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► **To cite this version:**

Victor Girard, Hubert Chapuis, Nicolas Brosse, Nadia Canilho, Laurent Marchal-Heussler, et al.. Biomass species and process contribution in a lignin first and ecofriendly approach for nanoparticles production. 2023. hal-04232814

HAL Id: hal-04232814

<https://hal.science/hal-04232814>

Preprint submitted on 9 Oct 2023

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ARTICLE

Biomass species and process contribution in a lignin first and eco-friendly approach for nanoparticles production

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Victor Girard,^a Hubert Chapuis,^a Nicolas Brosse,^a Nadia Canilho,^b Laurent Marchal-Heussler,^c and Isabelle Ziegler-Devin^{*a}

In order to handle with urgent energy and environmental issues, the development of circular economy supported by lignocellulosic biorefineries is essential right now. In this respect, lignin should no longer be seen as a waste or by-product, but as a renewable and abundant resource. This is why research has recently focused on the development of lignin nanoparticles (LNPs), which are opening up new value-added areas. However, to date, no study has focused on the contribution of the initial raw biomass species (hardwood, softwood, herbaceous) on same environmentally-friendly LNPs production process. This lignin-first integration work therefore provides information on chemical lignin structure and functional groups interaction for LNPs formation. To this end, a steam explosion (SE) pretreatment was carried out upstream of an ethanol-Organosolv treatment (OT) in order to extract pure lignin which is then reduced to nano size by anti-solvent precipitation. We show that initial raw biomass species such as lignin type (OL lignin compare to KL Kraft lignin) makes a significant difference to particle size (50 – 250 nm), aggregation and morphology in aqueous suspensions. The LNPs formed by this eco-friendly, simple, fast and high yields process (7 – 15 wt % LNPs of initial biomass waste), which can be upscaled for industrial purposes, are stable over 90 days-storage and have lower sizes than Kraft lignin. LNPs resulting from this work therefore have great potential for high added-value applications such as cosmetics and medicine.

1. Introduction

Recent Intergovernmental Panel on Climate Change (IPCC) report (AR6) highlights that excessive globalization and industrialization have led to unprecedented global warming of +1.1 °C compared to pre-industrial levels,¹ resulting in increased risks, such as climate change impacts and energy supply challenges due to non-renewable fossil fuels shortage.²

Following this severe environmental backdrop, lignocellulosic biomass biorefineries received increased attention since 2000s as it is one of the most promising ways to save energy using a sustainable, cheap, carbon-neutral, abundant, and renewable bioresource.^{3,4} Lignocellulosic biomass is mainly composed of 3 structural biopolymers namely cellulose, hemicelluloses (polysaccharides), and lignin (aromatic structure).⁵ In a bio-refinery approach, while polysaccharides are fully utilized for the production of pulp,⁶ biofuels,^{7,8} platform molecules,⁹ fibers,¹⁰ nanofibers,¹¹ lignin is still primarily used as an energy source.¹²

Lignin is a complex aromatic biopolymer and an essential component of the cell wall of lignocellulosic biomass (20-25 %

in hardwoods, 25-33 % in softwoods and 15-30 % in herbaceous).¹³⁻¹⁵ Lignin particular structure depending on biomass species¹⁶ is composed of three basic monomeric units named guaiacyl (G), syringyl (S) and p-hydroxyphenyl (H) which are interconnected by β -O-4 linkages, among others.¹⁷ Moreover, lignin chemical structure is also modified during extraction process.¹⁸ Due to lignin's aromatic structure composed of diverse functional groups, mainly aliphatic hydroxyl, carboxyl and phenolic hydroxyl groups, exclusive range of properties are underlined related to antimicrobial and antioxidant activity,^{19,20} encapsulation capacity to stabilize emulsions²¹ or UV-light absorption^{22,23,24}

A great deal of academic research has been carried out over the last few decades with the aim of using lignin in high value-added applications, particularly in the fields of adhesives,²⁵ antioxidants²⁶ and fibers²⁷ but very little has led to industrial developments. The main challenges to the development of large-scale applications for lignins are related to their chemical complexity, variability, the presence of impurities and their very dark color.^{28,29}

The concept of lignin-first refers to the use of lignin as a resource of interest and not as a co-product in a biorefinery process.³⁰⁻³² This approach which leads to lignin fractions whose composition, degree of purity and chemical structure are better regulated than in technical lignins, requires efficient and environmentally friendly pretreatment processes.^{33,34} Organosolv fractionation stands out as one of the most promising methods to perform lignin first removal.³⁵ In short, this sulfur-free lignin extraction from biomass is accomplished

^a Laboratoire d'Etude et de Recherche sur le MATériau Bois (LERMAB), Faculté des Sciences et Technologies, Université de Lorraine, F-54000 Nancy, France.

^b Laboratoire Lorrain de Chimie Moléculaire (L2CM), CNRS, Faculté des Sciences et Technologies, Université de Lorraine, F-5400 Nancy, France.

^c Ecole Nationale Supérieure des Industries Chimiques (ENSIC), Université de Lorraine, F-54000 Nancy, France.

using aqueous-organic solvent solution and allows the separation of biomass constituents in 2 distinct fractions, namely cellulose-rich pulp and lignin-hemicelluloses aqueous-organic solution called black liquor.³⁶ This pretreatment/fractionation technology shows great potential for new biorefinery concept by using solvents that are easy to recover and reuse like low molecular weight aliphatic alcohols such as ethanol, enabling the coexistence of traditional biofuels technologies with novel eco-friendly approaches.³⁷ Steam Explosion (SE) can be also considered as one of the most promising processes for biomass pretreatment and fractionation.^{38,39} SE is a thermo-mechanical-chemical treatment involving a heating step by water steam followed by an explosive decompression that leads to partial biomass deconstruction.⁴⁰ SE has shown a great interest for biorefinery perspective because it is an eco-friendly technology with poor energy requirement that can replace the initial grinding step (accounting for a third of the total energy cost of biomass deconstruction process).³⁷ Initially used to improve accessibility to cellulose for production of bioethanol by enzymatic hydrolysis,⁴¹ this process recently showed great potential for different industrial prospect (medium-density fiberboards depollution,⁴² biopolymer and platform biomolecules extraction,^{41,43} energy densification and pellets,⁴⁴ fibers production and cottonization for textile^{45,46}).

Biobased nanoscale technology is viewed as the potential next industrial revolution due to its wide-ranging benefits for new consumer needs in various domains including energy, transportation, agriculture, food, materials, electronics or medicine.⁴⁷ In 2016, more than 60 different countries initiated nanotechnology projects, and this market is expected to exceed US\$ 125 billion by 2024.⁴⁸ In recent years, there has been growing interest in LNPs, as lignin micronization overcomes some of the macrosized lignin limitations mentioned above and opens up new applications.⁴⁹ For now, LNPs have been produced using diverse techniques such as liquid precipitation,⁵⁰ aerosol processing⁵¹ and mechanical⁵² or ultrasound treatment^{53,54} Liquid precipitation or solvent shifting, are the most common method to synthesize LNPs by taking advantage of lignin insolubility in aqueous media.²⁴ Several experimental procedures have been developed such as addition of excess antisolvent into a lignin solution⁵⁵ or vice versa⁵⁶, acid precipitation⁵⁷ or dialysis^{58,49} Anti-solvent precipitation with water and ethanol appears to be an efficient way to produce LNPs for high added-value applications because it is eco-friendly, fast, simple, and low-cost.⁵⁹ Potential areas of applications of LNPs are very broad and include hybrid nanocomposites,⁶⁰ environment for water and soil depollution,⁶¹ medicine for drug delivery systems or tissue regeneration,⁶² cosmetic for antioxidant or UV-blocking cream preparation,^{53,63} or emulsions stabilizers⁶⁴. To date, the works reported in the literature on LNPs have mainly focused on Kraft lignin (KL). KL is a co-product of the pulp industry that contains impurities, particularly sulfur, which can make it unsuitable for many applications, thus limiting the potential uses of LNPs products.^{50,65}

Recently, only few papers^{50,66} studied the production of LNPs from Organosolv lignin (OL). The lignin source impact on LNPs production was studied and it was concluded that OL could be a serious candidate due to the high hydrophobicity and very poor water-solubility but also lowest molecular weights and polydispersity among technical lignins.⁶⁷ Another paper suggested that inherent Organosolv lignin properties impacted LNPs production, underlining the significance of choosing suitable initial lignin materials for particular applications.⁶⁸ To our knowledge, this work represent the only study that addresses the correlation of every biomass species (hardwoods, softwoods and grasses) and LNPs properties.

Lately, we demonstrated that SE followed by an ethanol-aqueous Organosolv delignification can be considered as an efficient method for high quality lignin extraction.⁴³ This hybrid pretreatment allowed the production of lignin with low repolymerization rate, rich in aryl ether patterns and with low molar mass and polydispersity. In the present work, LNPs have been produced by antisolvent precipitation of lignin isolated from beech, spruce wood and wheat straw by SE/Organosolv (SE/OL) combined pretreatments. Kraft lignin was also examined for comparison. The lignins were fully characterized by HSQC or 31P NMR and size exclusion chromatography (SEC). LNPs size distribution was examined by Dynamic Light Scattering (DLS) analysis and Transmission Electron Microscopy (TEM). The relationship between the plant species, the extraction process, the chemical structure of the lignin isolated and the morphology of the LNPs produced was studied and discussed. The final goal is the production of tailor made LNPs from biomass using an eco-friendly process and according to green chemistry principles.

2. Experimental

Separate steps of the project for the LNPs production and associated analyses from the raw biomass are summarized in **Fig. 2**.

2.1. Feedstock and Material

Waste from three different and locally available biomasses (Vosges Forest around Epinal in Grand Est Region, France) were used for this project, namely beech (*Fagus sylvatica* / Hardwood), spruce (*Picea Abies L.* / Softwood) and wheat straw (*Triticum* / Herbaceous). Wheat straw residues were specially provided from "Bergerie de Straiture" sheepfold (Ban-Sur-Meurthe-Clefcy, France). Commercial Kraft lignin (KL) was supplied and derived from the Lineo™ Prime W by Stora Enso process (CAS Number 8068-05-1).

2.2. Green Lignin Macro-Particles (LNPs) Extraction

Macrosized lignin was extracted using combined or single environmentally friendly processes (Steam Explosion pretreatment followed by Organosolv or Organosolv only). In both cases, before pretreatment biomass waste was coarsely crushed with a Retsch® cross beater mill SK100 into Ø8 mm particles.

2.2.1. Chemical characterization

The chemical composition was determined from National Renewable Energy Laboratory (NREL) labelled protocols and TAPPI method T222 before and after the pretreatment processes in order to quantify the impact on chemical structure. Briefly, 5g of wood powder were heated in a 600 °C oven for 24 h minimum for ash content (NREL/TP-510-42622). Whereupon other 2 g of same wood powder were extracted by Soxhlet extraction apparatus for 6h with toluene/ethanol 2/1 v/v (NREL/TP-510-42619). Then, free extractive biomass was used to determine acid insoluble lignin and monomeric sugar contents (NREL/TP-510-42618 and NREL/TP-510-42623). Use of High-Performance Anion Exchange Chromatography coupled Pulsed Amperometry Detection (HPAE-PAD, ICS-3000 Dionex™) with analytical column Dionex™ CarboPac PA-20 (3x150 mm) was used to analyse the monomeric sugars in liquid fractions. Monosaccharides were eluted at 35 °C with a flow rate of 0.4 mL/min according to the following composition: 99.2 % ultrapure water / 250 mM NaOH 0.8 %: 0-20 min; 75 % ultrapure water / 250 mM NaOH 20 % / NaOAc (1 M) - NaOH (20 mM) 5 % 20-37 min; 40 % ultrapure water / 250 mM NaOH 20 % / NaOAc (1 M) - NaOH (20 mM) 40 % 37-41 min. Wash and the necessary equilibration time were performed after each elution. The determination of fucose, arabinose, rhamnose, galactose, glucose, xylose, mannose, galacturonic acid and glucuronic acid was carried out by external calibration with standards. The chemical compositions of raw biomass waste used in this study is given in **Table 1**.

2.2.2. Steam Explosion (SE) Pretreatment

Before the SE treatment, 100 g of biomass (dry basis) was impregnated with distilled water under vacuum pressure for 30 min with the liquid/solid ratio of 10/1. Then the water impregnated biomass was loaded into a pressurized reactor under steam temperature of 200 °C for a residence time of 10 min, then followed by an explosion with pressure relief. After the treatment, liquid and solid phase were recovered and then separated by vacuum filtration. The solid phase was washed and placed in a 103 °C oven for 24 h, cooled in a desiccator for 1 h and then weighed. The associated mass loss was calculated according to the following equation:

$$\text{Mass loss (\%)} = \left(1 - \frac{\text{dry mass of solide residue (g)}}{\text{dry mass of initial biomass (g)}}\right) (1)$$

2.2.3. Organosolv Treatment (OT)

Organosolv treatments were performed using raw or SE pretreated material. In details, 100 g of biomass (dry basis) was treated at a temperature of 200 °C for 1 h in 60/40 v/v ethanol-aqueous (liquid/solid ratio of 10/1) in a pressurized 2L reactor (PARR® 4568 bench top reactor). The Parr reactor was equipped with a PID controller and thermocouple to ensure effective and repeatable treatment. After 1 h of treatment the reactor was quickly cooled in an ice bath in order to stop the reaction. Then solid phase was washed with twice OL reaction volume (60 % v/v ethanol-aqueous) and separated by vacuum filtration from liquid phase (Black liquor). As for the SE pretreatment, the solid

phase was washed and placed in a 103 °C oven for 24 h, cooled 1 h in a desiccator before weighing and then saved for further processing. The associated mass loss was calculated according to equation (1).

2.2.4. Lignin Recovery with Black Liquor Precipitation

The lignin contained in the liquid phase after OL treatment (black liquor) was separated by simple precipitation with distilled water. Thus, black liquor was diluted in distilled water 1:3 at low temperature in order to help the precipitation by reducing the solubility of lignin. After 1 h, the precipitated lignin was separated by vacuum filtration using glass microfibrils filter of 1.6 µm for optimal results. Subsequently, lignin was washed with 500 ml distilled water before being dried in a 40 °C controlled oven for 2 days. On one side the lignin was first weighed for yields according to equation (2), then ground to obtain LMPs and on the other side rich hemicellulose filtrate was stored at 4 °C for further analysis.

$$\text{LMPs extraction yield (\%)} = \frac{\text{dry mass of extracted lignin (g)}}{\text{dry mass of initial lignin (g)}} (2)$$

Where *dry mass of initial lignin (g)* was determined from the *raw lignin biomass content (%)* and the *initial dry mass of biomass (g)*.

2.2.5. Milled Wood Lignin (MWL) recovery

The method used in this study to extract beech and spruce MWL is based on preliminary works from our research team^{43,69}. The MWL yields were 1.81 % and 0.51 % for beech and spruce respectively (based on raw lignin biomass content).

2.3. Treated Biomass and LMPs Properties Characterization

In a lignin first approach, chemical composition of the processed biomass as well as the purity of the extracted LMPs were determined according to the methods described in section 2.2.1.

2.3.1. Lignin molecular weight characterization by SEC

Size Exclusion Chromatography (SEC) was performed in order to determine molecular weight distributions and average molecular weights of LMPs fractions. First, each lignin sample was dissolved in NaOH (10 mM and 5mg/mL concentration) under magnetic agitation for 24 h before filtering with 0.45 µm PTFE filters. A Shimadzu Prominence™ chromatography equipped with a Shimadzu SPD-20A UV detector (280 and 254 nm), a refractive index detector (RID, Shimadzu RID-20A) and a combination of Shodex™ GPC KF-806L and Phenogel™ 00H-0442-K0 columns was used for the analyses. The separation was performed at 35 °C and eluted with NaOH (10 mM) at a flow rate of 0.4 mL/min. Finally, the calibration curve was plotted using Aligent Technologies™ GPC/SEC calibration kits for pullulans standards (Aligent PL2090-0101) according to Steinmetz⁷⁰ et al. method with molar mass ranging from 667 to 344 000 Da.

2.3.2. Lignin structure analysis by HSQC NMR

Lignin structure was analysed by Heteronuclear Single Quantum Coherence (HSQC) Nuclear Magnetic Resonance (NMR). Briefly, 100 mg of purified and dried LMPs was dissolved in 500 μL of dimethylsulfoxide-*d*6 (DMSO *d*6 99.8 %) for the ^{13}C - ^1H HSQC analysis. Spectra were obtained with the Bruker™ Advance III 400 MHz spectrometer at 50 °C and relaxation delay of 25 s.

2.3.3. Lignin hydroxyl group content by ^{31}P NMR analysis

Lignin hydroxyl group content was determined by Phosphorus-31 NMR spectroscopy. The method was derived from published methodology⁷¹. Thus, 25 mg of purified and dried LMPs was dissolved in 400 μL of a mixed solution (A) of pyridine/deuterated chloroform (1.6/1 v/v) in a 2 mL vial. Then, 150 μL of other mixed solution of Chromium (III) Acetylacetonate 97 % (3.6 mg/mL of A) and Cyclohexanol (4.0 mg/mL of A) was added respectively, as the relaxation reagent and internal standard. Then, the solution was derivatized with 50 μL of 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) before being vortexed and analyzed on the Bruker™ Advance III HD 300 MHz spectrometer at 25 °C and relaxation delay of 2 s. All NMR data were processed using Topspin™ 4.1.0 software (Bruker Bio Spin).

2.4. Lignin Nanoparticles (LNPs) preparation

LNPs were prepared using very simple and green antisolvent precipitation method. For this purpose, first, each LMPs fraction was first dissolved in 80 % v/v aqueous ethanol, identified as the optimal concentration to solubilise lignin (**Supporting Information's**), and then placed in an ultrasonic bath for 1 h to completely solubilise the lignin solution of 10 mg/mL. Then, the solution was filtered by vacuum filtration with 0.45 μm nylon filter in order to remove possible aggregates. Lignin solubilisation yields for beech, spruce, wheat straw and KL were respectively 97.5, 98.7, 97.2 and 93.20 wt %. In order to produce LNPs, a KF Technology™ NE-1010 syringe pump was used to precipitate the lignin solutions in ultrapure agitated water (400 rpm) at 20 °C with a flow rate of 40 ml/min to reach a final concentration of 1 mg/mL. Final suspensions were practically aqueous (91/9 H₂O/EtOH v/v).

2.5. LNPs Characterization

2.5.1. Dynamic Light Scattering (DLS)

LNPs size distribution, size average, polydispersity index (PI) and ζ -potential of prepared suspensions were determined using a Malvern™ Zetasizer Nano ZS instrument. Measurements were directly conducted after precipitation at 25 °C by filling optical PS cells with 1.5 ml of LNPs suspension. Size distribution, size average and PI were determined with samples and measurements triplicate in back angle (174 °) Dynamic Light Scattering (DLS) analysis. Suspensions were stored at 4 °C and further measured at 25 °C in case of long-term stability tests. Lastly, ζ -potentials analyses were conducted on same instrument by using special folded capillary zeta cells (DTS 1070) at 25 °C.

2.5.2. Transmission Electron Microscopy (TEM)

TEM images of LNPs were taken using a FEI Philips® CM200 Transmission Electron Microscope (TEM) with accelerating voltage of 160 kV. Samples were directly prepared without contrasting by placing a drop of LNPs suspension (1 mg/mL) on a TEM grid and dried for 30 min.

3. Results and discussion

The main goal of this study was to produce customized LNPs from biomass by environmentally sustainable method and investigated how biomass type and extraction procedures affect the properties of resulting LNPs.

3.1. Green LNPs Extraction Process

Firstly, this study investigated lignin extraction under the same conditions on various processes (SE-OL for Steam Explosion and Organosolv or OL for Organosolv only) and different biomass species (B for Beech, S for Spruce and W for Wheat Straw) to determine SE impact and the best initial raw material for eco-friendly and high efficiency lignin isolation.

Delignification using clean processes was highlighted, with only water and ethanol used as chemical solvents. Treatment conditions are listed in **Table 2**. These conditions are both derived from previous studies⁴³. Despite the known benefits of acid catalysis to improve delignification,^{72,73} we chose to keep initial pH solvent mixture to ensure the most environmentally friendly treatment.

The lignin isolation results with the composition of residues after treatments are shown in **Table 2**. After the SE treatment, an increase in lignin yields in connection with both cellulose and hemicellulose decrease was observed compared to raw biomass. Indeed, time/temperature coupling leads to hemicellulosic sugars auto-hydrolysis as they are easily degradable⁴³. For cellulose, below 200 °C only amorphous part is affected⁷⁴. As wheat straw is a cellulosic sugars rich fraction with lower crystallinity⁷⁵ (around 40 %) compared to hardwoods^{76,77} (50-55 %) or softwoods^{76,77} (55-60 %), cellulose degradation was greater, resulting in higher mass loss (30.26 %). The lowest mass loss (13.94 %) was obtained for spruce with the highest lignin fraction. These results confirmed previous investigations⁷⁸ in which SE removes hemicellulose, alters cellulose structure by changing crystallinity and redistributes lignin, favouring cellulose accessibility.

Concerning OL pretreatment, a significant decrease in lignin content was observed after OL extraction due to aryl ether bonds cleavage³⁶. OL pretreatment also removed residual hemicelluloses, resulting in cellulose-rich pulp. Higher hemicellulose decrement was observed in the case of SE/OL which increase both lignin and cellulose contents especially for beech and spruce. Lower mass loss was obtained after SE/OL compared to OL treatment for the 3 types of biomass. These observations can be attributed to a more significant breakdown of the lignocellulosic structure following SE.

As a result, in a biorefinery context, SE/OL coupling offers the advantage of generating significant LNPs extraction yields depending on biomass species (68.82 %, 32.54 % and 49.08 %

for beech, spruce and wheat straw respectively and based on raw lignin biomass content in **Table 2**), while allowing optimal biomass valorisation with easy recovery of rich and undamaged hemicellulose in aqueous phase.⁷⁹ More particularly for wheat straw, coupling improved lignin extraction (44.76 % for OL versus 49.08 % for SE/OL) which can be due to the greater impact of SE on the chemical structure of herbaceous. In agreement with Nitsos³⁵ et al., best lignin production yields were obtained for hardwoods. Lignin extraction yields is interesting considering that extractions are performed without acid catalysis (H₂SO₄) as in the case of most publications^{36,80,81}. After characterization, the different lignin compositions were investigated as shown in **Table 2**. We can notice that, whatever the extraction conditions (whether for coupling or not), high-quality lignin's were obtained with purities above 93% for each biomass. Highest purities were obtained for wheat straw and spruce with values between 94.26 % and 96.35 %. Furthermore, according to literature,^{43,82} OL extracted lignin contains residual carbohydrates, likely derived from the lignin-carbohydrate complex. Highest sugar content was observed in case of OL extraction for wheat straw (1.78 %), spruce (1.73 %), and beech (1.24 %) compare to SE/OL as shown in **Supporting Information's** with predominance of glucose and xylose from degradation of cellulosic and hemicellulosic sugars fractions respectively.

To conclude this part, the use of eco-friendly SE/OL allowed to extract the purest lignin with high yields, while generating 2 others valuable fractions (i.e. rich cellulose solid pulp and aqueous concentrated xylose/glucose liquid). Moreover, as long as SE can replace the grinding step, the technology becomes even more attractive in terms of material and energy efficiency. Finally, SE allowed biomass chemical break down what could change lignin chemical structure as analysed in **Part 3.2**.

3.2. LMPs chemical characterization

Chemical characterizations were performed to establish relationship between the chemical properties of the produced LMPs and characteristics of the LNPs further generated.

Molecular weight (M_w) distribution

The molecular weight distribution curves determined from SEC analyses for all the produced lignins in comparison with beech and spruce MWL (labelled B-MWL and S-MWL) and commercial KL are shown in **Fig. 3**. The results of the calculated average molecular weight M_w from the distribution curves are presented in **Table 3**.

Analyzing both molecular weight distribution curves and average molecular weight of MWL reveals that SE/OL or OL treatments altered lignin chemical structure resulting in a decrease of the molecular weight and lower distribution (**Fig. 3**). SE pretreatment seems to only affect beech biomass by decreasing particle size (20.8 to 18.0 kDa for average M_w). For spruce and wheat straw, average molecular weights are equivalent between OL or SE/OL (15.7 and 15.6 kDa for spruce or 17.2 and 17.2 kDa for wheat straw). **Fig. 3** also shows a much wider M_w distribution (average M_w of 29.4 kDa) for Kraft lignin

compared to SE/OL or OL lignins suggesting that Kraft process has a different impact on lignin chemical structure.

NMR analysis

Chemical structure of SE/OL, OL, and Kraft lignins was characterized by two-dimensional heteronuclear single quantum correlation (HSQC) and phosphorous 31P NMR as shown in **Table 3**.

To begin, this study included results of assignments for ¹³C-¹H cross-signals based on literature⁸³ and including aliphatic side chains (δ C/ δ H 50-90/2.5-6) and aromatic region (δ C/ δ H 100-140/5.5-8) (**Supporting Information's ?**). β -aryl-ether (β -O-4), phenylcoumaran (β -5) and resinol (β - β) linkages amounts played a crucial role in assessing the degree of lignin depolymerization structure.¹⁸ **Table 3** resumed quantification of these main lignin linkages and aromatic regions. Comparison with MWL showed a significant decrease of β -O-4 (up to 50 %) linkages which can attributed to the well-documented^{36,84} solvolytic cleavage during OL treatment reducing also β -5 and β - β linkages. As expected, notable differences between each kind of lignin (B, S, W) can be observed here. As for molecular weight, differences on spruce lignin are minimal between SE/OL (β -O-4: 18.66/ β -5: 14.39/ β - β : 3.23) and OL (β -O-4: 17.89/ β -5: 13.71/ β - β : 3.06). For wheat straw and especially beech, where the chemical structure of the lignin is more easily depolymerized, changes were observed. For beech, SE pretreatment led to an increase of β -O-4 content (25.28 to 31.71 %) accompanied by a decrease of condensed phenolic structure especially Guaiacyl one which contributes to the significant increase in the S/G ratio. In the case of wheat straw, it appeared that SE exhibited enhanced depolymerization as β -O-4 levels decreased (16.06 to 13.58 %), often accompanied by reduced levels of condensation as for spruce. Chemical structure of KL in **Table 3** informs us that the Kraft process generates high depolymerized and recondensed lignin compared to SE/OL and OL treatments due to alkaline solvents. Higher S/G ratios for both beech and wheat straw suggest highest level of depolymerization with SE treatment. This result indicates that SE may have a beneficial impact on both depolymerization and condensation of lignin chemical structure as previously reported in several studies^{43,85}. **Table 3** also suggested that Kraft process is more severe for chemical structure which is likely to encourage lignin recondensation. Then, **Table 3** also shown hydroxyl content quantification (aliphatic -OH, phenolic -OH with syringyl -OH, guaiacyl -OH, p-hydroxyphenyl -OH and carboxylic acid -OH) on same lignin samples from 31P NMR spectra, providing additional chemical structure information's. As expected for spruce and wheat straw, a notable rise in phenolic -OH groups were highlighted for SE/OL compared to OL accessing the higher solvolytic cleavage of β -O-4 linkages. For beech, SE treatment led to both decrease of aliphatic and phenolic -OH with higher reduction for guaiacyl -OH which suggested potential beneficial impact of SE on lignin depolymerization and condensation during process. If we compare the results obtained for SE/OL or OL lignins with KL it can observe that phenolic -OH/aliphatic -OH ratio is higher for

KL. These observations are in line with the significant lignin degradation observed under Kraft process coupled with recondensation reactions detected by HSQC NMR.

It is evident from the data in **Table 3** that the delignification process, whether through SE/OL, OL, or Kraft methods, had a notable impact on LMPs structure.

3.3. Species and fractionation effects on LNPs formation and properties

In this study, solvent exchange precipitation with water as anti-solvent was used to prepare the LNPs. For this purpose's lignin should first be dissolved in an appropriate solvent which is a central step of the all process⁵⁶ and especially for industrial objective. Numerous studies have investigated the lignin solubility in conventional solvents such as tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), methanol, acetone or ethanol in order to understand factors that affecting lignin solubility^{86–88}. It is common for polymers to exhibit reduced solubility as their molecular weight increases, but lignin amphiphilic unique nature⁸⁹ suggested that lignin solubility would be more dependant of its chemical structure (Hildebrand theory), especially hydrophilic functional groups⁸⁶ and syringyl units⁸⁸. In contrast with literature^{90–93} on LNPs production by anti-solvent method, we have chosen to use ethanol as it can be considerate as the most environmentally and human health-friendly organic solvent despite its lower known lignin solubility⁸⁸. We therefore investigated the solubility of the produced SE/OL or OL LNPs in ethanol-water mixtures according Hildebrand theory where higher solubility is achieved when the solubility parameter of the solvent closely matches that of lignin. We have demonstrated in **Supporting Information's** that highest lignin solubility effectively appears for an ethanol concentration of 70-80 % improving lignin solubility factor by more than 20-25 % compared to pure ethanol for a 5 g/L lignin solution (solubility factor rises from 75 to 97-99 %). Once the ideal solvent composition has been found we prepared the lignin stock solutions according to the protocol in **part 2.4** before preparing LNPs by anti-solvent precipitation using a syringe pump to obtain high repeatability of results.

It has been reported in literature that the formation and properties of LNPs (size, shape and morphology) are dependent on several parameters such as the initial lignin concentration,^{94–97} the solvent addition rate,^{55,66} the solvent and antisolvent types⁵⁴ or proportions,^{98,99} the addition of shear forces⁵² and sonication^{53,100,101} or even a change in anti-solvent temperature and pH⁹⁵. In contrast, the initial biomass specie has been barely studied yet, despite its massive importance in a large-scale industrialization perspective. Here, we proposed as a lignin first approach, to exclusively focus on initial biomass type and lignin isolation process as an impact on further LNPs produced. The particle size distributions of the LNPs suspensions generated as described before and characterized by DLS are summarized in **Fig. 4**. First, all distributions are monomodal, attesting low dispersion and therefor interesting precipitation with different results depending on biomass type and fractionation process. Independent from SE/OL or OL, the size distributions of the

isolated lignins are lower than the KL one. Indeed, **Fig. 5** illustrates that KL (198.0 nm) exhibits a larger average particle size diameter compared to S-SE/OL lignin (136.8 nm), which represents the maximum particle size among the eco-friendly isolated lignin's. Both **Fig. 4** and **Fig. 5** also introduce significative differences between SE/OL and OL with lower distributions for SE/OL in case of beech and wheat straw compared to OL (89.2 – 95.2 nm and 115.3 – 121.1 nm respectively) suggesting that SE pretreatment would be able to reduce a bit LNPs size. Spruce seemed to have the higher particle size distributions with close results between SE/OL and OL methods (136.8 – 123.8 nm). Important feature for nanoparticles and especially for industrial purposes is stability over time which is rarely studied and for short periods⁹⁶. Here, we analyzed long-term stability of each suspension after 90 days at 4 °C storage which is 3 times longer than the highest period we have found in literature⁵⁸. Results are represented in **Fig. 5** where we noticed a very good stability over time especially for beech, spruce, and KL suspensions with size variations between 3 to 10 %. For wheat straw, size variation is around 15 % for both SE/OL and OL (71.9 – 86.8 nm and 121.1 – 138.6 nm respectively). Suspensions stability can be explained by highly negative zeta potential (-21.5 to -34.8 mV) indicating that large number of negative charges surround the LNPs, thus maintaining self-repulsion and electrostatic stability in water⁵⁸. Dynamic light scattering results were combined with TEM images shown in **Fig. 6**. A correlation is observed between DLS size distribution and microscopy images for each sample. However, we noticed once again differences between biomass species with, in case of beech, almost all LNPs being spherical and between 20 and 200 nm. In case of wheat straw, spruce and more importantly KL we observed varying two colors micelles around 100 nm with black center surrounded by a gray envelope that can produce flock-like effects. These fluffier particles could explain zeta potential and polydispersity results in **Fig. 5**. For zeta potential, values were less negative for softwood (-21.5 to -27.8 mV), which has the less spherical particles. For polydispersity, fluffier particles were also able to contribute to higher polydispersity due to hazardous shape. Here we have shown that both initial biomass type and biomass fractionation, upstream of the precipitation process had an impact of LNPs formations with different results in terms of size, shape, and morphology.

3.4. Formation mechanism of LNPs

For 10 years now, some works have focused on LNPs formation mechanism explanations involving Ouzo effect,^{99,102} self-assembly theory,^{24,89,103–105} classical nucleation theory (CNT)⁹⁸ or supersaturation theory (ST)^{106–108}. There is no unique answer, and all these global hypotheses can be confirmed in the way that they describe same mechanism of homogeneous nucleation in metastable region as illustrated in **Fig.7**. Nucleation phenomenon first described by LaMer¹⁰⁹ in 1950 is function of complex supersaturation condition influenced by solvent and anti-solvent type and proportions, temperature, mixing, addition rate or the solute concentration and type.^{106,107}

Global mechanism is therefore challenging because of different kinetics or chemical factors involved. In our work we only focused on solute chemical structure as a contribution to nucleation and growth process. Solute is a key factor of nucleation theory because it must exhibit low solubility in aqueous solutions to undergo nucleation and growth before the formation of final NPs and prevent premature dissolution.¹⁰⁶ Lignin amphiphilic character is therefore predominant for LNPs formation impacted by hydrophilic-hydrophobic interactions. In lignin, higher phenolic hydroxyl ($pK_a \approx 10$) and carboxyl content ($pK_a \approx 4$) is related to higher hydrophilicity rather than aliphatic hydroxyl groups ($pK_a \approx 17$) due to acidic nature.²⁴ In addition, it was previously reported⁸⁹ that non-covalent π - π interactions could contribute to lignin hydrophobic nature decreasing between aromatic rings in $S > G > H$. Once nucleation driven by supersaturation starts, hydrophobic parts are going to self-assemble as spherical nuclei and to growth by diffusion or coalescence with hydrophilic parts around the surface until stability is reached.⁸⁹ Increased hydrophobicity influenced by non-covalent interactions and low phenolic/aliphatic hydroxyl ratio will rise supersaturation, leading to diffusive growth then low aggregation and resulting into small LNPs size with spherical shape (Fig. 7 a - b). In contrast, hydrophilic lignin will lead to coalescence growth and LNPs fusion resulting in larger size and micelles formations (Fig.7 numbers c, d and g for spruce lignin).

Relationship between lignin chemical structure and LNPs size and morphology

By combining results from NMR, SEC, TEM and DLS analysis we were able to quantify the impact of lignin hydrophobicity concerning LNPs size. First, Fig. 8 indicates that lignin M_w has a lower influence than chemical structure even if in literature larger M_w is related to more hydrophobic character. Then, as explained before LNPs size and morphology appeared to be more linked to lignin chemical structure with functional units and hydrophobic/hydrophilic character. Indeed, Fig. 8 showed the correlation between LNPs size and lignin hydrophobic nature driven by S/G ratio (Fig.8 - a) and phenolic/aliphatic hydroxyl (Ph/A-OH) content (b). Thus, by increasing S hydroxyl content and reducing G hydroxyl content (Fig.8 c and d) led to smaller LNPs size (i.e. beech < wheat straw < spruce < KL). Then, combination with low Ph/A-OH ratio (b) led to ideal hydrophobicity to decrease LNPs size and produce spherical particles. On the contrary, increasing phenolic hydroxyl (higher Ph/A-OH ratio) in addition with high G hydroxyl content (b and d) led to higher LNPs size with micelles resulting of coalescence growth. Spherical LNPs with lower sizes (89.2 nm) were obtained for B-SE/OL lignin which contained lower Ph/A-OH combined with higher S/G hydroxyl content and vice-versa for KL (198.0 nm).

To conclude, we observed that feedstock type (hardwood, softwood or herbaceous) is an important parameter for LNPs self-assembly because it generates 29 % of LNPs size variation in our study (comparison of beech and spruce 92.2 – 130.3 nm). Then, lignin isolation process is also an important parameter because it can lead to LNPs size improvement of 34 % for our

production parameters (comparison between SE-OL, OL and Kraft process for spruce 130.3 – 198 nm). A clear improvement in particle shape and morphology is also visible as a function of feedstock and fractionation process which supports our study. It is known that spherical morphologies are preferable for cover applications such as nanocarriers in medicine or Pickering emulsions.¹¹⁰ Taking all these results into account hardwoods seemed to have the better lignin structure for small and spherical LNPs compared to grasses and especially to softwoods with chemical structure that favours coalescence growth and particle fusion during nucleation process. To the best of our knowledge, it's one of the first time that this type of lignin first approach with LNPs eco-friendly production has been reached.

4. Conclusions and prospects

In this study we were able to produce LNPs suspensions with attractive size (between 100 and 200 nm) that are stable over long-term period, customizable, repeatable, highly concentrated and produced by simple and eco-friendly method using only heat, water, and ethanol. Operating with various biomass type (hardwoods, softwoods, and herbaceous) and different LNPs isolation process (SE/OL or OL) but the same LNPs production method we demonstrated the correlation between lignin chemical structure and NPs properties (size, shape, and morphology). Both LNPs production methods were efficient depending on biomass type yielding between 32.5 and 69.7 wt % compared to initial lignin amount in the raw biomass and allowed us to create a range of high-quality LNPs with customizable properties as function of suitable characteristics (i.e., phenolic, and aliphatic hydroxyl groups composition and S or G units' quantities). For each biomass specie, lower Ph/A-OH combined with higher S/G hydroxyl content decreased the LNPs size justifying the hydrophobic nature of lignin as one of the parameters of supersaturation phenomenon and therefore of the resulting nucleation. Shape and morphology differences between hardwoods and softwoods LNPs can be explained by distinct nucleation mechanism resulting of hydrophobicity/hydrophilicity levels leading to more-or-less spherical structures. Accumulated knowledge in this study will be beneficial for the LNPs production from optimized raw materials. Even with soft condition, interesting steam explosion can generate more suitable lignin chemical structure for NPs production by self-assembly. Start from biomass residues has shown that a global process with lignin first approach is possible and even advantageous compared to pulping methods, as it produces LNPs with enhanced properties that can be optimized for industrial purposes, while at the same time answering to Green Chemistry principles.

Author Contributions

Victor Girard: Conceptualization, Investigation, Analysis, Writing - original draft **Nicolas Brosse:** Funding acquisition **Nadia Canilho:** Methodology, Investigation, Analysis **Laurent Marchal-Heussler:** Methodology, Investigation, Analysis **Hubert Chapuis:** Project

administration **Isabelle Ziegler-Devin**: Project administration, Funding acquisition, Methodology, Investigation, Analysis.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors thank the French Grand Est Region and the French National Research Agency through the ARBRE Laboratory of Excellence (ARBRE; grant ANR-11-LABX-0002-01) for the financial support. The authors also greatly acknowledge the “Plateforme PhotoNS” of the L2CM Laboratory, University of Lorraine and the CC3M of the IJL Laboratory, University of Lorraine.

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