

Short Commentary

Synthesis of Nanolignin Following Ozonation of Lignocellulosic Biomass

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Introduction

The non-food valorization of biomass represents a major axis of research currently animating a large number of scientists. Whether for energy purposes, replacing fossil fuels such as oil, or as innovative strategies for access to new bio-sourced products, modern valorization approaches are above all respectful of the principles of green chemistry, and generally refer to processes or to the use of eco-compatible products. Renewable polymers have emerged as an attractive alternative to conventional metallic and organic materials for a variety of different applications, due to their biocompatibility, biodegradability and low cost of production [1]. Renewable biomass can provide many industrial solutions as it is composed primarily of cellulose (30–35%), lignin (15–30%) and hemicellulose (20–35%). Among them, lignin is known as one of the main bio-resource raw material that can be used for the synthesis of environmentally friendly polymers, thus a good candidate for replacing regular industrial aromatic polymers and fine chemicals. Due to its chemical and structural diversity, lignin valorization remains a major challenge for achieving a viable biomass-based economy [2]. Lignin's are composed of polymerized monolignols and their derivatives. Particularly grass lignin's contain important amounts of alkenes yielding up to 10–15% by weight aldehydes [3].

Lignin extraction from lignocellulosic biomass

The lignocellulosic biomass has to be treated before any widespread utilization of its components. As a decrease in the lignin content in plants results in an increase in biodegradability, lignin removal from this biomass is a crucial pretreatment step [4,5]. A large number of chemophysical pretreatment approaches has been investigated on a wide variety of feedstock [6]. These methods require the use of hazardous materials such as acids, alkalis and/or organic solvents. They are currently four industrial processes to extract pure lignin: sulfite, kraft, organosolv and soda processes [7, 8]. Kraft pulping accounts for approximately 85% of the produced lignin. The delignification process is performed at high temperatures (170°C) and high pH 13 or 14, during which the lignin is dissolved in sodium hydroxide and sodium sulfide (white liquor) [9].

The sulfite process involves the reaction between lignin and a metal sulfite and sulfur dioxide, with calcium, magnesium or sodium acting as counter ions; the pH can vary between 2 and 12, and the temperature between 120 and 180 °C, with a digestion time of

1–5 h [10]. The soda process is typically used for the treatment of grass, straw and sugarcane bagasse, which accounts for 5% of the total pulp production [11]. The biomass is digested at temperatures that vary between 140 and 170 °C in the presence of 13–16% by weight of aqueous solution of sodium hydroxide. The soda lignin contains no sulfur which is not the case of the kraft and sulfite processes.

The organosolv process is based on the treatment of the biomass using organic solvents including ethanol, methanol, acetic and formic acid that are usually mixed with water at temperatures that range from 170 to 190°C [12]. The recovery and separation of the dissolved lignin and hemicelluloses can be done by precipitation of lignin or evaporation of the organic solvent, after adjusting the temperature, pH and concentration of the organic solvent. Organosolv pulping is one of the most efficient options for the further valorization of lignin and it also preserves the native structure of the lignin [13]. The obtained lignin is sulfur-free, with lower ash-content, and it has higher purity.

The removal of lignin by different technologies originates different product streams. Beyond the production costs and the environmental impact the lignin extraction method has to be selected depending on the use that will be given to the extracted lignin. In general, the kraft and sulfite processes allow extracting lignin at reasonable costs, while the organosolv method continues to be an expensive technology but still with high quality extracted lignin. However, the soda extraction process generates lower production costs and low environmental impact.

Ozonation of lignocellulosic biomass

Ozonation can circumvent the different issues of the above extraction processes that require the use of hazardous materials (acids, alkalis and/or organic solvents), as it is considered as a green process. Ozone (O₃) is a powerful oxidizing agent (E° = 2.07 V). It is one of the most promising lignocellulosic biomass oxidative pretreatment for selective lignin degradation with minimal effects on the hemicellulose and cellulose contents [14]. It provides low production of inhibitory compounds such as furfural and HMF (Hydroxymethylfurfural), and more importantly it requires no chemical additives during all the pretreatment process. However, ozonation demands high energy generation costs but this aspect can be avoided by optimizing the ozonation process. Ozone has a high affinity for phenol and polyphenols such as lignin and tannic acid. During ozonation lignin is converted to soluble products which to a great extent are biodegradable and thus yield a useful byproduct [15].

It has been reported the ozonolysis of grass lignin to selectively cleave aromatic aldehydes by limiting the reaction residence time to a few minutes for preventing over oxidation of targeted products [16], the ozonation was done in acidic media to avoid the production of secondary ozonides usually done at neutral pH media [17]. Ozone has been used to remove lignin from different biomass such as wheat and rye straw [18], cotton stalk [19], magazine pulps [20], among others.

Lignin presents a very complex assembly which limits enormously their interaction with host polymer matrices for industrial applications. It has been reported that only 2% of the annually extracted lignin from paper and pulp industry is used for applications such as fillers, adhesives and dispersants; the remaining lignin is burned as industrial waste for energy generation [21].

Synthesis of lignin nanoparticles

One way to overcome the limitations of lignin pointed out in the above section is to reduce the size of lignin particles until the nanometric size (less than 100 nm). At this scale, new functionalities and properties of materials are observed and used for a wide range of novel applications. As the size of the particles is reduced to the nanoscale range, the surface to volume ratio of the particles gradually increases which in turn increases the reactivity of the particles and changes their mechanical, electrical and optical properties [22] (Adusei-Gyamfi and Acha, 2016). These lignin nanoparticles hold huge potential for downstream valorization due to their unique morphology and abundant multifunctional groups. Thus the idea is to prepare lignin nanoparticles, which will greatly improve their reactivity and solubility with host matrices, and will provide a morphological and structural control of these structures for different high-value applications [21].

Several different methods have been published to synthesize nanolignin. Frangville et al. reported nanolignin obtained by precipitation in HCl. The resulting nanoparticles were crosslinked with glutaraldehyde, getting good stability over a wide range of pH [23]. Gilca et al. prepared nanolignin by sonication, they identified two main reaction patterns resulting in chain cleavage (depolymerization) and oxidative coupling (polymerization), both probably promoted by the hydroxyl and superoxy radicals generated by ultrasound [24]. Hydroxypropyl lignin nanoparticles were reported to be prepared by reacting an alkaline lignin solution with propylene oxide, then acidifying and centrifuging the mixture to precipitate the nanoparticles [25]. It has been reported also the use of a solution precipitation from alkaline lignin with either ethylene glycol or alkaline solution, which resulted in smaller nanoparticles [26]. Of all the methods mentioned above, the precipitation method in HCl seems to be the easiest for the synthesis of lignin nanoparticles.

Applications of lignin nanoparticles

As for the applications for lignin nonmaterial's, lignin shows unique properties such as antioxidant and antibacterial properties, ultraviolet absorption, and high toughness [27]. To produce novel materials with improved properties, nanolignin particles can be incorporated in polymers for use in food packaging with the properties mentioned above, such as polyvinyl alcohol/Chitosan (providing

UV absorbance, antioxidant and antibacterial properties), glycidyl methacrylate grafted polylactic acid (providing UV-absorbance and antibacterial properties), polylactic acid (providing UV-absorbance and antibacterial properties) [28], among others.

Lignin's are known by their free radical scavenging activity due to their complex phenolic structure, which make them recognized as efficient natural antioxidants [29]. The incorporation of natural antioxidants to food packaging materials has been widely studied in order to improve protection of light and/or oxygen sensitive products [30]. Lignin's have been proposed as antioxidants for polylactic acid films [31]. Lignin nanoparticles have been reported to exhibit higher antioxidant activity than neat lignin [26, 32, 33].

Nanolignin particles have also been involved in production of antimicrobial materials. Richter et al. [34] produced nanolignin loaded with silver ions and coated with a cationic polyelectrolyte layer capable of adhering to bacterial cell membranes. The nanoparticles killed both Gram-negative and Gram-positive bacteria while using at least 10 times less silver than conventional silver nanoparticles, thus reducing the environmental impact produced by silver nanoparticles. Films based on polylactic acid [35], chitosan, and/or polyvinyl alcohol [36] added with nanoparticles of lignin presented activity against Gram-negative bacteria, indicating that the films containing nanolignin particles could be used as antibacterial food packaging.

UV radiation accelerates oxidation rates in food [37] and also photodegradation of organic polymers [38]. The UV-absorbing capacity of lignin was tested by Yearla and Padmasree [32] by monitoring survival rates of UV-irradiated *E. coli*. In the absence of lignin compounds, the mortality of *E. Coli* was 100% after 5 minutes of UV exposure, while their survival was improved in the presence of lignin in proportion to their concentration. This study was done based on the fact that *Escherichia coli* suffer intracellular oxidative damage and death caused by UV radiation. In addition, because lignin nanoparticles have superior UV protection over ordinary lignin, the survival rate results were much better when nanolignin was used. Bionanocomposite films made of gluten-lignin nanoparticles have been reported to absorb UV radiation [99], thus these materials could be applied in food packaging with UV protective features, such as nuts and other food products that are prone to lipid oxidation.

Conclusion

Lignin as a renewable polymer is an attractive alternative to conventional metallic and organic materials due to its biocompatibility and biodegradability. Ozone has proved its efficiency as pretreatment method of lignocellulosic biomass for removing lignin. Ozonation is a green method requiring no hazardous compounds such as acids or alkalis, and needs moderate reaction conditions such as room temperature and atmospheric pressure. Lignin is a very complex polymer limiting its applications. One way to solve this problem is to reduce the size of ordinary lignin particles at the nanoscale, where new properties are being harnessed for novel applications. Lignin nanoparticles are good candidates for the next generation functional nanocomposites as they present very interesting properties such as UV light blockers, radical scavengers, and antioxidants very promising for potential applications in the food sector such as packaging.

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