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# Biomass Waste—A Source of Raw Materials

Matjaž Kunaver

**Abstract:** Biomass represents an immense and renewable source for the production of bio-fuels and valuable chemicals. A little amount of this is used in industry and the remaining is leftover in huge quantities. Agricultural crop residues, such as straw, corn stover, and wood and wood wastes such as leftovers from timber cutting, broken furniture, sawdust, residues from paper mills etc. contain appreciable quantities of cellulose, hemicelluloses, and lignin. Much effort has been devoted to converting these types of biomass into useful industrial and commercially viable products. In recent years, some effective processes have been found, such as thermochemical conversion, producing several platform chemicals from these renewable resources. Lignocellulosic biomass contains cellulose, hemicellulose, and lignin in various proportions. The first step towards the conversion of these basic ingredients into different basic chemicals is their separation. Each of these three biomass components can then be converted into different platform chemicals. Different reaction pathways and final products with high added value will be presented. One of possibilities of converting biomass is the liquefaction in glycols using mild acid catalysts. During the liquefaction reaction, lignocellulosic components are depolymerised to low molecular mass compounds with high reactivity, high hydroxyl group content, and can be used in many useful applications. The liquefied biomass can be used as a feedstock in the synthesis of polyesters, polyurethane foams, and adhesives with properties similar to those produced from crude oil feedstock. Nanocellulose, a carbon neutral and sustainable material with outstanding mechanical properties, is one of the most promising materials and has been a subject of recent interest. An overview of some applications and methods are presented in this contribution. The utilization of liquefied lignocellulosic materials can at least partially reduce the crude oil consumption, thus increasing the use of the renewable resources in large extent.

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## 1. Introduction

Biomass-based materials and wood in particular are among the more abundant renewable resources. Much effort has been devoted to converting these types of biomass into useful industrial and commercially viable products. Recently, considerable attention has been given to the preparation of environmentally friendly products from liquefied biomass materials. Some typical conversion processes are depicted in Figure 1. However, much remains to be done in synthesis, analysis,

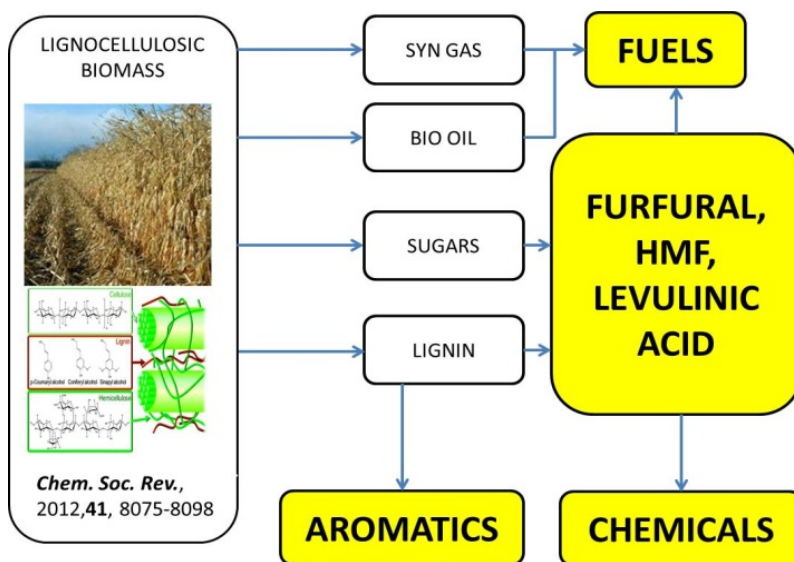
and characterisation if these new materials are to be exploited to their full advantage. Cai et al. [1] published a review of physicochemical properties and characterisation methods of lignocellulosic biomass. The knowledge of biomass properties and main components is essential for effective process development.

With respect to the liquefaction of wood, wood wastes, and other lignocellulosic biomass, earlier applications were mainly based on their use as fuels. A direct liquefaction of wood at high temperatures and pressures in order to convert it into a more usable fuel was achieved using different technologies, such as pyrolysis, plasma techniques, supercritical water gasification, and enzymatic conversion, thus providing a longer-term solution to the need to decrease the crude oil dependency [2–5]. With respect to the liquefaction of wood and wood wastes and their use as a liquid fuel, Rezzoug and Capart [6] used solvolysis in ethylene-glycol and catalytic hydrogenation as the second stage for the production of oils that possessed a high heating value. Seljak et al. [7] reported the results of a successful combustion of liquefied wood prepared in an acid catalysed reaction with polyhydroxy alcohols.

Since petrochemicals may soon be limited, considerable attention has been given to the selective conversion of biomass into chemicals such as 5-hydroxymethylfurfural and dimethylfuran by selective chemical catalysts [8–10]. The conversion of biomass by depolymerisation and fermentation is presently the approach with the most potential. Recent studies of acid catalysed depolymerisation with organic solvents has allowed to increase yields of basic chemicals such as furfural, hydroxymethylfurfural, and levulinic acid [11–13].

Although biomass-based lignocellulosic materials are complex and the liquefaction process of their components is not fully understood, three major transformation pathways are more commonly used.

- Fast pyrolysis at high temperatures and subsequent conversion into the liquid products and gaseous products that are used for energy production;
- Thermochemical conversion, at elevated temperatures and with the use of different liquefying agents and catalysts. Here, solvolysis and depolymerisation take place simultaneously with the liquid final product being rich in hydroxyl groups;
- Biochemical modifications (enzymatic conversion into ethanol and other depolymerisation products).



**Figure 1.** Biomass conversion pathways.

This review provides some references on conversion methods of biomass into some important chemicals and polymers. Because of numerous chemical products that can be manufactured from biomass, the interest in biomass conversion to chemicals has been a subject to many studies during the last few years. Researchers worldwide have developed methods to provide bio-based products from a wide selection of biomass resources and some processes are now suitable for scale-up production in industry. The industrial production of levulinic acid from tobacco wastes is one of the first applications and the isolation of 5-hydroxymethylfurfural, isosorbide,  $\gamma$ -valerolactone, nanocellulose, and other specialty chemicals will follow. Interests in the conversion of biomass to chemicals are strongly connected to the use of renewable resources instead of crude oil and the need to decrease greenhouse gas emissions. Therefore, due to the abundance and availability of biomass with no impact on food production, its utilization in the production of fuels and chemicals is highly promising.

This article presents some pathways for the production of chemicals from biomass. Special attention was given to thermoconversion methods, such as the liquefaction of biomass due to its simple chemical conversion process and equipment needed.

### 1.1. The Liquefaction Process

The liquefaction of wood and other lignocellulosic materials in the presence of phenol or polyhydroxy alcohols has been intensively studied by several authors [14]

and has been described in detail [15]. Such a liquefaction process is usually carried out at elevated temperatures and in the presence of an acid catalyst [16–18]. The liquefied wood contains depolymerized products from the  $\beta$  1–4 glucosidic bond cleavage of the cellulose and hemicelluloses molecules and from low molar mass oligomers. The complex structure of the lignin molecule is broken into smaller fragments. Several attempts to elucidate the mechanisms associated with the liquefaction of lignin, of cellobiose, and of cellulose have been published. The liquefaction of lignin with phenol has been studied on the basis of the behaviour of model substances, such as guaiacylglycerol- $\beta$ -guaiacyl ether. According to Lin et al., the dominant products were guaiacylglycerol- $\alpha$ -phenyl- $\beta$ -guaiacyl ethers, followed by guaiacol, triphenylethanes, diphenylmethanes, benzocyclobutanes, and phenylcoumaranes [19,20].

The behaviour of cellulose in acidic ethylene glycol and ethylene carbonate was studied by Yamada and Ono [21]. These authors proved the formation of ethylene glycol—glucosides in the early stage of liquefaction. These later decomposed into the 2-hydroxyethyl levulinate. Jasukaityte et al. [22] studied the liquefaction of different types of cellulose by monitoring the molar mass decrease and changes in degree of crystallinity during the reaction. They found that the less disordered regions degraded in the initial minute of liquefaction. The highly ordered cellulose regions remained relatively stable for a longer time. Kobayashi et al. [23] have undertaken research into the liquefaction of cellulose powder, of steamed lignin, and of mixtures of these two components in order to characterise the reaction process on the basis of the polyhydric alcohol nature of the materials. They found that the condensation reaction occurred only in mixtures of cellulose and lignin. Under these conditions, dimethyl formamide insoluble residue was formed, being similar in nature to wood. They suggested that a condensation reaction occurred between the depolymerised cellulose residues and the aromatic derivatives of lignin. Yan Shi et al. [24] studied kinetics of biomass solvolysis and found that glycerol was very efficient solvent due to higher polarity.

While a large number of papers have been published describing the liquefaction process, the characterisation of the product, and the reaction pathways, little information is available on the application of the more specialised techniques in biomass liquefaction. One of these is microwave-driven wood liquefaction, where microwave heating has been used in a very efficient and fast liquefaction of wood. The efficiency of liquefaction and the time needed for the complete liquefaction was reduced significantly [25,26]. Complete liquefaction was achieved in 20 min under the prevailing processing conditions. The use of ionic liquids for wood liquefaction is also considered to be specific due to the application of reagents and their recycling [27]. Zavrel et al. very efficiently dissolved wood chips in ionic liquids, an environment-friendly alternative to conventional methods [28].

A novel approach to very efficient energy input during the thermochemical conversion of lignocellulosic biomass into liquefied depolymerised products is the use of ultrasound technologies [29–31]. High-energy ultrasound has been used in liquefaction reactions with different wood waste materials. The most common wood waste materials were chosen in order to prove the efficiency of the ultrasound process and to establish a different way for recycling wood wastes found in large quantities in municipal waste deposits. The reaction times were shortened up to nine times when using the ultrasound process, with smaller residual particles and with no influence on the hydroxyl number of the final products.

Yamazaki et al. have studied the liquefaction of beech wood using supercritical alcohols with 100% yields [32]. Liquefied wood has a high reactivity due to a large amount of phenolic and alcoholic hydroxyl groups that are present. The hydroxyl value of the liquefied wood has been determined by several authors and is generally determined to be higher than 200 mg KOH/g. The value depends on the liquefaction time and on the ratio between the wood content and the liquefying reagents.

Although the liquefaction of biomass was studied in detail and its further use in polymer synthesis, its direct utilization in film formation was published by Budja et al. [33] and Briones et al. [34]. Authors produced polymer films from liquefied biomass with promising mechanical properties and with good future perspective in film production for agricultural applications.

## *1.2. Chemicals from Biomass*

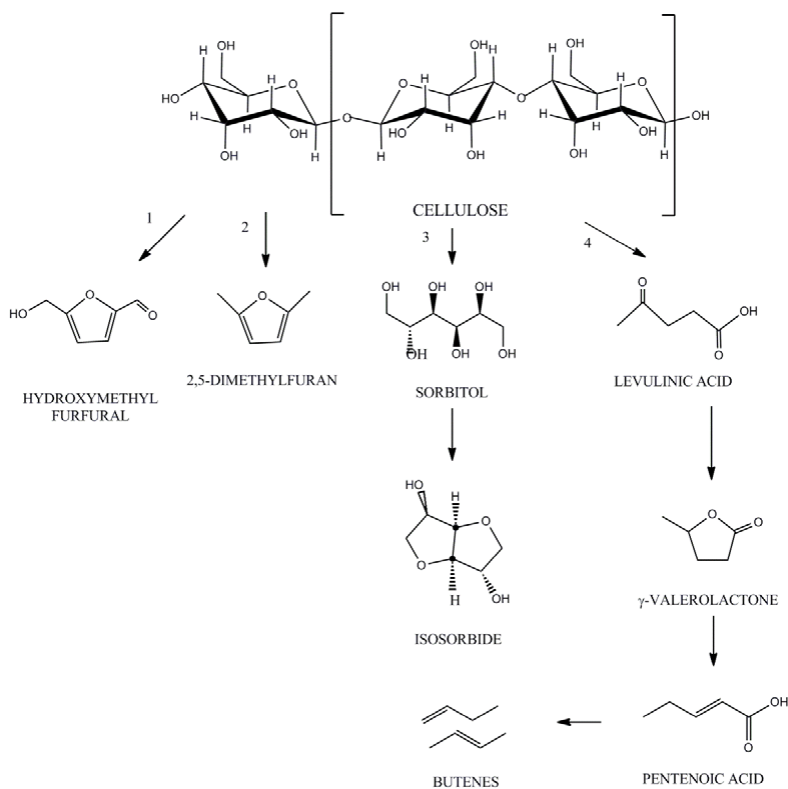
Biomass is primarily composed of cellulose (40–50%), hemicellulose (25–35%), and lignin (15–20%). The composition varies considerably depending on types of biomass, part of the plant etc. Cellulose is the major structural component of plant cell walls and is organized into fibrils, which are aligned parallel to each other, surrounded by a matrix of hemicellulose and lignin.

### *1.2.1. Cellulose*

The use of biomass as a natural source for industrial applications and for the production of chemical are today regarded as an alternative to petrochemical processes. In particular, cellulose as the most abundant renewable polymer has become an object of studies on how to obtain many valuable chemicals from biomass [11].

A multitude of different types of biomass has been tested, including algae, cultivated crops, agricultural waste, forest resources, etc. The term that is usually associated with such conversion is biorefinery. A variety of technologies have been used including fermentation, pyrolysis, thermochemical conversion, hydrothermal liquefaction, catalytic conversion, etc.

Some final and intermediate products, derived from cellulose are shown in Figure 2. Chemicals, such as 2,5-Dimethylfuran, 2,5-Dimethyltetrahydrofuran, are considered as the target chemicals for fuel. Isosorbide (1,4:3,6-Dianhydrohexitol) is a desired chemical that allows further chemical modifications through the conversion of the hydroxyl groups into other functional groups, which leads to monomers suitable for the production of polymers [35,36].



**Figure 2.** Cellulose conversion into different chemicals by biorefinery.

### 1.2.2. Hemicelluloses

Hemicelluloses, hetero polymers that are present along with cellulose in plant cell walls, contain xylose, mannose, galactose rhamnose, and arabinose. They can easily be isolated from plants by different purification methods using acids, organic solvents, and alkaline reagents. Other methods include steam explosion, ultrasonication, extrusion, and microwave irradiation. Further conversion into hydroxymethyl furfural, furfural, and even propionic acid can be achieved by reaction in a catalysed ionic liquid, fermentation processes, or hydrothermal processes [37–39].

### 1.2.3. Lignin

Lignocellulosic biomass is mostly cell wall material, and lignin is one of three principal components beside cellulose and hemicelluloses. Lignin serves as a binding agent, adding strength to the cell walls. It is a cross-linked amorphous polymer synthesized from aromatic alcohol precursors, p-coumaryl, coniferyl, and sinapyl alcohols and has a very complex structure. These precursors are linked together via radical coupling reactions to form a complex three-dimensional molecular architecture that contains a great variety of bonds with typically around 50%  $\beta$ -O-4 ether linkage [40]. The characterization and structure determination of lignin has been a challenge to scientists for many years.

Since it represents 30% of all non-fossil organic carbon on Earth, it is logical to explore the potential use of this natural polymer as a source of valuable chemicals, as shown in Figure 3. Lignin is extracted from biomass by physical, chemical, and biochemical treatments. Pulping processes that utilize extraction methods are based on ester and ether bonds cleavage and thus change the structure of lignin macromolecule into more simple and smaller ones. The product is different than the original lignin present in the plant cell. In general, we can distinguish two different extraction processes: sulphur and sulphur-free process. The product of the first one is the lignosulfonate and kraft lignin, while the second one gives organosolve and soda lignin.

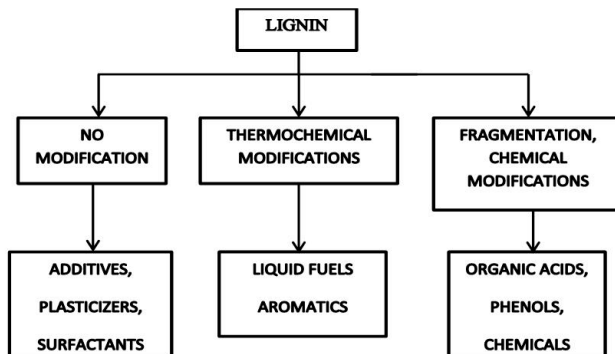


Figure 3. Summary of the uses of lignin.

Lignin without chemical modification can be used as a filler, anti-oxidant, UV-stabilizer, surfactant etc. The chemical modification of lignin [41] has much better potential for multiple applications and can be classified into three main categories:

1. Fragmentation;
2. Modification by creating new chemical active sites;
3. Chemical modification of hydroxyl groups.



## Fragmentation of Lignin

The fragmentation methods can be summarized into pyrolysis, hydrogenation, hydrolysis, oxidation, gasification, enzymatic oxidation, and microbial conversion processes. The products are very diverse, from syngas to phenols, cresols, phenol, vanillin, dimethylfuran, different organic acids etc. Lignin fragmentation has had two objectives: the study of the structure and the production of useful materials from waste lignin.

Lignin pyrolysis has been studied for many years with the abovementioned goals and is based on heating biomass at around 500 °C without oxygen. The degradation products are solid (tar), liquid (methanol, acetic acid, acetone, and water), and gaseous fraction (CO, CO<sub>2</sub>, CH<sub>4</sub>, etc.). Pyrolysis has been used predominantly for bio-oil production which can be used as a fuel.

Lignin oxidation with one of most common oxidants such as nitrobenzene, some metallic oxides, air, and oxygen is another way to obtain phenolic derivatives. Of course, the proper reaction conditions must be met to obtain products with high added value, such as vanillin, which is mainly used in the food processing industry. The lignin oxidation process can also provide some very useful basic chemicals for the chemical industry, such as vanillic acid, hydroxybenzaldehyde, syringic aldehyde, syringic acid etc.

One of the most promising methods is the thermochemical conversion—liquefaction of lignin. This method utilizes simultaneous solvolysis and depolymerisation. The resulting products are in hydroxyl groups and can be used as a feedstock in the preparation of polyurethanes, polyesters, and epoxy resins [42,43].

## Modification of Lignin

In order to increase the reactivity of these groups, several modifications have been studied, such as nitration, amination, alkylation, dealkylation, carboxylation, and halogenation. The common goal was to achieve better solubility in organic solvents, to increase chemical reactivity, and to improve mechanical properties and processing of lignin.

### Chemical Modification of Hydroxyl Groups

Special attention was given to the functionalization of phenolic and hydroxyl groups in lignin since they can be converted through esterification, etherification, oxidation/reduction, phenolation, reactions with isocyanates, or silylation. Such modifications improve the solubility of lignin. Demethylation is well-known method for dimethyl sulfoxide (DMSO) production. Here, two methyl groups are transferred from lignin to sulfur, which is further oxidized to DMSO. Esterified lignins can be used as a precursor of polyesters, epoxy resins, and elastomeric

materials. Etherification leads to polyols that can be used for the production of polyurethane foams. Hydroxymethylated lignin can substitute a certain part of phenol in phenol-formaldehyde resins. Variations with the use of glyoxal, furfural, and glutaraldehyde have also been published [44].

### *1.3. Adhesives*

Hydroxyl groups in liquefied lignocellulosics can also react with different reactive sites in thermosetting systems as well as in two component systems. Lee and Liu prepared a resol type of resin from liquefied bark that was used in particle board preparation [45]. Similarly, a phenol formaldehyde adhesive was prepared by Shenyuan et al. from liquefied bamboo [46]. Zhang et al. used Chinese fir and poplar in this context [47]. They tested the bonding strength of such adhesive in plywood, showing that the product successfully met the requirements. Gagnon et al. have undertaken research into the softwood bark pyrolysis oils and their use as adhesives for particle boards in combination with isocyanates [48]. Dos Santos et al. have used liquefied cork and wood to produce polyurethane adhesive [49]. Juhaida et al. liquefied kenaf core and prepared polyurethane adhesive for wood laminates [50]. Kunaver et al. applied a mixture of liquefied wood and melamine—urea—formaldehyde resin as an adhesive in wood particle board production [51].

The hydroxyl groups of the liquefied wood can react with epichlorohydrin, thus introducing the epoxy functionality. Kobayashi et al. prepared such epoxy compounds from the heartwood meal of Japanese cedar [52,53]. Kishi et al. prepared a wood-based epoxy resin from wood meal of German spruce [54]. The authors cured their epoxy resin precursors with suitable amino precursors. Such two-component systems were used as adhesives in plywood preparation, and good mechanical and physical properties were obtained.

### *1.4. Polyurethanes*

Liquefied lignocellulosic materials are considered to be an alternative feedstock for polymer synthesis. Recently, considerable attention has been given to the preparation of environmentally friendly polymeric products from liquefied biomass materials and their derivatives.

In the liquefaction process, the hydroxyl group-containing species in the wood components can be used as polyols for several different purposes. The polyhydric units that are present in the resulting liquefied/derivatised wood can be used in the creation of polyurethane foams, polyurethane resin precursors [55,56], and in the recently developed wood polyalcohol-based urethane adhesives [57]. Several authors have found a combination of PEG-400 and glycerine to be the most effective liquefying reagent [58,59]. Claims are made that greater than

95% liquefaction has been achieved in most experiments. Liquid wood can be used directly without any additional treatment. It is claimed that mixtures of such liquefied/derivatised mixtures can be directly used for the preparation of polyurethane foams [55]. Chen and Lu prepared rigid polyurethane foams from liquefied wheat straw [60]. The products are rich in ethylene oxide units and, due to the presence of extensive hydrogen bonding, have a highly hydrophilic character. Hu and Li produced rigid and semi-rigid polyurethane foams by using crude glycerol with high organic impurities [61]. The foams had suitable properties comparable to those derived from petrochemical-based chemicals. Lee et al. [62] have studied the thermal stability, biodegradability, and genotoxicity of a range of polyurethane foams that were produced from polyols made from waste paper. They found that the foams possessed the same thermal stability as those made from liquefied starch or wood. The foams were biodegradable to some extent. No mutagens or carcinogenic substances were found in water extracts from the foams. These materials are technologically simple and inexpensive to produce. It is stated that they can be used in agricultural and horticultural applications. D'Souza et al. [63] have liquefied bark at different reaction conditions and have found that the foams exhibited a high amount of open cell content when utilizing the polyol synthesized at lower temperature.

### *1.5. Polyesters*

The hydroxyl value of the liquefied wood has been determined by several authors and is generally determined to be between the equivalent of 200 and 500 mg KOH/g. The actual value depends on the liquefaction time. This large number of hydroxyl group sites means that the products have applications in those areas in which the hydroxyl component can be used in complex polyester synthesis. Yu et al. [64] liquefied corn stover in a mixture of ethylene glycol and ethylene carbonate and used the liquefied product as a polyol in a condensation reaction with different organic dibasic acids. The product was a completely crosslinked solid polyester, insoluble in most solvents.

Kunaver et al. [65] used the liquefied wood as a polyol in the polyester synthesis. Saturated polyesters are defined as polyesters whose components contain no polymerizable double bonds, the opposite of what occurs with alkyd resins and unsaturated polyesters. Saturated polyesters are synthesized by the condensation of bifunctional or polyfunctional monomers containing hydroxyl or carboxylic groups. The hydroxyl groups in the current investigation originate from liquefied wood. The polycondensation process takes place at temperatures of 150 °C to 260 °C. Water, as the main reaction byproduct, is removed from the system by the creation of a slight vacuum, gas stream condensation, or an azeotropic process. Čuk et al. [66] combined recycled PET polyester with liquefied wood polyester for the production

of polyurethane/polyisocyanurate foams. Glass transition temperature, density, and water absorption of the foam increased with increasing amount of glycerol in liquefied wood, and compressive stress also increased, while thermal conductivity was not affected.

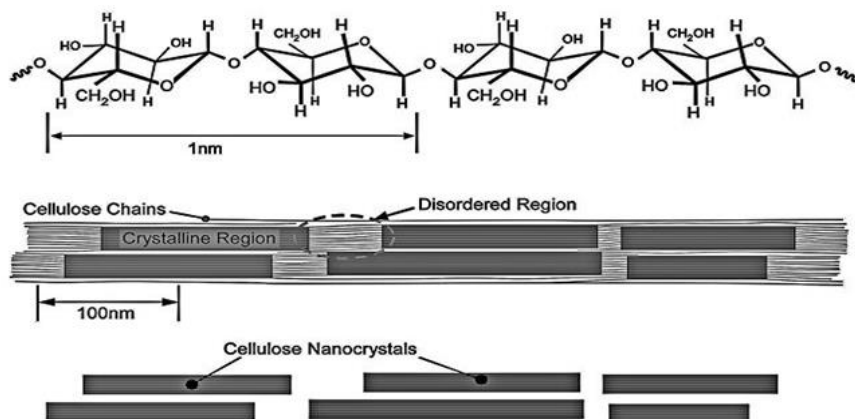
Some benefits could be expected from such systems. These include the incorporation of the biomass components into the polymeric compositions and, consequently, the provision of a certain degree of biodegradability. Esterification of a proportion of the hydroxyl groups reduces the reactivity of the liquid wood, a feature that is sometimes desired in polyurethane synthesis.

## 1.6. Nanocellulose

### 1.6.1. What Is Nanocellulose?

In recent years, there has been increasing interest in the development of biodegradable composite materials, so-called green composites. Natural fibers lack the high performance characteristics of many synthetic fibers. Cellulose acts as a framework in lignocellulosic materials and is based on highly oriented cellulose fibrils. Within cellulose fibrils, there are highly oriented regions, namely nanocrystalline cellulose, as presented in Figure 4.

Highly crystalline cellulose nanofibers (CNCs), present in natural plant bodies, have unique properties and have been identified as a new reinforcing agent in nanocomposites due to their low cost, availability, renewability, light weight, nanoscale dimension, and high aspect ratio [67,68]. The CNC has high strength due to its dense and ordered crystalline structure and therefore its axial Young's modulus is extraordinary, potentially stronger than Kevlar.



**Figure 4.** Cellulose nanocrystall regions in plant structure [69].

### 1.6.2. Nanocellulose Isolation

CNC is usually produced from native cellulose by isolation of its crystalline regions [70]. Different processes have been developed for the isolation of nanocrystalline cellulose from biomass. These include

- Chemical pulping where lignin is removed by a Kraft process;
- Steam explosion followed by hydrolysis;
- Acid hydrolysis;
- Microwave assisted hydrolysis;
- Mechanical structure breakdown.

The typical procedure currently employed for the production of CNC consists of subjecting the cellulosic material to strong acid hydrolysis under strictly controlled conditions of temperature, agitation, and time. Since it is quite difficult to achieve CNC with stable and controlled size (length) in a short duration of time. Kos et al. [71] developed an optimized process for rapid preparation of CNC using microwave heating, while Kunaver et al. [72] modified the process of biomass liquefaction in polyhydroxy alcohols and acid catalyst for the rapid and non-expensive isolation of CNC from different lignocellulosic sources. Ultrasound can be used as an additional source of energy.

### 1.6.3. Nanocrystalline Cellulose (NCC) Applications

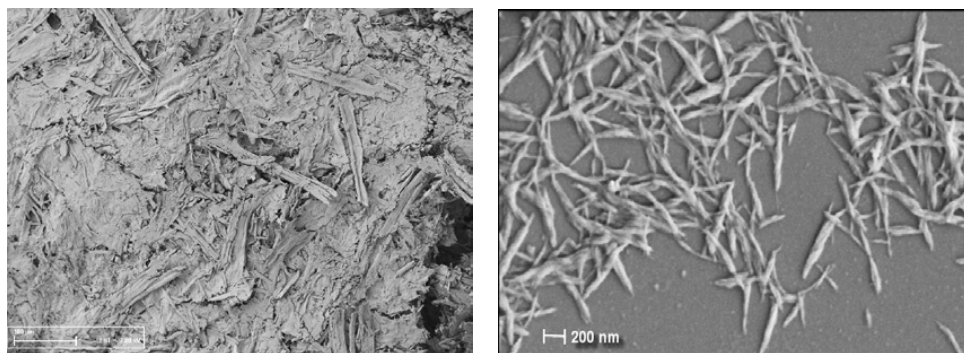
Many new nanocomposite materials with attractive properties have been prepared by physical incorporation of CNC into a natural or synthetic polymeric matrix and also holds promise in many different applications such as in nanopaper, coatings, adhesives, optical sensors, biomedical scaffolds, filtration membranes, electronic devices, foams, aero gels etc., which make NCC of significant interest from a scientific and industrial perspective [73–76]. Major studies over the last decades have been dedicated to use nanocellulose as a filler in nanocomposites to improve mechanical and barrier properties. It can be easily chemically modified due to the abundance of OH groups on the surface of the nanocellulose through the acetylation reaction, TEMPO oxidation, silylation, polymer grafting, all with the purpose of modifying the polarity of the nanocellulose surface and improving the compatibility with different polymer matrices. Due to nanocellulose's high functionality and so many possible chemical modifications, the material applications for nanocellulose are almost limitless.

## 2. Characterisation Techniques

A number of methods have been used for the process control and for the characterisation of products. Here, only the most commonly used are described.

### 2.1. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) Observations

Wood meal and wood residue, after the liquefaction reaction, can be micrographed on a scanning electron microscope. Samples must be sputter coated with a thin layer of gold to avoid electrostatic charging during scanning. Samples of nanocellulose must first be diluted and sonicated to prevent agglomeration. Both SEM and TEM micrographs give the information about the particle dimensions and the degree of agglomeration. An example of micrograph of wood residue after the liquefaction and nanocrystalline particles, isolated from wood meal, are shown in Figure 5.



**Figure 5.** Scanning electron microscopy (SEM) micrograph of wood residue after the liquefaction process (**left**). SEM micrograph of nanocrystalline cellulose isolated from wood meal (**right**).

### 2.2. Viscosity Measurements

The viscosity of polyesters and of the liquefied wood is measured using a rotational viscometer. Standard ISO 3219-1993 describes the measurement method.

### 2.3. Measurement of Hydroxyl Number and Acid Number of Liquid Biomass and of Liquefied Biomass Polyester Derivatives

The hydroxyl numbers of liquefied biomass and its derivatives can be determined using standard ASTM Standard D4274-05 [77]. The acid number is determined using standard ASTM D974-08 [78]. Both measurements are needed to control the process of polyester formation and for polyurethane foam preparation.

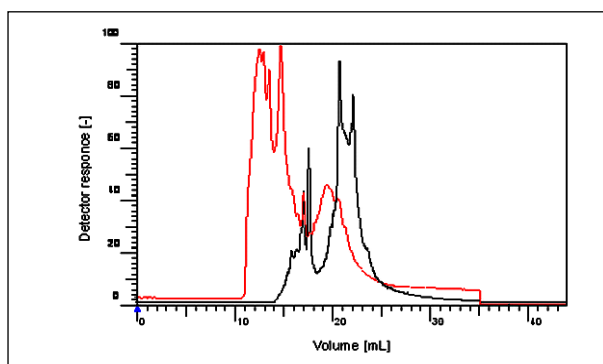
### 2.4. Fourier Transform Infrared (FTIR) Spectroscopic Analysis

Spectra are usually obtained using an FTIR spectrophotometer. The liquid/derivatised wood samples and the polyesters are each supplied on a NaCl crystal

as a thin film. Transmittance spectra are measured in the wavelength range from  $4000\text{ cm}^{-1}$  to  $500\text{ cm}^{-1}$ . The method helps to identify the characteristic functional groups in liquefaction products.

### 2.5. GPC Measurements

Gel permeation chromatographic (GPC) representations are obtained on a chromatographic system, consisting of isocratic pump, a refractive index detector and a diode array detector. Polystyrene standards are used for the calibration curve. The mobile phase is sometimes prepared from dimethyl acetamide containing 0.05 M LiBr. The latter is added in order to prevent interaction between the sample molecules and the stationary phase. A typical GPC curve of liquefied wood and of liquefied wood polyester is presented in Figure 6.



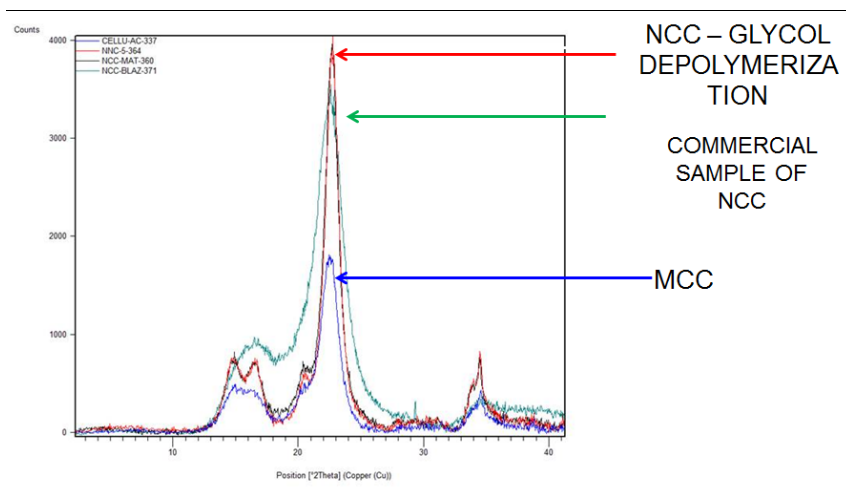
**Figure 6.** Gel permeation chromatographic (GPC) chromatogram of liquefied wood (black) and polyester synthesized from liquefied wood (red).

### 2.6. Particle Size Distribution from DLS Studies

The dynamic light scattering (DLS) technique is usually employed to find the statistical distribution of the particles present in nanocellulose or other biorefinery products.

### 2.7. X-Ray Diffraction

The crystallinity index of nanocellulose is usually calculated from X-ray diffractograms (Figure 7). The diffraction data are collected on a wide-angle X-ray diffraction instrument, equipped with Cu anode at wavelength  $\text{Cu K}\alpha$ . Diffractograms are measured in the 2-theta range from  $5^\circ$  to  $40^\circ$ . The most used method for the crystallinity index calculation is the Segal method [79] although this method suffers some inaccuracy due to the inaccurate amorphous peak position. The crystallite size can be estimated by using a well-known Scherrer equation [80].



**Figure 7.** X-ray diffraction (XRD) diffractograms of nanocrystalline cellulose and microcrystalline cellulose.

## 2.8. Differential Scanning Calorimetry (DSC)

The thermal behaviour, the melting temperature, and the crystallization temperature is measured using differential scanning calorimeter. Samples are heated from 30 °C to 350 °C under a nitrogen atmosphere.

## 2.9. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) analyses are used for the determination of an initial weight loss at low temperatures, the thermal degradation temperature, and the maximum decomposition temperature. Samples are heated at constant heating rate under nitrogen purging.

## 3. Conclusions

The possibilities of converting lignocellulosic biomass and biomass waste in particular into valuable chemicals and raw materials for further use in polymer chemistry are numerous. Intensive studies of this challenge have been governed for the last two decades. The biorefinery concept has been firmly established, and the only danger that has to be guarded carefully is that the production does not compete with food production. It provides new prospects of utilizing renewable resources for the production of energy, organic chemicals, and polymers through complex processing technologies. Lignocellulosic biomass, the most abundant sustainable feedstock on earth, contains cellulose, hemicellulose, and lignin in various proportions. The first step toward the conversion of these basic ingredients into



different basic chemicals is their separation. Each of these three biomass components can then be converted into different platform chemicals. One of the newest challenges is the isolation and application of nanocellulose, an outstanding material that is carbon neutral, sustainably recyclable, and non-toxic. It has the potential to become a true green nanomaterial that will be used in high-performance applications. The final cost of bioproducts depends upon the processing costs. Therefore, high tonnage, high yields, and the reduction of the synthesis steps are the most important development trends today and in the future.

All the products can be regarded as higher added-value materials, decreasing the dependency to the crude oil production, and at least not increasing the greenhouse gas emissions.

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