, the hornification that occurs during conventional drying in an airborne dryer is quite different from the forced hornification carried out in the laboratory at high temperature in the contact mode in relation to its effect on cellulose fibres.



(a) (b)

Figure 64 - Results on the network strength (a) and the strain (b) measured in the control and hornified pulps, after air dry-defibration in the hammermill at 3500 rpm.

5.4.5 Ultra-high-pressure treatment

The processing of foodstuff by high hydrostatic pressure (HHP) is known since 1899 when Hite [293] demonstrated that the shelf life of milk and other food products could be extended by pressure treatment. This is the technology of applying high hydrostatic pressure to materials by compressing the surrounding water and transmitting pressure throughout the product uniformly and rapidly [294]. Regarding cellulosic fibres, UHP treatment demonstrated structural modifications dealing with rearrangements of cellulose fibrils in fibres, forced hydration and enhanced accessibility. Recently, UHP was considered as an interesting tool to promote the introduction of chemicals or specific biomolecules inside fibres [136,158]. One of the effects of UHP treatment on the pulp fibres is the changes in fibre morphology and physical properties. Thus, the forced hydration of the cell wall leads to some increase in its thickness, fibre coarseness and fibres become more elastic and plastic [152,155,158]. At the same time, due to the forced hydration of cellulose fibrils and formation of strongly attached hydrate clathrates, the UHP treated fibres becomes less bonded each other via hydrogen bonding of free hydroxyl groups [136,158]. Furthermore, due to the forced hydration during UHP treatment, a part of the aggregate fibrils in pulp are separated, being swollen, thus increasing the accessible cellulose surface [155].

In order to investigate the impact of UHP on the fluff pulp properties, a never-dried cellulosic *Eucalyptus globulus* ECF bleached kraft industrial pulp was submitted to an UHP treatment at 400 MPa and 600 MPa for 15 min and 10 min, respectively. The treatment conditions were selected according to previous works dealing with cellulosic fibre modifications for papermaking and pulp functionalization [136,155,158,160]. The results presented in Table 32 evidence that the UHP treatment did not affect the pulp characteristics as concerns the kappa number, intrinsic viscosity and brightness. Contrariwise, the content of carboxylic acid groups was affected to some extent. Probably, under UHP treatment, some proportion of xylan from fibre surface was removed in solution due to the enhanced forced hydration and swelling of fibres. The forced hydration was confirmed by increased WRV after the UHP treatment when compared to never-dry pulp (negative hornification). The behaviour of water under high pressure promotes pressure-shift freezing and further fast thawing, non-frozen storage under pressure at sub-zero temperature, and different ice polymorphs [158,295]. Strongly attached water cannot be removed from pulp at 105 ºC and therefore the weight of treated pulp after drying at 105 ºC is higher that the weight of oven-dry untreated pulp. This amount of strongly bound water increases with the increase of applied pressure (Table 32).

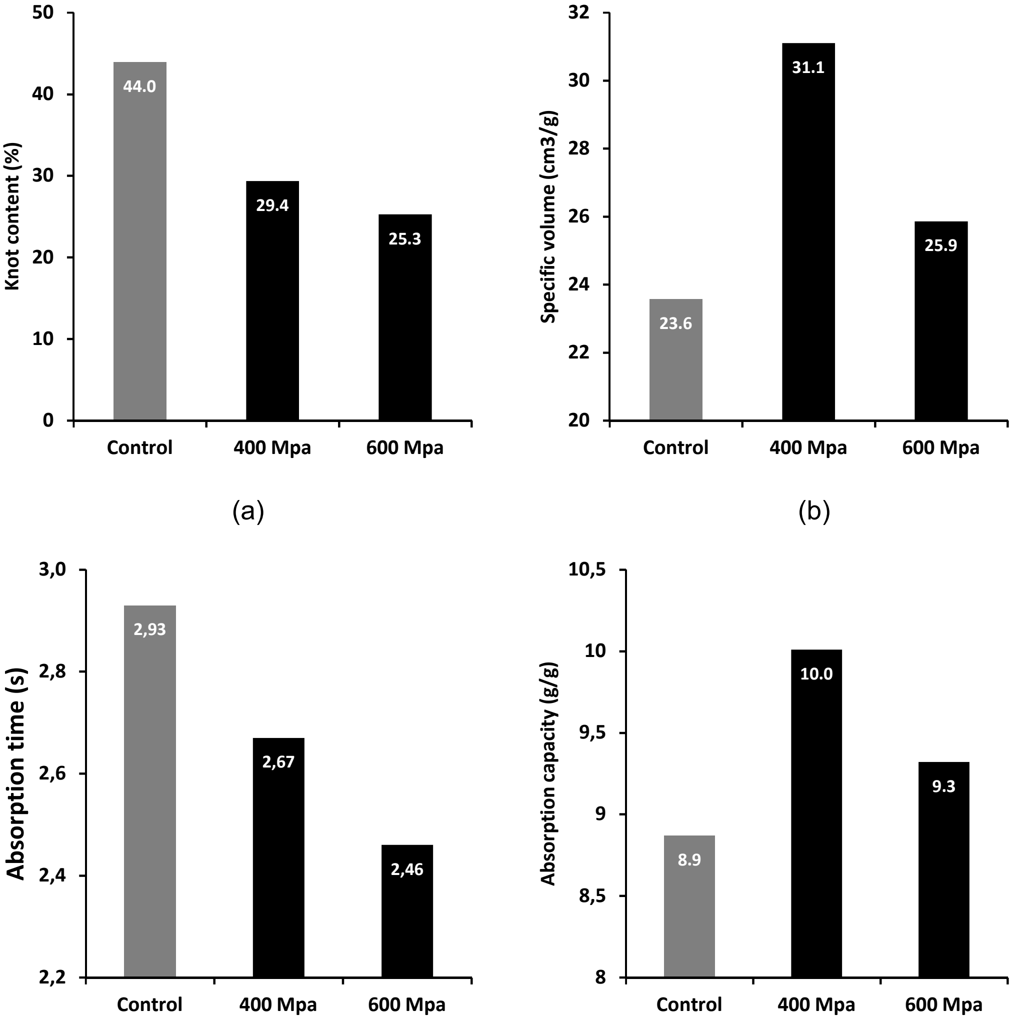
Table 32 - Results of kappa number, carboxylic acids, intrinsic viscosity, brightness index and water retention value in pulps modified with hyperbaric treatment.

	Kappa	**COOH meq/g**	**Viscosity dm^3/kg**	**Brightness %ISO**	**WRV %**
Control	2.3	9.5	932	91.1	117
400 MPa	2.1	8.6	929	90.6	126
600 MPa	2.2	8.8	930	91.3	131

The HP treatment promoted the decrease in the content of knots presented in fluff pulps after dry defibration (Figure 65 (a)). The forced hydration is enhanced by the increase of hydraulic pressure thus diminishing the amount of free OH groups on the fibre surface not involved in strong hydration complexes. Accordingly, the better separation of fibres under increased pressure is quite understandable.

UHP decreases the conformability of treated fibres, which explains the increase in the specific volume of air-laid pads made of treated fluff pulp (Figure 65 (b)). The maximum was reached after the UHP treatment at 400 MPa. It is believed that UHP treatment improves intrinsic fibre strength due to the favourable ordering and the increment of cellulose crystalline domains [155]. Furthermore, the increase of the specific volume improves the porosity and absorption capacity of fluff pulps and, consequently promotes the rise of water flux through fibres [296].

The results of the absorption time of pulp fluffs, illustrated in Figure 65 (c) demonstrated that UHP treatment increased significantly the absorption rate of air-laid pads. A possible explanation is the improved porosity of the pads constituted of treated fibres. In fact, the general features related to the porosity of pads (Figure 65 (b)) coincides with their absorption capacity (Figure 65 (d)).

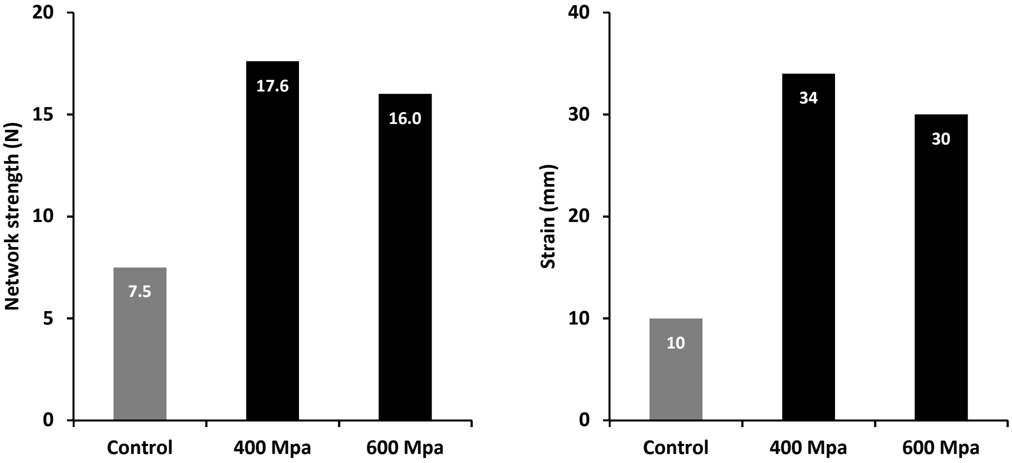


(a) (b)

(c) (d)

Figure 65 - Results of the UHP treatment on the knot content (a), specific volume (b), absorption time (c) and absorption capacity (d) of the pads made of untreated (control) fluff pulp and pulps modified at 400 and 600 MPa. Dry-defibration performed in a pilot scale hammermill at 3500 rpm.

The increased of network strength, more than twice, detected for HP-treated fluff pulps (Figure 66), reflect the increased intrinsic strength of fibres due to the favourable cellulose fibrils rearrangement leading to crystallites aggregation/accretion and diminishing the distortion of their surfaces [158,297] and the improved elasticity of the treated fibres. The increased deformation of the pads produced from UHP-treated pulps shows a more resilient fibre network. This is also a result of morphological changes in cellulose fibres that occurred in the UHP treatment (Table 33).



(a) (b)

Figure 66 - Effect of the UHP treatment on the network strength (a) and strain (b) of the pads made of untreated (control) and UHP-processed fluff pulps at 400 and 600 MPa. Dry defibration performed in a pilot scale hammermill at 3500 rpm.

Regarding the changes in fibre morphology, the UHP treatment showed small increase in curl and in coarseness of the pulp fibres (Table 33). In the UHP-treated fibres, the fibre length is slightly decreased while the fibre´s width maintained constant. Apparently, the fibre cell wall was swollen mostly due to the expansion of internal layers, because the fibre´s width did not change so much, but the fibre wall thickness increased noticeably (Table 33). Noteworthy that after dry defibration, the fibre´s length increased slightly, and the kink index decreased due to the fibre straightening. The increase in the length, curl and coarseness of the fibre favours the increase in the fibre network strength.

Since the coarseness of fibres and the knots content relate directly to the porosity of the air-laid fibre network and the porosity favours the absorption rate (Figure 65 (c)), the positive effect of the increased fibre coarseness and the decrease in knots after the UHP treatment obviously corroborate with the absorption time (Figure 67).

As could be mentioned, the high fibre density zones can disperse fluid throughout the entire surface of the absorbent fluff pad by virtue of excellent wicking properties, establishing a network of capillary action channels interconnecting the low fibre density zones (low coarseness) which have the task of permanently absorbing and retaining the fluid. The results revealed that both coarseness and curl affect positively the absorbency capacity and absorption time of the fluff pads (Figure 68).

Table 33 - Fibre morphology of the control pulp and modified pulps with HP treatment, before and after air dry-defibration, in the pilot-scale hammermill at 3500 rpm.

Before dry defibration	**Lc(w) ISO**	**Fibre width (W)**	**Curl**	**Mean fines**	**Coarseness**	**Fibre wall thickness**	**No. of kinks per fibre**	**Mean kink index**
	mm	µm	%	-	µg/m	µm	-	-
	(± 0.003)	(± 0.1)	(± 0.1)	(± 0.2)	(± 0.5)	(± 0.1)	(± 0.02)	(± 0.05)
Control	0.699	18.9	8.6	12.0	81	2.9	0.76	2.64
400 MPa	0.687	18.7	8.8	11.5	82	3.0	0.70	2.44
600 MPa	0.687	18.9	8.6	16.9	86	3.2	1.17	3.15
After dry defibration @ 3500 rpm	**Lc(w) ISO**	**Fibre width (W)**	**Curl**	**Mean fines**	**Coarseness**	**Fibre wall thickness**	**No. of kinks per fibre**	**Mean kink index**
	mm	µm	%	-	µg/m	µm	-	-
Control	0.671	19.3	8.6	14.9	73	2.8	0.79	3.36
400 MPa	0.697	19.1	8.9	16.3	83	3.1	0.67	2.25
600 MPa	0.684	19.1	8.9	17.9	84	3.1	0.71	2.42

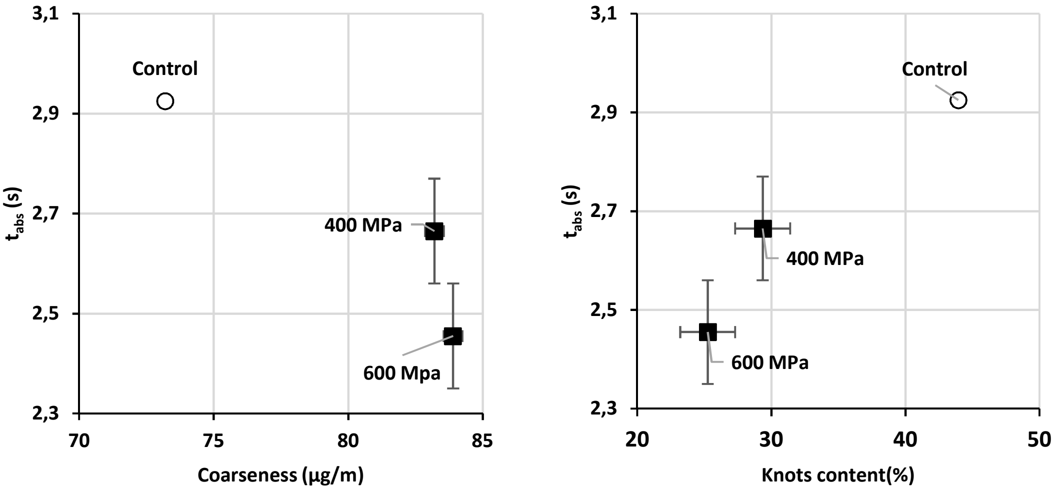


Figure 67 - Relationship between absorption time and coarseness (left figure) and knots content (right figure) of the control fluff pulp and the fluff pulps modified by HP treatment.

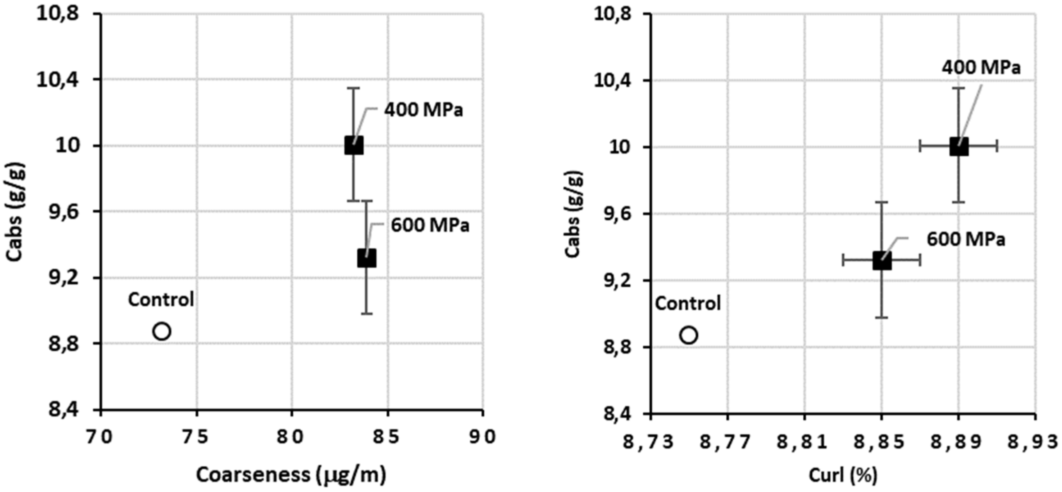


Figure 68 - Relationship between absorption capacity and coarseness of fibres (left figure) and curl (right figure) of the control fluff pulp and the fluff pulps modified by HP treatment.

5.5 Fluff based product prototype

The journey of building a product involves several steps to reach the level where it can be brought into production for customers. Each product has a specific target audience and solves its problems in some way. To assess, whether the product really solves its customer’s problems, an almost working model called a prototype is created and tested with the prospective users and stakeholders. For instance, a “working prototype” (i.e. a prototype which focusses more on function than form) will allow to check if the product is functional, easy to use and safe. Prototyping a product, will help to discover possible flaws within the operation of the product, which could have resulted in serious consequences.

There is a large variety of commercial products with fluff pulp, which majority have other different components, such as superabsorbent materials, chemical additives, among others. However, for example, a maternity, perineal and surgical pads have in its composition practically fluff pulp only, in order to be safe, soft, comfortable, easy to apply, and highly absorbent. Therefore, it was prepared at a pilot-scale a medical obstetric pad made of 100 % *E. globulus* bleached kraft fluff pulp and compared with that existing on the market (Figure 69).

According to the previously obtained results (section 5.3), the best formulation to obtain a fluff pad with enhanced absorption properties, resilient fluff pad, high network strength and low defibration energy (low knots content) corresponded to a pulp produced with specific conditions: kraft cooking with alkali charge of 15% (sulphidity 30%, temperature = 160 °C ± 2°C; retention time = 120 min ± 5 min) and an ECF bleaching sequence $D_{hot}E_PD_1P$.

The maternity pads are generally used after women giving birth, so the pad should be free of any contaminants and microorganisms to avoid possible infections. For that reason, it was previously added to *Eucalyptus globulus* bleached kraft pulp 0.3 %(w/w) of the antiseptic agent polyhexamethylene biguanide (PHMB), that can infiltrate bacterial cell membranes and kill bacteria. Testing has demonstrated that exposure to PHMB causes viral cell to clump together, forming aggregates [298]. This prevent invasion into the host cells, making PHMB a potential antiviral treatment. Several studies have shown that the product is safe in clinical use. Schnuch *et al.* demonstrated that in trials including 3529 patients, skin sensitisation to PHMB is low (approximately 0.5%), even when used concentrations (2.5% and 5%) [300,302].

Simultaneously, the bleached softwood fluff pulp of the commercial maternity & perineal pad (Figure 70) was evaluated on its absorbent properties, specific volume, knots content, network strength and fibre morphology.

Figure 69 - Prototype of a medical obstetric pad made of *E. globulus* bleached kraft fluff pulp.

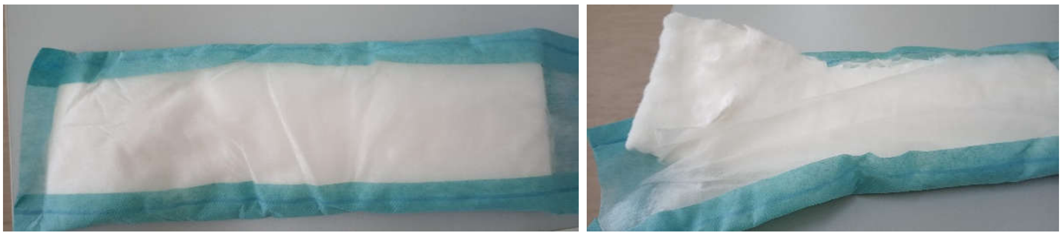


Figure 70 - Commercial maternity & perineal pad.

According to Figure 71 (a) the specific volume of the *E. globulus* fluff pad (prototype) is higher than the fluff pulp removed from the commercial product. This is an unexpectable result since the rearrangement of the softwood fibres after dry defibration is better than the hardwood fibres, which increases the specific volume. A possible explanation is the compressibility of the softwood fluff pulp in the commercial product, caused by the industrial line specificity. It is was not possible to simulate the effect of the compressibility in the prototype's fluff pad.

Regarding the network strength results (Figure 71 (b)), the fluff pulp from prototype presented a value of 13.4 N. After several attempts, it was not possible to determine the network strength of the fluff pulp from the commercial pad. As already observed in previously results, when the softwood network starts to deform, curled fibres starts to straighten before any slippage between them takes place, which means that a more flexible dry-formed network is formed when more curled fibres are present. Another possible explanation is the presence of the dusting phenomenon due to the high amount of fines content (Table 34) of fluff pulps from the commercial pad. The fines percentage affects the structure and the formation of the network pad, which may compromised the specific volume (Figure 71 (a)) and network strength of the fluff pulp.

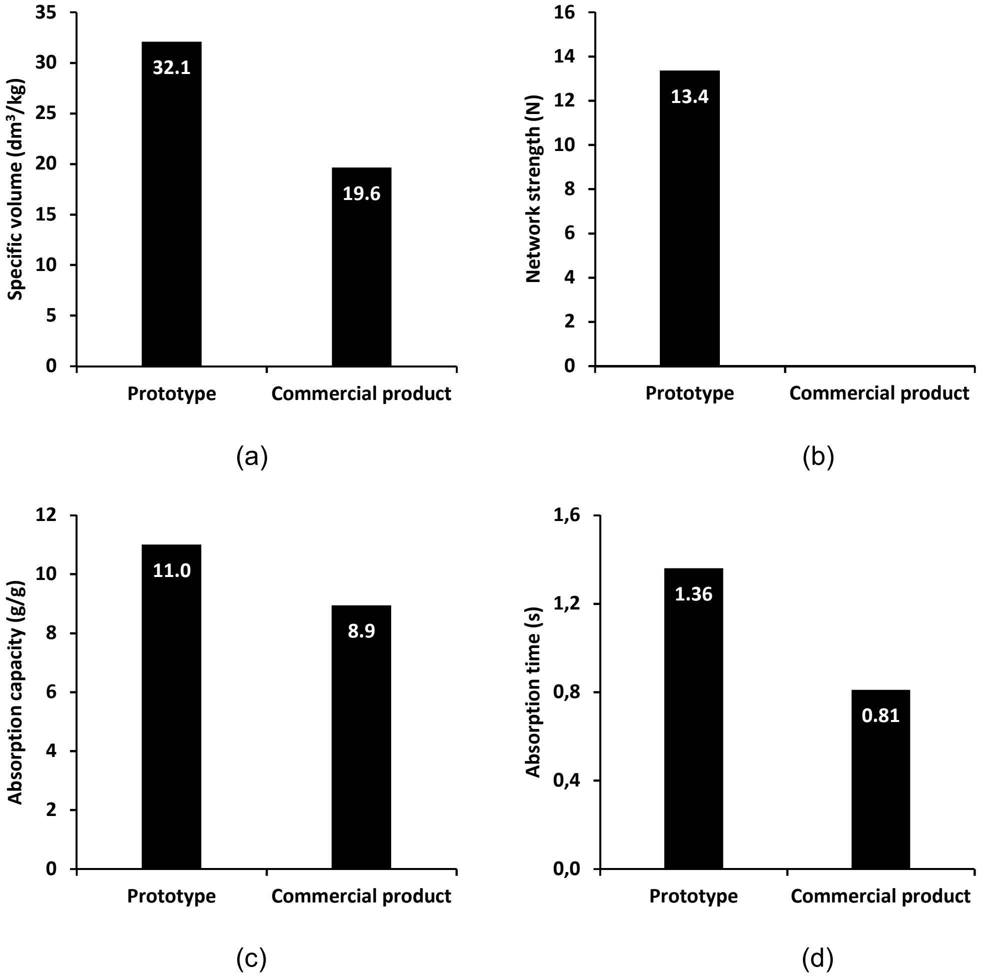
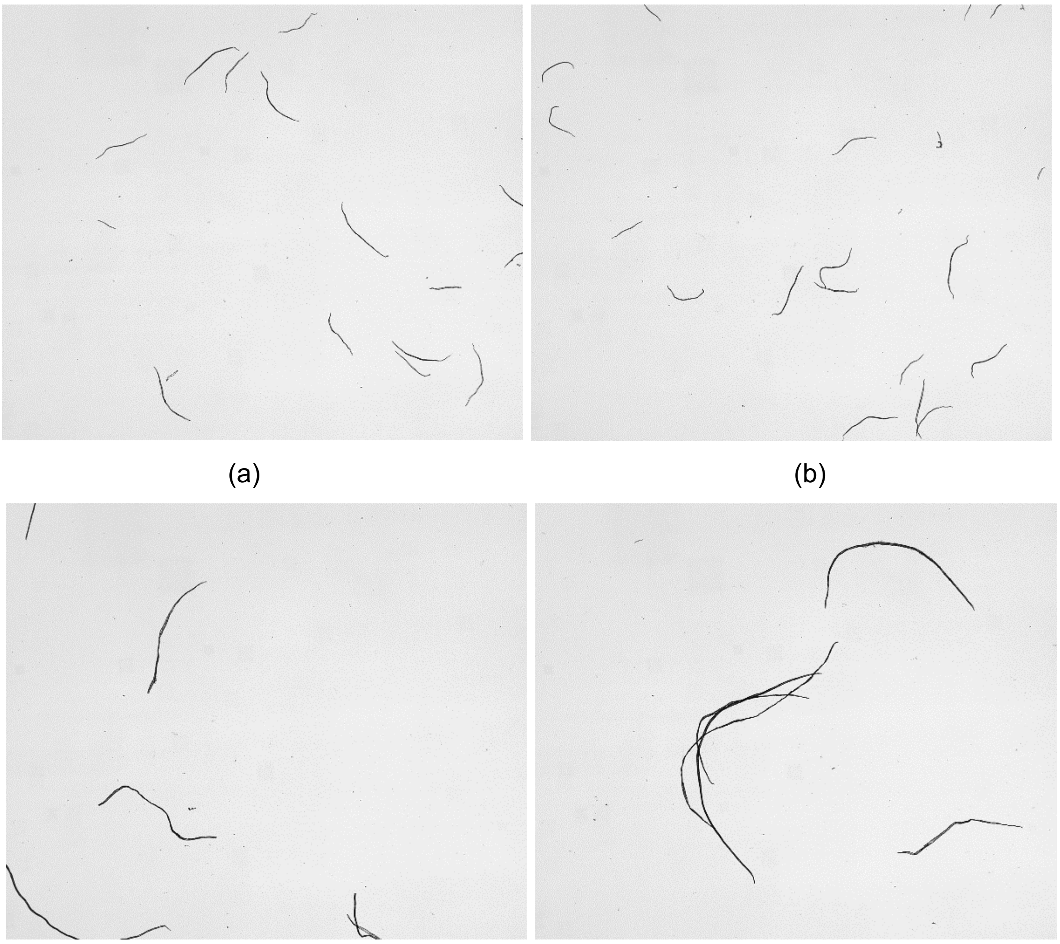


Figure 71 - Specific volume (a), network strength (b), absorption capacity (c) and absorption time (d) results of the medical obstetric pad made of *E. globulus* bleached kraft pulp and the commercial product.

As could be seen, the absorption capacity (Figure 71 (c)) is higher in prototype's fluff pulp compared to softwood commercial product, but the absorption time (Figure 71 (d)) of commercial product is lower than the prototype. The previous results unambiguously confirm that the fibre's network of hardwood and softwood influences significantly the absorption properties.

It was also investigated the fibre morphology of the hardwood fluff pulp (prototype) and the softwood fluff pulp (commercial product). Figure 72 clearly shows the difference between the fluff pulps, mainly in the fibre's length/width and deformations (kinks). It was evidenced the absence of knots content in both fluff pulps, which indicate that hardwood fluff pulp used in prototype has enhanced debonding properties.



(a) (b)

(c) (d)

Figure 72 - Fibres of *Eucalyptus globulus* bleached kraft fluff pulp (prototype) - (a), (b); and softwood fluff pulp (commercial product) - (c), (d).

Table 34 - Fibre morphology of the *E. globulus* bleached kraft fluff pulp (prototype) and the softwood fluff pulp (commercial product).

	Lc(l) ISO	**Lc(W) ISO**	**Fibre width**	**Curl**	**Mean Fines**	**Coarseness**	**Fibre wall thickness**	**Mean kink index**
	mm	**mm**	**µm**	**%**	**%**	**µg/m**	**µm**	
Prototype	0.876 ± 0.002	0.778 ± 0.003	18.5 ± 0.2	8.8 ± 0.1	7.0 ± 0.2	79.1 ± 2.3	2.8 ± 0.1	2.214 ± 0.036
Commercial Product	2.826 ± 0.073	2.012 ± 0.038	33.5 ± 0.1	8.5 ± 0.1	19.9 ± 1.0	256 ± 26	5.0 ± 0.6	0.853 ± 0.023

Product evaluation needs a perfect understanding of the criteria that influence the absorption process. It was relatively easy to understand the absorption mechanism of the *E. globulus* fluff pulps prepared at a lab-scale. However, these mechanisms are much more complex for commercial diapers constituted of the multifunctional cores consisting of different materials, such as fluff pulp, super absorbent powder, super absorbent fibres, nonwoven, crosslinked cellulose “curly fibre”, tailor made fibres and air laid cores with super absorbents. Laboratory tests only give an incomplete picture of product performance and consumer preferences [302]. Thus, consumer tests are fundamental for product testing and development of consumer products. Only a combination of laboratory and consumer tests can provide a precise and representative picture of product performance in consumer.

6 CONCLUSIONS

The results of the present study allow drawing several brief conclusions regarding the potential of *E. globulus* bleached kraft pulps in fluff applications that may be formulated as follows:

Fluff pulps produced by dry defibration of *E. globulus* kraft bleached pulps revealed an absorption capacity of the order of 10-12 g/g, which is similar or superior to that of commercially available softwood fluff pulps. At the same time, the absorption rate and fibre network strength of softwood fluff pulp are substantially greater than that of eucalyptus fluff pulp. These differences, however, can be significantly reduced by treating eucalyptus pulp with appropriate debonding agents, by selective xylosidic enzymes or by physical modifications (for example, accelerated hornification or ultra-high-pressure treatment). This properties and processes allow eucalyptus fluff pulp to be considered as a prospective material for manufacturing different nonwoven formulations.

Under the single pulp mill scenario, the pulping and bleaching conditions can induce variability within 15% in the absorption capacity and within 25% in the network strength of the fluff pulps. The processing conditions also induced nearly 20% variability in knots content upon dry-defibration of kraft pulps. The gentlest processing conditions for fibre strength and morphology ensure the best properties of fluff pulp. Among the favourable fibre morphological characteristics, the coarseness and the occurrence of deformations (curl and kink) are considered the most important. Both the kraft pulping conditions and the bleaching mode (ECF or TCF) affect the chemical composition and physical structure of the pulp fibres, which in turn effect their dry defibration behaviour and the properties of air-laid fluff pulp formulations. Pulps are easier to defibrate with less knot release when cooked at an increased active alkali (AA) and ECF bleached. TCF bleached pulps provide more rigid and coarser fibres than those of ECF bleached pulps. In turn, dry-defibrated ECF pulps possess more flexible and less deformed fibres than TCF pulps. Thus, coarser, stiffer and more deformed fibres of the TCF pulps are less conformable and provide a more porous and strong air-laid fibre network than that formed by the fibres of the ECF pulps. The network strength of TCF fluff pulps is 20 to 70% greater than that of ECF fluff pulps.

The absorption capacity of the eucalyptus fluff pulps is the result of multiple occurring factors, such as the knots content, fibre´s hydrophilicity and morphology and the water retention capacity of the fibre web, whose contributions are not always unambiguous. Since capillary suction is the main absorption mechanism in air-laid formulations, the porosity of the fibre network is a more important factor than the hydrophilicity of the fibres forming it. The porosity of the air-laid pads depends mainly the knots content and the morphology of the pulp fibres. A knotless pulp with coarse and deformed fibres (curled and kinked) is of the best performance. At the same time, the hydrophilicity and water retention capacity of the pulp fibres is the second of importance factor that determines the absorptivity of fluff pulp. Despite the similar accessibility of non-agglomerated fibres and fibres agglomerated in knots, the latter have less isosteric heat of adsorption in the monolayer than the former and, therefore, possess less wettability. Hence, the knots decrease the absorptivity of fluff pulp. The deformed fibres (curled and kinked) showed less monolayer capacity and the accessible surface, but higher isosteric heat of adsorption in the monolayer, when compared to non-deformed fibres. The last fact was explained by more disordered cellulose fibrils on the surface of deformed fibres, due to the distortion, microcompression, or even partial rupture of cellulosic lamellas. The effect of hemicelluloses on fluff pulp adsorption is quite ambiguous. From one hand, the water retention capacity of fluff fibres correlates positively with amount of carboxyl groups in pulp, i.e. with the residual xylan content. On the other hand, hemicelluloses provide less wettable fibre surface and weaken the air-laid fibre network under humidification.

The fibre network strength and the absorption capacity of air-laid formulations are not directly related. The network strength is sensitive to the knots content and increased to 5-60% when removing the knots from the fluff pulp. Besides the fibre morphology (fibre length, coarseness and deformations), having a decisive influence on the strength properties of air-laid pulp formulations, the physical structure of the cellulose in the fibre wall plays an important role. All kind of treatments favouring fibrils rearrangements in the fibre wall followed by their aggregation after pulp drying (hornification) improved the fibre network strength. This has resulted in the formation of stiffer and less conformable fibres forming a tighter network with higher resistance under moistening. Thus, the partial removal of the xylan from the fibre surface either during pulping/bleaching operations or by selective enzymatic hydrolysis of a bleached pulp permits the network strength raising until 50%. The accelerated hornification allows not only to improve radically the dry defibration of kraft pulp, but also to increase the fibre network strength of fluffed pulp almost twice. The kraft pulp treatment by ultra-high hydraulic pressure (UHP) leads to the rearrangement of the cellulose fibrils followed by their forced hydration resulting in the hydrated fibres containing strongly bound water. This reduces the interfibre bonding and thus improves the dry defibration of eucalyptus kraft pulp. As the UHP-treated pulp reveals coarser and more elastic fibres, the network strength of the treated fluff pulp increases more than twice.

The functionalization of eucalyptus kraft pulp with PHMB allows not only to acquire the antimicrobial function of the pulp, but also to radically improve its dry defibrillation and the strength of the fibre network in air-laid formulation. The prototype of maternity/medical obstetric pads made of eucalyptus fluff pulp modified by PHMB showed even better fluffiness and absorption capacity than the commercial product made of softwood fluff pulp with very good network strength and absorption rate.

7 SUGGESTIONS FOR FURTHER WORK

Further improvement of physical and chemical modification methods of eucalyptus bleached kraft pulp to enhance it absorbency properties and the strength of the air-laid formulation produced thereof. This includes the optimization of the accelerated hornification and UHP treatment conditions and the more detailed understanding of the mechanisms involved. As regarding a chemical modification of eucalyptus kraft pulps, a series of reactions of fibres with esterifying reagents aiming to improve radically the absorption capacity and the interfibre bonding in the air-laid formulations can be performed. These biodegradable materials can substitute the synthetic superabsorbents made from fossil resources in different fluff applications. The physical-mechanical and absorption properties of the dry fluff pulp formulations could be compared according to existing procedures.

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9 ORIGINAL RESEARCH

The following section of the thesis regards the original research developed along the PhD program.

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Article

Relationship between Surface Properties and Fiber Network Parameters of Eucalyptus Kraft Pulps and Their Absorption Capacity

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Abstract: Water absorption capacity is a key characteristic of cellulosic pulps used for different commodities. This property is influenced by the affinity of the pulp fiber surface with water, chemical composition of the pulp, morphology, and organization of fibers in the network. In this study, surface properties of six industrial *Eucalyptus* bleached kraft pulps (fluff pulps) dry-defiberized in a Hammermill, which were obtained by wood pulping and pulp bleaching under different production conditions, were studied while employing dynamic water vapor sorption and contact angles measurements. The absorption properties of air-laid pulp pads were analyzed following the absorbency testing procedure and the relationship between these properties and pulp's chemical composition and fiber network structure were assessed by multivariate analysis. The results showed that the accessibility of the fiber surface is related to the reduction of the contact angles, but, at the same time, to the longer absorption time and less absorption capacity of the fiber network. Therefore, the absorption properties of the pulps are not necessarily directly related to their surface properties. Indeed, absorptivity is related to the surface chemical composition, fiber morphology, and fiber network structure. Thus, surface carboxylic groups promote total water uptake, resulting in better absorption capacity. Greater fiber coarseness and deformations (curl and kink) provide a less wettable surface, but a more porous network with higher specific volume, resulting in more absorbent air-laid formulations.

Keywords: fluff pulp; absorption capacity; sorption isotherms; contact angles; surface wettability; principal component analysis

1. Introduction

Besides for papermaking, wood pulp has been used in absorbent products for many years, being part of common society's goods [1]. Non-paper application of dry-defiberized cellulosic pulps (fluff pulps) includes, but is not limited to, diapers, female hygiene products, air-laid absorbent toweling, surgical pence, and adult incontinence. Capacity expansions and new capacity start-ups are expected to grow in the fluff pulp sector for the next 2–3 years, mainly due to the rising of baby diapers market [2]. Recent interest in fluffy cellulosic materials is related to the low surface stability of SARS-CoV-2 on its surfaces, when compared to common steel and plastic materials [3]. Some strains of coronavirus only live for a few minutes/hours in cellulosic networks that, being a porous absorbable material, cause

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the virus to be stuck and dry. This fact opens new horizons in the manufacture of a wide range of disposable means of cleaning and protection using fluff pulps.

Fluff pulp is made of softwood or hardwood cellulosic pulps, which are produced by kraft or sulphite pulping [4]. The aim is to produce a pulp that can be well defiberized when dry [1,4]. Fluff pulps that are made of softwood pulps have a large fiber length distribution, i.e., the pulp contains long tracheid fibers (2–5 mm) and a relatively high content of fines (short fibers whose length is less than 0.4 mm). Long fibers hinder pulp defibering and fines produce dust [4]. Shorter fibers (e.g., libriforms in hardwood pulps) are easier to defiberize, but these fibers possess a weaker network than long fibers of softwood pulp in air-laid formulations. There is a prominent tendency in some applications to use fluff pulp that is made of hardwood instead of softwood pulp, for example, from *Eucalyptus* kraft pulp [5–7].

The main quality parameters of fluff pulps are related to their absorption capacity, absorption rate, and the air-laid network strength [7–9]. These quality parameters are negatively affected by undefiberized agglomerates (knots) in the fluff pulp. Among the factors that influence the absorption capacity of fluff pulps, the chemical composition of the fibers, the morphology, and their arrangement in air-laid network stand out [5–10]. The intrinsic absorbance of the fibers is related to their accessible surface, which, in turn, depends on the chemical composition and physical structure of the fibers, but also on their length, diameter and stiffness (fiber morphology). An increase in the length and mechanical deformation of the fibers positively contributes to the porosity and burst resistance of the fiber network. However, the importance of changes in the affinity of the fiber surface with water for the absorption capacity in relation to structural changes in the fiber network is not entirely clear. The penetration rate of water into porous fiber network via such important absorption mechanism as capillary suction can be described by the modified Washburn equation [11]:

$$\frac{dl}{dt} = \frac{\gamma_{lv}\, r\, cos\theta}{4\eta l} \tag{1}$$

where l is the distance penetrated into capillary of radius r in time t by a liquid of surface tension γ_{lv} and viscosity η. The contact angle θ between the drop of liquid and the fiber surface reflects the affinity of this liquid to the capillary surface formed by fiber's mesh.

According to Equation (1), an increase in wettability at the fiber-water interface (low θ) causes faster water penetration in the inner layers of the web. At the same time, the larger the average pore size in a given pulp network, the greater is the fluid flux inside the web. The maximum absorption capacity (C_{am}) of a sample with porosity ε and density ρ, for liquid with density ρ_l, per unit mass of dry solid medium, and assuming that there is no change in dimension under wetting and the entire pore space is filled up, can be expressed as follows [12]:

$$C_{am} = \frac{\rho_l}{\rho}\,\frac{\varepsilon}{1-\varepsilon} \tag{2}$$

Because the conditions for the manufacture of kraft pulp (wood pulping and pulp bleaching) affect the chemical composition of the pulp and the morphology of the fibers, these conditions can cause changes in the absorption capacity of the air-laid fiber network. The present work focuses on the characterization of the absorption capacity and affinity of the surface towards water of a set of bleached *Eucalyptus* kraft fluff pulps in order to determine the relationship between the former parameters and the chemical composition and the fiber morphology. Accordingly, fluff pulps were analyzed by capillarity absorption and thermodynamic methods, such as sorption isotherms, sorption enthalpies, and contact angle measurements.

2. Materials and Methods

Six industrially produced eucalypt kraft pulps, cooked, and elementary chlorine free (ECF)/totally chlorine free (TCF) bleached, under conditions that cover all the range of typically applied technological parameters at the CELBI kraft pulp mill (Leirosa, Portugal), were used in this study. The chemical analysis of kraft pulps (carboxylic group content (CG) and monosaccharide composition) and their fiber morphology were determined, as described previously [7]. Thus, CG was determined by conductometric titration according to the SCAN-CM 65:02 standard method. The sugar analysis was carried out as alditol acetates by GC after two-step Saeman hydrolysis. The morphology of the fibers after defiberization was analyzed using a Kajaani FS300 fiber analyzer (Espoo, Finland). Pulps were dry-defiberized by two-step passage in a pilot-scale Hammermill (Schuttle Buffalo, Model W6H, Buffalo, NY, USA) operated at 3500 rpm. Knot percentage was determined using a RETSCH® sieve shaker adapting to the norm SCAN-CM 37:85. The results of chemical composition and fiber morphology of pulps are presented in Tables 1 and 2, respectively.

Table 1. Carboxylic groups content (CG) and monosaccharide composition of pulps.

Pulp	**[CG] (μmol/g)**	**Monosaccharide Composition (%) ***					
		Glu	**Xil**	**Man**	**Gal**	**Ara**	**Ram**
1	92.0 ± 1.2	74.4	24.6	0.2	0.2	0.1	0.5
2	128.0 ± 1.9	72.6	26.4	0.3	0.2	0.1	0.4
3	84.0 ± 0.9	76.3	22.9	0.2	0.2	0.1	0.3
4	98.0 ± 0.9	72.2	26.8	0.2	0.2	0.1	0.5
5	116.0 ± 1.5	71.4	27.5	0.2	0.2	0.1	0.6
6	120.0 ± 1.9	72.4	26.3	0.4	0.2	0.4	0.3

* Sugars designations are as follows: glucose (Glu), xylose (Xil), mannose (Man), galactose (Gal), arabinose (Ara) and ramnose (Ram). The relative error in sugars analysis not exceeded of 3–5%.

Table 2. Fiber morphology parameters of defiberized eucalypt kraft fluff pulps.

Pulp	**Fiber Length (mm)**	**Fiber Width (μm)**	**Fines (%)**	**Curl (%)**	**Kink (%)**	**Coarseness (mg/m)**
1	0.781 ± 0.003	18.2 ± 0.01	30.7 ± 0.2	9.9 ± 0.1	45.3 ± 0.1	0.0703 ± 0.001
2	0.771 ± 0.002	17.7 ± 0.01	29.6 ± 0.4	11.0 ± 0.1	49.5 ± 0.2	0.0714 ± 0.003
3	0.775 ± 0.002	18.0 ± 0.01	30.8 ± 0.3	11.5 ± 0.1	50.2 ± 0.1	0.0710 ± 0.003
4	0.773 ± 0.003	17.9 ± 0.01	30.5 ± 0.4	12.0 ± 0.1	52.1 ± 0.3	0.0734 ± 0.004
5	0.776 ± 0.002	17.9 ± 0.01	29.9 ± 0.2	11.6 ± 0.1	50.0 ± 0.2	0.0710 ± 0.006
6	0.758 ± 0.004	17.8 ± 0.01	30.5 ± 0.3	12.8 ± 0.1	53.3 ± 0.2	0.0720 ± 0.005

Water sorption isotherms of defiberized kraft pulps without knots (**1**–**6** pulps) and of **2** pulp with knots (**2K** pulp) were obtained at 25, 30, and 35 °C and at relative pressure in the range between 0.05 and 0.95, while using the Dynamic Vapor Sorption Analyzer (DVS Adventure, Surface Measurement Systems Ltd., Wembley, UK). The experimental sorption data, i.e., equilibrium moisture content, X_{eq} and water activity (or relative pressure), a_w were fitted into the Guggenheim-Anderson-de Boer (GAB) model, since it is valid for high relative pressures ($P/P_0 \leq 0.90$, where P_0 represents the saturation pressure) and proves adequate for surface affinity studies of cellulosic pulps [13,14]. Equation (3) represents this model:

$$X_{eq} = \frac{X_m\,C\,K\,a_w}{((1-K\,a_w)(1+(C-1)K\,a_w))}, \tag{3}$$

where C and K are the GAB model parameters that are related to the heat of sorption in monolayer and in multilayer, respectively, and X_m is the monolayer capacity [13–19]. C, K, and X_m were estimated from the experimental results by non-linear regression analysis:

$$\frac{a_w}{X_{eq}} = \frac{(1-C)K}{X_m\,C}{a_w}^2 + \frac{C-2}{X_m\,C}a_w + \left(\frac{1}{X_m\,C\,K}\right) \tag{4}$$

Sorption enthalpies, ΔH_C and ΔH_K, and entropic accommodation factors between mono and multilayer, C_0, and between bulk liquid and multilayer of water molecules, K_0, as determined from Equations (5) and (6) [14,15,20]:

$$\ln C = \ln C_0 + \frac{\Delta H_K}{R\,T} \tag{5}$$

$$\ln K = \ln K_0 + \frac{\Delta H_K}{R\,T} \tag{6}$$

The net isosteric heat of sorption, ${Q_{st}}^{net}$, was obtained employing the Clausius–Clapeyron equation [14,15,21–25]:

$$\ln a_w = \left[\frac{-{Q_{st}}^{net}}{R}\frac{1}{T} + constant\right]_{X_{eq}} \tag{7}$$

However, because the sorption data were not determined at constant moisture content, a_w was calculated from Equation (8) for each X_{eq} value, at different temperatures, while using the GAB parameters that were obtained from experimental data [15,25].

$$a_w = \frac{2 + \left(\frac{X_m}{X_{eq}} - 1\right)C - \left(\left(2 + \left(\frac{X_m}{X_{eq}} - 1\right)C\right)^2 - 4(1-C)\right)^{\frac{1}{2}}}{2\,K\,(1-C)} \tag{8}$$

The fraction of occupied sites in the monolayer, ξ^{l_1} was calculated according to Equation (9) [8,16]:

$$\xi^{l_1} = \frac{C\,K\,a_w}{1 + (C-1)\,K\,a_w} \tag{9}$$

Contact angles were measured on laboratory handsheets (65 g/m^2 ± 2 g/m^2) prepared from **1–6** pulps, using a semi-automatic Rapid–Köthen sheet former, according to ISO 5269-1 standard procedure. The measurements were carried out in a Contact Angle System OCA20 goniometer (Data Physics, Filderstadt, Germany) that was equipped with a CCD camera and SCA20 software, while using the sessile drop method applying 3µL micro-drops of distilled water. At least 20 determinations were done per each sample and the obtained results were averaged.

The absorption tests were performed according to the Scandinavian procedure SCAN-C33:80 while using air-laid pads produced from pulps without knots (**1–6** pads) and with knots (**1K–6K** pads). Simultaneously, the specific volume, ν, absorption capacity,C_{abs}, and the absorption time, t, have been determined. This testing procedure allows for calculating the total volume (V_t) of each formed pulp pad and, therefore, determine its porosity, ε, according to Equation (10):

$$\varepsilon = \frac{V_t - \frac{m}{\rho}}{V_t}, \tag{10}$$

where m is the dry mass of the pulp pad and ρ is its intrinsic density, calculated as a weighted average of cellulose and xylose densities. The Xylan density was assumed to be equal to 1.20 g/cm^3 and the density of crystalline and amorphous cellulose of 1.59 and 1.40 g/cm^3, respectively [14]. It was assumed that the average degree of crystallinity of cellulose in *Eucalyptus* kraft pulp is 71% [14]. The proportions of xylan and cellulose (glucan) were inferred from the sugar composition of pulp that is presented in Table 1.

Multivariate analysis between surface and capillarity absorption properties of the studied pulps and their chemical composition and fiber morphology were obtained by principal component analysis, while using JMP14 software [26].

3. Results and Discussion

3.1. Sorption Isotherms and Sorption Enthalpies

Sorption isotherms for **1–6** pulps and the **2K** pulp, at 25 °C, 30 °C, and 35 °C are presented in Figures 1 and 2, respectively. The obtained isotherms are consistent with type II isotherms, typical of hydrophilic polymers, such as cellulose, possessing free hydroxyl groups, which are largely responsible for water sorption [14,27]. An increase in temperature induces a reduction in the equilibrium moisture content at a specific water activity, being more significant at higher a_w values, as should be expected for fibrous cellulosic materials [15,28]. The increase in the temperature increases the state of excitation of the water molecules and, consequently, decreases the attractive forces between them, due to an increase between their mutual distances. This decrease in binding energy between water molecules and the surface of the absorbent material results in the breakdown of these bonds, and, therefore, in a decrease of the equilibrium moisture content for a given water activity value. Figure 2 also shows that knots content did not significantly affect the equilibrium moisture content. This means that fibers in bundles maintained the accessibility comparable with that of well-separated fibers. In practice, inaccessible surfaces of aggregated fibers in cellulosic materials become accessible via the cleavage of intermolecular hydrogen bonds by water, thus promoting fiber swelling and increasing the effective surface area [14,19]. Hence, the agglomeration of fibers is not a problem for their accessibility inside the knots.

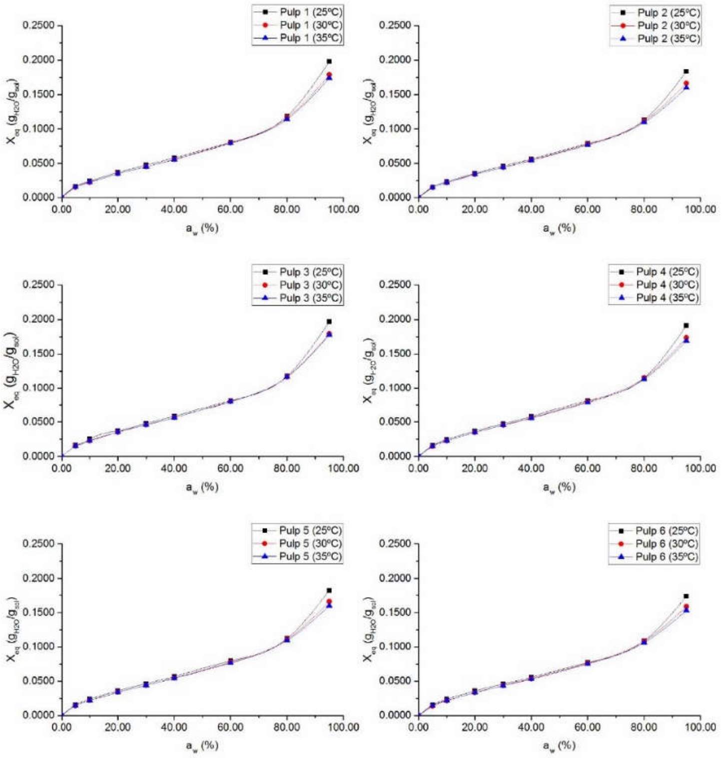

Figure 1. Sorption isotherms of pulps **1–6** without knots at 25, 30, and 35 °C.

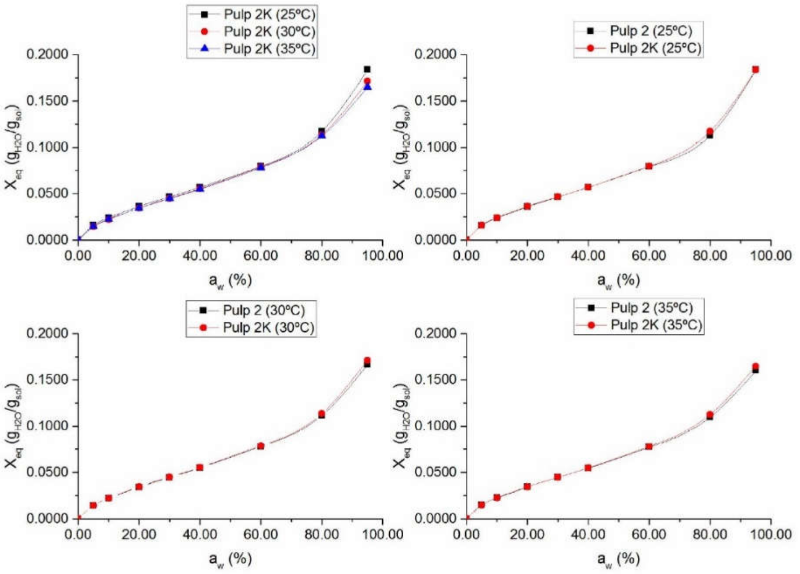

Figure 2. Sorption isotherms of fluff pulps with knots (**2K** pulp) and without knots (**2** pulp) at 25, 30, and 35 °C.

The sorption isotherms allow for evaluating the capacity of the monolayer (X_m) in the fluff pulp, while adjusting the GAB model to the experimental data and infer the effective parameters (Equations (3) and (4)). Only "free" hydroxyl groups not involved in strong intramolecular and intermolecular hydrogen bonding bind water molecules, thus forming a monolayer at low water activities ($a_w \leq 0.40$) [27,28]. This monolayer is discontinuous, because of randomly distributed free hydroxyl groups and their differences in accessibility. Bleached *Eucalyptus* kraft pulps contain notable amounts of glucuronoxylan, which is located essentially in the outer layers of the fibers [29]. Accordingly, the content of xylan and its chemical structure (mainly the quantity of uronic moieties) contribute to the absorption of water by the fluff pulps and must be considered in the interpretation of the results of the isothermal sorption.

Table 3 presents the obtained monolayer capacity values. This parameter measures the availability of active sites on the material for water sorption to occur [14–16] and it was used to estimate the specific surface area of the absorbent material, S as Equation (11):

$$S = \frac{X_m \, N_A \, A_m}{M} \tag{11}$$

where M is the water molecular weight, N_A the Avogadro number, and A_m the effective cross-sectional area of the water molecule (0.125 nm^2 for water at 298 K) [21]. X_m values and, consequently, S values decrease with temperature (Table 4). This result is in accordance with considerations of other studies that attributed this issue to a reduction in the total number of active sites for water binding as a result of physical or chemical changes on the fiber surface that is induced by temperature [14–21,28].

Table 3. Monolayer capacity values at 25, 30, and 35 °C.

	$X_m \pm dX_m$ ($\frac{g_{H_2O}}{g_{sol}}$)		
Pulp	**T = 25 °C**	**T = 30 °C**	**T = 35 °C**
1	0.048 ± 0.002	0.046 ± 0.003	0.046 ± 0.003
2	0.047 ± 0.003	0.046 ± 0.003	0.046 ± 0.003
3	0.047 ± 0.003	0.047 ± 0.003	0.047 ± 0.003
4	0.048 ± 0.004	0.047 ± 0.003	0.046 ± 0.003
5	0.048 ± 0.003	0.046 ± 0.003	0.046 ± 0.003
6	0.047 ± 0.003	0.046 ± 0.003	0.045 ± 0.003
2K	0.047 ± 0.002	0.046 ± 0.002	0.045 ± 0.003

Table 4. Specific surface area of pulps at 25, 30 and 35 °C.

	$S \pm dS$ ($\frac{m^2}{g_{sol}}$)		
Pulp	**T = 25 °C**	**T = 30 °C**	**T = 35 °C**
1	201 ± 8	194 ± 15	191 ± 12
2	196 ± 12	193 ± 15	191 ± 12
3	198 ± 12	195 ± 15	195 ± 12
4	200 ± 16	196 ± 15	193 ± 13
5	199+ ± 14	194 ± 15	191 ± 13
6	195 ± 11	192 ± 15	189 ± 11
2K	197 ± 7	194 ± 14	190 ± 12

Energy parameters *C* and *K* of the GAB sorption model are shown in Tables 5 and 6, respectively. Parameter *C* is essentially related to differences in enthalpy between monolayer (H_1) and multilayer (H_n), and it measures the binding energy of the forces between water molecules and the fiber surface [14–19]. The *C* values presented in Table 5 suggest that the effective binding force between water molecules and the surface of agglomerated and compact fibers (knots) is weaker than between water molecules and non-agglomerated fibers, since the *C* value for **2K** pulp is lower in comparison to *C* value for **2** pulp. Parameter *K* is related to differences between enthalpy in the bulk liquid (H_L) and multilayer [14,15]. *K* varies between 0 and 1; when it approaches one, water molecules that are beyond the monolayer are not structured in a multilayer and there is almost no distinction between multilayer molecules and bulk liquid. The lower the *K* value, the more sorbed molecules are structured in a multilayer [14,15]. The *K* values are very similar for all samples, varying in the range between 0.7 and 0.8 (Table 6), which indicate that the multilayer is structured and its properties are distinct from the bulk liquid [14]. The temperature has negative effect on *C* and positive effect on *K*, as it has already been reported for other cellulosic materials [14,15,28]. These results are consistent with the definition of these parameters, i.e., C decreases with increasing temperature due to the decreasing of monolayer binding energy and K increases with increasing temperature, which indicates that multilayer water molecules become more similar to those in bulk liquid, due to the increase of their excitation state.

Table 5. Energy parameter *C* at 25, 30, and 35 °C.

	$C \pm dC$ (adm)		
Pulp	**T = 25 °C**	**T = 30 °C**	**T = 35 °C**
1	10.7 ± 0.6	10.0 ± 0.9	9.8 ± 0.7
2	11.0 ± 0.5	9.9 ± 0.9	9.5 ± 0.7
3	12.0 ± 0.5	10.0 ± 0.9	9.5 ± 0.7
4	11.0 ± 0.5	9.9 ± 0.9	9.4 ± 0.7
5	11.0 ± 0.5	9.6 ± 0.9	9.4 ± 0.7
6	11.5 ± 0.5	9.8 ± 0.9	9.4 ± 0.6
2K	10.4 ± 0.4	9.8 ± 0.8	9.5 ± 0.7

Table 6. Energy parameter K. at 25, 30, and 35 °C.

	$K \pm dK$ (adm)		
Pulp	**T = 25 °C**	**T = 30 °C**	**T = 35 °C**
1	0.77 ± 0.05	0.78 ± 0.09	0.80 ± 0.08
2	0.76 ± 0.07	0.77 ± 0.09	0.78 ± 0.08
3	0.78 ± 0.07	0.78 ± 0.09	0.80 ± 0.07
4	0.76 ± 0.09	0.77 ± 0.09	0.79 ± 0.08
5	0.75 ± 0.08	0.77 ± 0.09	0.78 ± 0.08
6	0.75 ± 0.07	0.76 ± 0.09	0.78 ± 0.07
2K	0.78 ± 0.04	0.77 ± 0.08	0.80 ± 0.07

Enthalpy differences and entropy accommodation factors between monolayer and multilayer ($\Delta H_C = H_1 - H_n$ and C_0, respectively), and between bulk liquid and the multilayer ($\Delta H_K = H_L - H_n$ and K_0, respectively) revealed that ΔH_C are positive (Table 7), because the interaction of water with primary sorption sites is exothermic [15]. ΔH_K. values are smaller, because multilayer molecules interact less than monolayer molecules with the surface of the absorbent material and, consequently, multilayer molecules are less firmly bounded in comparison to the monolayer molecules [14–16]. These results show that the enthalpy that is associated with adsorbed water molecules follows the order: $H_1 > H_n > H_L$, i.e., the interactions of water molecules in the monolayer are stronger in comparison with the multilayer. The C_0 values are smaller than 1, because, from an entropic point of view, the water molecules have a larger degree of freedom in the multilayer. Similarly, the K_0 values are greater than 1 due to higher molecule's entropy of the molecules in the bulk liquid. K_0. values are larger than C_0 values because of a more significant entropic contribution due to the strongly increased number of configurations and mobility of molecules in the bulk liquid compared to molecules in the multilayer.

Table 7. Enthalpy differences and entropic accommodation factors between the monolayer and multilayer (ΔH_C, C_0) and between the bulk liquid and the multilayer (ΔH_K, K_0).

Pulp	$\Delta H_C \pm d\Delta H_C$ (kJ/mol)	$C_0 \pm dC_0$ (adm)	$\Delta H_K \pm d\Delta H_K$ (kJ/mol)	$K_0 \pm dK_0$ (adm)
1	7 ± 1	0.5 ± 0.2	−3.3 ± 0.2	2.9 ± 0.2
2	12 ± 3	0.2 ± 0.01	−2.1 ± 0.6	1.7 ± 0.4
3	16 ± 4	0.02 ± 0.01	−2.4 ± 0.6	2.0 ± 0.5
4	13 ± 3	0.2 ± 0.01	−3.0 ± 0.4	2.6 ± 0.4
5	13 ± 5	0.2 ± 0.01	−2.7 ± 0.2	2.3 ± 0.2
6	16 ± 5	0.02 ± 0.01	−2.9 ± 0.4	2.4 ± 0.4
2K	7 ± 1	0.7 ± 0.03	−2.0 ± 0.9	2.0 ± 1.0

The net isosteric heat of sorption is an important thermodynamic parameter, which measures the binding energy of the forces between the water vapor molecules and the absorbent material. It gives useful information regarding the sorption mechanism, since it can help to interpret the type of water binding that is occurring at a given moisture content [15,16,30–33]. The results presented in Figure 3 show the existence of three classes of water with a continuous transition from tightly bound water to free water molecules. In the monolayer region, water molecules are tightly bound to the material, corresponding to high interaction energy (high Q_{st}^{net} values). At increasing moisture content, net isosteric heat of sorption decreases, since most active sites become occupied and sorption occurs on the less active sites, which results in lower heats of sorption. Ultimately, Q_{st}^{net} approaches zero, which indicates that the total heat of sorption is equal to the heat of vaporization of pure water, i.e., the region where adsorbed water molecules behave as molecules in the liquid state with properties like those of the bulk liquid. The knots effect is well evidenced in Figure 3 for **2K** pulp, as there is a noticeable decrease in isosteric heat of adsorption in the monolayer region. This result is in accordance with the previous conclusion, i.e., the binding energy between aggregated fibers in knots and water molecules is weaker when compared to well-separated fiber-water binding forces. The maximum net isosteric heat of sorption, which can be theoretically defined as $Q_{st,max}^{net} = \Delta H_C + |\Delta H_k|$ [14], can be associated to physical interpretation of GAB parameters: Q_{st}^{net} and ΔH_C are related to sorption energy in monolayer and ΔK is related to multilayer interactions. In fact, a higher monolayer sorption enthalpy (ΔH_C) corresponds to a higher value of $Q_{st,max}^{net}$ (e.g., in the case of **3** and **6** pulps, Figure 3). It was also found a clear relation between Q_{st}^{net} and $|\Delta H_K|$: **3** and **6** pulps have the lowest multilayer sorption enthalpy, i.e., lower $|\Delta H_K|$ and, consequently, Q_{st}^{net} reaches zero at lower moisture content, demonstrating that these have a less structured multilayer and their water molecules have properties that are similar to bulk liquid.

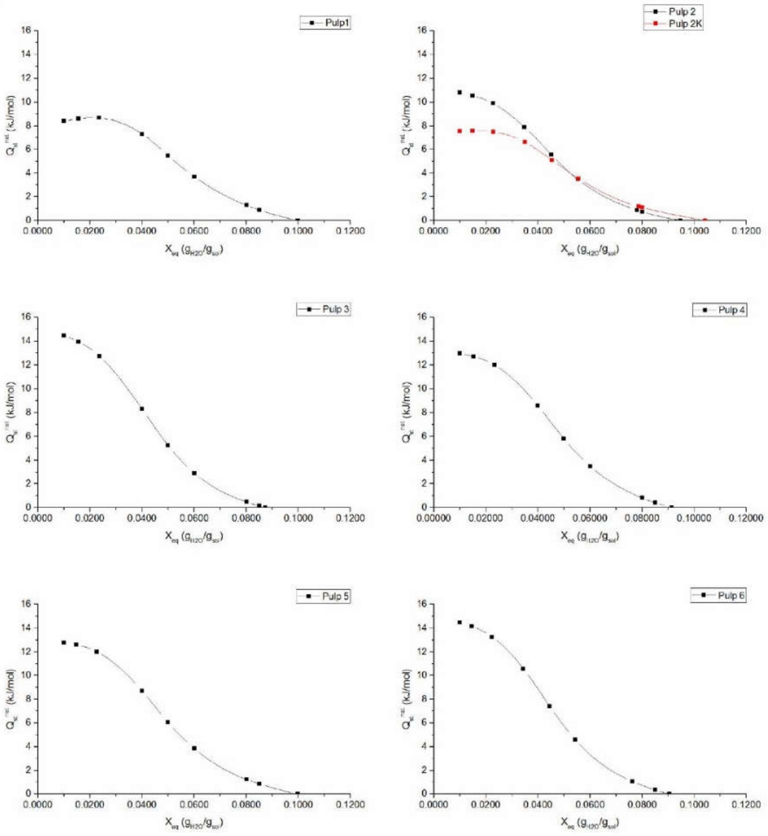

Figure 3. Net isosteric heat of sorption as function of moisture content derived from experimental sorption data for each pulp.

The fraction of occupied sites in the monolayer, ξ^{l_1}, plotted as a function of water activity, evidences the assumption of incomplete surface coverage of the adsorbent material and the formation of the multilayer (Figure 4). At low water activity values, the surface has more available sites for the water molecules to form hydrogen bonds with the surface and, therefore, there is a more pronounced growth in ξ^{l_1} at low relative pressure (up to a_w = 40%). As the monolayer of water molecules forms, the surface becomes less accessible due to the "jamming" of the adsorbate water molecules, favoring bonds between water molecules instead of bonds between water molecules and the surface [21]. For each pulp, the maximum fraction of occupied sites in the monolayer is higher than 96%, which indicates good surface affinity of the absorbent material for water molecules. As could be expected, by analogy with X_m, ξ^{l_1} values were negatively affected by temperature, especially at relatively low a_w (≤ 40%) (Figure 4).

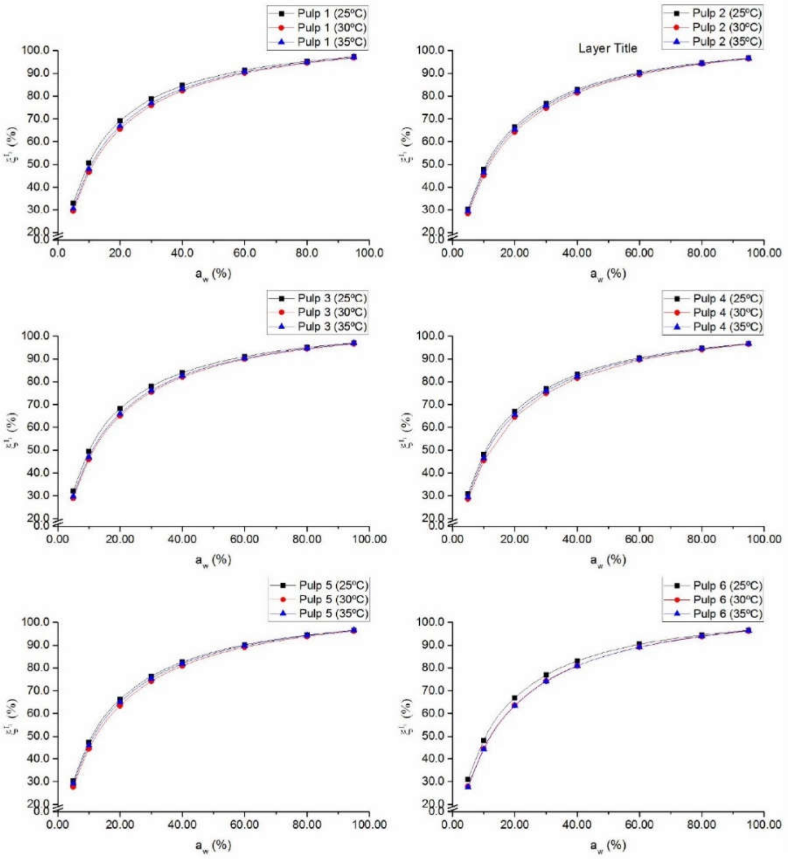

Figure 4. Fraction of occupied sites in the monolayer (ξ^{l_1}) for **1–6** pulps as a function of water activity at 25, 30, and 35 °C.

3.2. Contact Angles of Pulps

Contact angles, θ, were measured on laboratory pulp handsheets with smooth surface in order to minimize the effect of surface roughness. At least similar roughnesses were detected for all samples when evaluated by known Bendtsen test according to ISO 8791/2:2013, making the results of contact angle tests comparable. Contact angles varied between 17° and 27° (Figure 5), thus demonstrating common strong pulp wettability, as solid-liquid attraction largely prevailed over the liquid-liquid one [34]. The contact angles, that reflect the wettability of the handsheet surface, must relate to the affinity of the pulp fibers for water (i.e., X_m and S). Figure 5 shows that the wettability of the handsheet's surface is clearly related to fiber's affinity for water: the sheet with lower contact angle has been produced from the pulp that has better ability to retain water molecules on their surface (higher value of X_m). Hence, a surface with fibers that are more accessible to form hydrogen bonds with water provides higher hydrophilicity to the pulp, which, in turn, correspond to lower contact angles measured on handsheets formed from it. The experimental results unambiguously confirm that the wettability of the pulp handsheets and the affinity of the fiber surface with water are inextricably related. Pulps with extreme contact angles (e.g., **1** pulp with $\Theta = 17°$ and **6** pulp with $\Theta = 27°$, Figure 5) did not correlate univocally with their chemical composition (amount of hemicelluloses or carboxylic moieties, Table 1), or with their basic fiber morphology (average fiber length/width or coarseness, Table 2). On the other hand, a tendency of pulp´s contact angle to increase with fiber´s deformation (curl and kink, Table 2) was clearly traceable ($r^2 = 0.7$–0.8, figure not shown).

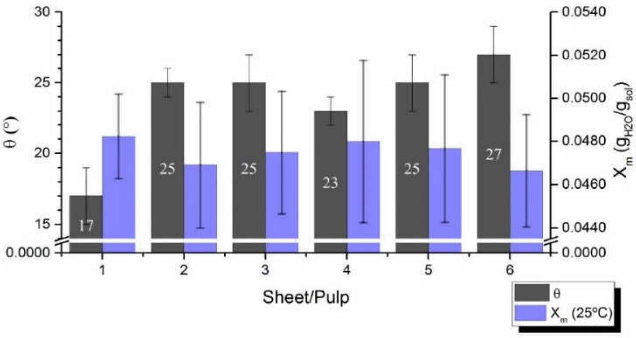

Figure 5. Monolayer capacity (X_m) of **1**–**6** pulps at 25 °C and the average contact angles of corresponding handsheets.

The deformations of the pulp fibers, such as curl and kink, are mostly irreversible being caused by distortion and compression of the fibril layers [35–37]. The misalignment of the fibril lamellas lead to wavy layers (Figure S1, Supplementary Materials), where some adjacent surfaces in the creases approach each other, forming intrafiber cross-links by hydrogen bonding of free hydroxyl groups [37]. As a consequence, the accessible area of the damaged fibers can be slightly reduced, which caused the lower monolayer capacity and the wettability of the fiber mesh, resulting in Θincrease. On the other hand, the surfaces of deformed fibers, which contain partially disordered cellulose fibrils, are more accessible when compared to surfaces of non-deformed fibers [36]. This fact can explain the larger ΔHc (Table 7) and Q_{st}^{net} (Figure 3) of more curled and kinked pulp fibers (Table 2) observed experimentally. These accessible surfaces of deformed fibers can also readily form the intensive hydrogen bonds between the fibers in the handsheets, thus contributing to the reduction in paper surface wettability (increases in Θ). Therefore, the contact angle of the fiber web reflects the apparent wettability of the surface and not necessarily just the intrinsic contribution of the constituent fibers [38]. Nevertheless, the contact angle is one of the most common and reliable analyses for assessing the wettability of cellulosic materials.

3.3. Capillarity Absorption

Porosity (ε), specific volume (v), absorption capacity (C_{abs}), and absorption time (t) of **1**–**6** pads without knots and **1K**–**6K** pads with knots revealed notable differences, depending on the fiber network structure in pads (Table 8). These differences influenced the absorption properties. Thus, the knots turn the fiber network much more compact (less bulky), negatively affecting the porosity of air-laid pads. However, this fact did not lead to the expected drop in C_{abs} of pads formed from knotted pulp compared to knotless one (Table 8), although within a series of **1–6** or **1K–6K** pads some tendency to decrease of C_{abs} was observed with the decrease in the specific volume of the pad. Furthermore, predicted by Equation (2) the maximal absorption capacity (C_{am}) of pads was more than five times greater than those obtained experimentally. This apparent discrepancy can be explained by the collapse of pad pores upon wetting. The contraction of the volume of the pad occurs essentially under the gravity of the absorbed liquid, due to the low mechanical resistance of the wet mesh [12]. Hence, the C_{abs} depended significantly on the strength of network under wetting. In this context, a certain positive effect of knots on the C_{abs} can be explained by the inclusion of rigid fiber bundles in the network that preserve it from collapse under moistening. As already pointed out, the accessibility of fibers within the knots is not much worse than that of disintegrated fibers (Figure 2). However, the monolayer sorption enthalpy (ΔH_C) and the net isosteric heat of sorption (Q_{st}^{net}) of fibers in knots are lower than those of well-separated fibers (Figure 3 and Table 7), due to the more intense interfiber interactions in the formers. This, together with lower pore size inside than outside of knots, must lead to the lower penetration rate of water into the pad (Equation (1)). Such behavior was experimentally confirmed for most of the evaluated pulps (Table 8).

Table 8. Porosity, specific volume, absorption capacity and absorption time of pads formed from pulps without (**1–6** pads) and with (**1K–6K** pads) knots.

Pad	*Knots* (%)	ε (%)	ν (cm^3/g_{sol})	C_{abs} (g_{H2O}/g_{sol})	t (s/g_{sol})
1	-	98.2 ± 0.1	18.3 ± 0.1	11.0 ± 0.1	0.95 ± 0.01
1K	26.9	97.8 ± 0.1	13.4 ± 0.1	11.2 ± 0.1	0.82 ± 0.01
2	-	98.3 ± 0.1	20.6 ± 0.2	11.3 ± 0.1	0.47 ± 0.01
2K	25.0	98.2 ± 0.1	16.4 ± 0.1	12.2 ± 0.2	0.59 ± 0.01
3	-	98.3 ± 0.1	20.6 ± 0.2	11.1 ± 0.1	0.60 ± 0.01
3K	24.9	98.2 ± 0.1	17.3 ± 0.1	10.8 ± 0.1	0.61 ± 0.01
4	-	98.2 ± 0.1	19.9 ± 0.1	10.9 ± 0.1	0.83 ± 0.01
4K	20.0	98.1 ± 0.1	15.2 ± 0.1	10.7 ± 0.1	0.91 ± 0.01
5	-	98.2 ± 0.1	20.3 ± 0.2	11.1 ± 0.1	0.61 ± 0.01
5K	26.2	98.1 ± 0.1	16.7 ± 0.1	11.4 ± 0.1	0.56 ± 0.01
6	-	98.3 ± 0.1	20.9 ± 0.1	11.6 ± 0.1	0.41 ± 0.01
6K	22.5	98.2 ± 0.1	16.4 ± 0.1	11.7 ± 0.1	0.50 ± 0.01

According to common knowledge, the strength of the network becomes better when using longer, coarser, and curvier fibers [10,12,39]. Among six examined pulps, which were obtained from the same wood specie and by similar processing mode, the fiber length/width and coarseness varied little (Table 2). However, the fiber deformation parameters of pulps (curl and kink) varied quite substantially. The minimal fiber deformations were registered for **1** pulp and the maximal for the **6** pulp. These pulps have the opposite surface affinity for water in terms of X_m, ΔH_C, Q_{st}^{net} and contact angles (Tables 3, 7 and 8 and Figures 3 and 5) and demonstrated the opposite absorption capacity and the absorption rate (Table 8). Contrary to expectations, more hydrophilic **1** pulp showed less absorption capacity and absorption rate than less hydrophilic **6** pulp. The only explanation is the structure of the fiber network of **6** pad**,** comprised of fibers that are more curled, kinked, and coarser than those of **1** pad, which promoted a more bulky/porous and robust structure than that formed in the **1** pad. Therefore, the structure of the fiber network is a more important factor affecting absorptivity than the intrinsic hydrophilicity of the constituent fibers, at least in the range of contact angles of ca. 15–30°.

On the other hand, the better absorption capacity and the absorption rate of **2** and **6** pulps in relation to **3** and **5** pulps does not match well to the proposition that the structure of the network is a unique dominant factor, because ε, υ, and the main deformation parameters of the fibers in pulps (curl and kink) did not vary significantly as to justify this assumption (Tables 2 and 8). At the same time, **2** and **6** pulps had one of the highest contents of carboxylic groups, which mainly belong to the glucuronoxylan that is present in the pulps (Table 1). The latter suggests that the chemical composition of the fibers also has an important contribution to absorption, because it is known that hemicelluloses and other components containing carboxylic moieties contribute largely to the swelling of the pulp [10,40]. The swelling of the polymeric network is one of the basic mechanisms in the absorption by porous materials [10,41].

Interestingly, the **4** pulp containing the high amount of the hemicelluloses and carboxyl groups (Table 1) and having the coarsest and most deformed fibers among the examined pulps (Table 2), allowing for porous and bulky pads, showed the worst absorption capacity, and the lowest absorption rate (Table 8). At least partially, these findings can be explained by the smaller number of knots in **4** pulp (Table 8) and one of the shorter lengths of fiber (Table 2).

The relationships between the surface properties of the pulp fibers, their chemical composition, and morphology with respect to the absorption capacity of the resulting air-produced formulations are not straightforward and multi-dependent, as can be seen from the above reasoning. To better trace these relationships, statistical analyzes of the absorption capacity in relation to the pulp properties were performed.

3.4. Multivariate Analysis

Principal component analysis (PCA) was used to monitor the main relationships between the absorption capacity of the studied pulps and their surface properties, chemical composition, and fiber morphology (Figure 6). The PCA reflects the correlation between the variables, expressing their contribution to the two principal components (PC), in terms of relative variation. Thus, two variables that are located at the same quadrant indicate a positive correlation, since them positively or negatively contribute to the two PCs, and this correlation is as stronger as closer they are. When located in opposite quadrants, two variables present have a negative correlation with each other, because they translate into opposite effects for the PCs. When located in parallel quadrants, two variables apparently have the same contribution to one PC and the opposite contribution to the other. However, it is necessary to consider the total variation that is explained by each of the PCs. In this case, component 1 (PC1) explains 69.9%, while the component 2 (PC2) explains only 14.9% of variations (Figure 6). Therefore, the correlations between the different variables will be analyzed, especially in relation to their contribution to PC1 describing mainly the fiber network properties.

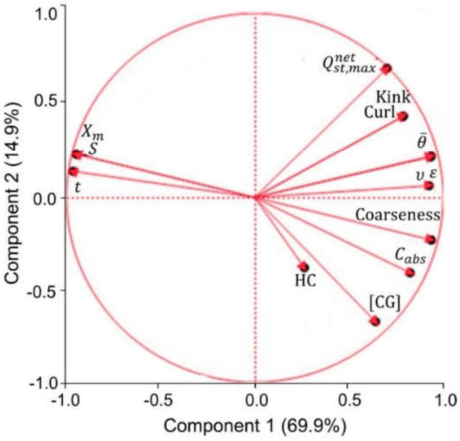

Figure 6. Principal component analysis (PCA) diagram elucidating the structure-property relationships of kraft fluff pulps **1–6**.

In general, the PCA supports previous conclusions that the affinity of the fiber surface with water, expressed by X_m and S and the surface wettability (measured by the contact angle, Θ), are not necessarily related to the improved capillarity absorption properties (C_{abs} and t). In fact, statistically, X_m and S have positive correlation with absorption time (t) and negative correlation with absorption capacity (C_{abs}). The opposite effect is verified in relation to the correlations between the average contact angle (θ) and these absorption properties. The PCA also shows that higher coarseness correlated with the lower accessible surface area (S) and the monolayer capacity (X_m) and the increased fiber deformations (kink and curl) to the lesser wettability of handsheet's surface, i.e., larger contact angles (Figure 6). The reasons for such correlations have been previously discussed when analyzing the affinity of the pulp surface with water (Section 3.2) and the relationship between the absorption capacity and the structure of the fiber network in air-laid pads (Section 3.3).

The expectable positive correlation was found regarding the presence of highly hydrophilic components in pulps (hemicelluloses and other polysaccharides containing carboxylic groups) and their absorption capacity (Figure 6). The absorptivity of pulps also positively correlated with fiber coarseness and, to a lesser extent, with curled and kinked fibers. In fact, the network with a higher coarseness of fibers usually exhibits better absorption properties, because these bulky fibers possess less interfiber bonding areas, resulting in a network with high specific volume, high porosity, and, therefore, improved absorbency. The positive contribution of deformed fibers to improve the specific volume (ν) and the porosity (ε) of air-laid pads has also been discussed previously and favored the pulp's absorption capacity. It is worth mentioning that the deformations of the fibers provided the greatest contribution to ν and ε of the pads. These deformations occurred during the production of kraft pulp, due to the variable cooking and bleaching processing conditions. These conditions also affected the chemical composition of pulp due to the variable degradation of hemicelluloses [42]. Dry defibration is another cause of fiber deformation, which depends on the manufacturing history, e.g., pulping and bleaching conditions.

Although the content of hemicelluloses (HC) in pulps is expectedly related to the carboxyl groups content (CG) (Figure 6), a much weaker relationship exists between the HC content and the absorption capacity (C_{abs}). HC usually contributes negatively to the air-laid fiber network strength due to the weakening of wet mesh, thus decreasing the network flexibility and leading to less curled fibers [8]. Consequently, the effect of HC on C_{abs} is not straightforward. On the one hand, HC favors the network swelling and water retention and, on the other hand, HC deteriorate the air-laid fiber network structure and strength.

HC contributed negatively to the wettability of the fibers in pads (negative contribution to PC2), according to the PCA data. Thus, the X_m and HC located, even in the opposite quadrants, indicating a negative correlation with each other (Figure 6). This feature is in line with the known fact that HC can negatively affect the wettability of the fiber web, resulting in an increase in Θ with the extent of HC present in the pulp [38,43,44]. The plausible explanation deals with intensive formation of hydrogen bonds between free hydroxyl groups on the surface of cellulose fibrils and amorphous hemicelluloses. As a result, the amount of free hydroxyl groups in the cellulose fibrils is decreasing and the interfibrillar space is reduced being filled with HC, thus diminishing the monolayer capacity of fibrils. The removal of moderate amounts of hemicelluloses can lead to better wettability of fibers, because the lower the hemicellulose content, the looser the cellulose fibrils network in fiber, and, consequently, fiber mesh will have higher specific volume and higher porosity. However, with a very low HC content, when the fibers are dried intensively, their surface is collapsed due to the intensive aggregation of fibrils within cell wall and the wettability of the fibers decreases [38,40]. Therefore, hemicelluloses can have both positive and negative effects on fiber wettability.

It is noteworthy that, among the studied pulps, the variations in HC content did not exceed 20% and the eventual direct relationship between the decrease in HC content (Table 1) and the increase in Θ of pulp fibers (Table 8) was not clearly detectable. It was recently reported that the capacity of pulp fiber to swell depends not only on the amount of hemicelluloses in eucalypt kraft pulp, but also on their location within the cell wall [45]. The last feature depended on the pulping severity, mainly the alkali load and the cooking temperature. Hence, it is reasonable to propose that the wettability and absorption capacity of kraft pulps in study also depended not only on the HC content, but also on the HC distribution in the cell wall of fibers.

4. Conclusions

The results of this work showed that the surface properties of industrially produced *Eucalyptus* kraft fluff pulp varied noticeably within the range of process conditions applied to the mill. In addition to wettability, the pulp fibers revealed significant morphological changes, mainly related to their deformations. The processing conditions also induced nearly 20% variability in knots content upon dry-defiberization of kraft pulps.

Despite the similar accessibility of non-agglomerated fibers and fibers agglomerated in knots, the latter have less isosteric heat of adsorption in the monolayer than the former and, therefore, possess less wettability. This, together with relatively low porosity, reduces the absorption capacity and increases the absorption times of air-laid formulations containing knots. At the same time, the better wettability of the fiber surface not necessarily related to the improved capillary absorption. The last largely depended on the fiber network structure, which, in turn, is affected by fiber morphology and the chemical composition of the pulp. The highly porous fiber network possessing high network strength and, less deformable when wetted, meets the best requirements for that purposes. The pulp production conditions favoring more coarse and deformed fibers (curled and kinked) are of great preference to produce a fluff pulp with good absorption capacity. The deformed fibers showed less monolayer capacity and the accessible surface, but higher isosteric heat of adsorption in the monolayer, when compared to non-deformed fibers. The last fact was explained by more disordered cellulose fibrils on the surface of deformed fibers, due to the distortion, compression, or even partial rupture of cellulosic lamellas.

The effect of hemicelluloses on fluff pulp adsorption is quite ambiguous. Despite improved water retention by hemicellulose-rich fibers, hemicelluloses provide less wettable fiber surface and weaken the air-laid fiber network under humidification. According to literature evidences, hemicelluloses decrease the deformability of fibers, thus resulting in less porous and less strong fiber network in air-laid formulations. Accordingly, the industrial conditions leading to pulps with diminished hemicelluloses content can be advantageous for the absorption properties of fluff pulps.

However, additional work is needed to more clearly trace the relationships between the fiber surface properties and their network parameters and absorptivity, using pulps from different production histories with a wider range of variation in the chemical composition and morphology of the fiber.

Supplementary Materials: The following supplementary data are available online at http://www.mdpi.com/2571-9637/3/3/20/s1, Figure S1: Schematic representation of a cellulosic fiber possessing curl (A) and kink (B) deformations.

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Potential of bleached eucalyptus kraft pulp for applications in nonwoven fibrous fabrics

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Abstract

A series of six industrial bleached hardwood kraft pulps produced from *Eucalyptus globulus* (BEKPs) under variable process conditions were dry-defiberized on a pilot scale hammermill at 3500 rpm and the nonwoven air-laid fabrics evaluated for their specific volume, absorption capacity/absorption rate and fiber network strength. The effect of non-defiberized fiber aggregates (knots) on the former properties was evaluated. Processual variations in pulping and bleaching conditions revealed variability within 15% in the absorption capacity of fluff pulps and within 25% in the network strength of the air-laid formulations. These variations were attributed to changes in the chemical composition of BEKPs and fiber morphology. The importance of pulp bleaching sequence on the quality of BEKPs for fluff applications was highlighted. BEKPs, having a high residual xylan content with a greater amount of uronic/hexenuronic moieties and coarser/deformed fibers, revealed the best performance in fluff applications. The coarseness was considered a critical morphological parameter of the fibers, strongly affecting the porosity of air-laid formulations, which determined the absorption capacity and the network strength. The absorption capacity of fluffed BEKP was comparable of commercial softwood bleached softwood kraft pulp (BSKP), although the latter showed almost triple the network strength of air-laid formulations produced with BEKP. BSKP proved to be much more vulnerable to dry defiberization conditions than BEKP and suffered a pronounced cut of fibers, producing larger amounts of fines (dust) and stronger undesirable peeling and straightening of fibers. BEKPs can be considered a promising raw material for fluff applications, whose basic properties can be adjusted according to the needs by varying conditions in the pulping and bleaching process steps.

Keywords

Absorption capacity, network strength, fluff pulp, fiber morphology, dry defiberization

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Introduction

Currently, the market for printing and writing papers is gradually decreasing due to the advanced development of electronic and digital media in modern societies.[1] Thus, in order to maintain the sector's sustainability, considerable attention is paid to new applications of cellulose pulp that are not related to papermaking. Besides dissolving pulps used for the production of rayon fibers, increasing attention

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is paid to the production of pulp fibers used for convenience items after being dry-defiberized (fluff pulps). These nonwoven fabrics constituted of fluff pulp include disposable diapers, female hygiene/care products, surgical pence, absorbent toweling, and adult continence.[2] Fluff pulp is made essentially of softwood cellulosic pulps, which are produced by sulfate (kraft) or sulphite pulping and should be easily dry-defiberized.[2,3] The softwood fluff pulps contains long cellulosic fibers (2–5 mm) possessing good absorptivity and the mechanical strength of air-laid formulations, but are difficult to defiberize and produce dust. Short fiber (*ca.* 1 mm) hardwood fluff pulps are an attractive alternative to softwood pulps though their applicability to air-laid formulations is much less studied.[3,4]

In the early 1980's, a wide use of so-called synthetic superabsorbents (SAPs) has resulted in a noticeable decrease of cellulosic fluff pulp content in certain hygienic products. However, more than 95% of SAPs are synthetic polymeric materials (mainly cross-linked polyacrylates) produced from non-renewable sources, which end disposal creates huge environmental concerns.[5] Furthermore, these SAPs do not contribute to the integrity of the absorbent non-woven fabric and, therefore, it has become important that the cellulosic fibers involved can contribute to the compression resistance in the absorption cores of hygienic products. Accordingly, significant efforts are made to develop new materials based on predominantly biodegradable natural resources that can fulfill the necessary functions in the absorption core of a disposable diaper. The key function of the cellulosic fiber in the core of a diaper, still containing up to 15% SAP, is to acquire and distribute the fluid in the core in a manner that it can be stored in the superabsorbent polymer.[6,7]

Total global fluff pulp demand is growing around 3–4% per year being induced by the improvement of living standards, demographic trends and economic growth of developing countries.[3] More than 90% of all fluff pulps are fully bleached chemical pulps, of which more than 90% are kraft pulps. The contribution of chemi-thermomechanical pulps (CTMP) is less than 10%. The web formation, wet pressing and drying of fluff pulps differ from the same production operations of conventional paper grade pulps. Moreover, these steps are critical for the quality and processability of the final product.[8,9] The conventional fluffs are derived from long-fiber coniferous species, such as southern yellow pine, known on the market as southern bleached softwood kraft pulp (BSKP).[2,3] Over time, the global fluff market has become increasingly centered on BSKP due to the grade's superior performance in absorbent hygiene applications and relatively low production costs. However, other raw materials and processes, such as softwood CTMP (chemi-thermomechanical pulps) and hardwood kraft pulps, are of growing technical and economic interest.[3,10,11]

The fluffiness (bulkiness of loosely laid fibers) and moisture absorption are the two most important quality parameters of the fluff pulp. According to its functionality, the fiber has the inherent characteristics of bulk, softness and high absorption. The intrinsic absorbency of fluff pulp, aside from its hydrophilic nature, is largely due to the length, diameter and stiffness of its fibers. Fluff pulps with an appropriate network structure and fiber's strength can carry a large amount of SAP, thus allowing a higher moisture absorption capacity. For application in absorbent products, cellulose fiber should have an increased length and strength, and the fluff pulp sheet requires a suitable burst resistance. A good network strength is generally obtained if, during the dry defiberization of a fluff pulp, the fibers are well separated with no formation of dense aggregates of fibers called knots. Therefore, a low knot content is assumed as a basic objective, with the lowest possible defiberization energy consumption, keeping the fibers intact. Excessive consumption of energy does not only result in economic losses, but also in other drawbacks, such as decreasing fiber lengths, dust formation and electrostatic charging of fibers, which in turn hampers the formation of an even web.[12,13]

The basic characteristics of hardwood fluff pulps, such as knot's contents, absorption capacity, wet compression behavior and network strength in an air-laid product can be improved by setting the conditions of pulp production and changing the pulp composition or by chemical modification of the pulp.[10,14] At the same time, the potential of *Eucalyptus globulus* bleached kraft pulp for such kind of applications is still little known. In this study, a set of typical paper-grade Bleached Hardwood Kraft Pulps from *E. globulus* wood (BEKPs), kraft cooked and Elemental Chlorine Free (ECF)/Totally Chlorine Free (TCF) bleached under variable industrial conditions, were evaluated for the fluff pulp applications and compared with the properties of commercial fluff BSKP.

Experimental

Kraft pulps

Six produced eucalypt (*Eucalyptus globulus*) kraft pulps, kraft cooked and ECF/TCF bleached at extreme industrial conditions at the CELBI SA kraft pulp mill (Leirosa, Portugal) were pre-selected to cover all the gamma of typically applied technological conditions. Changes in cooking conditions included some variations in temperature and the alkaline profile of the continuous digester. All pulps were delignified with oxygen before bleaching (two sequential O stages). The variations in the ECF (D_{hot}-E_P-D-P) and TCF (Q-(P_O)-P-P) pulp bleaching consisted of alterations in the temperature and reagent's profiles (D and P designate the chlorine dioxide and hydrogen peroxide stages, respectively, and E is the alkali extraction stage). H1, H2, H3, H5 and H6 were ECF bleached pulps and the H4 pulp was TCF bleached. Pulps were not subjected to any treatments with auxiliary reagents (e.g. debonding agents). These H1-H6 pulps and a reference industrial BSKP fluff pulp C1 were thoroughly characterized for the chemical composition, fiber morphology, intrinsic viscosity and physical properties.

Dry defiberization

The pulp sheets were torn into small pieces (width ≈10 cm) and dry-defiberized by two-step procedure in a pilot-scale hammermill (Schuttle Buffalo, Model W6H, Buffalo) operated at 3500 rpm. In the first step, the disintegrated fibers had to pass in a mesh with 5 mm openings and then in a mesh of 2 mm in the second step. All fluff pulps were thoroughly characterized for the fiber morphology, knots content, network strength, and for the absorption time and capacity.

Analyses of kraft pulps

The pulps were analyzed for the composition of neutral sugars as alditol acetates by GC after the Saeman hydrolysis.[15] Sugar analysis was performed using a DB-225 J&W analytical column (30 m × 0.25 mm id, 0.15 µm film thickness) on a GC chromatograph (Thermo Fisher Scientific Focus GC series) equipped with an FID detector, using a nitrogen carrier gas, with an injector temperature of 225°C, column temperature of 220°C and detector temperature of 250°C. The determination of the total amounts of acidic group content (the sum of carboxylic and sulphonic acid groups) in pulp was carried out by conductometric titration according to SCAN-CM 65:02. The hexenuronic acid residues content was assessed by UV-vis method after the hydrolysis with sodium formate buffer at pH 3.[16] The fiber morphology of the dried fibers before and after defiberization were analyzed on a Kajaani FS300 fiber analyzer (Espoo, Finland). At least five determinations were carried out for each sample and the results were averaged. Viscosity (intrinsic viscosity) was determined according to a standard procedure, as described in ISO 5351:2010. Isotropic handsheets with a target grammage of 65 g/m^2 ± 2 g/m^2 were produced according to ISO 5269-1 using a conventional semi-automatic Rapid–Köthen sheet former. The laboratory handsheets were conditioned at 23 ± 1°C and 50 ± 2% relative humidity (RH) before and during the tests, in order to evaluate the structural, optical and mechanical properties. The main physical properties were evaluated according to standard ISO procedures, for example, the tensile strength index according to ISO 1924-2:2008, tear resistance according to ISO 1974:2012 and burst resistance according to ISO 2758:2001.

Analyses of fluff pulps

Knot percentage was determined using a RETSCH® sieve shaker adapting to the norm SCAN-CM 37:85. This device uses a series of standard ASTM mesh screens to separate fluff into knots and accepts. In this test procedure, knots are the fraction that is retained on an ASTM 12 mesh screen. The equipment for the formation of pads, a test piece former (described in more detail in the norm SCAN-C 33:80), is shown schematically in Figure 1. In a typical procedure, 3.0 g of defiberized fibers were introduced through the inlet tube (1) and further disintegrated in the funnel. The continuous suction of air forced the fibers to pass to the support of the pad. The apparatus is connected to a vacuum line maintaining a constant air stream from the inlet to the outlet tube, applying a pressure difference of 0.14 bar. The formed pulp pads had a diameter of 50 mm. After adjusting the pulp weight to exactly 3.0 g, the pad was subjected to absorption and specific volume tests and measurement of the absorption time under a constant pressure of 2.5 kPa applied to the pad. By weighing the wet test piece, the absorption capacity was calculated as the relative increment of the pad mass before and after the soaking in water.[17]

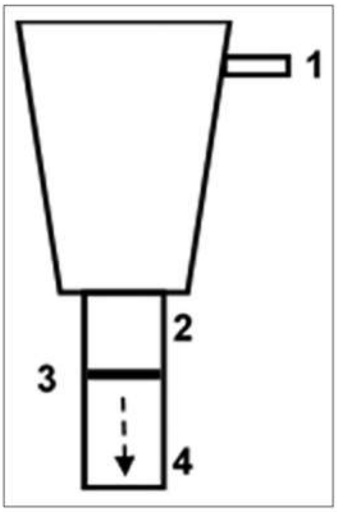


Figure 1. Schematic overview of test piece (pad) former.
1 – Fiber feed; 2 – Pad holder; 3 – Wire screen; 4 – Air suction.

The network strength was examined using air-laid formed pads (according to SCAN-C 33:80) on the sample crash tester SC-500 (IDM, Spain). Figure 2 illustrates the experimental design. A cylindrical test piece having a weight of 3.0 g and a diameter of 50 mm is prepared in an air-laid former as described above. The test piece is placed in a burst chamber installed in a stress-strain apparatus operated in compression mode with a velocity of 100 mm/min. A piston (diameter 2.0 cm) was then forced through the pad and the highest force was recorded just before the pad ruptures. This force, required to burst the test piece, was registered and reported as the strength of the pulp network.

The specific volume, absorption time and absorption capacity were determined accordingly to SCAN-C 33:80. This SCAN-test method describes the preparation of test pieces of fluff pulp and a procedure for their use in determining the specific volume and the absorption properties. A fluff specimen of about 3.0 g mass and 50 mm diameter is prepared using the air-laid former by sucking the material from a container through a cylindrical enclosure onto a fine wire screen according to the method described previously (Figure 1). The test piece was placed on a perforated plate in contact with fluid, in a vertical position and at a load of 2.5 kPa, as shown in Figure 3. The height of the specimen was determined before the fluid contacts the material. The test piece was then allowed to absorb water (25 ± 1°C) from below and the time required for the waterfront to reach the top surface was measured and reported as the absorption time.

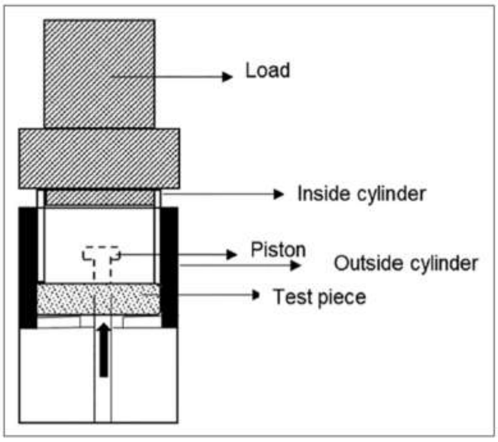


Figure 2. Schematic overview of instrument used to measure the network strength.

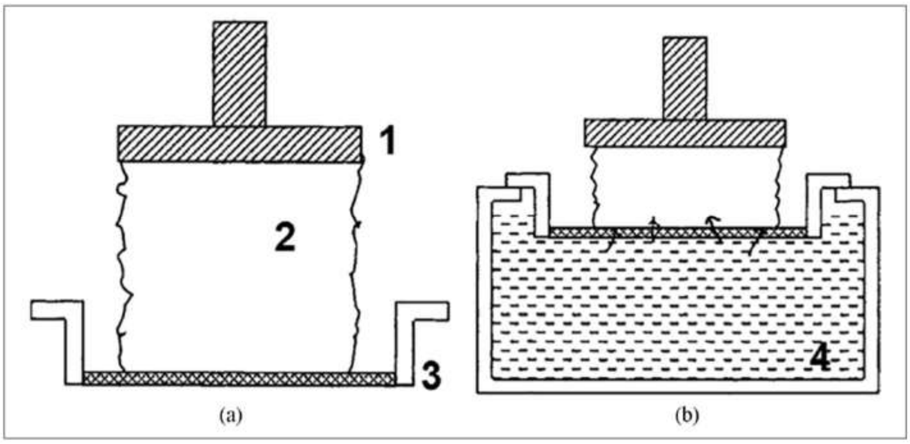
In a water retention test, a sample of defiberized pulp (0,200 g ± 0,005 g oven-dry weight) was sealed inside a heat sealable teabag and submerged in a 0.9% saline solution for 30 minutes at 22 ± 2°C. After 30 min saturation time, the bags were let drip for three minutes. Thereafter, the fluff pulp samples were placed in a centrifuge bucket and centrifuged at 3000 rpm for 3 minutes (22 ± 2°C). Immediately after stopping the centrifuge, the test pad is transferred to a pre-weighed glass plate and weighed. The water retention value (WRV) is defined as the weight of retained water per gram of dry pulp (g/g).

Results and discussion

Composition and properties of kraft pulps

A series of six industrial BEKPs (H1–H6) produced under varied cooking and bleaching conditions were pre-selected to cover the gamma of typically applied technological parameters. A commercial bleached loblolly pine softwood fluff pulp C1 was used for the comparative reasons. Pulps H1, H2, H3, H5 and H6 were bleached by Elemental Chlorine Free (ECF) sequence $\mathrm{OOD_{H}(P_{O})D_{1}P}$, whereas H4 pulp was bleached by Total Chlorine Free (TCF) bleaching sequence $\mathrm{OOQ(P_{O})PP}$. Some physical properties of examined pulps are presented in Figures 4 and 5.

Despite similar origins of unbeaten eucalypt pulps, they still showed about 20–35% variations in their basic strength properties. Tensile strength is defined as the breaking force divided by the width of the paper strip. The nature of the



(a) (b)

Figure 3. Test for the absorbency performance of a fluff pulp. The image on the left (a) shows a pad before wetting under a 2.5 kPa load supplied by a pressure plate 1, where 2 is a tested sample and 3 is a perforated plate. The image on the right (b) shows the sample immersion in water from bath 4 (accordingly to SCAN-C 33-80).

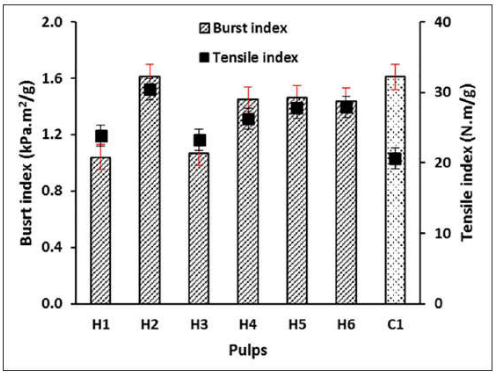


Figure 4. Results on burst and tensile index of eucalypt kraft H1–H6 pulps and softwood kraft C1 pulp.

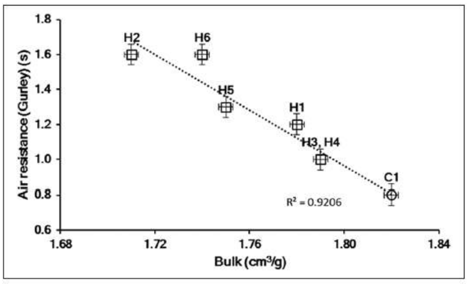


Figure 5. Correlation between air resistance (Gurley test) and the bulk of eucalypt kraft H1–H6 pulps and softwood kraft C1 pulp.

breaking (fracture) is dependent on the degree of the bonding in the paper sheet. A high degree of bonding leads to a large propagation of fiber breaks, whereas a poorly bonded fracture zone is when fibers are pulled out of the network as the fiber-fiber bonds break.[18] Figure 4 clearly shows that H2 pulp has the highest tensile and burst index while H1 and H3 pulps have the lowest values. The H4–H6 pulps showed similar resistance properties, being intermediate to those detected for H2 and H1/H3 pulps. This may be due to the particular combination of pulping and bleaching conditions. Despite the high burst index of the softwood C1 pulp, the tensile index value is one of the lowest. This behavior may be explained by the morphologic characteristics of the pulp. The last are reported to be dependent on lumen width, fiber diameter, specific gravity, Runkel ratio, percentage of fines and coarseness.[19,20] Softwood fibers are larger and thicker than hardwood fibers and form limited bonding areas between the fibers in the web. Bursting strength is mainly affected by the way in which fibers are bonded together in paper sheet, where fiber length and fine elements account for 99.9% and 98.9% variations in the burst index respectively.[21] Softwood fibers are much longer than the ones observed in hardwood and form a greater number of contacts between the fibers, thus demonstrating a reasonable burst resistance, even of unbeaten pulps.

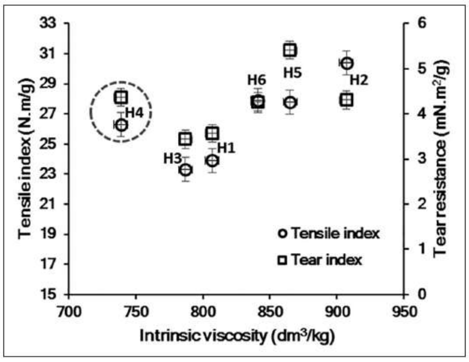


Figure 6. Dependence of tensile strength (○) and tear resistance (□) on the intrinsic viscosity of eucalypt pulps. The TCF H4 pulp was out of the general trend of other ECF pulps and marked with a circle.

Figure 5 illustrates a good correlation ($R^2 = 0.9206$) between air resistance and bulk in both hardwood and softwood pulps. Probably, fibers from softwood pulp (C1) are not only longer, but also more collapsed when compared to fibers of H2 and H6 pulps, because the former pulp has a lower tensile strength. Collapsed fibers that arose under hornification are less flexible and have a lower bonding area, therefore they will create a network with much lower density and higher bulk.[22] Wood fibers have circular or rectangular cross sections, but may flatten or collapse during the web forming. Under lateral pressure, such as wet pressing, drying or calendaring, the pulp fibers collapse and change the tube structure into a double-layered strip.[23] In addition, softwood pulp has coarser fibers that should create a web with higher porosity and bulk compared with the collapsed ones. The paper made of collapsed fibers usually have higher bending stiffness and is easier to dewater.[24] At the same time, softwood long-fiber pulp demonstrated a predictably higher tear strength (14.4 mN.m²/g for pulp C1 and around 3.0–5.0 mN.m²/g for H1–H6 pulps), due to the higher number of fiber-fiber contacts in the mesh than in short-fiber hardwood pulps.[22–24]

Most of the strength properties are affected by the degree of polysaccharide degradation during pulping and bleaching operations. A clear dependency of tensile strength and tear resistance from the intrinsic viscosity of ECF bleached eucalypt pulps is demonstrated in Figure 6. It is noteworthy that TCF-bleached eucalypt pulp (H4), suffered the excessive oxidative depolymerization of polysaccharides[25] and was out of this trend.

A clear relationship was noted between the pulp's intrinsic viscosity and the content of carboxylic groups (Figure 7). In hardwood pulps, the amount of carboxylic groups is

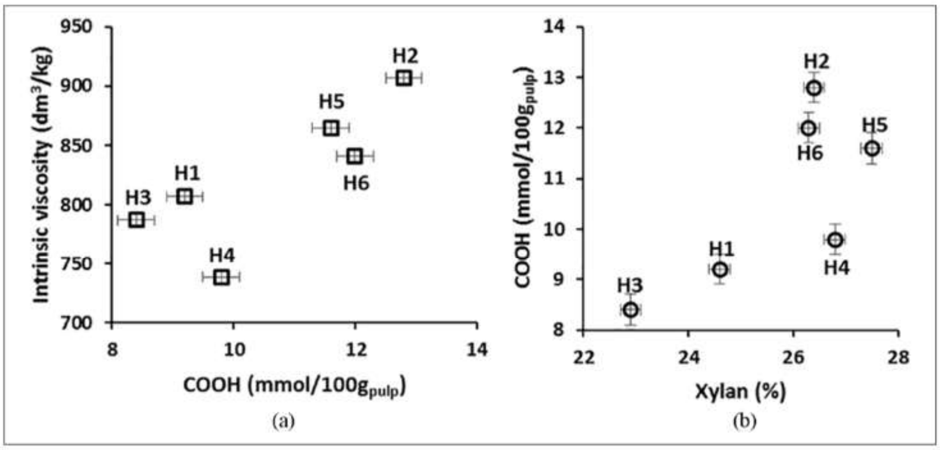


Figure 7. Relationship between carboxyl group content in eucalypt pulps and their intrinsic viscosities (left figure) and the xylan content (right figure).

Table 1. Monosaccharide composition and the carboxyl groups content in BEKPs and BSKP.*

Samples	Ramnose %	Arabinose %	Xylose %	Mannose %	Galactose %	Glucose %	HexA mmol/100g	COOH mmol/100g
H1	0.5	0.2	24.6	0.2	0.3	74.2	0.66	9.2
H2	0.5	0.2	26.4	0.2	0.3	72.4	2.00	12.8
H3	0.3	0.1	22.9	0.2	0.3	76.3	0.33	8.4
H4	0.5	0.2	26.8	0.2	0.3	71.9	3.40	9.8
H5	0.6	0.2	27.5	0.2	0.3	71.1	1.21	11.6
H6	0.4	0.4	26.3	0.4	0.5	69.4	0.59	12.0
C1	0.5	0.8	11.2	6.9	0.1	80.4	0.26	6.0

*The relative error in sugar analysis has not exceeded 3%.

mainly associated with the presence of glucuronoxylan, whose degradation depends upon the severity of cooking.[26] The positive effect of the carboxyl group content on the amount of xylan in the pulps, assessed by the sugar's analysis (Table 1), confirms this trend (Figure 7). Consequently, the positive relationship between the viscosity and the amount of carboxyl groups in the pulps could be explained by different pulping conditions, when the more drastic degradation of xylan with cleavage of the uronic moieties coincided with the stronger degradation of the cellulosic chains. Again, H4 pulp bleached by TFC sequence was distant from other ECF-bleached pulps (Figure 7). This fact suggests that the excessive degradation of the pulp polysaccharides in the oxidative bleaching stages (O, P_O and P) is also harmful for xylan that loses part of the uronic moieties.

Dry defiberization and changes in fiber morphology

All eucalypt bleached kraft pulps (H1–H6) were dry-defiberized to obtain fluffed pulps using a pilot hammermill operated at 3500 rpm. The fluffing conditions were selected from the previous work done on the dry defiberization of birch kraft pulp, showing the best development of fluff network strength at defiberization intensity as higher as 3000 rpm.[27] An industrial finished sheet of fluff pulp must have certain physical properties to be easily defiberized into a uniform fluff material, inducing minimal damage to the fibers and consuming as little energy as possible.[2] These specific properties are conferred to the finished sheets in the last stage of pulp production during the drying of the cellulosic pulp slurry.

Due to the different drying equipment (design features related to the sheet former, press and the drying sections) and conditions (residence time and temperature profile in drying section), the density of the finished fluff pulp sheets is inferior to that of conventional paper grade pulp.[27] In addition, so-called debonding agents are added to the fluff pulp to diminish the interfiber bonding. Due to lack of industrial eucalypt fluff pulp, we used conventional paper grade pulp in this study. Therefore, dry defiberization was hampered by a relatively dense pulp sheet to being

Table 2. Fiber morphology of eucalypt and softwood pulps before and after dry defiberization with a pilot scale hammermill.

Pulp sample		H1	H2	H3	H4	H5	H6	C1
Fiber length, (mm) (±0.002)	Sheet	0.847	0.863	0.849	0.852	0.852	0.867	2.510
	Defiberized	0.781	0.771	0.775	0.773	0.766	0.758	0.731
Fiber width, (μm) (±0.1)	Sheet	17.3	17.7	17.5	17.5	17.5	17.6	30.1
	Defiberized	18.2	17.7	18.0	17.9	17.9	17.8	27.0
Curl, (%) (±0.1)	Sheet	16.1	15.1	14.9	16.3	15.2	16.1	17.4
	Defiberized	9.9	11.0	11.5	12.0	11.6	12.8	9.2
Coarseness, (mg/m) (±0.0003)	Sheet	0.100	0.105	0.103	0.103	0.104	0.104	0.294
	Defiberized	0.0703	0.0714	0.0710	0.0734	0.0710	0.0720	0.1781
Kink angle, (°) (±1)	Sheet	57	56	56	58	56	57	44
	Defiberized	129	128	128	128	128	126	124
Fines, (%) (±0.2)	Sheet	19.5	20.4	20.2	20.0	20.0	20.2	42.8
	Defiberized	30.7	29.6	30.8	30.5	29.9	30.5	73.3
Knots, (%) (±0.2)	Defiberized	26.9	25.0	24.9	20.0	26.2	22.5	1.5

processed. This was not the case for the C1 commercial softwood pulp, which was produced industrially with the addition of debonding reagents.

Fiber morphology is an important parameter of the fluff pulp because of the direct relation to the structure of air-laid fiber network and the absorption properties of corresponding formulations. According to practical considerations, the fiber length of fluff pulps should be as high as 2 mm and the fines content should be as low as possible, because of the dusting problems.[17] Long fibers have more fiber-fiber contacts and a bolstered continuity in the structure and therefore form a stronger network when compared to short fibers.[27,28] The absorptivity of the fibers is related to their accessible surface, which, in turn, depends on the chemical composition and physical structure of the fibers. Usually, an increase in wettability of the fiber surface causes faster water penetration in the inner layers of the web. At the same time, fiber length, diameter and fiber wall thickness determine the capillary size of the absorbent structure (wet and dry) and its strength. For example, the larger the average pore size in a given pulp network, the greater is the fluid flux inside the web. Hence, taken into consideration the importance of fiber morphology, eucalypt fluffed pulps were analyzed based on changes in fiber length and shape that are summarized in Table 2.

Unlike softwood C1 pulp, that suffered notable fiber cuts upon fluffing, all eucalypt kraft pulps demonstrated less than 10% loss in fiber length, being finally comparable with the length of softwood fluff pulp (Table 2). Simultaneously, the percentage of fines in H1–H6 pulps increased up to ca. 30% in contrast to ca. 70% in C1 pulp. Apparently, the applied defiberization intensity was excessive for the C1 pulp. In fact, the optimum defiberization intensity of hardwood and softwood pulps is not the same and is lower for softwoods.[27] Softwood pulp (C1) has fibers with larger diameters than eucalypt hardwood pulps (Table 2). In addition, the coarseness of softwood fibers was more than twice of hardwood fibers. The fibers with larger fiber diameters and thicker walls have stiffer networks than fibers with small diameters and thin walls and demonstrate usually an improved compression resistance both in the dry and wet states, providing both resiliency and better holding capacity.[27]

The deformation of pulp fibers was evaluated through changes in curl and kink defects (Table 2). Fiber deformations occur during pulp production (pulping and bleaching procedures) and due to the strong mechanical action in dry defiberization. The noticeable decrease of fiber curl (from *ca.* 20–35%) upon defiberization can be explained either by partial straightening or by strong kink of fibers occurred during the process (up to 280% increase). This straightening of fibers play a negative role on the critical strain of air-laid product when analyzing the network strength, because the network starts to deform when curled fibers begin to straighten before any slippage between them takes place.[8,9] The kinks are local deformations, such as knees and wrinkles in the fibers. They are detected as changes in the direction of the main axis of the fibers within a limited distance of the fiber. The number of local deformations of the fiber may, on average, be one per fiber, meaning that the fibers in general have weak points, which negatively affect the fiber strength. From another side, kinks favor the bulk of pulp and the porosity that is important for the absorption of water.

Fiber coarseness, expressed as a dry fiber mass per unit length, decreased more than 30% after dry defiberization (Table 2). The coarseness results from the multiplication of the area of the cross section by the density of the cell wall and depends on the diameter of the fiber, thickness and density of the cell wall and cross section of the fiber, and contributes significantly to fiber network structure.[26,27] As a rule, a higher coarseness presupposes greater resistance of the fiber network and, in this sense, dry defiberization impairs its properties and is more critical for softwood fibers (Table 2).

As expected, the fines content increased after dry defiberization of both hardwood and softwood pulps (Table 2).

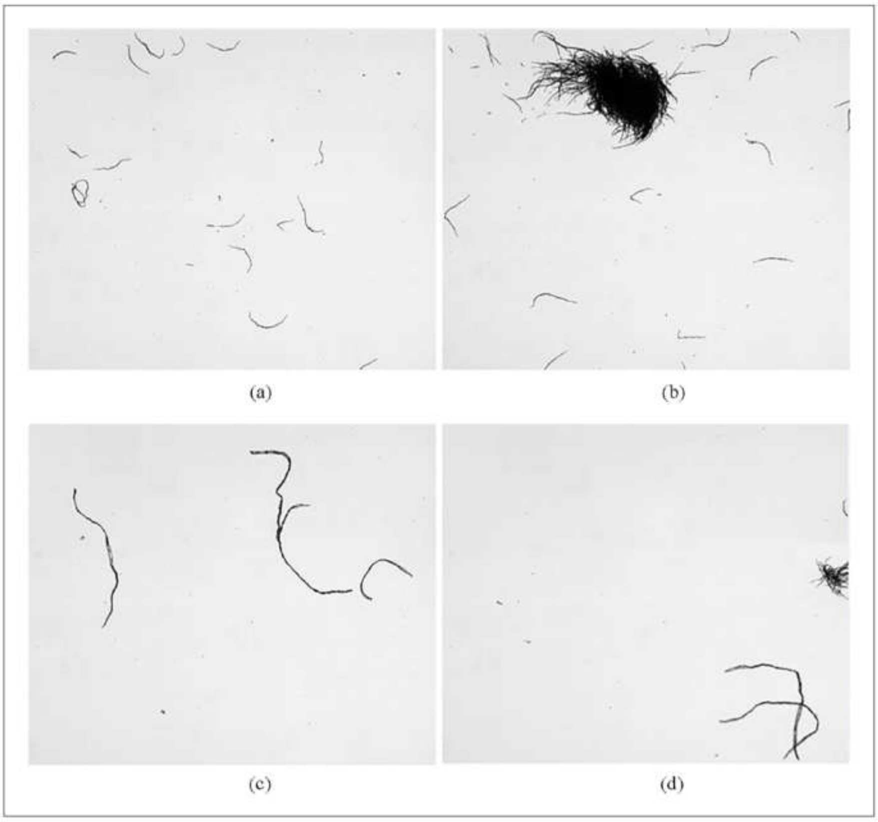


Figure 8. Fiber morphology of eucalypt and softwood fluff pulps after dry defiberization: (a) eucalypt fibers without knots, (b) eucalypt fibers with knots, (c) softwood fibers without knots, (d) softwood fibers with knots.

In chemical pulps, fines include ray cells and parenchyma cells in addition to cell wall shivers. During dry defiberization, the cell wall was peeled out, to some extent leading to shivers formation, which explains the notable increase in fines content of fluffed pulps. Another source of fines could be the short cuts of fibers that arose under mechanical degradation. According to obtained results, the formation of fines was more critical for softwood than for hardwood pulp.

Knots content

Under dry defiberization, complete separation of fibers cannot be achieved and a certain amount of agglomerated fiber bundles (knots) is still present in fluffed pulp. Hardwood fluff pulps showed a knot content range of 20–27% while softwood fluff pulp (C1) had a knot content less than 2% (Table 2). These results can be explained by different intensity of interfiber bonds in two types of pulps, predetermined by their pulp sheets density. Hardwood paper-grade pulp sheets (H1–H6) had a density of about 1.300 g/cm^3 while the commercial C1 softwood fluff pulp sheet, for the fluff needs, possessed a density of less than 0.650 g/cm^3. In addition, the industrial C1 pulp was doped with debonding agents facilitating the defiberization. Pulp sheets with lower density are easily defiberized and have less amounts of knots. For example, in H1–H6 series, H4 pulp showed the lowest knots content being more bulky than other pulps (Figure 5). However, the correlation between knots content and the pulp bulk was not straightforward. It should be noted that the knots in the hardwood pulps were larger and denser than those of the softwood pulp (Figure 8). This difference in knots morphology can affect the absorption properties of fluffed pulps, because the knots negatively affect the porosity and the wettability of air-laid fiber networks.[27]

Absorption properties and specific volume

The absorption capacity of the fluffed pulp corresponds to the ratio between the mass of water absorbed by a standard air-laid test piece (pad) and the initial mass of the pad, while the absorption time is the time required for a standard pad to be completely saturated by absorbed water when tested under specified conditions.[29] Noteworthy that during water uptake, the fibers swell and thus lead to narrowing of capillaries in the network and decrease in the fluid uptake. In fibrous materials, majority of the fluid is absorbed in spaces between fibers and only a small fraction is absorbed in internal structure. Any fluid diffusing into the internal structure will do so by the fiber swelling and expanding into the air spaces within the web. Furthermore, the process of absorption involves breakage of cross-links between the fibers, which causes a loss in modulus, in bending rigidity of fibers and, consequently in the ability of the fibrous network to maintain its pore structure under pressure.[30–33] Although absorption velocity and capacity are not independent of each other, the rate of absorption is controlled by the effective radius of the pores or capillaries between the fibers and the contact angle formed between the fiber surface and the liquid. The absorption capacity also depends on the fiber morphology, strongly affecting the network porosity.[30–32]

According to the data of Figures 9 and 10, absorption capacity of H1–H6 pulps varied within *ca.* 15% and, in most cases, were negatively affected by elimination of knots. At the same time, the specific volume of the air-laid pads was *ca.* 25% higher after the removal of knots (Figure 9). The latter fact is explained by the less dense air-laid network constituted by well-separated fibers. The apparent controversy between the increase of fiber network porosity and the decrease in absorption capacity of pads prepared with knotless pulps can be explained by the collapse of pad pores upon wetting. The contraction of the volume of the pad occurs essentially under the gravity of the absorbed liquid, due to the low mechanical resistance of the wet mesh.[30] Hence, a certain positive effect of knots on the absorption capacity can be explained by the inclusion of rigid fiber bundles in the network, that preserve it from collapse under moistening.

By a set of properties, such as absorption capacity and velocity, H2 and H6 pulps show the best results, possessing also the most porous network structure (the highest specific volume). The H1 and H4 pulps showed the lowest absorption capacity and the longest absorption time (Figures 9 and 10). Since the absorption of fluffed pulp is positively affected by the specific volume/porosity of the fiber network,[29–32] the greater absorptivity of pulps H2 and H6 is quite understandable. These pulps showed also the shortest absorption time (Figure 10) due to the large capillary in the corresponding pads, as predicted by the modified Washburn equation[30] that describes the penetration rate of capillary suction:

$$\frac{dl}{dt} = \frac{\gamma_{lv}\, r\cos\theta}{4\eta l} \qquad (1)$$

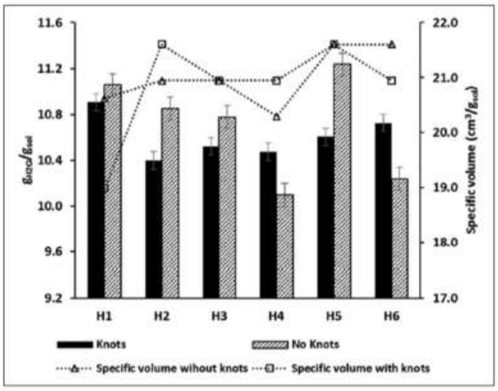


Figure 9. Absorption capacity and specific volume in fluff pulps (H1–H6) with and without knots.

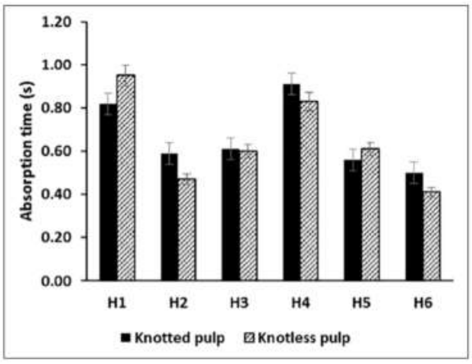


Figure 10. Absorption time revealed by eucalypt fluff pulps (H1–H6).

where l is the distance penetrated into capillary of radius r in time t by a liquid of surface tension γ_{lv} and viscosity η. θ is the contact angle between the drop of liquid and the fiber surface.

The high porosity of air-laid pads constituted of deknoted H2 and H6 pulps can be explained, at least partially, by the coarsest, longest and highly deformed fibers (Table 2). However, within the narrow range of variations in fiber morphology, it was difficult to establish reliable relationships between them and the absorption capacity of the corresponding pulps. The highest absorption capacity of H2 and H6 pulps coincides with the highest content of carboxylic groups belonging mostly to the glucuronoxylan (Figure 7). The hemicelluloses containing carboxylic groups contribute largely to the swelling of the pulp.[5] The swelling of the polymeric network is one of the basic mechanisms in the absorption by porous materials.[5] The importance of the chemical composition of fluff pulp on its absorption can be demonstrated by the correlation between water retention and carboxyl group content in hardwood pulps (Figure 11). Carboxyl groups present in the glucuronoxylan confer hydrophilicity to the fibers and, consequently, contribute to the water absorbing properties of the fluff pads. The water retention of the softwood C1 pulp was out of the trend revealed for the hardwood H1–H6 pulps and showed higher values (2.7 g/g) with lower content of carboxyl groups (6.0 mmol/100 g) in the pulp. This behavior can be explained by a high proportion of fines (>70%) in defiberized softwood pulp that improve water retention due to their high specific surface.

The smallest specific volume (i.e. the smallest porosity) was apparently the main factor of lower absorption in the pads produced from the pulps H1, H3 and H4 (Figure 9). This also explains, to some extent, the longest absorption time with these pulps, due to the smaller diameter of capillary. The shortest length and the lowest coarseness of fibers in H1 and H3 pulps (Table 2) could be one of the factors that contributed negatively to the network porosity. On the other hand, pulps H1, H3 and H4 also contained a low amount of carboxyl groups, thus contributing less to the intrinsic water retention of the fiber mesh.

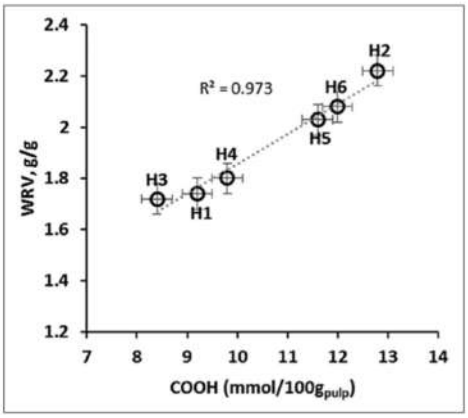


Figure 11. Correlation between the content of carboxyl groups in H1–H6 pulps and the water retention values (WRV) of corresponding fluff pulps.

Surprisingly, pads produced with C1 pulp showed similar absorption capacity (10.4 g/g) compared to pads produced with hardwood pulps (H1–H6) while possessing almost double specific volume (44.0 cm^3/g). At the same time, the absorption time (0.40 s) was shorter for softwood (C1) than for hardwood (H1–H6) pulps. The plausible explanation of such results is the unusually strong collapse of porous network structure of C1 pulp under moistening and external pressing. This behavior could be a result of significant fiber damage detected for softwood fluff pulp under applied conditions of dry defiberization (Table 2). Indeed, along with very short fiber fragments (fines content of ca. 70%), the fluffed pulp contained very long fibers so that the average fiber length was comparable to that of hardwood fluffed pulps. The comparable absorptivity of hardwood and softwood fluff pulps makes the former also attractive in different formulations of convenience items. Thus, the partial replacement of softwood pulp with hardwood pulp in fluff application improves the absorptivity of obtained formulations, thus allowing reducing the use of synthetic SAPs.[11]

It seems that the effect of chemical composition of fluff pulps on its absorption is not limited to the amounts of hemicelluloses only (e.g. glucuronoxylan in hardwood

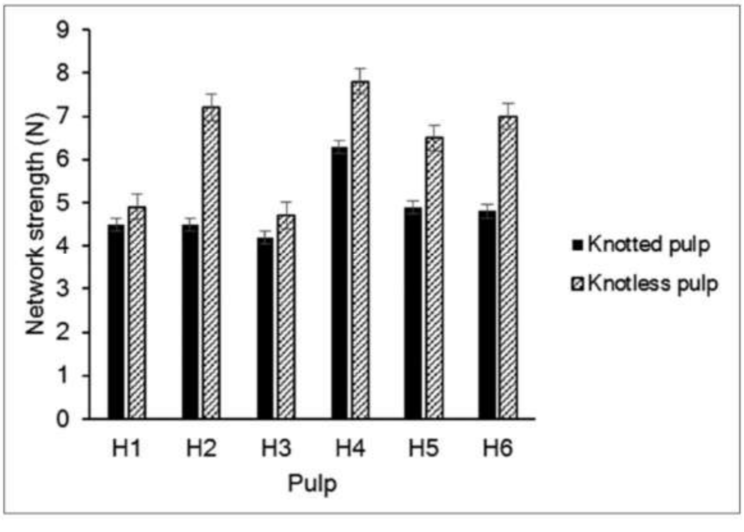


Figure 12. Network strength of air-laid pads produced from eucalypt kraft pulps (H1–H6).

pulps), but also their chemical structure and the localization in the fiber cell wall. When the variation in xylan did not exceed 10% in H1–H6 pulps, the variation in uronic moieties was as high as 25%. Hence, the variation in pulping and bleaching conditions induced structural differences in xylan in terms of its substitution with uronic moieties (both the original 4-*O*-methyl-α-D-glucuronic acid (4*O*MeGlcA) and its hexenuronic acid (HexA) derivative). The bleaching sequences affected not only the amounts of uronic moieties (detected through the amount of carboxyl groups) in pulps, but also the proportion between 4*O*MeGlcA and HexA (Table 2). Thus, if ECF-bleached pulps (H1–H3, H5 and H6) possessed a relatively small amount of HexA (0.3–2.0 mmol/100 g), the TCF-bleached H4 pulp contained 3.4 mmol/100 g of HexA (about 35% of total uronic moieties). Since the pKa of HexA and 4*O*MeGlcA are similar (3.0 and 3.1, respectively),[33] the contribution of these uronic moieties to ion-exchange capacity and pulp swelling must be comparable. In addition to their quantity, the allocation of xylan in the fibers plays an equally important role in the swelling and mechanical properties of eucalypt kraft pulp.[35] In turn, the location of the residual xylan depends on the pulping severity, mainly the alkali charge and the cooking temperature.[35] Thus, the absence of a clear impact, either on the water retention in the pulp (WRV) or the absorptivity of air-laid pads from the xylan content in eucalypt kraft pulps, could be explained by other associated factors, such as the structure and the location of the residual xylan in pulps.

Network strength

All eucalypt (H1–H6) and the reference softwood (C1) fluffed kraft pulps were evaluated for the network strength (NS) of air-laid pads assessed by measuring the maximum force which the network could withstand and the work of deformation to break in the shear mode with a standard designed equipment (Figure 2). In all essays, the knotless fluffed pulps showed a greater network strength than corresponding knotted pulps (Figure 12). This trend is usually explained by the decrease in the misshapen and inhomogeneous spaces in the pads, which result in undefined break points.[14,36] Another important factor affecting the network strength is the fiber length, which explains much stronger NS of C1 (17.5 N) than that of hardwood pulps (H1–H6). Despite strong detrimental effect of dry defiberization on the fiber's length (Table 2), still a considerable fiber fraction in C1 possessed much longer fibers than H1–H6 pulps. Long fibers provide more fiber-fiber contact points per fiber, which enhances network strength. Similar features were reported previously while comparing birch and softwood fluff pulps.[27]

Among H1–H6 pulps, the largest NS values (⩾7.0 N) were obtained with H2, H4 and H6 pulps. There was no clear impact of fiber length and its deformation parameters (curl and kink) on NS, though some positive correlation was traced between NS and fiber coarseness ($r^2 = 0.60$). In fact, the highest NS detected for the H4 pulp, possessed the highest coarseness and one of the highest fiber deformations (Table 2). Thus, the coarseness of the fiber seems to be one of the most relevant factors that strongly affected the NS of the hardwood pulps under study. Additionally, it explains the aforementioned NS superiority of the softwood fluff pulp having more than twice the fiber coarseness (Table 2). The NS of the air-laid fiber network was positively correlated (Figure 13) with the tensile strength and burst resistance of the wet-formed webs discussed previously (Figure 4). Hence, previous discussions concerning the factors that affect the mechanical properties of wet-formed handsheets are valid to some extent for the air-laid formulations and can be used to predict the network strength of the air-laid formulations. Thus, as in the case of wet-formed webs, the H2 pulp presented the highest NS

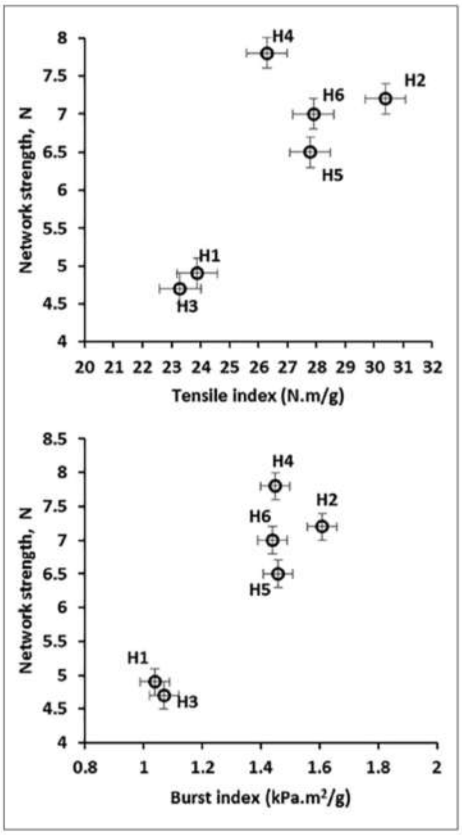


Figure 13. The relationship between the network strength of air-laid pads and the tensile (upper image) and burst (lower image) resistance of the corresponding wet-formed webs of eucalypt kraft pulps (H1–H6).

among ECF pulps and the pulps H1 and H3 the lowest, while H5 and H6 pulps showed intermediate NS values.

Noteworthy that the pulp showing the highest NS is not necessary the one with the largest absorptivity. Thus, H4 pulp showed the highest NS value (Figure 12), but the lowest absorption capacity (Figure 11). At the same time, H2, H5 and H6 pulps revealed both a relatively large network strength and the absorption capacity. Abnormal behavior of H4 pulp could be assigned to the relatively low porosity of the air-laid pad (Figure 9). The porosity is the major factor determining the absorptivity of the hardwood fluffed pulps, being even more important that the hydrophilicity of the fibers.[32,37] Other factors affecting the absorptivity are related to the collapsibility of wetted network and its water retention ability. The last parameters are also effected by the xylan content in pulp and this dependency is fairly ambiguous.[26,31] It has been found that the removal of moderate amounts of xylan from a hardwood fluff pulp (up to 50% of the initial) leads to an increase in the collapsibility of the air-laid fiber network when wet, while the removal of large amounts of xylan (up to 80% of the initial) decreases the network's ability to collapse under wetting.[27] This fact was explained by the hornification of the pulp fibers with the elimination of xylan and improvement of the network stiffness. Speculating these findings and taking into account a similar amount of xylan in H4 and in H2, H5 and H6 pulps (Table 1), it can be proposed that the lowest absorptivity of H4 pulp, when compared to H2, H5 and H6 pulps, is due to the weaker water retention of the former pulp (Figure 11), rather than due to the increased collapsibility of the network under wetting. This argument is also relevant when explaining the low absorptivity of H1 and H3 pulps, which show the lowest water retention capacity (Figure 11).

Among ECF-bleached eucalypt kraft pulps, the pulping conditions used for the production of H1 and H3 pulps can be considered the least suitable for the production of fibrous material for fluff applications. These pulps demonstrated the lowest basic mechanical properties, intrinsic viscosity, content of residual xylan and amount of carboxylic groups (Figures 6 and 7). In terms of fiber morphology, H1 and H3 pulps showed the shortest average fiber length and the lowest coarseness (Table 2).

Conclusions

The results of this study showed that for the same hardwood specie (*Eucalyptus globulus*), industrial production conditions can significantly affect pulp properties for fluff applications. In particular, the pulping and bleaching conditions can induce variability within 15% in the absorption capacity of fluff pulps and variability within 25% in the network strength of the air-laid formulations. These differences in fluff pulp performance are related both to the variations in the chemical composition and structure of its components and to the fiber morphology. BEKPs that have high intrinsic viscosity, high residual xylan content with a greater amount of carboxyl groups, higher coarseness and deformed fibers can be considered the most suitable for fluff applications. In addition to the length, the coarseness of the pulp fibers was considered a critical morphological parameter, strongly affecting the porosity of air-laid formulations, which corroborated with its absorption capacity and network strength. Nevertheless, further studies are needed involving different sources of hardwood fibers with wider variation of chemical composition and morphology (fiber length, coarseness and deformations) to trace more clearly the relationship between the fiber properties and their air-laid network parameters and absorptivity.

Being dry-defiberized under the same conditions, the specific volume of *eucalyptus* fluff pulp is almost half that of softwood fluff pulp, with comparable level of absorption capacity. However, the network strength of air-laid formulations produced with softwood fluff pulp is almost triple than that produced with *eucalyptus* fluff pulp. Softwood kraft pulp is much more vulnerable to dry defiberization conditions than *eucalyptus* pulp and undergoes strong fiber cutting and peeling, producing large amounts of fines (dust). The losses in coarseness (*ca.* 50%) and in the curl of softwood fibers (*ca.* 40%) due to the straightening under dry defiberization were more pronounced than those being characteristic of hardwood fibers (*ca.* 25% and 30%, respectively). Through the set of obtained results, BEKPs can be considered a promising raw material to substitute, at least partially, softwood pulps in the market of fluff pulps.

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Effect of cooking and bleaching conditions on the properties of eucalyptus kraft fluff pulps

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Abstract

A series of *Eucalyptus globulus* kraft pulps were cooked under the same conditions (160 ºC, 2h) using different active alkali (AA) charges of 13%, 15%, 17% and 18%. All pulps were further oxygen delignified (100 º C, 1h) and bleached using the elemental chlorine free (ECF) and the totally chlorine free (TCF) sequences. The obtained bleached pulps were dry-defibrated on a pilot scale hammermill at different intensities (rpm) and analysed for knots content, absorption capacity and air-laid fibre network strength. These fluff pulp parameters were related to the chemical composition of pulps, fibre morphology and the physical structure of the cellulose assessed by solid-state ^{13}C nuclear magnetic resonance spectroscopy (^{13}C NMR). Being dry-defibrated, pulps cooked at an increased AA revealed a reduction of the knots and the ECF pulps showed better defibration ability than TCF pulps. It was concluded that absorption capacity of the fluff pulps is the result of multiple occurring factors, such as the knots content, fibre´s hydrophilicity and morphology and the water retention capacity of the fibre web, whose contributions are not always unambiguous. This explains the non-evident dependence of the absorption capacity of fluff pulps on cooking and bleaching conditions. At the same time, the fibre network strength was sensible to the conditions of pulping and bleaching and always increased with the increase in cooking AA. The network strength of TCF fluff pulps was 20 to 70% greater than that of ECF fluff pulps.

Keywords: Bleaching, *Eucalyptus globulus*, fluff pulp, kraft pulping, absorption capacity, hornification, network strength, dry defibration

Introduction

Fluff cellulosic pulp refers to dry-defibrated pulps mainly used in the absorbent core of personal care products such as disposable diapers, adult incontinence products, female hygiene/care products, surgical pence, absorbent towelling, among others (Parham and Hergert 1980). The most important technical properties of fluff pulps are the high absorption capacity and the rate of absorption, specific volume of air-laid formulations (wet and dry), network strength, brightness, bulk after wetting, compression and spring back (Brill 1983; Murji and Brisebois 1995; Levlin and Söderbjelm 1999). Chemical fluff pulps are essentially made of softwood pulps, which are produced by sulphate (kraft) or sulphite pulping and should be easily dry-defibrated (Parham and Hergert 1980; Young and Barlow 2007). However, the type of cellulosic fibre may not be critical, depending on the applications, and different fibre sources suitable for applications in fibrous nonwoven fabrics can be used. In addition to chemical pulps, the chemi-thermomechanical pulps (CTMP) produced from softwood, hardwood or a combination of hardwood and softwood can be used for fluff applications (Young and Barlow 2007). Nevertheless, more than 90% of all fluff pulps on the market, growing at around 3 to 4% per year, are fully bleached chemical pulps, of which more than 90% are kraft pulps.

The conventional pulp sheet for fluff applications is manufactured following the chemical pulping/bleaching operations transforming the cellulose fibres into a non-woven mat by one or more wet forming processes typified by the conventional Fourdrinier process. Low density dried pulp mat (*ca.* 0.6-0.7 g/cm^3) is usually rewound into continuous rolls for shipment to the customer (Tanner and Koller 2004; Jakkola and Sealey 2013). A low density of the fluff pulp sheet is a key pre-requisite to dry defibration of fluff pulp without significant amounts of fibre agglomerates (knots), which deteriorate the properties of air-laid formulations (Brill 1983; Lund et al. 2012; Hubbe et al. 2013). The amount of knots can be reduced by increasing the intensity of dry defibration, but the excessive energy input leads to the cutting of fibres and a high content of fines (dusty material). In order to disperse the dry pulp into individual fibres with less energy, several types of debonding agents have been used to reduce the bonding strength of the pulp in sheet (Wiley 2014; Shaanxi et al 2016). Softwood pulps, possessing long fibres (2-5 mm) are harder to defibrate than short-fibre hardwood pulps and produce dust (Parham and Hergert 1980; Lund et al. 2012). However, shorter and less coarse hardwood fibers reveal a weaker network strength than long fibers of softwood pulp in air-laid formulations (Lund et al. 2012). This is the main reason why conventional fluff pulps are produced from long-fibre softwoods that dominate the fluff market (Parham and Hergert 1980; Young and Barlow 2007). At the same time, hardwood pulps can introduce several complementary properties to softwood pulps (Sealey et al. 2014) or even replace them in certain fluff applications (Jordao and Neves 1989). Last facts explain the growing technical and economic interest in hardwood fluff pulps (Foelkel 2007; Eucafluff 2019).

The basic quality parameters of fluff pulps, such as the absorption capacity, the absorption rate and the air-laid fibre network strength are strongly affected by the chemical composition of the fibres, their morphology and arrangement in the mesh (Jordao and Neves 1989; Chatterjee and Gupta 2002; Lund et al. 2012; Hubbe et al.2013). Since capillary suction is the main absorption mechanism in nonwoven cellulose fibre webs (Chatterjee and Gupta 2002), the absorption capacity of fluff pulps strongly depends on the porosity of the air-laid formulations, which, in turn, is sensitive to the fibre length and morphology (e.g. coarseness, curl and kink). Longer and coarser fibers form a more porous and stronger network (Jokinen et al. 1991; Askling at al 1998a, 1998b; Lund et al. 2012). The porosity is also promoted by curled and kinked fibres. In fluff cellulosic materials, majority of the fluid is absorbed in spaces between fibres and only a reduced fraction is absorbed in internal structure. Hence, the porosity of the web is a more important factor for absorptivity that the hydrophilicity of constituent fibres (Azevedo et al. 2020). During water uptake, the fibers swell and thus lead to narrowing of capillaries in the network and decrease in the fluid uptake. The absorption involves breakage of cross-links between the fibers in the network, which causes a loss in modulus and bending rigidity of fibers and, consequently in the ability of the fibrous web to maintain its pore structure under pressure. The collapsed wet web retains much less water that could be predicted by intrinsic porosity of dry web (Chatterjee and Gupta 2002; Azevedo et al.

2020). Under these circumstances, the intrinsic water retention capacity of fluff pulp is gaining importance. The last is dependent on the swelling capacity and, therefore, closely related to the chemical composition and morphology of the fibres. Since pulping and bleaching conditions affect these characteristics of cellulosic pulp it could be expected that basic properties of fluff pulps might be vulnerable to the processual conditions of their production.

The effect of pulping and bleaching conditions on the basic properties of fluff pulps is poorly studied, especially for hardwood fluff pulps. However, brief analysis of a series of industrial bleached kraft eucalypt pulps clearly demonstrated that changes in pulping conditions (alkali load and temperature) and the bleaching approach (ECF or TCF) revealed variations in knots content after dry-defibration within 20%, absorption capacity within 15% and network strength of the air-laid fibre webs within 25% (Azevedo et al. 2020; Rebola et al. 2020). In addition, changes in bleaching conditions play a no less important role than changes in cooking conditions. In particular, it was pointed out that pulp bleached by the TCF sequence showed an advantage over ECF bleached pulps in terms of fibre network strength, but not always in terms of absorption capacity and absorption rate. However, multiple variables of industrial process did not allow to trace unambiguously the relationships between the processual conditions and fluff pulp properties. To avoid such an ambiguity, in this study, laboratory-cooked eucalypt kraft pulps, under controlled conditions and with variable alkali load, were laboratory ECF and TCF bleached to similar brightness and dry-defibrated applying varying defibration intensities. The fluff pulps were evaluated for their fibre morphology and analysed for general chemical composition and supramolecular cellulose structure employing solid-state ^{13}C NMR. The absorption capacity/absorption rate and the air-laid fibre network strength of eucalypt fluff pulps were assessed and related to the morphology, chemical composition and physical structure of fibres, with regard to the cooking and bleaching conditions applied.

Materials and methods

Characterization and chemical analysis of *E. globulus* wood

The chips used in the lab cooking experiments were prepared from freshly cut logs supplied from controlled plantations of Iberian *Eucalyptus globulus*. The wood chips were screened by a chip classifier according to SCAN-CM 40. The wood chips used in the experiments correspond to the large accept chips (13 mm holes) and the small accept chips (7 mm holes). The chips did not contain bark or knots. The basic density of the wood chips (567 kg/m^3) was determined according to SCAN-CM 43. The chips had a dry solid content of 56.3% (according to SCAN-CM 39) and were stored in a conditioning room at 23°C ± 2°C and RH 50%. The content of wood extractives in air-dried sawdust (40-60 mesh) was determined in a Soxhlet apparatus, with acetone as the solvent, according to SCAN-CM 49. The analysis of acid insoluble lignin (Klason lignin) of previously extracted wood was carried out according to TAPPI T222 om-88 and the sugar analysis was carried out according SCAN-CM 71 employing a conventional Saeman hydrolysis and the derived sugars were analysed by anion-exchange liquid chromatography and pulsed amperometric detection (PAD).

Conventional kraft cooking and analyses of kraft pulps

A conventional kraft cooking was carried out in a MK laboratory digester with a capacity of approx. 1.0 kg of dry chips. The industrial white liquor (cooking liquor) was adjusted with addition of NaOH or Na_2S to reach the desirable active alkali of 13-18% (as Na_2O) and the sulphidity of 30%. After filling the digester vessel with a white liquor (liquid-to-wood ratio 4, initial temperature ca. 30 ºC), the temperature in the digester was raised within 10 min to 130°C followed by the chips impregnation for 30 min. After that, the temperature was increased to 160°C within 5 min. The temperature was kept constant at 160°C for 120 min to maintain the H-factor nearly 800. The delignified chips were removed from the digester, disintegrated in demineralized water and screened using a 0.15 mm screener. The rejected material was collected and dried overnight at 105°C ± 2°C to determine their content. All cooking experiments were performed in duplicate. All pulps were centrifuged to 20-25% dry content (ISO 638) and evaluated with respect to yield, kappa number (ISO 302) and intrinsic viscosity (ISO 5351). The hexenuronic acid content was determined according to the dual wavelength method proposed by Chai et al. (2001), which was adapted by Pedroso and Carvalho (2003) to *E. globulus* samples. The carboxyl content of pulps was determined following the ion-exchange method TAPPI T 237 cm 08. The unbeaten pulp samples were also characterized with respect to total lignin (TAPPI T222 om-88 for Klason lignin and TAPPI UM T250 for soluble lignin). ISO brightness was determined for unbeaten screened pulp according to ISO 2470. In the water retention test, a sample of defiberized pulp (0,200 g ± 0,005 g oven-dry weight) was sealed inside a heat sealable teabag and submerged in a 0.9 % saline solution for 30 minutes at 22 ± 2°C. After 30 min saturation time, the bags were let drip for three minutes. Thereafter, the fluff pulp samples were placed in a centrifuge bucket and centrifuged at 3000 rpm for 3 minutes (22 ± 2°C). Immediately after stopping the centrifuge, the test pad is transferred to a pre-weighed glass plate and weighed. The water retention volume (WRV) is defined as the weight of retained water per gram of dry pulp (g/g). Isotropic handsheets with a target grammage of 65 $g/m^2 \pm 2$ g/m^2 were produced according to ISO 5269-1 using a conventional semi-automatic Rapid–Köthen sheet former. The contact angles, using distilled water, were determined by the sessile drop method as described elsewhere (Azevedo et al. 2020).

Oxygen delignification

The oxygen delignification of kraft pulps was carried out in 1L stainless steel pressurized reactor PARR (Model 4842) at 100 ºC, alkali load of 2.5% and oxygen pressure of 5.0 bar for 60 min. The unbleached kraft pulp consistency was approx. 6%. The oxygen-delignified pulp was filtered off, washed with distilled water and stored at 4 ºC (*ca.* 25% consistency). The delignified pulps were analysed for the kappa number, intrinsic viscosity and ISO brightness according to the same methodology as unbleached kraft pulps.

Bleaching

The oxygen delignified pulps were subjected to final bleaching trials. The bleaching experiments, at pulp consistency of 10%, were carried out in a sealed polyethylene bags placed in a constant temperature water bath at programmed temperature, under periodical shaking. The elemental chlorine free (ECF) $D_{hot}E_PD_1P$ bleaching sequence, with a final peroxide stage (P), was applied to simulate the existing industrial bleaching trial (where D denote the bleaching stage of chlorine dioxide and E_P the alkaline extraction reinforced with hydrogen peroxide). The totally chlorine free (TCF) $AE_PP_1P_2$ bleaching sequence included the first acid extraction stage, an alkali extraction stage reinforced by hydrogen peroxide (E_P) and two consecutive peroxide stages (P_1 and P_2). Table 35 resumes the bleaching conditions for the ECF and TCF sequences.

Table 35 Bleaching conditions applied to the ECF $D_0E_PD_1P$ and TCF $AE_PP_1P_2$ sequences.

Bleaching sequence	Bleaching Stage	ClO_2 kg/t	H_2O_2 kg/t	pH	Temperature, °C	Time, min
ECF	D_{hot}	20	-	3.0 – 3.5	92	120
	E_P	-	4.0	10.5-11.5	100	50
	D_1	7.0	-	3.5	74	60
	P	-	3.5	10.5-11.5	85	70
TCF	A	-	-	3.5	100	120
	E_P	-	17.0	11.0-12.0	95	50
	P_1	-	5.0	10.5-11.5	92	60
	P_2		5.0	10.5-11.5	95	70

(1) In the E_P stage, the NaOH load was 2.5% and 2.0 kg/tpsa of $MgSO_4$ was added. No chelating agent was introduced in the E_P stage. In all bleaching stages, the pulp consistency was 10%.

The bleached pulp was filtered off and thoroughly washed with distilled water after each treatment. The properties of the bleached pulps were analysed to determine the kappa number, the intrinsic viscosity and ISO brightness according to previously referred standard procedures.

Formation of pulp sheets

The bleached wet pulp was disintegrated according to ISO 5263-1. A suspension of ca. 5.0% pulp consistency was transferred to a conventional sheet former (Rapid–Köthen sheet former) to prepare the low density laboratory sheets of pulp for the subsequent dry defibration. The suspension was stirred and then dewatered, by allowing it to dry for 5 sec. The formed pulp sheet of ca. 1500 g/m^2 was involved in three layers of blotting paper (Binzer & Munktell filter GMBH) and pressed at around 5kPa for 10 sec. The sheet was gently removed from the wire and air-dried in a conditioning room at 23°C and 50% RH. The density of pulp sheets varied between 0.6 and 0.7 g/cm^3.

Dry defibration and knot content

The pulp sheets were cut into strips (width ≈ 10 mm) and dry defibrated in a pilot scale hammermill Schutte Bufallo (Schuttle Buffalo, Model W6H, Buffalo) operating at 2500, 3000 and 3500 rpm. The rate of the inlet feed of the sheets was almost constant and the disintegrated fibres had to pass in a mesh with 5 mm openings in the first run and, afterwards, in a mesh of 2 mm openings in the second run. The obtained fluff pulp was kept in sealed polyethylene bags without tamping. Knots content evaluation was adapted to the norm SCAN-CM 37:85. After dry defibration, the obtained fluff pulp was passed through a RETSCH® sieve shaker. This device uses a series of standard ASTM mesh screens to separate fluff into knots and accepts. In this test procedure, knots are the fraction that is retained on an ASTM 12 mesh screen.

Dry forming of pads and the network strength

The air-laid pulp formulations (pads) were formed using a standard test piece former according to SCAN-C 33:80, which is described in more detail elsewhere (Lund et al 2012; Rebola et al. 2020). The weight of defibrated fluff pulp in the pad was always 3.0 g and the pad diameter 50 mm. The network strength of air-laid pads was determined according to the method developed in the Papirindustriens Forskningsinstitutt (PFI) in Norway (Brill 1983), on which the SCAN-C 33:80 is based on. According to the method, a cylindrical test piece (pad) is mounted on a sample holder being pre-pressed at a load of 2.5 kPa for 30 s. The sample holder has a mobile steel plate with a hole in the centre with a diameter of 20 mm for the movable piston. This plate puts a load (5 kPa) on the periphery of the test piece to fix it when tested. The test piece is placed in a burst chamber installed in a stress-strain apparatus SC-500 (IDM, Spain) operating in compression mode with a velocity of 100 mm/min. A piston (diameter of 20 mm) is then forced through the pad and the highest force is recorded just before the pad ruptures. A more detailed description of the testing equipment can be found elsewhere (Lund et al 2012; Rebola et al. 2020).

Specific volume and absorption properties

The specific volume, absorption time and absorption capacity were determined accordingly to the SCAN-C 33. This SCAN-test method describes the preparation of test pieces of fluff, a procedure for their use in determining the specific volume and the absorption properties of the fluff. A fluff specimen of about 3.0 g mass and 50 mm diameter (pad) is prepared using air-laid former as described above. The test piece was placed on a perforated plate in contact with fluid in a vertical position and at a load of 2.5 kPa. The height of the specimen was determined before the fluid contacts the material. The test piece was then allowed to absorb water (25 ± 1°C) from below and the time required for the waterfront to reach the top surface was measured and reported as the absorption time. A more detailed description of the testing equipment can be found elsewhere (Lund et al 2012; Rebola et al. 2020).

Fibre morphology

The fibre morphology of the dried fibres, before and after dry defibration, were analysed using an L&W Pulp Fiber Tester (Morphology Test), according to ISO 16065-2. The fluff pulp was soaked according to the relevant part of ISO 5263. The recommended mass fraction used in ISO 16065 was 0,004% to 0,010% for hardwood pulp. In order to get accurate measurements, the suspension was diluted using demineralized water.

Solid State Nuclear Magnetic Resonance Spectrometry (CP-MAS ^{13}C-NMR)

Solid-state Cross Polarization – Magic Angle Spinning ^{13}C Nuclear Magnetic Resonance (CP-MAS ^{13}C NMR) spectra were registered on a Bruker Advance 400 spectrometer. The CP-MAS ^{13}C NMR spectroscopy was used to study a cellulose crystallinity index (*CrI*), which describes the relative amounts of crystalline and amorphous cellulose phases. Samples were packed into a zirconia rotor sealed with Kel-F^{TM} caps. The rotor's spinning speed was 12kHz, contact time 1 ms, ca. 7000 scans with a 90° proton pulse were collected with a recovery delay of 2.5 s. Glycine was used for the Hartman-Hahn matching procedure and as external standard for the calibration of the chemical shift scale relative to tetramethylsilane ($(CH_3)_4Si$). CP-MAS ^{13}C NMR spectra were registered using air-dry pulp samples (ca. 14% humidity).

The crystallinity index was determined from the relationship between the integration areas of the ordered ($A_{86-92\,ppm}$) and amorphous ($A_{79-86\,ppm}$) C-4 signals in cellulose (Liitiä et al. 2000):

$$CrI,\% = \frac{A_{86-92\,ppm}}{A_{86-92\,ppm} + A_{79-86\,ppm}} \tag{1}$$

The lateral fibril dimensions and fibril aggregates were determined by methodology proposed by Wickholm et al. (1998), according to the model of a fibril with a square cross-section:

$$q = \frac{4n-4}{n^2} \tag{2}$$

where q is the fraction of intensity of the signal of accessible and inaccessible surfaces to assess fibril dimensions or the fraction of intensity of the signal of accessible surfaces only to assess the dimensions of fibril aggregates; n is the number of cellulose polymers perpendicular to the cross-section along one side of the square fibril cross-section. The assumed square fibril aggregate cross-section n can be converted to a lateral dimension expressed in nm using a factor of 0.55 nm per chain (Krässig 1993).

Results and discussion

Cooking and bleaching of kraft pulps

A meticulously selected Iberian *E. globulus* wood was kraft cooked under controlled conditions (160 ºC, 120 min) using the same liquor sulphidity (30%) and variable active alkali (13, 15, 17 and 18% as Na_2O). The obtained kraft pulps were delignified by oxygen and subsequently ECF $D_{hot}E_PD_1P$ and TCF $AE_PP_1P_2$ bleached to similar brightness. The results of cooking revealed progressive delignification of the pulps obtained with an increase in the load of active alkali (AA), showing a kappa number ranging from 19.2 for AA13 pulp to 13.3 for AA18 pulp (Table 2). The total cooking yield fell in the same order and the screened yield reached the maximum at AA of 15-17%. The intrinsic viscosity ([η]) of the pulps gradually decreased with the increase in AA due to the enhanced alkaline hydrolysis and cellulose peeling reactions (Ershova et al. 2012). These results are similar to those previously reported for the kraft cooking of *E. globulus* wood (Pedroso and Carvalho 2003; Pinto et al. 2005a).

Under kraft cooking conditions, 4-*O*-methylglucuronic acid (MeGlcA) residues in glucuronoxylan of eucalypt wood undergo alkali hydrolysis and demethoxylation with formation of terminal hexenuronic acid (HexA) groups, whose amount strongly depends on the liquor alkalinity (Daniel et al. 2003). In the unbleached pulps, the content of HexA increased with the increase of AA from 13 to 15%, being further decreased with AA of the liquor of 17 and 18% (Table 2). Similar features were observed previously for kraft cooking of eucalyptus wood with variable alkalinity and explained by the simultaneous formation/degradation of HexA and the xylan dissolution in spent liquor (Daniel et al. 2003).

Table 2 Results of laboratory kraft cooking of *E. globulus* wood, oxygen delignification and ECF/TCF bleaching of pulps.

	Parameters	AA 13%	AA 15%	AA 17%	AA 18%
After Cooking	Total yield, %	57.5	55.5	55.0	53.1
	Pulp screened yield, %	51.2	54.0	54.2	52.6
	Kappa number	19.2	15.6	14.5	13.3
	IK lignin, *	16,5	12,3	11,4	10,4
	Total lignin, %**	3,1	2,3	2,1	1,9
	HexA, mmol/kg pulp	32,2	38,9	36,3	34,2
	Brightness, %	31.0	35.7	36.1	38.3
	$[\eta]$, cm^3/g	1280	1200	1060	980
After O_2 delignification	Kappa number	12,5	9,8	8,5	7,4
	IK lignin, *	9,5	6,5	5,5	4,8
	Total lignin, %**	1,8	< 1,0	1,0	< 1,0
	HexA, mmol/kg pulp	31,3	34,1	36,9	33.0
	Brightness, %	43.5	47.2	53.9	57.2
	$[\eta]$, cm^3/g	1250	1115	955	830
After ECF bleaching	Kappa number	1.1	1.2	< 1.0	< 1.0
	Brightness, %	89	89	91	91
	HexA, mmol/kg pulp	2.5	1.8	2.1	3.0
	$[\eta]$, cm^3/g	830	740	685	645
After TCF bleaching	Kappa number	5,0	5,0	3,7	3,4
	Brightness, %	80	82	84	85
	HexA, mmol/kg pulp	9,6	16,8	13,8	15,3
	$[\eta]$, cm^3/g	630	580	545	480

*the fraction of Kappa number belonging to the lignin (IK lignin = Kappa number – 0.086[HexA]), where [HexA] is the content of HexA, mmol/kg

**the sum of insoluble (Klason lignin) and acid-soluble lignin.

Oxygen delignification allowed *ca.* 50% delignification of kraft pulps (Table 2), thus accounting for significant savings of bleaching reagents in subsequent bleaching (Sixta et al. 2006). Due to the greater brightness gain for pulps cooked with 17 and 18% AA in delignification with oxygen, the final brightness of these pulps was higher in ECF and TCF bleaching with the same load of bleaching reagents (Table 2). Due to the poor reactivity of (HexA) residues in the residual xylan of pulps during oxygen delignification (Vuorinen et al. 1999; Costa and Colodette 2007), its contents were quite similar before and after the oxygen stage. The content of HexA residues decreased drastically upon bleaching, being more accentuated for the ECF bleached pulps. The last fact is explained by readily degraded HexA residues by ClO_2 in D stages. TCF pulps still contained considerable amounts of HexA even when applying the A stage at the beginning of the sequence. In general, ECF pulps showed higher brightness and intrinsic viscosity than corresponding TCF pulps.

Chemical composition of bleached pulps

All bleached pulps revealed a relatively low content of extractives (<0.1%). The content of the residual lignin was substantially higher in TCF pulps that in the ECF pulps (Table 2) reflecting much less effective delignification in bleaching stages with hydrogen peroxide than with chlorine dioxide. Sugars analysis showed that glucuronoxylan, the main hemicellulose in eucalypt wood, was largely retained in bleached pulps, although its content in ECF pulps is higher than that of TCF pulps (Table 3). This fact could be explained by predominance of alkaline bleaching stages in TCF sequence. In addition to the backbone degradation, the oxidative alkaline bleaching stages induce xylan migration and its partial removal from the cellulosic fibre surface (Dahlman et al. 2003). During kraft pulping, the xylan is partially removed in liquor due to its degradation and swelling of the fibre cell wall (Gomes et al 2020). Alkali-induced degradation affects not only the xylan backbone, but also the MeGlcA and HexA residues α(1→2)-linked to xylopyranose units, whose alkaline hydrolysis raises with alkali charge (Pinto et al 2005b). Accordingly, the changes in the severity of cooking conditions, expressed as a variable alkali charge, negatively affected the xylan retention in ECF and TCF pulps. Therefore, the observed coincidence in simultaneous reduction of pulp's viscosity and content of carboxyl groups (Tables 2 and 3) is due to the increased alkali load in cooking, when the more drastic degradation of xylan with cleavage of the uronic moieties coincided with the stronger degradation of the cellulosic chains.

Table 3 Monosaccharide composition and content of carboxyl groups in ECF and TCF kraft pulps.*

Pulp samples	Ramnose %	Arabinose %	Xylose %	Mannose %	Galactose %	Glucose %	COOH mmol/100g
ECF13	tr.	0.2	14.9	0.2	0.3	84.4	8.9
ECF15	tr.	0.2	14.4	0.2	0.3	84.9	6.7
ECF17	tr.	0.1	13.9	0.2	0.3	85.5	5.1
ECF18	tr.	0.1	13.3	0.2	0.3	86.1	4.8
TCF13	tr.	0.1	13.4	0.2	0.3	86	9.3
TCF15	tr.	0.1	13.0	0.2	0.3	86.4	9.5
TCF17	tr.	0.1	12.4	0.2	0.2	87.1	8.1
TCF18	tr.	0.1	11.3	0.2	0.2	88.2	8.0

*The relative error in sugar analysis did not exceed 3%. The pulp designations include the bleaching sequence (ECF or TCF) and the active alkali (AA) employed for their production (AA=13-18%).

The results of sugar analysis also showed the presence of minor amounts of glucomannan and arabinogalactan in bleached pulps. The last one might be structurally associated with glucuronoxylan (Evtuguin et al. 2003). Noteworthy that the amount of carboxyl groups was higher in TCF than in ECF bleached pulps (Table 3). Since carboxyl groups belong mostly to the MeGlcA and HexA residues in the residual xylan of pulps, the former fact is attributed, at least partially, to a better preservation of HexA residues in TCF bleaching (Table 2). However, the oxidation of polysaccharides in oxidation bleaching stages with formation of carboxyl groups cannot be completely excluded. Since carboxyl moieties are the main functional groups responsible for bulk and fibre surface charge of kraft pulps, its content have a big impact not only on the ion-exchange properties and fibre swelling ability (Grignon and Scallan 1980; Scallan and Tigerstrom 1992), but also on the fibre flexibility, inter-fibre bonding and mechanical properties of the pulp sheets (Zhang et al. 2006; Chen et al. 2013).

Dry defibration of pulps

The dry-defibration of ECF and TCF bleached pulps was carried out under the same conditions using laboratory hammermill with variable intensities (2500, 3000 and 3500 rpm). The increase in milling intensity clearly revealed a reduction in knots content of dry-defibrated fluff pulps (Figure1). Similar features were previously reported for birch kraft pulps (Lund et al. 2012). A particularly accentual decrease in knots content was registered when the milling intensity increased from 3000 to 3500 rpm. ECF bleached pulps cooked at different AA showed better defibration ability than corresponding TCF bleached pulps.

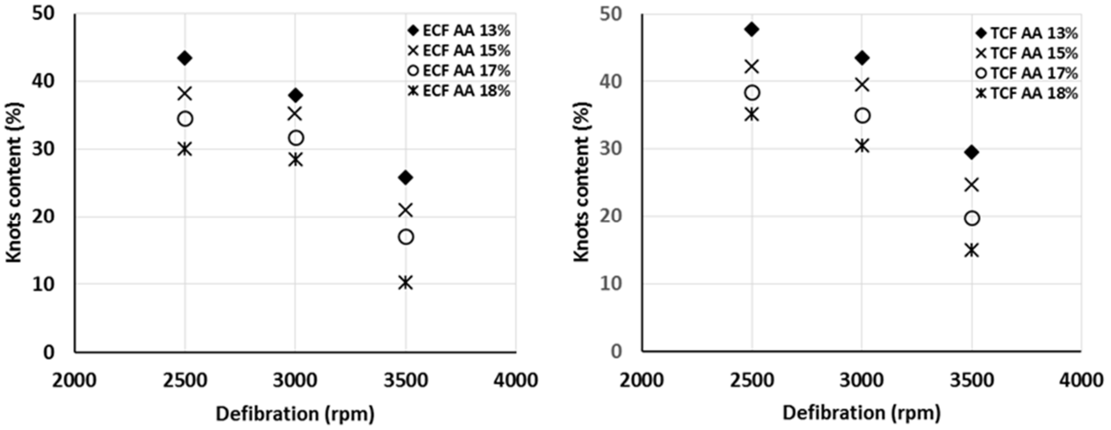

Fig. 1 Effect of defibration intensity on knots content in dry-defibrated ECF and TCF fluff pulps. The standard deviation for the knots content was *ca.* 4.0%.

The pulps cooked at an increased AA always show a reduction in knots (Figure 1). This fact can be associated with more delignified pulps containing less residual lignin and hemicelluloses (Tables 2 and 3), that are more susceptible to hornification under drying. Such pulps possess less flexible and conformable fibres, with less bonding capacity in pulp sheets (Lund et al. 2012). Nevertheless, this justification is not completely valid when comparing the dry defibration of ECF and TCF bleached pulps (Figure 1). The contents of residual hemicelluloses are lower in TCF than in ECF pulps (Table 3) and the bonding capacity between fibres in TCF pulp sheets should be weaker than in ECF pulp sheets. However, the TCF pulps were harder to defibrate that the ECF pulps (Figure 1). The plausible explanation consists in differences of fibre morphology detected between ECF and TCF bleached pulps (Table 4). Thus, TCF pulps have coarser fibres than ECF pulps, which can be important for dry defibration. The fact is that longer and coarser fibres need more energy for defibration (Parham and Hergert 1980; Lund et al. 2012). In addition, the TCF pulp fibres were more kinked during dry defibration that the fibres of ECF pulps (Table 4), which could deteriorate their effective separation and enhance the already pronounced tendency of eucalypt fibres to flocculate in air-laid processes (Larkomaa et al 2014).

Table 4 Fibre morphology of eucalypt kraft pulps before and after dry defibration using a pilot scale hammermill.*

Pulp Sample		**ECF13**	**ECF15**	**ECF17**	**ECF18**	**TCF13**	**TCF15**	**TCF17**	**TCF18**
Fiber length, (mm) (± 0.003)	Sheet	0.765	0.768	0.766	0.764	0.796	0.785	0.787	0.784
	Fluffed	0.761	0.757	0.758	0.758	0.754	0.752	0.746	0.746
Fiber width, (µm) (± 0.1)	Sheet	19.4	19.1	19.0	19.1	19.0	18.9	18.7	18.7
	Fluffed	19.5	19.1	19.1	19.1	18.5	18.2	17.9	18.0
Curl, (%) (± 0.1)	Sheet	8.8	8.7	7.9	7.9	8.8	8.8	8.8	8.8
	Fluffed	9.3	9.9	9.0	8.7	8.7	9.8	9.0	8.8
Coarseness, (mg/m) (± 0.0003)	Sheet	0.0659	0,0649	0.0641	0.0639	0.0751	0,0720	0.0753	0.0785
	Fluffed	0.0653	0.0645	0.0625	0.0627	0.0714	0.0718	0.0685	0.0686
Kink, (%) (± 0.2)	Sheet	38.1	38.4	35.0	34.3	27.8	28.7	29.7	29.9
	Fluffed	37.9	40.5	38.0	36.9	42.0	42.4	40.1	39.2
Fines, (% in length) (± 0.3)	Sheet	33.8	32.9	31.9	32.8	36.2	34.1	34.1	34.8
	Fluffed	42.6	34.2	33.4	34.4	38.3	35.0	35.0	36.2

*-pulp designations denote the employed bleaching sequence (ECF or TCF) and the active alkali used in the kraft cooking (13, 15, 17 and 18%).

Since ECF and TCF bleached pulps have the same delignification history, including oxygen delignification, the major changes in fibre morphology took place during the final bleaching and further drying. Alkaline stages in TCF bleaching led to a more extensive removal of xylan from fibres than in ECF bleaching stages (Table 3). Accordingly, such TCF pulps are more susceptible to hornification than ECF pulps (Oksanen et al. 1997). The hornification of eucalypt bleached kraft pulps increases exponentially with the decrease of xylan content (Rebuzzi and Evtuguin 2006). The hornification deals with the collapse of the fibre surface and the fibre stiffening and shrinkage (Minor 1994; Weiss 1998). Consequently, the fibres become more consolidated and contracted. This could explain a slightly higher coarseness of TCF than ECF pulps. To confirm this proposition, in a separate laboratory trial made with bleached kraft pulp, purposefully dried at 140 ºC to enhance the hornification, the increased fibre coarseness have been detected from 73.5 µg/m in never-dried pulp to 85.8 µg/m in hornified pulp. In addition, the increased hornification of pulp makes fibres stiffer (Oksanen et al. 1997; Rebuzzi and Evtuguin 2006) and this fact affects the dry defibration (Lund et al. 2012). Evidently, the more flexible fibres of the ECF pulps were more difficult to kink than the relatively rigid fibres of the TCF pulps. In turn, the less flexible fibres from TCF pulps were harder to curl during dry defibration than the more flexible fibres from ECF pulps (Table 4). This difference in the deformation of fibres from ECF and TCF pulps, under dry defibration, should affect the physical properties of air-laid formulations constituted thereof.

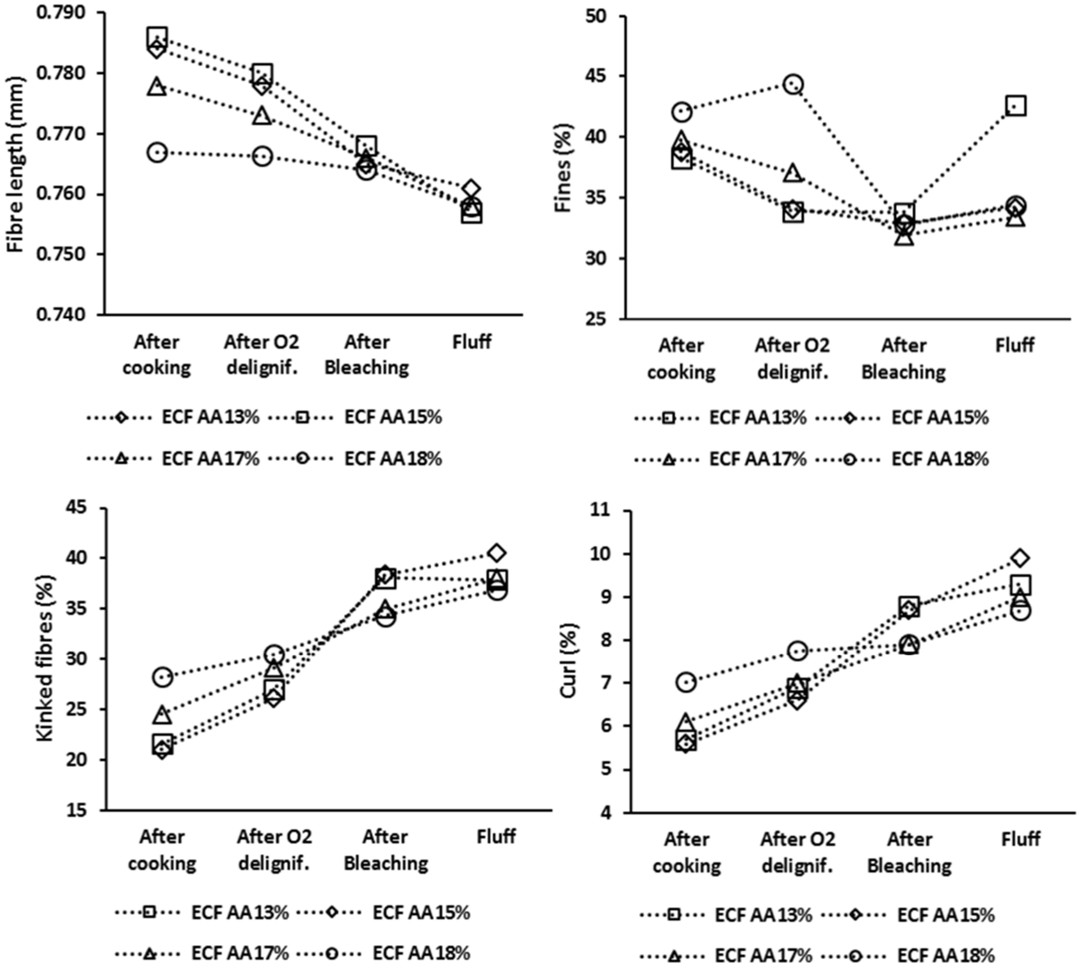

Fig 2 Changes in fibre morphology occurred after kraft pulping at AA from 13 to 18% during oxygen delignification, ECF bleaching and dry defibration of fluff pulps.

The drop in fibre length after dry defibration was relatively small for all bleached eucalypt pulps (within 5%). Previously, similar trend was reported for the dry defibration of ECF and TCF eucalypt industrial pulps (Rebola et al 2020). It should be noted that the decrease in fibre length and the increase in fibre deformations were observed in all steps of fluff pulp production after cooking (i.e. after oxygen delignification, bleaching and dry defibration). However, the most pronounced aforementioned morphological changes occurred during the pulp bleaching

(Figure 2). Noteworthy is the tendency of fibers to deform after the ECF bleaching, showing more pronounced kink and curl when compared to fibres of TCF bleached pulps (Table 4).

Absorption properties

The absorption capacity of fluff pulps is largely dependent on the uptake and retention of fluid by the void volume of the fibre web (Chatterjee and Gupta 2002; Hubbe et al.2013). Accordingly, an air-laid fibre network should have high enough specific volume with enhanced mechanical properties and reduced inter-fibre bonding without compromising the absorbent properties. Furthermore, the architecture, stability and surface properties of an interfibre capillary system have a major effect on fluff absorbency. Therefore, the absorbent capacity is related directly to individual fibre characteristics, such as coarseness, stiffness and length, which control fluff pad resilience.

Pads with a higher specific volume possess a good resiliency and should have higher water absorption capacity. The last affirmation was not quite fair regarding the results on absorption capacity of ECF and TCF eucalypt pulps in study (Figure 3). Thus, the air-laid fibre formulations made of TCF pulps showed slightly higher specific volume (higher porosity), but somewhat lower absorption capacity than pads made of ECF pulps. Among ECF pulps, those cooked with increased AA tended to increase absorption. The opposite tendency was observed with TCF fluff pulps (Figure 3). The absorption time always followed a declining trend with an increase of cooking AA for both ECF and TCF pulps. However, TCF pulps showed slightly shorter absorption times than ECF pulps. In general, variations in absorption capacity were smaller than would be expected from variations in pads porosity.

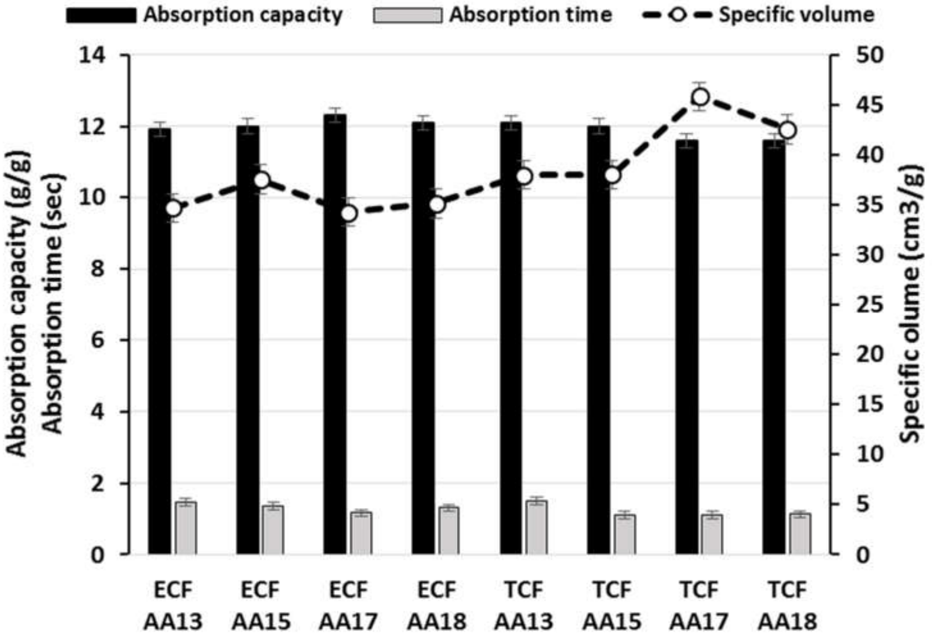

Fig. 3 Absorption capacity and absorption time of ECF and TCF fluff pulps cooked at variable active alkali (AA) from 13 to 18%.The specific volumes of air-laid pads were measured at the compression load of 2.5 kPa.

The porosity of the air-laid fibre network is commonly affected by the fibre morphology, being promoted by the fibre length, coarseness and deformations (Askling et al. 1998a; 1998b; Lund et al 2012). Therefore, the higher specific volume of pads made from TCF pulps (Figure 3), which have greater coarseness and kink (Table 4) than ECF pulps, is not surprising. It must be noted that during the wet absorption test, under external compression load, the porous fibre network collapses to significant extent due to the low mechanical resistance of the wet web. The resistance of the wet web depends largely not only on the flexibility of individual fibres under moistening (Gupta and Hong 1995), but also the amount of knots in the formulation (Rebola et al. 2020). Knots not only negatively affect the specific volume of the air-laid formulations; they also have less absorption ability than disaggregated fibres (Azevedo et al. 2020). In addition, the water retention capacity of the pulp also contributes substantially to the absorption capacity, which in turn is related to the swelling of the fibres. In knotless industrial eucalypt fluff pulps, the water retention was directly related to the content of carboxyl groups in pulps and positively correlated with the absorption capacity of fluff pulps (Rebola et al. 2020). However, this was not the case in the present study, where no clear relationship was found between the amounts of carboxyl groups in the ECF or TCF knotted pulps and their absorption capacity (Table 3, Figure 3). Apparently, in the pulps cooked with increased AA, the decrease in hemicelluloses and in the content of the carboxyl groups did not lead to the expected decline in the absorption capacity due to the simultaneous decrease in the knots content of fluffed pulps (Figure 1). At the same time, there are other contributing factors such as, for example, some increase in the fibre surface hydrophilicity with removal of moderate amount of hemicelluloses (Liukkonen 1997; Koljonen and Stenius 2005). The contact angles of the pulp handsheets were always smaller with the increase in cooking AA, in both ECF and TCF bleached pulps. For example, the contact angle of handsheets dropped from 38 and 43° in ECF13 and TCF 13 pulps, to 31 and 33° in ECF18 and TCF18 pulps, respectively. The increase in fibre hydrophilicity positively contributes to the absorption capacity of fluff pulps, occurring predominantly via the capillary suction mechanism (Chatterjee and Gupta 2002). In this sense, more hydrophilic ECF pulps promote better capillary suction than TCF pulps.

Another factor that affects the absorption capacity of the pads is the change in the physical structure of the cellulose, expressed in the rearrangement of the fibrils, leading to their aggregation after drying (hornification), which results in more collapsed and rigid cellulosic fibers (Rebuzzi and Evtuguin 2006). According to previous studies on the hardwood fluff pulp, the removal of xylan by alkaline extraction leads to less flexible fibres that form an air-laid fibre network with a more resilient structure, capable of less deformation when wetted under external compression load (Lund et al. 2012). The changes in supramolecular structure of cellulose in pulps cooked at different AA and bleached by ECF/TCF sequences have been studied employing solid-state ^{13}C NMR (Figure 4).

Practically no significant changes were detected in cellulose crystallinity among studied pulps and the *CrI* varied between 0.46 and 0.48 (Table 5). However, the CP-MAS ^{13}C NMR spectra of kraft pulps showed some differences regarding the lateral fibril (D_L) and, especially, fibril aggregate dimensions (D_A). Thus, the increase in cooking AA led to a small increase in the D_L and to a noticeable growth in D_A. This fact indicates the progressive coalescence of cellulose fibrils in the fibre cell wall with increasing severity of processing conditions, also known as a part of hornification mechanism. As known, under conditions of kraft pulping, the cellulose fibrils in the fibre cell wall tend to coalesce due to the purification of its surface from lignin and hemicelluloses and a plasticizing effect of the reaction medium (Ioelovitch et al. 1991; Hult at al. 2001). Some neighbouring co-oriented cellulose fibrils may even join surfaces showing a small increase in crystallite width due to cocrystallization. This fibril coalescence is promoted by the cooking alkalinity and increases the aggregation of fibrils during pulp drying, i.e. enhances the hornification (Rebuzzi and Evtuguin 2006, Ferreira et al 2020). Hence, the severity of the pulping conditions affected the supramolecular structure of the cellulose, which in turn altered the physical properties of the fibres.

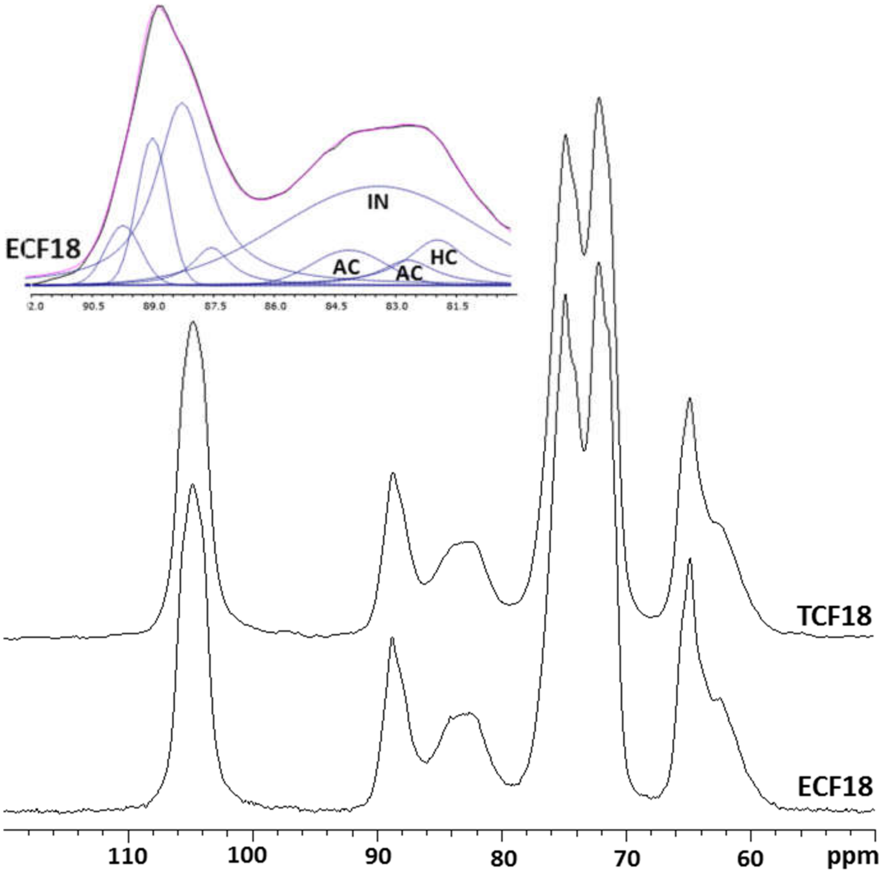

Fig. 4 Typical CP-MAS ^{13}C NMR spectra of ECF and TCF bleached kraft pulps cooked at active alkali 18% (ECF18 andTCF18, respectively). The expanded spectrum region of ECF18 pulp at 80.0-92.0 ppm depicts the deconvolution peaks assigned to hemicelluloses (HC) and accessible (AC) and inaccessible (IN) cellulose surfaces used for the calculations for the lateral dimensions of fibrils and fibril aggregates.

Table 5 Crystallinity index (*CrI*) and average transversal fibril (D_L) and aggregate dimensions (D_A) of ECF and TCF pulps cooked at different active alkali (AA).*

Pulp	Crystallinity index (*CrI*) (±0.1)**	Lateral fibril dimension (D_L) (±0.1 nm)**	Lateral aggregate dimension (D_A) (±0.3 nm)**
ECF13	0.47	4.9	7.2
ECF15	0.47	4.9	7.2
ECF17	0.46	5.2	7.5
ECF18	0.46	5.2	7.5
TCF13	0.47	5.4	8.0
TCF15	0.47	5.4	8.0
TCF17	0.47	5.6	8.2
TCF18	0.48	5.7	8.6

*-pulp designations are the same as in Table 4; **- data obtained by CP-MAS ^{13}C NMR

The pulp hornification is greater in TCF than in ECF pulps due to the more severe alkaline peroxide bleaching stages involved in the former sequence (Table 1). This follows from the more pronounced fibril aggregation in fully bleached TCF than ECF bleached pulps (Table 5) and the lower detected water retention value (WRV) (Figure 5). Apparently, the pulp hornification is one of the explanations for the absence of clear correlation between the amount of carboxyl groups in pulps (Table 3) and their water retention capacity (Figure 5). Hornification decreases the fibre surface and the WRV of the pulp and contributes negatively to the absorption capacity of the fluff pulp. Accordingly, it can be concluded that the observed absorption capacity of the ECF and TCF fluff pulps (Figure 2) is the result of multiple factors that occurred simultaneously (knots content, fibre's hydrophilicity and morphology and physical structure of the cellulose), whose contributions are not always unambiguous.

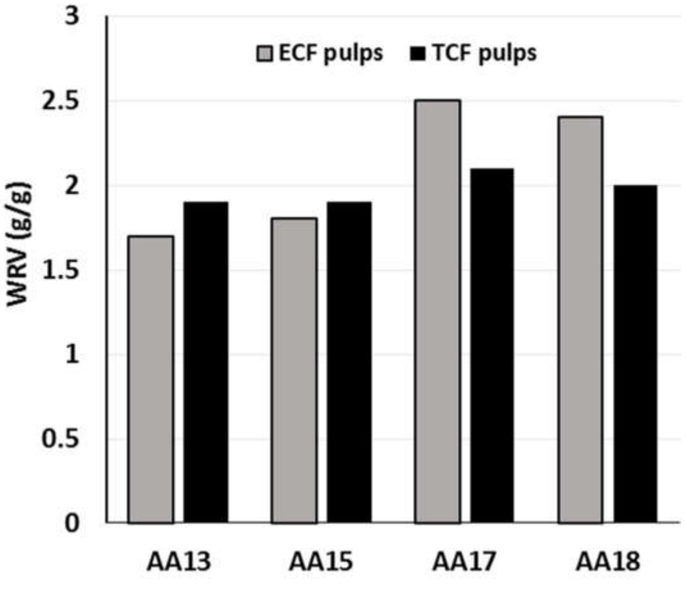

Fig. 5 Water retention volume of ECF and TCF fluff pulps cooked at variable active alkali (AA) from 13 to 18%.

Network strength of fluff pulps

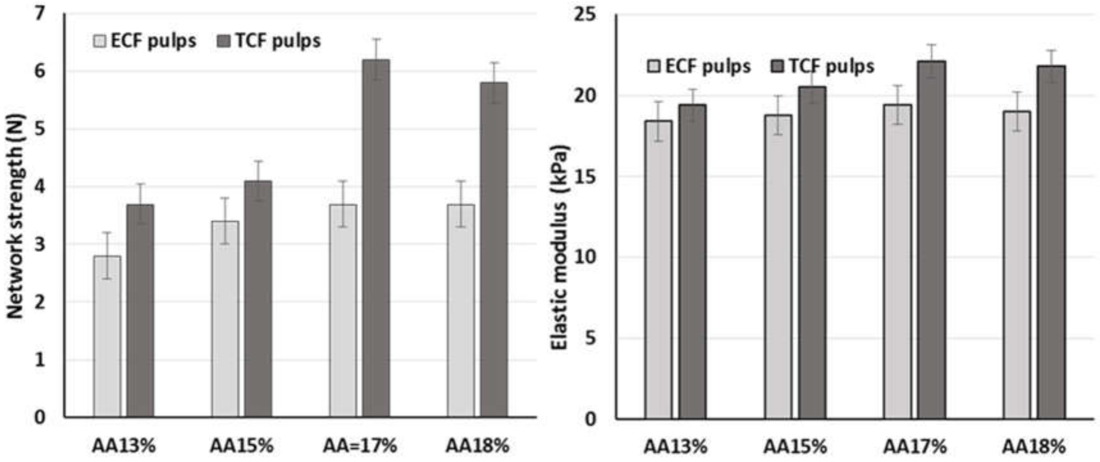

Fig. 6 Network strength of ECF and TCF fluff pulps cooked at variable active alkali (AA) from 13 to 18%.

The network strength (NS) analysis of air-laid fluff pulp formulations were carried out after their dry defibration at 3500 rpm. In this case the knots content in fluff pulps was minimal (Figure 1). A similar trend was observed for ECF and TCF pulps with regard to the increase in NS with higher cooking AA (Figure 6). This behaviour can be explained, at least partially, by the reduction of the knots in dry defibrated eucalypt kraft pulps cooked with an increased AA (Figure 1). The knots usually bolster misshapen and inhomogeneous spaces in pads, which result in undefined break points (Brill 1983; Lund et al. 2012). As it was clearly demonstrated in our previous study, the elimination of knots from eucalypt fluff pulp increases greatly the NS of the pads (Rebola et al. 2020). For the kraft pulps cooked at the same AA, NS values were greater for the pulps bleached by TCF than by ECF bleaching sequences (Figure 6). These differences were especially noticeable for the high cooking AA. Meanwhile, since the knots content in dry-defibrated TCF pulps were always higher than in ECF pulps, the greater NS of the former cannot be explained by the amount of knots only.

Taking into consideration that the fibre morphology (fibre length, coarseness and deformations) has a decisive influence on the strength properties of air-laid pulp formulations (Askling et al.1998a; Lund et al. 2012), it can be proposed that the coarser and more kinked fibres of the TCF than of ECF pulps (Table 4) contributed substantially to the higher NS values of the former. This was also the main argument to explain the higher NS values of the industrial TCF than of the ECF fluff pulps (Rebola et al. 2020). However, the discussed above dependencies on the physical properties of the eucalypt pulp fibres from the kraft cooking and bleaching conditions show that these factors must also be considered. Thus, the increase in the cooking AA can be associated with stiffer and less conformable fibres in fully bleached pulps, especially those bleached by TCF sequence. Such fibres provide more porous and rigid fibre network. Thus, the elastic modulus (*E*) was increased for both ECF and TCF fluff pulps with the increase of the cooking AA. Apparently, more rigid and deformed fibres (curled and kinked) are arranged in a network so that the slippage of the fibres under load is less pronounced. In general, the proportional compression deformation of air-laid pads (ε) under load (2.5 kPa) was smaller for TCF than for ECF fluff pulps (Figure 7). However, the dependence of the ε from the cooking AA was not univocal and had a tendency to decrease for TCF fluff pulps and to increase for ECF fluff pulps.

Noteworthy that the absorption capacity and the network strength of fluff pulps are not clearly interrelated (Figures 3 and 6). Indeed, the absorption capacity was not significantly affected by either the cooking or bleaching conditions. However, a clear trend was observed for ECF fluff pulps to increase absorption capacity with increased cooking AA, while the opposite trend was observed for TCF fluff pulps (Figure 3). At the same time, the network strength was sensible both to the pulping and bleaching conditions and always increased with increased cooking AA (Figure 6). The network strength of TCF fluff pulps was 20 to 70% greater than that of ECF fluff pulps.

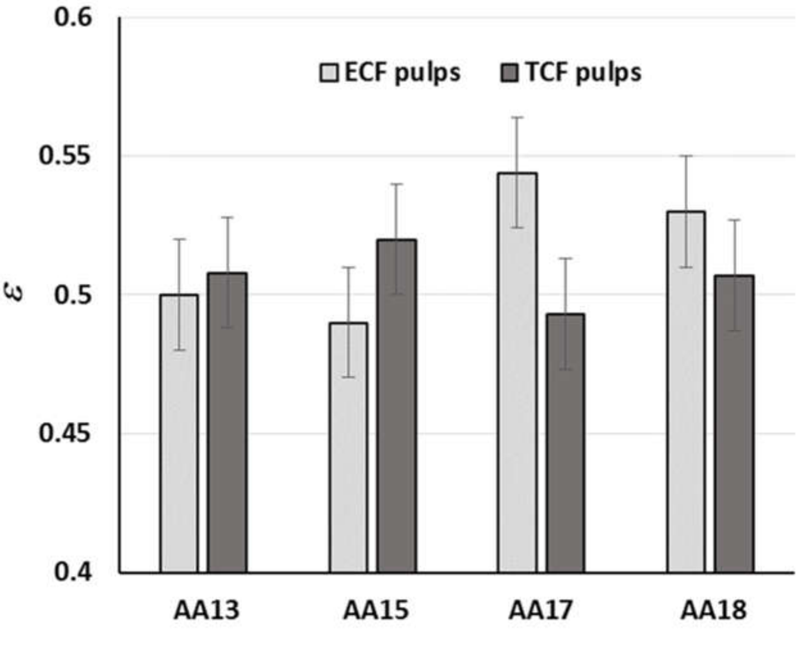

Fig. 7 The proportional compression deformation of air-laid pads (ε) made of ECF and TCF fluff pulps cooked at variable active alkali (AA) from 13 to 18%.

Conclusions

The results of this study showed the importance of kraft pulping conditions and the bleaching mode for the properties of eucalypt fluff pulps. The increase in active alkali (AA) in cooking provides progressively delignified and bleachable pulps with variable chemical composition affecting the physical structure of cellulose and fibre properties. The further bleaching (ECF or TCF) enhances the differentiation among the pulps regarding their behaviour in dry defibration, absorption capacity and mechanical properties of air-laid formulations. Thus, the bleaching mode (ECF or TCF) affects the pulp's composition and fibre morphology that, in turn, influences their dry defibration behaviour. Pulps are easier to defibrate with less knot release when cooked at an increased AA and ECF bleached. TCF bleached pulps provide more rigid and coarser fibres than those of ECF bleached pulps. In turn, dry-defibrated ECF pulps possess more flexible and less deformed fibres than TCF pulps. These features predetermine the structure and the strength properties of air-laid formulations. Thus, coarser, stiffer and more deformed fibres of the TCF pulps are less conformable and provide a more porous and strong air-laid fibre network than that formed by the fibres of the ECF pulps. However, the fibre network strength and the absorption capacity of air-laid formulations are not directly related. It was concluded that absorption capacity of the fluff pulps is the result of multiple simultaneously occurring factors, such as the knots content, fibre's hydrophilicity and morphology and water retention capacity of the fibre web, whose contributions are not always unambiguous. This explains the non-evident dependence of the absorption capacity of fluff pulp on cooking and bleaching conditions.

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