XII Iberoamerican Congress on Pulp and Paper Research

28th June to 1st July 2022

Book of Abstracts

Marc Delgado-Aguilar, Quim Tarrés, Fernando Julián, and Francesc X. Espinach (eds.)

GIRONA

Tracing the path to a circular bioeconomy

Universitat de Girona

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LEPAMAP PRODIS

XII Congreso Iberoamericano de Investigación en Celulosa y papel 2022 (CIADICYP)

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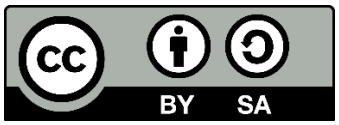

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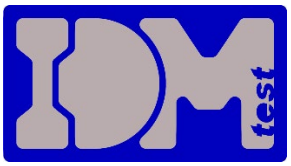

Índex

ORAL SESSIONS

Plenary sessions
(Tuesday 28th June 2022)

Bio-based materials from a high content of Renewables: oilseed and lignocellulosics as feedstock

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Studies concluded or in progress have aimed to add value to raw materials derived from lignocellulosic and oilseed biomass targeting to meet society's expectations and contribute to the advancement of the circular bioeconomy. In this context, lignin and cellulose obtained from woody or non-woody sources (Figure 1), woody lignosulfonate, triglycerides of ricinoleic acids (the main constituent of castor oil, CO), linoleic and oleic (main constituents of soybean oil epoxidized, ESO) (Figure 1), have been used as reagents in syntheses, with simultaneous formation of bio-based films or composite matrices. Plant fibers (short fibers or mats) and microcrystalline cellulose (MCC) have been used as reinforcement in bio-based matrix composites, and nanocrystalline cellulose (CNC), lignin, and cellulose as films or electrospun mats additives. CO has also been used as a dispersant in CNC-reinforced electrospun mats and a compatibilizing agent in lignocellulosic fibers-reinforced hydrophobic matrices (e.g., polyethylene reinforced with curaua fibers). Against this background, the Recycled PET (rPET) electrospun mat showed considerably higher Young's modulus when CO was used as a dispersing agent for CNCs in rPET, compared to the mat rPET/CNCs. Lignin (or lignosulphonate), and MCC, acted as polyols in the synthesis of polyurethanes. In addition to additional polyol, CO worked as a dispersant of solid reagents in the solvent-free reaction media. Such syntheses, under appropriate conditions, have led to films or composite matrices. It has been possible to use high concentrations of MCC as a polyol; the films have exhibited many good properties, including non-cytotoxicity; films with antiviral properties are underway. Regarding composites, the use of MCC as reinforcement, combined with cellulosic blankets (a type of hierarchically reinforced hybrid composite), has led to materials with excellent impact resistance. Epoxy matrix composites synthesized from lignosulphonate (or lignin) and ESO, hierarchically reinforced, are in progress.

Figure 1. Raw materials from lignocellulosic and oilseed biomass

Polysaccharide-based nanocarriers For Biotechnolgical and Medical applications

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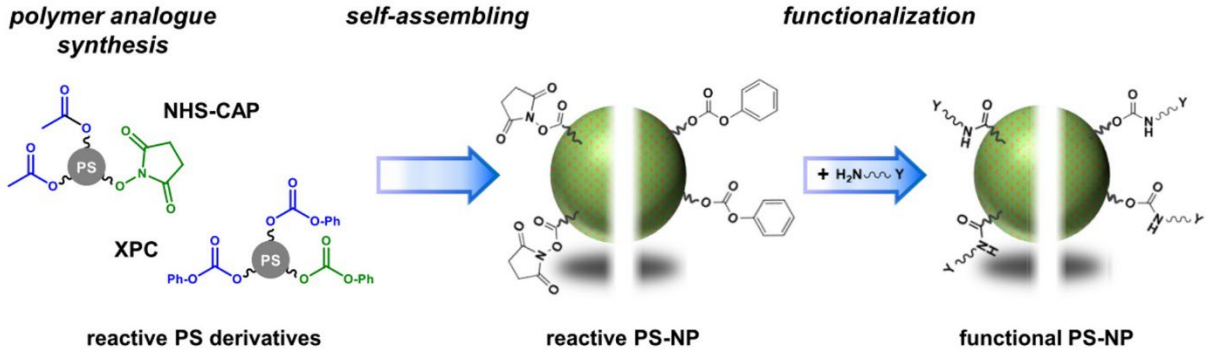
Nanoparticles (NP) can easily be obtained by self-assembling hydrophobic polysaccharide derivatives. Due to their inherent biocompatibility and facile preparation, they are highly attractive for (bio)medical applications, e.g., immobilization of drugs, antibodies, and sensors like dyes.

Ready-to-use NPs with reactive groups are of interest that enabled direct immobilization of biomolecules. For instance, NP with activated NHS (N-hydroxysuccinimide)-ester groups could be obtained from cellulose acetate phthalate (CAP). The NHS-ester moieties are useful for the immobilization of amines [1]. The NHS-CAP products formed spherical NP in the range of 200-400 nm.

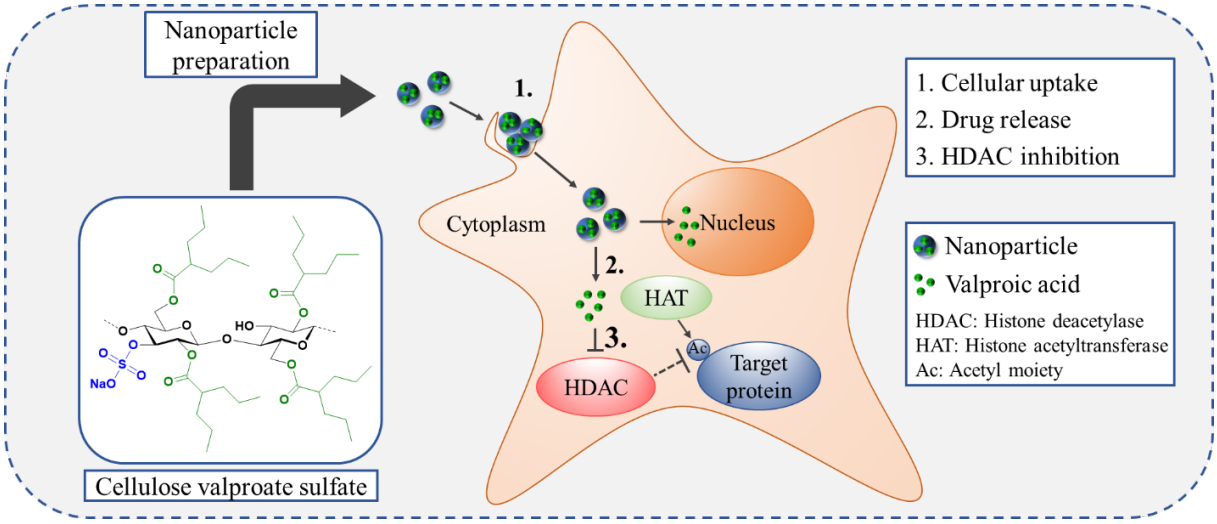
On the other hand, xylan phenyl carbonates (XPC) with different degrees of substitution were prepared under homogeneous reaction conditions applying ILs. The derivatives showed a high reactivity towards various types of functional amines leading to the formation of carbamates [2]. The carbonate groups acted as reactive and hydrophobic groups, thus, enabling the self-assembling of XPC into NP with diameters of 100-200 nm:



The NP with reactive moieties (NHS-esters and aryl carbonate moieties) were stable under aqueous conditions and enabled direct immobilization of amine-functionalized dyes and enzymes under aqueous conditions with high coupling efficiencies of up to 90 %. Moreover, the novel NP was demonstrated to be non-cytotoxic.

The development of bio-based NPs as drug containers is of increasing interest to circumvent common treatment disadvantages such as rapid drug metabolization, short serum half-life, and side effects. The histone deacetylase inhibitor valproic acid (VPA) is known for its anti-inflammatory as well as anti-cancer activity. Here, recently developed VPA-loaded NPs based on cellulose- and dextran VPA esters were modified with sulfuric acid half-ester moieties to improve intracellular drug release. The NPs show rapid cellular uptake, are non-toxic, highly biocompatible, and can induce histone H3 hyperacetylation.

Thus, they represent a potent drug delivery system for the application in a variety of treatment issues, such as inflammation, sepsis, and defined cancer types. In addition, the flexible NP-system offers a broad range of further options of modification, e.g. for targeting strategies and multi-drug approaches [3,4]:



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Engineered (nano)cellulose for advanced paper-based materials in sustainable packaging

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After the 20th century, which was the century of petrochemistry and our civilization's debt to the ecosystem of our planet, it is time to move on to the 21st century which will undoubtedly be dedicated to the bio-economy. The fossil resource tends to saturate our environment and atmosphere with CO2 but also become depleted. One solution is to use biomass and more precisely the superstar of the biomass, i.e the cellulose.

Cellulose is fascinating in its structure, but above all, this material is biobased, biodegradable, non-toxic, biocompatible with living organisms, available everywhere in the world, and not expensive. For more than 20 years, I have therefore directed all my research to the development of new cellulose engineering to enable the production of a new generation of high-performance cellulosic materials. The Paper industry with all its supply chain and large-scale process facilities is becoming a key partner to develop such solutions. Our society is expected paper-based solutions in sustainable packaging as it is the only material that is recycled (not recyclable), biodegradable and biobased. However, the challenges are still numerous to bringing high barriers and new functions or to create 3D shaped materials.

The main idea detailed during this talk is to use the engineered (nano) cellulose in paper to overcome these classic issues.

A specific focus will be proposed on (i) optimizing the production of a new generation of nanocellulose (by using twin-screw extrusion), (ii), giving them new functions (i.e. antibacterials, molecule release, hydrophobic), and (iii) proposing high-performance applications in paper-based packaging (barrier solutions). An introduction about the new Cellulose Valley chair will also be proposed.

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New Advances to Approach Circularity with Wood, Fibrillated Lignocelluloses and Biomass Residuals

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I introduce three emblematic cases associated with our recent work that highlight the great possibilities of circularity in the bioeconomy based on forest biomass and residuals. First, I discuss a processing route that transforms low-value wood (residual, damaged, decayed, disposed, or fractured) into a lightweight and strong structural materials. The process involves delignification, combined with partial dissolution and regeneration, to expose cellulose fibrils originally present in the cell walls. The latter form strong hydrogen bonding networks at interphases, leading to a 'healed' wood with a mechanical strength that exceeds that of typical metals and commercial laminated wood. Moreover, recyclability as well as excellent resistance against organic solvents are demonstrated, providing a promising valorization and sustainability pathway for low-value wood (1). Following similar approaches, I next discuss an option for the valorization of biomass, in this case, blueberries pruning residuals and food waste and losses, sourced from agroforestry operations that can be used to produce added-value products, including platform chemicals and value-added materials (2-3). Along with such examples, I briefly show the premise of new routes for the production of fibrillated cellulose (4-5). Finally, I gave an example of a facile strategy to synthesize all-green SUPs based on chitin nanofibers. The latter is demonstrated for their facile recyclability and biodegradability in natural environments, addressing the limitations of circularity and end of life of non-renewable products (6). Given the low cost of the raw materials, their natural micro-structural design, and self-adhesion, these presentations show fully sustainable alternatives to products based on non-renewable carbon.

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Biocomposites

(Tuesday 28th June 2022)

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Cellulose nanomaterials and their use in composites, from laboratory to industrial scale

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The research on cellulose nanocomposites started *in the* late 1990s in Grenoble, France. Since that, the research on cellulose nanomaterials has had incredible growth and *many* papers are published every year. A large part of the research is focusing on the separation processes of the nanomaterials but the number of papers on composite manufacturing processes and on applications has increased every year [1, 2]. This lecture gives some ideas about how cellulose nanomaterials can be used in composites and what type of properties can be achieved. *Composite* manufacturing processes such as extrusion, impregnation of nanofiber networks, and preparation of super lightweight foams are discussed.

Processing of bionanocomposites has focused on solvent casting and some other *laboratory-scale* methods, however, our group *has* used common composite processing methods which can be upscaled [3-7]. We have developed an extrusion process where the nanomaterial is fed into the extruder as a liquid suspension and this process can lead to good dispersion of the nanomaterial if compared with processes where the nanomaterials dried before blending with the polymer [3,4]. The dispersion of the nanomaterial in a polymer matrix is critical and we have shown that if the nanomaterials are well dispersed, they can increase the polymer properties already in very low concentrations. We have showed that if the nanocrystals or nanofibers are oriented, they are further increasing the reinforcing effect [8-10]. Solid-state drawing of PLA nanocomposites with cellulose nanofibers resulted in increased strength and toughness of the composites by 70 % and 200% [10]. Another process *that* is interesting is to use the nanofiber network as a preform in resin infusion processes. Nanofiber networks are very stiff and strong but also very dense with low permeability. We have worked with preform development *that* could allow a common vacuum infusion of a thermoset resin into the network [5,7,11,12].

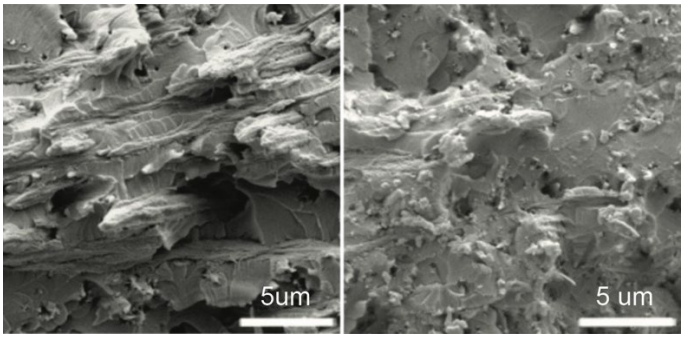

Figure 1. Cellulose nanocomposite with good interfacial adhesion with bioepoxy as matrix.

In addition, demonstration of scale up operations of selective nanocomposites for automotive and building applications are also presented and discussed. [13-15]

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Industrial scale melt processing of renewable cellulose nanofibers/polyamide-6 composites

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As a renewable alternative to petroleum-based materials, wood or plant-based materials offer a greater prospect in the transition towards sustainable replacements. Native to wood, cellulose nanofibers (CNF) form the major load-bearing component and possess tremendous potential as a reinforcement material in polymeric matrices. This study focuses on nanocellulose-based composites prepared and characterized bio-(nano)composites with high cellulose weight/volume fraction. The influence of nanoscale reinforcement or nanostructure on the macroscopic properties of the nanocomposites was investigated. Distinct prominence was given to the effect of nanocellulose dispersion and nanocellulose/polymer interface on the physical characteristics of biocomposites.

On an industrial scale, it is a challenge to achieve cellulose-based nanocomposites due to dispersion issues and high process temperature sensitivity. The conducted study describes methods to develop mechanically strong and thermally stable polyamide 6 (PA6) and cellulose nanofibers composites capable of withstanding high processing temperatures. With PA6 being a very technical polymer matrix to be reinforced with CNF, good dispersion was achieved with the help of a high-speed kinetic mixer and also prevent the CNF from excess thermal degradation by implementing an extremely short processing time. The published paper [1] presents an industrially feasible method to produce PA6/CNF nanocomposites with high CNF composition processed by a high-speed kinetic mixer (GELIMAT®) followed by compression molding to obtain homogenous and thermally stable nanocomposites aimed for high-performance applications. PA6 was reinforced with three different wt.% formulations (5, 15, and 25 wt.%) of cellulose nanofibers. The resulting nanocomposites exhibited a significant increase in Young's modulus and tensile strength with CNF content, owing to the effective melt processing and the surface charge density of the CNF, which necessitated the dispersion. The thermal stability and polymer crystallinity concerning CNF composition for the PA6/CNF nanocomposites were examined by TGA and DSC analysis. Rheology studies indicated that the viscosity of the composites increased with an increase in CNF composition. Overall, this work demonstrated an industrially viable manufacturing process to fabricate a new generation of PA6/CNF nanocomposites.

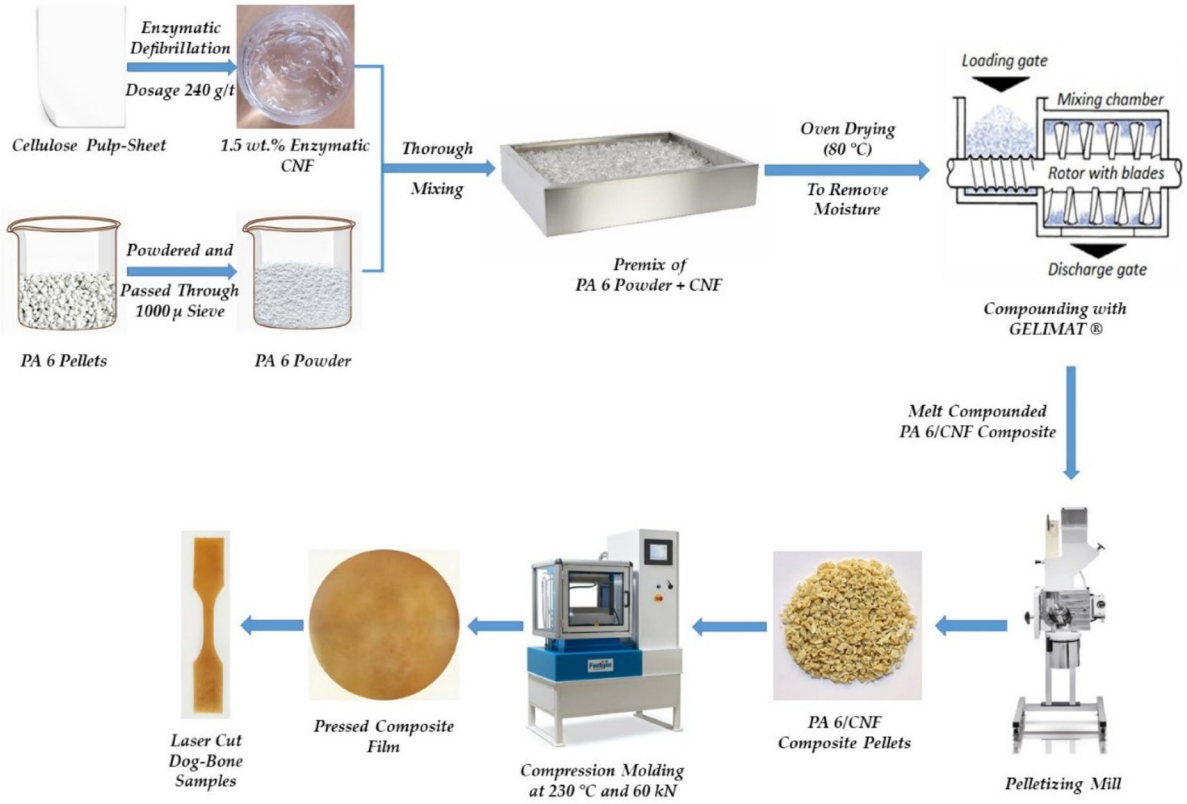

Figure 1. Schematic representation of the manufacturing process for PA6/CNF nanocomposites. [1]

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Magnetic polyvinyl alcohol/cellulose nanofibers blend beads

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Access to secure water resources is widely recognized of key importance for living organisms, so any potentially harmful substances must be conveniently removed from both the industrial wastewaters and the already polluted natural water bodies. In the research of materials suitable to be used as environmental remediation devices, it is important to consider not only their capability towards the defined aims but also the costs and ecological impacts of the employment of certain starting materials as well as the implied preparation methodologies. In this sense, cellulose, the most abundant and widely spread natural polymer on Earth, has been considered for the development of adsorbents for water treatments[1].

On the other hand, micro-and nano-structured materials have attracted attention as promising water remediation devices due to their large surface areas and specific active sites to which the pollutants can be easily bonded[2]. Particularly, the generation of magnetic materials offers the possibility to remove the material, once the water treatment has finished, by the simple use of an external magnetic field. Magnetic materials, such as films and beads containing iron oxide nanoparticles, have demonstrated good activities as pollutants removers. Recently, simple polyvinyl alcohol (PVA)-based magnetic beads able to remove cationic and anionic dyes from aqueous systems were prepared and reported[3]. To progressively turn our research work as green as possible, favoring circular economy and bio-economy, the replacement of synthetic PVA with nano-cellulose obtained from agricultural waste was deeply studied. Specifically, in the present research work, lignin-free cellulose nanofibers (CNF) obtained mechanically from wheat straw by previous optimized procedures were considered to prepare PVA/CNF magnetic beads containing iron oxides, and the obtained materials were completely characterized and further tested as potential adsorbents for water remediation. It is important to remark that the *in-situ* generation of the magnetic nanoparticles not only makes the preparation procedure a simple one, but also the so-obtained materials are expected to be better reinforced than those containing blend fillers.

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Producing cellulose-reinforced biocomposite films from biomass using ionic liquids

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Biomass and its lignocellulosic components are complex polymeric materials underutilized for their impressive mechanical properties. As the structural support material of plants, lignocellulosic biomass derives its strength and stiffness from the microscopic morphology of its cells, whose walls are composed of precisely aligned cellulose microfibrils known to have exceptional tensile properties. These microfibrils are reinforced by agglomerations of lignin and hemicellulose, making biomass a natural composite. However, as fluid transport is necessary even in the dead structural support tissue of plants, much of the volume of lignocellulosic biomass is void. Physical densification has been shown to improve its mechanical performance. [1] Therefore, chemical densification, by way of **selectively dissolving the non-cellulosic fraction of biomass in ionic liquid to form a cellulose-microfibril-reinforced biopolymer composite**, should also yield improved mechanical properties. Unlike physical densification, this process is intrinsically scalable, as it is not limited by the size of feedstock particles.

Ionic liquids are salts with sufficiently low melting points to be conveniently used in liquid form. They are stable, non-flammable, and offer immeasurably low vapor pressures, meaning they are safer to transport, work with, and dispose of than traditional polymer solvents. They may also be reused after mixing with lighter solvents like water by vacuum distillation, making them a relatively sustainable choice for polymer dissolution. In that biomass is renewable, it may also be sustainable—though far more so when it derives from forestry or agricultural waste, which comprise the majority of available lignocellulosic biomass (the largest stream of non-edible biomass globally). [2]

The two primary challenges associated with this manufacturing process are the same: dissolving highly polymerized lignin from whole biomass and regenerating lignin to form a solid film during ionic liquid removal. Essentially, depolymerizing and depolymerizing lignin. To address the first challenge, ionic liquid chemistry and dissolution conditions were optimized. To address the second, two methods were tested: radical polymerization of the dissolved non-cellulosic portion of biomass; and partial dissolution of cellulose to form a solid matrix for other biopolymers during regeneration. Related parameters such as curing, drying, and regeneration conditions were also optimized.

Dynamic mechanical performance and microstructure of thin films produced using this method (which preserves the native cellulose-I structure) were compared to those of biomass films containing fully dissolved and regenerated cellulose (cellulose-II), and to those of films made from equivalent mixtures of extracted lignocellulosic components. The effect of biomass composition on this performance, modulated directly in component mixtures and by wood species in biomass films, was also investigated. The produced composites may offer a sustainable alternative to traditional glass fiber-reinforced polymers for high-volume structural applications.

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Discovering potential of hemp fiber materials

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The key principle of circular bio-economy intends converting waste material produced by one industry into the valuable source for the other processes. Hemp fibers (HF) along with the advantage of being valuable agricultural waste material versus the virgin wood pulp usually used for the pulp and paper industry, have much more benefits. Unlike the botanically limited size of the wood-based fiber, the length of HF can be adjusted by choosing different parts of hemp stem (long fibers, shives, or mixed) or processing type and intensity, furthermore HF is highly responsive for fibrillation, thus opening opportunity for a wide variation of properties. HF has been acknowledged as suitable for combination with different conventional pulps, as well as with non-traditional fiber-like substances, such as fungal hyphae, which has been recognized as an appropriate blend for innovative bio-based materials [1].

In the presented research HF was obtained from hemp stem and shives by Kraft pulping. HF showed intense micro-fibrillation during the beating process using both conventional PFI mill and high-performance blender, achieving up to 91°SR. Highly fibrillated HF was used for obtaining extra thin (40-70 μm) and at the same time extra-strong paper (tensile index up to 62 N·m/g) with low grammage (9-16 g/m^2) and low air permeability (10-30 ml/min). Differently pre-processed HF was mixed with recycled fibers (RF), cellulose nanofibrils (CNF), and fungal fibers (FF) in various combinations and tested for their mechanical and air permeance properties. Results showed the potential for developing paper sheets with a wide range of strength and air permeability values. The amount of HF in fiber combinations was the main factor responsible for mechanical performance. Higher fibrillation of HF improved the strength even more, however, caused drainage problems and should be controlled. The most successful combination in terms of strength was a mixture of HF with different fiber lengths in addition to 3-5% CNF when tensile index reached 70 N·m/g. Most of the HF materials showed rather low air permeability, which can be increased significantly by adding 30-70% fungal hyphae pulp. Obtained HF-FF material had unique structure and has potential for further development.

A wide range of results confirmed the potential of HF as an appropriate and attractive component for the development of natural fiber-based materials potentially suitable for a variety of targeted applications. HF can be added to conventional pulps or recycled fiber compositions for higher strength, and the influence of HF can be adjusted via choosing the processing parameters or mechanical or chemical pretreatment of fibers and by varying the composition.

Acknowledgment

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Properties of panels from residual hemp particles

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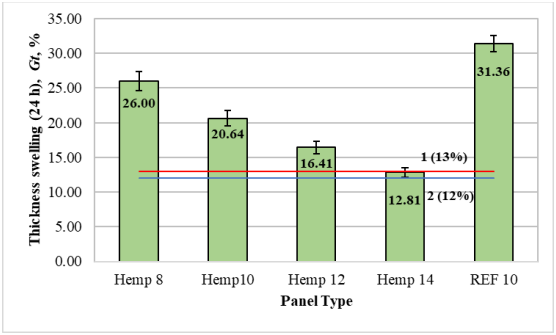
The growing production of wood-based panels and the global shortage of wood raw materials necessitate the search for alternative raw material sources [1]. Non-wood lignocellulosic residuals are promising raw materials for that purpose [2]. Stems of industrial hemp are characterized by the high strength of their fibers, with a low bulk density of the material. At present, mainly hemp plants' long fibers are separated from the stems, and the leaf mass is also used. That remains a residual of hemp particles and small amounts of fiber [3].

This report presents a study on the effect of the resin content on the properties of panels produced from residual hemp particles. The chemical composition of the hemp raw material has been determined, and the content of both short and long fibers has been established. The fibers are left in the composition of the panels, thus increasing the contact areas between the particles and reducing the pore space. The boards are manufactured with a set density of 650 kg.m^{-3} and a change in resin content of 8 to 14% (Hemp 8 to Hemp 14). A wood particle board with a resin content of 10% (REF 10) was also produced. The adhesive system comprises 90% urea-formaldehyde (UF) resin and 10% melamine-formaldehyde (MF) resin. It was found that panels from hemp particles and fibers have very good properties, exceeding these of wood particleboard, Figure 1 A) and B). It is not recommended to use more than 10% resin content when panels are used in a dry condition and up to 12% for humid conditions. Increasing the resin content to 14% will make the product more expensive and increase formaldehyde emissions from the boards.

A)



B)

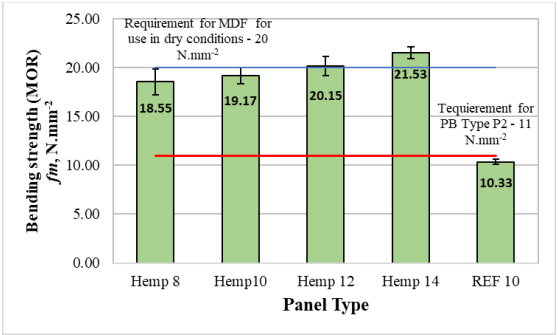


Figure 1. A) Thickness swelling; B) Bending strength

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Nanocellulose-reinforced pla biocomposites: masterbatch-like dispersion approach

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The use of nanocellulose, both in the form of cellulose nanofibers (CNF) and cellulose nanocrystals (CNC), as reinforcement of polylactic acid (PLA) has been a topic of great interest during the last decade. The successful incorporation of CNF into PLA matrices could significantly improve its mechanical, rheological, and barrier properties while maintaining its features in terms of biodegradability and biocompatibility. However, the inclusion of CNF is still a challenge, particularly in the presence of water, the lack of appropriate dispersion methodologies, and the low affinity between cellulose and PLA. To overcome these limitations, several strategies have been reported, including the use of surfactants, plasticizers, or solvent-based processing techniques. However, the use of such strategies usually hurts properties or they are not upscalable.

For all the above, the purpose of this work is to elucidate the feasibility of incorporating high dosages of CNF into a thermoplastic starch matrix (TPS), which contains unknown fractions of PLA, to be later blended with PLA. This is based on a masterbatch-like approach, where TPS acts both as a carrier and a compatibilizer between CNF and PLA. To achieve the proposed objective, CNF were prepared using mechanical and enzymatical methods. Later, they were concentrated to 8 - 10 wt% of consistency (moisture content ranging from 92 to 90 wt%), solvent-exchanged with polyethyleneglycol (PEG), and incorporated into the TPS at 30 wt% of CNF content using a Brabender mixer. The resulting high CNF content TPS composites were blended with PLA at different fractions, processed using hot pressing to obtain testable films, and characterized in terms of mechanical, thermal, and rheological properties.

The obtained nanocomposites exhibited improved tensile and thermal properties due to the presence of the CNFs. Although the original properties of PLA were not reached, the resulting materials exhibited good performance in terms of processability and mechanical properties. It was found that the presence of CNFs was beneficial, although at a certain point the nanostructured reinforcement tends to agglomerate, jeopardizing their reinforcing potential. This work provides a new paradigm for understanding the production of nanocellulose-reinforced composites, particularly in systems where the interface is crucial.

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All cellulose composites based on thermoplastic cellulose esters and micronized pulp fibers

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Cellulosic substrates are appealing for the development of sustainable materials given their abundance, low cost, biodegradability, and good mechanical performance [1]. In composites, cellulose fibers have been mainly used as reinforcement elements, given that they are not soluble in traditional solvents and cannot be melt-processed. However, its esterification grants thermoplasticity to the fibers, which in addition to the reinforcing action, extends its exploitation as matrices, thus allowing the production of All Cellulose Composites (ACC). Nonetheless, the use of thermoplastic cellulose esters often requires plasticizers to make melt-compounding attainable [2].

In the present work, ACCs were manufactured by melt-mixing a thermoplastic cellulose ester with micronized cellulose fibers from bleached eucalyptus kraft pulp (Figure 1). A sustainable, non-toxic, and commercially available plasticizer was used. The obtained composites were characterized regarding their processability, morphology, mechanical and thermal performance, and the main results will be presented and discussed.

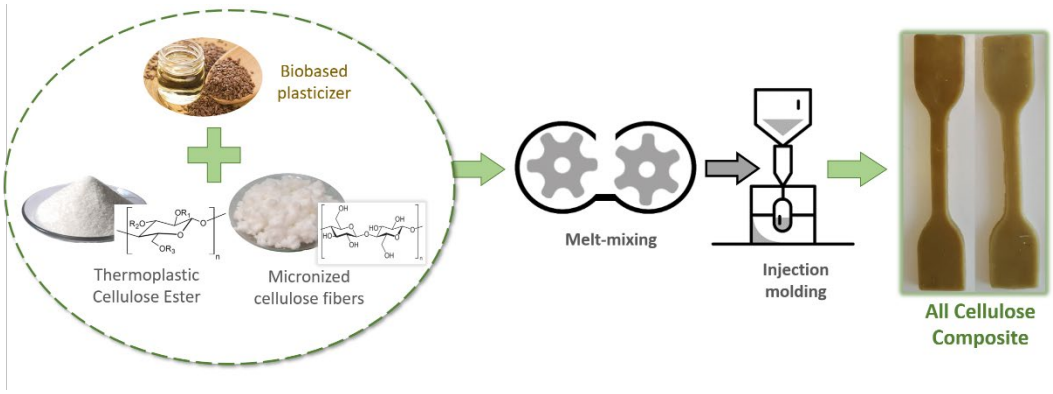

Figure 1. Schematic illustration of the production of the ACCs developed in this study.

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Acknowledgments:

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Influence of compounding parameters on the tensile properties and fibre dispersion of injection moulded polylactic acid (PLA) and TMP fibre biocomposites

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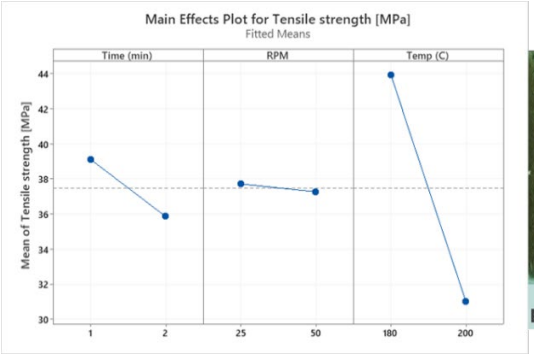
Thermomechanical pulp (TMP) fibers can serve as renewable, cost-efficient, and lightweight reinforcement or filler material for thermoplastic polymers such as poly(lactic acid) (PLA). The reinforcing ability of TMP fibers can be reduced due to various factors, e.g., insufficient dispersion of the fibers in the matrix material, fiber shortening under processing, and poor surface interaction [1].

When compounding fibers and biopolymers, the aim is to achieve a homogenous dispersion of fibers in the matrix while maintaining the fiber length [2]. The compounding process is controlled by the compounding time, screw rotation speed, compounding temperature, and the screw design. The parameters time, speed, and temperature are investigated in this work.

A two-level factorial design was created and PLA together with TMP fibers and an industrial and recyclable side stream were processed in an Xplore twin-screw micro-compounder accordingly. From the obtained biocomposites, dogbone specimens were injection moulded. These specimens were tensile tested, and the compounding parameters evaluated. Scanning electron microscopy (SEM) and three-dimensional X-ray microtomography (X-µCT) images were acquired to get insight into the microstructure and to gain information about fiber orientation and dispersion that could affect the micromechanical performance of the biocomposites.

The temperature turned out to be the major influence factor on tensile strength and elongation, while no significant difference was quantified for the tensile modulus. A temperature of 180 °C, screw speed of 50 RPM, and less compounding time of 1 min. turned out to be the most beneficial set-up for compounding PLA with TMP and industrial side stream.

Based on the structural and mechanical characterization, finite element analysis was performed in Abaqus 2017 to demonstrate a tool for evaluating potential applications for the here presented biocomposites.



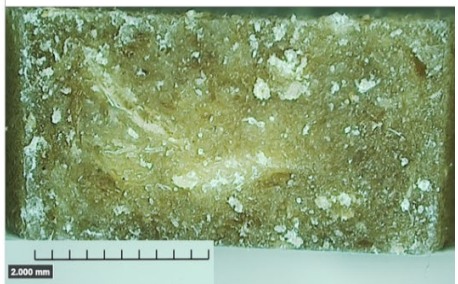


Figure 1. Main effect plots of important compounding parameters on tensile strength (left) and microscopy picture of the breaking surface of the biocomposite compounded at 180 °C, 50 RPM, and for 1 min. (right).

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The effects of biocomposite formulations on the mechanical properties and 3D printability of filaments for fused deposition modelling

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Biocomposites of poly(lactic acid) (PLA) and kraft pulp fibers were prepared. The effects of the compounding temperature, the type of kraft fibers (bleached (B) and unbleached (U)), and the elastomer poly(hydroxyalkanoate) (PHA) on the mechanical properties of the biocomposites were investigated. Compounding at 180 °C had a positive effect on the tensile strength. Biocomposites with 30% kraft fibers showed an increase in the tensile modulus from 3074 MPa to ~4800 MPa. The addition of PHA to the formulations (50% PLA/20% PHA/30% kraft) resulted in a moderate increase in modulus (PLA+PHA+U: 3838 MPa, and PLA+PHA+B: 3312 MPa). The tensile strength increased in PLA+kraft biocomposites, while a reduction in strength was observed for PLA+PHA+U and PLA+PHA+B.

The type of fiber had a significant effect on the modulus of the biocomposites containing PHA. Biocomposites with unbleached fibers (PLA+PHA+U) presented a higher modulus and strength than biocomposites with bleached fibers (PLA+PHA+B). The unbleached fibers contain lignin, which has been reported to act as a compatibilizer between the fibers and the PLA matrix, therefore improving the mechanical properties of the biocomposites [1].

Manufactured filaments of PLA, PLA+PHA+U, and PLA+PHA+B showed similar printability of complex geometries, demonstrating that unbleached pulp fibers could also be utilized in the preparation of biocomposites with good mechanical performance and 3D printing properties.

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Evaluation of the micromechanics properties of long flax oriented fibers as a starch polymer reinforcement

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In the present work, long flax fibers (LFF) were used as reinforcement for a starch-based polymer (PTA). The authors prepared composite material plates and standard specimens were cut from such plates. The specimens were cut out keeping the fibers highly oriented in the direction of the tensile loads to be applied during the tensile test (Figure 1). Additionally, single fiber tests were performed at different gauge lengths.

It was found that composite materials adding 32.07% wt. flax showed a mean tensile strength of 100.80 MPa and a mean Young's modulus of 14.90 GPa. Knowing that PTA properties were 5.85 MPa and 0.16 GPa, respectively, the composite's tensile strength and modulus were 17.23 and 93.16 times higher than the matrix.


a


b

Figure 1. Photography of the fracture section of the specimens

The results showed the expected decrease in the tensile strength of the fibers when their length increased. This is due to the increasing probability of finding a defect in the fiber surface. It was found that long fibers returned tensile strength as predicted by using micromechanics. On the other hand, the intrinsic Young's modulus of the fibers showed noticeable changes with the length of the fibers. This was unexpected, as Young's modulus is a fundamental property. Additionally, the obtained results were lower than those obtained from the Rule of Mixtures. The main reason explaining the differences can be due to partial fiber slippage from the tensile test equipment clamps. This results in overestimating the fiber deformations.

Waste as a resource: municipal solid waste derived, lignocellulosic biomass-reinforced, polylactide laminated composites for advanced engineering applications

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A linear resource consumption model, e.g. the 'take-make-dispose' model, of fossil-derived products, is at the heart of our industrial economy. Manufacturers convert raw materials into products that can be sold to consumers, who discard these when they no longer serve a purpose. Whilst manufacturers have attempted to improve the resource efficiency of their products by integrating renewable energy into their manufacturing chains, less thought has been given to the materials used and their disposal after the products' useful life comes to an end. Manufacturing processes based on consumption instead of the restorative use of resources will ultimately negatively affect the supply chain of many consumer products. As a result, the 7th EU Environmental Action Programme stressed the importance of transforming the EU into a resource-efficient and low carbon economy zone, with a particular focus on turning waste into a resource, with more prevention, reuse, and recycling by 2020, e.g. a circular bio-economy model. In this context, municipal solid waste (MSW) could serve as a low-value feedstock for the production of high-value advanced materials for engineering applications. MSW is composed of either mixed domestic residual waste or waste rejected from sorting and recycling processes (MRF rejects) and contains significant quantities of paper/card (lignocellulosic) based materials. The use of lignocellulose derived from residual mixed waste has several inherent sustainability credentials including waste disposal diversion, reduction of GHG emissions, enhanced sustainability, and the move away from the food-vs-fuel debate. Also, there is sufficient year-round availability and established collection infrastructure.

In this presentation, we discuss the processing of lignocellulosic biomass in MSW into high-performance composite materials. The MSW-derived lignocellulosic biomass was first bleached and refined to remove impurities from this waste feedstock, followed by vacuum filtration and heat consolidation to produce a lignocellulosic fiber network with high stiffness and strength. The lignocellulosic fiber networks were then stacked with polylactide (PLA) films to produce high-performance lignocellulosic fiber-reinforced PLA laminated composites. At a lignocellulosic biomass loading of 35 wt.-%, the resulting laminated composites showed a flexural modulus of ~6.4 GPa. This represents a 40% increase over neat PLA and is comparable to randomly oriented glass fiber-reinforced polymer composites. More importantly, the strong performance of the composites was not sacrificed when compared with PLA, which is often the case when lignocellulosic biomass was used as a reinforcement. The mechanics of using high stiffness high strength fiber network as 2D reinforcement, viscoelasticity, thermo-mechanical properties, and moisture sensitivity of the MSW-derived lignocellulosic fiber-reinforced PLA laminated composites will be presented. The green credentials of incorporating lignocellulosic biomass from MSW into PLA quantified using lifecycle analysis will also be discussed in this presentation.

Energy and Environment (Tuesday 28th June 2022)

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Modelling of a small scale biorefinery and evaluation of its sustainability in a local context

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The concept of the biorefinery is one of the pillars of the bioeconomy, which promotes the diversification of transformation paths of bioresources. The integration of biorefineries in territories embody its belonging to the bioeconomy, and evokes the sustainability of biorefineries as independent facilities, and as an integrated entity of the territory, impacting the territorial socio-economic and environmental components. As opposed to large-scale biorefineries, small-scale biorefineries can be explored as a potential design of biorefineries, implemented in territories to valorize the corresponding biomass and create a socio-economic dynamic. In this context, our study aims to model the implementation of a biorefinery system, namely a small-scale biorefinery, in a local context, and evaluate the sustainability of its implementation on the economic, social, and environmental dimensions. In a first step, multifactorial statistical analysis is conducted to characterize the scale-based designs of biorefineries, particularly defining the small-scale biorefineries. In a second phase, the modeling for evaluation of the implementation of biorefinery systems is subjected to the integrated modeling assessment framework. The model is a coupling of logistical, mass & energy balance, cost-benefit analysis, and multi-criteria decision analysis for the triple bottom line. In parallel, the scenarios of potential biorefineries were evaluated to discern the most sustainable and efficient valorization path or combination of paths. This work provides a solid basis for further developments in small-scale biorefinery definition and the integrated assessment modeling of implementation of biorefineries in the bioeconomy.

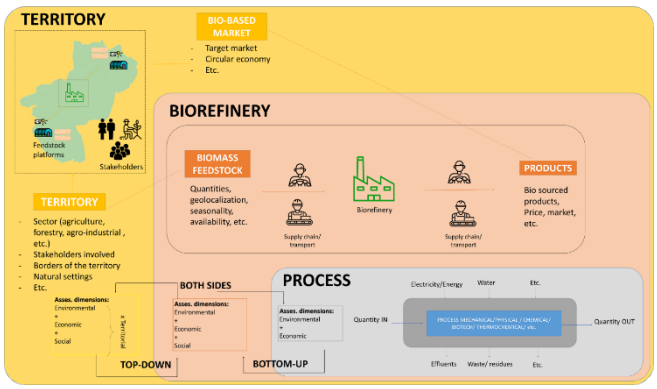

Figure 1. The framework of assessment of the integration of the biorefinery in the territory

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Thermodynamic view for vapor pressure, boiling point, and heat of dissolution of Kraft black liquors

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Boiling point elevation, vapor pressure, and heat of dissolution are essential black liquor properties for heat exchangers and evaporators design. Since black liquor is a complex mixture, theoretical calculations of these properties and their estimation is a challenging task.

On the other hand, the application of experimental data without a theoretical analysis is limited, even very practical, bringing in his history a lack of knowledge about experimental running errors and misconceptions about colligative properties.

In this work a Gibbs-Helmholtz equation view and Pitzer's method for calculating the activity coefficients are presented first, followed by a theoretical estimation and experimental literature data for water inorganic electrolyte solutions of Na_2CO_3, Na_2SO_4, $Na_2S_2O_3$, and the mixture Na_2CO_3-Na_2SO_4. Then, for the organic compound in water, sugar (fructose and glucose), a thermodynamic view is presented for estimating boiling point elevation, with literature experimental data and semiempirical equations for properties estimation.

Several experimental apparatuses for the determination of boiling point elevation (rise), vapor pressure, and heat of dissolution measures are briefly described aiming to discuss the source of errors in the experimental data. Also, the interdependence between the Gibbs-Helmholtz and Clapeyron equations is discussed. Furthermore, the thermodynamic relationship between vapor and liquid in equilibrium is described as the electrolyte thermodynamic equilibrium and analyzed under electrolyte fugacity coefficients. It is important to review the several boiling phenomena and the limits of defining boiling for high solid contents. The colligative properties also concern heat capacity estimation (vapor pressure and enthalpy dependence), but this is not discussed here.

Finally, literature experimental data and semiempirical estimation of vapor pressure, boiling point elevation, and heat of dissolution for several black liquors are presented here and analyzed from a colligative properties point of view. A very extensive and comprehensive reference list is presented in this work.

Pretreatment of agroindustrial waste by ozonolysis to obtain bioenergy

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An increase in population and urbanization have increased the world's consumption and cost of production of fossil fuels, causing them to have low availability and a vulnerability to climate change. This problem generates great energy challenges and causes an intense search for energy substitutes, which must align to fulfill the seventh sustainable development goal (SDG7), established by the United Nations (UN) and UNESCO in the 2030 agenda. Biorefineries based on lignocellulosic waste appear to be a promising route toward renewable energy production [1]. Lignocellulose is the most abundant and renewable material available on earth for bio-fuel production. In Mexico, particularly in Jalisco, both sugar cane and tequila industries are thriving in the economic sector. These processes generate tons of agro-industrial residues whose final disposal is complicated. As we know, this kind of material is composed of three main fractions: cellulose, hemicellulose, and lignin, which makes it a promising raw material to obtain biofuels.

Recently, a promising chemical pretreatment is the use of ozone as an oxidizing agent for the degradation of aromatic compounds such as lignin, with 85% degradation and selectivity[2]. Therefore, the objective of this work was to evaluate the behavior of three different materials, sugarcane bagasse (BCa) and agave bagasse with and without cooking (BAC and BAS), subjected to ozone pretreatment, on the production of biomethane, using optimal conditions previously determined. In Table 1, the results of the quantity of BMP produced by the materials (BAC, BAS, and BCa) pretreated with ozone and enzymatically hydrolyzed are presented. The material that produced the most methane was BCa (270 NmL CH_4 / g SV added). This could be because this material was the one that presented a higher content of carbohydrates of C5-C6 sugars. For the enzymatic hydrolysates of BAC and BAS, the BMP values achieved were relatively lower (256 and 246 NmL CH_4 / g SV 184 added) respectively.

Tabla 1. Biochemical methane potential and kinetic parameters estimated with the modified Gompertz model.

Parameters	BAC	BAS	BCa
BMP (NmL CH_4/g SV)	256.98	246.93	270.85
H max (mL/g SV)	264.17	245.25	253.39
λ (h)	0.2	0.6	0.1
R max (mL/g SV-h)	131.39	293.95	77.24
R2	0.99	0.98	0.99
YCH_4 (NmLCH_4/g COD)	211.27	250.36	250.41
COD removal (%)	99.33	99.34	98.92
SV removal (%)	95.35	95.83	94.83

BMP: Biochemical methane potential; H max: maximum methane yield; R max: maximum methane production rate; λ: lag phase; R2: correlation coefficient; TS: Total solids; COD: Chemical oxygen demand; VS: volatile solids.

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Masterbatch strategy in papermaking: assessment of an easily deliverable micro-/nanofiber-reinforced market pulp

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In a context where paper is expected to partially replace single-use plastics in the near future, the bulk incorporation of cellulosic or lignocellulosic micro- and nanofibers (MNFs) is regarded as a convincing way to improve the mechanical and barrier properties of the end product [1]. Nonetheless, despite the bright business prospects for this market [2], distribution still presents an unresolved challenge. MNFs are produced as dilute (3 wt.% or less) aqueous suspensions and conventional drying results in irreversible agglomeration, hindering redispersion. Hence, transporting MNFs involves either large volumes of water or an insurmountable loss of usability. Our strategy to undertake this challenge was using a high fraction of lignocellulosic MNFs to reinforce a high-yield pulp, as schematized in Fig. 1. This reinforced pulp can then be used as a bulk additive in papermaking, not unlike a so-called "masterbatch" in plastics manufacturing. After obtaining enhancements of paper dry strength by up to 62% at lab scale, an upscaling, a techno-economic evaluation and an environmental assessment of the process were proposed. Overall, this pathway grants water recovery in the nanocellulose production site and, in what pertains to transportation, fuel savings and lower CO_2 emissions.

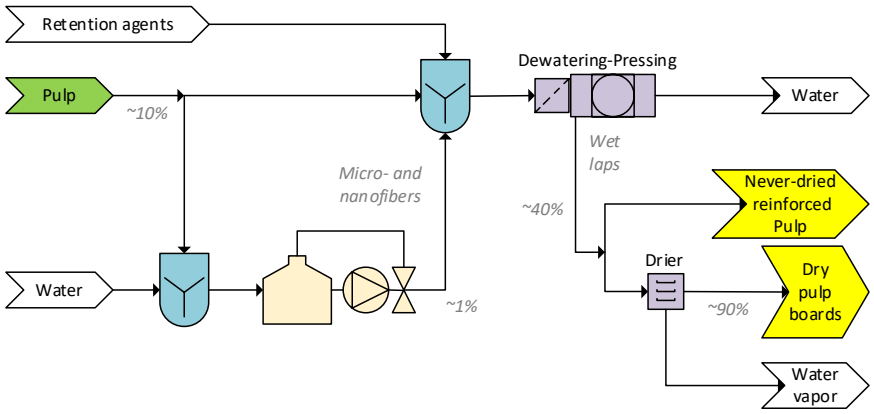

Figure 1. Flowchart of the production of a reinforced pulp to be delivered to a paper mill.

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Z-ECF and Z-TCF bleaching of softwood kraft pulp

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The use of chlorine-based reagents during pulp bleaching leads to several concerns related to the production of toxic compounds in both the paper itself and in the process water. Fortunately, it is possible to reduce their use of oxygen-based chemicals. Today kraft cooking is typically followed by OO-D-Eop-D in case of ECF bleaching or OO-Z/D-Eop-D in case of Z-ECF bleaching. A final hydrogen peroxide stage can complete these standard bleaching sequences for higher brightness ceiling and stability.

It is well agreed Z-ECF bleaching allows for similar or better pulp characteristics than ECF bleaching with hardwood pulp. However, that point is still a matter of concern with softwood pulp for some experts. The present paper reviews different lab and industrial results showing the competitiveness of environmentally friendly Z-ECF bleaching considering pulp quality, chemistry, and economic aspects.

Modelling and simulation in pulp bleaching processes to minimize water consumption

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Pulp and paper production is one of the industrial sectors with the highest consumption of water, resulting in strong environmental burdens, especially in areas with water scarcity. To achieve acceptable sustainable production indicators, there is a strong pressure to minimize the environmental footprint of water consumption in this process. Bleaching is the section of the pulp mill that contributes the most to water consumption and generation of wastewater (6 - 10 m^3/tAD pulp), because of pulp washing between the different bleaching stages. The efforts implemented in industries to reduce water consumption have resulted in counter-current pulp washing schemes. In addition, fresh water has been partially replaced by condensates from the concentration of black liquor and white water from the pulp drying machine. These measures have led to the accumulation of the so-called non-process elements (NPE), process elements, and various anions [1].

A typical elemental chlorine-free bleaching sequence usually comprises stages with ClO_2 and alkaline extraction stages with NaOH, making pH vary greatly, ranging from 2 to 10,5. At higher pH, two phenomena occur that can compromise pulp quality, bleaching efficiency, and operability, namely, the formation of precipitates and the adsorption of NPE on the fiber [1]. Adsorption of NPE on the active sites of the fiber occurs at basic pH since under these conditions, the functional groups are deprotonated, easily binding to cations [2]. Thus, globally it is necessary to minimize water consumption while limiting the precipitation and adsorption phenomena. An approach to minimizing water consumption in the bleaching line in a sustainable way involves modeling and simulation, allowing a quick understanding of the evolution of a system when changes are introduced in the process. WinGEMS is a simulator commonly applied in the pulp production processes. This software contains specific modules for pulp production, but it is very limited in terms of chemical equilibrium, not allowing the prediction of the pH in each stream, nor the precipitation and adsorption phenomena. To attain more accurate simulations, it is necessary to strengthen the software with chemical speciation models (pH and precipitation prediction) and adsorption models. A possible solution is to couple WinGEMS with other software for determining the chemical speciation (HSC Chemistry), together with the implementation of simple models for adsorption equilibrium. This solution can be implemented by exporting data from each stream to a spreadsheet where the chemical speciation can be performed directly, using the HSC Add-ins functionality. With the pH and chemical equilibrium data, it is possible to simulate the adsorption equilibrium in MATLAB. The resulting data are returned to WinGEMS, where equations are implemented to correct the values of the stream components, according to the simulation results. Globally, this strategy of modeling and simulation supports decisions to reduce water consumption in the pulp industry.

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Impact of the Bleaching on the yield improvement obtained by high alkali impregnation

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The main process used for chemical pulp production is kraft cooking and its chemistry has a crucial impact on the final properties of the fibers. Approximately 50% of the component are lost in the cooking process due to lignin and some carbohydrate dissolution, leading to a low yield. High alkali impregnation (HAI) has proved to be an efficient way to increase the kraft yield (Brännvall 2018). Recently, it was also seen that the yield improvement can be maintained after oxygen delignification and mechanical properties can be improved (Esteves, et al 2022). However, yield preservation after bleaching processes was not studied so far. This study aims to evaluate how bleaching with either chlorine dioxide or with hydrogen peroxide can affect the final yield and strength for samples obtained with standard and high alkali impregnation.

High alkali impregnation leads to a higher chemical diffusion rate and can increase the rate of the stopping reactions over the rate of the peeling reactions. This phenomenon leads to higher yield, mainly due to glucomannans preservation. To study the effect of process modifications, pulps delignified by kraft cooking with standard or high alkali impregnation were compared after oxygen delignification and bleaching with two different bleaching chemicals – chlorine dioxide or hydrogen peroxide. The chemical composition, viscosity, brightness, and mechanical properties were studied.

The study showed that enhanced impregnation by high alkali improves pulp yield without negative effects on strength. The yield improvement achieved by HAI was preserved along with both types of bleaching sequences (2% for chlorine dioxide and 4% for hydrogen peroxide). A similar tensile index was obtained for both samples, regardless of the bleaching chemical used.

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Forest, Pulp and Paper (Tuesday 28th June 2022)

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High Calcium Content of Eucalyptus dunnii Wood Affects Delignification and Polysaccharide Degradation in Kraft Pulping.

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Eucalyptus dunnii, cultivated in plantations in various locations in Uruguay, have shown slow delignification during kraft pulping. The investigations on both lab-scale and industrial scales have suggested that calcium plays an important role in this phenomenon. The calcium in wood appears to be present in the form of crystals in the lumen. Based on previous works, it is known that depending on the growth site, the calcium content in wood varies highly, and in some cases, pulping is difficult. This problem was investigated using wood with different calcium contents (705 to 1500 mg/kg). Conventional kraft cooking experiments on wood were performed and supported with the preliminary characterization of wood and obtained pulps. We also hypothesized that the amount of calcium affects the cellulose degradation in pulp and tested this hypothesis with carbohydrate compositional analysis and pulp viscosity measurements. The investigated eucalyptus dunnii samples had similar chemical composition irrespective of calcium content. Higher xylan and pectin content was only observed in wood chips with the highest calcium content (4668 mg/kg). There was a significant difference observed in kraft pulping concerning calcium content present in the wood, whereas the higher calcium content gives slower delignification. No significant effect has been observed in the content of hexeneuronic acid with the different calcium content in wood in this study. The higher calcium content in wood resulted in higher yield losses in kraft pulping and increased degradation of cellulose and hemicellulose. However, the results from pulping experiments indicated that the increased effect on delignification and carbohydrate degradation occurs already in the wood samples with lower calcium content, thus the problems seem to be associated with the calcium itself. The higher pulp yield and pulp viscosity losses for wood with a higher calcium content are most likely explained by increasing alkaline hydrolysis. In our work we also suggest a possible explanation for the chemical reactions involving calcium in the kraft cook, decreasing the rate of delignification and increasing the rate of carbohydrate degradation.

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Thermally modified wood of Acacia *melanoxylon* Preliminary results

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Due to the urban development and the continuous growth of cities, architects, engineers, and constructors are choosing sustainable materials. Wood is a natural, sustainable, and low-carbon material. However, wood presents some disadvantages (e.g. hygroscopicity and anisotropy), that can be overcome by thermal treatments [1]. The wood thermal modification only requires temperature and an oxygen-free atmosphere, it does not use any kind of chemical products and improves some wood properties such as dimensional stability, water resistance, and biological attack resistance [1]. *Acacia melanoxylon* is among the most widespread invasive plants in Europe. Today, Acacias are widely naturalized and have become an environmental problem in Southwestern Europe, particularly in Portugal. Its presence can be a threat to native species and has been declared ‘‘invaders’’ due to its rapid growth rate, prolific production of seeds with high longevity, and germination stimulated by fire. Acacia wood has very interesting mechanical properties which can be used in building construction, façades, walkways, and decks, among others. This study aimed to thermally modify Acacia wood in collaboration with a Portuguese company, Santos & Santos. Then the unmodified (A) and modified (MA) woods were exposed to weathering in two different environments (urban and industrial/maritime) and the color, chemical, and morphological changes were evaluated over time. The wood color was determined by a portable spectrometer measuring the CIELab parameters. The summative chemical analysis (e.g. total extractives and lignin contents) was made and the lignin monomeric composition was accessed by analytical pyrolysis (Py-GC/MS). Additionally, the samples were characterized by scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS). The treatment induced a decrease in the soluble lignin content (1.1% for A and 0.70% for MA) and an increase in Klason lignin (17.2% for A and 27.0% for MA), which can be caused by a lignin degradation during the thermal treatment [2]. Py-GC/MS showed a decrease in S/G ratio in modified wood (2.2 vs. 1.7), caused by an increase of G-lignin units and a decrease of S-units in the modified acacia wood. This could be explained by lignin modifications during the treatment [2]. Through SEM/EDS analysis, some cracks in fibers and particles were detected in samples exposed to both environments. Some deposition of dust, aerosols from pollution, and salt particles were found in woods exposed to the industrial/maritime environment. Likewise, woods from the urban environment also had some deposition of dust. The study is still running and for that reason is not possible to present all the results, namely those from the analysis of the weathered samples.

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An approach to the fibre furnish selection for tissue paper based on statistical geometry

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The tissue segment represents one of the most promising in the paper industry in terms of stable growth in the coming years. The quality attributes of tissue products establish the achievement of important differentials in a scenario of fierce competition between manufacturers. Although the formation of tissue paper is not measured and monitored, in the industrial process, it is essential to recognize its importance for the development of key quality properties. This work presents a theoretical approach to the aspects of the fibrous composition of furnish, used for tissue paper production, through an analysis based on statistical geometry, using the Poisson distribution to evaluate the structure of the sheet formed at the wet end of the tissue machine, but before creping, considering typical base paper of the tissue industry. The results of this study show the influence of morphological and structural parameters of cellulosic fibers and the effects of pulp blends, containing short hardwood fibers and long softwood fibers, on the distribution of coverage and corresponding local grammage, in the paper sheet. Lower basis weight coefficients of variation have been observed by incorporating total or predominant content of short hardwood fibers in the furnish composition. This approach represents a useful reference for practical considerations in the industry for the selection and optimization of the paper stock recipe, given the uniformity of tissue paper formation.

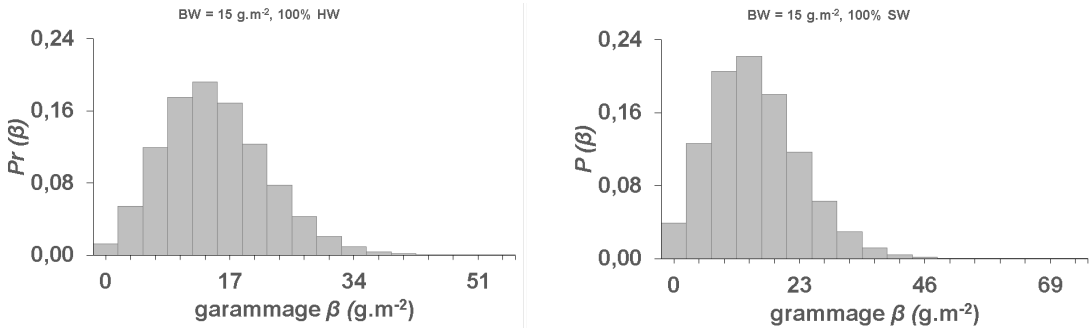

Figure 1. Histograms of grammage for 15 g.m^{-2} tissue paper with 100% short fiber hardwood content (left) and 100% long fiber softwood content (right), as given by the Poison distribution.

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Acacia biomass exploitation: a tool to reduce wildfires risk in unmanaged forestlands – Acacia4FirePrev project

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Acacias species have been considered invasive species, spreading all over Europe, particularly in Portugal, covering over 18 500 ha[1], where the most problematic species are *A. dealbata*, *A. longifolia*, *A. melanoxylon* and *A. saligna*. *Acacias* eradication is unfeasible, and their management requires high investment and long-time actions due to the sprouting ability and large and resilient seed banks.[2] However, managing these ecosystems is a task that should be addressed, since climatic conditions, the abandonment of rural areas, and fuel accumulation (due to the lack of forest management) are increasing the *Acacia* invasions with changes in fire behavior and regime.

Acacia4FirePreve project (https://www.acacia4fireprev.com/, Figure) proposes novel uses for *Acacias* and their residues, resulting in economic benefits through harvesting biomass from invasive populations. The idea is to use Acacia biomass better, creating high added-value products that provide an economic instrument to landowners while mitigating *Acacia* invasion and reducing overall fire risk.

Two sites are being monitored in Lisbon (litoral of Portugal) and Silvares (interior of the country). The *Acacias* were removed, and at the moment, more relevant species are being installed: flowering species to help bees in honey production (*e.g. Lavandula*) and endemic species of each region, to avoid soil erosion and maintain sustainability; in Lisbon: *Crataegus monogyna*, *Olea europaea, Myrtus communis, Pistacia lentiscus, Phillyrea latifolia, Phillyrea angustifolia, Rhamnus alaternus,* and *Arbustus unedo* where the chosen species, but in Silvares, *Erica*, *Lavandula* and *Juniperus* species were more adequate for these purposes.

Anatomical and chemical procedures characterize the collected material (wood, flowers, and bark). The objective is to have an overview of its characteristics. At the same time, products are being developed, such as pellets, and their characteristics are being evaluated. These products could provide income to forest owners, which have an important role in preserving the forests.

Another important goal of the project is to increase the awareness of the society (in particular young students, but also the forest owners) on the urgent need for *Acacia* control to protect our habitats and reduce fire risk. This is an ongoing task, achieved through social engagements and citizen science through activities such as the Bioblitz, an activity developed in Tapada da Ajuda (Lisbon) where volunteers could see the different Acacias species learned how to identify them. For this activity, a guide was produced to identify *Acacia* species (https://www.acacia4fireprev.com/ciencia-cidada).

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Dissolved cellulose on alkali conditions for multidimensional hierarchical structures

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A novel mechanism for cellulose dissolution and regeneration in aqueous alkali-based systems is proposed. The fine-tune and control of shear stress forces, chemical environment, temperature, and time allows the production of different cellulose dopes, which are suitable to produce multidimensional materials 1D (filaments), 2D(films), and 3D (meshes). The 1D spun filament materials are produced from a wet-spinning system with cellulose concentrations in the range of 7 -12 % w/w, exhibiting similar tenacities to those reported for viscose textile fibers. Following analogous procedures, 2D printed films with tensile strength in the range of 37 - 47 MPa and 3D printed wet auxetic meshes with an average tensile strength of 115kPa and average Poisson's ratio of -0.2 are produced. The material's properties are studied using different techniques such as small-angle X-ray scattering (SAXS), Ultraviolet-visible spectrophotometry, scanning electron microscopy (SEM), and rheology. The results suggest that several factors such as cellulose concentration, dope rheology, and fibrils orientation profoundly impact the materials' mechanical and optical performance. The mechanical and in-vitro biocompatibility results suggest that these materials can be used as a platform to manufacture textiles and biomedical wearable patches or meshes. The results are an essential contribution to the development of environmentally friendly cellulose-based materials

Characteristics chemical in the fiber and relationship on softness in tissue paper

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The consumption of tissue paper is a product demanded globally, products essential called "commodity", as consumption goes hand in hand with a demographic explosion. The tissue paper is found in different presentations and qualities, the principal market will be indexed by its price by demand, in which the properties of tensile resistance and softness are the main characteristics that consumers demand. The demand for fibers has increased to satisfy the main groups of paper.

In this work, two long-fiber pulps and one short-fiber pulp were evaluated, mixing the long fibers with the short fiber at 50% each to estimate their resistance and characteristics with three commercial samples of toilet paper and two samples of toilet paper and facial use. The chemical composition of the virgin fibers was evaluated. The samples were evaluated for both dry strength and softness by TSA under the same conditions. With the fibers, laboratory sheets of 20 g/m² and thickness of 45µm were formed. Which presented HF values of 70.3 units in the short fiber and 43 and 44 units in the long fibers and in mixtures the values were similar. In both the TS7 interpreted as the softness point, the units for short fiber is 99 units and for both long fibers, it was 68 u. In each of the mixtures, the determined value was 96.5 and 91.4 units, respectively. The modulus of deformation did not vary for any of them, with an average value of 0.89 mm/N, while commercial facial samples show HF of 86 and 88 units. In TS7 11.7 and 9.6 unit and its deformation modulus is 3.1 and up to 2.6. These samples were evaluated comprehensively. Regarding the chemical composition, the hardwood fiber presented a percentage of holocellulose of 97.32% and alpha cellulose of 79.22% and after its formation, the value of holocellulose decreased by 7 percentage units. Therefore, to satisfy the demanded parameters, the incorporation of chemical products, technology in production, and the improvement of forest plantations for the maturity of the fibers are of greater relevance.

	Fiber S	Fiber L1	Fiber L2	Fiber S/Fiber L1 (50/50)	Fiber S/Fiber L2 (50/50)	Facial Paper
Gramage	20.66+/- 0.5	20.72+/-0.6	21.02+/-0.2	19.57+/-0.7	20.56+/-8	33+/-4
Thiknes, µm	46+/-1.0	46+/- 2.0	49+/-1.0	46+/-1.0	48+/-2.0	62+/-0.5
HF	70.3 +/- 0.0	43.5 +/-5.0	44.5+/-5.0	39+/-1.14	41+/-0.3	86.79+/-1.36
HS7	99+/-10	68.5+/-7.5	68.2+/- 8.2	96.5+/-1.73	91.4+/-0.6	11.66+/-1.0
HS750	48.4+/-6.6	29.6+/-2.9	33.4 +/-7.2	48.6+/-5.1	51.3+/-16.2	23.65+/5.0
D(mm/N)	0.884 +/-0.0	0.866+/-0.0	0.876+/- 0.01	0.892+/-0.01	0.878+/-0.01	3.1+/-0.05
Bulk	2.315 +/-0.01	2.278 +/-0.01	2.331 +/0.01	2.294+/-0.01	2.404+/-0.0	5.208+/-0.01
Extratives, %	1.84 +/- 0.2	0.67 +/- 0.3	2.61+/- 0.5			
Lignine, %	0.84+/- 0.03	1.33+/-0.05	1.75+/-.09			
Holocellulose, %	97.32+/-0.3	98 +/- 0.5	95.64+/-1.1			
hemicelulosa	18.1+/-0.5	23.5+/-2.0	16.07+/-0.9			
a-celulosa	79.22+/-0.7	74.5+/-1.7	79.57+/-0.4			

Table 1. HF values in the structure paper and chemical composition of the fibers.

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Innovation in Polysaccharides

(Wednesday 29th June 2022)

Novel enzymatic tools for the deconstruction of cellulose

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Lytic polysaccharide monooxygenases (LPMO) are a novel class of enzymes abundant in fungi that act at the surface of cellulose. LPMOs cleave cellulose chains by an oxidative mechanism with a type II copper active center coordinated by a histidine brace. Oxidative cleavage of cellulose leads to the formation of oxidized glucose units at different positions resulting in the formation of aldonic acids at the C1 position and/or 4-ketoaldoses (gemdiols) at the C4 position.

In our laboratory, we investigate the use of lytic polysaccharide monooxygenase (LPMO) enzymes as an innovative tool to facilitate fibrillation for the fabrication of nanofibrillated cellulose.[1, 2]

Micro- and nanofibrillated cellulose has attracted much interest because of its attractive properties including high aspect ratio, high strength and stiffness, low density, transparency, and low thermal expansion. Despite their outstanding properties, micro- and nanofibrillated cellulose remains underemployed because of several constraints associated with its manufacture. Generally, cellulose fibers are disintegrated into fine fragments by mechanical refining methods. However, these processes involve high-energy consumption and tend to damage the nanofiber structure by reducing molar mass and crystallinity. In this field, LPMO enzymes can be viewed as an environmentally friendly tool to facilitate cellulose fibrillation.

Our studies provide direct evidence of the LPMO action on cellulose with the modification of accessible and inaccessible surfaces surrounding the crystalline core of cellulose fibrils. The chain breakage induces modifications of the cellulose network and weakens the fiber cohesion promoting their disruption. Besides the formation of new initiation sites for conventional cellulases, we provide the first evidence of the direct oxidative action of LPMOs with the mechanical weakening of the cellulose ultrastructure.

Therefore, LPMOs can be viewed as promising candidates for enzymatic modification or degradation of cellulose fibers including the preparation of nanofibrillated cellulose.

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Sustainability aspects of cellulose-based material solutions

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A sustainable circular economy requires innovative, systemic technological solutions, taking into account social and environmental sustainability as well as disruptive business models. Cellulose-based innovations may have a pivotal role in supporting a decarbonized and circular bioeconomy. To achieve the goal, it is essential to understand and monitor sustainability aspects and the circularity opportunities of emerging technologies as early as possible. In this paper, all sustainability aspects, economic, environmental, and social ones, are discussed related to circular cellulose-based applications.

The majority of environmental impacts are determined in the design stage. A systemic transformation requires a holistic view of the benefits and challenges in favor of agile decision-making and optimal choice of applications. The consumer attitudes towards novel bio-based solutions have been studied through both qualitative and quantitative surveys. Improved communication is a key element to raise awareness among consumers.

There has been a need to develop a science-based method to quantify positive climate impact systematically. A developed indicator, handprint [1], refers to the beneficial environmental impacts that organizations can achieve and communicate by offering products and services that reduce the footprint. Determining a carbon handprint requires calculating two carbon footprints: baseline solution and handprint solution. The carbon handprint shows the positive impacts to mitigate climate change. As a case study, additive manufacturing by using thermoplastic cellulose-based composite material will be discussed. 3D printing of cellulose-based materials for electrical insulation components, automotive components, and decorative elements in cruise ships has been scaled-up. To ensure circularity aspects, it has been studied that composite material can be recycled at least 7 times without losing the material properties [2].

Figure 1. 3D-printable cellulose-based composite material

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Man-made Cellulose Fibers in the View of Sustainability and Circularity

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Although only a minor fraction of global pulp production is dissolving pulp, which is used for the production of wood-based cellulose fibers, these applications create general awareness. This is as both the textile and the nonwoven value chains are facing several challenges. On one hand, the demand for fibers is raising as the world population and wealth are increasing, but there are problems associated with the production of fibers and their use – recognized by policy and consumers alike.

Fashion is accountable for a relevant share of greenhouse gas emissions and other environmental topics and therefore is addressed by the recently published EU strategy for sustainable and circular textiles. For nonwovens, the European Single-Use Plastic Directive is an important regulative as wipes are also covered by this directive. So, the fiber industry (together with its value chain partners) needs to operate in a (more) sustainable way.

Made from the renewable resource wood man-made cellulose fibers (like viscose or lyocell) can make a substantial contribution to the solution of these sustainability challenges and bear a huge potential.

This talk gives an overview of the basic processes and current developments in the field of man-made cellulose fibers from an industrial point of view. One important topic is the recycling of textiles as they contribute a significant amount to today's waste. Another topic covered is biodegradability as an end-of-life option – especially for single-use products. The concept of renewable carbon for materials as a complement to decarbonization (for energy) is presented also.

Figure 1. REFIBRA™ technology

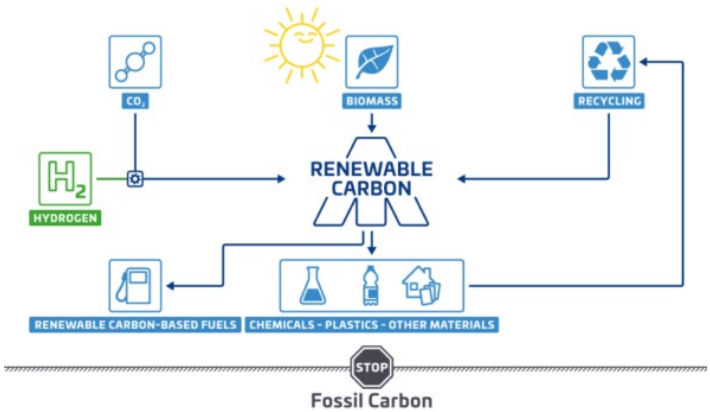

Figure 2. Renewable carbon concept (© nova-Institute)

Natural fibers based composite materials: challenges, innovations, and recent trends

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The development of biobased chemicals and materials is of enormous significance nowadays given the ever-growing awareness of environmental issues and the related efforts to implement a sustainable bioeconomy. For example, natural fibers-based composites have emerged in the last decades as a sustainable alternative to the conventional composites with synthetic fibers, such as glass fibers, for application in several areas, such as in the automotive, packaging, and building and construction industries. The natural fibers-based composite market has been thriving, with several available products, and with the forecast indicating a continuous growth in the future [1].

In this talk, the main challenges, innovative solutions, and prospects in the field of cellulose-based composite materials will be highlighted and discussed. Additionally, some contributions of our research team (BioPol4Fun Research group of CICECO- Aveiro Institute of Materials) to this area will be also presented.

References

[1] Global biocomposites market size by fiber (wooden fiber and non-wood fiber), by end-use industry (building & construction, transportation, consumer goods), by geographic scope and forecast, https://www.verifiedmarketresearch.com/product/biocomposite-market/ (accessed on Jun 01, 2022).

Acknowledgements: This work was carried out within the scope of the project CICECO – Aveiro Institute of Materials (UIDB/50011/2020 & UIDP/50011/2020). FCT is also acknowledged for the research contract to C.S.R.F. (CEECIND/00464/2017).

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Paper-based visual indicators for the rapid detection of heavy metal pollution in water

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It is needless to explain the popularity of pH paper, or why Helen and Alfred Free's paper pads attained massive success for urine analysis in the twentieth century. The key advantage of paper as the substrate of rapid and user-friendly indicators for aqueous solutions lies in its ability to wick water while not being dissolved by it [1]. Its biodegradability, its low cost, and its availability all around the world, and from many different materials, add to the pile of reasons to bet on paper-based detectors. All in all, we aim to contribute to the field of paper-based sensors, especially in the context of water pollution detection in developing countries, where rapid industrialization outweighs the progress of environmental monitoring. Paper strips were coated with sensing complexes or molecules, using oxidized nanocellulose both for thickening and for protection from aerial oxidation.

The sensing strips reported in this work fall into two categories. Some are colorimetric, displaying a color change under natural light (naked eye) [2]. An example is shown in Fig. 1: 3,3',5,5'-tetramethylbenzidine (TMB) turned blue in presence of Fe(III), selectively, while it required peroxide to display a visual response toward Hg(II) and Cu(II), or a strong acid to detect Cr(VI). Dithizone, which turns reddish in presence of trace amounts of Hg(II), Pb(II), or Cd(II), was also used in suspensions for paper coating. The challenge of its insufficient stability was undertaken by crosslinking nanocellulose with ascorbic acid, a potent antioxidant agent. Another class of responsive substances is based on a luminescence on/off mechanism, requiring excitation under ultraviolet radiation to detect the presence of a certain pollutant. Examples of this are europium(III) and terbium(III), which need to be complexed with different ligands to display significant emissions. They have their luminescence drastically quenched by a competing heavy metal ion [3].

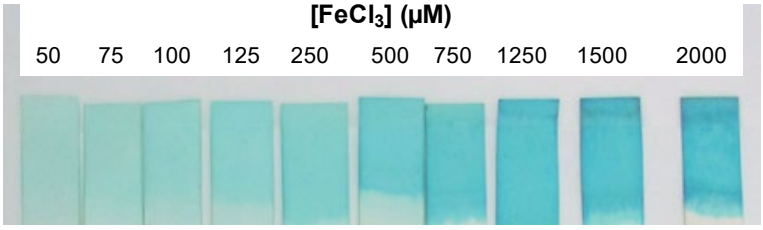

Figure 1. Picture taken under the natural light of TMB-impregnated paper strips after immersion in iron(III) chloride solutions in the micromolar or millimolar range.

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Structural curl related problems in paper: diagnosis of fiber orientation two-sidedness

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Curl is an out-of-plane deformation known to promote problems to end-users, namely printer jams. Troubleshooting activities should therefore be set in place by papermakers to speed up the search for the root cause (or causes) of the curl phenomena and the implementation of timely actions to solve or mitigate the detected problems. Curl can be caused by structural asymmetry over the thickness direction (ZD) of paper. The main papermaking source behind the development of this type of structurally related curl is fiber orientation (FO) two-sidedness. With this in mind, the goal of this work is to develop and test a systematic diagnosis procedure to screen for the possible existence of FO two-sidedness in paper with the potential to generate curl-related problems.

The proposed procedure to apply in curl troubleshooting activities for the diagnosis of FO two-sidedness includes two steps. The first step consists of applying the hot bend method, in which sample stripes are kept in contact with a heated (150 ºC) bent plate for 1-3 seconds, followed by the immediate measure of the produced curl magnitude. The method shows the sample potential to develop curl, while also suggesting the probable root causes behind the phenomena, namely the possible existence of FO two-sidedness. If needed, the second step is applied, consisting of a methodology that combines a sheet splitting technique with image analysis, to determine the FO in ZD. The procedure was tested on two types of laboratory anisotropic sheets, single layer, and double layer. Three single layer sheets were prepared for a defined anisotropy level, to be used as the control group: low level (L), intermediate (I), and high (H). On the other hand, two double-layer sheets were prepared, with the bottom and top halves presenting different anisotropy levels (bottom/top): (L/H) and (I/H).

The control (single layer) sheets presented a reduced potential for the development of curl, with negligible differences being observed between the FO of the two halves. In contrast, the hot bend method indicated high curl potential for the double layer sheets, probably due to FO two-sidedness. This result was confirmed by the sheet splitting-based method, with differences in FO between the two halves being consistent with the values obtained for the control sheets. In summary, the proposed procedure shows potential to use in curl troubleshooting activities in the industry, to diagnose FO two-sidedness in the paper.

Acknowledgments

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Cationic cellulose as a potential biobased flocculant for papermaking

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Mineral fillers (such as precipitated calcium carbonate - PCC) are typically used in papermaking formulations to reduce cost and improve optical properties. The much smaller size of these fillers compared to the wire mesh of the forming section of the paper machine causes them to be dragged away during the dewatering step. Therefore, retention agents are used to minimizing losses of mineral fillers, being the cationic polyacrylamides (C-PAM) the most commonly used retention agent. However, environmental concerns regarding the use of synthetic polyelectrolytes led to the search for new biobased alternative flocculants. Cellulose appears as a logical candidate to serve as the backbone for the production of biobased flocculants since it is the most abundant biopolymer on earth.
In the present work, cationic celluloses with distinct degrees of substitution and morphology (fibers, micro/nanofibrillated celluloses, polyelectrolytes), were produced by covalent bonding of quaternary ammonium groups into bleached Eucalyptus kraft pulp - BEKP. The potential of the cationic celluloses to flocculate PCC was evaluated by monitoring the size distribution of the flocs using laser diffraction spectrometry (**Fig.1**). The same samples were incorporated into papermaking furnish formulations to access the filler retention and drainability. All the results were compared against a commercial C-PAM.

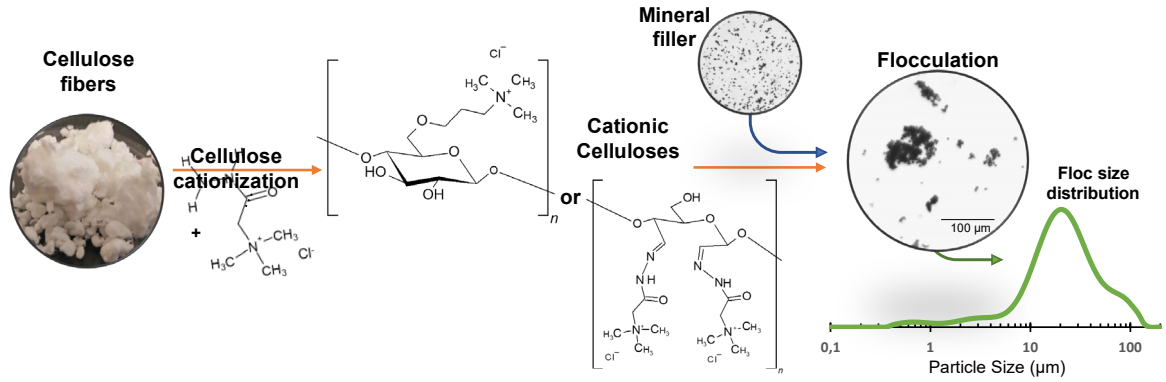

Figure 1. Preparation of cationic celluloses by functionalization of cellulose fibers with quaternary ammonium groups for flocculation of mineral fillers.

Acknowledgements
This work was supported by the Project inpactus – innovative products and technologies from eucalyptus (Project N. º 21874 funded by Portugal 2020 through European Regional Development Fund (ERDF) in the frame of COMPETE 2020 nº246/AXIS II/201). The authors also want to acknowledge the Project ToxApp4NanoCELFI (PTDC/SAU-PUB/32587/2017, from the Foundation for Science and Technology, Portugal), the Network CYTED Nanocelia - Transferencia Tecnológica sobre Aplicaciones de Nanocelulosa en Iberoamérica, and the Strategic Research Centre Project UIDB/00102/2020, funded by the Fundação para a Ciência e Tecnologia (FCT).

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Effect of nanofibrillar cellulose obtained from bamboo (Guadua Angustifolia Kunth) on physical and mechanical properties of paper made with virgin and recycled fiber

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Improvement searching in the paper industry has developed the use of raw materials, modifications, and additives for its production, opening a path for the implementation of nanotechnology. Nanocellulose is a promising element that would improve properties.

The scope of this study was to evaluate the effect of nanofibrillar cellulose (NFC) obtained from bamboo (*Guadua Angustifolia* Kunth), as an additive in three types of paper made with virgin bamboo fiber, recycled fibers from DKL, and the mixture of both, to evaluate the behavior of the physical and mechanical properties of the papers. NFC was obtained by applying a chemical pretreatment with the TEMPO oxidant and a mechanical treatment with a high-speed homogenizer. NFC was added in mass during the elaboration of the bamboo paper, DKL paper, and the mixture of both fibers (50/50) in the concentrations of 0, 2, 4, and 6 % for each type.

Research revealed that CNF of *Guadua Angustifolia* Kunth influenced the physical properties, highlighting. Density improvement in all three types of paper by adding 6% CNF. In addition, a 92% reduction in Gurley permeability in the mixed paper was noticed. Regarding the mechanical properties, increases in tension and traction were observed when adding 6% CNF to the DKL paper. For the folding property, increases of 4 and 5 times more were obtained in the bamboo and mixed paper, this by adding 4 and 6% of CNF, respectively.

Therefore, it is verified that the addition of CNF in the paper influences the physical and mechanical properties, which are linked to the final product to be produced and its application.

Recyclability of papers containing cellulose nanofibers

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Recovered paper is widely recognized as an efficient and eco-friendly cellulose source for paper and board production with important effects on reducing waste. As it is known, recycling cycles cause a decrease in mechanical paper properties due to cellulose fiber degradation and the use of nanocelluloses (NC) in papermaking can contribute significantly to improving the recycled paper quality, especially its mechanical properties [1-2]. Although their implementation at an industrial scale is developing very slowly, recovered papers containing NC will come to paper mills in the next future.

Therefore, it is necessary to study its effects on the different stages of the process, including the deposit formation due to the interactions with the dissolved and colloidal material (DCM) present in process water from recovered paper, to evaluate the possible changes in the operational conditions of the recycled process. The presence of DCM in white waters is directly related to the formation of adherent deposits (stickies, secondary stickies, white pitch) when destabilization occurs due to sudden changes in the system [3].

This work aims to study the effect of the cellulose nanofibers (CNF) contained in a recovered paper on deposit formation using the method developed and patented by UCM Research Group, deposition tester (Pat. No. 98901981.5). In the first stage, handsheets were obtained at a lab-scale from a mixture of liner (65%) and fluting (35%) cardboard, adding different ratios of CNF (0.5, 1.0, 2,0, 3,0 wt.%) and using a 2% of starch as retention agent. CNF was produced from bleach eucalyptus pulp and obtained by TEMPO-mediated oxidation, followed by a mechanical treatment by homogenization. The handsheets obtained were disintegrated in a lab pulper at 3,5% of consistency, under standard conditions, and diluted at 1%. Depositability tests were carried out on pulps using the improved deposition tester made of stainless steel [5]. The tests will be carried out in triplicate by inserting the deposition rotor into 1800 mL of the pulp at a temperature of 50ºC, for 1 hour and 400 rpm (rotor speed). The deposits collected on both external and internal stainless steel films were scanned and analyzed using an image analysis system (ImageJ), resulting in the percentage or mm^2 of surface covered by deposits (total stickies). For the determination of secondary stickies, the deposition test will be carried out in the same conditions but adding the volume of poly-ethylene-imine (PEI) necessary to destabilize the DCM.

The results show that the methodology is reproducible, with a relative error between 2 and 8%. It has also been proven that the formation of secondary stickies, due to the destabilization of DCM is greater than that of microstickies in all cases. Moreover, the deposit formation decreases when the concentration of CNF in handsheets is higher, obtaining reductions of up to 35% of the area covered for microstickies and 48% for secondary stickies. Therefore, the presence of CNF in recovered papers improves the recyclability of these new papers.

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Comparison of Wood and Non-Wood Market Pulps for Tissue Paper Application

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A comparison among eleven pulps at a laboratory scale using uncreped hand sheets was performed to evaluate the performance of non-wood pulps for tissue paper manufacturing and determine how those fibers can be used to replace or complement commercial wood pulps in tissue paper products. A complete characterization of fiber morphology and hand sheet properties (softness, water absorbency, strength) was performed at different mechanical refining levels. Results show that fiber morphology has a significant impact on tissue paper properties. Market pulps having a combination of long fibers with a high coarseness to width ratio and low content of fines can provide superior bulk, softness, and water absorbency. Long fibers having thin cell walls can be used to impart strength. Bleached bamboo soda can replace virgin hardwood kraft pulps to provide excellent softness and water absorbency at unrefined or very low refining levels. Bleached bamboo soda pulp can also replace virgin softwood kraft pulps to impart good softness, water absorbency, and strength at higher refining levels. Bleached and semi-bleached wheat straw sulfite pulps presented similar properties as recycled pulps (deinked and old corrugated containerboard pulps) because they impart good strength and water absorbency but much lower softness when compared to virgin hardwood and softwood kraft pulps

Bio-based products from non-woody resources (Wednesday 30th June 2022)

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Production and characterization of novel mixed-mode polysaccharide beads for protein adsorption and purification

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Research in protein adsorption is of great interest because it is the key step of downstream purification in the pharmaceutical and food industry. Different low-cost biopolymers have drawn the attention of the scientific community in this application for their outstanding biological characteristics and wide availability. In this work, we have produced new mixed-mode polysaccharides beads, characterized them, and examined their application in protein separation and purification. Composite polysaccharide beads were produced by combining pullulan, agar, and guar gum with alginate. Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), nitrogen physisorption, swelling ratio, and carboxyl group content were performed to characterize the beads. Protein adsorption was measured using bovine serum albumin (BSA) and a protein mixture produced in a bioreactor. The kinetics of protein adsorption was studied using Pseudo-first-order (PFO) and Ho and McKay Pseudo-second-order (PSO) models. Langmuir, Freundlich, and SIPS adsorption isotherm models were applied to study the mechanism of adsorption. Weber and Morris's intra-particle diffusion model was used to elucidate the diffusion mechanism and rate-limiting step. Our research showed very promising results for protein adsorption and purification using composite polysaccharide beads.

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Biochar-based wastewater treatment to combat antimicrobial resistance

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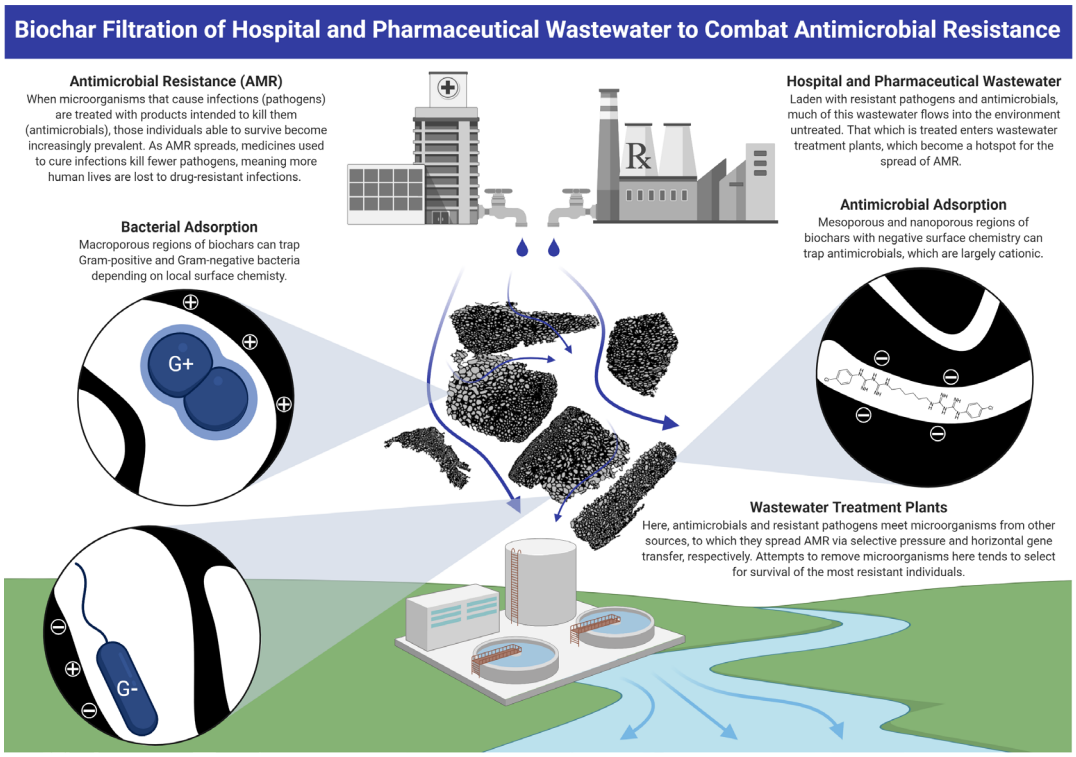
Antimicrobial resistance (AMR) is driven in part by environmental reservoirs of antimicrobial-resistant organisms and genes, as well as antimicrobials themselves, which drive resistance via selective pressure. According to the UN, 80% of all wastewater flows into the environment untreated. When wastewater is treated, treatment plants can act as hotspots of horizontal gene transfer from resistant to non-resistant organisms. There is therefore an urgent need to filter wastewater from sources rich in resistant bacteria and antimicrobials, like hospitals and pharmaceutical plants, before they reach environmental reservoirs where resistance can spread. Biochars produced from waste lignocellulosic biomass are ideal for this purpose, as they are highly adsorbent, affordable, and sustainable, with morphologies and surface chemistries that are tunable by choice of production conditions. Here, we link peak pyrolysis temperatures and alkaline pretreatment of walnut shell biochars to their filtration performance, showing these materials are suitable for in-line filtration of wastewater to combat AMR.



Designing the valorization of bay tree pruning waste through the extraction and microwave-assisted upgrading of polysaccharides into methyl levulinate

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One of the most important objectives and where the success of biorefineries lies is the valorization of lignocellulosic biomass, specifically in the fractionation and application of agricultural and agri-food residues. In this sense, bay tree pruning waste (BTPW), a very interesting agricultural by-product, has been used in the present study for the extraction and purification of polysaccharides, as well as their subsequent conversion into a high added-value product such as methyl levulinate (MLA), an important flavoring compound in the food industry and platform molecule for the synthesis of relevant chemicals such as γ-valerolactone (Figure 1).

Thus, firstly, the extraction of polysaccharides was optimized by autohydrolysis, studying different extraction temperatures and times (160-200 ºC and 30-75 min, respectively). Subsequently, an exhaustive analysis of the obtained fractions was performed, reaching the optimum autohydrolysis conditions for BTPW at 160 ºC for 45 min. The as-obtained polysaccharide fractions were found to be mainly composed of glucose (181.30 mg/g), xylose (172.41 mg/g), and galactose (45.44 mg/g), with a number-average molar mass of 6.04 KDa and a weight-average molar mass of 183.4 KDa.

The next step of this study was the simultaneous conversion of C5 and C6 sugars from the BTPW-polysaccharide fraction into MLA by MW irradiation. This MW-assisted reaction was also explored in terms of operating temperature and reaction time, in conjunction with the addition of H_2O in a methanol-rich medium using $Al_2(SO_4)_3$ as an acid catalyst. The results pointed out that MLA could be successfully obtained with an MLA yield of almost 40% from BTPW polysaccharides [1].

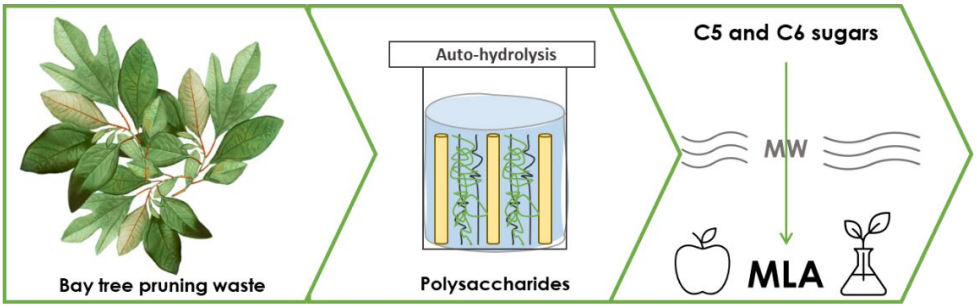

Figure 1. Scheme for BTPW polysaccharides extraction and subsequent MW conversion into MLA.

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Combination of green solvents for efficient sugarcane bagasse fractionation

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Biorefineries are facilities that aim at integrating processes and equipment to convert biomass into products of higher added value, such as fuels, biomaterials, chemical intermediates, and energy [1]. In Brazil, sugarcane bagasse, a readily available agro-industrial residue mainly composed of cellulose, hemicelluloses, and lignin, is the most abundant raw material for this industrial activity. To make the most of this material, fractionation strategies have been studied to allocate each of its main components to more noble applications than burning for power generation [2]. Therefore, this work addresses an unprecedented combination of green solvents [3] applied to the fractionation of sugarcane bagasse: a deep eutectic solvent (DES) composed of choline chloride and oxalic acid, ethanol (pure or hydrated), and carbon dioxide (CO_2).

Initially, an organosolv strategy at 170 °C was proposed to promote delignification: DES+CO_2+EtOH in a two-level and three-variable design of experiments evaluating the effects of solids loading, DES to biomass mass ratio, and the amount of CO_2. The results of this stage pointed to a lignin removal greater than 75% and virtually total maintenance of glucans. The kinetic study of these effects was carried out at three temperatures between 150 and 190 °C, confirming the best results regarding delignification at 170 °C. In addition, in this set of experiments, the retention of xylans was close to 20%, indicating that the system would be benefited from the addition of water, which would cause a greater extent of hydrolysis of cane bagasse hemicelluloses. Therefore, the replacement of anhydrous ethanol with hydrated ethanol (20% water) was studied in kinetics at temperatures from 130 to 170 °C. In this stage, a lignin removal greater than 90% was observed, accompanied by glucans retention greater than 80%.

After treatment, the lignin residue was precipitated by ethanol removal, followed by water addition and refrigeration. The precipitated residues were characterized in terms of their carbohydrate content, resulting in levels below 3 wt%. FTIR spectra demonstrated the presence of bands typical of technical lignins derived from herbaceous plants. In parallel, the distribution in apparent molecular masses was evaluated by high-performance size exclusion chromatography. The lignins obtained in the best yield conditions presented low average apparent average molecular masses, in the range of 2000 to 3000 $g.mol^{-1}$, with a dispersity around 5. In general, this work attested to the technical feasibility of using green solvents for the efficient fractionation of sugarcane bagasse into three distinct fractions that could be exploited for a variety of industrial applications.

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Hybrid nanocellulose/TiO_2 aerogels for NO_x pollution control by photochemical oxidation processes

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In this work, an innovative colloidal procedure for the synthesis of nanocellulose/TiO_2 hybrid aerogels as inorganic-organic heterostructures for the photocatalytic degradation of NO_x gases is proposed. This process allows the production of composite aerogels with high homogeneity and dispersion, which can be formed by a simple and conventional freeze-drying method. The resulting mixture of materials was formed into an aerogel format by immobilizing titanium dioxide nanoparticles (TiO_2NPs) on cellulose nanofibers (CNFs) through colloidal processing. To improve the dispersion/stabilization in liquid media and to favor the electrostatic interaction between TiO_2NPs and the surface of CNFs, the surface of TiO_2 was modified by adsorbing different amounts of a cationic polyelectrolyte such as polyethylenimine (PEI). The TiO_2-PEI suspension was added to a CNF dispersion (0.3 wt%) at different percentages (5, 20, 50, 50, 100, and 200% on CNF dry weight) causing a three-dimensional and attractive network between the components. Subsequently, aerogels were produced from the stable TiO_2-PEI-CNF suspensions by a freeze-drying process obtaining ultralight and high porosity aerogels. The photocatalytic activity of the different aerogel samples towards NO_x oxidation in a laminar flow reactor was analyzed. The heterostructured aerogels were further characterized in terms of physical and mechanical properties, chemical structure, and morphology.

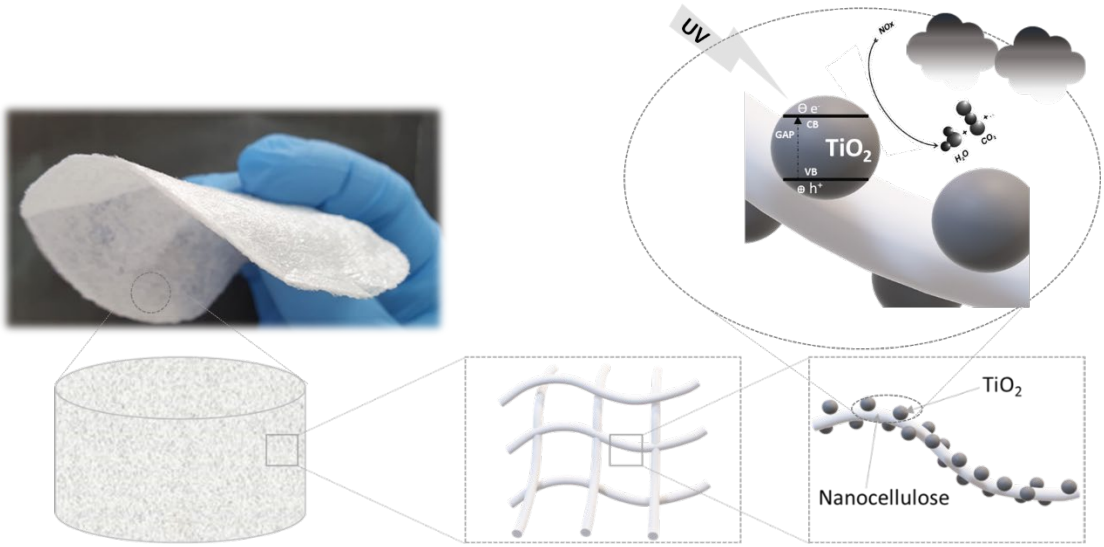

Figure 1. Photochemical oxidation action by the CNF/TiO_2 hybrid aerogels

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Nanocellulose production and modification (Thursday 30th June 2022)

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Preparation and characterizing of cellulose micro/nano fibrils using oxalic acid and different mechanical pre-treatments.

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In the last decades, the production of nanocellulose obtained from the cell walls of wood fibers and plants through a different process has gained a lot of attention due to their interesting properties [1]. In this study, we examined the production of cellulose micro/nano fibrils (CMNFs) obtained from bleached eucalyptus pulp (BEP). For this, a chemical pretreatment was performed using oxalic acid at two concentrations: 25% and 50 wt.%, considering two different mechanical treatments: a) a rotating homogenizer Ultra-turrax-type after chemical treatment or b) a PFI mill refining before chemical treatment. Finally, the mechanical fibrillation for the production of CMNFs was performed by pressurized homogenization considering 5 and 15 passes. The FTIR spectrum and the increase in carboxylic groups determined by conductometric titration of CMNFs confirm the carboxylation of cellulose produced by the chemical treatment. The CMNFs were characterized by the determination of nanofibrillation yield, transmittance and surface charge. The results show that the best-performed values of nanofibrillation yield (76.5%), transmittance (72%) and charge surface (73 µeq/g) of CMNFs were obtained for PFI refining, 50 wt.% of oxalic acid and 15 passes by pressurized homogenization. Besides, the morphology of the microfibrillated cellulose (CMF) and nanofibrillated cellulose (CNF) fractions were analyzed by SEM and TEM microscopy, respectively. The aspect ratio (p = length/diameter) of CMNFs was determined by sedimentation and shear viscosity methods. The highest aspect ratio determined by TEM was observed for the CNF obtained through PFI mill refining and 25wt.% of oxalic acid (p = 96.3), and no significant difference was observed by increasing the number of steps. The aspect ratio values determined by the sedimentation method agree with those of TEM microscopy. Besides, a strong relationship between the intrinsic viscosity of the CMNFs dispersions and their aspect ratio was observed. Films of CMNFs were formed and it was observed that the nanofibrillation yield, more than their aspect ratio, influences the film strength.

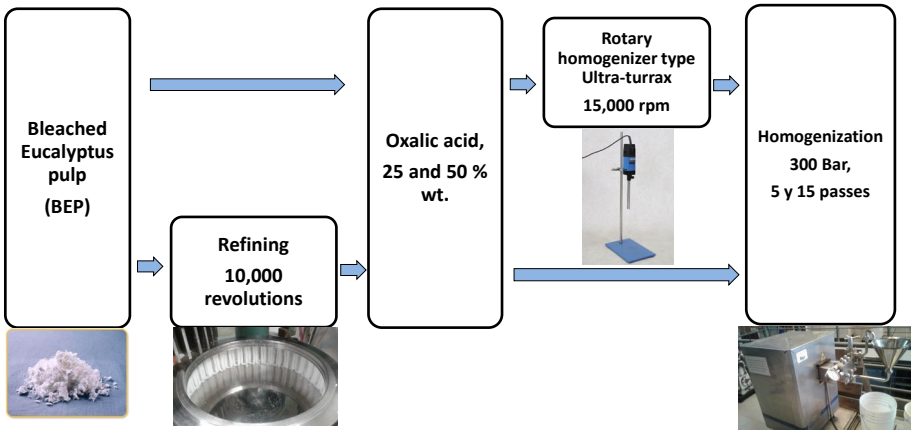

Figure 1. CMNF preparations

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Transformation of colombian agroindustrial by-products in nanocellulose: characteristics and potential applications

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The agricultural industry in Colombia is an important economic sector, with a growth of over 3.3 % during the first trimester of 2021 [1]. This is reinforced in over 6 million Ha of crops [2], and production of close to 58 million tons during the year 2020 [3]. This activity produces an important amount of by-products, for instance, during the harvest of bananas, only 12 wt.% of the plant is exploited, while the rest is underused [4]; this is also evident in the cocoa production, where only 10 wt.% of the plant is utilized [5].

These by-products can be transformed to obtain high-value nanotechnological products, such as cellulose nanofibrils (CNFs) [4,5]. CNFs are cellulosic nanoobjects obtained by the mechanical disintegration of cellulose and comprise amorphous and crystalline zones. They have a broad range of applications as rheological modifiers [6], stabilizers [7], and Pickering emulsifiers [8], among other uses, which make them desirable for paper, electronic, chemical, biomedical, and food industries [9]. The exploitation of fibrous by-products from the Colombian agroindustry could lead to possible inclusion in a developing market projected to reach 1,053.09 million USD by 2027 [10].

To obtain a cellulosic product, cocoa shells and banana rachis were processed by the KOH-5 method [11], followed by mechanical homogenization [12]. The morphology of the resultant product influences its properties, it was assessed by atomic force microscopy; the identification of cellulosic functional groups was performed by infrared spectroscopy (FTIR), and the crystallinity index was measured by X-ray diffraction. Due to its potential use as a food ingredient, cytotoxicity and genotoxicity were measured for the banana-derived cellulose as well. In both cases the obtained cellulose showed a three-dimensional network of fibril bundles, with diameters between 40 and 60 nm, sub-fibrillated fractions were still present. FTIR spectra were typical of cellulose I, the presence of peaks associated with fat was evidenced in cocoa shells; a crystallinity index of 56.12 % and 71.36 % was obtained for banana and cocoa shell CNFs, respectively. CNFs from banana rachis up to 1 wt. % did not show cytotoxicity or genotoxicity in CaCo-2 cells, which could be considered for possible *in*-vivo tests for its eventual incorporation as a novel food additive.

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Sustainable production of cellulose nanofibers: From lab-scale to synergic applications in industry

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Cellulose nanofibrils (CNFs) are nanomaterials obtained by defibrillation of cellulose fibers from different raw materials. Before mechanical fibrillation, some pretreatments such as chemical, mechanical or enzymatic allow facilitating the separation of the fibers, increasing the yield of nanofibrils. The high number of applications where CNFs can be used to improve the final product properties (papermaking, cement, biomedical applications, stabilizer in emulsions…) is due to their desirable properties, such as high strength, surface area or reactivity, together with their biodegradability, and renewability. Despite the CNF potential and the promising results obtained at the laboratory scale, their implementation in the industry is being delayed due to some limitations found during industrial trials. Even though on a laboratory scale the mechanical properties of cardboards are improved using the most common procedure to obtain highly fibrillated CNFs, TEMPO-mediated oxidation (TMO), and mechanical treatment, other challenges require their study to apply CNFs on an industrial scale [1].

Among them, the CNF quality is not proportional to the improvement of the properties, requiring the selection of the optimal quality for each application, based on the improvement of the properties and the added value that CNFs apport in the final product. Although highly fibrillated CNFs prepared from TMO reduce the energy requirements, the cost of reagents and catalysts increases significantly and does not always show an improvement of properties compared with other cheaper CNFs, such as those produced by low consistency refining. In addition, TMO reaction also presents some improvements to make the process more sustainable. The monitorization of oxidant consumption during TMO and the characterization of oxidized pulp with the time allowed us to see that the carboxyl group production was carried out mostly in the first minutes of reaction when the oxidant consumption is higher. Longer reaction times produce the dissolution of more cellulose in the medium. These facts would allow the reduction of time in TMO reaction and the reuse of part of the reaction medium due to a lower amount of cellulose being dissolved, reusing part of the medium with catalysts in several cycles [2].

Another limitation to implementing CNFs on an industrial scale is some technical challenges of CNF characterization, which difficult for the knowledge transfer from the laboratory to the industry due to unexpected differences observed after industrial trials. Three of these challenges are the application of gel point methodology for CNF suspensions, the dispersion of CNF hydrogels before their addiction to other polymer matrices as well as the development of a methodology to determine the branching degree of CNFs and CMFs. Finally, the cost of CNF production is high for its industrial application exclusively as reinforcement agents like products for packaging or substitutes for other high resistance and less sustainable materials. Therefore, to make feasible CNF production is necessary to find synergic applications beyond the limits of the paper industry, to use part of the CNFs at the mill, and the other to sell in local markets. Therefore, delving into new applications from different sectors is required, for instance, the use of CNFs as water-oil emulsifiers and stabilizers for the food industry or to remove contaminants from wastewater such as flexographic inks [3].

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Production and characterization of lignocellulose nanofibrils from Pinus radiata pressure groundwood pulp

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Lignocellulose nanofibrils (LCNFs) are a type of cellulose nanofibrils (CNFs) that contain lignin. The presence of lignin in the fibrils affects the mechanical-enzymatic process production of cellulose nanofibrils and modifies the morphology, the surface of fibrils produced, and the rheological behavior of suspensions, which is key in the development of applications for this material [1, 2]. This work aims to understand the effect of lignin on the mechanical-enzymatic production process of LCNFs and the morphological, superficial, and rheological properties of LCNF suspensions. Lignin harms the mechanical-enzymatic processes, generating larger fibrils, with less homogeneous size distributions, and with lower zeta potential. In addition, the composition of the fibrils changes, and part of the lignin is removed and dispersed into the solvent in the form of lignin nanoparticles (Figure 1). These nanoparticles are neutral and can be deposited on the surface of the fibrils. Regarding rheological properties, fibrils with lignin are less flexible than bleached fibrils due to the cementing capacity of lignin, increasing the hydrodynamic volume that these structures occupy per unit mass. In the semi-dilute region, lignin acts as a control agent for the viscosity in the suspensions due to its hydrophobic characteristic, which forms weak aggregates, poorly hydrated, and hydrodynamically smaller, which generate less resistance to flow.

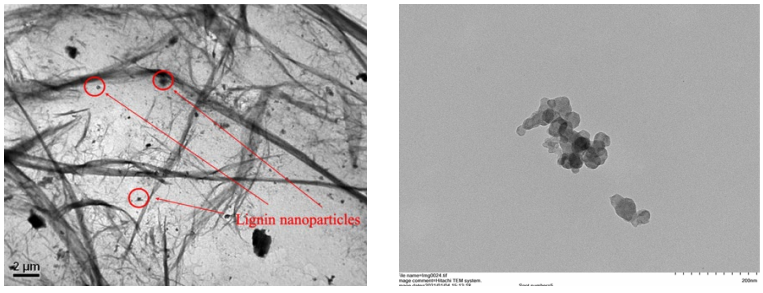

Figure 1. Micrograph TEM of LCNF and lignin nanoparticles (scale: 200 nm).

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Optimization of reagents consumption in TEMPO-mediated oxidation of *Eucalyptus* cellulose to obtain cellulose nanofibers

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This study is focused on the optimization of a chemical pretreatment based on the catalytic oxidation reaction by 2,2,6,6, tetramethyl-1-piperidinyloxy (TEMPO). This is one of the most common methods for the pretreatment of cellulose to reduce the cost of the production of cellulose nanofibers (CNFs). This study analyzes the ways to reduce the consumption of reagents while the quality of the final CNFs is maintained.

The reaction was carried out at different times and modifying both the concentration of the NaClO and the amount of the catalysts (TEMPO and NaBr), using *Eucalyptus* cellulose as raw material. Results are summarized in **Table 1**. The amount of carboxyl groups obtained by traditional TEMPO conditions [1], is higher than with the proposed conditions, 1.7 and 1.1 mmol COOH/g respectively. However, it is possible to reduce the reaction time from 2 hours to 45 minutes and obtain a sufficiently good quality of the CNFs. Moreover, the cellulosic pulp yield is higher under the proposed conditions (0.025 mmol/g TEMPO and 0.5 mmol/g NaBr) and a similar diameter of CNFs is obtained. With the optimized conditions, the catalyst can be reduced up to 75% compared to the most widely used catalyst doses (0.1 mmol/g TEMPO and 1 mmol/g NaBr). Therefore, it is possible to produce CNFs with lower environmental impact contributing to the sustainability of the industrial production of TEMPO-mediated oxidation CNFs.

Table 1. Comparison of traditional and proposed TEMPO-mediated oxidation conditions

	Traditional Conditions	***Proposed conditions***
Reaction		
NaClO (mmol/g)	5	5
TEMPO (mmol/g)	0.1	0.025
NaBr (mmol/g)	1	0.5
Oxidation time (min)	120	45
Oxidized pulp and CNFs properties		
Carboxyl groups (mmol/g)	1.7	1.1
Cellulosic pulp yield (%)	57	79
Diameter of CNFs (nm)	14-26	16-30
Catalyst cost (€/kg cellulose recovered)	136	27

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Kinetic study of tempo-mediated oxidation and real-time monitoring strategy

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The present work shows the feasibility of using sodium hydroxide consumption during TEMPO-mediated oxidation as an effective real-time monitoring system of the catalyzed reaction and provides kinetic information of the reaction as a function of the process conditions. A bleached kraft eucalyptus pulp (BKEP) was selected as raw material and subjected to TEMPO-mediated oxidation at different reaction conditions. The kinetic study was performed using varying the temperature (5 – 35 °C), the oxidizer amount (5 – 15 mmol/g), and the TEMPO catalyst amount (2 – 32 g/kg). This provided a three-dimension factorial plan able to provide the dependence between carboxyl content and time for different reaction conditions.

It was found that regardless of the process conditions, the NaOH addition exhibited a linear relationship with the carboxyl content of the fibers, which indicates that the evolution of the reaction could be directly monitored using considering the amount of NaOH per gram of fiber. In addition, the effect of temperature and catalyst was elucidated, obtaining the kinetic constant of the reaction as a function of temperature and catalyst. Further, as the temperature was varied during the experimental work, the activation energy was properly obtained through the Arrhenius equation. The system was assumed to be homogeneous, although heterogeneities are known due to the morphology of the reacting species (fibers). From the study of the temperature, kinetic constants ranging from 0.58 to 5.50 s^{-1} were found, responding to a first-order reaction system. Further, the activation energy was quantified to be around 73.70 kJ/mol for an addition of 16 g/kg of TEMPO, which is following previously reported data [1,2]. Regarding the study of the effect of TEMPO catalyst, kinetic constants ranging from 0.47 to 3.63 s^{-1} were found, indicating that extra catalysts do not benefit the rate of reaction, while high temperature does (30 °C).

Finally, regarding the oxidizer amount, changes in the kinetic constant were observed, which indicates that changes in the limiting reagent occurred. This last part of the study deserves further research in terms of heterogeneous catalytic systems, as changes in morphology may occur, exposing further primary alcohol groups and, thus, affecting the reagent concentration.

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Prediction of cellulose micro/nanofibers aspect ratio and yield of nanofibrillation using machine learning techniques

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Cellulose nanofibers (CNF) have a wide range of applications in nanocomposite production, tissue engineering, and food packaging, among others, due to their biodegradability and good mechanical and barrier properties. To accelerate the development of this class of material, machine learning techniques constitute a convenient tool to reduce experimental efforts required for the design of new nanocellulose applications, for the modeling and characterization of biobased nanocomposite products. [1,2].

In the present work, 20 different types of lignocellulose micro/nanofibers (produced from Spruce and Pine softwoods and by different pre-treatment and fibrillation techniques according to [1]) were used as training and testing datasets aiming the development and evaluation of three machine learning models for the prediction of two CNF relevant properties: aspect ratio and yield of nanofibrillation. The models used were Random Forests (RF), Linear Regression (LR), and Neural Networks (NN). The performance of these models was evaluated by comparing Root Mean Square Error (RMSE) and R^2, showing that NN provided the best results for both properties, followed by LR and finally RF. NN models for aspect ratio resulted in RMSE=6.31 and $R^2 = 0.96$, and for yield of nanofibrillation they were RMSE=0.70 and $R^2 = 0.98$. For both properties, NN model topology was 5-10-1, which means 5 inputs, 10 neurons in the hidden layer, and 1 output. The hidden layer involved sigmoid activation function for the aspect ratio and rectified linear unit activation function for the yield of nanofibrillation. Five easily measured inputs were used for the aspect ratio: Total lignin (wt.%), Cellulose (wt.%), Hemicellulose (wt.%), Extractives (wt.%), and HPH Energy Consumption (kWh/kg). Similarly, the yield of nanofibrillation included 5 inputs relatively easy to obtain: HPH, Extractives (wt.%), Cationic Demand (μeq/g), Transmittance at 600 nm, and Consistency index "k". In both cases, the NN models trained here provided very good estimates of aspect ratio and the yield of nanofibrillation, being able to capture the effect of the applied energy along the fibrillation process. Also, aspect ratio NN modeling involved the chemical composition of the mechanically pretreated fiber and HPH, which are low-cost operation variables, whereas the yield of nanofibrillation required easy-to-measure variables as inputs. Finally, further machine learning studies will be conducted considering the continuous insertion of new data combined with the model optimization to improve the prediction performance and generalization capacity.

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Cellulose nanofibers from fique residues: isolation and characterization

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After cotton, fique fiber bundles are the second most important commercial fibers in Colombia. They are extracted from the leaves of the endemic species traditionally called fique or cabuya plants (*Furcraea cabuya* and *Furcrae macrophylla*). Fique cultivars are spread in at least ten regions around the country, and the production of the fibers is the main economic activity for thousands of farmers [1]. These bundles have several applications, such as, the manufacture of large sacks for the packaging of agricultural products, for instance, coffee and cocoa; and in recent times, they have been increasingly used in textiles, handcrafts and composite materials. These applications promote the internal demand of this product. Fibers represent only 4 wt.% [2,3] of the whole fique leave, and the remaining 96% is constituted by juice (55 wt.%) and bagasse (41 wt.%) [4]. Fique bagasse (FB) is composed of cellulose, hemicellulose, lignin, lipids, and proteins. This composition is a reliable source of lignocellulosic biomass, as well as to obtain cellulose nanofibers (CNF) [5][6]. In this work, fique bagasse was used to isolate fiber bundles and cellulose nanofibers. For this propose, an alkaline treatment using KOH at 5 wt.% and an additional mechanical process using a Supermasscoloider Mazuko MKCA6-2 (grinder), were used. Fique fibers and cellulose nanofibers were characterized through proximal analysis, FT-IR (Fourier Transform Infrared Spectroscopy), X-ray diffraction, colorimetry, rheology, and electronic microscopy to understand the effects of the treatments on the chemical structure and composition of the final product. In addition, AFM (Atomic Force Microscopy) was used to analyze the morphology of the CNF. The samples evidenced diameters between 5 and 60 nm. These results show that fique bagasse is, indeed, a promising alternative source for supplying fiber bundles and cellulose nanofibers.

Keywords:

Fique bagasse, fiber bundles, nanofiber cellulose, hemicellulose, lignin

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Membranes (Thursday 30th June 2022)

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Sustainable MFC acetylation by citric acid for the production of films combined with polyols for barrier packaging application

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This study evaluates the effect of acetylated microfibrillated cellulose (MFC) combined with polyols on the final properties of films. Bleached eucalyptus commercial pulp was mechanically fibrillated using a simple disk refiner. The MFC obtained was acetylated for 60 min at 90-95°C in acetic anhydride using 0.5 mmol/mmol glucose units of citric acid as a sustainable catalyst. The degree of substitution (DS) was determined on the acetylated MFC (MFC-A) according to the ASTM D817-12 standard. 15 g/m^2 films were prepared using solvent casting (drying at 50°C) combining MFC with glycerol (Gly): 100%MFC, 75%MFC/25%Gly (MFC without acetylation), and 75%MFC-A/25%Gly (acetylated MFC). Tensile index (TI), elongation at break (EAB), E modulus, water vapor permeability (WVP), water absorption (WA) (TAPPI T831), and transmittance at 600 nm (T_{600}) were measured on the obtained films. The overall migration food (OML) was determined using food simulants: distilled water, 15% v/v ethanol solution, and 3% w/v acetic acid solution.

The MFC-A reached a DS of 0.254. The transparency of the films increased ($p<0.05$) after the addition of glycerol to MFC without acetylation (transparency: 56.6%). On the opposite, the films with MFC-A showed lower transparency values (transparency: 41.7%), and the aspect of the film was visually more opaque. The thicknesses varied in the range of 21.9-35.6 µm. The incorporation of glycerol decreased the TI values, and the decrease in MFC (without acetylation) + GLY was greater than the combination with acetylated MFC (100%MFC: 65.1 Nm/g, 75%MFC/25%GLY: 23.5 Nm/g and, 100%MFC-A/25%GLY: 30.3 Nm/g, respectively). The EAB values increased with the addition of the plasticizer. The increase in EAB in the sample with MFC without acetylation was up 3 fold higher than (12.7%) the elongation of the 100% MFC sample (4.72%). The film with acetylated MFC achieved an EAB of 7.12%. The barrier properties were higher for the films with the acetylated MFC. The WA was higher for the MFC films (without acetylation) combined with glycerol (23.7%) than the WA for films with MFC-A (2.38%). The addition of glycerol increased the WVP of the film in unmodified MFC (from 132 to 157 m^2 day kPa). But, the film containing the acetylated MFC showed a lower value of WVP (77.6 m^2 day kPa). The OML values were less than 60 mg/Kg (maximum established by standard) for all the simulants, except for the 75%MFC/25%GLY films, where the OML in 15%v/v alcohol was 69.2 mg/Kg. The soil aerobic biodegradation will be tested in the following weeks.

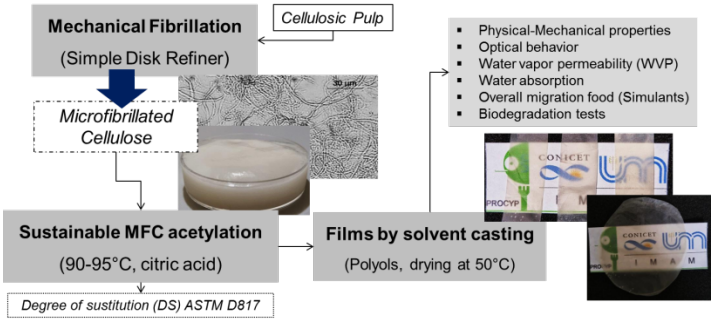

Figure 1. Applied methodology

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Preparation and characterization of biobased films reinforced with micro/nano-fibrillated cellulose

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Xylan (Xyl) is a polysaccharide that can be obtained from lignocellulosic materials. The combination of Xyl with another natural polyelectrolyte of opposite charge, chitosan (Ch), allows for obtaining films with excellent oxygen barrier properties [1]. However, due to the hydrophilic nature of these polymers, this property as well as the water vapor permeability are affected by the relative humidity of the environment. Nanofibrillar cellulose is a material that possesses advantageous properties and characteristics such as high specific surface area and biodegradability. Although this material presents hydroxyl groups that make it hydrophilic, it has been found that the water vapor permeability decreases when it is incorporated into a polysaccharide matrix [2].

In this work, micro/nano-fibrillated cellulose (MNFC) was obtained from commercial dissolving spruce pulp (Mw cellulose: 225 kDa). The pulp was pre-refined in a PFI mill (12000 revs), followed by a chemical treatment (oxalic acid 50% p/p, at 90°C for 60 min) and then, a mechanical treatment (Ultraturrax homogenizer and a high-pressure homogenizer, 10 passes at 300 bar). Then, the nano-fibrillated fraction (NFC) was obtained by centrifugation of the whole suspension. The nanofibrillation yield was 65.4%. Both fractions, MNFC and NFC, were characterized by complementary techniques, namely optical microscopy, AFM, polyelectrolyte titration, zeta-potential, and dynamic light scattering.

Furthermore, xylan extracted from poplar wood was used in combination with chitosan (mass ratio 60/40 Xyl/Ch) to prepare films containing different amounts of MNFC and NFC (0%, 3%, 5%, 7%, 10% wt.). They were characterized by determining the transparency, water vapor barrier properties at 50% HR and 23ºC, swelling capacity, and mechanical properties. It was found that by increasing the amount of MNFC or NFC, the water vapor barrier properties were improved indicating better interactions between nanocellulose and the matrix. Besides, the transparency of the films was decreased, mainly due to the presence of high amounts of MNFC. Particularly, when 5 wt.% MNFC was added, the stress at break increased 27% (up to 67 MPa), and elongation increased 56% (up to 11%). However, when higher amounts of MNFC were used, more opaque and rigid films were obtained.

All these results suggest that the addition of low amounts of nanofibrillar cellulose allows for obtaining Xyl/Ch films with better barrier and mechanical properties.

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Overcoming the dewatering challenges of nanopapers

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Nanopapers are an emerging category of paper that contains a significant quantity of some nanomaterial(s). Nanopapers have novel functional properties for various applications such as energy storage, packaging, etc. Micro-nano fibrillated cellulose (MNFC) is one of the most important constituents in many nanopapers. One of the main challenges for the wide-scale application of MNFC is poor water removal properties. This is due to the small size, large surface area, and high swelling ability of MNFC fibrils. [1,2]

Herein, we used different approaches to investigate the possible solutions to improve the dewatering of high MNFC content papers. One approach was the addition of in-situ generated cationic micro-nano bubbles to the furnish. They adsorb onto anionic fibers, which subsequently flocculate and float and structure the furnish. We learned that MNFC preferentially adheres to the cationic bubbles, which then enriches the top layer and avoids sheet sealing.[3]

This gave the idea of multilayer forming to overcome sheet sealing which is a significant problem in the dewatering of nanopapers. Sheet sealing might be related to the plugging of the forming wire or the formation of a very dense exit layer. In multilayer forming, the MNFC is introduced as a second layer on top of the fibers layer, which is bigger and less conformable than MNFC fibrils. This approach could prevent sheet sealing and facilitate dewatering. It was found that a thin layer of fibers on the exit layer with a grammage as low as 5 gsm was enough to improve the dewatering of MNFC significantly.

We investigated another approach to disrupt sheet sealing which is the application of high-frequency hydraulic pulse during filtration. It appears that a mechanical force can improve the dewatering of nanopaper by breaking the agglomeration of the fibers and creating flow channels. A novel drainage analyzer includes a pulsator apparatus that was designed and built in our laboratory.

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Nanocellulose membranes enriched with an *eucalyptus globulus* leaves extract for anti-aging skin-care applications

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Bacterial nanocellulose (BNC), with remarkable physical and mechanical properties, is a versatile carrier of bioactive compounds for skincare applications [1]. In the present study, BNC membranes were loaded with glycerol (as plasticizer and humectant agent) and the hydro-distillation extract of *Eucalyptus globulus* Labill. leaves (HDE), for application as sheet facial masks (Figure 1). The membranes with different HDE contents (1–3 μg cm^{-2}) are resistant and highly malleable in dry and wet states, with comparable or even identical mechanical properties to those of a commercial BNC mask. Furthermore, the HDE conferred a dose-dependent antioxidant activity to the BNC masks, and upon 3 months of storage at 22-25 °C and 52% relative humidity (RH) or 40 °C and 75% RH, the antioxidant activity, and the macroscopic aspect of the membrane with 2 μg cm^{-2} of HDE, was maintained. Lastly, the masks are non-cytotoxic toward human keratinocytes (HaCaT) and mouse fibroblasts (NIH/3T3) cells, and the membrane containing 2 μg cm^{-2} of HDE, promoted a drop in the senescence-associated β-galactosidase activity in the NIH/3T3 cells, which corroborates the potential of the membranes as bioactive facial masks for anti-aging applications.

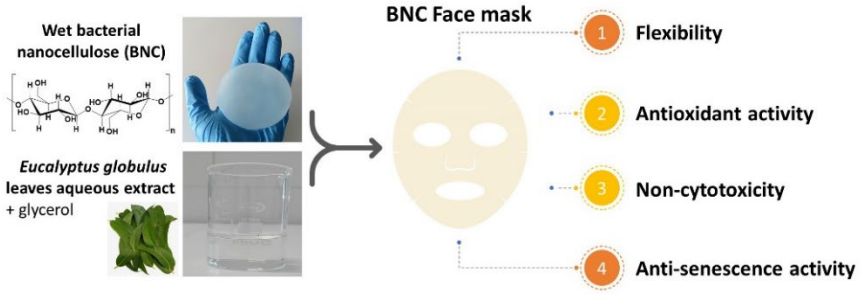

Figure 1. Schematic representation of the preparation of the BNC bioactive masks.

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Ion-conducting membranes of nanocellulose & lignosulfonates for application in fuel cells

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Nanocelluloses are being exploited for the assembly of naturally derived ion-exchange membranes for application in polymer electrolyte fuel cells (PEFCs) [1]. In the present study, fully biobased ion-exchange separators, composed of bacterial nanocellulose (BNC) and lignosulfonates (LS) (Figure 1), were fabricated by diffusion of an aqueous solution of the lignin derivative (LS) and a natural-based cross-linker (tannic acid) into the wet BNC nanofibrous three-dimensional structure [2]. The obtained ion-exchange membranes showed good thermal-oxidative stability of up to about 200 °C and high mechanical performance with a maximum Young's modulus of *ca*. 8.2 GPa, along with good moisture-uptake capacity with a maximum value of *ca*. 78% after 48 h. In addition, the blend of the robust BNC with the conducting LS conferred ionic conductivity to the membranes, reaching a maximum of 23 mS cm^{-1} at 94 °C and 98% relative humidity. Hence, these flexible water-mediated ion conductors might be a sustainable alternative to the traditional ion-exchange membranes for application in PEFCs [2].

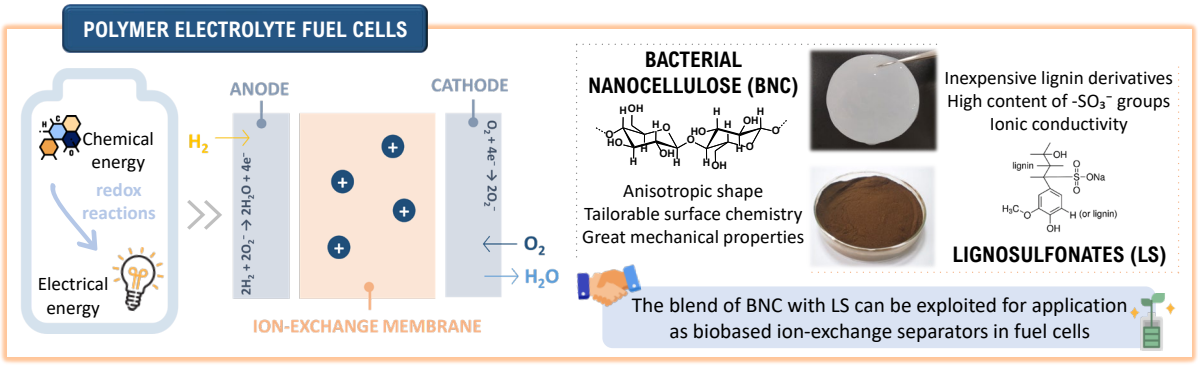

Figure 1. Schematic representation of the work developed in this study.

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Cellulose-based actuators prepared by tailored modification and assembly

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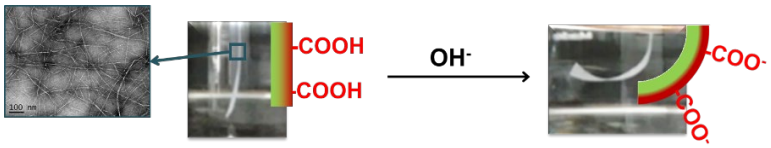
Nanocelluloses have attracted much interest because of their excellent properties including high aspect ratio, high strength and stiffness, low density, transparency, and low thermal expansion.[1, 2] There are two main types of nanocelluloses: cellulose nanofibers (CNF) obtained by mechanical fibrillation of the fiber, and cellulose nanocrystals (CNC) prepared by acid hydrolysis of cellulose fibers, which specifically solubilizes the amorphous regions in the fibers.

The surface properties of cellulose (charge, polarity) can be tuned by different strategies. The most common is the modification of the hydroxyl groups by oxidation, etherification, or esterification. Another innovative strategy is the selective modification of reducing ends. Thus, taking advantage of the chemical polarity of cellulose I, where all cellulose chains are arranged in a parallel way, we can selectively modify the aldehyde functionalities at reducing ends.[3]

In this work, we present different strategies to modify the cellulose structure and achieve outstanding properties. Combining tailored modification and assembly techniques, we have succeeded in fabricating actuators that respond to different stimuli (humidity, pH, solvent).[4] We designed CNF bilayer films differing in charge at each layer to obtain graded films. Hence, the resulting films contained a higher concentration of charged groups on one side of the film than on the opposite side, so pH changes result in charge-dependent asymmetric deprotonation of the two layers. The electrostatic repulsion separates the nanofibers in the film, thus facilitating an asymmetric swelling of the film that triggers macroscopic bending.



Our study provides direct evidence of the possibilities of cellulose-based materials. Besides its environmentally friendly properties, cellulose can be viewed as a promising candidate for the fabrication of advanced materials showing controlled response to external stimuli.

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Conductive nanocellulose-based substrates for more sustainable sensors and biosensors

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In the current worldwide situation of environmental crisis, a new paradigm toward a more sustainable model is needed. The appearance of the Internet of Things (IoT), and specifically in the medical area (Internet of Medical Things, IoMT), together with personalized medicine will be the maximum expression of personal health monitoring. High demand for sensors is then expected, pushing to produce simple, low-cost, and disposable diagnostic devices. The common materials used in the microfabrication of these sensors (electrodes and substrates) are usually toxic, critical raw materials, or simply, they are not biodegradable. So, we have a situation that we cannot ignore and forces our society to think about our future with a more sustainable and environmentally friendly approach. This is the reason why we propose to rethink and redesign the materials and sensor technology for the fabrication processes in a more eco-friendly and sustainable manner contributing to the first steps of the circular economy.

In this sense, novel nanocellulose substrates are used to manufacture microsensors, using economic and sustainable technologies such as digital printing or additive manufacturing. The overall concept is exploiting cellulose and nanocellulose with novel functional properties, for the formulation of green materials to be used in advanced, biodegradable, and disposable printed electronics. Electroconductive substrates are here developed by combining the nanocellulose with sustainable and biocompatible conductive elements (ie graphene or conductive polymers). The chosen manufacturing methodologies follow the principles of green chemistry. Synergies between conductive materials are studied in ternary hybrid nanocomposite formulations, for which improved conductive properties are attained. Conductivities higher than 1 Scm^{-1} were registered for 50:50 binary formulations with conductive polymers or about 50 Scm^{-1} for binary formulations with reduced graphene oxide. Ternary formulations increased by 3 or 4 times the electrical conductivity of each conductive element in the formulation. The electrochemical behavior was determined using the specific capacitance that attained more than 100 Fg^{-1} in ternary compositions [1].

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High added-value macromolecules from lignocellulose

(Thursday 30th June 2022)

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Tracing the path to a circular bioeconomy

Lignocellulosics an opportunity in the development of the bioeconomy andthe circular economy: New bioactives and materials

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The natural resources available to the world's population are limited. Global challenges such as the increase in the world population, climate change, and the degradation of ecosystems force us to seek new forms of production and consumption that are sustainable from an economic, social, and environmental point of view. To meet these challenges, how food, products, and materials are produced and consumed must be improved by developing a sustainable bioeconomy.

For the development of the bioeconomy to be successful, it needs to be endowed in its essence with circularity and sustainability. In line with that of the bioeconomy, the circular economy pursues the most efficient use of finite resources, extracting the maximum value and use from all raw materials, products, and waste, promoting energy savings and reducing greenhouse gas emissions. Greenhouse effect.

The biomass industrialization valorization of grains and cereals is considered an opportunity for the countries where agro-industrial activity is one of its main economic activities, rendering new higher-value products with a concomitant solution to waste accumulation issues. To that end, in this work we describe and characterize bioactive compounds generation from rice husk by semisolid fermentation, obtained from 100 g of the material at room temperature and 60% humidity with mixed cultures of Phanerochaete chrysosporium and Gloeophyllum trabeum.

The extract was evaluated in different germicide activities with Fungus and bacteria with application in solution, films, and fabrics. The results exhibited that the extract displayed germicide activity in all cases. The solid fermentation residue was washed with distilled water and was irradiated in a Gama cell at 72 kGrey of gamma radiation to separate Nano cellulose and Nano silica as secondary products This study has shown that it is feasible to prepare specific enzymatic extracts capable of directing the degradation of lignin towards oligomers or monomers that exhibit variable and functional structural characteristics. processes to obtain compounds to this end, we obtained 40% of veratryl alcohol from the transformation of lignin. Additionally, the germicidal activity showed total inhibition in bacteria and fungi reveals a potential application in medicine and agroindustry.

On the other hand, the process residues are transformed into Nano cellulose and Nano silica with a 60% recovery, which allows us to think of a biorefinery process that leads to circularity.

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Valorization and Characterization of Hardwood and Softwood Lignins from Sulfite Liquors

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Lignin is the most abundant natural phenolic polymer in the world. It is an amorphous, three-dimensional biopolymer arising from the polymerization of three basic units: p-hydroxycinnamyl, coniferyl, and sinapyl alcohol.[1],[2] Sulfite pulping is the most predominant lignin-producing process, generating lignosulfonates.[2]

This work aims to evaluate the structural characteristics of lignins obtained from hardwood (LHSL) and softwood (LSSL) sulfite liquors. Lignins were obtained after ultrafiltration and freeze-drying of the sulfite liquors and characterized based on inorganic content, nitrobenzene oxidation, ^{13}C NMR, and molecular weight determination (**Figure 1**). The structural characteristics achieved allow evaluating the potential of each lignin through depolymerization to produce added-value phenolic monomers. Hardwood and softwood lignins were submitted to alkaline oxidation with oxygen and the reaction conditions were optimized to obtain a final oxidation mixture with the maximum yield of phenolic monomers. As expected, through oxidation with O_2 hardwood lignin generates mostly syringaldehyde while lignin from softwood mainly produces vanillin; moreover, a slower reaction time and the interruption of O_2 admission avoid the degradation of the oxidation products in the final oxidation mixture for both lignins, more evidenced to hardwood lignin due to its higher reactivity. From the results, it is possible to conclude that a phenolic aldehyde-rich oxidation mixture could be obtained, confirming the viability of lignin as raw material to produce added-value products.

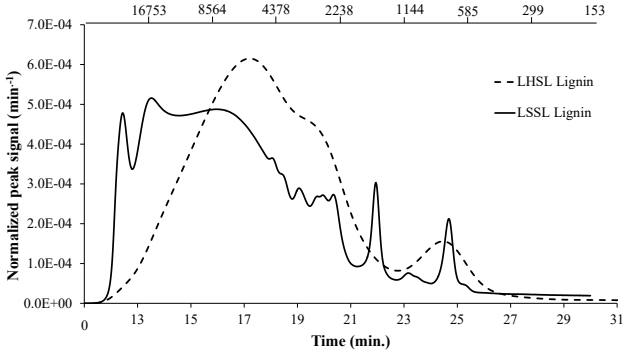

Figure 1. Molecular weight distribution curves obtained from GPC analyses of LHSL and LSSL lignins.

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Improving the fractionation of kraft black liquor by optimizing the operating conditions of the ultrafiltration process

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The separation of hemicelluloses and lignin using membrane ultrafiltration (UF) has propelled the valorization opportunities instead of the conventional use of industrial black liquor (BL). BL is an attractive bioresource as it contains 95-97% of lignin and 30-50% of hemicelluloses of wood biomass used for pulping operation. The separation of these biopolymers from BL can lead to their conversion into value-added products. In this sense, a difference in their molecular weight/ size makes them suitable for separation by the membrane filtration process.

In this work, hemicellulose, which has a comparatively higher molecular size than lignin, was concentrated in the retentate stream using suitable pore size UF membranes. While lignin due to its lower rejection was separated in the permeate stream with lesser impurities and controlled molecular size distribution. Further, the separation of these components was improved by optimizing the process parameters like temperature and pressure, favoring higher rejection of hemicelluloses than lignin. For effective separation of both components, temperature and pressure are the most important parameters for the membrane filtration process, where the molecular transport phenomenon is controlled by pressure while the temperature can influence separation by influencing the viscosity of the feed solution and solubility of solutes.

The effect of temperature (40–80 ºC) and pressure (1–4 bar) on rejection was studied using ZnO-based polyethersulfone UF membranes. It was observed that the rejection coefficients of hemicellulose and lignin varied with both temperature and pressure, which influenced their concentration in the retentate and/or permeate streams. The pressure studies revealed that the rejection of both components increased with pressure. The study of the temperature effect showed that the rejection of both lignin and hemicellulose was highest at the lowest studied temperature, and it reduced on increasing the temperature. However, increasing the temperature beyond a limit, the lignin rejection increased, and hemicellulose rejection remained stable. Therefore, at optimal temperature and pressure conditions, effective separation of both components from the BL was achieved during the UF process.

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Fractionation of Norway spruce wood using γ-valerolactone for production of advanced biofuels

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A novel fractionation method based on γ-valerolactone (GVL) [1] is proposed for producing advanced biofuels from softwood using Norway spruce (*Picea abies*) as a wood model. The results of our experiments show that the proposed method allows the fractionation of woody biomass into its three principal components (cellulose, hemicelluloses, and lignin) in a single step under relatively mild conditions. Fractionation is performed with a GVL/water mixture containing a very small amount (less than 0.5 g/100 g biomass) of sulfuric acid and at a temperature below 200 °C. The treatment leads to solubilization of hemicelluloses and lignin without affecting cellulose to a large extent, and it results in a cellulose-enriched solid fraction and a liquor containing hemicellulosic saccharides and solubilized lignin. The effects of the operational conditions (GVL concentration, temperature, and residence time) on the efficiency of the treatment were evaluated. The recovered cellulose displayed enzymatic digestibility values that are comparable with results achieved after acid pretreatment at temperatures 25 – 40°C higher than those used for GVL fractionation. The resulting hydrolysates can be fermented to ethanol. The solubilized lignin was precipitated from the liquid fraction by using water as an anti-solvent. The recovered lignin, which had high purity, and low carbohydrate content, was characterized by pyrolysis-gas chromatography/mass spectroscopy (Pyrolysis-GC/MS), Fourier-transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR), and high-performance size-exclusion chromatography (HPSEC). Hydrothermal liquefaction (HTL) can be applied to lignin for producing bio-oils that can be considered for formulating diesel- or gasoline-like fuels [2]. A short-lasting high-temperature dehydration process was evaluated for converting to furan aldehydes the hemicellulosic saccharides remaining in the liquid fraction after lignin precipitation. The furan aldehydes 5-hydroxymethylfurfural (HMF) and furfural resulting from hemicelluloses are of high interest for producing 2,5-dimethylfuran (DMF) and 2-methyltetrahydrofuran (MTHF), which can be used as biofuels [3]. Hence, with the proposed process, a modern biorefining concept allows directing the three main components of softwood biomass to biofuels, namely cellulosic ethanol, lignin-derived bio-oils, and furan biofuels. To the best of our knowledge, this is the first study where a GVL-based biorefining method is applied to Norway spruce for the production of three kinds of advanced biofuels.

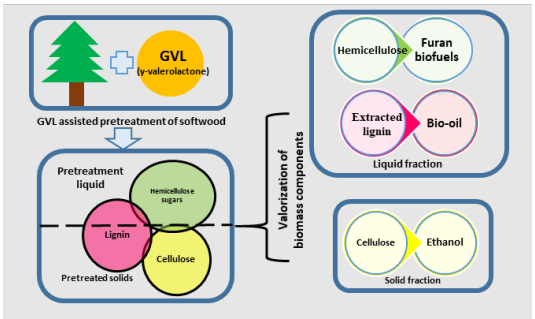

Figure Schematic outline of GVL-based fractionation of softwood and valorization of biomass components.

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Application of cold alkaline extraction process of the elephant grass to optimize the energy use and valorization of the hemicellulosic fraction

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There is a growing scientific and industrial interest in the generation of energy and valorizable compounds derived from the fractionation of lignocellulosic biomass for use in the bioenergy and materials industry by using plant species from industrial crops that do not interfere with food uses. (Yadav et al., 2019).

In this context, in which the main motivation is to achieve the sustainability of the processes and the commitment to the circular economy, the optimization of the energy use of the Elephant grass is addressed through the previous selective extraction of the hemicellulosic fraction by Cold alkaline extraction (CAE). Elephant grass is described as an excellent alternative to other wood materials (Marafon et al., 2021) for energy use by direct combustion, with significant lignin (20.86%) and hemicelluloses (27.4%) contents.

To optimize energy use, a composition central experimental design is applied operating in the following ranges: NaOH concentration 80-120 g L^{-1}; operation Time 30-90 minutes and operation Temperature 20-40 ° C. Optimizing the operating conditions (T 30 ºC, NaOH concentration 100 g L^{-1} and operation Time 30 min) achieves an increase of 4 % in the High Heating Value (19.151 MJ / kg) concerning the starting raw material consequent to the maintenance of the concentration of elemental C and the increase of 4.86 % in the elemental H content concerning the raw material. In addition, an environmental improvement is achieved by reducing the sulfur content by 46.9% in the solid phase post-Cold alkaline extraction compared to the raw material. They are advantageous operating conditions concerning those described by other authors with materials such as sugarcane bagasse or wheat straw (García et al. 2013; De Carvalho et al., 2016).

In addition, under the indicated conditions a relatively selective separation of the hemicellulose fraction from the cellulose and lignin fractions is achieved. 30.1% of the hemicellulose fraction is incorporated into the recoverable liquid phase while 93.0% of the cellulose and 82.1% of the lignin initially present in the raw material remain in the solid phase.

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Hardwood *Kraft* Pulp for the Production of Prebiotics

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Over the past years, there has been an increasing demand for functional foods, mostly for their positive effect on the immune response. In particular, the consumption of prebiotics, a substrate that is selectively utilized by host microorganisms, has been related to several health benefits [1]. More recently, due to the global covid-19 pandemic, their use as a prophylactic method to improve the immune system and minimize the inflammation caused by SARS-CoV-2 infection has been largely under study [2].

In this work, the pulp and paper industry answers to prebiotics increasing demand, as xylooligosaccharides (XOS), emerging prebiotics derived from xylan, is produced from a hardwood *kraft* pulp. This substrate, mainly composed of cellulose and hemicellulose, with 16 – 23% of xylan, although rarely used for XOS production, is widely produced and available in this industrial sector, representing a very promising and low-cost raw material.

The pulp (substrate) was directly submitted to enzymatic hydrolysis, the greenest known option for XOS production, without the need for any pretreatment. The most relevant experimental conditions were studied and optimized, considering not only the maximization of XOS yield but also the economic and environmental impacts of the process, with a particular focus on the reduction of the use of chemical products.

Yields of XOS above 6%(m/m) per initial pulp and 30%(m/m) per xylan in this substrate were obtained. The polymeric distribution of XOS in the hydrolysate was mainly composed of xylobiose and xylotriose (> 95%), oligosaccharides to which the highest prebiotic effect is attributed [3].

In conclusion, this work proposes and validates an ecofriendly process to produce prebiotics directly from a hardwood *kraft* pulp. The production of these high-value products represents an excellent alternative for the pulp and paper industry to diversify/ innovate the pulp usage and improve its competitiveness, also with excellent repercussions in the food and pharmaceutical markets.

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Protective effects of extracts from eucalyptus globulus biomass in alzheimer's disease *in vitro* and *in vivo* models

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Alzheimer's disease (AD) is the leading cause of dementia worldwide and involves progressive impairment of cognitive function. An increasing number of neuroprotective compounds from natural origin have been identified with potential anti-AD properties. *Eucalyptus globulus* is widely used by the pulp, paper, and wood industry which generates large quantities of residual biomass (bark, leaves, and branches) whose valorization can represent a significant contribution to the circular economy. *E. globulus* is employed as herbal tea and therapeutical purposes since its by-products are a source of bioactive compounds. This work evaluates the *in vitro* and *in vivo* effect of extracts obtained from *E. globulus* biomass in AD features.

Cytotoxicity was evaluated by the MTT assay. The anti-inflammatory effect was evaluated by Griess assay and RT-PCR. ROS production and mitochondrial membrane potential were investigated by Amplex Red and TMRE assays, respectively. The extracts were evaluated for their ability to reduce Aβ production by ELISA whereas its blood-brain barrier (BBB) permeability was studied by PAMPA assay. The effect of anxiety and cognitive deficits after intranasal administration to APP/PS1 mice was assessed by open field and fear conditioning tests.

The *E. globulus* extracts showed an anti-inflammatory effect in cerebral immune cells, namely LPS- and Aβ-stimulated microglia, decreasing the nitric oxide production and the expression of pro-inflammatory mediators. In neuronal cells, the extracts attenuated cell death induced by Aβ, and ameliorated mitochondrial membrane depolarization, ROS production, and Aβ secretion in neuronal cells expressing an AD-related mutation. One of the extracts demonstrated the ability to cross the BBB and its intranasal administration to APP/PS1 mice model of AD reduced Aβ brain levels ameliorated anxiety and interfered with fear memory acquisition.

Overall, these results suggest a protective role of extracts obtained from *E. globulus* biomass on AD-like pathology and cognitive impairment and its beneficial action may be attributed to the capacity to reduce Aβ production together with anti-inflammatory and antioxidant actions. Consequently, these extracts could be used as raw materials to develop food and pharmaceutical supplements useful for AD prevention or treatment.

Acknowledgments: This work was carried out under the Project inpactus – innovative products and technologies from eucalyptus, Project N.º 21874 funded by Portugal 2020 through European Regional Development Fund (ERDF) in the frame of COMPETE 2020 nº246/AXIS II/2017

Biopolymers, biofuels and enzyme-assisted technologies

(Thursday 30th June 2022)

Biorefinery utilization of quinoa residues for producing biofuels and biopolymers

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Lignocellulose biorefining is a solid pillar in the transition from the current fossil-based economy toward a bio-based economy. Biorefining of residual biomass allows producing fuels, chemicals, and materials that are today produced from fossil resources. In biorefining, biomass constituents are selectively separated, and the resulting fractions are used for producing relevant marketable products.

Using local residues as raw materials for biorefineries is important for sustainable development. In Bolivia, quinoa (*Chenopodium quinoa* Willd.) is an important crop. Huge amounts of stalks and seed coats are accumulated during quinoa harvest and processing, and they can be considered raw materials for local biorefinery initiatives. Our research aims at proposing a biorefinery process to be applied to quinoa residues from Bolivian Altiplano using our know-how on lignocellulose bioconversion and the asset of robust microbial strains isolated from extreme environments in that region. The proposed process consists in treating quinoa stalks in a sequence including extraction of saponins, acid hydrolysis of hemicelluloses, and enzymatic saccharification of cellulose for producing hydrolysates to be used in bioconversion processes with different alternative microbes.

In such a process, saponins are extracted with aqueous ethanol, the saponins-free material is subjected to sulfuric-acid-catalyzed hydrothermal pretreatment (SA-HTP) for separating a stream of hemicellulosic sugars and a cellulignin stream that is then saccharified with commercial cellulases. The extracted saponins can further be processed into value-added products or can be used for enhancing the enzymatic saccharification of cellulose. The produced hydrolysates are suitable substrates for producing ethanol or bacterial biopolymers. The residual lignin from the enzymatic saccharification can be upgraded for value-added applications.

The process is based on our experimental results including (i) evaluation of different procedures for extracting saponins from quinoa stalks and seed coats; (ii) assessment of SA-HTP of saponins-free quinoa stalks; (iii) study of the enzymatic saccharification of SA-HTP-pretreated quinoa stalks; (iv) investigation of the effect of quinoa saponins as additives in the cellulose saccharification; (v) isolation and identification of halotolerant bacteria from high-salt environments in the Bolivian Altiplano; (vi) evaluation of cellulosic and hemicellulosic hydrolysates as cultivation media for the yeasts *Saccharomyces cerevisiae* and *Scheffersomyces stipitis* and the halotolerant bacteria *Bacillus atrophaeus* and *Halomonas boliviensis*; (vii) characterisation of bacterial exopolysaccharides and polyhydroxyalkanoates produced in quinoa stalk hydrolysates; (viii) upgrading of residual lignins resulting from cellulose hydrolysis. Our preliminary trials reveal that biorefining of quinoa residues for producing biofuels and chemicals is a suitable process that deserves attention as an industrialization alternative for quinoa-producing areas, specifically for Bolivian Altiplano.

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Laccase-catalysed polymerization of kraft lignin from eucalyptus globulus

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Lignin, a heterogeneous biopolymer that is present in the cell wall of plants, has historically been a waste product from cellulosic pulp industry. In these processes, side-stream lignin is usually burned as a way of generating energy to cover part of the needs of the pulping industry. Nevertheless, in recent years, an interest in the valorization of lignin for the development of high-value-added products has emerged. Due to the great heterogeneity of this biopolymer, it may be necessary to modify lignin for its use in certain applications. One of the possible modifications is its polymerization by using enzymes, a sustainable process that can expand the use of lignins in applications that require high polymerization degrees such as dispersants and surfactants.

This work aims to study the oxidative polymerization of lignin by using laccase enzymes. For that, a commercial fungal laccase from the ascomycete *Myceliophthora thermophila* and a bacterial laccase isolated from *Streptomyces ipomoeae* were used to treat *Eucalyptus globulus* kraft lignin, recovered by acid precipitation from black liquor (industrial waste). To study and optimize the influence of some variables in these processes, a Response Surface Methodology RSM Design using a Central Composite Design with two continuous variables (enzyme concentration and reaction time) and three levels for each variable was used. The experiment consisted of thirteen runs of which five are center points and four are axial points (alpha= ±1.414). As output variables, phenol content and molecular weight of the resulting lignins were studied. Moreover, structural characterization of enzymatic treated lignin, by FITR and NMR analysis, and antioxidant activity were also evaluated.

Results showed that in the case of bacterial laccase, the enzyme concentration was the most influential variable in the kraft lignin polymerization reaction within the range studied, while for fungal laccase the most influential variable was the reaction time. Nevertheless, in both cases the higher the laccase concentration or the longer the reaction time, the higher the polymerization achieved in the studied lignin (referring to polymerization as lower phenolic content and higher molecular weight). FTIR and NMR characterization spectra corroborated polymerization results obtained from the RSM Design.

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Xylanase stage in ECF pulp bleaching and its impact on the environmental footprint of the pulp mill and the pulp properties

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The current regulation for emissions of Adsorbable organic halides (AOX) in the production of bleached ECF pulp in the EU is between 0,03 and 0,3 kg/ADt (ADt = tonnes of air-dry pulp expressed as 90% dry content) [1]. Chlorine dioxide, ClO_2, is responsible for the generation of AOX, and reduction of ClO_2 charge and/or optimization of the bleaching sequence can result in lower AOX emissions in the pulp mill effluents and reduced organic halogens (OX) in the final pulp products, which improves the pulp quality profile. Reducing bound halogens, OX, improves the overall sustainability profile of the pulp mill.

The charge of the bleaching chemicals as ClO_2, H_2O_2, and NaOH can be reduced by enzymatic treatment of the pulp. Reduced ClO_2 consumption not only results in a reduced amount of toxic AOX in the water effluent and lower OX in the final products, but it also will lead to reduced energy consumption. When ClO_2 is reduced or replaced by H_2O_2 in the production of ECF-light (one ClO_2 stage) bleached pulp, the energy demand is decreased due to the different energy demands in the production of these two bleaching chemicals [2]. The estimated energy savings are about 125 kWh/t pulp as a result of xylanase boost and reduction of the ClO_2 in the bleaching plant [3].

The purpose of our studies was to evaluate the environmental impact of xylanase in ECF bleaching sequence as well as the pulp properties including the pulp yield. The effect of xylanase stages was studied both before and after the oxygen delignification stage.

Our results concluded a Kappa number reduction of up to 20% with the tested commercial xylanases, regardless of if the xylanase treatment is before or after the oxygen delignification. The achieved Kappa number reduction is foreseen to result in corresponding savings of ClO_2 or other bleaching chemicals in the bleaching sequence as well as in energy savings to produce the bleaching chemicals. The final pulp viscosity seems not jeopardized. Furthermore, the yield loss in the xylanase stage is in the range of the yield loss in the oxygen delignification or EOP stage for the corresponding Kappa number reduction. However, the BOD and the COD of the bleaching effluent plant are reduced, since the pulp is entering the bleaching plant with a lower Kappa number and higher brightness and the generated effluent from the xylanase stage is burned in the recovery boiler during the regeneration of the chemicals. The cutting-edge limits of max 0,05kg AOX/ADt pulp can be achieved by ECF-light bleaching sequence, employing xylanase treatment, already at the entrance of the effluent plant, which will allow closing of the water loop further in the bleach section of fiberline. Another environmental-related aspect is that the energy demand in the ECF-light sequence is about 70% lower than in ECF sequence, due to the lower energy cost related to the production of H_2O_2 compared to ClO_2.

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Bio-based products from non-woody resources (Wednesday 30th June 2022)

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Co-products of sunflower cultivation, a promising source of biostimulatory molecules and construction materials

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The BioSUNmulant project (EU, FACCE SURPLUS, 2020-2023) aims to create a value chain of sunflower biomass [1]. Bioactive ingredients are extracted from sunflower co-products (*i.e.*, stalks and heads) through extrusion. Bioactive extracts are expected to be valorized as innovative and ecologically-friendly agricultural products. Besides, the remaining fibrous solid materials are used for obtaining bio-based construction materials, generating economical values with a lower environmental footprint.

First, aqueous extracts of sunflower (SE) were produced continuously from the co-products. The liquid/solid (L/S) extraction was carried out through twin-screw extrusion. Various operating parameters were optimized, *i.e.*, the incoming solid particle size, the screw profile in the L/S separation zone, the filling ratio of the machine, the pH of the extracting solution, the number of injection points, and the total L/S ratio. From optimal configuration, the extraction yield was 64.4% (w/w) (in proportion to the initial water-soluble compounds) in one single pass.

Then, the use of the SE extracts as biostimulatory products were evaluated [2]. The addition of SE to Arabidopsis (*Arabidopsis thaliana* L.) seedlings grown *in vitro* showed a dose-dependent response, with high concentrations causing severe growth inhibition. However, when priming seeds with SE, a small but significant increase in leaf area was observed at a dose of 5 g SE freeze-dried powder per liter. SE also improved the salt stress tolerance of the crops by reducing the production of reactive oxygen species (ROS) (*e.g.*, hydrogen peroxide) by about 30%. This ROS reduction was due to the presence of antioxidant agents in SE, and to the activation of ROS-eliminating enzymes. Polyphenols, carbohydrates, proteins, and other compounds detected in SE may have contributed to this bioactivity.

Lastly, residual solid (RS) generated at the extruder outlet was processed into cohesive boards through hot pressing. Optimal board (*i.e.*, 37 MPa flexural strength, 4.6 GPa elastic modulus, and 33% thickness swelling) was produced under 30 MPa pressure, 200°C temperature, 3 min molding time, and with 9.1% (w/w) sunflower protein isolate added as a natural binder. According to NF EN 312, it can be used as a type P2 board, *i.e.*, for interior fittings (including furniture) in a dry environment. In the future, for P3 and P4 types, a thickness swelling lower than 21% will be required. As a second way of valorization for RS, thermal insulation blocks with low density and thermal conductivity were also produced.

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Suitability of raspberry waste *(Rubus ideaus L.)* for nanocellulose obtention and its application in edible films and coatings.

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Agriculture has been fundamental for human development, however, large-scale mechanization and the increase in world population have led to the overexploitation of natural resources resulting in the massive generation of waste.

As a consequence of its accumulation, the need arises to find new ways of valorization, always from a sustainable and environmentally friendly point of view. In this sense, the cellulose present in this waste has suitable characteristics to be used as an alternative to petroleum-derived polymers, reducing the excessive use of plastics that we find today.

In this work, the viability of raspberry (*Rubus ideaus L.*) waste in obtaining nanocellulose and its application as a reinforcement agent in the development of food films and coatings using chitosan as a polymeric matrix was studied.

The results demonstrated the suitability of both the raspberry residue and the processes carried out to produce cellulose nanofibers, reaching nanofibrillation yields >95% for both TEMPO pre-treatments TO5 and TO10 in CNF samples. The application of LCNF and CNF in the development of films improved their mechanical and optical properties. Specifically, tensile strength, elongation percentage, and UV light blocking, with results of 41.8 MPa, 10%, and 88% for 1% LCNF-TO10, 1% CNF-TO5, and 15% LCNF-TO5, respectively. Regarding the application in food coatings, the coated raspberries improved their firmness values, and the microbial load remained below control after 7 days of storage.

Nanocellulose production and modification (Friday 1st July 2022)

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Modeling fibrillation in the mechanical production of lignocellulosic micro/nanofibers using neural networks

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The complex nature of typical (ligno)cellulosic micro-nanofiber (LCMNF) production systems is one of the main difficulties in the development of adequate monitoring instruments. Despite the huge efforts that were made in the last 20 years for the development of reliable and robust monitoring techniques, most micro-nanofiber properties cannot be measured online. Worse yet, off-line measuring of LCMNF properties can be very laborious. Besides, there is the difficult task of relating the raw material properties (which can usually be evaluated in the lab, such as the chemical composition, surface chemistry, rheological parameters, among others) and final end-use properties (mechanical performance, recyclability, barrier properties, etc.). These challenges can be faced efficiently with the help of machine learning modeling techniques, which make use of computational resources and statistical tools for efficient handling of massive datasets to predict relevant and/or time-consuming properties, as in the case of morphological features of LCMNFs. Among these modeling techniques, artificial neural networks (ANN) have been long recognized as one of the most powerful.

The present work proposes the use of neural networks to model the relationship among a set of easy-to-measure operation variables and initial fiber characteristics to the morphological features of mechanically obtained LCMNFs. The calibration dataset was constructed using data from Pine pulps described in an earlier work of this group [1] including just 15 samples that had undergone thermomechanical, kraft, and bleached kraft treatments. The selection of input variables of the fibrillation process was carried out thoroughly, combined with the interpretation of the behavior of the actual process conditions, allowing us to identify that the aspect ratio could be properly described by four main inputs: cellulose contents, applied energy, the mean fiber length and the mean diameter of the pre-treated pulps. The neural model based on these 4 inputs and 4 neurons in the hidden layer showed excellent correlation with the dataset used in the calibration (R=0.9993), validation (R=0.9989), and testing (R=0.9984) stages. As further proof of the validity of this ANN model, additional tests were performed for different species, including samples of spruce BTMP and also of non-wood species (hemp and sisal). The neural network model provided excellent predictions of aspect ratio for hemp samples, and adequate predictions for spruce BTMP and (to a greater extent) for sisal fibers, which encourages the use of the neural network approach to the modeling of the fibrillation process during the mechanical production of micro-nanofiber materials from different sources.

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Formation of hydrogels by extraction and acid hydrolysis of ivory nut endospermic nanocellulose

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The ivory nut is a peculiar seed obtained from a group of palm trees of the *Arecaceae* family, which includes three genera native to South America: *Phytelephas*, *Aphandra*, and *Ammandra*. Vegetable ivory has been economically exploited for centuries in Ecuador, Colombia, Peru, Panama, Brazil, and Bolivia due to its usefulness for manufacturing a range of artifacts, such as buttons and jewels for the fashion industry. With a view to the valorization of the residues from this industry, this work presents a methodology for the fractionation of the seed endosperm of *Phytelephas aequatorialis* Spruce into its most important components: mannan, cellulose, and fatty acids. Given that the ivory nut endosperm does not contain lignin, its fractionation protocol was designed to include the organic extraction of fatty acids, the alkaline dissolution and regeneration of mannans, and the acid hydrolysis and functionalization of cellulose. In particular, various sets of experimental parameters (temperature, sulfuric acid concentration, and hydrolysis time) were tested for their ability to yield stable nanocellulose hydrogels after ultrasonication. The most stable gel (1% solid content) was obtained after 4-h hydrolysis at 30° with 8 M H_2SO_4 of the extracted cellulosic fraction. The described protocol offers a way to valorize the endospermic cellulose residue of ivory nuts after mannan extraction by preparing nanocellulose-based hydrogels as a potential material for further utilization in various industrial applications.

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Self-assembly of asymmetric and symmetric end-grafted cellulose nanocrystals

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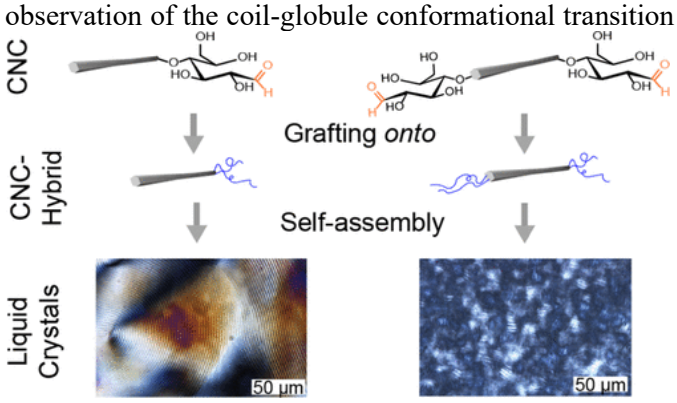
Cellulose nanocrystals (CNCs) are intriguing nanomaterials, not only due to their outstanding thermomechanical properties but also by their self-assembly into chiral liquid crystal (LC) phases [1]. Such chiral LC phases of CNCs have been observed primarily in aqueous suspensions above a critical concentration, at which mesophases with a "fingerprint" texture, associated with their chiral nematic pitch, begin to appear. The CNCs have a right-handed twist along their longitudinal axis, which favors the formation of left-handed LC phases. This makes CNCs an especially convenient model system to investigate chirality transfer across different length scales. Moreover, chiral assemblies of a variety of colloids have contributed to recent technological developments in heterogeneous enantioselective catalysts, chiral plasmonics, separation/sorption media, and chiral sensing, among others [2].

Among the external factors that can be used to manipulate the chiral nematic pitch of CNCs, such as ionic strength, ultrasound, *etc.*, reducing end group (REG) modification of different CNC allomorphs remains less explored. The REGs on CNCs extracted from cellulose I (CNC-I) allomorphs are exclusively located at one end of the crystallite, whereas CNCs extracted from cellulose II (CNC-II) allomorphs feature REGs at both ends of the crystallite, such that grafting polymers onto the REGs affords asymmetric and symmetric end-grafted CNCs, respectively. In this work, a neutral hydrophilic polymer, poly[2-(2-(2-methoxy ethoxy)ethoxy)ethylacrylate] ($POEG_3A$), was grafted onto the REGs of two different CNC allomorphs via reductive amination. The grafting of $POEG_3A$ onto the CNCs was evidenced by Fourier transform infrared (FTIR) spectroscopy, atomic force microscopy (AFM), and the observation of the coil-globule conformational transition of the grafted $POEG_3A$ chains. Furthermore, we investigated the self-assembly of end-tethered CNC-hybrids to discover the formation of chiral nematic phases observable by polarized optical microscopy. We hypothesize that the introduction of $POEG_3A$ to the REGs of CNC allomorphs does not disturb the surface of the CNCs along the rods, allowing the modified CNCs to effectively pack and form helicoidal assemblies despite the presence of the end-grafted polymers.



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Production and application of chemically modified nanocellulose: From the laboratory to a pilot plant scale

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The reinforcement of different materials with nanocellulose fibers (CNF) is a very interesting alternative since small proportions of CNF make it possible to substantially increase their mechanical properties. However, a fundamental requirement for this reinforcement is that the CNFs are distributed homogeneously. If this does not happen, fiber agglomeration will weaken the material considerably.

At the Technological Development Unit (UDT) of the Universidad de Concepción, Chile, we developed chemically modified CNFs, substituting up to 10% of the hydroxyl groups of the cellulosic chain with acetyl groups. Our acetylated CNFs disperse easily in various hydrophilic and hydrophobic media, and stay stable in time, without reagglomeration. The reinforcement of urea formaldehyde adhesives and PLA plastics show promising results.

Currently, we are upscaling the technology to a pilot level. The main challenge is not only to produce acetylated CNF with the desired characteristics but also to conceive a process that makes it possible to recover and recycle the acetic acid in a simple way, with low energy requirements.

Nanocellulose applications (Friday 1st July 2022)

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Novel sustainable developments in lignocellulose-based electronics, diagnostics and energy storage devices

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The global digitalization of production chains and the daily life of the citizens is followed by an increase in the production of electronic waste rapidly, the amount of e-waste is expected to reach 74 Mt by 2030, almost doubled in just 16 years [1]. The global consumption of material resources is expected to more than double between 2015 and 2050. There is a growing need for sustainable and renewable solutions to avoid problems of overconsumption and fossil-based raw material usage. Our ambition is the implementation of bio-based materials as a new normal in printed and hybrid electronics, diagnostics, wearables, optics, and energy storage devices. Simultaneously activities are going to develop green digital components to enable even more sustainable electronic systems. Novel lignocellulose-based materials offer a wide selection of substrate and structural material components including biobased, compostable, and recyclable materials depending on end-application needs. There is also a great potential to address new desired functionalities (*e.g.* antimicrobiality, material integrated sensoring, integrated lighting) through biobased matrix.

In this paper, the multidisciplinary approach of VTT combining the competences from printed and hybrid manufacturing with biomaterial development will be described. The structure-processing-performance interrelations will be described with examples of the use of wood-based nanocellulose, biobased thermoplastic polymers, and lignin extracts for different end-use applications. Eco-design approach and end-of-life methodologies for hybrid concepts will be discussed as they are a relevant part of sustainable future manufacturing and material development in future markets. This paper concludes the benefits of renewable material utilization and efficient manufacturing methods toward a carbon-neutral society in sectors like flexible electronics and energy storage devices.

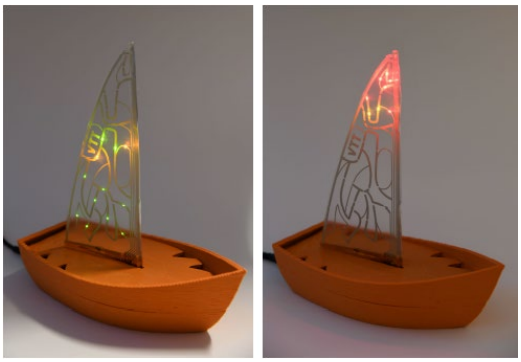

Figure 1. BIOBOAT − A sensor for a clean indoor air - manufactured by using bio-based materials

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Materials based on nanocellulose from agave bagasse with potential uses in energy

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In recent years, there has been a growing demand for electronic devices that are environmentally sustainable and there is a high interest in the application of these devices using nanocellulose as a basic component for their biodegradability, biocompatibility, resistance, and flexibility properties compared to other materials. The nanocellulose is the result of a chemical or mechanical modification of the cellulose, which allows obtaining a material that has at least one of its dimensions in the nanometric range. Cellulose is a linear biopolymer consisting of 100 to 14,000 glucose subunits linked by β-1,4 glycosidic bonds [1]. Although cellulose is the most abundant polymer on earth, there is a formidable demand for sustainability to use agroforestry waste to obtain cellulose and minimize the ecological footprint of the timber forest. To cope with this concern, agave bagasse has been used as raw material for the isolation of cellulose and nanocellulose [2,3]. Agave bagasse is abundant in the state of Jalisco, Mexico, because is a residual of major relevance to the agro-industries associated with alcoholic beverages of tequila. The objective of this research is to show various potential energy applications of agave bagasse nanocellulose. One of the applications is as a triboelectric generator (TENG), which is one of the emerging technologies that can take advantage of the mechanical energy dispersed in the environment to convert it into electricity [4]. The other application is to prepare electroconductive films based on nanocellulose doped with TIO_2 and reduced graphene oxide (RGO). Although the nanocellulose is not an electrical conductor which is essential in an electronic device, modifications have been made through chemical or physical processes, using materials such as conductive polymers or metal nanoparticles thus allowing the continuous flow of an electric current thanks to dopants and resistance and flexibility on the part of the nanocellulose. The material obtained was characterized by different techniques such as IR spectroscopy, SEM microscopy, X-ray diffraction, and its electrical capacity was tested with the four-point probe method and a dynamometer power supply. The results showed that the doped nanocellulose films had good interaction thanks to the presence of hydroxyl groups of the nanocellulose and the TiO_2-RGO mixture generating strong mechanical properties and showing electrical conductivity. This work offers a wide possibility for the production of electro-conductive films, which can have potential applications in smart clothes, armaments, and electrical devices.

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Transfer Imprinting of Photonic Microparticle Array through Self-Assembled Nanocellulose 'Glue'

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Paper-derived photonic devices have been investigated as a sustainable and low-cost alternative for conventional optics while printing nanocellulose colloid offers great potential for designing patterned micro/nanostructures with efficient light management capabilities. Here we described a hierarchical photonic structure composed of polystyrene microspheres and cholesteric self-assembled nanocellulose, acting as a polarization-sensitive retroreflective coating and microlens array. Micropatterned photonic films are prepared by casting an aqueous nanocellulose suspension onto a monolayer of polystyrene microspheres substrate through evaporation-assisted transfer imprinting lithography, integrating a bulk cholesteric matrix and patterned surface. By directing light at the as-assembled polystyrene surface, an enhanced structural color develops from the circularly polarized light retroreflection. Whereas when light traveling across the photonic film, the transparent layer of polystyrene microspheres form into plano-convex microlens to converge the transmitted light into the focus plane and reduce centimeter-scale illuminated image into a high-fidelity miniaturized replica. This simple method, combining self-assembly with imprinting lithography, is expected to pave the way for designing custom-tailored optics with novel functions.

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Gellan gum-nanofibrillated cellulose based bioinks for 3d bioprinting applications

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Three-dimensional (3D) bioprinting is promoting a great advance in many biomedical fields, including disease research, and drug investigation, among others. This technique consists of the deposition of bio-inks (biomaterials and cells) in a previously defined special pattern in a layer-by-layer approach. Natural polymers, such as gellan gum (GG), are interesting for the development of bio-inks due to their gelling temperature, crosslinking mechanism, and biocompatibility [1]. Nonetheless, the mechanical properties of GG are poor, which limits its printability and structural stability. One strategy to overcome this limitation is the development of nanocomposite hydrogels, using for example nanofibrillated cellulose (NFC) [2]. Here we combined NFC with GG in four different NFC:GG mass proportions, namely 90:10, 80:20, 70:30, and 60:40. All obtained inks were non-cytotoxic to HaCaT cell line, printable, and showed a shear-thinning behavior and shear recovery properties making them feasible for extrusion bioprinting applications.

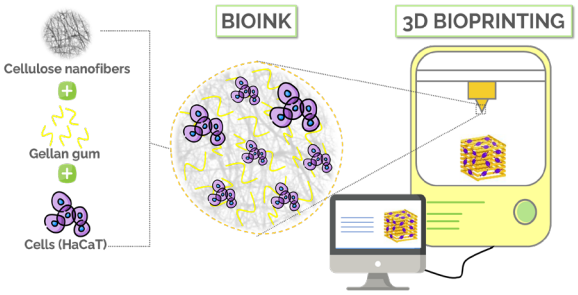

Figure 1. Schematic illustration of the production of NFC:GG bioinks for 3D-bioprinting.

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Bacterial Cellulose Network from Kombucha Fermentation reinforced Poly(methyl methacrylate) composites

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Kombucha tea is a healthy beverage produced by a consortium of bacteria and yeasts which has been commonly called tea fungus. The name is related to the ability of some of the bacteria in the consortium to produce a floating cellulose hydrogel that is used as a support for bacteria during the process [1]. The consumption of this tea has increased in the last years around the world due to its beneficial antioxidant, antimicrobial and digestive properties [2]. Nevertheless, the cellulose hydrogel produced during the tea fermentation is a by-product of the process and it's scarcely used, although the cellulose produced consists of a high-quality cellulose nanofiber network. Bacterial cellulose, such as the produced in Kombucha's fermentation, is a unique form of cellulose in nature with long fibres but nanoscale diameters building a 3D network that leads to exceptional properties. Those properties made it a potential reinforcement for polymers. Moreover, as a by-product, its use allows the revalorization of a residue in agreement with the objectives of climate change and sustainability, the sustainable development goals for 2030.

Nanocellulose reinforced polymer composites are still a challenging technology. The dispersion of nanoreinforcements is complex and the difficulty increases with polar reinforcements such as nanocellulose [3]. Thus, the use of the Kombucha cellulose (KBC) could represent an improvement for nanocomposite production due to its tridimensional structure with individualized nanofibers, providing the correct dispersion of the reinforcement in the nanocomposite. Nonetheless, to maintain the 3D network of KBC, it is necessary to avoid melt blending procedures. Generally, solvent exchanges and supercritical dryings are necessary [4]. These processes are expensive, complex, and usually, not environmentally friendly.

In the present work [5], KBC was used as reinforcement for poly(methyl methacrylate) (PMMA). PMMA is an amorphous polymer with high transparency, good mechanical properties, and chemical and heat resistance. In order to avoid commonly expensive compounding processes, PMMA was polymerized by water emulsion polymerization. The aqueous form of the dispersion of PMMA enhanced the impregnation of the KBC pellicles and maintained the KBC network during the process (Figure 1). Previously to the composite production, KBC was characterized. Kombucha cellulose showed high mechanical properties related to the nanoscale diameter of the fibres and its three-dimensional structure. Moreover, the thermal stability of the material was high due to the purity and crystallinity of KBC. When membranes were used as reinforcement a correct interaction between the fibres and the polymer was found. The stiffness of the nanocomposite films was doubled by the addition of 8% of KBC regarding the pure polymer. Tensile strength was slightly reduced, unexpectedly, but could be related to the strong and rigid KBC network reducing the flexibility of the nanocomposite and enhancing the crack propagation in the material, breaking the material in an earlier stage. This is in agreement with the poor tensile deformation and the brittle structure observed in the scanning electron microscope. The strengthening capability of the KBC nanocomposites was demonstrated by

micromechanical analysis. In addition, the thermomechanical and thermal analyses showed the shift of the glass transition and degradation temperature to higher values, indicating improved thermal stability in the nanocomposites by KBC presence.

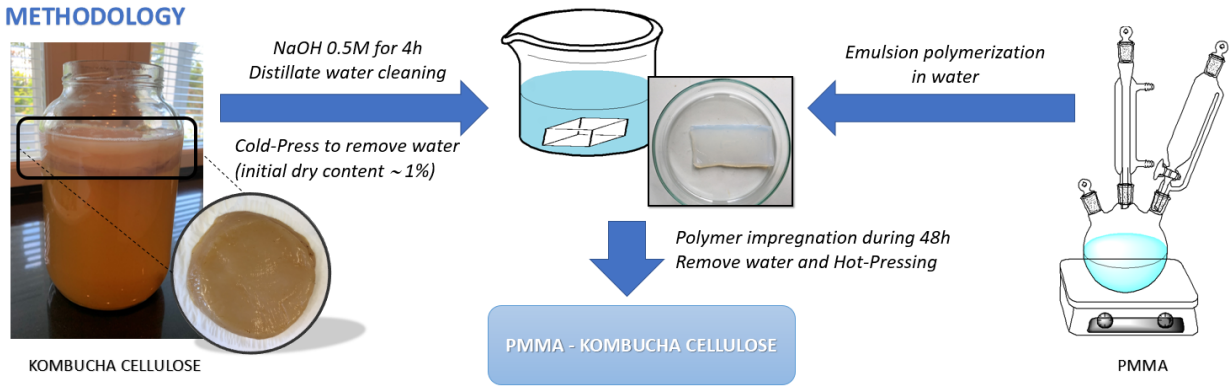

Figure 1. Schematic procedure of KBC reinforced PMMA nanocomposites

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Twin-screw extrusion for the production of nanocellulose-PVA gels with a high solid content: insight on the disintegration mechanism and properties of the resulting nanopapers

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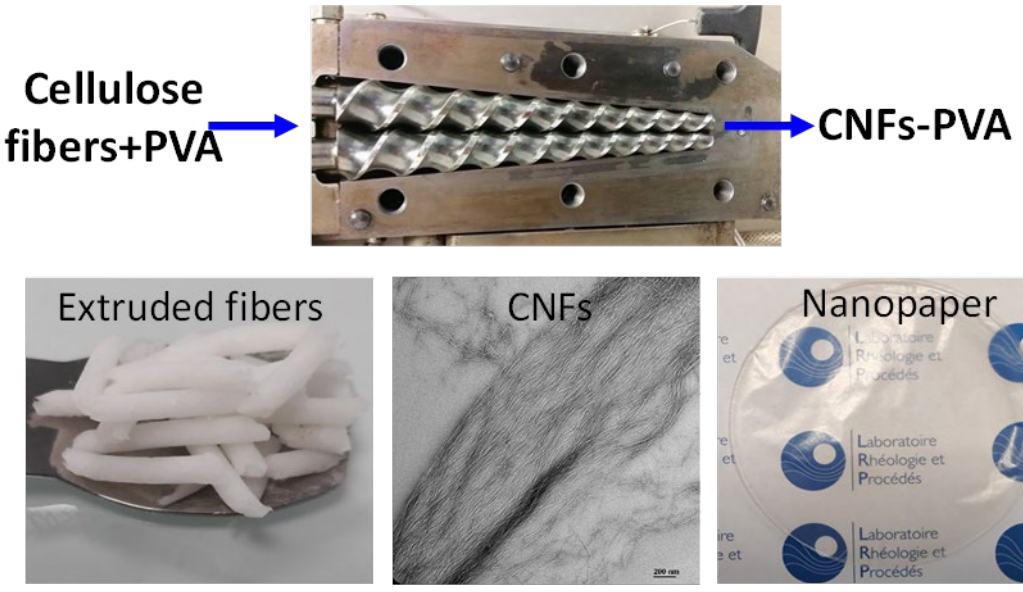
Twin-screw extrusion (TSE) is a recent strategy successfully used for the preparation of nanocelluloses with different functionalities at high solid contents (exceeding 10 wt%). However, many aspects concerning the mechanism of disintegration and the role of fiber pretreatment are yet to be elucidated. In this work, oxidized fibers were extruded in the presence of polyvinyl alcohol (PVA) to produce a high-consistency nanocellulose gel at 15 wt% solid content. The influence of the origin of the fibers (never-dried *vs.* dried pulps) and the oxidation treatment on the efficiency of fiber disintegration into nanocellulose was evaluated by porosity measurement based on dextran exclusion. It was also shown that combined TSE and rotor-stator dispersion or sonication homogenization during several minutes contributed to enhancing the defibrillation of the extruded fibers at the nanoscale. Beyond its aptitude to facilitate the extrusion process, the presence of PVA promoted the formation of nanocellulose-PVA gels ready for use in multiple applications, including paper coating or flexible packaging, additives, and nanopapers. Our results highlight the great potential of TSE to produce gels of nanocellulose dispersed in a water-soluble polymer with a high solid content and the method to significantly increase the nanoscale fraction in a much less energy-consuming manner.



Biopolymers, biofuels and enzyme-assisted technologies

(Friday 1st June 2022)

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Fermentation improvement to favour the production of bioethanol from eucalyptus bark

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Advanced biofuels are envisioned as readily available options to allow the transportation market to comply with greenhouse gas emissions reduction targets with no need for significant restructuring. However, the high production cost is one of the main challenges hindering large-scale bioethanol production from agro-industrial residues, such as *Eucalyptus globulus* bark [1].

Accordingly, two different approaches were followed in the present work. First, urea was used as an inexpensive nitrogen source [2], and then other commercially available nutrients were also tested, replacing the traditional and costly ingredients, such as yeast extract and peptone [3]. These assays were carried out at the Erlenmeyer scale using Ethanol Red® commercial strain. Second, the spent yeast, one of the main by-products of the fermentation process, was evaluated as inoculum in successive fermentations. This method not only decreased the time and costs associated with pre-inoculum and inoculum preparation but also could lead to microbial cells with higher tolerance to the stressful fermentation conditions [4,5]. For that purpose, at the end of a bioreactor assay, biomass was collected and separated by centrifugation from the fermentation broth [6], and finally transferred to the new consecutive fermentations at flask assays.

Results showed a decrease in bioethanol productivity when urea was used. However, despite being slightly lower than usual, good performance was attained by combining urea with less concentrated yeast extract. Promising results were achieved with other low-cost and market-ready available nutrients. Concerning the use of spent yeast, its use as inoculum in successive fermentations was well accomplished. Overall, this work suggests the potential of these two approaches, although an economic analysis will be crucial to determine the cost-benefit of each alternative.

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Acknowledgements

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Sustainable solvent extraction of inhibitors in the bioethanol producction from steam exploded eucalyptus globulus

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Concerning current human development, the depletion of natural resources, and the need to seek environmental and energy sustainability, the production of bioethanol from lignocellulosic biomass has attracted great attention. One of the key challenges facing lignocellulosic bioethanol production in a biochemical way is the disposal of degradation compounds generated during the thermochemical pretreatments of the biomass. Among them, phenolic compounds produce an inhibitory effect on both hydrolytic enzymes and fermenting microorganisms, decreasing ethanol production [1]. To overcome inhibitory effects and maximize productivity, inhibitors extraction with sustainable solvents may be a potential way not only to improve enzymatic convertibility but also to obtain antioxidant extracts [2].

This work proposes the evaluation of inhibitors extraction using different solvents in two different parts of the bioethanol production from steam-exploded eucalypt (*Eucalyptus globulus*). On one side, the liquid fraction (hydrolyzed) obtained after the steam explosion and subsequent enzymatic hydrolysis was subjected to liquid-liquid extraction (LLE) before bioethanol fermentation. On the other side, the pretreated material obtained after the steam explosion was subjected to a solid-liquid extraction (SLE) before the enzymatic hydrolysis to increase both the sugar production and, consequently the bioethanol yields. Two types of sustainable solvents, 2-methyltetrahydrofuran (2-MeTHF) as a bio-based solvent and a eutectic solvent based on menthol and octanoic acid (Mth:Oct) were investigated as extractive agents, in comparison to the use of the conventional solvent ethylacetate (EA). The extraction processes were carried out under pre-optimized conditions by magnetic stirring for the hydrolyzed and by orbital shaker or microwave-assisted extraction for the pretreated material. The total content of phenolic compounds, reducing sugars and antioxidant activity of the extracts were determined. Moreover, the sugars and ethanol production during enzymatic hydrolysis and fermentation, respectively, were also evaluated.

The inhibitors extraction results were promising, as solvents tested were able to extract a higher proportion of phenolic compounds than sugars, improving both enzymatic hydrolysis and fermentation process. In addition, the sustainable solvent extractions applied in this study allowed the recovery of phenolic compounds with antioxidant capacity, offering revalorisation options and additional value to a biorefinery. These results have important implications for competitive and sustainable biofuel production.

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Upgrading Enzymatic Hydrolysis Residue from Biochemical Conversion of Softwood Using GVL

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Global energy demand is increasing rapidly and the use of fossil energy sources is associated with sustainability problems. Hence, renewable energy resources attract a great deal of attention. Bioethanol, the most widely used liquid biofuel, is employed in various blends. Due to restrictions concerning the use of feedstocks based on starch and sugar, cellulosic ethanol, i.e., ethanol produced from lignocellulosic materials, has become highly relevant. However, the production of cellulosic ethanol from lignocellulose using biochemical conversion generates huge amounts of residue. The enzymatic hydrolysis residue (EHR) is the major by-product of these plants. EHR is the solid material remaining after the saccharification of polysaccharides, and lignin is its main constituent. γ-Valerolactone (GVL) is a green solvent that has shown high potential for lignin solubilization [1]. In this work, GVL was used to solubilize the lignin portion of EHR, and water was applied as an anti-solvent to precipitate the solubilized lignin from the treatment liquor.

EHR from the Biorefinery Demo Plant was provided by SEKAB E-Technology AB (Örnsköldsvik, Sweden). The compositional analysis revealed that the EHR contained 54% (w/w) lignin, 43% (w/w) cellulose, and 4% (w/w) hemicelluloses. EHR was treated with GVL/water mixture at different liquid-to-solid ratios (LSR) and temperatures. After the treatment, the solid and liquid portions were separated using vacuum filtration. For precipitating lignin, an adequate volume of water, as an anti-solvent, was added to the liquid portion, and the mixture was left to stand at 5°C overnight. After that, the supernatant was poured off, and the precipitated lignin was washed with hot water. The obtained lignin was dried at room temperature and characterized using pyrolysis-gas chromatography/mass spectroscopy (Py-GC/MS), Fourier-transform infrared (FTIR) spectroscopy, heteronuclear single-quantum coherence nuclear magnetic resonance (HSQC NMR) spectroscopy, high-performance size-exclusion chromatography (HPSEC) and compositional analysis.

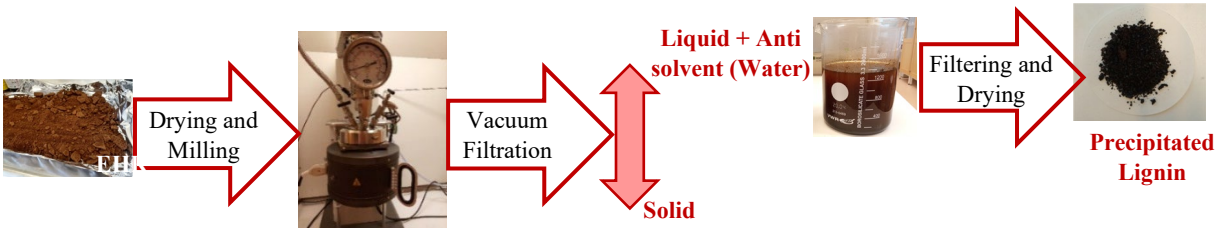

Figure 1. Simplified representation of the process

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Methanol purification, a-recovery+ case mönsterås

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ABSTRACT

Methanol is one commodity used for the synthesis of chemicals, such as MTBE, acetic acid, dimethyl ether, and formaldehyde. Methanol is used also as a transportation fuel alone or mixed with other fuels like gasoline. It is one of the reactants used for biodiesel production at transesterification reaction. By using purified methanol from the pulp mill side streams, 100 % fossil-free biodiesel can be produced.

Methanol is mainly formed during the sulphate cooking by alkali-catalyzed elimination of methanol from the 4-O-methylglucuronic acid residues in hemicellulose. Methanol yield is around 6-15 kg/ADT depending on the wood type. Cooking produces also organic sulphur compounds, as the sulphide- and hydrogen sulphide ions react with the lignin. A large amount of methanol formed during the cooking ends up in black liquor. Due to methanol's high volatility, it vaporizes together with water into the evaporator foul condensate.

Methanol is recovered at the foul condensate stripper and afterward can be liquefied from the stripper off-gases. Foul condensate contains also volatile sulphur compounds like H_2S, methyl mercaptan, and dimethyl sulfide, but also less volatile sulphur compounds, which will end up in methanol when treated in the stripper. The recovered methanol concentration is fairly high (>74 w-%), but as mentioned, it contains sulphur compounds normally over 5 w-%. Water, ethanol, acetone, nitrogen, and turpentine are the other main impurities. As such, the raw methanol is hardly transportable due to its heavy impurity content, thus it is burnt in the recovery boiler.

ANDRITZ has built and commissioned at Södra Cell, Sweden a 5000 t/a process for raw methanol purification. The production start-up and commissioning have been smooth, reaching its nameplate capacity and product purity >99.99 w-% faster than ever expected. The process has proven its capability of producing purified biomethanol. Process, which is the first in the world of its kind, is suitable for producing 100 % fossil-free fuel reducing significantly its end users' CO_2 footprint.

In the mentioned process, raw methanol is acidified with sulphuric acid to neutralize ammonia into a recovered ammonium sulphate solution. Acidification makes also the volatile sulphur compounds, like H_2S and methyl mercaptan, more volatile and easier to vaporize. The solubility of terpene compounds also reduces significantly, thus making the separation by decantation easier.

The next step uses patented liquid-liquid extraction technology to remove the remaining sulphur components by organic extractant. After the extraction, the extractant is regenerated by stripping the sulphur components away with steam. Extractant is circulated as regenerated to be used again in the extraction. In the last step, the methanol is purified in a series of distillation stages to remove acetone, ethanol, and water to finally recover the methanol as odorless purified methanol comprising the pure biomethanol grade purified methanol.

Keywords: Pulp and Paper, Methanol, Methanol purification, Biomethanol, Biodiese

Coatings (Friday 1st July 2022)

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New developments in paper coating with micro-/nanofibrillated cellulose for improving printing quality

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Within the current trends of papermaking, the use of micro-/nanofibrillated cellulose (M/NFCs) is raising increasing interest due to their excellent strength and barrier properties. In contrast, their bulk addition is still challenging for paper machines, due to their detrimental impact on drainage. Towards a satisfactory solution, recent works highlight paper coating as a suitable stage of the paper manufacturing process to use M/NFCs. In this regard, this study aims at evaluating the effect of M/NFCs, produced using different pretreatment methods (mechanical (m-MFCs), enzymatical (e-MFC), TEMPO-mediated oxidation (t-NFC), and cationic (c-NFC)) on paper printing properties.

M/NFCs were applied in combination with other coating components such as starch, cationic starch, a tri-block copolymer (P123), precipitated calcium carbonate (PCC), a sulfonated optical brightening agent (OBA), and alkyl ketene dimer. Different concentrations of M/NFCs were used in starch-based formulations and in combination with the aforementioned components to coat the base paper sheet. A Mathis laboratory roll coater was used, and printing quality was evaluated as reported elsewhere [1]. Briefly, all coated papers were printed using an inkjet printer; the gamut area was evaluated using ‘‘X-Rite Eye One XTreme UV Cut’’ spectrophotometer, and QEA PIAS-II spectrophotometer was used for optical density, print-through, and inter color bleed.

It was observed that the printing quality improved significantly when M/NFCs were used in combination with cationic starch and Pluronics. Among all M/NFCs, m-MFC and e-MFC were identified as the most effective to improve the gamut area and other key printing quality parameters, both from economic and technical points of view. Unlike m-MFC and e-MFC, c-NFC often reduced the whiteness of coated papers due to an observed quenching effect of OBA in presence of positive charges, and t-NFC is not also a good option since it involves an additional load of expensive chemical pre-treatment.

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Approaching Young's modulus changes during aqueous coating

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Currently, research on paper focuses on the reduction of grammages with constant mechanical characteristics and the functionalization of papers to obtain specific surface properties. These characteristics can be obtained by coating the paper surface with suitable aqueous coating color. The quality of the coating depends on the triplet: paper/coating color/coating process. Here, an aqueous starch-based color is used with known rheology [1]. Nevertheless, when coating very lightweight papers, wrinkles may appear at the exit of the coating area. A coupling between water absorption on one side and buckling phenomena has to be studied. The water phase, from the coating color, goes into the fiber network, causing runnability issues [2] and a reduction in mechanical properties, especially Young's modulus *E*. The objective of this work is to estimate the evolution of *E*, via a tensile tangent modulus E_{xx}, as a function of the quantity of water contained in the paper.

The technique used is the Cobb method (ISO 535). A fitting with least squares regression method is performed considering that the studied system is linear, first or second order, and responds to a Heaviside step function. Table 1 gives the parameters from the fitting between Cobb experimental data and the data from the least square method. It shows that the first-order model gives a 1:1 correspondence between modeled and experimental values. However, there is a lack of information between 0 and 12 g_{water}/m^2_{paper} that hinders the correlation.

*Table 1: Parameters obtained from water absorption model (for parity plot: data model= **slope***data experimental)*

Model	K ($g_{water}.m^{-2}_{paper}$)	τ_1 (s)	τ_2 (s)	***Slope*** from parity plot	Parity plot R^2
First-order model	21.69	-	18.90	0.996	0.979
Second order model	21.02	<0.01	17.58	0.980	0.977

To evaluate what is happening in a short time, data are subjected to Darcy's law, Lucas-Washburn's model, coupling between these two models proposed by Cummins et al [3] and Gong-Sinton's model [4]. Other experimental methods are also tested: ultrasonic liquid penetration measurement (ULPM), electrical resistance measurement of paper, and measures of the wet expansion of paper under one-sided contact with water (WSD). Nonetheless for ULPM, the penetration phenomena must be known to interpret the results properly: the ultrasound curves slopes cannot be simply interpreted as water penetration speed. Moreover, the sample holder type can change the interpretation of the results (influence of entrapped air bubbles) [5]. The electrical resistance measurements are still under investigation. From WSD measurement, the evolution of the strain versus time and web tension is obtained. The stress-strain curve is determined for different contact times. Thus, E_{xx} can be obtained as a function of time. Finally, the evolution of E_{xx} versus the amount of water absorbed by the paper is plotted. It could be simulated to determine the process conditions that prevent wrinkles formation during coating.

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Electrospray Deposition of Cellulose Nanofibers on Paper: Overcoming the Limitations of Conventional Coating

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While the potential of cellulose nanofibers to enhance the mechanical and barrier properties of paper is well-known, there are many uncertainties when it comes to how to apply them [1]. In this work, we use not only bulk addition of micro-/nanofibers and bar coating with oxidized nanofibers, but also a combination thereof and, as a key element of novelty, electrospray deposition of nanofiber dispersions. Characterization involved testing the strength of uncoated and coated paper sheets, their resistance to airflow, their Bendtsen roughness, and their apparent density, plus visualizing their surface and cross-sections by scanning electron microscopy. As expected, bulk addition was enough to attain strengthening to a great extent, but this enhancement was limited to approximately 124%. Conveniently, the surface adds to the resulting sheets by bar coating achieved a drastic improvement of air resistance, but not in strength, and using high nanocellulose concentrations (3%) was both futile and technically unfeasible. However, replacing this conventional process with electrospraying helped us overcome these apparent limitations, allowing for vast enhancements in both barrier and tensile properties. It is concluded that electrosprayed nanofibers, owing to their uniform deposition and favorable interactions, become an outstanding binder between fibers (and/or fines).

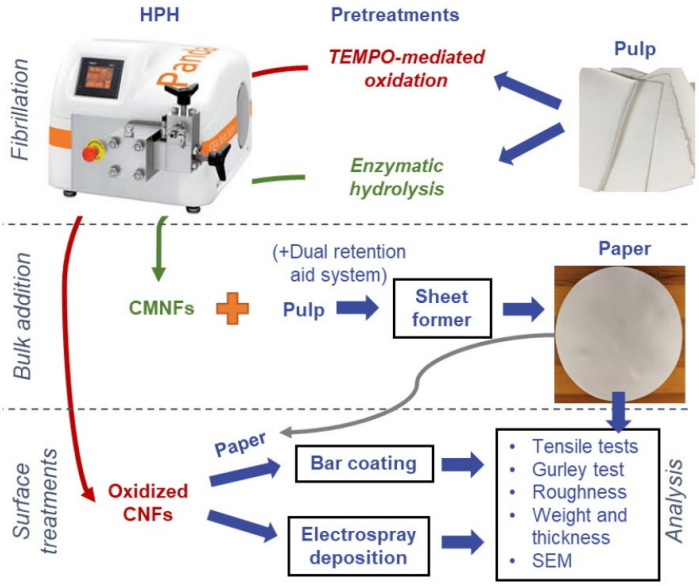

Figure 1. Diagram of the general experimental procedure, including fibrillation, sheet forming, bar coating, and electrospray deposition.

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Eco-sustainable hydrophobic and antimicrobial coatings for textiles

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The current Covid-19 pandemic has shaken both society and the scientific/medical world. It has led to a steady increase in concern and research. Mostly new research considerations related to medical treatment or vaccine development. However, a key point to consider is that of means of protection, mainly those related to high-performance textiles for applications such as face masks or other medical or protective textiles. Innovation is presented as the tool per excellence to generate new products and processes that offer solutions to the challenges posed. Among them, is the development of new coatings with improved properties for application in textiles. A large number of studies have been carried out in the field of protective materials such as the use of recyclable materials for masks, the development of antimicrobial and bioactive filters, the use of materials to improve oxygen saturation when masks are used or the development of masks with the capacity to self-purify thanks to UV light [1]. In the development of sanitizing textiles, the main innovations have been based either on the incorporation of an antimicrobial agent on the fiber or through the application of a surface finish coating, with the agent acting by diffusion or by contact [2]. Today, the concept of the bioeconomy has evolved through the development of bio-based products, but with high technological performance. In this context, cellulose nanoparticles, obtained from cellulose, the most abundant natural polymer, eco-sustainable and non-toxic [3], are considered raw materials for the development of eco-sustainable coatings with high technical performance. Thus, new eco-sustainable coatings based on modified cellulose micro/nanofibres have been obtained. In this way, the nanofibres have been endowed with antimicrobial, antiviral, and/or hydrophobic functionalities and have been applied to textiles. The results have shown increased contact angles (hydrophobia) of the samples and antimicrobial capabilities.

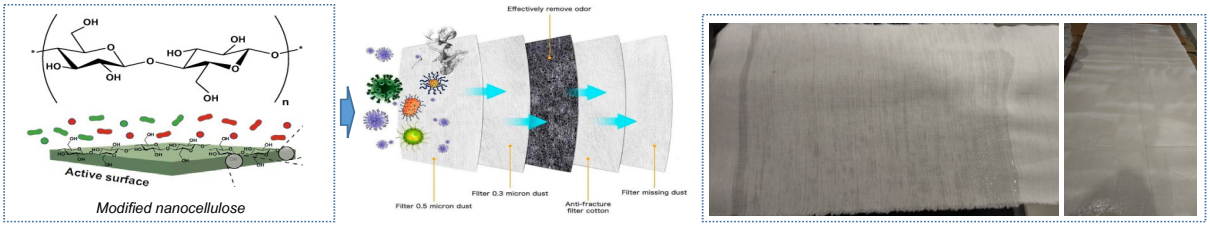

Figure 1. Nanocellulose on Eco-sustainable textiles

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Circular pacakging barriers for single-use cellulose fibre-based moulded products

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The use of bio-based and biodegradable or/and recycled materials **contribute** to **sustainable** material flows and helps to secure the availability of materials for future generations. Growing environmental awareness, the scarcity of fossil-based resources, and challenges related to plastic waste management have resulted in an increased interest in the packaging sector to find circular barrier solutions. Some biomolecular compounds derived from wood, agro-food, and seaweed biomass (nanocelluloses, hemicelluloses, pectins, alginates…) have shown a great potential to be used as grease and oxygen/air barrier solutions. However, biomolecules are quite sensitive to water (liquid and vapor) and therefore, their use is challenged when moisture/liquid, grease, water vapor, and oxygen resistance are simultaneously required.

Thus, new approaches/concepts are still needed to improve the barrier performance properties of bio-based materials and make them competitive with the traditionally used petroleum-based barriers. One of the big challenges to overcome here is to develop competitive bio-based solutions able to retain their biodegradability or be reused without producing deleterious effects on the environment and human health. To develop sustainable and competitive barrier solutions appropriate technologies and raw materials are required, as well as suitable characterization methods for evaluating performance, degradability, and/or recyclability to promote a safe introduction into the marketplace. Nevertheless, for wide commercial implementation-specific material target properties must be met while ensuring compliance with current regulatory requirements.

Raw material selection will be determined by end-user requirements, and they may be combined to fulfill the required target properties. In this study, we developed different bio-based dispersion barrier solutions with an enhanced moisture and grease barrier properties to be applied on single-use cellulose fiber-based molded packaging products for target applications related to fruit and vegetable storage, on-the-go foods, and biscuits and cakes.

Projects (Friday 1st July 2022)

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Knowledge development for the future use of nanocelluloses in a sustainable and competitive paper industry in Spain

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Nanocelluloses (NC) have unique properties due to their nanoscale size, fibril morphology, and large surface area that open many application areas in different industrial sectors. Moreover, the global market for NC is expected to grow at compounded annual growth rate (CAGR) of 21.3%, although Biobased Markets estimate the growth of 30%.

Despite the excellent properties of NC and the high interest shown by the research and industrial community, the NC market is still far from reaching its full potential at the industrial scale. Research, in the last decade, has been focused on the production of NC and their characterization, as well as on the development of knowledge and proof of concepts to improve the properties of the final products.

Despite so much fundamental research, little is known about the effectiveness (or side-effects) of the NC application on a larger scale as in paper and board production. This justifies the high number of non-successful industrial trials, which are related to the side effects of NC production and application. Therefore, more specific research is required to fulfill the industrial needs related to NC production process, control and optimization, the effects of NC in the papermaking process, and, finally the recyclability of NC-contained papers. These issues are related to process stability and competitiveness and prevent the implementation of NC on an industrial scale.

CON-FUTURO-ES is a three years project structured in 5 Work Packages (WP): WP1 focused on NC production monitoring, control and optimization, with different pre-treatments routes and fibrillation strategies; WP2 focused on how implementing NC in papermaking production processes; WP3 develops new NC coated papers for replacing single-use plastics, WP4 focused on closing the product life cycle with recyclability studies of NC-containing papers, and, finally, in WP5 technical guides and protocols for the industry will be elaborated, based on the results obtained at the four previous WPs.

The results of CON-FUTURO-ES will contribute to i) the development of environmentally friendly paper solutions, with the development of biodegradable and recyclable paper products replacing single-use plastics; ii) the improvement of recycled paper products' quality and fibers life, and iii) the replacement of non-biodegradable polymer coatings.

The impact on the Society will be the development of new bio-based products, consolidating the University-Industry cooperation to minimize the risk of innovation. The intended results of the project are therefore orientated towards a clear added value for the economy and the society contributing to Challenge 2 of the national research plan.

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Valorization and knowledge transfer for the industrial implementation of nanocellulose in paper manufacturing

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In the last decade, interest in the development of nanostructured lignocellulosic materials, as well as their application in various sectors, has experienced unprecedented growth. This interest, evidenced by the exponential increase in the number of scientific publications, is mainly due to the inherent characteristics of these materials, as well as their potential use for many applications (1). Among the various sectors in which NC presents opportunities, the paper sector is, without a doubt, the one that will take on the greatest role in the industrial deployment of this nanomaterial. In a conservative scenario, it is expected that in 2030 the total demand for NC will amount to 74,000 tons worldwide, of which approximately 60% will be demanded by the paper and cardboard sector (Future Markets Inc. 2020).

Today there are still some limitations of a technical and economic nature that are slowing down the transition from laboratory scale to industrial scale, both in terms of production and application (2). The UCM and UdG research teams have been working in the field of NCs since the beginning of the 2010-2020 decade, having jointly participated in various research projects. The project that is presented was born to respond to the demands of the paper industry through the transfer of the acquired know-how.

The main objective of the CONVALOR-NC project is the valorization and transfer of know-how in the production of cellulose nanofibers and their application in the paper sector. The project is based on the following pillars:

• Necessary development for the conversion of the research results into a value creation process.

• Demonstration on a semi-industrial scale by carrying out trials with end-users.

• Establish communication channels on nanocellulose with the society and with the industry.

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Sustainable and Alternative Fibers: A Revolutionary Initiative towards Implementing Non-wood Fibers for Consumer Goods

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The sustainable and alternative fibers initiative (SAFI) is a global effort aiming to create knowledge and foster technological developments that promote responsible and sustainable practices to produce fibers from non-wood sources (e.g., agricultural residues and fiber crops). This global effort is evaluating both technical (feedstock preparation, pulping technologies, bleaching, mechanical refining) and socioeconomic (supply chain, techno-economics, life cycle analysis, and consumer perception) aspects to demonstrate the potential of non-wood fibers to make bio-based products (e.g., market pulp, hygiene tissue products, packaging, textiles, and nonwoven), normally made of cellulose obtained from woody sources [1] [2] [3]. In this presentation, we are sharing our research approach and preliminary results.

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POSTER SESSIONS

Biocomposites

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Effect of chitosan or nanoclay addition on barrier properties of packaging paper coated with starch

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An alternative to the extensive use of plastic in food packaging could be their replacement with paper-based products. However, paper and paperboard are permeable to water, gases, and greases, preventing their use in perishables food packaging. Previous studies showed that these materials could acquire barrier properties through surface treatment with some biopolymers and nanomaterials. This study aims to evaluate barrier properties in packaging paper coated with blends of a commercial cationic starch with chitosan or montmorillonite nanoclay. Four different coating suspensions were prepared using 15% in total weight of starch with 2% and 4% in total weight of chitosan or nanoclay; in addition, a 15% starch coating was used as reference.

A 70 g/m^2 white kraft paper was coated with a 200 µm wet thickness of each coating suspension, using controlled coating equipment (model K10, RK Print-Coat Instruments Ltd., Herts, UK) with a micrometric adjustable blade. The wet coating was dried using a hot air stream and finally, the coated papers were smoothed out. Bendtsen and Gurley air permeance tests were performed and water vapor transmission rate and static and dynamic contact angles were determined. The grease barrier was evaluated by turpentine test and by surface repellency to castor oil.

Results obtained showed that the roughness and thickness of the initial paper increased after coating. All coatings increased air resistance at least 10 times; outstanding, air permeance decreased 400 times with the blend starch with 2% chitosan. The vapor transmission rate was not modified by any of the coatings. The 4% chitosan-coated papers revealed noticeable decreases in water absorption rates, while nanoclay-coated samples showed similar values to the base paper. In terms of grease barrier, none of the treatments reported improvements compared to the control sample of starch.

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Effect of fiber content on pcl-based composites for multi-material 3D-printed structures

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In its early stages, 3D printing was limited to a short range of filaments in terms of materials (mainly ABS, PLA, and PVA). However, in recent years, other materials have been developed, including neat matrices and composites. This wide range of filaments, together with the research related to materials development for Fused Deposition Modelling (FDM), has pushed the development of objects designed to be printed with different materials in different sections, also called multi-material 3D-printed objects.

Although there are several examples of multi-material structures, there is further research needed on improving the interface between the materials, as they tend to be weaker than the materials themselves. This is usually caused by a low affinity between the selected polymer matrices, which could be easily solved by taking the advantage of the differences that fiber content on composites may impart on the resulting properties of the material while keeping chemical affinity, as they have a common matrix.

The present work aims at elucidating the suitability of fiber-reinforced polycaprolactone (PCL) composites at different reinforcement content to obtain multi-material-like structures with an improved interface. To achieve this objective, a commercially available bleached kraft eucalyptus fiber was selected and compounded with PCL at different fiber contents, ranging from 0 to 30 % by weight. The resulting materials were characterized in terms of mechanical, thermal, and rheological properties, and processed in a filament extruder to be later printed by FDM. In terms of printing, different strategies were adopted, such as gradually increasing the fiber content in the z-axis using several layers or, on the other hand, combining two significantly different materials (i.e. 0 and 30 wt% reinforced composites) to determine the different behavior of the printed object depending on where the stress was applied, as well as the interface region. The results showed a good printability of the obtained materials, as well as an improved adhesion between layers. In addition, the presence of fibers indicated that they can contribute to the anisotropy of the materials, exhibiting excellent mechanical properties.

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Effect of hot-pressing temperature on properties of fibreboards bonded with hydrolysis lignin and phenol-formaldehyde resin

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Increasing requirements for formaldehyde emissions from wood-based panels are becoming increasingly difficult to achieve with conventionally used resins [2]. That requires partial or complete replacement of this type of adhesives. The use of bio-based lignin binders is a possible solution to this problem. That would also lead to the recovery of significant amounts of waste lignin, which is currently used mainly for heat energy [1].

This report presents a study on the effect of hot-pressing temperature on the properties of eco-friendly fibreboards. The adhesives were 12% based on dry fibers, and the adhesive system was composed of 80% hydrolysis lignin and 20% phenol-formaldehyde resin. A modified hot-pressing regime with low initial pressure, subsequent high pressure, and final cooling was also used [3].

It has been found that after 170° C, the effect of hot-pressing temperature on the strength properties of the panels is insignificant. In comparison, the waterproof properties show a noticeable improvement by increasing the temperature to 200° C. That study shows that quality eco-friendly fiberboards with hydrolysis lignin as a primary binder can be produced by optimizing hot-pressing temperature.

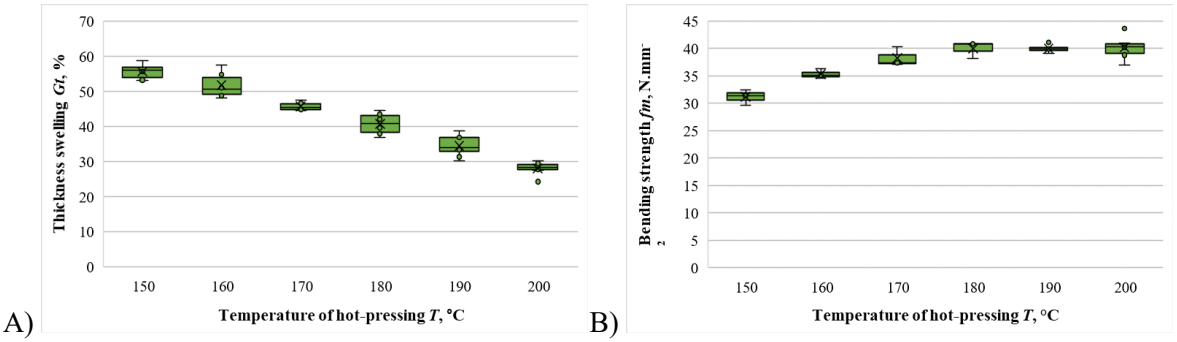

Figure 1. A) Thickness swelling; B) Bending strength

Acknowledgments

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Polyhydroxy-3-butyrate reinforced barley waste composites for agriculture purposes

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Introduction.

Plastics for agriculture are usually single-use plastics because they could not be recycled due to the high degradation produced by the environmental conditions. Thus, all these plastics used in agriculture contributes to the environmentally problematic. In addition, as an adequate and consciousness collection of them is done, the poor state of them at the end use due to the climatic conditions let to its presence in the environment in some forms. Nonetheless, the benefits of plastics use in agriculture has made them indispensable in the field. Therefrom, it is necessary to replace these materials for materials with sustainable ones.

Polyhydroxyalcanoates (PHA) are promising biopolymers with an increasing interesting in the industry as renewable materials. being polyhydroxy-3butyrate (PHB) the most representative [1]. Nonetheless, the mechanical and chemical stability of PHA, in long term applications, like the proposed in agriculture, is reduced due to its biogradability capacity. The preparation of composites materials of PHA reinforced with natural fibers could be a solution. Barley waste is a common by-product from agriculture in the France-Spain border. This waste is usually consumed as animal feed. However, it could be a potential reinforcement fiber for PHA and represents the revalorization of a residue.

In this work, an analysis of the behavior of PHB-barley reinforced composites under specific simulated environmental aging has been performed. Composites materials from 4 different fibres produced from barley waste were prepared, analyzed and used as reinforcement for PHB. The composites were characterized and then submitted to an accelerated climate aging test. The test simulated the weather conditions of a continental region and was carried out for 1, 2 and 4 weeks. Afterward, the samples were characterized and compared with neat PHB to understand the effect of fiber type in the stability of the samples.

Materials & methods

Composites materials were prepared by kinetic compounding using a Gelimat mixer. The mixer was fed with PHB and 0-30 wt% of Barley fibres (previously conditioned). The already prepared material was pelletized, dried and injection-molded to obtain bone-like samples for mechanical characterization.

The samples were submitted to environmental simulated aging using a Xenotest Alpha equipment, programmed according to ASTM D2565. After different exposition periods of time, the samples were characterized mechanically (tensile test), water uptake and surface morphology.

Results & discussion

An observation of the samples (optical microscopy) after aging is the loss of color of the samples (Figure 1A), becoming clearer a long with the exposition time. A loss of weight was also observed (gravimetrically) together with the darkening of the water of the tank used to supply humidity to the experiment. On the other side no changes were visually observed in the inner part of the material (Figure

1, right). This result is related with degradation process that PHB suffers due to the environmental conditions (radiation and humidity).

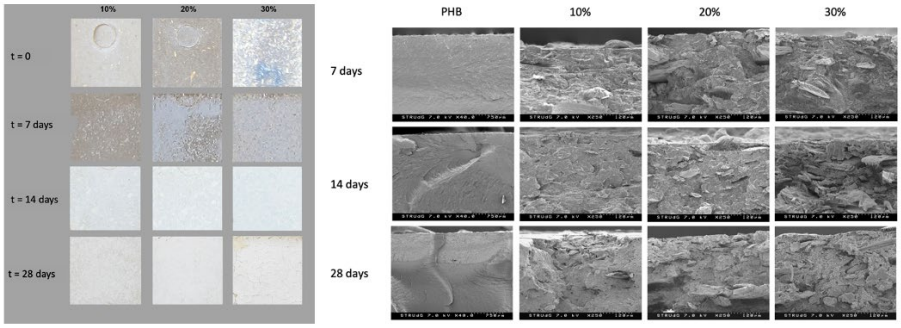

Figure 1. Left) Optical microscopy; right) SEM microscopy of samples of PHB reinforced with different contents of barley fibres previously defibrated.

The mechanical study revealed an important drop of ultimate tensile strength (UTS) (Figure 2, left) mainly related with the degradation process derived from the radiation and humidity [2]. Water uptake behavior study also informed about an increase of capacity to absorb water (Figure 2, right) derived from the creation of oxidized groups on the surface of samples increasing polarity on the surface of the material (higher water uptake).

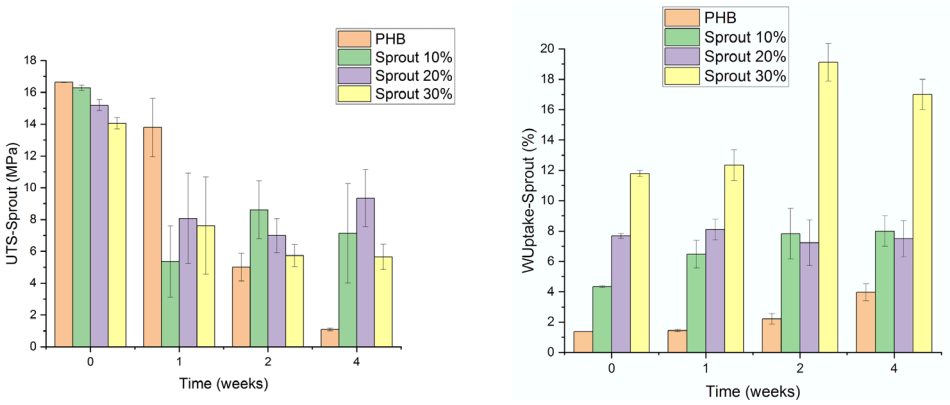

Figure 2. Evolution of the UTS (left) and the water uptake behaviour (right) of PHB composites.

Conclusions

The incorporation of fibres to PHB do not avoid degradation of the material although a slight decrease was observed. These kind of composites, structural during a period of time and later degraded can be a potential candidate to be used as agricultural plastics to be eliminated after working use directly in the field.

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Adsorbents derived from xylan hemicellulose with removal properties of pollutant metals

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Hemicelluloses are heteropolysaccharides composed of different sugar units. They are low molecular-weight biopolymers with a degree of polymerization from 80 to 200. Their chemical modification provides materials with different properties and uses, allowing the generation of products of greater value and utility [1]. The chemical modification of hemicellulose through the insertion of carboxyl, sulfonic, amide groups, etc., favours its hydrophilic nature and its ability to adsorb polluting ions [2]. This study aims to develop bioadsorbents, derived from hemicellulose xylan, that are capable of adsorbing copper(II), cadmium(II), and lead(II) ions under different experimental conditions. Specifically, previously extracted xylan (XYL) hemicellulose is chemically modified by inserting methacrylate groups (XYLMA) to incorporate vinyl groups into the polymeric structure that are useful for reacting with synthetic monomers, such as 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) to obtain hydrogels with different adsorption capacities for contaminating ions (see Figure 1). The hydrogels (H) were synthesized in different proportions, where HA3 and HA5 correspond to hydrogels with 30 and 50% m/m of XYLMA. The results show that all the synthesized hydrogels were capable of adsorbing contaminating ions with high adsorption efficiency during short periods. But those hydrogels with a higher content of XYLMA, a decrease in the swelling capacity in water and in the adsorption capacity of polluting ions is observed. HA3 and HA5 hydrogels have an adsorption capacity of 182.0 and 112.7 mg g-1 Cd(II), 66.2 and 42.8 mg g-1 Cu(II), 193.3 and 184.9 mg g-1 Pb(II) at 25°C, respectively. This result shows that modified XYL hemicelluloses can be employed as renewable adsorbents to remove Cu(II), Cd(II), and Pb(II) ions from aqueous solutions.

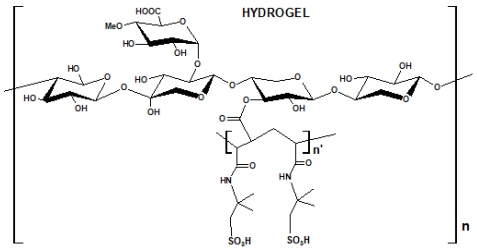

Figure 1. Xylan-derived adsorbent

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Feasibility study of injection planting pot from rice straw fiber

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Agriculture is one of the priority economic activities in Cambodia, which contributes about 21% to the GDP. Rice is regarded as the main staple crop, approximately 3.328 million hectares with a total production yield of around 11 million tons per year. Vegetables are an important part of a healthy diet, promoting human body growth and preventing illnesses related to heart, cancer, or digestion. Vegetable farming in Cambodia remains conventional and labor-intensive, but the situation is even worse as the labor in agriculture is reducing in particular adult groups, causing approximately 70% of daily fruit and vegetables to be imported from neighboring countries and others. The reduction of labor in agriculture due to the low production yield and profitability, compared to the jobs in industry and service. For a larger farm, the issue is lacking mechanization and supporting tools. To solve the issue, the government accepted and promoted farm mechanization improvement with conservation agriculture technology and system for sustainable intensification goals.

The promotion of small-scale mechanization may contribute toward a bigger impact on local vegetable production and increase productivity and profitability. Another problem encountered by seedlings vegetables in a plastic tray were damaged, thus biodegradable containers had been considered to substitute the plastic ones and for environmentally friendly. In this regard, rice straw fibers were studied in previous research for the possibility to make binderless fiberboard ought to be able to make a binderless planting pot.

The present work aims at injecting biocontainer for vegetable seedlings and cropping from rice straw fiber-reinforced poly lactic acid (PLA) composites at different ratios. To achieve this objective, a commercially available PLA was selected and compounded with rice straw at different fiber contents, ranging from 40 to 60 % by weight. The present work is expected to obtain an appropriate biodegradable planting pot usable for seedling crops and applies it with the no-till vegetable transplanter. The planting pot will be tested for its end-life, biodegradability, and performance with vegetable transplanter in Cambodia conditions using a conservation agriculture system and greenhouse cropping. The work will not only provide benefits to vegetable growers but also to rice producer farmers and other businesses.

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The use of agave tequilana weber nanocrystalline in reinforcement acrylic hidrogels

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Nanocrystalline cellulose (NCC) was prepared from Agave *tequilana Weber* blue variety via acid hydrolysis. The NCC was used in forming acrylic acid/acrylamide hydrogels (AA/AM), (80/20 w/w), crosslinked with N-N-methylene bisacrylamide (MBA) at addition levels of 1, 2, 4, and 8 wt% of the monomeric phase. The NCC was dosed at 0.1, 0.5, and 1.0 wt%. Two synthesis routes were used. In the first route, polymerization was performed immediately after mixing the components. In the second route, the mixture of the components was kept at 2 °C ± 1 °C for 24 h before the polymerization (thermal treatment). All the hydrogels were characterized by nuclear magnetic resonance (NMR), water absorption tests, scanning electron microscope (SEM) analysis, and rheology tests. The hydrogels that were subjected to the thermal treatment reached the equilibrium after approximately 72 h. The un-treated hydrogels reached the equilibrium after approximately 58 h. The thermally treated samples had a lower swelling degree and the swelling degree decreased as the crosslinking degree and the NCC concentration increased. The swelling kinetics followed the Schott's pseudo-second-order.

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From Traditional Use of Fique Fibers (Furcraea spp) to Novel Bionanocomposite for Wastewater Depuration Technologies

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The *Furcraea spp* plants, commonly known as fique plants, are endemic to Colombia and traditionally used to extract stiff fibers for crafts, cord, ropes, sacks, and packaging materials manufacture. Fique fibers are mainly cellulose, lignin, and hemicellulose. Previous studies in our laboratory have demonstrated that cellulose in fique fibers can act as a matrix for synthesizing transition metal oxides. Furthermore, supported nanoparticles (NPs) on the surface of the natural fibers have enormous potential to develop technologies for wastewater depuration. We describe here the fabrication of different bionanocomposites based on cellulosic fique fibers (FF) decorated with magnetite (Fe_3O_4) and manganese oxide (MnO_2) NPs. The materials FF/Fe_3O_4 and FF/MnO_2 bionanocomposites are used as a catalyst for the color removal (CR) of indigo carmine (IC) solutions. Cellulose in FF undergoes different treatments, which result in a heterogeneous and positively charged microstructure with channels and cavities acting as nanoreactors, facilitating size control, dispersion, and stabilization of the Fe_3O_4 and MnO_2 NPs via an ultrasonic-assisted co-precipitation method. The assembly of the FF/Fe_3O_4 and FF/MnO_2 bionanocomposites was monitored using FESEM, XPS, ATR-IR, XRD, and TGA. UV-vis spectroscopy was used to assess the bionanocomposite catalytic activity and cyclability on IC solutions CR. The FF/Fe_3O_4 bionanocomposite removed up to 90% of the color present in IC colored samples through Fenton-like reactions within 5 minutes for up to 10 cycles (CR up to 80%) with no effect on dye color removal efficiency. For another hand, FF/MnO_2 bionanocomposite, after 14 cycles of use, can discolor up to 90% of indigo carmine solutions without H_2O_2 addition. To the best of our knowledge, biocomposites synthesized here overcome the price-performance ratio of any previously reported fique nanocomposite applied in water treatment and enable an effective route to obtain novel cellulose-based materials for future technological applications in the degradation of dyes.

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Thermal stability of poly(lactic acid) and polyamide bioblends

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The thermal stability, as well as potential changes in degradation mechanisms of PLA in PLA/bio-based PA 10.10, were analyzed. In this case, a matrix of a rheological modified PLA by reactive extrusion was employed, adding 10-50% of biobased PA as the second phase. PLA/PA bioblends (with a predominantly biosourced PA10.10) were prepared by melt blending to overcome the advanced brittleness of PLA and also to improve its thermal stability in melt processes.

The temperature at which 5% of the mass is lost (T_5) increased from 315 to 321°C when increasing PA content from 10 to 50% (at a nominal heating rate of 10 K/min). On the other hand, the temperature at which 95% of the mass is lost (T_{95}) varied erratically in the range 455-540°C. Similar conclusions were obtained at the other heating rates employed in this study.

Empirical and theoretical solid-state mechanisms were tested to elucidate the best kinetic model: n-order, autocatalytic, random scission, F1, F2, F3, R1, R2, R3, D1, D2, and D3. Three different strategies were used for this goal: standardized conversion functions, IME (integral mean error) indexes, and y(α) master plots, which revealed that the most probable mechanism for the thermal degradation of PLA was random scission of macromolecular chains.

The kinetics of the thermal degradation was analyzed by using the general analytical equation (GAE) when the reaction mechanism is the random scission of macromolecular chains (as it was shown in this work):

$$ln\left[\beta\,\frac{-ln\left(1-\alpha^{1/2}\right)}{T^2\left(1-2\left(\frac{R\,T}{E}\right)+6\left(\frac{R\,T}{E}\right)^2\right)}\right]=ln\frac{A\,R}{E}-\frac{E}{R}\frac{1}{T}$$

The activation energies so obtained were: 154, 170, 204, 205, and 180 kJ/mol for bioblends containing 10, 20, 30, 40, and 50% of PA. These results indicated that activation energy increased when increasing PA content, thus showing the protecting effect of PA on PLA matrix (especially for PA content until 30-40%). Indeed, activation energy increased by 16 kJ/mol when PA content raised from 10 to 20% and it increased by 34 kJ/mol when PA content raised from 20 to 30%. The activation energy remained almost constant when increasing PA content from 30 to 40%. On the opposite, an activation energy decrease of 25 kJ/mol was observed when increasing PA content from 40 to 50%, the latter likely due to an inversion of phases, caused by a high content of PA. Therefore, the bioblend containing 30% of PLA showed an excellent thermal behavior against degradation. This result is following previous rheological and morphological analyses. Finally, PLA/PA bioblends with a content of 30-40% of PA present an interesting potential in the manufacture of cellulose/PLA composites and nanocomposites.

Keywords: PLA; PA; bioblend; thermal stability; kinetic models; reaction mechanisms; random scission of macromolecular chains.

Coatings

Natural polyelectrolyte complexes with micro/nano fibrillated cellulose for improving paper barrier properties

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Paper-based materials are often considered for food packaging applications due to their biocompatibility, recyclability, and excellent mechanical properties. Even though, coating processes are necessary to improve their oxygen and water vapor barrier properties. In this regard, xylan (Xyl) has received great attention due to its excellent oxygen barrier properties. It is also an abundant natural and non-food-based polymer that has the potential to replace current petroleum-based coatings.

In this work, polyelectrolyte complexes (PECs) of Xyl and chitosan (Ch) were prepared. The effect of different amounts of micro/nano fibrillated cellulose (MNFC) (0, 5; 10; 15; 20% wt.) on the rheological behaviors of the PECs colloidal suspension, as well as in the properties of the coated paper, were studied.

Xyl was obtained by alkaline extraction (NaOH 150%/wood) in a 50 L rotary reactor for 120 min at 90°C and then, it was precipitated using ethanol in a 1:1 v/v liquor: ethanol ratio. MNFC was obtained from commercial dissolving pulp. The fibers were first mechanically refined and chemically treated with oxalic acid (50% w/w) at 90°C for 60 min, as described elsewhere [1]. Finally, MNFC were obtained by 10 passes at 300 bar in a high-pressure homogenizer at 1% wt. The nanofibrillation yield was 65.4% and the MNFC acid groups surface, determined by polyelectrolyte titration at pH 8.0, was 86.9 µeq/g. The average diameter of the nanofibers measured by AFM was 20 ± 4 nm.

Coating suspensions (PECs-MNFC) were prepared by adding MNFC to the Ch solution, followed by the addition of Xyl solution, under continuous stirring at pH 5.0. The total solid of the coating formulation was 2.5% and the mass ratio of PECs used was 70:30 Xyl: Ch. The shear viscosity of the coating suspensions increased when MNFC was increased from 0 to 20 wt%. Besides, the oscillatory frequency sweep test showed higher elastic modulus (G´) when MNFC content was increased. Thus, a stronger network is formed indicating an increase in the number of contact points that reduce the mobility of the PECs, resulting in a higher viscosity and elasticity system.

A commercial paper (basis weight of 80 g/m^2) was used as base paper (BP) for coatings, using a Mathis laboratory coater coupled with a pre-drying infrared system. The thickness of the coatings ranged between 15.50 and 19.60 µm. The Gurley air permeability test showed 0 mL/min for all the coated papers. On the other hand, the contact angle with water increased from 84.7 to 92.9 when increasing the MNFC content from 0 to 20 wt%. Results showed that these coatings formulations have the potential to increase the barrier properties of paper for food packaging applications.

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Structural characteristics of cellulose nanocrystals from kraft pulp for application in the wood industry

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Cellulose from eucalyptus kraft pulp was hydrolyzed using sulfuric acid under different thermophysical conditions. As a result, the effect of the reaction conditions and the structural characteristics of the cellulose nanocrystals (CNCs) obtained were analyzed. The CNCs indicated a morphology described as individualized rod-like particles [1-2], with average diameters less than 50 nm and with a different size distribution. Zeta potential values (around -25 Mv) indicated that the CNC suspensions are stable, with no tendency to agglomerate and precipitate [3-4]. These features allow direct CNC applications in wood. One of the main difficulties in wood impregnation is the disruption of any material into the wood caused by plugging of the pits in wood fibers. By presenting CNC sizes of 50 nm, in addition to its stable dispersion in a solution, it will allow an adequate penetration without obstruction in the wood.

In the analysis of CNCs characteristics, significant Pearson correlations were established between CNCs crystallinity, CNCs yield, and crystallites interplanar distance ($\Delta d/d$). Thermogravimetric (DTG) profiles showed two stages of CNCs degradation, where the second stage of CNCs degradation showed a significant correlation with the sulfur content of CNCs. In our analysis, the crystallographic parameters showed a correlation with the mechanical behavior of CNCs, as the potential variation between crystal plane spacings is related to the stress and strain present in the crystallites of CNCs.

This study provides new knowledge about CNCs, improving the information for CNC-based industries and the processability of CNCs for the development of new materials, specifically oriented to the application in the forestry and wood industry.

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Paper coatings based on biopolymers for Single-Use Plastics (SUPs) replacement

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According to the European Union (EU), 80% of the sea litter is plastic and 70% of it belongs to single-use plastics (SUPs) [1]. Some examples of these SUPs are food packaging, plates, plastic cutlery, cotton swabs… In addition, 40% of the plastic demand in Europe is for food packaging fabrication, which is the most pollutant SUP generating the biggest environmental problems (Figure 1).

Due to the broad use of SUPs and the inevitable accumulation of them in our ecosystem, this research considers the possibility of creating a paper coating based on starch to substitute the food wrapper plastic based on fossil fuels. The created films were prepared with modified acetylated starch, sorbitol, and fillers such as kaolin or micro-cellulose. The synthesized biodegradable films require barrier properties for the final application such as humidity, grease, and/or gas. The best water absorption and vapor barriers were achieved by increasing kaolin content to 12% according to the starch quantity. In the case of micro-cellulose, the best results for these barriers were achieved by increasing the amount of starch and micro-cellulose in the mixture. Good grease barrier properties were obtained using kaolin, but not with micro-cellulose. Overall, increasing kaolin and micro-cellulose in the formulations leads to better barrier properties and more resistant coatings for the possible packaging.

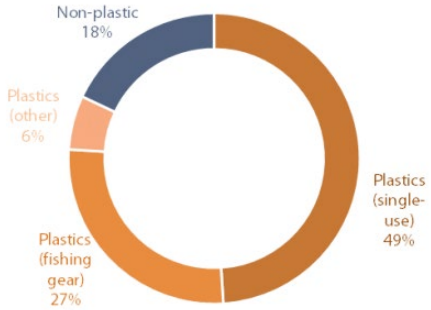

Figure 1. Marine litter found on EU beaches (2016) [2].

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Paper coated by bioplastic for single use plastics replacement

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The search for new materials has historically been linked to development, as new and better materials have been continuously sought to replace the previous ones to meet the needs of the moment. Within the materials, plastics or polymers have supposed a great revolution because they are very moldable, easy to process, and cheaper compared to metals and ceramics. Among the wide variety of applications in which polymers can be found, European Union (EU) has classified plastic cutlery, straws, balloon sticks, and cotton swabs as single-use plastics (SUPs). As the name suggests, these plastics are only used once, and in some cases, their use is only a matter of seconds. In addition to this, these plastics have other problems. On the one hand, they are synthesized from petroleum non-renewable sources and since it is running out, these plastics have an expiration date. On the other hand, once these materials are used they are thrown away and there is not an adequate way to dispose of them properly. Sometimes plastics are disposed into dumpers to degrade (taking thousands of years) or they can be incinerated, but carbon dioxide is emitted which contributes to an increase in the greenhouse effect. Moreover, in some cases, plastics are not disposed of properly and end up in the environment. Even more, 80% of the garbage found in the sea is plastic. To avoid all these issues, it is necessary to replace the SUPs with materials that have a natural origin and faster degradation. For this reason, bioplastics or biopolymers which can be obtained from plant biomass (such as corn starch) or animals (like chitosan from crab shells) are good candidates to replace typical plastics.

The main objective of this work is to produce paper covered with bioplastics to obtain good barrier properties to grease, moisture, water, and water vapor and substitute SUPs. To achieve this aim, starch will be used as bioplastic and inorganic fillers such as talc and calcium carbonate are added in different percentages (0, 3, 6, 9, and 12%). The obtained biofilms are characterized using COBB-60 test for quantifying the water permeability, the KITT test to measure grease resistance, water vapor resistance through the water vapor pressure (WVP) method, and changes in hydrophilicity/hydrophobicity by contact angle measurement. The results show a higher resistance to water at 6% of talc and $CaCO_3$, while the KITT test shows a trend between the number of fillers and grease tolerance achieving the maximum resistance by adding 12% fillers to biofilms. No tendency between fillers and permeability is observed using WVP. Finally, using contact angle, it has been determined that the surface of biofilms is more hydrophobic increasing filler percentage. Also, the coated paper needs to wrap the food without breaking, therefore a plasticizer such as D-sorbitol has been added to the bioplastics to check the breaking resistance of the material. This was checked using a scanning electron microscope (SEM), observing that by adding high amounts of filler and plasticizer-coated paper, it is easier to break not being able to use it for the application proposed.

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Energy and Environment

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Heat recovery system design for the paper machine at pulpa cuba paper factory

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The drying process consumes the largest percentage of steam and energy in a paper mill.

The drying section of the paper machine currently operates without a heat recovery system, part of which is operated and is disabled and with potential capacity for heat recovery, which affects the indicators of thermal efficiency of drying and heat recovery. industry.

This study aims to identify potential energy savings and opportunities for heat recovery in the paper machine by applying heat integration methods. The energy evaluation included the application of the methodology for the heat balance in the paper machine and the Pinch Analysis Method for the synthesis, analysis, and design of the network of heat exchangers in the drying of the paper with the use of HENSAD. and Aspen Energy Analyzer.

The design of a heat recovery system in the drying section achieves that in the heat exchange between the vegetable steam and the condensate of the cylinders it is possible to raise the temperature of the condensate in the boiler by 12.5 ^{o}C.

Determining potential annual savings of 93 t of fuel oil and 46 680 m^3 of water through Heat Integration allows for assessing an investment project feasibility for heat recovery in the paper factory.

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Prospective characterization of lignocellulosic biomasses to obtain biorefinery fractions of interest in asphalts

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There is a growing interest in the renewable use of ligocellulosic biomass to obtain chemicals and other products. One of these is asphalts (bituminous asphalt mixture), in which polyphenolic or fiber derivatives can be incorporated into bitumen (high viscosity liquids that come from petroleum [1]) with previous modifications to improve its thermomechanical behavior [2].

In this sense, there is a growing interest in the use of renewable raw materials for the formulation of "reactive" prepolymers that can be used to modify the bitumen [3] or the incorporation of derivatives of cellulosic fibers. This is a very complex field in which multiple raw materials (in this case: wheat straw, Populus Wood, and *Eucalyptus* wood) and polymers have been tested to incorporate bitumen and facilitate its emulsification and demulsification. Traditionally, these fiber and lignin have been obtained from biomass fractionation processes such as the kraft process (widely used in the pulp and paper industry).

So, the objective of this work was to apply an environmentally friendly fractionation process to obtain cellulose from wheat straw, Populus Wood, and *Eucalyptus; second, these cellulosic pulps were introduced into asphalts* (bituminous asphalt mixture) which get rheologically modified. Specifically, cellulose has been obtained from the kraft process.

Cellulosic pulp from these different biomasses was mixed with B50/70 bitumen at 6.5% by weight of cellulose at a temperature of 165ºC, when these mixtures were analyzed by fiber, oscillation, and flow analysis, it was found that certain properties of asphalt improved as the number of fibers per gram increased or other physical properties of the fibers improved. It has been observed that cellulose prevents the decantation of the asphalt engraving during transport. It also modifies rheology and viscosity. Cellulosic fibers can also occupy part of the bitumen gaps making the product (asphalt) “greener” and more sustainable. Eucalyptus pulp is the best, followed by Populus pulp and wheat straw pulp.

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Pyrolysis kinetic, thermodynamic and product analysis of different leguminous biomass by Kissinger-Akahira-Sunose and pyrolysis-gas chromatography-mass spectrometry

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Fast-growing leguminous are environmentally friendly options for energy production and high added-value compounds such as bio-oils, char, and biogas (methane, hydrogen, and others).

A series of experiments were designed through thermogravimetric analysis of *L. leucocephala, C. proliferus, P. alba,* and *S. sesban*, to determine their performance in thermochemical treatments with pyrolysis at low heating rates. The behavior of the TG and DTG curves (Figure 1) was studied, besides, the activation energies and the most prominent thermodynamic parameters were obtained by isoconversional KAS method.

In addition, gas samples were extracted through adsorption tubes to analyze the most important volatile organic compounds at the different peaks of degradation (hemicellulose and cellulose) using gas chromatography/mass spectrometry (Figure 2).

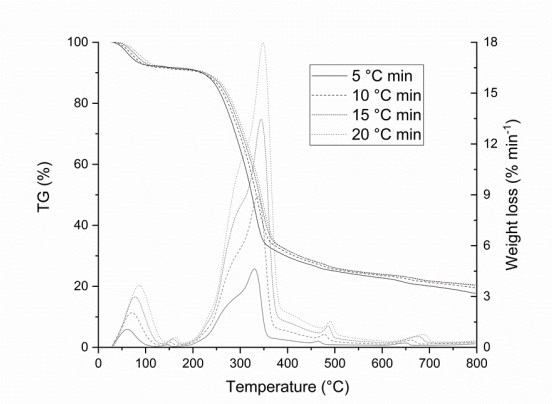

Figure 1. TGA and DTG analysis of *P. alba* at different heating rates (5, 10, 15, and 20 °C min^{-1})

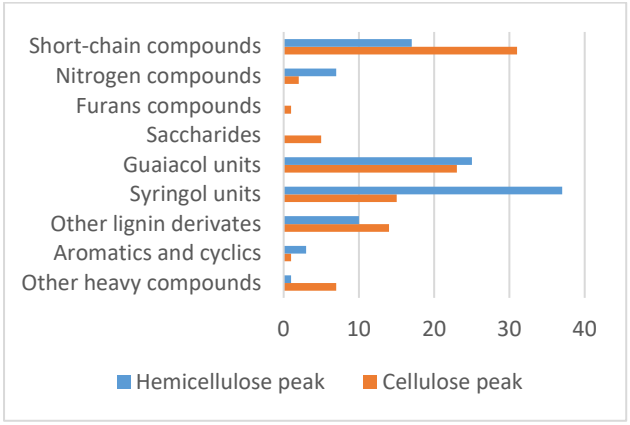

Figure 2. Comparison of the different main groups of compounds by Py-GC/MS of degradation of *L. leucocephala*

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Life Cycle Assessment of Softwood and Eucalyptus Cultivation for Pulp Production.

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The increase of greenhouse gasses (GHG) concentration in the atmosphere, thriving of algae and aquatic plants, acid rains, and biodiversity reduction are some of the multiple consequences related to the industrial activities of humanity. Agriculture, forestry, and land use are responsible for 22% of global GHG emissions (IPCC, 2019). Some of the products from these activities such as the biomass produced in managed and natural forests is vital to supply the pulp and paper industry. To develop a complete analysis of the sustainability of pulp-based products the establishment and management of the forests have to be assessed. Life cycle analysis (LCA) is a reliable methodology to evaluate the environmental burdens related to each one of the life stages of a product. In this work, the LCA methodology was used to evaluate the environmental impact of three significant sources of cellulose: Northern Softwood (British Columbia, Canada), Southern Softwood (Southeastern USA), and Eucalyptus (Brazil). The production of Northern softwood chips shows the most significant environmental impacts in each environmental category, despite the avoidance of fertilizer use. Trees in Canada are harvested mainly for the production of lumber. Therefore, wood chips are a co-product of the sawmill, carrying with them the environmental burdens of the upstream processes.

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Forest, Pulp and Paper

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Floristic composition of forest species for timber use in living fences

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The degradation of forest ecosystems is due to several factors among them: The growth of urban areas, forest fires, pests and diseases, natural disasters, and land-use change, among others. Deforestation in our country has caused the loss of that biological wealth that tropical forests have due to the elimination of natural habitats and forest species with a diversity of uses, highlighting timber.

The incorporation of forest species in agricultural systems is a good option, to increase wooded areas, within the agroforestry practices of greater acceptance among producers are the living fences, which have an ecological function by connecting natural ecosystems with agricultural activities; in addition to native species of multiple-use including timber. Therefore, the objective of this study was to identify forest species and the diversity of uses in rural areas. The work was carried out in the Ejido Tepames, in the state of Colima. 10 sampling sites of 2 x 500 m were drawn, on both sides of the road, for a total of (10,000 m^2). All individuals with DAP equal to or greater than 7.5 cm were registered.

The results indicate a total of 45 species (8 timber for sawmill); *Pithecellobium dulce* (Roxb.) Benth., presented 288 individuals, with an IVI value of 94.02 and a total volume of 177.57 m^3, dominating in all the variables evaluated. Of the timber species, *Enterolobium cyclocarpum* (Jacq.) Griseb., stands out with 18 individuals, with an IVI value of 21.79 and a volume of 40.31 m^3, demonstrating the importance of these species at the study site. It is concluded that the timber trees for sawmilling in live fences, represent ecological benefits, due to the connectivity between agricultural patches and forest masses, also highlight their economic value by obtaining various products such as poles, firewood, fruits, shade, and fodder in agricultural activities.

Figure 1. *Crescentia alata* Kunth fodder and medicinal use

Figure 2. *Tabebuia rosea* (Bertol.) DC., timber use

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Methodology to characterize the fiber orientation in zd of paper sheets: development and testing

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Variation of fiber orientation (FO) over the thickness direction (ZD) of paper, also known as FO two-sidedness, is the main cause behind the development of curl. This phenomenon can promote printer jams and cause other handling and conversion problems for end-users. The capability to characterize the FO in ZD of paper is therefore required for curl troubleshooting activities in the industry. Thus, the goal of this work is to develop an efficient methodology to determine the FO in ZD of paper sheets, for use in curl troubleshooting related tasks. The methodology should also be affordable and reproducible in industrial environments (namely in the site quality laboratories).

Typical methodologies used to determine FO in ZD are based on confocal laser scanning microscopy and sheet splitting techniques. The latter type is preferable, being cheaper and easier to implement. As a result, the methodology developed in this work was based on a sheet splitting procedure, consisting of three steps: i) sheet splitting, using a commercial hot laminator based technique; ii) multilayer image collection, applying a commercial flatbed scanner to acquire images of the obtained layers; iii) multilayer image analysis, employing an image analysis (IA) algorithm based on a gradient approach to estimate the FO distribution function for each layer.

The methodology was applied/tested on commercial and laboratory anisotropic sheets. Around 12 layers/sample were attained unscathed by the applied splitting technique. The splitting technique does not have a significant impact on the orientation angle (θ_{max}, the direction of maximum orientation of the FO distribution function) values of layers obtained for laboratory sheets. Higher sheet size is preferable (e.g., A4 size) for testing, to improve the precision of the measurement of the basis weight of the layers. The IA method presented a high internal consistency, accurately detecting offset angles introduced at the imaging step. The overall FO of the samples determined by the developed methodology was similar to the values obtained with the widely used tensile stiffness orientation (TSO) technique. In summary, an affordable and easy-to-implement methodology to characterize the paper FO in ZD was developed. This methodology can be efficiently applied in curl troubleshooting activities in the paper industry.

Acknowledgments

This work was carried out under the Project inpactus – innovative products and technologies from eucalyptus, Project N.º 21874 funded by Portugal 2020 through European Regional Development Fund (ERDF) in the frame of COMPETE 2020 nº246/AXIS II/2017.

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Development of fiber-based products with improved barrier, surface, and mechanical properties to be used as substitutes of single-use-plastics

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Due to the current environmental situation of the European Union, immersed in a "revolution" to minimize waste generation (urban and industrial), new directives and regulations have been approved to intensify the recycling of materials and contribute to a circular economy. Considering the severe problem of the large plastic production of single-use packaging and the management of this waste, it is clear that there will be several challenges in this field over the next years. NC-based products provide renewable, technical, and sustainable benefits to packaging materials, enhancing paper properties, and conferring them unconceivable characteristics with current products and technologies [1]. Knowledge of the performance of NC-based products for packaging applications, such as mechanical performance and barrier properties, will promote the potential substitution of single-use plastic products [2].

Food packaging materials must comply with some structural requirements, no permeation of oil and grease into the material, resistant to liquid water, and high oxygen and water vapor barrier. This work has as its main objective the development of NC-based coating formulations to obtain these properties. Coating formulations have been prepared using NC, sodium montmorillonite (MMT), AKD, ASA, PVA, Pullulan, among others. In the first phase, coating formulations have been developed to improve each of these properties individually. Subsequently, the combination of the resulting formulations has been studied to provide the paper with multi-functionality.

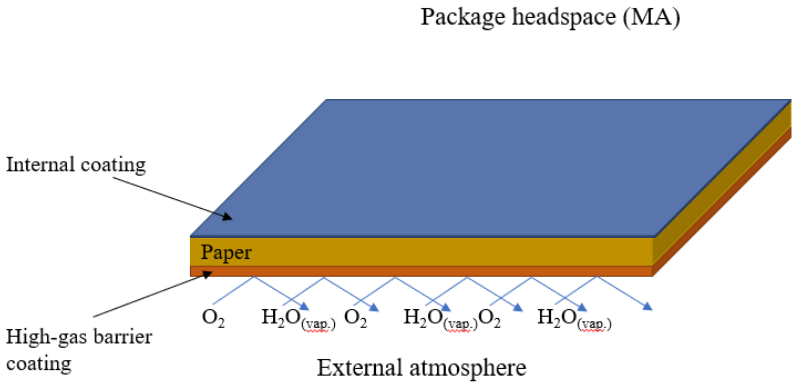

Figure 1. Scheme of paper coating mechanism

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Hydrogels fabricated from different cellulose sources and their performance for sorption purposes.

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Hydrogels were fabricated from dissolving grade and unbleached kraft pulps through the N-methylmorpholine N-oxide (NNMO) route. Bleached kraft pulps from *Eucalyptus globulus* and *E. nitens* were purified via cold caustic extraction (CCE) with 5% and 10% (w/v) NaOH and activated with dilute acid hydrolysis (samples coded as CCE5-H and CCE10-H, respectively) to produce dissolving grade pulp. The morphology, molecular and supramolecular structure of pulp, and sorption performance of the fabricated hydrogels were determined. A higher degree of crystallinity (CrI) was observed for cellulose in CCE10-H hydrogels. CCE10-H hydrogels also resulted in denser structures with lower swelling than CCE5-H hydrogels. The adsorption capacities of methylene blue (MB) particles were 36–51 mg/g for CCE5-H hydrogels and 27–33 mg/g for CCE10-H hydrogels. Hydrogels fabricated from *E. nitens* dissolving pulp exhibited higher capacities for adsorption of MB than hydrogels derived from *E. globulus* dissolving pulp, which was attributed to the lowest CrI and intrinsic viscosities of *E. nitens* pulps. Unbleached kraft pulps from *E. globulus* and *Pinus radiata* were subjected to activation through acid hydrolysis with 10% and 3% H_2SO_4, respectively (samples coded as E-H10 and P-H3, respectively) to achieve similar intrinsic viscosities (540 ml/g) for hydrogels production and further comparison.

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Effect of coating thickness with cellulosic nanofibers on barrier properties of packaging paper

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Today's society demands more sustainable packaging to replace plastic boxes and sacs widely used in transport and for sale perishables goods. Paper and cardboard packaging obtained from natural sources are recyclable and biodegradable, which could be an alternative to plastic containers. However, paper and cardboard show a clear competitive disadvantage compared to plastics, which is the lack of barrier properties to water, greases, and gases. They can acquire barrier properties and extended functional performance through coating with plastics or aluminum foil, among others. Nevertheless, it is mandatory to use friendly barrier coating materials such as certain biopolymers to obtain plastic-free packaging.

Several studies report that cellulose nanofibers (CNFs) films, produced by different methods, had high hydrophobicity and low water and air permeability. However, lamination of paper and board with CNFs films is economically unfeasible to obtain a competitive packaging. Therefore, this work studies the effect of coating with increasing amounts of three commercial CNFs on the barrier properties of a packaging paper

Mechanical (CM), TEMPO mediated oxidation (CT) and carboxymethylated (CC) CNFs were coated on commercially recycled flutings. Paper samples were coated using a K Control Coater (K202) and an adjustable blade micrometer to deposit the coating suspension (solid concentration of 2% in CNFs). The samples were dried against a highly polished surface at 85 ºC for 5 min. To increase the coat pick-up in CNFs coated samples, coating and drying steps were repeated to deposit five or ten layers of each CNFs. The barrier properties of the CNFs coating papers were evaluated in terms of air Gurley permeance, static and dynamic contact angle (wettability rate), water vapor transmission, and grease resistance and repellency.

CC coatings led to the lowest air permeance values, even at low coating weights. CT was also able to reduce air permeance at low coating weights, while a higher amount of CS had to be applied to obtain good results. For all CNFs, the static contact angles were noticeably decreased compared to the value of the base paper; and no influence of coat weight deposited was detected, except for CS. Only the papers coated with CC showed significant decreases in wetting rates; i.e., CC coatings significantly slowed down the absorption of water into the paper. In addition, CC-coated samples showed high resistance and repellency to grease, these results were achieved even with a low pick-up. None of the papers coated with the different CNFs showed changes in vapor transmission.

Antibacterial papers made from agave bagasse fiber doped with silver nanoparticles and chitosan

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In this research, the antibacterial properties of a paper prepared from agave bagasse cellulose fibers doped with silver nanoparticles and chitosan are studied. It is relevant to design materials with antibacterial properties since there are bacteria such as *Staphylococcus aureus, Staphylococcus epidermidis, Pseudomonas aeruginosa, Klebsiella pneumoniae, Proteus mirabilis, Serratia marcescens, and Escherichia coli*, among others, which are generated by infection in surgical wounds and this represents the largest percentage of all hospital infections [1]. It is important to note that these bacteria have developed resistance to a variety of antibiotics over time; therefore using an antibacterial material in wound care could help reduce infection [2]. Surgical wound infections can occur during surgery or the post-surgical period. The origin of the infecting microorganisms can come from the colonization sites of the patients themselves or the nosocomial environment and hospital personnel [1]. The antibacterial properties of silver nanoparticles are already known [3]. However, the combination of silver nanoparticles with cellulose and chitosan fibers has been little studied. Green synthesis of silver nanoparticles was performed and the spherical shape and small size between 20nm and large between 50nm were confirmed by UV-Vis spectroscopy. This was confirmed by TEM and additionally, in this investigation, the agave bagasse cellulose, chitosan, and the composite material were characterized by IR spectroscopy and mechanical tests. Cellulose and chitosan were extracted from agro-industrial residues such as agave bagasse [4] and shrimp shell [5] to enhance their applications. A decrease in the growth of the *Escherichia coli* bacteria was observed in the paper prepared from agave bagasse cellulose fibers doped with different concentrations and sizes of silver and chitosan nanoparticles, demonstrating that it is a material with potential use in dressings for wound care.

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Effect of coating based on lignin-starch mixtures on packaging paper

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Nowadays, it is well known that plastic packaging wastes are polluting different ecosystems; in particular, a large amount of plastic waste accumulating in the oceans is very disturbing. Thus, the world governments have established policies to reduce the amount of plastic in the market products. One possible solution to this global problem would be to replace the plastics in packaging with environmentally friendly materials, such as paper and cardboard, which could be a feasible alternative because they are recyclable and biodegradable. However, cellulosic materials do not have barrier properties to liquids and gases; therefore, the development of barriers on the paper surface using sustainable biomaterials should be a science-technologist priority. The purpose of this work was to study the effect of applying coatings made with mixtures of lignin and commercial starch on Kraft paper and evaluate the effect on the barrier properties.

In this work, coating mixtures were made with commercial starch and lignin obtained from the ethanol-water fractionation of lignocellulosic biomass. An L_9 orthogonal array scheme which nine experiments was used to evaluate the effect of the coating on Kraft paper. The responses considered were starch content (%w/w), lignin content (%w/w), coating wet thickness (µm), and heat treatment temperature (ºC) of coated sheets. For each one, three levels were tested to minimize the signal-to-noise ratio. The experiments were carried out randomly to avoid any kind of bias. The barrier properties of the papers coated with mixtures of starch and lignin that were evaluated are *Gurley air resistance (GAR)*, *short compression strength (SCS)*, and *static contact angle (SCA)* as a measurement of surface *hydrophobicity* and *water vapor transmission (WVT)*.

Under the conditions evaluated in this study, it was determined that the best combination of parameters for the GAR was using the minimum assessed value for each variable. The SCS increased with the starch content and temperature of heat treatment. On the other hand, the hydrophobicity of the paper is mainly affected by the amount of lignin in the mixture and the temperature of heat treatment. Finally, the evaluation of *WVT* indicates that is mainly influenced by the starch content and wet thickness. After determining the optimal process conditions, a confirmatory test was carried out for each response variable, which allowed to obtain improvements of up to 100 times for *GAR*, increases of 30% for *SCS,* and 15% for hydrophobicity, and *WTC*.

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Influence of surfactant additives in the kraft cooking of *e. Globulus* mixtures with *e. Urograndis* or *e. Nitens*

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Eucalyptus globulus wood is the main source of short fiber for the Portuguese paper industry due to its high density, pulp yield, and outstanding fibers for the production of high-quality paper. Despite the clone selection and the good silvicultural and fertilization practices foresting the productivity, the incorporation of wood from other *Eucalyptus* species, such as *E. urograndis* and *E. nitens* is still required to achieve the mill production capacity. In general, as compared with *E. globulus*, these species require more severe conditions in kraft pulping to reach the same kappa number (higher concentration of alkali and/or temperature). Therefore, the incorporation of *E. urograndis* and *E. nitens* in kraft pulping, even with a dominant proportion of *E. globulus*, leads to a decrease in pulp yield compared to that obtained from the sum of individual species pulping.

Several strategies to maximize the yield and keep the competitive advantage of the eucalyptus kraft pulp have been evaluated, such as individual impregnation and optimization studies regarding temperature, time, and alkaline charge for each mixture. Another strategy encompasses the utilization of cooking additives, testing the additive dosage and the effect in eucalyptus mixtures. The scope of this work is the improvement of the pulping performance, concerning pulp yield and/or kappa number through the use of additives during kraft cooking. For that, the influence of three commercial additives (based on surfactants) was studied in the kraft pulping of mixtures of 70% national *Eucalyptus globulus* with 30% *Eucalyptus urograndis* or *Eucalyptus nitens* to obtain pulps with kappa number 15 and 18, using loads between 0 to 1 kg of additive per ton of dry wood. The experiments were carried out in an MK digester, keeping constant the cooking conditions for each chip mix and each kappa number.

It was possible to verify the beneficial influence of the additives, both in the yield and the KN. Under optimal conditions it was possible to improve yields of 2.3% in the *Eucalyptus globulus/urograndis* mixture and 1.9% in the *Eucalyptus globulus/nitens* mixture, also observing cases where KN decreases one unit.

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TCF vs ECF bleaching of prehydrolysis kraft pulp

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In recent decades, the growing demand for regenerated cellulose fibers, particularly viscose fibers, has resulted in considerable growth in dissolving pulp production [1]. The main processes used to produce dissolving pulps are based on sulphite pulping and prehydrolysis-kraft (PHK) pulping. The last one provides a pulp with higher alpha-cellulose content; however, a two-step process is needed. To reach the high requirements of dissolving pulp, hemicellulose and lignin must be removed from the raw material. PHK process is based on the auto/acid hydrolysis of the lignocellulosic materials to enhance hemicellulose removal before kraft cooking [2].

In this work, the performance of prehydrolysis treatment in batch and flow-through reactors (FTR), as well as the cooking and bleaching behaviors of the different prehydrolysed materials, are compared.

When compared to a batch prehydrolysis system, the prehydrolysis carried out in the FTR produced an unbleached pulp with lower viscosity (800 cm3/g vs 1120 cm3/g), lower kappa number (6.3 vs 8.6) and lower hemicellulose content (3.6% vs 8.8%), showing the positive effect of this system in the prehydrolysis treatment. In addition to the effect on the pulp's chemical compositions, the variation of flowrate in the flow-through reactor changed the pulp structural features; the viscosity and the molecular weight distribution changed significantly, which are crucial aspects for cellulose dissolution.

In this study, total chlorine-free (TCF) and elemental chlorine free (ECF) bleaching sequences were applied to PHK unbleached pulps produced in a flowthrough reactor to assess the influence of prehydrolysis conditions on the bleaching effectiveness, with a particular emphasis on molecular weight distribution and its effects on dissolution. These results will be compared with the post enzymatic treatment, where a reduction of 38% in viscosity was achieved using an enzymatic mix *Celludase* for 1-hour treatment at 40ºC.

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Acknowledgements

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Solvent exchange: effect on cellulose fibers dissolution in LiCl/DMAc

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The molar mass distribution is a key characteristic of cellulosic polymers for their characterization and applications. However, the application of size exclusion chromatography (SEC) for the analysis of these samples is often limited by their poor solubility in solvent systems, such as Lithium Chloride/N, N-dimethylacetamide (LiCl/DMAc).[12] Thus, an activation step is crucial for opening the crystalline structure to enhance the diffusion of the solvent system to regions that are tightly packed and less accessible.[3]

This work aims to present a study of different activation methods by using the solvent exchange technique for the dissolution of cellulose fibers in the LiCl/DMAc system for Size Exclusion Chromatography (SEC) analysis. This methodology is applied to different cellulose fibers (dissolving pulp from *Eucalyptus globulus* wood chips, waste paper, and waste cotton from the textile industry). The preliminary results indicate, for all tested activation solvent systems, that full dissolution occurs for prehydrolysis kraft pulps, while partial dissolution results for cotton and wastepaper fibers, as shown in Figure 1. Considering that none of the systems was fully effective for all the fibers due to their unique characteristics, the pre-treatments' effects were evaluated by the dissolution extent and obtained molecular weight distribution. The most appropriate system for each cellulose fiber was discussed in terms of interactions and its' properties.

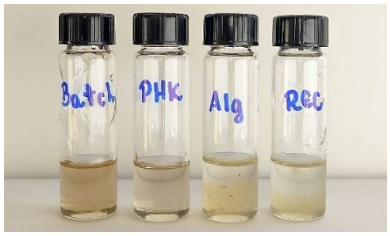

Figure 1. Preliminary results of activation by H_2O-MeOH-DMAc system.[3]

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Characterization of cellulose fibers and their potential for lyocell process

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The world's textile production has almost doubled in the last 10 years from 58 million tons in 2010 to 109 million tons in 2020.[1] The textile industry is one of the most threatening production systems for the environment, considering its consumption of water, energy sources, and large amounts of solid waste, wastewaters and air pollutants generated by its processes.[2]

Cotton is the most consumed natural fiber in the textile industry, and the most critical environmental impacts associated with its production are water consumption (2.6% of the global amount), land occupation, emissions, and usage of chemicals.[3] Following the sustainable concept, the demand for regenerated cellulose as a material for the textile industry has increased. For many years, the viscose process has been the most dominant in such matters. However, in the early '80s, the Lyocell process was introduced as an environmentally friendly alternative, using N-methyl morpholine-N-oxide (NMMO) as a non-toxic, environmentally harmless, and biodegradable solvent.[4,5] Nevertheless, some dissolving pulp's properties are required for lyocell processes, such as high α-cellulose content, a moderate degree of polymerization (DP), and high purity (low metal ion and ash content). The balance of these properties is required to ensure fiber dissolution and mechanical strength preservation.[4]

This work aims to evaluate the influence of the cellulose properties of different raw materials (dissolving pulp from *Eucalyptus globulus* wood chips, recycled paper, and cotton textile waste) on the performance of its dissolution in NMMO. Following this proposal, this work characterizes fibers by physical and chemical methods. Preliminary results indicate that cotton textile waste may require pretreatment and wastepaper should be delignified and its hemicelluloses extracted to improve solubilization.

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The effect of epoxidized compounds on the structure of Kraft pulp cellulose films

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Cellulose, the most abundant biopolymer on earth, is the best solution to replace the enormous amount and variety of "petro-plastics" [1]. Films obtained by cellulose regeneration could be a practical solution for a new generation of bio-based films with useful properties. The presence of functionalities in these films that promote crosslinking is expected to improve mechanical and thermal properties. Some researchers have already attempted to use crosslinking agents to create covalent bonds between the hydroxyl groups of cellulose to enhance its performance. However, some of the agents used are not environmentally friendly, such as epichlorohydrin [2], which is classified as a probable or likely human carcinogen by several international health research institutes and groups [3]. In this work, pre-hydrolyzed kraft cellulose was dissolved and mixed with the epoxidized crosslinkers, such as diethylene glycol diglycidyl ether, ethylene glycol diglycidyl ether, and 1,4-butanediol diglycidyl ether. The cellulose/crosslinker solutions were applied to glass plates and regenerated under suitable conditions. The resulting hydrogels were then regenerated to films and dried under optimized conditions. The films were further characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), swelling, contact angle measurement, dynamic scanning calorimetry (DSC), and thermal analysis (TGA), and their tensile properties were also evaluated.

Figure 1. Kraft pulp cellulose films crosslinked with epoxides.

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Acknowledgments: The authors acknowledge the Project HIGH2RPAPER-POCI-01-0247-FEDER-049716 for financial support.

Pulp and handsheets potential of pre-treated *E.* globulus stumps in a biorefinery context

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E. globulus stumps are a sidestream of the pulp industry that are uprooted and used as biofuel for energy and heat conversion at the end of the tree exploitation cycle. Stumps are more recalcitrant for pulp production than stemwood because they have higher contents of total extractives (13.0-17.4%), total lignin (24.0-25.5%), and less holocellulose (62.9%)[1]. To solve this problem, a pre-treatment route before pulping was envisioned to remove/diminish extractives and hemicelluloses contents and enhance the pulping chemicals accessibility in the lignocellulosic matrix, thus improving the delignification process of stumps.

In this work, industrial chips from eucalypt stumps were attained from a Portuguese Pulp and Paper Industry and prepared for: i) summative chemical analysis (11.9% of extractives, 25.2% of lignin, and 62.9% holocellulose), ii) pre-treatment testing five procedures: liquid hot water (LHW), alkaline peroxide (AHP), oxalic acid (OA), sodium xylene sulfonate (SXS) and iron (III) chloride ($FeCl_3$), iii) untreated and treated stumps used for kraft pulping, iv) production of handsheets and properties characterization (bulk density, burst, tear and tensile indexes, and stretching).

The chemical composition of the pre-treated stumps changed after the treatments: extractives decreased on all treatments except for $FeCl_3$ (10.0%) and SXS (14.2%); total lignin increased in all samples except for AHP (24.5%) and SXS (23.0%); glucose content increased except for LHW treatment (39.6%)[2]. The kraft pulps produced with untreated stumps presented a yield, Kappa number, and degree of polymerization of 49.4%, 18, and 3789, respectively. These same properties on pulps produced with pre-treated stumps varied considerably; yields ranged from 30.7% ($FeCl_3$) to 53.9% (AHP), while Kappa number varied from 10 (SXS) to 41 ($FeCl_3$).

Relatively to the handsheets, only those produced from LHW pulp showed a considerable improvement compared to untreated stumps pulp. LHW pre-treatment favored the elimination of extractives, thus enhancing the delignification by the kraft liquors, so the resulting pulp had good characteristics for sheet formation. On the contrary, the FeCl3 pre-treatment induced a high degree of deconstruction upon the fiber material, and the pulp attained was inadequate for handsheets production.

Overall, stumps are an interesting raw material for pulping, and their valorization may be increased if pre-treatments are applied. LHW improved the pulp physical properties while AHP, SXS, and OA showed potential for dissolving pulps. $FeCl_3$ pre-treatments can be used if a chemical deconstruction is aimed.

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Characterization of the retention of cellulose nanofibrils in papermaking

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The paper and cardboard industry needs to improve the quality of its products to meet customer demands. Several additives and other alternatives are used to increase the properties in papermaking, such as mineral fillers to improve the optical properties, cationic starch, the refining of the fibers as a strength agent, or cationic polyacrylamides as a retention agent [1]. An emerging option as a strength additive, although still expensive, is the use of cellulose nanofibrils (CNFs) to enhance the mechanical properties of paper and cardboard products. CNFs are nanomaterials obtained by defibrillation of cellulose fibers from different sources. Before mechanical fibrillation, some pretreatments such as chemical, mechanical or enzymatic facilitate the separation of the fibers, increasing the nanofibrillation yield. In addition, in a circular economy approach, CNF implementation in papermaking can be addressed through the in-situ production from a cellulose stream of the same process of paper manufacture [2].

One of the challenges in the application of CNFs in papermaking is the study of their retention in papermaking, to minimize their loss through the filters and paper machine. Currently, there are scarce methods that develop this challenge, requiring analytical techniques and image analysis, making difficult the application in industrial environments [3]. This research aims to quantify in a simple way the CNFs retained in papermaking by the analysis of the water process. Two different raw materials to prepare handsheets have been studied: recycled newsprint and cardboard. CNFs added to the pulp were obtained from a bleached eucalyptus pulp (NBSK) obtained by TEMPO pretreatment with sodium hypochlorite and 3 homogenization passes.

To quantify the CNF retention in the pulp, a dynamic retention tester, commonly available in paper mills, has been used. On it, the pulp and the white water containing fines and non-retained CNFs were obtained. This filtrate was characterized using UV-spectrophotometer. Several peaks were obtained in the graphical representation of the transmittance derivative vs. the wavelength, identifying characteristic peaks from CNFs and fines (Figure 1). Different mathematical models (peaks, area, the relation between them…) were proposed to optimize the calibration of the method.

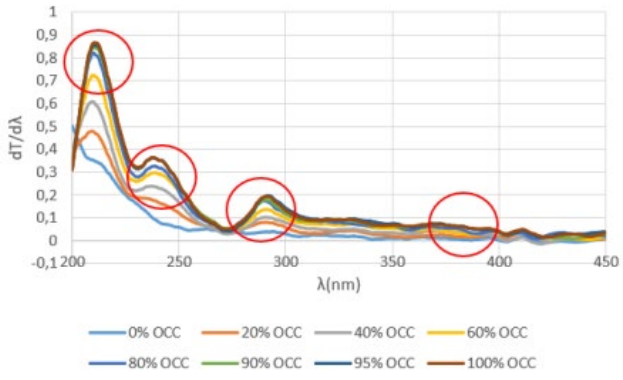

Fig. 1. Representation of the transmittance derivative vs. wavelength.

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Interaction of the cellulose nanofibers with the dissolved and colloidal material in paper recycling

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The paper recycling industry is one of the most sustainable industries contributing to the circular economy since used as raw material recovered papers [1]. However, the use of recovered fibers as raw material has the drawback of the high number of contaminants that are introduced into the papermaking process and accumulated in form of dissolved and colloidal material (DCM) in process water. The composition of DCM, which mainly comes from pulp, fillers, recycled water, and the chemicals added during the papermaking processes, is very complex. In addition, the presence of DCM in white waters is directly related to the formation of adherent deposits (stickies, secondary stickies, white pitch) when destabilization occurs due to sudden changes in the system [2-3].

Shortly, the recovered paper containing nanocelluloses (NC), added to improve the mechanical properties of recycled papers, will reach recycled paper mills. If NC is released during the papermaking process, it may interact with the DCM. The effect of the NC contained in the recovered paper on the composition, behavior, and concentration of DCM and, thus, on the stability of the production process is unknown yet. Therefore, it is necessary to study the interaction of the non-retained NC with DCM and fillers present in the white waters and their effect on the deposit formation during papermaking.

This work aims to study: (1) the effect of cellulose nanofibers (CNF) on the formation of adherent deposits during papermaking; (2) the interaction of CNF incorporated in bulk on pulp depositability; and (3) the interaction of non-retained CNF with DCM present in white water on white water depositability.

Two raw materials have been studied, coated paper and bleached eucalyptus pulp, adding different amounts of a CNF in pulps or white waters. It was produced from eucalyptus and obtained by TEMPO-mediated oxidation, followed by a mechanical treatment by homogenization. In the first stage, the white water is obtained at a lab-scale in similar conditions to the papermaking process and characterized. A second stage consists of a deposition test carried out using a deposition tester, developed and patented by the Research Group, to obtain the adherent deposits microstickies and secondary stickies. The deposits are quantified by an image analysis system.

The results show that, in the case of coated paper, the deposits produced are mainly secondary stickies, while in the case of eucalyptus pulps, mainly microstickies are produced. On the other hand, the interaction of the CNF with the pulp is greater when a destabilizing agent is not added, as observed with the decrease in the formation of microstickies when the addition of CNF in bulk increases. Finally, the interaction of the non-retained CNF with the DCM present in the white water depends on the DCM from the raw material used.

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Marine biomass from Posidonia Oceanica as raw material for nanocellulose production and its application in papermaking

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The increasing demand for renewable resources makes that waste could be an important source to produce new materials such as cellulose nanofibrils (CNFs), due to the low costs of waste and the benefits to the environment. In recent years, several agricultural or industrial residues have been researched for nanocellulose production [1], whereas the use of marine biomass has been used to a lesser extent. *Posidonia Oceanica* is a marine plant endemic to the Mediterranean Sea that grows forming extensive underwater prairies. The drop in the temperatures in autumn and the arrival of storms make the leaves of Posidonia Oceanica dragged to coastal areas. The accumulation of hundreds of tons of *Posidonia Oceanica* on the beaches of the Mediterranean Sea hurts tourism, as well as environmental and health problems [2].

The objective of this work is the recovery of *Posidonia Oceanica* as a raw material to produce CNFs through bleaching and mechanical nanofibrillation. Firstly, an alkaline pretreatment with NaOH and a high temperature was prepared to dissolve the lignin and to obtain the cellulose pulp. Then, the pulp was bleached at pH 12 using $NaClO_2$. From the bleached pulp, CNFs were obtained by three different treatments: (i) PFI refining; (ii) High-Pressure Homogenization (HPH) at 600 bars and 6 passes; and (iii) chemical oxidation catalyzed by TEMPO followed by HPH at 600 bars and 2 passes.

Pulps were characterized initially and after each pretreatment by measuring ash, extractives, lignin, cellulose, and hemicellulose. Results show a very high amount of hemicellulose in the pulp that is almost maintained with the treatments. After the bleaching process, the lignin content noticeably decreases by more than 90% whereas the amount of cellulose increases from approximately 10% to almost 30%. This cellulose content allows *Posidonia Oceanica* can be used as a raw material for CNF production, despite the high content of ashes from inorganic compounds due to the presence of typical mineral salts in marine biomass such as silica or weddellite. The CNFs obtained were morphologically characterized by the measurement of the polymerization degree, the cationic demand, the nanofibrillation yield, and the transmittance at 400 nm and 800 nm. The best characteristics of CNFs were obtained by chemical pretreatment with TEMPO followed by HPH.

CNFs obtained from *Posidonia Oceanica* by the different treatments were applied as a reinforcement agent in papermaking to obtain cardboard. Mechanical properties such as tensile strength, short-span compression test (SCT), and tear strength were measured to evaluate the recycled cardboard enhancement. Cardboard handsheets prepared with 3% of CNFs produced with TEMPO and HPH and 0.5% of cationic starch as retention agent showed the best results with an increase of 11% in the tensile index, an improvement of 9% in SCT index, and maintaining the tear of the samples respect to the cardboard only with cationic starch. Therefore, *Posidonia Oceanica* is a promising raw material for the production of CNF of suitable quality for its application as a reinforcing agent in papermaking.

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Cationic nanofibrillated cellulose as flocculant in recycling papermaking

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The paper industry is an example of a sustainable industry since it transforms natural and renewable raw materials into different recyclable products using increasing more environmentally friendly technologies. However, one of its main problems today is the process's dependence on the use of unsustainable flocculants to improve solid retention and drainage rate and achieve high productivity. Therefore, considering more sustainable alternatives is key to continuing to improve paper manufacturing processes [1].

During the last ten years, nanofibrillated cellulose (NFC) has gained great interest due to its environmental advantages, since they are renewable and biodegradable, as well as its mechanical properties, thermal stability, and low density, high specific surface, etc. Cationic nanofibrillated celluloses (CNFC) could be alternative biodegradable and renewable flocculants to improve the retention and drainage of paper processes [2]. There are some studies on the feasibility of using CNFCs as flocculant, but all of them use virgin fiber cellulose sources, thus there is a lack of knowledge on the use of CNFCs from agroforestry residues such as rapeseed or corn stalks as flocculants in paper recycling [2, 3]. The objective of this research is to study the feasibility of producing and using CNFC from different agroforestry wastes as an alternative to synthetic flocculants in the wet-end of paper recycling machines.

CNFC was produced from rapeseed and corn stalks which were previously pulped using the organosolv process. The organosolv pulps were bleached with NaClO and cationized with an aqueous solution of 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC). Finally, cationic cellulose pulps were homogenized at high pressure. The flocculation efficiency of CNFC was studied on deinked pulp by monitoring the particle chord length distribution in real-time. CNFC induced the formation of soft flocs (Figure 1). A dynamic drainage analyzer (DDA) was used to determine the efficiency of CNFC as retention agents in the retention and drainage process. Drainage time decreased down to 43% with 5,5 kg of CNFC per ton of paper. Obtained results proved that CNFC can improve the wet end of the paper machine and can be a sustainable alternative for traditional flocculants.

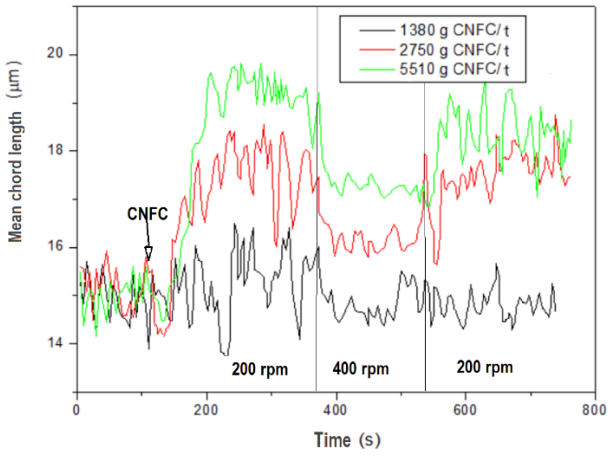

Figure 1. Flocculation of deinked pulp with CNFC from corn stalk.

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Recyclablity of packaging papers with nanocellulose coatings

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The widespread use of plastic materials in packaging is a major environmental problem. Plastic packaging has advantages such as low cost, lightweight, versatility, heat sealing**,** and good mechanical and barrier properties (1). However, many of them are neither compostable nor biodegradable, which has a high environmental impact due to the difficulty of recycling them.

To reduce this problem, new packaging alternatives are being developed based on the use of cellulose fiber-based packaging, which is a biodegradable and recyclable material. These materials have disadvantages in some of their properties, such as low impermeability to air and humidity and low resistance in dry and especially wet conditions. To alleviate these limitations and favor the use of paper and cardboard in applications where these properties are limiting, papers are being reinforced with different polymers, sometimes obtaining good results.

These coatings must be compatible with the recycling of the paper by the usual means so that the new packaging does not affect the life cycle of these products, with high recycling rates.

In this work, the recyclability of papers that have been reinforced with a coating of commercial nanocellulose (mechanical, chemical, and carboxymethylated) is studied.

The recyclability is studied by observing the variation of rejects on a Sommerville sieve after the samples are pulped under fixed conditions. Together with this parameter, the process performance is determined, and the process water is characterized in terms of conductivity, pH**,** and COD.

The results obtained show increases in Sommerville rejects compatible with good recycling of the materials and changes in other parameters are also acceptable for appropriate recycling of nanocellulose coated papers.

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Chemical characterization of different morphological parts of acacia dealbata and potential biological activities of extracts

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Acacia dealbata is an invasive species of the Portuguese eucalyptus and pine forests. Although this species produces wood suitable for good quality fiber cellulose, its wood is mainly used for furniture, the gum of bark for tanning production, and flowers have been used in the flavor industry [1].

In Portugal, *A. dealbata* is considered a by-product of the forestry exploitation of *Eucalyptus globulus* wood for pulp and paper production, and therefore, this biomass is left in the forest or is used essentially for power generation [1]. In the last years, some studies have reported that *A. dealbata* is particularly interesting as a source of added value compounds [2]. Notwithstanding, there is no detailed study on the composition of the lipophilic and phenolic fraction of the different morphological parts of *A. dealbata* envisaging their integrated exploitation. In this vein, a systematic study was conducted on the lipophilic and phenolic composition of the bark, wood, and leaves as well as on the cytotoxicity of the extracts obtained. The composition of the lipophilic extracts was analyzed by GC-MS, while polar extracts were analyzed by UHPLC-DAD-MS^n. In the lipophilic fraction, different families of compounds were identified, such as fatty acids, sterols, and triterpenic compounds. Flavonoid glycosides and procyanidins were amongst the most relevant phenolic compounds identified. All extracts were evaluated for their cytotoxicity in different types of cells.

In conclusion, this study is an important contribution to the knowledge of the lipophilic and phenolic fraction of *A. dealbata*, promoting its exploitation as a resource of valuable compounds.

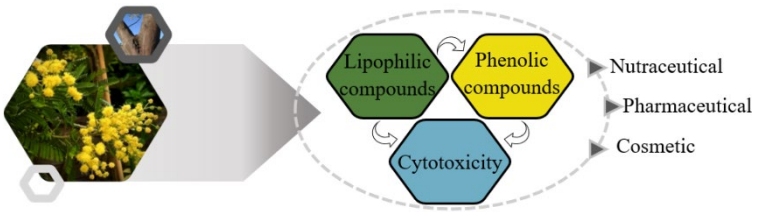

Figure 1. Illustrative scheme of the work carried out for the chemical characterization of *A. dealbata.*

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Conversion of carbohydrates to organic acids using Lewis acid catalysts in aqueous medium

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The use of renewable resources to produce fine chemicals, pharmaceuticals, biofuels, and biobased materials has been pushed by the urgent need to replace harmful petrochemicals in a wide range of industrial activities [1]. This way, biomass-based biorefineries help promote sustainable alternatives that elicit lower carbon footprints and greenhouse gas emissions. Carbohydrate conversion to organic acids has an important role in this scenario for their possible transformation into several high value-added chemical intermediates, fuel, and food additives, and biobased polymeric materials [2]. In this study, sugarcane molasses containing sucrose, glucose, and fructose were converted to organic acids such as levulinic and lactic acids using different Lewis acid catalysts in aqueous media. Emphasis was given to lactic acid due to its application in polymer synthesis to produce biocompatible and biodegradable plastics based on poly(lactic acid) (PLA). Aluminum and zinc nitrate and chloride were used in two reaction systems based on conventional and microwave heating. Stainless steel (SS) and glass reaction vessels were used for this purpose, respectively. The conversion was evaluated by liquid chromatography at different reaction times and temperatures. Regarding the catalysts involved in this study, aluminum catalysts promoted higher product yields compared to zinc. Lactic acid coming from the retro-aldol reaction of fructose was often obtained in the highest yield, compared to other reaction products (Figure 1). Reactions carried out in SS reactors inside a muffle (conventional heating) presented higher yields of lactic acid (65%) compared to those carried out in a microwave reactor (36%). Besides lactic acid, a small amount of formic acid, levulinic acid, and 5-(hydroxymethyl)-furfural (5-HMF) were obtained as co-products from dehydration. The temperature regime was a critical parameter to achieve high yields and good selectivity for lactic acid in these reaction systems. The best condition for lactic acid production was obtained in 90 min using conventional heating due to the gradual increase in reaction temperature up to 195 °C. $Al(NO_3)_3$ had the best catalytic performance, producing 65 mol% lactic acid, 14 mol% levulinic acid (14 %), 21 mol% formic acid, and only 4 mol% 5-HMF. Regarding heating efficiency, approximately 60 min were required to reach 180 °C using conventional heating, while the corresponding heating time in the microwave reactor was only 2 min.

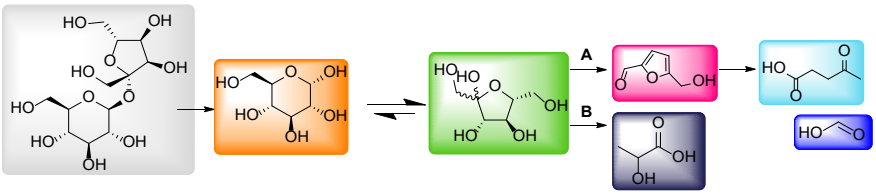

Figure 1. Conversion of carbohydrates to organic acids by dehydration (A) and retro-aldolic (B) reactions.

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Organosolv fractionation of cane bagasse using aqueous ethanol and organic acids in the presence of supercritical co2

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A new sugarcane bagasse pretreatment technology was developed based on organosolv fractionation [1] with aqueous ethanol in the presence of an organic acid catalyst and supercritical CO_2 ($scCO_2$). Different process conditions were investigated and the decision parameters for the best pretreatment process were based on the rates of glucan recovery and delignification [2]. Reactions were carried out with 6 g of cane bagasse in a 100 mL stainless-steel high-pressure Parr reactor in which CO_2 was injected with the aid of an Isco syringe pump. Acetic, citric, and oxalic acids in 60 mL aqueous ethanol were used for cane bagasse delignification at 170 °C for 60 min in the absence and presence of $scCO_2$. Initially, various ethanol concentrations in water (up to 80 vol.%) and CO_2 injection loads (up to 50 g) were applied, with the three organic acids fixed at 1% (w/v). The best solvent mixture was ethanol 60 vol.% since higher titers favored esterification to the corresponding ethyl esters. All acid catalysts added to pretreatment increased hemicelluloses and lignin removal, but the highest delignification rates were obtained with oxalic acid regardless of CO_2 addition. CO_2 injection did not cause an increase in glucan recovery or lignin removal from cane bagasse, but pretreatment was made more homogeneous due to the better diffusivity of the pressurized organic solvent [2]. Also, the use of CO_2 was more advantageous when the pretreatment was carried out at shorter reaction times. After defining the best organic acid, ethanol concentration, and CO_2 injection load (25 g), a preliminary optimization study was carried out using an experimental design to study the effect of variables such as temperature (150-190 °C), reaction time (0-30 min) and oxalic acid concentration (0.5-1.5%, w/v) in $scCO_2$-assisted aqueous ethanol organosolv process. The best condition was 170 °C for 15 min using 1% (w/v) of oxalic acid, in which a high glucan recovery (89 ± 4%) and a high delignification yield (86 ± 2%) were obtained. Cellulosic materials arising from these conditions were submitted to enzymatic hydrolysis using Cellic CTec3 from Novozymes, resulting in a glucose conversion of 74.3 ± 0.2% after 96 h. This value was about 11 times greater than that obtained from untreated cane bagasse. Therefore, the $scCO_2$-assisted, oxalic acid-catalyzed aqueous ethanol organosolv pretreatment process was able to change the structure of sugarcane bagasse and make the glucans, mostly present as cellulose, much more available for saccharification by enzymatic hydrolysis. The concentrated pretreatment liquors allowed the recovery of lignin in relatively high yields using water as an anti-solvent. The isolated lignin contained low carbohydrate content and a spectral fingerprint that was very similar to high-quality technical lignins. Furthermore, the aqueous phase derived from this process had low concentrations of acetic acid, furfural, and hydroxymethylfurfural, suggesting good potential for fermentation processes such as cellulosic ethanol production.

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Utilisation of corn fiber to furfural

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Corn fiber is a co-product of a significant amount, obtained during the corn wet-milling process for the starches production and is usually sold as relatively low-value animal feed after mixing with heavy steep water and dried [1]. It is well known that the corn pericarp contains much more arabinoxylose and relatively less cellulose and lignin. Methods for selective hydrolysis and separation of xylose and arabinose have been studied and productions of food additives have been proposed [2,3]. Another study suggested the conversion of xylose to ethanol and of arabinose catalytically to ethylene glycol, propylene glycol, and glycerol [1,4]. The effectiveness of the proposed technologies is not high, and the corn fiber product is continuously used as animal feed. The purpose of the present study is to investigate the hydrothermal and diluted acid hydrolysis of corn fiber as a pretreatment step to find a solution for the cost-effective utilization of this biomass.

Industry corn fiber was used in this investigation and the content of pentosans, lignin, cellulose, ash, and hot water solubility substances was determined according to standard analytical procedures. Dilute acid hydrolysis was performed in 2l stainless steel autoclaves under the sulfuric acid charge 1% on dry pulp, liquid to solid ratio 10:1, initial temperature 100°C, maximum temperature 130°C, heating time 60 min, and reaction time at maximum temperature 20 and 40 min. The hydrothermal hydrolysis was carried out at a liquid to solid ratio of 10:1, at temperatures 160° and 190°C for 20 to 40 min. The total solubility substances and content of glucose, xylose, arabinose, furfural, and HMF were determined according to the NREL Technical Report on a Dionex HPLC system by Shodex RI detector.

A comparison of the results obtained after corn fiber hydrothermal hydrolysis at moderate temperature and acid hydrolysis shows that in both cases the dissolved substances are over 60% with minimal destructive processes of sugars. After hydrothermal hydrolysis mainly oligosaccharides are found, while after acid hydrolysis mainly monosaccharides with molar ratio Xyl:Ara:Glu=1.2:1:1 are observed. The amount of arabinose obtained should be taken into account when developing a strategy for optimal utilization of corn fiber. The formation of 22.3% furfural is detected in pentosan analysis of corn fiber. That is the reason to propose a simplified technology for the transformation of all C5 sugars to furfural. Utilization of corn fiber to furfural seems to be more effective than complicated sugar separation or converting it to bioethanol.

Acknowledgments

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Biopolymers, biofuels and enzyme-assisted technologies

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Integrated configuration for bioethanol production from primary sludge and *eucalyptus globulus* bark: evaluation of several operating conditions

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Over the past few years, the energy crisis has led to an increased worldwide interest in bio-based fuels, particularly second-generation bioethanol production. Concomitantly, the pulp and paper industry has invested in its production within an integrated biorefinery, focusing on valorizing the residues generated throughout the production process.

The main goal of the present work was to study the influence of several parameters in bioethanol production following a simultaneous saccharification and fermentation process, with (PS-SSF) and without (SSF) a non-isothermal pre-saccharification. Two lignocellulosic residues from the pulp and paper industry were assessed, namely primary sludge (with and without pretreatment with HCl) and *Eucalyptus globulus* bark (previously submitted to a kraft pretreatment). The following operating conditions were evaluated: a) the pre-saccharification time at 50 °C (6 *vs* 24 h); b) the fermentation temperature (30 *vs* 38 ºC); and c) the impeller type (Rushton turbine *vs* Anchor type impeller). For that purpose, all the assays were carried out using a solids loading of 8 %, a total suspension mass of 350 g, and an enzymatic loading of 25 FPU $g_{carbohydrates}^{-1}$. A commercial enzyme consortium from Novozymes and a yeast strain from ATCC were used in all assays.

Firstly, it was found that an additional pretreatment of primary sludge with HCl favored the fermentation performance. Moreover, the longer pre-saccharification time showed to be advantageous, particularly for the pretreated primary sludge fermented at the lower temperature, with a boost on maximum ethanol concentration more than 2-fold when the pre-saccharification period was prolonged from 6 to 24 h. For *E. globulus* bark kraft pulp, an improvement of only 6% was observed. Concerning the fermentation temperature increase, the operation at 38 ºC more than doubled the ethanol production for pretreated primary sludge, in both cases with the shorter pre-saccharification period. In contrast, the increase in the maximum ethanol concentration was almost negligible for *E. globulus* bark kraft pulp. Regarding the impeller type, a slightly higher ethanol concentration was obtained in a much shorter time using the anchor type impeller for the pretreated primary sludge, while with the *E. globulus* bark, it was the opposite.

Concluding, the effect of operating conditions is highly dependent on the feedstock. It was also found that *E. globulus* bark resulted in higher ethanol production for almost all the conditions evaluated.

Acknowledgments

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Valuable chemicals from pyrolysis of lignoforce^{tm} lignins

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Being the second most available biopolymer on Earth, lignin is an outstanding candidate for the replacement of fossil derivatives in the chemical industry by acting as a source of building blocks for additives, polymers, antioxidants, resins, and other carbon-based materials (1). Besides that, pulp and paper mills produce huge amounts of lignin (75,000 metric tons per year), making it easily accessible for fractionation and conversion to sustainable bioproducts. However, lignin is still largely underutilized by industry. Today, lignin overproduction in biorefineries including pulp and paper mills offers the prospect for sustainable developments oriented to the chemical recovery of aromatic compounds and other platform chemicals (2). In this work, lignin samples isolated from hardwood (LFHL) and softwood (LFSL) species by the LignoForce™ process were pyrolyzed at 550 °C to produce liquid streams (pyrolysis oil) containing low molecular mass compounds. The liquid products were separated into two phases and characterized by GC-MS, FTIR, acid number (AN), ^{31}P NMR, Folin-Ciocalteu, and Karl-Fischer titration. Formic and acetic acids besides a vast range of phenolics including chemicals such as catechol, pyrogallol, and guaiacol were identified in pyrolysis liquids. By comparing the hydroxyl content of lignin (3) before and after pyrolysis, a significant increase in total phenolic compounds was observed and further characterized by GC-MS, demonstrating that an aromatic-rich matrix is released upon thermal conversion. These monomers are important precursors for synthesizing fuel additives, chemical intermediates, polymer precursors, renewable hydrocarbons, and green antioxidants.

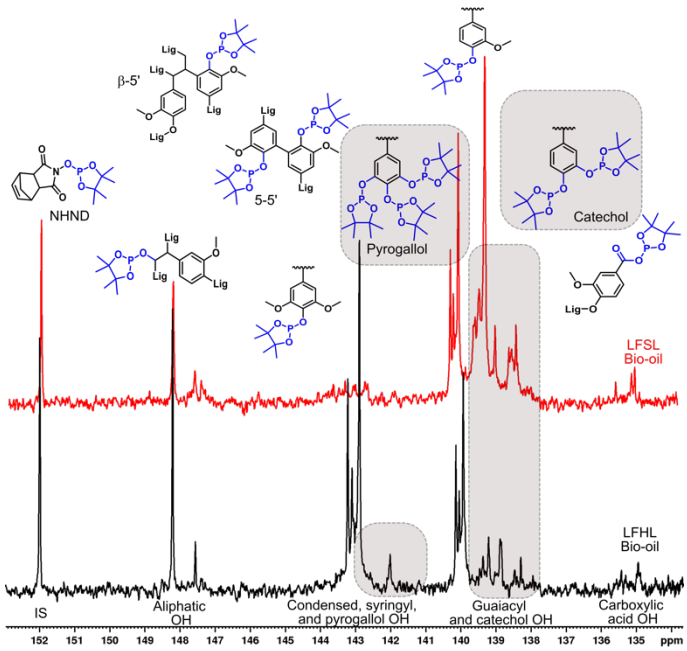

Figure 1. ^{31}P NMR spectra of phosphitylated phenolic-rich bio-oils derived from hardwood (LFHL) and softwood (LFSL) LignoForce™ lignins, with embedded structures indicating the signal attribution. IS, internal standard. NHND, *endo*-N-hydroxy-5-norbornene-2,3-dicarboximide

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Optimization of the simultaneous saccharification and fermentation strategy for 2g ethanol production in a pine sawdust biorefinery

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The objective of this work was to evaluate the second-generation bioethanol (2G) production from a pine sawdust soda-ethanol pulp by simultaneous hydrolysis and fermentation (SSF) to obtain the best conditions for scaling up the process [1].

Factorial experimental designs with central points were employed to evaluate the combined influence of enzymatic load, temperature, and time on bioethanol yields. The Statgraphics Centurion software was used to assess the experimental design results at a 95% confidence level. The used pulp had the following chemical composition: 80.18% Glucans, 7.20% Xylans, 0.29% Galactans, 8.40% Mannans, and 3.67% Lignin. Cellic® Ctec2 cellulolytic enzymes and *Saccharomyces cerevisiae* IMR 1181 (SC 1181) yeast were employed. A strain recovery technique to reactivate preserved yeast colonies used in previous work is described.

This study allowed defining suitable conditions for each processing stage, which can be adjusted to achieve maximum bioethanol production. The calculated fermentation yield values fit the experimental values, establishing the validity of both obtained models, Model I for the first 24 hours and Model II from 24 to 72 hours. The optimal fermentation yields were 63.2% and 81.9% for Models I and II, respectively. The best conditions found by the experimental designs were 30 FPU g^{-1} glucans, 39°C and 24 h for Model I, and 30 FPU g^{-1} glucans, 35°C and 72 h for Model II.

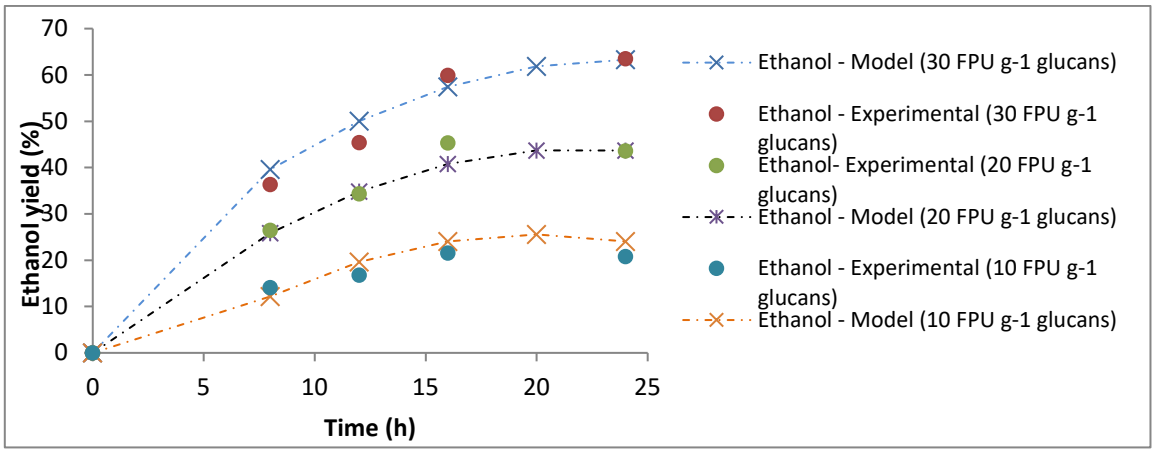

Figure 1. Experimental and theoretical (Model I, first 24 hours) fermentation yields al 39°C

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Optimization of organosolv-pretreated wheat straw saccharification

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In biorefinery applications, lignocellulosic residues stand out above the rest raw materials because it represents the largest carbon source on the planet since it is the main component of the plants. Therefore, lignocellulosic biomass has been considered one of the possible solutions to reduce the dependence on fossil fuels. Within the lignocellulosic raw materials, wheat straw is one of the most suitable for biofuels production thanks to its high sugar content, low cost, wide availability, and renewable character [1]. However, due to its complex structure, lignocellulosic materials need previous operations also known as pretreatments, to render them more reactive and adequate to be transformed into medium- and high-value products. In our case, acid-organosolv, an aqueous-organic solvent-based technique, was used as pretreatment of wheat straw [2].

In this research, some critical conditions for enzymatic saccharification process of lignocellulosic materials were studied to set the optimum values that enhance the yield of the reactions and maximize the sugar production. These operations were: enzymatic concentration, as enzymes are the principal actors in the hydrolysis reaction, buffer solution concentration, and pH and solids loading. This study aimed to obtain a complete analysis of the reaction products, so an evaluation of both liquid (HPLC) and solid phase (FTIR-ATR) was carried out.

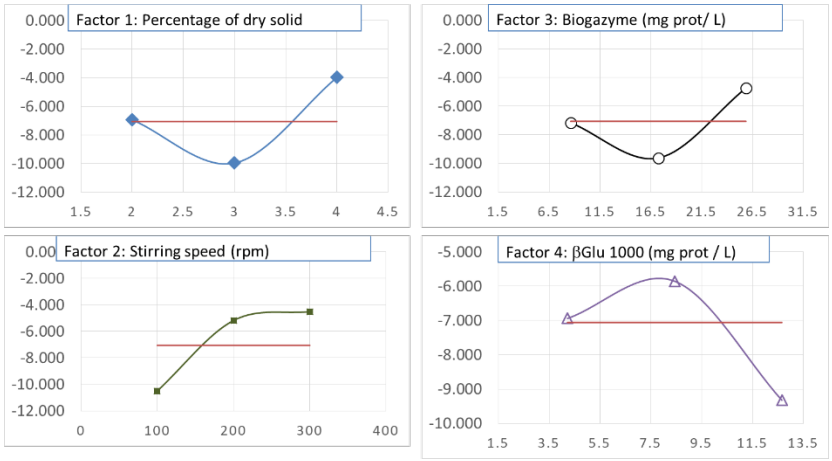

Figure 1. Taguchi L9 optimization of the saccharification process

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Design of a biorefinery for bioethylene production and lignin recovery from forest industrial waste

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Pine sawdust is a lignocellulosic waste from the primary processing of wood, highly available in Argentina. It could be a promising raw material to produce second-generation (2G) ethanol and its derivatives, like bioethylene-based products. 2G bioethanol production requires sawdust fractionation to achieve high cellulose yields. Lignin, a relevant source of aromatic organic compounds to obtain high-valued and carbon-neutral lignin-based products, is generated as a byproduct. Currently, only a low percentage (2%) of the generated lignin, principally in pulp manufacturing processes, is destined for other applications such as biomaterials; the remainder goes to combustion processes for energy generation. This work assesses two potential scenarios for pine sawdust valorization in a biorefinery frame. Organosolv pretreatments were applied to obtain bioethylene, lignin, fermentable sugars, and energy production.

The raw material was pine sawdust from a local industrial sawmill (Misiones, Argentina). Two cases of organosolv pulping were studied: (I) alkaline pulping with NaOH and ethanol recovery, and (II) autocatalyzed pulping only with ethanol recovery. **Figure 1** shows the pulping conditions. Mass and energy balances, yields, lignin availability as a byproduct, and economic parameters (investment, production cost, others) were compared and analyzed.

Delignification is 25% higher per ton of dry sawdust in Case I, whereas 88 kg and 111 kg of bioethylene per ton of dry sawdust are obtained in Cases I and II, respectively. The energy consumption for Case I is almost three times higher than in Case II. Bioethylene production plus lignin and sugars recovery are promising alternatives for this low-cost raw material in Argentina. Techno-economic evaluation allowed the feasibility of both cases at different scales of comparison.

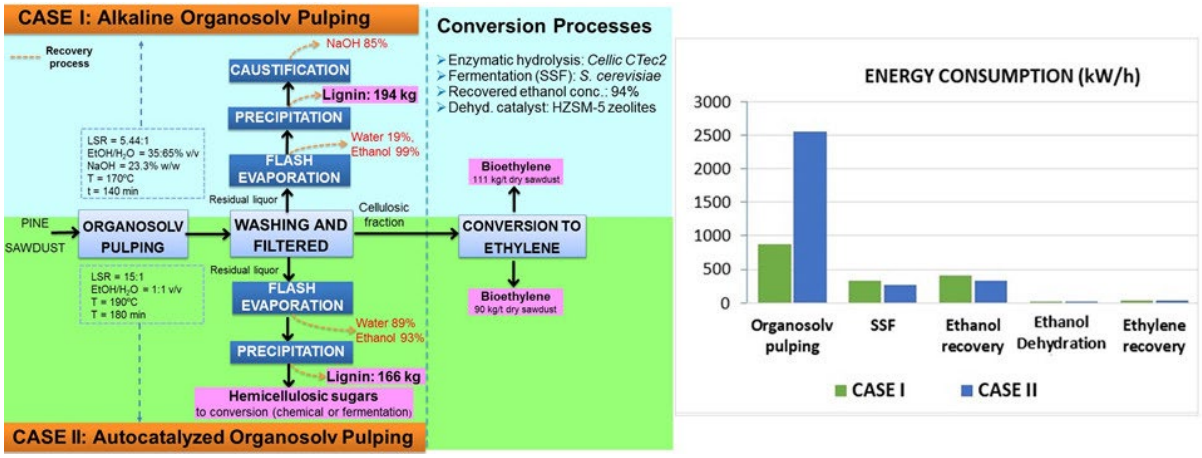

Figure 1. Pine sawdust organosolv pulping and conversion processes to bioethylene.

Process design for obtaining polymers from sugarcane bagasse autohydrolysis spent liquors in a biorefinery

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The design of biorefinery processes requires several factors assessment like available biomass, involved process, and obtained products, among others. Several products could be obtained to valorize the biomass in a biorefinery. In the last years, polymers production has gained attention. This study assesses sugarcane bagasse valorization in a biorefinery frame (see Figure 1). The proposed layout considered PHB and levulinic acid (LA) production through a fermentative pathway. Mass and energy balances were developed. After autohydrolysis, the residual solid was used for the energy production of char and tar. Two alternatives were evaluated for the fermentation step of the liquid fraction (with and without acetate addition).

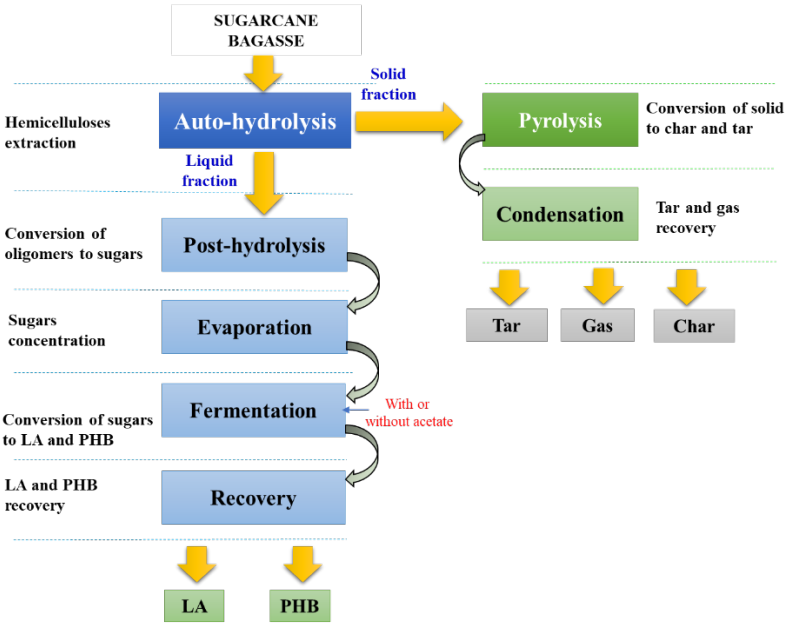

Figure 1. Proposed processes for biomass valorization.

It is possible to obtain between 5 and 31 kg of PHB and between 24 and 54 kg of LA per dry ton of sugarcane bagasse from the autohydrolysis spent liquor, and 227 and 162 kg of char and tar, respectively, from the solid fraction. Regarding energy consumption, autohydrolysis consume about 760 kWh per ton of dry biomass pretreated. For liquid fraction valorization, the concentration step is the process with the highest energy consumption (about 2345 kWh per dry ton of biomass). The pyrolysis step gases could satisfy the energy demand for the solid fraction treatment. The future steps of the present study are to develop a techno-economic assessment to evaluate the feasibility of the proposed scheme and determine critical factors.

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Bioethanol production using pinneapple and banana agroindustrial residues

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Costa Rica is one of the main banana and pineapple producers and is the major pineapple exporter worldwide. Agroindustrial processing of these fruits generates huge amounts of waste that cause environmental problems. The study's objective was to use mashed banana process by-products and pineapple juice obtained from the peels to produce bioethanol via fermentation, after treating the residues enzymatically. These residues have a high potential due to their sugar content and can be used as examples of the use of a circular economy.

Banana juice (168g/L±4 sugar content) was obtained after treatment with amylases and glucoamylases. Nutrient supplementation effects, as well as juice type (juice A and B), were studied using a 2^2 factorial design. Juice A was clarified enzymatic banana juice and Juice B was commercial purified banana juice. Fermentation was carried out on 7L bioreactors. Microorganism (*Saccharomyces cerevisiae*), temperature (30°C), pH (4.5), aeration, stirring (75rpm), and inoculum concentration (1.5g/L) were constant parameters. The logarithmic growth phase evaluated by optical density began from 0 hours and lasted 23 hours after. Ethanol production and sugar consumption (quantified by HPLC) were determined during fermentation. There was no significant difference ($p>0.05$) in cell growth rate ($0.078\text{-}0.088h^{-1}$) whether the substrate was supplemented or not. Sugar consumption was faster when using commercial juice. Ethanol concentration was higher (72g/L) when using juice B than when using juice A (62g/L). Nevertheless, there was no effect of supplementation ($p<0.05$). Ethanol yield concerning theoretical value was higher when using juice A (90%) than that obtained with juice B (83%). Final fermentation time was affected by supplementation as well as juice type, and varied between 31 and 48 hours, corresponding to supplemented juice A and non-supplemented juice B, respectively. The higher productivity was achieved using supplemented juice A.

Pineapple peels were milled and moisture, sugar content (HPLC), soluble solids (°Brix), and pH were determined. Milled peels were pressed, clarified, and sterilized to obtain the juice, and fermentation was evaluated with *Saccharomyces cereviseae* and *Zymomonas mobilis*, as well as different supplementation media (A and B), using a 2^2 factorial design. Fermentation was carried out on 5L working volume bioreactors; temperature and pH were maintained at 30°C and 4.5 for both microorganisms. *Saccharomyces* fermentation was held at 75 rpm and *Zymomonas* at 20 rpm. The moisture of pineapple peel was 86.27±1.10, the sugar content of juice was 87.71±1.67 (g/L), soluble solids 11.6±0.5, and pH of 4.16±0.52. There was no effect when supplementing juice ($p<0.05$). The logarithmic growth phase evaluated by optical density began from 2 hours and lasted 14 hours after with *S. cerevisiae*. 100% of sugars were consumed and ethanol production was 37.22g/L at 23 hours (81% of the theoretical value). Glycerol production reached 4.9g/L. Fermentation time ended at 23 hours. The lag phase for *Zymomonas* ended after 3 hours and the logarithmic phase ended at 21 hours of fermentation. 94% of sugars were consumed and ethanol concentration reached 40.20 g/L (88% of the theoretical value). No glycerol was detected.

This research showed that the use of banana and pineapple agroindustrial residues to produce bioethanol without the need for nutrient addition was feasible.

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Xylanase pre-bleaching treatment of oxygen-delignified eucalypt kraft pulp

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Increasingly restrictive environmental regulations in the last decades, and in the years to come, have forced the pulp and paper industry to shift towards an environmentally friendlier paradigm, mainly regarding pulp bleaching operations. The development of elemental chlorine-free (ECF) bleaching technology was the main result of the efforts made to decrease the release of chlorinated organic compounds, which are toxic hazardous species produced during chlorine bleaching, to the environment. Since the 1990s, biobleaching technology has been one of the most investigated alternatives to the established chlorine dioxide bleaching, mainly through the application of xylanases. A xylanase pre-treatment of pulp before an ECF bleaching sequence has been shown to allow substantial chlorine dioxide savings and to decrease the number of organochlorinated compounds released to the process effluents, as well. Nowadays, this enzymatic technology is already employed at the mill scale.

In this work, a pre-bleaching enzymatic treatment (X), employing a commercial endo-xylanase, was optimized and applied on oxygen-delignified eucalypt kraft pulp, which was then subjected to an ECF bleaching sequence. Thus, an OXDE$_P$DD bleaching sequence was studied. The main goals of this study were, besides the customization of the enzymatic technology to the existing industrial bleaching sequence, chemical reagent savings, the decrease of bleaching's environmental impact, and the improvement of both pulp quality and process economy.

Two combinations of time and enzyme dose were observed to reach maximum chemical savings during ECF bleaching**:** one of shorter duration, and higher xylanase dose; and another one, longer, yet applying a lower dose. Both tested conditions allowed the reduction of total chlorine dioxide and sodium hydroxide doses applied in bleaching in 12 and 10%, respectively. Despite being regarded as a rather bleach-promoting step, the xylanase treatment caused some delignification itself, as seen by the release of lignin and lignin degradation products into the treatment's effluent. Besides, the brightness stability of enzyme-treated fully bleached pulps was improved, which was associated with the decrease in hexenuronic acids content. Furthermore, X did not cause a significant impact on the papermaking properties, did not alter the cellulose fraction in the pulp, and thus did not affect pulp viscosity, either. However, the enzymatic stage was seen to cause yield loss, which was associated with the removal of xylans from pulp, which are the direct targets of xylanase action. Also, X was observed to cause slight fiber fibrillation and to increase the degradation degree of the xylans that remain in the fibers afterward. As expected, the enzymatic treatment caused a significant increase in its effluent's COD, but the reduction in chlorine dioxide dose did not translate into AOX reduction in the same proportion.

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Effect of alkalization and supramolecular structure of cellulose on enzymatic treatment of *Eucalyptus nitens* and *Pinus radiata* kraft pulps

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Cellulose I is the dominant cellulose polymorph in woods and plants and can be converted to cellulose II by alkaline treatment. When cellulose swells in an alkaline solution, a complex with alkali ions and water molecules, known as Na-cellulose I, is formed. When alkali is washed out, the Na-cellulose I complex is converted into Na-cellulose IV, which has an antiparallel chain packing with a two-chain monoclinic unit cell. When Na-cellulose IV is dried, it resulted in a stable cellulose II crystal. Therefore, the original parallel crystal structure of cellulose I am converted to the antiparallel cellulose II polymorph. On the other hand, several studies have demonstrated the use of commercial cellulases as a tool for controlling pulp viscosity and improvement of fiber reactivity for cellulose derivatives and saccharification. In this sense, the supramolecular structure of cellulose (i.e. crystallinity, polymorphic type, among others) can have a significant effect on enzyme performance. This work aimed to assess the effect of alkaline treatment and supramolecular features of cellulose on the enzymatic treatment of *Eucalyptus nitens* and *Pinus radiata* pulps. Bleached kraft pulps were treated with NaOH at different concentrations (from 5 to 35%, w/v), coded as CCE5, CCE10, CCE17.5, and CCE35. After each treatment, the chemical composition, fiber biometry, intrinsic viscosity, carboxyl content, specific surface area (SSA), crystallinity CrI) and saccharification were determined. Results indicated that the intrinsic viscosity of eucalyptus (730 – 420 mL/g) was higher than pine (625 – 410 mL/g). The carboxyl content ranged from 0.080 to 0.033 mmol/g and from 0.032 to 0.021 mmol/g in eucalyptus and pine, respectively. The SSA of eucalyptus samples (89–21 m^2/g) was higher than the values of pine samples (20–5 m^2/g). Eucalyptus CrI ranged from 60 to 44%, while pine CrI went from 71 to 44%, decreasing as alkali concentration increased. Regarding the cellulose polymorphs, cellulose II was first detected in eucalyptus after CCE10, while in pine it was detected after CCE17.5. Regarding enzymatic hydrolysis, the samples were treated with the commercial cellulase (Cellic CTec3) and with endoglucanase from *Aspergillus niger* to evaluate the glucose conversion rate and the increasing of cellulose reactivity and accessibility for dissolving pulp purposes, respectively. In both cases, differences were detected among the treatments and more interestingly, between both species, showing that fiber architecture and supramolecular features are more determining in pine than in eucalyptus, according to the alkalization conditions used.

Acknowledgments:
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High added-value macromolecules from lignocellulose

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γ-valerolactone as a green solvent for the delignification of sugarcane bagasse

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Biorefineries based on lignocellulosic biomass have become relevant for reducing emissions and replacing fossil resources. Sugar platform biorefineries employ carbohydrates sugars derived from cellulose and hemicelluloses. Carbohydrates and lignin form a complex structure, so they must be separated by delignification using chemicals and specific experimental conditions. The application of green solvents is a strategy that will allow process optimization with minimal environmental impacts. γ-valerolactone is a promising candidate because it is a bio-based organic solvent with low toxicity, high water solubility, low melting point, high boiling point, and lower recycling costs [1]. This study evaluated γ-valerolactone as an organosolv treatment for the delignification of sugarcane bagasse. It could be a green option to include in a lignocellulosic biorefinery.

The delignification conditions of sugarcane bagasse in a mixture of γ-valerolactone and water were analyzed using a Draper-Lin central composite experimental design evaluating four factors: temperature, time, γ-valerolactone concentration, and sulfuric acid load. This last one was used as a catalyst in concentrations lower than 0.01M. The liquor/solid ratio was 10:1. Pulp yield, ISO brightness, total structural carbohydrates, lignin content, delignification percentage, intrinsic viscosity (η), and crystallinity index were evaluated as response variables.

Results showed that high levels of the variables produce lower yields, lignin content, and η (minimums values of 40.5 wt%, 2.32 % on dry basis (odb), and 140 mL/g,) in addition to higher brightness, delignification, and crystallinity index (maximums values of 58.1% 96.2%odb, and 80.0%). The η correlated with pulp yield (r=0.95) and crystallinity index with total lignin content (r=-0.98). The optimization for delignification, η, and glucans using the Desirability function indicated that the treatment at 152 ºC, for 60 min, 43 wt% of γ-valerolactone, and 0.0083 M of sulfuric acid produce theoretical maximums of 89%odb delignification, η=791 mL/g, and 84%odb of glucans in the pulp. These results prove that acid, even at low concentrations, is needed for delignification, and its effect is significant for all the response variables. However, there was an appreciable amount of shives, possibly because of the acid media.

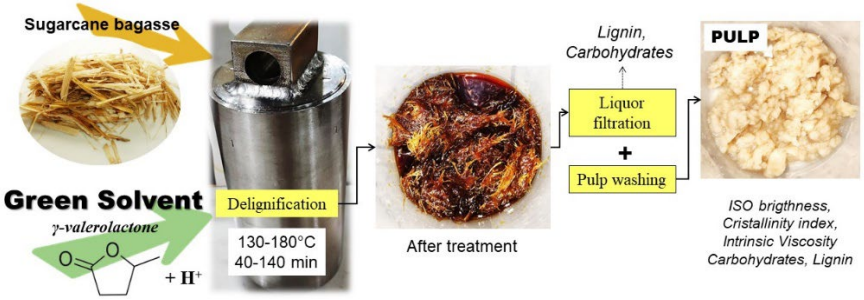

Figure 1. Applied methodology

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PLA / lignin biobased composites 3D printing for food packaging industry

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There has been great growth in waste from the agricultural industry due to the increase in the population, as well as the overproduction of food to meet the nutritional needs of this. To manage this waste, it is necessary to implement a circular economy model, that replaces the linear economy, where the waste generated is revalued, lowering by this the production costs. From agri-food, residues are possible to extract compounds such as cellulose, lignin, hemicelluloses, or different compounds.

In this work, the lignin contained in vine shoots is used to obtain PLA for the development of food packaging. Vine shoots are treated using a soda pulping method. The lignin contained in the residual liquors is obtained by an acid precipitation process. Once the lignin is isolated, a PLA-Lignin composite is generated for 3D printing. PLA granules are impregnated with lignin and introduced into an extruder obtaining a 2.85 mm diameter filament. This filament is used to make 3D printed packaging that has been digitally designed. This method allows easy addition of various components to the material used as the basis for the realization of any design, many of these materials being biodegradable.

With the development of this composite, the aim is to prolong the useful life of foods thanks to its antioxidant properties, as well as to study the variations in the mechanical properties of the PLA/lignin composite. To evaluate the mechanical properties, resistance tests are carried out using type 1BA specimens according to ISO 527-2. In addition, a global food migration study is carried out to indicate the protection capacity of the food composite against external agents.

Eucalyptus globulus leaves as source of chemical compounds with successive fractionation

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The chemical composition of the cuticular membrane in young and mature leaves of *Eucalyptus globulus* will be characterized after hydro-distillation for essential oil production. Leaves are covered by a continuous extracellular membrane of soluble and polymerized lipids called the cuticle or cuticular membrane, chemically consisting of waxes that serve as waterproofing barrier and the biopolyester cutin that functions as structural support. Cuticular waxes include very long-chain fatty acids (VLCFAs), their derivatives, and other secondary metabolites such as triterpenoids and flavonoids, while cutin consists of esterified fatty acids and hydroxylated and epoxy hydroxylated fatty acids mostly with 16 and 18 C chain lengths.

Young and adult leaves from *E. globulus* Labill. were collected from a eucalypt arboretum located in the fields of the School of Agriculture, University of Lisbon (ULisboa), in Lisboa. Whole fresh leaves were submitted to hydro-distillation. Extraction of cuticular waxes and cutin was made in the hydro-distilled whole leaves and isolated leaf cuticles after cellulases and pectinases treatment. The cuticular waxes were extracted with dichloromethane yielding a solution containing both epi- and intracuticular waxes, and cutin was depolymerised by a sodium methoxide-catalyzed methanolysis. The cuticular waxes and cutin monomers were analyzed by GC-MS.

The cuticular waxes obtained as dichloromethane-soluble extractives include mainly aliphatic compounds and some aromatics. Aliphatic molecules account for approximately 76% of the total cuticular wax compounds in adult leaves and cutin is composed mainly of aliphatic ω-hydroxyacids, representing approximately 69% of cutin [1].

The solid residue obtained after the removal of cuticular waxes and cutin was chemically analyzed regarding summative composition given a subsequent chemical valorization.

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Wood prehydrolysis in a flow-through reactor: hydrolysate characterization

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Hemicelluloses and other organics extraction from hardwood chips before kraft pulping process is usually done with hot water, dilute acid, or steam in kraft dissolving pulp production [1]. The obtained pre-hydrolysates are rich in different compounds, mainly in sugars (as hemicelluloses), glucose, and lignin. The capacity of recovering high-value compounds from this stream is important to enhance the sustainability of prehydrolysis-kraft (PHK) process, valorizing these compounds instead of using them to produce energy by incineration. For example, xylooligosaccharides (XOs) extracted from wood by enzymatic, hot water or acid hydrolysis treatment can be used as probiotics[2].

In this work, the prehydrolysis step was studied using both a flow-through reactor (FTR) and a batch reactor. In the FTR, different flowrates (residence time) and temperatures were applied to assess the effect of these parameters on the released compounds throughout the pre-treatment and to evaluate the best conditions to achieve the highest quantity of high-value compounds. The hydrolysates were characterized by High-Pressure Liquid Chromatography (HPLC) by following the release of xylooligosaccharides and monomeric sugars from the raw material in the process.

Results have shown that a lower residence time (higher flow rate) of the extracted compounds in the FTR provides XOs with a higher degree of polymerization (DP) (Fig 1) and lower amounts of xylose. On the other hand, the hemicelluloses extracted yield exhibit a low sensitivity to the prehydrolysis conditions; the yield range between 61% and 70%.

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Different kraft lignins sources for electrospun nanoestructure production

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The large quantity of residual lignin generated mainly from the pulp and paper industry is currently underexploited. Normally, it is burned to produce energy i.e., heat and electricity, which covers part of the needs of the pulping industry. However, about 60% of residual lignin is left over after supplying the requirements of this industry. Therefore, the search for the valorization of this residual lignin into high value-added products is currently on the rise. In this context, the production of lignin nanostructures by the electrospinning technique can extend or improve the applications of this waste. For example, in the case of biolubricants production (where lignin can act as a thickener in the mixture with vegetable oil), the high porosity, small size, and high surface/volume ratio of the lignin nanostructures could induce the formation of a three-dimensional network with a much greater capacity to promote physical interactions between the oil and the thickener.

This work studies the influence of the characteristics of different residual Kraft lignins (from eucalypt, poplar, and olive tree pruning, OTP) on the electrospinning process to obtain nanostructures. Firstly, the different Kraft lignins (KL) were characterized by ^{1}H, ^{13}C NMR, and two-dimensional NMR, SEC, FTIR, TGA, and DSC; and their chemical composition was also analyzed by standard analytical methods. As it is known, the addition of cellulose acetate (CA) improves the electrospinning process of lignins. Therefore, solutions of KL/CA solutions at 30 wt.% and with a KL:CA weight ratio of (70:30) were prepared and then were physicochemical and rheologically characterized. After, the resulting lignin/CA electrospun nanostructures were morphologically characterized by SEM.

Results showed that electrospun membranes based on eucalypt/CA and poplar/CA showed uniform nanofibers with a few beaded fibers and cross-linked, while electrospun OTP/CA membrane presented micro-sized particles connected by thin fibers. Understanding the properties of these nanostructures could help to optimize their use in different applications including biolubricants production.

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Intensification of the lignocellulosic biomass fractionation process with ethanol-water by liquor reuse

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The pre-treatment is a key step in the lignocellulosic biomass (LCB) preparation for hydrolysis and sugar conversion. The main drawback of pre-treatments is the costs of energy and product concentration stages. In the case of the water-solvent fractionation treatment, the increase of the energy involved in the solvent recovery is relevant. An approach to address this handicap is to re-use the spent liquor as cooking liquor for successive treatment steps by feed-backing a fraction of the spent liquor of the previous stage. However, this reuse can lead to an accumulation of several compounds, which can negatively affect subsequent stages of the lignocellulosic waste valorization, such as the fermentation stage. In a previous work [1] LCB fractionation with ethanol-water (EW) including liquor re-use (EWR) was studied. In this work, EW and EWR fractionation processes are compared counting energy, water, and ethanol needed. Process simulation was implemented in Aspen Plus v9.0 for a plant processing 100 ton/d of dry wheat straw for several L/S ratios. Experimental conditions for EW and EWR and yields are given elsewhere [1].

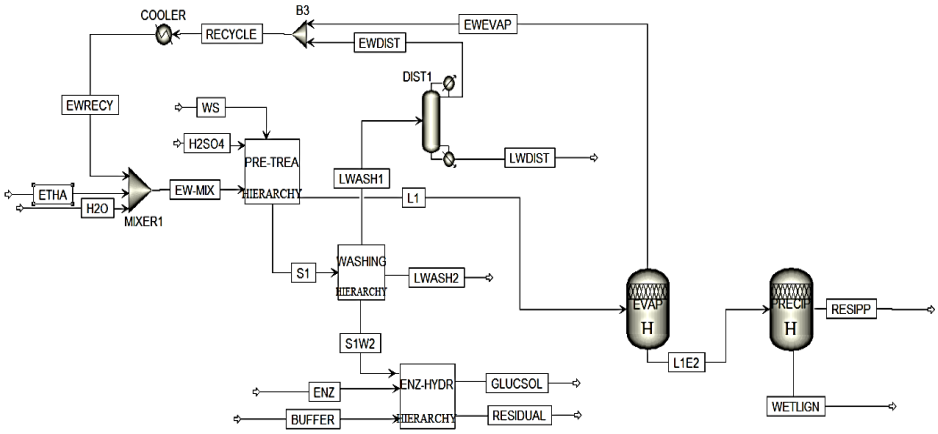

Figure 1. EW process flowsheet

A Non-random two-liquid property method was used and components in Aspen database were used. ASPEN Plus EWR implementation was conducted by considering batch pre-treatment reactors. Each pre-treatment mass balance considers the experimental yields. The spent liquor of the n-1th pre-treatment step is used in the nth step. The results of the economic and energy comparison yield clear advantages for the EWR compared to the EW treatment, with savings of 35-40% in energy (depending on the L/S used), 57-68% in ethanol consumption, and only a small increase of 6-8% in water consumption. Equipment expenses also decrease with an impact of a 6-13% reduction in costs.

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Obtaining furfural by isothermal autohydrolysis from agricultural by-product

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The peak of circular bioeconomy in the production of high added-value compounds and biofuels has been made evident due to new policies of several countries in the reuse, valorization, sustainability of biomass as raw material, and the biorefinery [1]. Furfural could be obtained from lignocellulosic biomass and this chemical is one of the key "green" in biorefinery [2, 3]. Furfural is the only organic compound derived from biomass that can replace the crude oil-based organics used in industry [4]. One of these biomasses is wheat straw, an underused agricultural by-product, which is an interesting raw material due to its abundance.

The objective of this work was to apply an environmentally friendly fractionation process to obtain furfural from wheat straw. Specifically, isothermal autohydrolysis (temperature 220-250ºC and residence time 0-60 min) was used to solubilize hemicelluloses as xylooligosaccharides and pentoses (principally xylan and araban). They were dehydrated for furfural [5].

A central composite experimental design was used to optimize furfural production. With this design, not only the best-operating conditions were obtained (time of 0-47 min to reach the isothermal operation temperature- and temperature of 220ºC), but it was also observed the increase in severity factor RO drecreased the content of furfural, xylose, and hemicellulose extracted in the liquid phase, by the degradation of hemicellulosic derivatives.

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Membranes

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Combined effects of glycerol/sorbitol plasticizers on the properties of cnf films

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This study aimed to evaluate the effect of plasticizers on the properties of cellulose nanofibers (CNF) films. CNF was produced from ECF bleached commercial pulp by TEMPO-oxidation and mechanical fibrillation. The films were obtained by a solvent casting technique and dried at 50°C. The mixtures included the CNF suspension with glycerol/sorbitol (G/S): 0G/50S, 10G/40S, 20G/30S, 30G/20S, 40G/10S, and 50G/0S. Further, for evaluation of the effect of drying temperature, samples 50G/0S were dried at 25°C (air drying) and 60°C (oven-drying). The film characterization comprehended physical-mechanical properties, optical behavior, water absorption, water vapor barrier (WVP), and aerobic biodegradation in the soil (period: 25 days).

The film thicknesses obtained were in the range of 23.0-65.0 µm. All films except those dried at 25°C showed air bubbles (Figure 1. a). The incremental drying temperature increased the diameters of air bubbles: 587-875 µm (50°C), and 627-1167 µm (60°C). The highest temperature developed more quantity of air bubbles. The transmittance at 600 nm values was reduced with the addition of plasticizers, obtaining decreases of about 26% in 50G/0S films and 7% for 0G/50S. The plasticizers addition decreases the E modulus values in all cases showing that the elasticity increases with the addition of the polyols. The highest decrease was for the application of 50% w/w of glycerol with a reduction of 92.7% (E=0.36 GPa). The opposite effect occurs with sorbitol, where the E modulus values are higher as the sorbitol load increases (E= 0.87 GPa for 50% w/w sorbitol).

The plasticizer addition influenced the barrier properties. The samples containing glycerol decreased their WVP as the percentage added increased until reaching a minimum with the load of 50% w/w glycerol (43.5 g/m^2 day kPa). The sample with only 50% w/w sorbitol did not vary significantly from the control (WVP=201g/m^2 day kPa). The water absorption decreased for plasticized films, the decrease being higher with increasing sorbitol load (up to 30.4% decrease for 0G/50S sample). The film's biodegradation after 25 days reached values of about 50% in weight loss. Although no significant difference was observed between samples, upper values were obtained for glycerol higher content films.

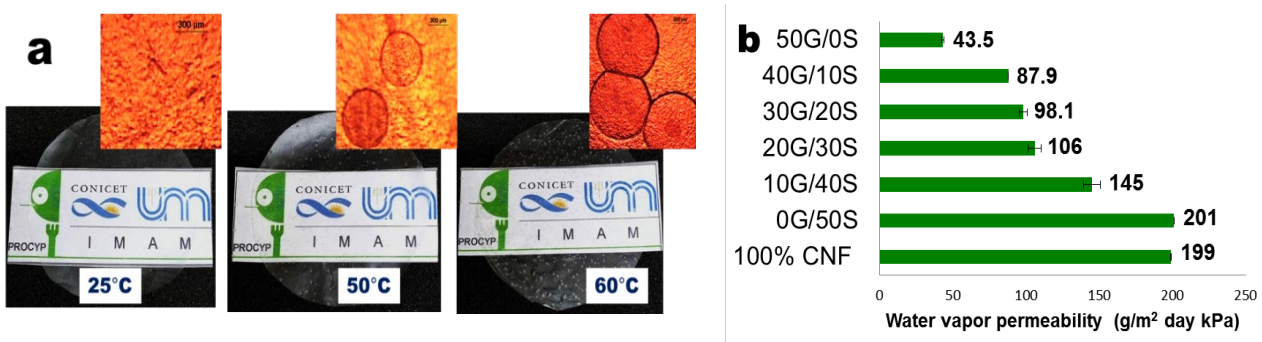

Figure 1. a) Films 50G/0S dried at different temperatures, and b) WVP values

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Influence of lignin content and plasticizer load in nanocellulose/sorbitol films

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This study evaluated the effect of adding incremental loads of sorbitol on the final properties of cellulose and lignocellulose nanofibers (CNF and LCNF). Unbleached (Kappa number: 20) and bleached (Kappa number: 3.1) pine pulps were TEMPO-oxidized and nanofibrillated using a colloidal grinder. Films were acquired from each nanocellulose suspension by solvent casting using varying loads of sorbitol (25% w/w and 50% w/w). The samples were dried at 50°C. The film characterization included: physical-mechanical properties, water vapor barrier behavior (WVP), optical characteristics, and biodegradation after 25 days. Overall migration limit (OML) (to evaluate the application in food packaging) was measured using distilled water, 15% v/v ethanol, and 3% w/w of acetic acid as food liquid simulants.

Films thicknesses were in the range of 23.0-79.0 µm. The incremental loading of sorbitol improved the elasticity of the films ($p<0.05$) (Figure 1): 4.90 GPa (100% CNF)-0.87 (CNF + 50% w/w), and 2.82 GPa (100% LCNF)-0.89 GPa (LCNF + 50%w/w). The nanocellulose type and sorbitol loading significantly influenced ($p<0.05$) the transmittance at 600 nm (T_{600}). The total color difference (ΔE) was influenced only by the nanocellulose type (ΔE=3.27-3.74 in CNF, and 6.00-7.08 in LCNF). The T_{600} values decreased with sorbitol addition up to 10% for the highest sorbitol load.

The WVP values varied from 99.4 to 201 g/m^2 day kPa. The sorbitol load showed significant differences ($p<0.05$): the 50% w/w load showed a negative effect since it increased the WVP value compared to the controls. The type of nanocellulose did not significantly influence WVP values, but the trend showed lower values for CNF films. The biodegradation after 25 days increased with the addition of sorbitol, of up to 50.7% in weight loss. The sorbitol addition increased the OML value over the limit for all simulants (OML>100 mg/Kg for 25% w/w sorbitol, OML>200 mg/Kg in 50%w/w sorbitol films).

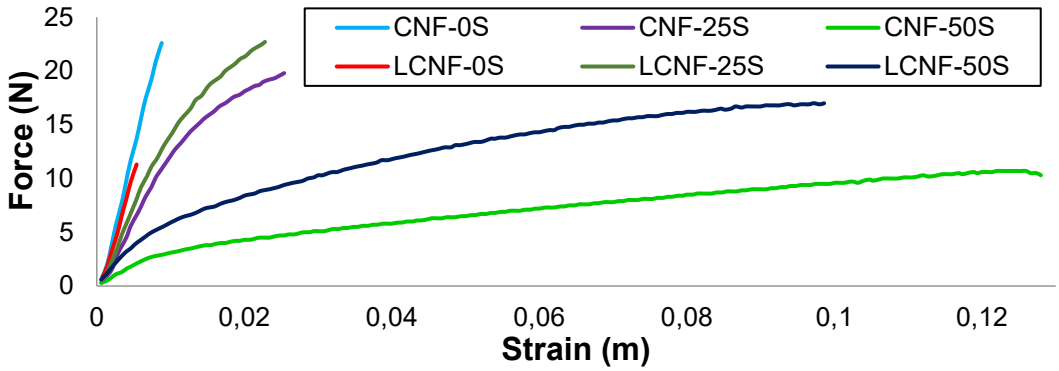

Figure 1. Force vs. Strain for all films

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Plasticizer polyols/mfc films production for single-use primary food packaging

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This study evaluated the changes in physical, mechanical, optical, and barrier properties of microfibrillated cellulose (MFC) films whit food-grade polyols addition. MFC was obtained from pine sawdust pulp using a simple disk refiner. The films were acquired by solvent casting mixing 75%w/w MFC and 25% w/w of three polyols (sorbitol, mannitol, and glycerol) and dried at 50°C. The characterization included: physical-mechanical properties, optical behavior, and water vapor permeability (WVP). Finally, the aerobic biodegradation in soil of films was evaluated (15 days period).

The visual appearance of films varied according to the applied polyol (Figure 1. a). The combinations between MFC and sorbitol had a similar appearance to the control. In the case of the sample containing glycerol, the films mostly stuck to the Petri dishes, making it difficult to remove them. The films were sticky and ripped without effort. The mannitol films were very brittle, with typical white spots of the polyol crystallization in the framework. Significant differences were observed in the film's transmittance values at 600 nm ($p<0.005$), being higher for the samples with the addition of sorbitol (T_{600}=9.23%) and mannitol (T_{600}=13.4%). However, the values for the films with the addition of glycerol (T_{600}=5.97%) were lower than the control (T_{600}=3.87%).

The thickness range was 26.0-48.0 µm. The addition of sorbitol and glycerol increased the elongation at the break of the films (8.25% and 23.7%, respectively). The tensile index values decreased when adding the plasticizers obtained (up to 80% lower). The E modulus values decreased 25.2% with the addition of sorbitol and 52.9% with glycerol (an increase of elasticity in both cases). The addition of mannitol increased 5.13% E modulus concerning 100% MFC film (Figure 1. b).

The incorporation of polyols in MFC decreases the WVP in all cases ($p<0.005$): 180 g/m^2 day kPa (100% MFC), 118 g/m^2 day kPa (sorbitol), 92.0 g/m^2 day kPa (glycerol), and 159 g/m^2 day kPa (mannitol).

All samples showed evidence of biodegradation. The MFC films combined with sorbitol and glycerol reached 100% biodegradation after 15 days. The MFC/mannitol films attained a weight loss of 72.3%.

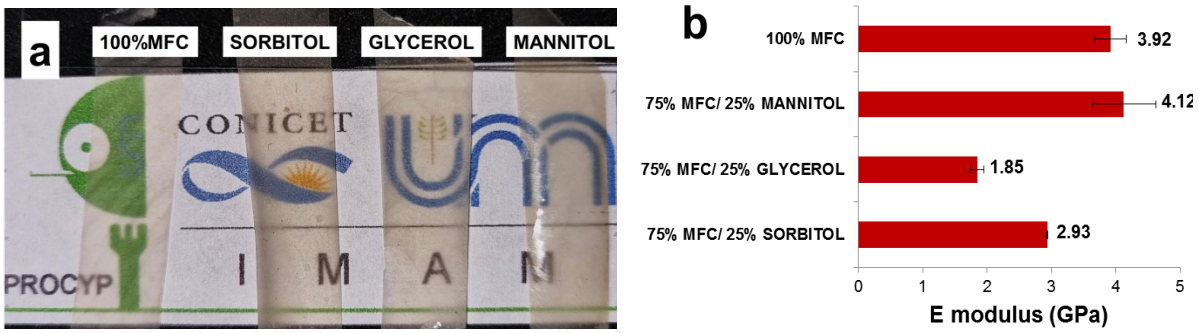

Figure 1. a) Optical aspect for films, and b) E modulus values

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Improving nanocellulose film properties by adding isolated kraft lignin

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Nowadays, there is a strong need for replacing petroleum-based plastic materials with renewable, biodegradable, and bio-based ones, to cope with environmental pollution and ecological problems. Biopolymers made from lignocellulosic biomass could be used as a sustainable alternative. Specifically, nanocellulose is one of the most versatile bioproducts that can be obtained in a lignocellulosic biorefinery. Strong, transparent, and flexible films can be produced from nanocellulose. However, these films did not present active properties such as antioxidant capacity and UV-shielding, which are required for some applications, especially in food packaging. For this reason, the addition of some compounds such as lignin, a subproduct generated in lignocellulosic biorefineries and pulp industries, can provide these properties to nanocellulose films.

The objective of this work was to produce nanocellulose films with enhanced properties by adding isolated kraft lignin. For that, nanocellulose (denoted by TOCNF) was produced from *Eucalyptus globulus* bleached kraft pulp by TEMPO-mediated oxidation pretreatment followed by microfluidization. On the other hand, the black liquor obtained during the pulping process was used to isolate kraft lignin by acid precipitation. Then, two different protocols for the addition of lignin to TOCNF suspension were compared. In the first one, the TOCNF suspension (0.3%) was mixed with a 0.3% aqueous suspension of kraft lignin. In the second one, lignin was diluted in acetone: water (9:1) before the addition to the aqueous TOCNF suspension to allow the formation of lignin nanoparticles (LNP) by solvent shift. For each protocol, the resulting materials were used to prepare films with increasing concentrations of lignin: 2.5%, 5%, 10%, and 20%. Finally, films were characterized by FTIR spectroscopy and TGA, and their antioxidant capacity and water vapor permeability (WVP) were determined.

It was observed that the addition of lignin to the TOCNF suspension improved barrier properties (lower WVP) of the resulting films, especially when lignin was in form of nanoparticles: $1.6 \cdot 10^{-11}$ $gm^{-1}s^{-1}Pa^{-1}$ for TOCNF and $1.3\text{-}0.9 \cdot 10^{-11}$ $gm^{-1}s^{-1}Pa^{-1}$ for TOCNF with LNP. However, when bulk lignin was added at a high load (20%) a negative effect was observed in WVP ($2.0 \cdot 10^{-11}$ $gm^{-1}s^{-1}Pa^{-1}$). On the other hand, the antioxidant capacity of lignin-containing films was directly related to the lignin content, increasing to a greater extent when lignin was present in the films in form of nanoparticles (34.7 mg Trolox equivalent per g of a film with 20% LNP) compared to bulk lignin (26.4 mg Trolox equivalent per g of a film with 20% lignin). Finally, similar slight increases in thermal stability were observed when either LNP or bulk lignin was added. Therefore, the addition of lignin by forming LNP in-situ in the TOCNF suspension seems to be a more efficient protocol for improving nanocellulose film properties

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Exploring Agro-industrial by-products to Produce Novel Electroconductive Nanomaterials

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Nanocellulose is a promising material for producing biocomposites due to its mechanical properties. By decorating nanocellulose surface with conducting polymers a new generation of materials with a wide range of applications can be obtained. Among those polymers, Polypyrrole (PPy) is especially promising for commercial applications due to its facile synthesis, high conductivity, and biodegradability. In this work, we show how conductive cellulose-based nanopapers can be obtained. Three different kinds of highly oxidized cellulose nanofibers (CNF) are involved in the chemical polymerization induced adsorption process of PPy on the surfaces of oxidized CNFs in aqueous media. The resulting CFN/PPy nanocomposite was evaluated by X-ray photoelectron spectroscopy (XPS), Fourier transformed infrared (FTIR) spectroscopy, scanning, and transmission electron microscopy (SEM and TEM respectively), Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy. Morphological characterization clearly shows the formation of core-shell structures in which PPy nanoparticles are covering the CNF's surface. The resulting CNF/PPy nanocomposites presented diameter sizes in the range of 70 – 90 nm, which are relatively higher in comparison to the initial CNF's diameters. XPS analysis shows a centered N1s peak at 399.1 eV indicating a successful integration of PPy in the CNF structure. FTIR spectra show signals around 3350 cm^{-1} and 1600 cm^{-1} which indicate that CNF has changed into CNF/PPy nanocomposite. Moreover, electrochemical characterization indicates that the composite fabricated exhibits excellent electrical conductivity in comparison to uncoated CNF or pure PPy. The resulted CNF/PPy nanocomposite synergistically combines the electronic characteristics of conducting polymers with the structural advantages of bio-based cellulose polymers. This nanocomposite is being explored as a matrix for the chemical and electrochemical deposition of metal nanoparticles. Finally, in this work, we show that these nanocomposites are useful for developing sensing devices.

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Nanocellulose applications

Nobel nanocellulose-based separators for Lithium-Sulfur batteries (LISA Project)

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On the one hand, Lithium-Sulfur batteries (LSBs) have received increasing attention over the past years due to their extraordinary theoretical energy density (2600 W h kg^{-1}), and theoretical specific capacity (1675 mA h g^{-1}), environmentally friendliness, and low cost. However, LSBs also present several drawbacks such as polysulfide (PS) shuttling, swelling cathodes, thermal runaway, and Li dendrites formation among others [1]. Studies to tackle these problems have been focused to improve electrodes or electrolytes but also to modify and prepare new separators able to stop PS diffusion. On the other hand, nanocellulose (NC) based materials are promising candidates for LSBs due to natural abundance, low-cost production, chemical modification, and good mechanical and thermal properties [2]. Moreover, NC chemical structure can improve electrolyte's wettability compared with commercial polyolefin separators to avoid the PS shuttle effect [3]. In LISA project, a European H2020 project formed by 13 partners, NC-based separators are fabricated via electrospinning for LSBs. Electrospun NC nanofibers membranes can provide tuneable thickness, porosity, and mechanical strength among other properties, which are crucial properties to LSBs separators. Finally, and according to the electrochemical tests, it is demonstrated that these separators are promising for LSBs.

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Cyto-genotoxic effects of distinct micro/nanocelluloses in human osteoblastic and mice fibroblastic cells

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The unique characteristics of micro/nanocelluloses (MNCs) have been boosting their use in a wide variety of industrial and biomedical applications. With the expected decrease in their production cost, it is likely to observe an even faster-growing adoption of these materials in the coming years.
With the increasing use of MNCs comes an increased likelihood of human exposure to these materials, raising concerns about potential human health effects. The number of studies on the potential adverse effects of MNCs is still scarce and sometimes inconclusive.
The present study aims to shed some light on the impact of human exposure to cellulose-based nanomaterials. For that, three MNCs were produced from bleached *Eucalyptus* kraft pulp using different pretreatments. A microfibrillated (CMF) and a nanofibrillated cellulose (CNF) were respectively obtained by enzymatic and TEMPO-mediated oxidation pretreatments followed by high-pressure homogenization. In addition, cellulose nanocrystals (CNC) were obtained by acid hydrolysis with diluted sulfuric acid.
The potential cytotoxicity of the MNCs was evaluated *in vitro* in two mammalian cell lines (human MG-63 osteoblasts and mice V79 lung fibroblasts) by the MTT and the clonogenic assays, and the genotoxicity was assessed by the micronucleus assay.
Cytotoxicity was observed by the clonogenic assay in V79 cells, particularly for CNC, but not by the MTT assay. CNF induced micronuclei in both cell lines and nucleoplasmic bridges in MG-63 cells. CMF and CNC induced micronuclei and nucleoplasmic bridges in MG-63 cells, but not in V79 cells.
From the results, it was concluded that under the tested conditions all MNCs present cytotoxicity and genotoxicity, although at different concentration levels, which may be related to their physicochemical differences, to the availability for cell uptake, and differences in the DNA damage response of the cell model.

Acknowledgments

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Hybrid nanocellulose/CuO aerogels with antimicrobial properties by Colloidal Processing

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The current work investigates the possibility of creating cellulose-based three-dimensional structures incorporating copper oxides nanoparticles (CuO NPs) with a contact-active antimicrobial functionality. Such materials are suitable for applications in which a porous structure combined with antibacterial properties is desired, for example, in packaging, hygiene and healthcare products, filtering media, and so on.

In this sense, an innovative colloidal processing route has been proposed to manufacture nanocellulose/CuO hybrid aerogels from high homogeneous and well-dispersed suspensions. The loading and immobilization of CuO NPs on cellulose nanofibers (CNFs) were carried out in a previous wet step through a heterocoagulation methodology and then the inorganic-organic heterostructures were shaped by a conventional freeze-drying method.

To improve the dispersion/stabilization in liquid media and to favor the electrostatic interaction between CuO NPs and CNFs, the surface of CuO was modified by adsorbing different amounts of a cationic polyelectrolyte (polyethylenimine, PEI). The CuO-PEI suspension was added to a CNF dispersion at different percentages on CNF dry weight causing a three-dimensional and attractive network between both components.

Finally, the antibacterial activity of the different spongy samples was analyzed for *Escherichia coli*. The resulting aerogels were additionally characterized in terms of physical, and mechanical properties, chemical structure, and morphology.

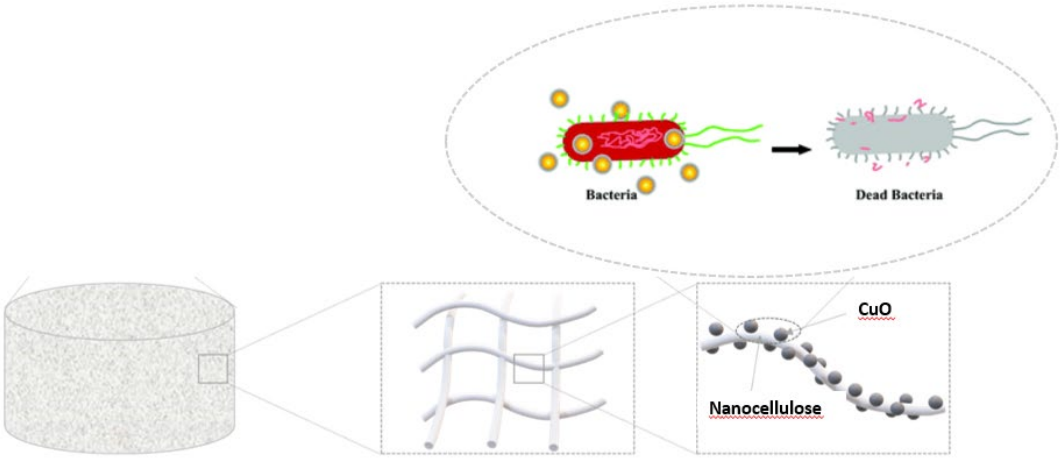

Figure 1. Hybrid aerogels as inorganic-organic heterostructures with antimicrobial properties

Nanocellulose production and modification

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Evaluation of Fibrillar Nanocellulose (NCF) of Bolaina blanca (*Guazuma crinita)* wood from a plantation in Ucayali, Peru.

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Currently, a part of society has a predisposition to use eco-friendly products. Therefore, there is great interest in seeking natural sources with high availability capable of being used compatibly in industries that produce products suitable to replace and/or reinforce traditional ones.

Cellulose is the most abundant renewable polymer on the planet, used in a wide variety of applications. It has been demonstrated that cellulose at a nanometer scale has quite attractive characteristics for being light, strong and with mechanical properties superior to other materials such as Young's modulus and tensile strength with values of 130 GPa and 7.5 GPa respectively at an average density of 1.6 g/cm3 [1]. The topic of nanocellulose is a field of research with many advances and contributions, however, there are still potential sources of cellulose that require greater depth of knowledge for the elaboration of this material, such as the lignocellulosic sources found in different crops of forest species that are currently being promoted, such as crabgrass.

The “bolaina blanca” is one of the species with the highest production in Peru, due to its rapid growth and being harvestable from an early age. It is also a type of wood of great demand, used in construction, furniture, and moldings. According to FAO in 2011, in Ucayali alone, the production of this species increased by 500%, and its demand raised from 20,000 to 110,000 m^3/year between 2006 and 2011.

Taking as a premise the potential production of “bolaina”, it is necessary to promote its use for the creation of products other than timber products. All this is to originate products with added value in a world market that shows a tendency in biodegradable products to reduce global pollution.

In the present research, fibrillar nanocellulose (NCF) was obtained from “bolaina blanca” (*Guazuma crinita*), providing data on the conditions of its synthesis by mechanical treatment, as well as its characterization by analytical techniques (SEM, XRD, TGA, FTIR, UV-Vis).

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Ozonization as alternative pretreatment in the production of cellulose nanofibers

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Cellulose nanofibers (CNFs) are nanomaterials produced from a wide variety of cellulose sources, using different types and intensities of pretreatment, and varying the severity and types of mechanical treatments. The applications where CNFs can be used to improve the final product properties are varied (such as papermaking, biomedical applications, food industry, oil absorption) due to their exceptional properties, such as high strength, surface area, reactivity, transparency, biodegradability, or renewability, among others [1]. Nowadays, the most used process to obtain highly fibrillated CNF is those that use a chemical pretreatment that facilitates the subsequent fibrillation using mechanical fibrillation. Among these chemical pretreatments, TEMPO-mediated oxidation (TMO) is the most relevant using sodium hypochlorite as oxidant and TEMPO and NaBr as catalysts. However, the TMO reaction also presents several drawbacks, and many factors could be studied to make the process more sustainable such as the recovery of catalysts, the minimization of reagents and catalysts, the reduction of reaction times, or the use of alternative pretreatments to maintain the quality of CNFs.

An alternative pretreatment to TMO is the use of ozone. Ozonization is commonly used as a bleaching agent in papermaking because of its high oxidizing power. Ozone removes the lignin but, at the same time, produces partial depolymerization of the cellulose, and the removal of amorphous cellulose, to a higher extent than the use of chlorine [2]. These facts would justify the use of ozonization as pretreatment of the cellulose pulp to facilitate the subsequent mechanical treatment. Northern bleached softwood kraft (NBSK) pulp was first refined before the ozonization for 2 hours at pH 5-6, due to the sample was not possible to pass by high-pressure homogenization (HPH) without the previous refining due to the clogging of the equipment. Results show a slight increase of carboxyl groups from 0.12 to 0.26 mmol/g pulp and a decrease in the polymerization degree from 1150 to 480 monomers from the sample only refined to the sample also ozonized. CNFs obtained after HPH still have some clogging problems requiring the dilution of the sample until 0.7%. In addition, a higher ozonization time produces the decarboxylation of the C6 of the anhydroglucose units [3].

These results make us to consider other options such as the use of TEMPO and NaBr to accelerate the ozone reaction and produce BrO^- ions which led to oxidize the cellulose. This reaction must be carried out at alkaline pH to reduce the production of bromates in the reaction with the ozone [4]. Results showed that although the carboxyl groups are maintained, the polymerization degree decreased up to 200 monomers, facilitating the HPH around 1% consistency without clogging.

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Bacterial nanocellulose production: properties on static and agitated processes

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Bacterial nanocellulose (BNC), due to its characteristics and its high potential for functionalization, has proven to be a remarkably versatile and attractive biomaterial for different applications, such as surface coating of different materials, manufacturing of composites, etc. BNC can be obtained with several microorganisms under different. There are two possibilities as to how to carry out the production process, in static or with agitation, being the first one much more studied than the second process. In static production, several microorganisms and carbon sources have been studied, together with the medium composition and operational conditions (pH and temperature) [1]. However, there is no clear comparison of the characteristics and properties of the BNC obtained by both static and agitated operations. In this work, these characteristics are compared.

Experimental runs have been performed on both production processes, using *Komagataeibacter sucrofermentans* CECT-7291, with a Hestrin-Schramm medium (HS), a pH of 5.5, and a temperature of 30 ºC. In the case of agitated production, the runs have been performed in Erlenmeyer in a shaken incubator at different agitations. BNC production was evaluated under dynamic conditions considering the effects of agitation on production yield, on the characteristics and physical, optical, and surface properties using standardized analytical methods. As a control, the properties of commercial vegetal nanocellulose (CVN) and BNC produced in static conditions were analyzed. In addition, the storage in activated state of the strain was evaluated, for which the BNC obtained in the first cycle was compared with that produced with the microorganism stored in activated form for 5 cycles.

The results obtained showed marked differences at the macroscopic level when evaluating the main effects of different agitation speeds and cell aging on BNC production. In addition, a 45% increase in BNC production yield was found when using 80 rpm agitation, so this speed was considered optimal among those studied. At 120 rpm, a notable decrease in performance was observed, as well as a delay in the appearance of the first signs of BNC production. No significant differences were observed in the physical properties (grammage, thickness, crystallinity, and composition) between the different BNC obtained. However, differences in viscosity (degree of polymerization) were observed, related to the dispersion method used to obtain the suspensions, but not to the production conditions evaluated. On the other hand, after 5 cycles of active storage, the production yield was reduced, although its maximum production was also observed with agitation of 80 rpm. This may be related to the fact that *K. sucrofermentans* strains stored in activated form can be affected by bacterial senescence or spontaneously transformation into non-cellulose-producing mutants.

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Effect of homogenization pressure on the obtaining of cellulose micro/nano fibrils. Interaction with a natural complex.

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Cellulose-based materials such as cellulose nano/micro fibrilar (MNFCs) can be used in novel applications in various technological fields. The use of CNFs intended for the substantial improvement of paper properties is the one that promises the highest volume of consumption. In this work, the effect of the pressure of the homogenizer on the characteristics of the micro/nanofibrillar celluloses (CMNFs) obtained from a commercial bleached eucalyptus pulp (BEP) was evaluated. For this, a chemical pretreatment was performed using oxalic acid at two concentrations: 25 wt.% and 50 wt.% followed a mechanical pre-treatment using a PFI mill refiner at 10,000 revolutions. The fibrillation process was performed using a high-pressure homogenizer at 0.75 wt.% of consistency, with the following sequence: 2 passes at 300 bar, and then, 3 passes at 300, 600, and 900 bar. Therefore, six different CMNFs were obtained, which were characterized with measurements of nanofibrillation yield by centrifugation, the transmittance at 800 nm, surface charges using z-potential, and size by dynamic light scattering (DLS). The results show that when the pressure of the homogenizer increases and the concentration of oxalic acid (50 wt.%), the nanofibrillation yield, transmittance, and surface charges values of the CMNFs increase, and the hydrodynamic diameter decreases. In addition, cationic polyelectrolyte complexes (PECs) were formed by adding the chitosan solution (CS) to xylan (X) solution, at pH 5.0, under continuous stirring and with a mass ratio CS/X of 20/80. The charge and size of the PECs were determined using a zetasizer nano. The results were +4.7 mV and 314.6 nm. Then, the colloidal interaction between CMNFs and PECs was analyzed by curves of turbidity and surface charges. Finally, the retention and drenability of CMNFs when it was added to recycled unbleached softwood fibers and different dosages of PECs were studied in a Britt Dynamic Drainage Jar system at pH 7,0 and 0.01N NaCl. It is desired to obtain high retention values of the CNFs with an acceptable drainage rate in the formation process, aspects that are critical in the application of CNF in the paper.

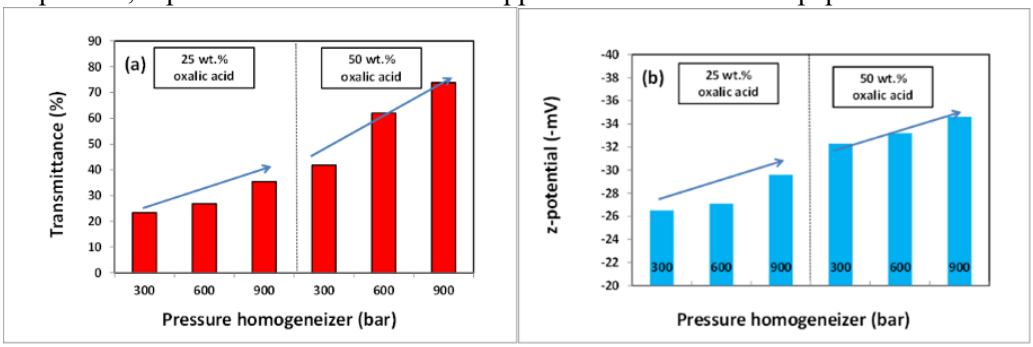

Figure 1. (a) Transmittance and **(b)** z-potential of CMNFs dispersions as a function of high-pressure homogenizer.

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Biotechnology for the production of bacterial cellulose

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Cellulose is the main component of biomass. The use of cellulose has grown over the last decades and continues to increase thanks to its availability, intrinsic properties, and the sustainability and renewability of its resources, mainly from trees and plants. The natural association of plant cellulose with hemicellulose and lignin can be a drawback in some cases [1]. Instead, bacterial cellulose possesses some characteristics that can be favorable, compared to plant cellulose, such as purity, crystallinity, and degree of polymerization, also with numerous applications in medicine and industry [2]. Among different bacteria, the genders *Acetobacter* and *Gluconacetobacter* are regularly used to produce forms of bacterial cellulose. Still, however, high production costs due to culture media, low yields, and operative costs are present in the regular production of bacterial cellulose. In the current work, agro-industrial residues were tested as nutrients for the production of bacterial cellulose using *Komagataeibacter xylinus* bacteria [2, 3]. Pellicles of bacterial cellulose was extracted in the Hestrin-Schramm medium, and compared to those from alternative media formulated with different carbon sources. In particular, hydrolyzed liquor from asparagus husks (LHE) and artichoke bracts (LHA), with reducing sugar content of around 12-13 g/L were tested as carbon sources. Yields of nearly 2 g/L were obtained after 21 incubation days. Bacterial cellulose pellicles made of homogeneous, compact, and 3D structures of micro and nano cellulose fibrils were extracted. FTIR spectra of the bacterial cellulose corresponded to type I cellulose fibrils, with crystallinity index of about 86% and 82%, respectively for LHE and LHA carbon sources. The results demonstrate that agro-industrial residues such as asparagus husks and artichoke bracts can replace expensive substrates in the production of bacterial cellulose by using *Komagataeibacter xylinus* bacteria. The final bacterial cellulose pellicles and films revealed remarkable physical and morphological properties.

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