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# **Treball Final de Grau**

Production of high value-added nanocellulose from agriculture biomass waste

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Primer de tot, m'agradaria agrair a tota la meva família el suport incondicional que m'han proporcionat sempre, tan en els bons moments però sobretot en els dolents.

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## SUMMARY

With the growing concerns about the environmental effects of fossil-oil based products, the research for a more sustainable source has started. In that context, biomass is a possible sustainable resource since it is an abundant and renewable material. Biomass is defined as any organic material that comes from plants or animals, such as wood, forest and agriculture residues or energy crops.

Lignocellulosic biomass is formed by three principal compounds (cellulose, hemicellulose, and lignin) that can be used as raw materials for bio-based products. Bionanomaterials are an interesting bio-based products since reducing materials to nanoscale can improve the properties of those products. Cellulose for its properties, such as high mechanical strength, high crystallinity and aspect ratio, and its biodegradability is an interesting material to convert to the nanoscale, producing nanocellulose. Depending on the production process different types of nanocellulose exist, such as cellulose nanocrystals, cellulose nanofibrils or bacterial nanocellulose. Nanocellulose is an interesting nanomaterial for the variety of applications in different industrial fields like biomedical, electronic and composite industries

This work is focused on designing a process to produce cellulose nanocrystals and nanofibrils from agriculture biomass wastes. Different alternatives have been studied from bibliographical resources in order to be able to design a sustainable and productive process. The process design is separated in three main stages, selection and preparation of the raw material, pre-treatment of the lignocellulosic biomass to separate its main compounds and production of the nanocellulose.

**Keywords**: Nanocellulose, cellulose nanocrystals, cellulose nanofibrils, agriculture biomass wastes, hemicellulose, lignin

# RESUM

El creixement de la preocupació per l'efecte mediambiental dels productes derivats dels recursos fòssils, ha obert la porta a la recerca de fonts més respectuoses amb el medi ambient. La biomassa ha sorgit com una opció de producció de productes derivats sostenible perquè es un material renovable i abundant en la naturalesa. La biomassa es pot definir com qualsevol material orgànic de procedència animal o vegetal, alguns exemples podrien ser la fusta, els residus forestals o agraris.

La biomassa lignocel·lulósica està formada per tres components principals com són la cel·lulosa, hemicel·lulosa i la lignina, que es poden utilitzar com a matèria prima per la producció de materials de base biològica. Dins d'aquests biomaterials els d'escala nanomètrica són molt interessant, ja que poden millorar les propietats dels materials on s'implementin. La cel·lulosa, per les seves propietats com l'alta resistència mecànica, alta cristal·linitat o que es un material biodegradable fa que sigui molt interessant transformar-la a escala nanomètrica per obtenir nanocel·lulosa. Depenen del procés que s'utilitzi per produir nanocel·lulosa se'n poden obtenir diversos tipus com la cel·lulosa nanocristal·lina, la cel·lulosa nanofibrilada o la nanocel·lulosa bacteriana. La nanocel·lulosa té aplicacions en industries d'àmbits molt diferents, des de la biomedicina fins l'electrònica.

L'objectiu d'aquest treball és el disseny d'un procés per la producció de cel·lulosa nanocristal·lina i nanofibrilada a partir de residus de biomassa agrària. S'ha estudiat les diverses alternatives existents per poder dissenyar un procés que sigui sostenible i productiu. El procés dissenyat es pot separar en tres seccions, selecció i preparació de la matèria prima, pretractament de la biomassa per separar els components principals i la producció de nanocel·lulosa.

**Paraules clau**: Nanocel·lulosa, cel·lulosa nanocristal·lina, cel·lulosa nanofibrilada, biomassa, residus de biomassa agrària, hemicel·lulosa, lignina

# **1. INTRODUCTION**

### 1.1. BIOMASS A GREEN RESOURCE

Nowadays, society is based on products from fossil resources, but with the growing concerns about environmental pollution that is produced during the production process and the products life cycle of fossil-based products, the research for a more sustainable source has been one the public eye on the recent years. In these conditions, biorefineries and bio-based products have been identified as essential to reduce the use of fossil resources [1].

The resource of bio-based products is biomass. Biomass can be defined as any kind of organic material available that comes from plants or animals, such as wood, forest residues, agricultural wastes, or energy crops [2]. Biomass is the most abundant natural and renewable material on the planet, with an approximate production of 1,3x10<sup>10</sup> metric tonnes per year. This makes biomass a sustainable source for a great number of potential materials and applications.

In the present, direct combustion of biomass to produce energy, anaerobic digestion for biogas production, and biomass with great amounts of cellulose used for pulp and paper manufacture are the main applications. Although with the growing interest in bio-based products other applications with greater value are being studied. From lignocellulosic biomass, biofuels like bioethanol are produced, and bio-based nanomaterials are studied as a future market.

Biomass can be obtained from very different places. Agricultural activities and forest residues produce a huge amount of lignocellulosic biomass because of intensive agriculture, these wastes have the potential to become the raw material for many applications, and at this moment most of this material is not being used as a resource to produce high value-added compounds. *Table 1* shows different agricultural and forest wastes and their annual production worldwide [3] and *Table 2* shows the biomass residues produce in Spain annually.

Fibre source	World production (10 <sup>3</sup> tons)	Origin
Bamboo	10.000	Stem
Oil palm fruit	23.500	Fruit
Sugarcane bagasse	75.000	Stem
Banana	200	Fruit
Coir	100	Stem
Wood	1.750.000	Stem
Pineapple	1200	Leaf
Rice straw	28.900	Stem
Rice husk	26.750	Fruit/grain
Jute	2500	Steam
Kenaf	770	Steam
Flax	810	Steam
Sisal	380	Steam
Abaca	70	Steam
Kapok	100	Steam

Table 1. Annual production of different lignocellulosic wastes [3]

Table 2. Spain annual biomass waste generated

Sources of biomass waste	Annual production (10 <sup>6</sup> tonnes)
Crops	40
Agriculture	31
Forest	19
Stockbreeding	74
Industrial	85
Domestic	21

### 1.2. LIGNOCELLULOSIC BIOMASS

Lignocellulosic biomass fibers are a complex compound as they are made of polysaccharides, phenolic polymers, and proteins that represent the essential cell walls of woody plants [4]. Lignocellulosic biomass composition is mainly formed by three types of polymers, cellulose, hemicellulose, and lignin [5]. Others minor compounds present in the fibers, aggregates, are commonly referred to as ashes and extractives. Those minor components can be soluble in water or organic solvents such as resins, phenols or low molecular mass carbohydrate or insoluble like carbonates, oxalates and silica, which is really abundant in different types of straws.

The structure of lignocellulosic biomass can be observed in *Figure 1*, where cellulose molecules form crystalline and amorphous regions, on the other hand, microfibrils of cellulose interact with each other using hydrogen and van der Waals bond to remain united, hemicellulose connects lignin with cellulose fibers and gives the rigidity to the lignocellulosic biomass [6].



Figure 1. Lignocellulosic biomass structure and compounds formulas [4]

Composition of cellulose, hemicellulose and lignin varies from all different sources of lignocellulosic material having different percentages within the biomass. Depending on the products that want to be obtained the raw material has to be chosen carefully to provide the highest production. Some ftors that also can affect the composition of the biomass are the age

and stage of growth of the biomass itself [7]. In *Table 3*, information about the composition of different lignocellulosic materials is given.

In the following sections of the introduction, will be described in more detail the structure of the lignocellulosic biomass fibres. As mentioned before, the main compounds of biomass are cellulose, hemicellulose and lignin, which are the compounds that will be detailed.

Lignocellulosic biomass	Cellulose (%)	Lignin (%)	Hemicellulose (%)	Ashes (%)
Switchgrass	5-20	10-40	30-50	5-6
Miscanthus	38-40	24-25	18-24	5,5
General Grasses	25-40	10-30	25-50	-
Municipal solid waste	33-49	10-14	9-16	-
Corn cob	42-45	14-15	35-39	3.53
Corn stover	38-40	7-19	24-26	6,8
Sugarcane bagasse	42-48	20-42	19-25	-
Rice straw	28-36	12-14	23-28	19,8
Wheat straw	33-38	17-19	26-32	3,74
Oat Straw	31-37	16-19	27-38	-
Rye Straw	33-35	16-19	27-30	-
Rice husk	28-36	26-31	18-21	17,27
Barley Straw	31-45	14-19	27-38	-
Bamboo	26-43	20-32	15-26	0,2-5
Corn leaves	26,93	15,18	19,49	10,95
Cotton	85-90	-	-	0,8-2
Softwood	38-46	22-34	23-31	1-5
Hardwood	38-49	16-30	20-40	2-8

Table 3. Composition of diferrent lignocellulosic biomass sources [8] [9] [10]

#### 1.2.1. Cellulose

Cellulose (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)n is the principal compound of vegetal and animal cell wall and the most abundant polymer on the planet. It is a polysaccharide with a straight chain between 200 and 10.000 of D-glucose united by a glycosidic or ether bond  $\beta$ ,1 $\rightarrow$ 4 between the first and fourth carbon of the chain [4].

The numerous hydroxyl groups present in the glucose from one chain create hydrogen bonds with other chains forming the known as microfibrils, where there are crystalline structures that give resistance and amorphous regions which give elasticity to the fibres. The presence of amorphous regions in the microfibrils facilitates the penetration of chemical reagents which gives the capacity to alter the structure of the cellulose. Another property of cellulose for which is starting to gain attraction to produce bio-based products is that is biodegradable.

In *Figure 1*, it can be observed the cellulose structure with a great number of straight chains. On the other hand, *Figure 2* shows the smaller unit of the cellulose polymer known as cellobiose.



Figure 2. Section of the cellulose chain. Cellobiose [13]

#### 1.2.2. Hemicellulose

Hemicellulose constitutes the non-cellulosic polysaccharides in the lignocellulosic biomass fibres. It is a heteropolymer with shorter chains than cellulose, ramified, and amorphous without crystalline zones. Hemicellulose is formed by different monomeric sugars. The principal monomeric sugars that hemicellulose is formed are three hexoses and two pentoses. Glucose, mannose, and galactose are the hexoses and xylose, and arabinose are the pentoses [14]. These monosaccharides are represented in *Figure 3*. Hemicellulose is linked with cellulose by hydrogen bonds and with lignin by ester and ether bonds. The utilisation of hemicelluloses to produce high value-added products is more difficult than cellulose since it is a less homogeneous polymer [4].



Figure 3. Scheme of the principal monomeric sugars of hemicellulose

#### 1.2.3. Lignin

Lignin is the third principal compound in abundance of lignocellulosic biomass. Lignin does not have a particular structure defined as it is formed by a combination of three aromatic hydrocarbons that are presented in *Figure 4*. As it is a combination of those three phenolic polymers, lignin is very ramified and has an amorphous structure. Normally, lignin from softwoods is mainly made of coniferyl alcohol and hardwoods lignin is a combination of sinapyl and ciniferyl alcohols [15]. Lignin also has a minor part of paracoumarly alcohol, the third aromatic compound.



Figure 4. Principal aromatic polymers present in lignin

#### 1.3. NANOCELLULOSE

In recent years, the development of new nanomaterials has experimented a big increase in a lot of different fields, such as biomedicine, electronics, or wastewaters treatment [14]. A nanomaterial can be defined as a material whose size is on the scale of 1 to 100 nm. If a material size is reduced to nanoscale its properties can change being able to design nanomaterials with the properties that one desires. The biggest nanomaterial producer is the United States followed by Europe, and Asia [17].

As nanomaterials are a growing market, the search for environmentally green nanomaterials has also started. Cellulose is one of the most studied materials to convert to nanoscale because of its properties, such as high mechanical strength, high aspect ratio, crystallinity, and adjustable surface chemistry [20]. Also, because it is easy to obtain, exists in large quantities, is renewable, and is a biodegradable material. A comparison between nanocellulose and other materials is shown in *Table 4*. Nanocellulose was first produced by Nickerson and Habrle in 1947 and Ranby in 1949 using acid hydrolysis [18][19], since then, understanding of nanocellulose has exponentially improved.

Depending on the nanocellulose production conditions and the cellulose origin, different types of nanocellulose can be obtained. The standardized classification of nanocellulose by the Technical Association of the pulp and paper industry (TAPPI) is the following, three different types of nanocellulose are distinguished. Cellulose nanocrystals (CNC), also known as cellulose whiskers, cellulose nanofibrils (CNF) also named nanofibrillated cellulose or microfibrillated cellulose, and finally bacterial nanocellulose (BN). BN will not be described in this thesis as the aim is to obtain nanocellulose from agriculture and forest wastes and not from the bacterial organisms.

Material	Density (g/cm³)	Tensile Strength (MPa)	Tensile Modulus (GPa)	Cost (\$/kg)
High strength steel	7,9	600	210	~1
Aluminum 6061-T6	2,7	275	70	~2
E-glass fibre	2,5	3.500	80	~2
Carbon fibre	1,8	4.500	230	>20
CNC	1,5	7.500	135	4-10

Table 4. Comparison of different materials utilised in the industry to CNC

In the following sections of the introduction, CNC and CNF will be described and their possible methods of production. Finally, a study of the actual situation of the nanocellulose market and its applications will be done.

#### 1.3.1. Cellulose nanocrystals (CNC)

CNC has a short rod-like shape or whisker shape that has the following dimensions, 2-20 nm of diameter and 100-500 nm of length depending on the production process and the operating conditions [13]. As mentioned before, cellulose has amorphous and crystalline regions within the fibres, CNC is made by removing those amorphous regions obtaining a high crystalline material. The removal of amorphous regions is mainly done by acid hydrolysis of these zones.

#### 1.3.2. Cellulose nanofibers (CNF)

CNF are structures longer than CNF with diameters of 50-30 nm and lengths up to micrometres. These structures are large cylindrical and flexible fibres that in a suspension form a hydrogel [14]. CNF is mostly isolated by mechanical methods which use the forces produced by the mechanical treatment to disrupt the cellulose fibres. However, enzymatic hydrolysis has started to gain the attraction of the researchers. CNF composition is made by crystalline and amorphous regions, unlike CNC.

#### 1.3.3. Production of nanocellulose

Nanocellulose production can be performed by different types of methods that can be classified as mechanical, chemical, and biological. As mentioned before, depending on the type of nanocellulose that wants to be manufactured there are more suitable methods than others.

Directly using these methods to attack the lignocellulosic biomass has been the most used procedure. This type of process has low yields because of the complex lignocellulosic structure of the biomass, requiring high energy and chemicals to use these treatments. To make more accessible the cellulose fibres and lower the energetic and chemical demand of the process, lignocellulosic biomass has to use pre-treatments, removing most of the hemicelluloses, lignin, and minor compounds present in the materials [22]. Also, the removed lignin and hemicellulose can be transformed into by-products with commercial value, such as phenolic resins or xylose syrup. The use of pre-treatments for nanocellulose production is very similar to the use that the pulp and paper industry does since the raw material is very similar [21].

Nanocellulose production can be divided into two main processes, the pre-treatments to fractionation the lignocellulosic material into their main compounds and cellulose transformation to nanocellulose by the diverse methods existing.

#### 1.3.3.1. Pre-treatments

Pre-treatments can be categorised as chemical, physical, or a combination of both and biological pre-treatment [22]. In this subsection, different options of pre-treatments for the removal of hemicellulose and lignin will be described.

#### Physical pre-treatments

Physical pre-treatments are used basically for size reduction of the lignocellulosic material [26]. Some examples of these types of pre-treatments are shredding, grinding, or milling (ball milling, two-roll milling, hammer milling, colloid milling, and vibro energy milling), these pre-treatments increase the surface area making easier the isolation of nanocellulose with further pre-treatments and methods [25].

#### Chemical pre-treatments

Chemical pre-treatments have been massively studied by the pulp and paper industry in order to remove lignin from the cellulosic material [22]. There are three main chemical pre-treatments that have been investigated and scaled up to industrial productions, which are acidic, alkali and sulphur dioxide pre-treatments.

Acid pre-treatments is centred in the hydrolysis of hemicellulose and the amorphous parts of cellulose using acids, such as H<sub>2</sub>SO<sub>4</sub>, HCl, or H<sub>3</sub>PO<sub>4</sub>. Normally this type of pre-treatments uses diluted acids because degradation of cellulose has to be minimized, and also because hemicellulose hydrolysis and separation increases. It can be performed at high or low temperatures (120 °C-180 °C) depending on the reaction time (30-90min) [26].

Sulphur dioxide pre-treatment has various advantages respect the acidic pre-treatment using sulphuric acid. SO<sub>2</sub> is a gas, this eases its addition to the process as it can be added with or ahead of the lignocellulosic stream. Another advantage is that it is better this distribute within the biomass facilitating the reaction [25].

Alkaline pre-treatment uses principally NaOH, KOH or Ca(OH)<sub>2</sub> as alkaline agents. Alkaline hydrolysis efficiency depends on the treatment conditions and lignin content of the lignocellulosic biomass. Alkaline pre-treatment is more effective in low lignin content materials like agriculture biomass waste [25]. One of the most used pre-treatments of lignocellulosic biomass in the industry is the alkaline aggregating Na<sub>2</sub>S to accelerate the process delignification, this treatment is commonly known as the kraft process [11]. Another variation of the alkaline treatment is using a catalyst to substitute the Na<sub>2</sub>S in the kraft process to eliminate

the sulphurs content in the resulting biomass and the wastewaters, one catalyst that has been investigated is the anthraquinone (AQ), which is a non-toxic aromatic compound that is regenerated during the process without creating additional residues.

#### Physico-chemical pre-treatments

There is a great variety of physico-chemical pre-treatments, with the likes of steam explosion, liquid hot water (LHW), wet oxidation (WO), ionic liquids, organoslov process, ammonia fibre explosion (AFEX), among others. The most used in industrial applications will be the ones that will be described.

Steam explosion uses steam at high temperature and pressure for an amount of time to treat lignocellulosic biomass. This pre-treatment has two phases, the first one is the hydrolysis of hemicellulose with the hot steam, the second one is an explosive decompression that helps to destroy the rigid structure of the fibres making the fractionation of the biomass easier [29][30].

LHW is a similar pre-treatment to stem explosion, the difference is that LHW uses liquid water (160-240 °C) in the steam place and, therefore, it has to operate at high pressure to maintain the water in the liquid phase [22]. This pre-treatment is interesting because of its high hemicellulose recovery and its environmentally green nature as it does not use acids or chemical catalysts. On the other hand, needs a high amount of water and energy to operate because of the pressure and liquid phase of the water [25].

WO is an oxidative pre-treatment where the lignocellulosic biomass is treated with water and oxygen, or air injected at high pressure at temperatures around 100 °C and higher. This process with lignocellulosic biomass forms phenol aldehydes and furaldehydes from the hydrolysis of hemicellulose which is counterproductive as they are inhibitors of the isolation methods of nanocelluose. This negative effect can be solved by using an alkaline agent with the WO.

AFEX is a very similar pre-treatment to the steam explosion, the difference is that liquid ammonia is used in the place of steam. Liquid ammonia interacts with the biomass at high pressure and temperature range of 60-100 °C [25] for a determinate period of time and then a decompression is made. This pre-treatment is more suitable to produce biofuels than nanocellulose because cellulose is hydrolysed and has a high recovery percentage of sugars

from hemicellulose, which after the pre-treatments will be fermented and transformed to bioethanol.

Organoslov process consists of the utilisation of a mixture of organic solvent with inorganic acid catalysts, such as HCl or H<sub>2</sub>SO<sub>4</sub> fractionating the lignin and hemicellulose in the biomass. Some organics solvents that are commonly used are methanol, ethanol. The Organoslov process solubilizes almost all hemicellulose and removes a high amount of lignin, this happens because of the hydrolysis of the lignin and hemicellulose internal bonds [22]

#### Biological pre-treatments

Biological pre-treatments are an eco-friendly method as it does use enzymatic hydrolysis to remove lignin and hemicellulose. This pre-treatment has different advantages in comparison with physical, chemical, or physico-chemical pre-treatments, such as low energy requirements, high yields of delignification and hemicellulose removal and that does not generate toxic residues [22]. Although the advantages are important it has a greater disadvantage that is a slow process, to achieve high yields the residence time is up to two weeks [28] which is not suitable for an industrial process.

It is worth mentioning that although all these pre-treatments have been described separately, a combination of various pre-treatments can be the best way to fractionate the lignocellulosic biomass, because some of them are more suitable for hemicellulose removal and others for lignin. The combination of different pre-treatments must ensure that cellulose is not degraded, as the objective of the pre-treatments is to obtain a pure stream of cellulose to produce high quantities of nanocellulose.

#### 1.3.3.2. Nanocellulose isolation methods

Different types of nanocellulose exist and with this, different methods of production are needed to obtain one or another. For CNC chemical and biological methods can produce them, on the other hand CNF can be isolated by mechanical and biological treatments. *Biological treatment* 

Enzymatic hydrolysis consists in the use of enzymes to produce nanocellulose. Cellulose structure is complex with amorphous and crystalline regions, because of this, different enzymes have to be used in order to obtain nanocellulose. Cellobiohydrolases attack the crystalline part of cellulose and endoglucanases hydrolyse the amorphous parts. Although enzymatic hydrolysis

has low energy demands, does not use chemicals producing wastewaters that have to be treated and is an eco-friendly method, it has a big disadvantage which is that reaction times is too elevate [31]. Because of this enzymatic hydrolysis is used in combination with other methods normally mechanical ones.

#### Mechanical treatments

There is a great number of different mechanical treatments that are being used in the industry. Some examples of this type of treatment are high-pressure homogenization (HPH), grinding, refining, ball milling, and cryocrushing

The first treatment is HPH, which is a great method for the refining of cellulose pulp. In this method, cellulose pulp passes through an extremely small nozzle with high pressure, the shear and impact forces that are applied cause the defibrillation of the cellulose fibres into the nanoscale [27].

Microfluidization is a very similar method to HPH, as it uses the shear and impact forces to defibrillate the cellulose as well. The difference is that microfluidiziers have a small chamber in a specific geometry, such as Y or Z-shape where the stream of cellulose pulp is introduced at high pressure [21], whereas in HPH the device has a small gap between the impact ring and the valve letting through nanosized material. In these methods, there is a correlation between the number of passes through the homogenizer and the CNF size [27].

In the process of grinding, cellulose pulp passes through two stones (disks), one of them is fixed and the other one rotates. The shearing forces created between the stones enables the defibrillation of cellulose into nanofibrils, CNF. The friction of the disks produces heat, evaporating the water present in the pulp and increasing the solid content in the mixture [21]. Refining is a similar process to grinding because the procedure is the same, the difference is that refining can be done in different devices, such as disk refiners, PFI mills, beaters, and directly using a grinder. Refining is usually used as a secondary treatment because needs another intensive mechanical treatment to effectively produce nanocellulose [21]

Ball milling consists of a hollow cylindrical vessel that is filled with balls, the container rotes producing collision between the balls and the cellulose, breaking the cellulose fibres. The balls are made of metal, ceramic or zirconia [27].

Cryocrushing is another CNF production methods, in this treatment cellulose with water is frozen using liquid nitrogen and after it is crushed applying impact and shear forces breaking down the frozen cellulosic content in the mixture.

Although the CNF production by this method is widely used, it has an important disadvantage which, is the big energy consumption. Because of this, a mechanical treatment has to be combined with another mechanical, chemical or biological treatment in order to be more economic and less energy intensive.

#### Chemical treatments

Acid hydrolysis is the principal existing chemical treatment for the production of nanocellulose and more specifically, CNC. Acid hydrolysis attacks the amorphous parts of the cellulose fibres removing them, obtaining the crystalline part of the fibres almost pure. Diverse acids can be used, such as H<sub>2</sub>SO<sub>4</sub>, HCl, or H<sub>3</sub>PO<sub>4</sub>, or HBr. Sulphuric acid is most used as it initiates the esterification process in cellulose [27]. Acid hydrolysis with sulphuric acid helps the dispersion of the nanocrystals solution, this is because of sulphates ions that are impregned on the cellulose surface after the hydrolysis. For the optimization of this treatment there are different variables that have to be chosen correctly, which are temperature, reaction time, and acid concentration [33].

Another chemical treatment that has gained the attraction of the researchers is the TEMPO (2,2,6,6-Tetramethylpiperidinyloxy) oxidation of cellulose. This treatment dissolves TEMPO and NaBr with NaClO as an oxidation catalyst [11]. This process can selectively oxidise hydroxyls groups that are on the cellulose surface to carboxylate [32], *Figure 5* shows the TEMPO oxidation reaction mechanism. TEMPO oxidation has to be combined with other treatments in order to start to be economically viable, normally is used before a mechanical treatment to reduce the energy needed in the mechanical process. This treatment can be used for CNC and CNF production, although industrially is more common for CNF production.



Figure 5. Reaction mechanism for TEMPO oxidation process of cellulose [34]

#### 1.3.4. Process alternatives in the industry

For CNC the most common process is acid hydrolysis using 64% sulphuric acid, the scheme of this process is shown in *Figure 6*. Different companies use this method, being CelluForce the biggest, which has yearly a production of 260 annual tonnes (*Table 5*).



Figure 6. Block diagram of acid hydrolysis method for production of CNC

On the other hand, CNF production has more variety of processes used in the industry. TEMPO oxidation and mechanical treatments are the most used in the industry, *Figures 7 and 8* show the production process of CNF using these two methods. Some companies have searched other routes to produce CNF like VTT which uses a combination of chemical and enzymatic treatments. Different companies and their process and capacities for CNF production are showed in *Table 6*.



Figure 7. Block diagram for production of CNF by TEMPO oxidation



Figure.8 Block diagram for production of CNF by mechanical treatment

As mentioned before some companies have searched for alternatives process to improve nanocellulose production or making more economically viable the process. American Process created a process (AVAP) that ensures high quantities of nanocellulose production and lower energy and chemical consumption than other processes. Also, the crystallinity of the nanocellulose produced by AVAP increased arriving to 90% [35]. This process uses SO<sub>2</sub> as a delignifying agent and ethanol to help SO<sub>2</sub> to penetrate the biomass fibres. Ethanol is regenerated with SO<sub>2</sub>, cellulose pulp passes through a bleaching and mechanical process that the company does not specify and produces a mixture of CNF and CNC.



Figure 8. Scheme of the AVAP process for production of nanocellulose

#### 1.3.5. Nanocellulose market

Nanocellulose industry has been growing in recent years. As new procedures that make nanocellulose production economically viable are conceived. In 2014 the nanocellulose market was around 250 million \$ with an estimated growth (CAGR) of 19% to 2019, this estimated growth was confirmed as the nanocellulose market increased to 295 million \$. Finally, its potential growth is set to reach a market value of around 1.000 million \$ in 2027 [23].

Tables 5 and 6 illustrate the different companies that produced nanocellulose and their respective nanocellulose production capacities, separating CNC and CNF. These tables also show the process used to produce CNC and CNF and the company location. This information is from 2018.

Producer	Process	Capacity
CelluForce, Canada	sulphuric acid hydrolysis	260
American Process, USA	SO2 fractionation	130
Melodea, Sweden	sulphuric acid hydrolysis	35
Alberta Innovates, Canada	acid hydrolysis	5
U.S. Forest Products Lab, USA	sulphuric acid hydrolysis	3
Blue Goose Biorefineries, Canada	catalytic conversion	2
FPInnovations, Canada	sulphuric acid hydrolysis	Pilot
Hangzhou Yeuha Technology Co., China	Proprietary	Pilot
Sweetwater Energy, USA	Reactive extrusion	Pilot
Tianjin Haojia Cellulose Co., Ltd., China	Modified and unmodified	Pilot

Table 5. CNC production companies and their capacities in annual tonnes (2018) [24]

Producer	Process	Capacity
Nippon Paper, Japan	TEMPO, carboxylated	560
University of Maine, U.S.	Mechanical	260
American Process, U.S.	SO2 fractionation	130
CelluComp, UK	chemical pretreatment	100
Chuetsu Pulp and Paper, Japan	aqueous counter collision	100
Oji Paper, Japan	phosphate esterification	40
Sugino Machine, Japan	oblique collision	26
Seiko PMC, Japan	modified hydrophobic	24
SAPPI, Netherlands	Chemical	5
VTT, Finland	chemical, enzymatic	5
Tianjin Haojia Cellulose Co., Ltd, China	TEMPO, carboxylated	3
Dai-ichi Kyogo (DKS), Japan	TEMPO	1
U.S. Forest Products Lab, U.S.	TEMPO, mechanical	<1

Table 6. CNF production companies and their capacities in annual tonnes (2018) [24]

In Spain nanocellulose market still is small, but in recent years has started to grow, with the same growth as in Europe. Most of the companies that are beginning to produce nanocellulose are in pilot scales where they produce nanocellulose depending on the demand of the client. Some examples of these companies are Tecnalia, ITENE or Aidanano.

#### 1.3.6. Applications

Nanocellulose, for its gifted properties like high thermal properties, high mechanical strength with low weight, transparency and biodegradability is attractive for many different industries [13]. Nanocellulose applications have been used in several different fields, such as the paper and packaging industry, in electronics, biomedical and cosmetics applications, or in the composite industry.

For the biomedical industry, nanocellulose could be a game changer, as pure nanocellulose is nontoxic and biocompatible with humans. Because of this, it can be used in health care, personal hygiene, and cosmetics [27]. Right now, nanocellulose is being used as an agent in wound dressing as it adheres well with the wound and can be detached with ease as skin recovers [20]. But the most promising applications in this field are being investigated with the likes of blood vessel replacements or implants of soft tissue [13].

The paper and packaging industry is the industry at this moment that uses more nanocellulose. This is because of the urge to find a replacement of the synthetics polymers from petrochemical sources [20]. Diverse studies have shown that adding nanocellulose to packaging materials can maximize their mechanical and barrier properties [3].

For other industries, nanocellulose is also being used or is in the investigation to search for applications. In electronics, nanocellulose can be used because of the improved conductivity and flexibility [20], these properties can help to produce paper-based sensors, flexible electrodes to name some of the possible applications. In the automotive industry, nanocellulose is being used as bumper beams, front ends, underbody shields and dashboards, where nanocellulose is introduced in the thermoplastics matrix to increase their performance and nonbrittle fracture [3]. Nanocellulose has also been used in films, foams, or coating in the composite industry as a reinforcing agent,

Nanocellulose applications are starting to be used in very different industries as a possible substitute for the products produced by petrochemical and other non-renewable sources. As it is at this moment, nanocellulose still has a large path until its production will be able to replace the classical products, because of the difficulty to put up an economically viable process for its production at industrial size. For that reason, investigation for the design of a viable process for nanocellulose production must be done.

# **2. OBJECTIVES**

The main aim of this project is to develop production process of nanocellulose from agriculture biomass waste, by studying the state of the art of technologies that are being used at this moment in the industry. Therefore, this project has the following objectives:

- Study of the state of the art of nanocellulose production and its potencial applications
- Purpose a process design of nanocellulose production from agriculture biomass waste ensuring its economic and environmental viability without compromising the capacity production of the process.

# **3. METHODOLOGY**

The methodology followed to design a possible path to nanocellulose production process has been the following:

Firstly, a study of the raw material has been made, in order to determine the product composition and availability. Secondly, a study of the different available technologies in the industry is made, gathering basic information of the process. Thirdly, deciding which technologies are more suitable to the process it is wanted to design, based on analysing and studying the information collected in the second point.

# 4. PROCESS DESIGN

In this section, it is used the methodology described before to achieve the design of the nanocellulose production process. Focusing on the decisions made to select each unit and the auxiliary equipment.

### 4.1. PROCESS FLOW DIAGRAM (PFD)

The process flow diagram for the process designed it is shown in Figure 9.



Figure 9. Process flow diagram of nanocellulose production from agriculture biomass waste

### 4.2. PROCESS DESCRIPTION

The process design in this work to produce nanocellulose can be divided in four different stages. The early stages (steps one and two) are used to obtain cellulose free from other components like hemicellulose, lignin, or other impurities present in the biomass. The latest stages (steps three and four) are the methods to produce cellulose nanocrystals (CNC) and cellulose nanofibrils (CNF). The design process is as follows

Firstly, there is the biomass selection, which type, composition, and quantities needed to obtain our product. Also, the raw material must be treated to reduce its particle size to proceed to the next stage of the process.

In the second stage, the crushed biomass material enters a hydrothermal pre-treatment used to remove the hemicellulose present in the biomass. Separation is made by washing and filtration of the solution that comes from the hydrothermal pre-treatment.

The next step is an alkaline delignification followed by washing and filtration to separate most of the lignin from the cellulose. The resulting flow stream from the delignification enters to a WO unit where the lignin and impurities that remain in the biomass are removed obtaining almost pure cellulose.

The final stage is put down to a chemical procedure (acid hydrolysis) to produce CNC and mechanical treatment is used to produce CNF. With these two differentiated paths the cellulose obtained in the previous stages is converted to nanocellulose.

In the following sections of this work will explain in detail all the stages in the process and why these were selected. It will also describe what can be done with the by-products obtained during the process, such as hemicellulose and lignin, to improve de viability of the process and to reduce waste. Another topic that will be treated is the reutilisation of the wastewaters from the process produced in the hydrolysis or during the filtrations to reduce the environmental impact.

### 4.3. RAW MATERIAL SELECTION AND PREPARATION

The production of high value-added nanocellulose from agriculture lignocellulosic waste starts from the raw material selection and preparation. It is important to know the origin and composition of the raw material to be aware of in which conditions enters the process. Another important design parameter is the production capacity of the production process.

Biomass selection is very important, because depending on the origin of the waste the content of cellulose, hemicellulose, lignin, and other aggregates in the fibres change. Considering that, this work will be using forest and agriculture lignocellulosic wastes.

The next step is evaluating the composition of these wastes to be able to know their composition. As forest and agriculture wastes can be from all kinds of origins and types, the composition of the biomass used will be an average following the different bibliographical sources found. *Table 7* shows the different compositions of lignocellulosic biomass that will be used in this work.

Lignocellulosic biomass	Cellulose (%)	Lignin (%)	Hemicellulose (%)	Ashes (%)
Corn cob	42-45	14-15	35-39	3.53
Corn stover	38-40	7-19	24-26	6,8
Sugarcane bagasse	42-48	20-42	19-25	-
Rice straw	28-36	12-14	23-28	19,8
Wheat straw	33-38	17-19	26-32	3,74
Oat Straw	31-37	16-19	27-38	-
Rice husk	28-36	26-31	18-21	17,27
Barley Straw	31-45	14-19	27-38	-
Softwood	38-46	22-34	23-31	1-5
Hardwood	38-49	16-30	20-40	2-8

Table 7. Composition of agriulture biomass and forest wastes [8] [9] [10]

From *Table* 7 and doing the average of the different biomass source it is obtained a raw material composition of 38,5% cellulose, 20,1% lignin, 28% hemicellulose and 13,4% ashes.

The first step of the process is to reduce the size of the biomass to another that it is suitable for the next stage in the process. It is important to reduce the size of the biomass to improve the ratio of surface area-volume because it eases the separation of cellulose from the other components present in the biomass [37]. The selection of the unit operation to reduce the size depends on the type of product that is going to be downsized because the most important property for the reduction of the size is the hardness of the material [38]. Most of the biomass used is wood, which is relatively soft, so the equipment that has to be used is cutting equipment. If the hardness of the product to downsize were much higher milling equipment will be needed.

Considering all the conditions explained above it has been selected a grinder machine to reduce the size. To ensure that almost all the material is the same size after the grinder, sieve analysis is the following equipment in the process. The biomass powder that does not pass the sieve will be reintroduced in the grinder to reduce the size.

### 4.4. HYDROTHERMAL PRE-TREATMENT

Agriculture biomass waste is formed by cellulose, hemicellulose, lignin and aggregates, but for nanocellulose production, almost pure cellulose is needed. Therefore, hemicellulose, lignin and the other aggregates have to be removed from the fibres to obtain the purest cellulose possible. Consequently, the best pre-treatment to remove hemicellulose from the biomass is going to be selected in this section. This pre-treatment must be efficient on different types of agricultural biomass, economically viable and must recover the maximum possible quantity of hemicellulose [26]. In *Table 8* there is a comparison from different pre-treatments, their conditions, and how they affect the lignocellulosic biomass.

A key challenge is how to separate all these different compounds to ensure that cellulose pulp with a high percentage of cellulose is obtained because it is the source of nanocellulose production. Examples of pre-treatments for fractionation of the biomass can be hydrothermal, alkaline, acidic, ionic liquid or biological pre-treatment. Among these, there are some pretreatments, such as the biological one, which is not suitable for the present process because of their large reaction time, which can last days or weeks [28]. Others that are commonly used in the pulp and paper industry, such as alkaline and acid-chlorite pre-treatment are not appropriate because of the contents of the resulting pulp. For instance, the acid-chlorite pre-treatment, known as bleached kraft pulp, yields about 80% cellulose, 12% hemicellulose, 1% lignin and the rest are extractives and ashes [39]. Analysing the pulp content, it becomes evident that it is a great process for delignification as lignin is almost inexistent, but hemicellulose content it is too high for the present process needs, making the next steps less efficient.

Unlike pre-treatments commented before hydrothermal pre-treatment has been selected as the pre-treatment used to remove hemicellulose effectively as it has been proved that works at a commercial scale [26]. Furthermore, the cost for this treatment are low because it does not use high concentrated acids and the primary reaction medium is steam or hot water. It can be added an acid agent, such as chloride or sulphuric acids, in low concentrations to accelerate the fractionation of biomass. For our purpose has to be discussed if acidification makes a good impact on our process.

The most important variables for this type of pre-treatment are reaction time, temperature and pressure that takes place in the reactor. Hydrothermal pre-treatment typical conditions are high temperatures 160-240 °C, reaction times from minutes to various hours and 1-3,5 MPa depending on the biomass that is being used [29].

Steam or liquid hot water (LHW) can be used in this type of treatment. Steam conditions uses steam at a high temperature and pressure, at the end of the residence time a decompression is done to bring to atmospheric pressure the reactor. It can be made by reducing slowly the pressure in the reactor or making a sudden change in the pressure causing a steam explosion. The decompression makes that the water inside the cells vaporizes expanding the fibres. During all this process hydrolysis of hemicellulose take place as it is the most accessible part of the biomass to be hydrolysed.

Steam pre-treatment is very sensitive to the conditions that are being used. As the severity of the conditions increases, cellulose can be solubilized and lignin content in the biomass also increases [26], which is an inconvenience as the main objective of the pre-treatments is to reduce the content of hemicellulose and lignin.

An acid catalyst can be added to the reactor to lower the severity of reaction conditions. However, for raw materials like woods and agriculture biomass wates, which are our raw materials, there is no need to use an acid catalyst as the hemicellulose in these residues is acetylated, which allows the biomass to go through autohydrolysis [40]. As hydrolysis goes on there is the formation of oligomers. At increased reaction times and temperatures, oligomers turn in monomers, mostly pentoses and hexoses, which are unstable in these conditions and can undergo further reactions to form furfural or formic acid, that are harmful to the fibres. For all these reasons steam pre-treatment is not considered the most suitable option for the process.

On the other hand, there is the hydrothermal pre-treatment using LHW, this pre-treatment is less affected by the severity of the conditions, making it easier to work with [29]. Hemicellulose using this method can be fully solubilized [41]. The conditions described in [41] for full hemicellulose hydrolysis are 200-230 °C and 0-15 minutes of residence time. Lower temperatures require more residence time, but more hemicellulose can be removed. In addition, the resulting biomass has higher percentage of cellulose as the temperature is lowered because it is more difficult to solubilize the cellulose. As mentioned before in the steam treatment, hydrolysis is taking place also in the LHW pre-treatment. Therefore, as it increases the temperature and the residence time in the reactor, degradation of the xylose to furfural happens poisoning the fibres.

Therefore, hydrothermal pre-treatment using liquid hot water has been selected as the best option to produce nanocellulose. The conditions that will take place in this pre-treatment are 180 °C with a residence time of 20 minutes. Under these conditions yields of 80-85% of solubilized hemicellulose have been reported [42]. Also, the process has to be held to a 5 MPa of pressure to maintain the water in liquid phase. All these conditions are selected to obtain a solid with the maximum percentage of cellulose possible, this is the reason because not all hemicellulose is solubilized [41]. Temperature below 200 °C can be used to not degraded noticeable quantities of cellulose and higher residence time is to obtain higher hemicellulose solubilization as the fibres are hydrolysed more time. A batch reactor is used for this type of pre-treatment as they need less energy and water to operate [60].

The biomass solid resulting from the hydrothermal pre-treatment will be sent to washing and filtration equipment to ensure that all the hemicellulose solubilized is separated from the biomass. Hemicellulose will be sent to the recovery section, where it will be valorised to obtain a product that can make the process more economically viable. Biomass solid will be sent to the next equipment in the process, which is the delignification unit.

Pre-treatment	Chemical	Temperature/ Pressure	Reaction time	Hemicellulose removal	Lignin removal	cost
Dilute acid hydrolysis	Acid	≥160 °C	2-10 min	+	+	+
Alkaline hydrolysis	Base	1	1	-	+	++
USE	1	160-260 °C	2 min	+		-
ACSE	Acid	160-220 °C		+		-
LHW	None	180-230 °C	45 s-30 min	+		-
AFEX	Ammonia	90 °C	30 min	-	+	-
CO <sub>2</sub> explosion	CO <sub>2</sub>	56,2 bar	1	+		
Biological	7	25-35 ℃	>1 week	+,-	+,-	-

Table 8. Comparison of different pre-treatment methods for lignin and hemicellulose removal [29]

+, major effect -, minor effect /, no information

### 4.5 ALKALINE DELIGNIFICATION

The biomass that arrives to this stage is made up of cellulose, lignin and residual hemicellulose that could not be solubilized and separated in the previous equipment. To obtain a solid with a high concentration of cellulose, lignin has to be removed. The aim of this subsection is to select one or various pre-treatments to solubilize lignin and separate it from the cellulosic content of the biomass, without damaging the cellulose being held in the fibres of the biomass.

The most common pre-treatments of delignification are acid treatment, alkaline treatment and kraft delignification [13]. Other pre-treatments are feasible for this application due to their residence time, temperature or since they are more effective to solubilize a fraction of the biomass that has been extracted in previous stages of the process, such as hemicellulose. On the other hand, a combination of different pre-treatments for delignification has started to be used in the industry, because of their capacity to extract high quantities of lignin and preserve the cellulose from being damaged during the process as delignification in various stages the conditions are less severe [43]. Biological treatment although it has high yields of lignin solubilization and is an environmentally conscious process with low energy demands, has reaction times way higher than other treatments [11][28]. Treatments such as LHW or steam, cannot be used because they are less effective. They could hydrolyse the cellulose of the biomass reducing the production of nanocellulose, which is the objective of this process. Another disadvantage is that they can produce by-products that would difficult the access to cellulose in the next sections.

Kraft process is an alkaline treatment that uses NaOH and Na<sub>2</sub>S as catalyst to accelerate delignification, it is the principal process for the production of cellulose pulp used in the paper industry. Although it is a treatment highly studied and with great results and lignin content is reduced to 1%, it is not a suitable choice because of the sulphur content in the resulting biomass which has to be treated for their recovery and reduced the environmental impact, also some compounds, such as hydrogen sulphide can produce a strong bad smell around the production plant.

Another process for delignification is an alkaline pre-treatment followed by an acid-chlorite treatment. Firstly, sodium hydroxide 4-20 wt% is used to facilitate hydrolysis and raise the surface area of the cellulose in the fibres. Continuing with acid chlorite at 60-80 °C to remove lignin and break the links in the fibres to solubilize hemicellulose [64]. This kind of treatment can achieve increase the amount of cellulose present in the biomass from 43% to 84% [44].

All these delignification processes described before have issues regarding environmental impact as their wastewaters have sulphurs and chlorites that can elevate the economic costs of operation because of the wastewaters treatment. Also, reaction times for alkaline chlorite are high and could last from 4 to 12 hours [13]. Another reason for not considering this pre-treatment as optimal is because in alkaline-chlorite treatment yields of cellulose fraction even though are quite high, with other methods can be obtained purer cellulosic stream.

The first delignification process chosen is an alkaline pre-treatment with AQ as a catalyst. Various reports demonstrate that soda-AQ pulping can be comparable with the conventional kraft process pulp in terms of yields and residence times [46][61]. Compared to kraft pulping this method has lower pollution in the air and wastewaters from the plant because it eliminates sulphurs from the process. AQ catalyst effect and the hydrosulphide ion used in the kraft process are equivalent. *Figure 10* shows the catalyst effect of AQ in soda pulping. Also, the strength properties of soda-AQ are no better than the conventional kraft pulp [45]. With alkaline

treatment using anthraquinone yields up to 70% of delignification are achieved [46]. In addition, relatively low quantities of cellulose are solubilized during this treatment.



Figure 10. Mechanism reaction of soda-AQ delignification [61]

Conditions for this treatment are 160 to 170 °C with an alkaline component such as NaOH in between 20 and 40% in dry solid basis and residence time from 10 to 150 minutes [46]. For the process in the making, low residence times with high delignification are preferred. This can be achieved by increasing the temperature of the treatment and changing the liquid to solid ratio. This last change increases the alkaline concentration in the process because the alkali-to-solid ratio does not vary, producing a decrease in the reaction time to obtain the same yields of delignification. For all these, the conditions selected for the soda-AQ delignification are, 170 °C, 20% of NaOH on dry solid basis, 0,1% of AQ as a catalyst, liquid to solid ratio of 6 and residence time of 30 minutes.

After the alkaline treatment to separate the material that has been solubilized, washing and filtration are needed. All the wastewaters will be sent to lignin recovery to obtain a by-product, this is shown in Figure 9.

Although lignin content is reduced by 70 % in the described treatment, it can be further reduced by introducing another treatment after the soda-AQ delignification. As mentioned before, the selection of delignification method must have a low environmental impact without decreasing the separation of lignin that wants to be achieved and being economically viable.

Normally after an alkaline treatment, a chlorine-based treatment is needed to solubilize the remaining lignin, this process is known as bleaching. This process is not as environmentally conscious as others because of the residual chlorite that stays with the biomass after the delignification and the chlorite that goes to the wastewaters which have to be treated. Although acid-based pre-treatment accomplishes great lignin extraction, the same delignification can be achieved with chlorite-free treatments, such as wet oxygen delignification [43].

Wet oxygen delignification has various variables that can affect the delignification process. Oxygen pressure, temperature, reaction time and percentage of alkali introduced are the most important ones. Yields vary from 81 to 88% depending on the conditions that the treatment takes place [45]. In other bibliographical sources, it can be observed that yields vary with the type of biomass that enters the process, with a range from 70 to 95% of residual lignin removal [47][48].

WO has been the pre-treatment selected, the optimal conditions of the process are selected from the bibliographical sources cited before, where experiments with different conditions were made. The alkaline percentage goes from 2 to 4%, but 3% can achieve the most consistent and high yields for different conditions. Temperatures ranges are from 80 to 140 °C, high temperature could lead to degradation of the cellulose in the treatment, for this and analysing the different sources 100 °C is the temperature selected. Oxygen pressure extends to 3 to 8 MPa. Oxygen pressure can decrease with the increase of alkaline concentration, because of the intermediate concentration of alkaline, oxygen pressure is also in the middle of the range, selecting 6 MPa. Reaction time has a big span from 15 to 150 minutes, although it is recommended to not surpass 60 minutes as degradation of the biomass could happen and yields would be compromised [49]. Finally, low concentration of additives need to be added to protect cellulose fibres from depolymerization and alkaline oxidations [49], in our case 0,1% of MgSO<sub>4</sub> is the additive.

After oxygen delignification, the resulting pulp is filtrated to separate the lignin from the high cellulosic yield pulp, the liquid filtrated is sent with the stream of lignin extracted from the first delignification process for its further valorisation, *Figure 9*.

### 4.6. PRODUCTION OF NANOCELLULOSE.

Nanocellulose can be produced for various methods, which are classified as mechanical, chemical or biological. Nanocellulose properties change depending on the production method, distinguishing cellulose nanocrystals (CNC) that can be made by chemical treatments and cellulose nanofibrils (CNF) that can be obtained by the three types of methods. Commonly a combination of methods is effective to reduce energy costs and obtain higher yields of nanocellulose production.

The aim of this section is to select the optimal path to produce each type of nanocellulose incorporating these treatments as the final step in the process described during this section of the work. Production of CNC and CNF in the same plant enables product versatility, meaning that different products with different properties are obtained.

The almost pure cellulosic stream resulting of the wet oxidation is divided to enter to the CNF and CNC production process, *Figure* 9.

#### 4.6.1. Production of cellulose nanocrystals (CNC)

Firstly, the selection will be focus on the path to obtaining CNC. The most usual treatment to produce CNC is acid hydrolysis. Strong acids such, as sulphuric acid or hydrochloric acid are among the utilized acids. Although acid hydrolysis is commonly used, other routes can be used, such as oxidation methods and a combination of acid or oxidation treatments followed by mechanical treatment.

Mechanical treatments cannot be used by themselves to manufacture CNC because the crystal part of the cellulose is degraded reducing the high crystallinity of CNC. Considering that, mechanical treatments can only be used as a final step for purification or separation of the nanocrystals produced before for another treatment [50].

The aim of cellulose oxidation is to oxidize primary hydroxyls groups of cellulose. This oxidation has to be selective because only the primary hydroxyls have to be oxidized. To ensure this, it is used the TEMPO selective oxidation reaction, where sodium hypochlorite, sodium bromide are utilized with TEMPO as a reaction catalyst [13]. TEMPO process is effective in cellulose with low crystallinity because hydroxyls are more accessible [51], *Figure 5* shows the reaction mechanism for the TEMPO oxidation. These conditions are best suitable for CNF production because it is formed by crystalline and amorphous parts of the cellulose biomass. For TEMPO oxidative manufacture of CNC in productive yields, has to be combined with acid hydrolysis, making it a high production cost process and highly chemical consuming [11][13].

With oxidation discarded as an effective method of production of CNC, it is going to be selected the best conditions to accomplish a high yield of CNC with acid hydrolysis that ensures the properties of the product will not be affected.

The first topic for this selection is deciding which is the acid that is going to be used. Sulphuric acid has been the most used acid for nanocellulose production, although recently other acids have been studied, such as hydrochloric acid, hydrobromic acid and organic acids. Most of the acids cannot compete with sulphuric acid because of the high colloidal stability of the nanocrystals manufactured by this method [36]. Another factor is the size of the crystals produced, many acids like hydrochloric or hydrobromic produce nanocrystals with aggregates that need further treatments to separate them. This is the case of using hydrochloric acid, which can produce CNC with yields up to 90% [36] but need an extra treatment like TEMPO oxidation to eliminate the aggregates. Hydrolysis of sulphuric acid has its flaws, for example, the CNC surface area contains residual sulphuric, which is difficult to eliminate without damaging the CNC produced [52].

Sulphuric acid hydrolysis can produce high quantities of CNC with high yields if the operational conditions are selected correctly. The controlling factors of the operation conditions are acid percentage in the mixture, reaction time and temperature, these factors have been documented for many years. Other factors less studied in nanocellulose production like acid-pulp ratio or particle size could affect the yield as it happens in similar processes involving lignocellulosic biomass for example production of biofuels [22]

For many years sulphuric acid hydrolysis has been using a standard sulphuric percentage of 64 wt% but it might not be the best as recent studies have shown [53]. For sulphuric acid at 64 wt%, low yields of CNC are obtained, in the range of 30-45% [11][35]. Lower percentages around 50 wt% also produce really low yields of 25%, this can be because there is not enough depolymerization of cellulose, making that the rest of cellulose is partially hydrolysed and not converting to CNC. Seeing this, the maximal yield of CNC production needs a sulphuric content in the range of 56-62 wt%, because lower concentrations cannot hydrolyse cellulose and higher concentration deteriorate the cellulose to oligomeric and monomeric sugars that cannot be recovered and used [54]. Within the range of 56-62% of sulphuric acid content, yields up to 70% of CNC are achieved [54].

As it is shown the percentage of acid in the solution is the dominant effect, with this optimized, other factor have to be studied for further improving the CNC yield and its properties. Temperature and time can affect some properties like crystallinity and the crystals length of nanocellulose [52]. Acid hydrolysis temperature does not need to be high because it will

accelerate the decomposition of cellulose to sugars but it cannot be lower than 35 °C because reaction time to get to the maximal yields will be too high [53]. Temperature has an impact on crystal length, as temperature increases length does the opposite, and high reaction times increases crystallinity because biomass is more time exposed to hydrolysis eliminating the amorphous parts of cellulose. With that said and considering the bibliographical sources an optimal time and temperature are 50°C and 60 minutes.

To finalize, the resulting CNC must be quenched to end the hydrolysis reaction and to separate the solubilize content that stayed in the surface. The wastewaters from this process will be treated because of the sulphuric presence. Before obtaining the final product CNC has to surpass a dialyse treatment to control the residual sulphuric that has stayed in the surface area of the CNC.

#### 4.6.2. Production of cellulose nanofibrils (CNF)

CNF is mainly produced by mechanical treatments in the industry, but there are more options for its manufacture, such as enzymatic hydrolysis or TEMPO oxidation method.

Enzymatic hydrolysis has a huge disadvantage that has been cited different times in this work, which is the reaction time, to achieve significant yields several days must pass. Another disadvantage is the high costs of the enzymes [31]. In order to remediate this a combination between enzymatic hydrolysis and mechanical treatment could be done, this combination needs high concentrations of enzymes to reduce its reaction time and make more accessible the fibres to the mechanical process, which increases the costs of the process.

The other process that has been studied is the TEMPO oxidation, this treatment has different disadvantages that must be addressed. The first one is the chemical consumptions costs and the second one is not obtaining sufficiently high yields compared to mechanical treatments needing an extra defibrillation method to solve it [55].

The method of production of CNF has to be chosen from the variety of mechanical treatments existents. The pre-treatments use in the design of this process helps the mechanical treatment have access to the cellulose fibrils reducing the energy needed for this process. Nanocellulose yields from the different types of mechanical treatments are very similar, not making it the primary condition to determine which mechanical treatment suits best the process. The main condition is that the energy consumption of the process is the lowest possible

maintaining the high yields and properties of nanocellulose. If only one mechanical treatment is used the energy demand is very high making the process not viable, therefore a combination of two or more mechanical treatment should be used [56].

Ball milling has issues with the quality and homogeneity of the product as CNF size is not uniform causing possible problems to the following treatments or not being able to be used in some applications decreasing the fields that could be applied [21]. Another treatment that is discarded is microfluidization because of its nature of clogging while using long fibres [20] [57].

Other treatments that do not have the disadvantages mentioned before are grinding, refining and HPH. HPH is a common method for CNF production as a final element of the process. Other mechanical treatments to ensure that cellulosic material is partially converted to CNF favors this treatment decreasing energy consumption [27], the only disadvantage of HPH is that temperature has to be controlled because the mechanical forces produced in the device created heat generation. Grinding is formed by two stones, one is fixed and the other rotates producing shearing forces, the distance of these two disks could be adjusted reducing the chance of clogging. Also, grinding could be assimilated to a type of refiner known as disk refiner [20]. Apart from disk refiners, PFI mills refiners are the other devices most used in this mechanical method. Refining is a great treatment for CNF production as it is easy to operate and has high mechanical efficiency.

Therefore, CNF production in this project will be using a refiner followed by an HGH treatment. Comparing PFI mill and disk refiners it is observed that PFI mill energy consumption is huge compared to disk refiners, also, the amount of time needed to obtain high yields is lower with disk refiners. Disk refiners operation conditions are from 800-1600 rpm and residence times from minutes to hours [58][59]. CNF and the residual cellulosic material that the refining process has not been able to convert, enter the HPH where cellulose is almost completely transformed to CNF. Finally, the operational condition of HPH that has to be determined is the pressure, HPH have a range from 100-150 MPa [21]

### 4.7. BY-PRODUCTS RECOVERY AND WASTEWATER TREATMENT

From the process design made, *Figure 9*, different residual streams have to be treated in order to recover by-products that can be further valorised. From the washing and filtration after the hydrothermal pre-treatment a stream with sugars from hemicellulose hydrolysis can be valorised. Lignin recovery from soda-AQ and WO delignification can undergo another recovery and valorisation to obtain other products. Finally, the wastewaters from sulphuric acid hydrolysis have to be processed to eliminate the acid presence and reduce the wasterwater contamination.

#### 4.7.1. Hemicellulose and lignin recovery

Hemicellulose is formed by different monosaccharides that formed diverse structures. When hemicellulose is hydrolysed those monosaccharides are liberated and can be used to produce high value-added by-products, such as alimentary additives, drugs, bioethanol, xylitol, or furfural.

From those possible products, bioethanol production could fit well with nanocellulose production process in order to increase the biomass conversion to valuable products and give versatility to the biorefinery. The hemicellulose conversion to bioethanol is a well-known process, therefore is a great process for hemicellulose valorisation

The residual stream from hydrothermal pre-treatment consisting of a huge amount of water with hydrolysed hemicellulose as monomeric sugars is transported to a bioethanol plant where is going to be used as raw material.

The streams from alkaline-AQ and WO treatments contain water, high lignin content which can be recovered for further applications and residual hemicellulose and aggregates that have been degraded during the process. Lignin recovery and valorisation is more difficult than the other compounds present in the lignocellulosic biomass because of the complex structure it has. Therefore, in the pulp and paper industry and existing nanocellulose companies normally use lignin as a source of energy for the process. [62] Purpose different processes for lignin separation from the alkaline pulping treatments streams, membrane separation and acidification for lignin precipitation are the two methods investigated. Although these methods separate up to 90% of lignin in acidification and 75% in membrane separation, further studies have to be done to ensure that these processes are economically viable in the context of a biorefinery.

Therefore, the stream with lignin content will be used as energy source to reduce the energy demand of the process.

The stream main compounds are water, lignin and residual hemicellulose and aggregates. The process used to produce energy from this kind of streams is by incinerating the content in the stream, to do so, liquid content of the stream has to be evaporated to elevate the solid content. After the evaporation, the solid content is transferred to a recovery furnace where it is burn obtaining steam that can power the process *Figure 9*.

#### 4.7.2 Acidic wastewater treatment

After the acid hydrolysis the wastewaters must be treated to remove the acidic content from the water and recover the sulphuric acid to reuse it, reducing the chemical demand of the process. The conventional methods for acid regeneration are highly economical and energetically demanding such as combustion of the diluted acid or evaporation of the acid and water mixture [63]. Therefore, other methods have to be explored, such as polymeric membrane equipment, which forms a retentate of a greater concentration of acid than the original stream and another retentate with a high concentration of water. This process can be done several times obtaining the acid concentration desired.

### 4.8. PROCESS SUMMARY

This subsection will summarize the conditions of the equipment in the process that has been designed, the equipment conditions are in *Table 10*. Also, it will provide an approximated capacity of nanocellulose that could be produced by this process, utilising 1 tonne of agriculture biomass waste as calculating bases with the composition that has been approximated in section *4.3. Raw material selection and preparation* of this work and it is represented in *Table 9*.

Cellulose	Hemicellulose	Lignin	Ashes
38,5	28	20,1	13,4

Table 9. Average composition of the lignocellulosic biomass that enters the process

Equipment	Conditions
Grinder and sieve	Size reduction of the biomass
Hydrothermal pre-treatment (LHW)	T=180 °C, t=20 min, Hemicellulose yields 80-85%
Soda-AQ delignification	T=180 °C, t=30 min, 20% NaOH, 0,1% AQ, Liquid to solid ratio of 6, Lignin yield 70%
Wet oxidation	T=100 °C, t=60 min, O₂ pressure=0,6 MPa, 3% NaOH, 0,1% MgSO4, Lignin yield 70-95%
Sulphuric acid hydrolysis	T=50 °C, t=60 min, 56-62% H <sub>2</sub> SO <sub>4</sub> , CNC yield 70%
Disk refiner	800-1600 rpm
High pressure homogenizer (HPH)	P=100-150 MPa

Table 10. Equipment conditions of the nanocellulose production process design

Diverse considerations have been made in order to be able to calculate the quantities that exit every equipment of the process. For cellulose, it is considered that 1% is degraded on the hydrothermal LHW pre-treatment as the conditions are slightly favourable for cellulose to be hydrolysed. For hemicellulose, in the LHW pre-treatment it is known the percentage that is hydrolysed and removed, *Table 10*. On the other hand, hemicellulose removal in soda-AQ and wet oxidation has been appointed as an approximation based on other delignification processes, with a 40 and 20% in each equipment. Lignin in LHW pre-treatment has been considered the same degradation as cellulose with a 1%. Finally, ashes are the extractives, some of these aggregates are soluble and easy to remove but a residual part of the ashes are insoluble. Therefore, it is considered that 75% of the ashes can be eliminated in each equipment, resulting in a low percentage in the pulp before entering the final stage of the production process, all the quantities for each component of the lignocellulosic biomass are specified in the *Table 11*.

Compound	Raw material (kg)	LHW (kg)	Soda-AQ (kg)	Wet oxidation (kg)
Cellulose	385	381,15	381,15	381,5
Hemicellulose	280	49	29,5	23,6
Lignin	201	198,99	59,7	10,45
Ashes	134	33,5	8,37	2,09

Table 10. Lignocellulosic compounds quantities that exit the pre-treatment equipment of the process

The cellulosic material that enters the final stage of the process has a 91,3% of cellulose, 5,6% of hemicellulose, 2,5% of liginin and a 0,5% of ashes. This stream is divided into two equal streams for CNC and CNF production. As mentioned before in this work, CNF production by the mechanical process selected, it is considered to fully convert the cellulosic stream into CNF. On the other hand for CNC production the conversion rate is exposed in *Table 10*. The nanocellulose quantities for each production process it is displayed in *Table 11*.

Table 11. CNC and CNF production capacities per tonne of biomass.

CNC (kg)	133,5
CNF (kg)	190,75

Finally, in *Table 12*, hemicellulose and lignin quantities that have been removed to be valorised as bioethanol and energy are shown. As it can be observed, huge quantities of hemicellulose and lignin are separated. Therefore, it is very important to valorise those by-products in order to reduce waste and to make more viable the process.

Table 12. By-products	of the process and their	quantities recuperated
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Hemicellulose sugars (kg)	231
Lignin (kg)	188,54

# 5. CONCLUSIONS

The aim of this project was to design a process to produce high value-added products, such as nanocellulose. Therefore, the study of the state of the art of nanocellulose production and the process design has achieved the following conclusions:

- Agricultural biomass waste can be used as raw material for nanocellulose production processes, because of their lignocellulosic matrix formed by cellulose, lignin and hemicellulose.
- Nanocellulose production by only one step (mechanical, biological, or chemical treatment) is not sustainable as the conversion is too low compared to the costs of these types of processes.
- Pre-treatments are needed to fractionate the biomass into their main components (cellulose, hemicellulose, lignin), decreasing the operational costs of the production process as cellulose is more accessible after the pre-treatments.
- The design process has great hemicellulose and lignin recovery, which are further valorised to bioethanol in a bioethanol plant with hemicellulose sugars as raw material and generation of energy from lignin, making the process more versatile, reducing waste, and decreasing energy consumption. Also, the process is environmentally friendly because the acidic wastewaters generated in the sulphuric acid hydrolysis are treated to recuperate the H<sub>2</sub>SO<sub>4</sub>.
- The process design in this project has an approximated capacity of 133kg of CNC and 190,75kg of CNF per tonne of agriculture biomass waste.
- CNC and CNF produced can be applied to several industrial fields, standing out biomedical, electronic and composites industries.

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# ACRONYMS

TAPPI	Technical Association of the Pulp and Paper Industry
CNC	Cellulose nanocrystals
CNF	Cellulose nanofibrils
BN	Bacterial nanocellulose
LHW	Liquid hot water
WO	Wet oxidation
AFEX	Ammonia fibre explosion
HPH	High-pressure homogenization
TEMPO	2,2,6,6-Tetramethylpiperidinyloxy
AVAP	American Value Added Pulping
USE	Uncatalyst steam explosion
ACSE	Acid catalyst steam explosion
AQ	Anthraquinone