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## Cascade extractions of coffee silverskin: Towards zero solid waste valorization of a byproduct

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### ABSTRACT

In a former study it was shown that extracting cycles of coffee silverskin using the previous water extract as solvent with fresh material, results in a caffeine-rich aqueous extract and insoluble fibers. In the present work, we observed that: (1) the concentration in sugar, electrolytes, chlorogenic, ferulic, caffeic acid and antioxidant power increases in the water fraction during the extraction cycles. As a remarkable result the ratios of caffeine to sugar, polyphenols and antioxidant power remains also constant; (2) lignin- and cellulose-rich insoluble fibers can be solubilized using successively the green solvents gamma-valerolactone and N-methylmorpholine N-oxide. Using cascade extractions, it is possible to separate and recover all constituents of coffee silverskin as solid substances as well as liquid fractions, making it possible to leave no solid waste behind.

### 1. Introduction

Silverskin is a byproduct of coffee production, an outer skin separated from the green coffee bean during torrefaction in the first crack, a moment that takes its name from the loud noise it emits (Nolasco et al., 2022).

In a recent study, we performed water extraction cycles of the coffee silverskin, targeting caffeine (Chemat et al., 2024). The extraction cycles were carried out by using the extract of cycle  $n-1$  ( $n$  being the number of cycle) as solvent for the next cycle with fresh biomass. To extend the number of cycles achievable, it was reported that the loss in hydration water of the fibers had to be compensated at each cycle. Caffeine concentration was found to increase until cycle 11, then a plateau was reached. Two products were generated by the process, a caffeine-rich aqueous extract and a biomass depleted in caffeine. The final extract was proposed to be used as natural ingredient for caffeinated beverages and foods or as a substrate for further caffeine isolation. The residual solid consisted largely of insoluble fibers, as evidenced by the low loss of substance in the thermogravimetric analysis (TGA). Those two products, the caffeine-rich aqueous extract and the caffeine-free solid fibers, have both beneficial effects on human health (Iriundo-DeHond et al., 2019).

**Abbreviations:** TGA, Thermogravimetric analysis; GVL, Gamma-Valerolactone; GPC, Gel permeation chromatography; NMMO, N-Methylmorpholine N-oxide; THF, Tetrahydrofuran; CASA, Cysteine Assisted Sulfuric Acid; Mw, Mass average molecular weight; Mn, Number average molar mass; PDI, Polydispersity Index; LiCl, Lithium chloride; LiLF1, Lithium polyoxyethylene octyl ether carboxylate.

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In this study, we first analyzed the composition of the extract obtained through successive extraction cycles to evaluate its potential for formulation. A possible co-extraction of sugar, electrolytes, chlorogenic acid, ferulic acid and caffeic acid was examined. The evolution of the antioxidant power was also studied to confirm the activity of the aqueous caffeine concentrates.

The presence of chlorogenic acid and its evolution in the aqueous fractions was reviewed in light of a recent article by [Nemzer et al. \(2022\)](#), which showed an important association of this molecule with caffeine ([Adams et al., 2002](#)). Since the pH of normal coffee is between 4.8 and 5.1, chlorogenic (pKa 3.36), caffeic (pKa 4.8) and ferulic acids (pKa 4.58) are mostly present in their ionized and water-soluble forms ([Genaro-Mattos et al., 2015](#); [Food Crumble, 2022](#); [Saini et al., 2020](#)). Therefore these anions may be involved in the increase of the solubility of caffeine in water, just like sodium salicylate, which has been shown to be a potent hydrotrope for aqueous caffeine solubilization ([Shen et al., 2023](#)). However, it was hypothesized that the presence of salting-out sugars and magnesium and calcium minerals in the silverskin could have a counteracting effect on its solubility ([Grundl et al., 2017](#)). Therefore, sugar concentration was determined and pH and conductivity measurements were taken after each water extraction cycle.

The remaining exhausted coffee silverskin was further utilized for additional extractions. The residual solid fibers can be classified as lignocellulosic biomass, consisting primarily of cellulose, hemicellulose, and lignin. Among these components, lignin is particularly noteworthy, as the largest natural source of aromatic molecules. Lignin, is typically constituting 20–30 % of lignocellulosic biomass and provides plants with protection and structural stability ([Gioia et al., 2020](#)). It is primarily made up of three aromatic subunits, syringyl, *p*-cumaryl and coniferyl alcohol, which are interconnected through various ether or carbon bonds. The composition of lignin varies depending on the type of biomass. For example, lignin from softwoods, such as pine or spruce, is predominantly composed of coniferyl alcohol, whereas lignin from hardwoods, such as oak or birch, is mainly comprised of syringyl and coniferyl alcohol. Although most lignin is currently burned to offset the energy consumption in paper production, it holds great potential as a material for future applications. Due to its composition, it is considered a promising alternative resource for various petroleum-based applications, such as the synthesis of epoxy resins or the production of biofuels ([Cheng et al., 2023a](#); [Gioia et al., 2020](#); [Momayez et al., 2022](#); [Shaukat et al., 2023](#); [S. N. Sun et al., 2019](#); [S.-L. Sun et al., 2014](#)). Isolating such a renewable resource from waste products like coffee silverskin would be an ideal approach.

In the second part of this study, the insoluble solids fibers were further extracted using gamma-valerolactone (GVL), a green solvent that can be recycled by distillation as it does not form a water azeotrope. The recovery of GVL can be efficiently achieved by initially separating any remaining water through simple distillation, followed by vacuum distillation at 60 °C and 10<sup>-3</sup> bar. Alternative methods, such as liquid-liquid extraction, have proven challenging due to GVL's high miscibility with most solvents and its strong solubility for dissolved biomass molecules. GVL is a non-toxic, biodegradable liquid with a high boiling point (207 °C) and low vapor pressure (3.5 kPa at 80 °C). It can be produced from biomass via various pathways ([Horváth et al., 2008](#)) ([S. Zhang et al., 2018](#)), including selective hydrogenation of biomass-derived levulinic acid ([Tang et al., 2014](#)). This makes GVL a key component in a global eco-responsible cycle. This approach aligns with the philosophy of using guaiacol cholinium to extract lignin, which can then be depolymerized to produce guaiacol monomers for fresh solvent preparation ([Huang et al., 2022](#)). GVL exhibits excellent lignin dissolution properties, even dissolving larger quantities compared to other good solvents like THF, acetone or ethyleneglycol and remains stable up to 150 °C, making it a highly efficient extraction solvent for coffee silverskin lignin. Additionally, GVL has advantageous swelling properties, which facilitate the penetration of solvent components into the lignocellulosic structure, enabling the degradation of all its constituents ([Cheng et al., 2023a](#)).

After extraction, the purity, chemical composition and polymer size were determined using UV–Visible spectrometry, 1D and 2D-NMR spectroscopy and gel permeation chromatography. Light microscopy observations were conducted before and after lignin extraction. Following the selective extraction of water-soluble, hydrophilic materials and lignin through a cascade extraction process, a further step was taken. The complete solubilization of the remaining cellulose-rich fraction was achieved using N-methylmorpholine N-oxide (NMMO) ([Rosenau and French, 2021](#); [Vinogradov et al., 2023](#)).

For the moment, European legislation bans the use of coffee waste as food ingredients ([Lachenmeier; Walch, 2023](#)). This restriction does not seem to be justified as it goes against the FAO global goals for sustainable development, which the European Union agreed on ([FAO and the Sustainable Development Goals, 2022](#)).

## 2. Material and methods

### 2.1. Biological materials and chemicals

#### 2.1.1. Biological material

The biomass used was coffee silverskin from Guatemalan Robusta, without any transformation following the first crack. The material was shipped in large quantity and stored in a dry environment. Coffee silverskin was provided by the company Rehorik (Regensburg, Germany).

The material was from the same batch as the one used in the previous study by [Chemat et al. \(2024\)](#). Comparison and graphics referring to caffeine were made using the caffeine content determined in grams. They are reported in Supplementary Information (SI), chapter 1.

#### 2.1.2. Chemicals

2.1.2.1. *Chemicals for extraction of water-soluble compounds.* Sodium carbonate 99 % (CAS 144-55-8) from Sigma Aldrich; Folin-Ciocalteu phenol reagent (CAS 12111-13-6) from Sigma Aldrich; gallic acid (98 % CAS 149-91-7) from Thermoscientific; methanol (HPLC, Isocratic grade CAS 67-56-1) from VWR Chemicals; DDPH (2,2-Diphenyl-1-picrylhydrazyl CAS, 1898-66-4); caffeine standard 99,7 % by Thermoscientific (CAS 58-08-2); chlorogenic acid standard 95 % by Sigma Aldrich (CAS 327-97-9); caffeic acid (3,4-

Dihydroxycinnamic acid) standard 99 % by Acros Organics (CAS 331-39-5); ferulic acid 99 % (*trans*-ferulic acid) standard by Sigma Aldrich (CAS 1135-24-6); formic acid 98 % (CAS 64-18-6) by VWR Chemicals; Acetonitrile HPLC LC-MS grade (CAS 75-05-8) from VWR chemicals; glucose standard (D-(+)-Glucose monohydrate (CAS 14431-43-7) 97.5–102.0 % anhydrous basis from Sigma Aldrich; phenol (purified by redistillation 99 % CAS 108-95-2) by Sigma Aldrich; sulfuric acid (95–97 % analytical grade, CAS 7664-93-9) by Sigma Aldrich.

**2.1.2.2. Chemicals for extractions of water-insoluble compounds.** Gama-Valerolactone (anal. grade, CAS 108-29-2) was provided by KVT-Technology/Glaconchemie (Graz, Austria). Sulfuric acid (95–98 %, CAS 7664-93-9), L-cysteine (98 %), DMSO- $d_6$  (99.8 %, CAS 2206-27-1), N-methylmorpholine N-oxide monohydrate (NMMO) (>99.5 %, CAS 70187-32-5) were purchased from Merck KGaA (Darmstadt, Germany). Tetrahydrofuran (THF) (anal. Grade, CAS 109-99-9) was purchased from Fisher Scientific GmbH (Schwerte, Germany). Polystyrene standards (ReadyCal-Kit fir GPC No. PSS-pskitr1) were purchased from PSS Polymer Standards Service (Mainz, Germany). Lithium Chloride (>99 %, CAS 7447-41-8), lithium hydroxide (>99 %, CAS 1310-65-2) were purchased from Carl Roth GmbH & Co. KG (Karlsruhe, Germany). Polyoxyethylene octyl ether carboxylic acid (AKYPO LF1) (CAS 53563-70-5) was purchased from Kao Chemicals GmbH (Emmerich, Germany). The ionic liquid LiLF1 was prepared by stirring a LF1/water/LiOH (20 g/10 g/1.18 g) for 24 h at room temperature with subsequent drying at 75 °C.

## 2.2. Water extractions and analysis of the water phase throughout the cycles

The first extraction cycle was performed by mixing 100 mL of demineralized water and 4 g of coffee silverskin under stirring in a 60 °C warm water bath for 15 min. After extraction, the mixture was strained, the extract was weighed, and the water lost in process was compensated. Meanwhile the exhausted biomass was dried in a vacuum desiccator for 24 h. The extract was then used as the solvent for the next extraction. These steps were repeated until the 15th cycle, a few cycles after reaching a plateau. After each cycle, the samples were weighed and 5 mL of the sample was collected for analysis, then the water-loss was then compensated.

### 2.2.1. pH and conductivity measurements

During the sampling part of the extractions, the pH and the conductivity were measured using a multi-parameter portable meter MultiLine® Multi 3630 IDS, with both results displayed on the same screen and taken simultaneously.

### 2.2.2. Determination of sugar content

The sugar content was estimated by the Dubois method (DuBois et al., 1956), the results were expressed in mg of glucose equivalent per gram of dry matter. A calibration curve was established using glucose as the standard and following the same preparation steps as for the other samples. A volume of 500  $\mu$ L of sample, and the same volume of a solution of phenol at 5 % were put in contact inside of a flask. A volume of 2.5 mL of sulfuric acid (98 %) was introduced and the mixture was allowed to react for 10 min. After this time, the samples were vortexed for 10 s before being left resting for another 15 min. Then, the samples were kept at 35 °C for 30 min. The samples were measured using a UV-visible spectrophotometer, Libra 22 from Biochrom, at 490 nm.

### 2.2.3. Antioxidant power, total polyphenol content and polyphenols concentrations

To quantify the antioxidant power of the extracts, three types of analytical methods were used, the DDPH, the Total Polyphenol Content (TPC) on microplate and a UPLC targeting specific polyphenols content.

The antioxidant capacity was measured by diluting the samples with methanol to obtain 50  $\mu$ L which was added to 50  $\mu$ L of a DDPH solution. The microplate was placed under the plate reader and the results were read at 520 nm.

For the analysis of total phenols content in the extract, a volume of 20  $\mu$ L of diluted samples was mixed with 80  $\mu$ L of a solution of sodium bicarbonate at 75 g/L and 100  $\mu$ L of the Folin-Ciocalteu agent. The samples on the microplate were put under the plate reader FLUOstar Omega from BMG LABTECH and the absorbance was measured at 750 nm. The results are given in gallic acid equivalent.

The analysis of the content in caffeine, chlorogenic, ferulic and caffeic acids was done using a Waters UPLC Acquity H class plus system with a PDA detector, and an Acquity UPLC BEH C18-Column (1,7  $\mu$ m, 50 mm  $\times$  2,1 mm). The run was 12 min, with a constant elution flow of 8 mL/min. The mobile phase was made of (A) water with 0.1 % formic acid and (B) acetonitrile. The elution gradient was chosen as follows: from 0 to 4 min, 98 % (A); from 4 to 6 min, 70 % (A); from 6 to 6.50 min, 2 % (A); from 6.50 to 8 min, 2 % (A); from 8 to 8.50 min, 98 % (A); the gradient remains at 98 % (A) until 12 min. The chromatograms were registered at 273 nm for caffeine and 322 nm for the other polyphenols, the retention time were 4.75 min for caffeine, 3.71 for chlorogenic acid, 5.50 for ferulic acid and 2.75 for caffeic acid. The analysis of the chromatograms was done with Empower 3.0 software, all in triplicate, with the results given as average values.

## 2.3. Extractions of water-insoluble fibers and analysis of the products

### 2.3.1. Extraction of lignin from water-extracted coffee silverskin

The remaining solid fibers were separated into their components using an Organosolv extraction method. In a 250 mL round-bottom flask, a mixture of GVL/water (9/1) with 0.075 mol/L sulfuric acid (98 %) was used as solvent, with 10 w% of solid coffee silverskin loading. The extraction mixture was stirred for 120 min at 140 °C, cooled in an ice bath for 15 min and filtered through a Büchner funnel to separate the residual cellulose. The filtrate, containing lignin and hemicellulose, was added to a 10-fold double distilled water to precipitate lignin. The precipitated lignin was collected using a Büchner funnel and dried in a vacuum desiccator for 3 days. The remaining yellow transparent hemicellulose solution was retained as a byproduct of the process. The solvent, a mixture of GVL and water (1:10), was removed by vacuum distillation to obtain pure hemicellulose. Various extraction parameters, such as time, temperature, GVL/water ratio, solid loading, and acid concentration, were adjusted for different lignin extractions. Some samples

also received ultrasonic treatment for 30 min at 60 °C, in the ultrasound system medical ultrasonic bath USC 300 T from VWR LMS Consult GmbH (Brigachtal, Germany). The found optimum extraction conditions were: 9/1 GVL/water, 5 w% solid, 0.075 M sulfuric acid, 140 °C, 120 min, with ultrasonic pretreatment before acid addition. Details on the optimization of the extraction parameters are provided in SI, chapter 2.

### 2.3.2. Determination of the lignin content and purity determination of lignin samples

The lignin content was determined via the Cysteine Assisted Sulfuric Acid (CASA) method as described by Lu et al. (2021). A stock solution of 0.1 g/mL L-cysteine in 72 % sulfuric acid was prepared. Between 10 and 20 mg of biomass (ms) were dissolved in 1 mL of stock solution over 2 h of stirring at room temperature and diluted to 100 mL (VL) with double distilled water. The UV-visible absorbance was measured at 283 nm ( $A_{283\_biomass}$ ) to determine the lignin content using Equation (1). The molar absorption coefficient  $\epsilon$  was determined to be 17.25 L/g cm.

$$\text{CASA Lignin [\%]} = (A_{283\_biomass} \times VL) / (\epsilon \times L \times ms) \times 100\% \quad (1)$$

UV-visible spectroscopical experiments were performed on a double-beam UV-visible spectrophotometer from PerkinElmer Lambda 19 UV/Vis/NIR (Dodgau, Germany). Samples were filled into micro-UV cuvettes with an optical path length L of 1 cm from Brand GmbH & Co.KG (Wertheim, Germany) and measured against a reference sample at 25 °C. UV-visible spectra were recorded in a range from 200 nm to 400 nm.

The lignin purity was also determined by the CASA method. Purity determination was based on the CASA method of Lu et al. (2021), with the following modification. This method was enhanced by incorporating a straightforward correlation of absorbances to measure the “loss of lignin in a representative biomass samples modeled with extracted lignin”, which reflects the lignin purity. This modification of the CASA method was internally validated, more details are provided in SI, chapter 3. To this end, 10 mg multiplied by the percentage of lignin present in the respective biomass was dissolved in 1 mL of stock solution and then diluted to 100 mL with double distilled water. Equation (2) was used to calculate the lignin purity by dividing the absorbance at 283 nm of the extracted lignin sample ( $A_{283}$ ) by the absorbance at 283 nm when using the respective biomass source as substrate ( $A_{283\_biomass}$ ).

$$\text{Lignin purity [\%]} = (A_{283} / A_{283\_biomass}) \times 100\% \quad (2)$$

### 2.3.3. Thermogravimetric analysis of lignin samples

Lignin samples were analyzed using a PerkinElmer thermogravimetric analysis device. Measurements were done under synthetic air (80/20) with a flow rate of 25 mL/min. The temperature range studied was comprised between 50 and 700 °C with a heating rate of 10 °C/min.

### 2.3.4. NMR analysis of lignin samples

NMR experiments were conducted using an Avance III HD 400 spectrometer (400.13 MHz Proton, 5 mm BBO 400 SB BB-H-D sample head with Z-gradient). Samples were dissolved in DMSO- $d_6$  at a concentration of 60 mg/mL, stirred until fully dissolved and then transferred into NMR glass tubes. 1H NMR and 2D-HSQC-NMR were performed on selected samples to assess the aromatic and bonding composition of the extracted lignin. The spectra were analyzed using SpinWorks software.

### 2.3.5. Gel permeation chromatography

Gel permeation chromatography (GPC) was used to separate polymers and determine their molecular weight distribution. All samples chosen for GPC analysis were stored at 120 °C for several days before being diluted in tetrahydrofuran, setting concentrations to approximately 1.5 mg/mL, followed by stirring for at least 24 h at room temperature. The lignin solutions were then filtered into screw-cap flasks with PTFE septa using a 0.2  $\mu\text{m}$  syringe filter to prevent larger particles from blocking the column. The GPC system employed was the Malvern Viscotek 270-03 setup with a Malvern GPC100 column (Malvern, United Kingdom). The flasks were placed in the autosampler, and 150  $\mu\text{L}$  of each sample were injected into the system with a 1:45 split and a flow rate of 1 mL/min. A refractive index detector was used to monitor the separation. Molecular weight values, including the mass average molar mass ( $M_w$ ), number average molar mass ( $M_n$ ), and the Polydispersity Index (PDI), were determined based on the retention times of lignin samples, using calibration standards provided by PSS Polymer Standards Service (Mainz, Germany).

### 2.3.6. Light microscopy of used coffee silverskin

Coffee silverskin samples, both before and after a specified number of extraction steps, were examined using a Nikon Eclipse E400 light microscope with  $\times 4$ ,  $\times 10$ ,  $\times 20$  and  $\times 50$  magnification lenses. Pictures of each sample were captured via a Canon EOS 650D digital camera connected to the microscope and an adjacent computer. The surface and fiber composition were evaluated based on these images.

### 2.3.7. Solubilization of the remaining cellulose

The remaining cellulose was solubilized in a mixture of NMMO monohydrate and GVL. A 60/40 (NMMO/GVL) composition was used for optimal dissolution of cellulose residues at 80 °C under continuous stirring in a 50 mL round-bottom flask. The additives LiCl or LiLF1 were added in small quantities of 2 w% in the solvent mixture. To ensure the removal of most of the lignin, three consecutive extractions were performed on the coffee silverskin, resulting in a cellulose residue that was mostly lignin-free. When working with NMMO, it is important to be aware of the hazards associated with transition metal ions, which can induce autocatalytic decomposition that may become uncontrollable very quickly (Rosenau and French, 2021).

### 3. Results and discussion

#### 3.1. Evolution of the water phase composition during the water extraction cycles

##### 3.1.1. Evolution of the pH and conductivity

The pH and the conductivity were measured for all cycles during the extraction process, their evolution throughout the process can be found in Fig. 1(a).

Following the pH evolution of the extract during the process, allows to control if the biomass undergoes significant changes in its composition and in which ionic form the extracted compounds are present. The pH of the extract became slightly more acidic, going from 5.8 to 5.5. This change of less than 0.3 is not considered relevant. The electrical potential of the compounds in the extracts is not altered, thus preventing subsequent reactions or conformational changes. As the pH remained above 5, it could be assumed that chlorogenic acid was strongly ionized and that caffeic and ferulic acids were partially ionized, with pKa of 3.36, 4.8 and 4.58 respectively (Adams et al., 2002; Genaro-Mattos et al., 2015; Saini et al., 2020). Since the pH of a standard cup of coffee is around 5 (Food Crumble, 2022), the pH values of the extracts obtained via this process are comparable to that of a beverage.

During the process, the conductivity increased with the number of the extraction cycles. The evolution of conductivity throughout the process was similar to the one observed for caffeine concentration. Starting at 2.885 mS/cm after the first cycle, conductivity logarithmically rose to 10.175 mS/cm until after the 11th cycle. For all further cycles, the conductivity value remained stagnant. This increase corresponds to an increase in electrolyte concentration. They might occur with the formation of salts from the mineral part of the silverskin or from quaternary ammonium salts coming from trigonelline formed during torrefaction (Narita and Inouye, 2014; Riedel et al., 2014; Taguchi et al., 1985), see Fig. 1(b). It could also be the result of the extraction of ionized polyphenols, amino acids, peptides and proteins (Narita and Inouye, 2014). In Fig. 1(c), the conductivity value is plotted as a function of caffeine concentration in the extract solution. The conductivity rose linearly with the increase in caffeine concentration in the extract solution. This behavior suggests that all electrolytes are extracted with a similar efficiency as caffeine and a constant ratio can be obtained by diluting the extract with the highest caffeine concentration.

##### 3.1.2. Evolution of the sugar content

The evolution of the sugar concentrations (g/L) versus the number of water extraction cycles is reported in Fig. 2(a). The sugar concentration had an initial value of 1.950 g/L after the first cycle, which increased to about 11.429 g/L after the 11th cycle, where it reached a plateau. Towards the 15th cycle, the sugar concentration increased only slightly more, up to 13.103 g/L. The curve is comparable to that of caffeine concentration, see SI chapter 1, and of the conductivity versus the number of cycles, see Fig. 2(a), with the concentration increasing until it reaches a plateau. A comparable ratio of extraction efficiency can be postulated for all the a priori hy-

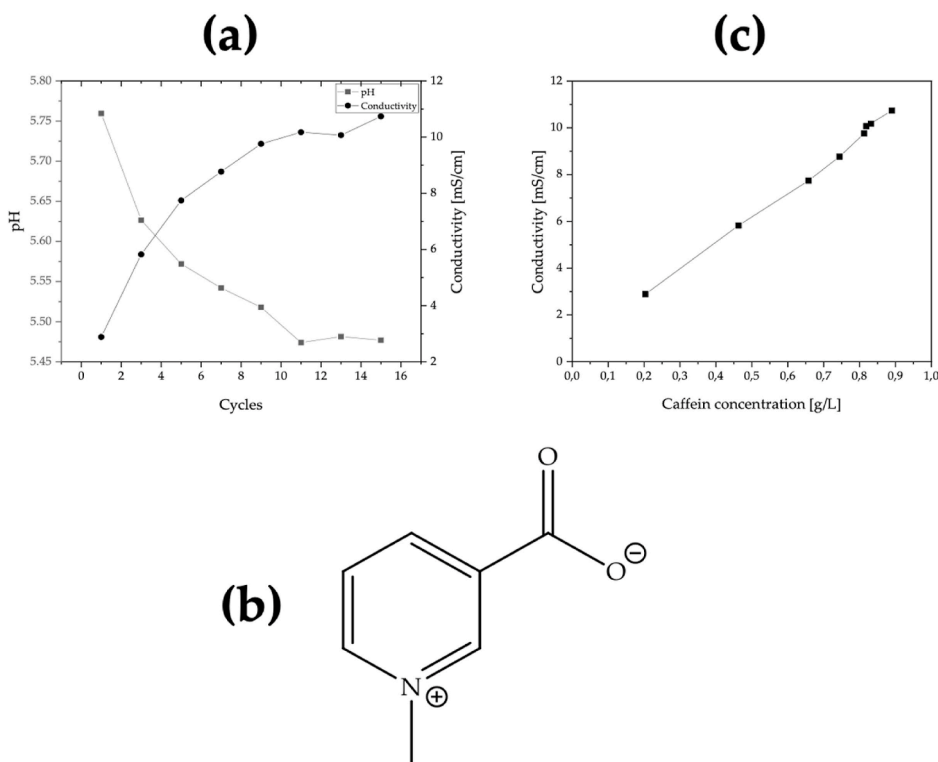


Fig. 1. (a) Evolution of pH and conductivity versus water extraction cycles; (b) Trigonelline structure; note that the molecules can be partially charged depending on the pH value in the solution; (c) Electrical Conductivity versus caffeine concentration in the extract.

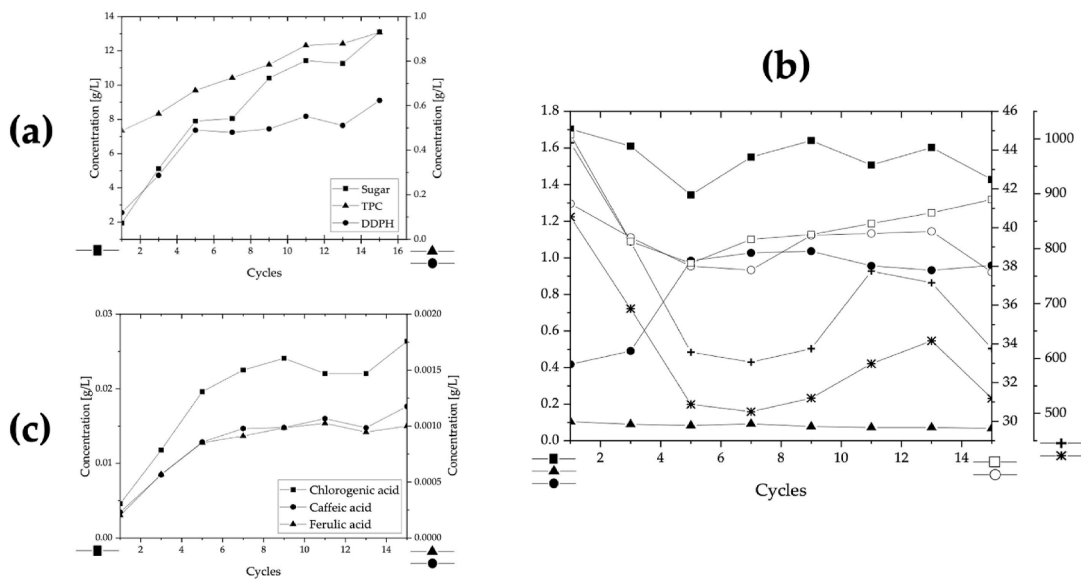


Fig. 2. (a) Evolution of the concentration (g/L) in sugars, total polyphenolic content and of the antioxidative power versus water extraction cycles; (b) Comparison of the ratio caffeine/compounds of interests (On the right y axe: sugars -▲-; TPC -●-; antioxidative power -■-. On the left first y axe: caffeic acid -○-; ferulic acid -□-. On the y axe at the extreme left: polyphenols (chlorogenic acid + caffeic acid + ferulic acid) - + -; chlorogenic acid -\*-). (c) Evolution of chlorogenic acid, caffeic acid and ferulic acid concentrations (g/L) as a function of the number of extractive cycles.

drophilic molecules and not only for the charged electrolytes. The constant values of the caffeine/sugar ratio during all the cycles performed are depicted in Fig. 2(b). The plateau observed during the caffeine cycle extraction was at a value of 4.25 g/L, which was below 10 g/L, the caffeine solubility in water at 60 °C (Arnaud, 2005). This can be attributed to the salting-out effect of electrolytes and sugars. All analytical methods were performed under glucose equivalence.

According to the Regulation (EC) No. 1924/2006 of the European Parliament and of the Council on nutrition and health claims made on foods, a liquid could be approved as low in sugar if the concentration is inferior to 2.5 g of sugar per 100 ml, which is equivalent to 25 g/L. With a sugar concentration at the 11th cycle of 11.429 g/L, the extract could be considered as a low sugar liquid. It would be interesting to use the extract as an ingredient for alternative beverages, as it would be suitable for people with sugar sensitivity.

### 3.1.3. Evolution of the total polyphenol, chlorogenic, caffeic, ferulic acid contents and of the antioxidant power of the water phase

The antioxidant properties of coffee silverskin derives from its polyphenolic content. Therefore, three analytical methods were established to assess the polyphenol concentration, the polyphenol composition, and the antioxidant capacity.

When compared with each other, see Fig. 2(a), the TPC and the antioxidative power have an evolution with numbers of extractive cycles that is comparable to the one of caffeine, see SI chapter 1, with a rise of their amounts with increasing number of cycles until reaching a plateau. The TPC, whose results are given in gallic acid equivalents, started at 0.488 g/L and reached 0.870 g/L after 11 cycles. In parallel, the antioxidative power started at 0.120 g/L of extract and plateaued after the 11th cycle at 0.552 g/L of extract, the results being expressed in Trolox equivalents. These measurements only allow us to quantify the presence of antioxidants, but not to detect their molecular nature.

Therefore, UPLC analysis experiments were performed for a better understanding of the polyphenol composition. The concentrations of chlorogenic, caffeic, and ferulic acids are represented in Fig. 2(c), while the evolution of caffeine concentration is reported in SI, chapter 1.

Caffeine with a concentration of 0.832 g/L after the 11th cycle is the main reason for the antioxidant capacity of this extract, when compared to the concentration of the other polyphenols, namely chlorogenic acid with 0.0220 g/L, caffeic acid with 0.0017 g/L and ferulic acid with 0.0015 g/L.

A similar behavior in the content of all analyzed compounds was reported after each addition of cycles. For all, a steady increase in the content was found until reaching a plateau at the 11th cycle, with slight variations thereafter. The ratio of caffeine to compound of interest remains relatively constant for all cycles, as it can be seen in Fig. 2(b). The cycles were followed up to 15 cycles to see the different behavior of the compounds, but as shown in the previous study, stopping this process after 11 cycles is a better option. This ensures a high antioxidant content without the risk of any significant losses and co-extracted waste materials.

Further studies on the interactions between products within the extracts and on ways to enhance their overall solubility would be advisable. Nevertheless, the analysis performed may already help to prepare convenient extracts for different applications, be it in cosmetics or food/beverages.

### 3.2. Extractions of lignin and solubilization of cellulose from the remaining solid fraction

#### 3.2.1. Extraction of solid components and optimization

Using the CASA method and gravimetric analysis following the lignin extraction, the biopolymer content of coffee silverskin samples was determined. The results showed a lignin content of 21 %, cellulose content of 18 %, hemicellulose content of 18 % and fiber content of 70 %. Lignin extractions were carried out under found optimum conditions: 9/1 wt ratio GVL/water, 5 w% solid loading, an overall concentration of 0.075 mol/L sulfuric acid in the extraction mixture, 140 °C, 120 min and ultrasonic pretreatment before acid addition, (S. N. Sun et al., 2019; S.-L. Sun et al., 2014; Cheng et al., 2023b; Gioia et al., 2020; Momayez et al., 2022; Shaukat et al., 2023). Three separate extraction steps with fresh solvent were performed in triplicates, each resulting in further increase in lignin yield while maintaining a high purity. The results are shown in Table 1. Purity determinations were made using the CASA method (Lu et al., 2021), the corresponding spectrum can be found in SI, chapter 3.

The nearly complete extraction of lignin from coffee silverskin, as indicated by the lignin content determination and consistent purity of around 96 %, underscores the effectiveness of the optimized extraction conditions. Given these results, a single extraction step might suffice for obtaining lignin from exhausted coffee silverskin, thereby conserving solvent. To further optimize solvent use, mixing the liquid from a single extraction with fresh coffee silverskin could balance efficient lignin extraction with reduced solvent consumption. However, for the best valorization of the whole coffee silverskin sample, also including the polysaccharide residue, achieving maximum lignin extraction remains beneficial. This is considered once more in subsection 3.2.4, when it comes to dissolution of the solid residue. The resulting lignin, in comparison to light-brown lignin from spruce wood, was dark brown or black and had a rich smell. The color was deemed to come mostly from small residues of melanoidins present even after several liquid extraction cycles. These melanoidins are created from chlorogenic acids already during the roasting process of coffee beans. In this process, they lose their original aromatic structure and become a dark mixture of polymers. Aromatic molecules, like chlorogenic acids, can usually act as a solubilizer for lignin. They prohibit a strong stacking of lignin molecules in organic solvents by forming pi-pi-interactions with lignin structures (Alghooneh et al., 2017; Bobková et al., 2022; Hunter and Sanders, 1990). However, with the loss of their aromatic structure during the coffee bean roasting process, the created melanoidins do not contribute to the solubilizing effect anymore (Bobková et al., 2022; Santal and Pal, 2013; H.-Y. Wang et al., 2011). This might be a reason why lignin from coffee silverskin is less easy to dissolve in DMSO- $d_6$  or other organic solvents as for example lignin extracted from spruce wood. After successfully extracting lignin, both hemicellulose and cellulose were also recovered. Cellulose remained as solid fibers, while hemicellulose was mostly degraded into xylose and monosaccharides in the GVL solution. To achieve complete solubilization of all components in coffee silverskin and facilitate future valorization of this waste product, it was decided to dissolve cellulose using bio-based solvents, building on existing processes.

The solubility of natural coffee silverskin cellulose is comparable to that of common cellulose solvent mixtures. Although cellulose and hemicellulose both have significant applications, lignin was prioritized for application screening due to its valuable polyaromatic structure. The extracted lignin was thoroughly analyzed to explore its potential applications, focusing on efficient methods to degrade it into monomeric compounds useful for bio-based resins, potentially replacing bisphenol A. Efforts are currently underway to improve the lignin isolation process to ensure a consistent, low-condensation lignin solution that can be quantitatively cleaved into monomeric compounds.

While cellulose already has several applications, improvements in its dissolution process are also being investigated in this work. Further details on cellulose dissolution will be discussed in Chapter 3.2.4.

The hemicellulose-solution, which was separated at the end of the lignin extraction process, offers promising avenues for further research. Hemicellulose has great potential for pharmaceutical and biomedical applications due to its interesting antimicrobial and gel-building properties. It can be used to create films and hydrogels for drug delivery, which can help in cancer therapy (Qaseem et al., 2021), or wound dressing after hydrophilization modifications (Farhat et al., 2017). Moreover, hemicellulose can be utilized as a precursor for synthesizing furfural, a versatile platform chemical. Furfural can be further converted into various bio-based solvents, thereby contributing to the production of sustainable and eco-friendly chemical alternatives.

In our work, hemicellulose is primarily degraded into xylose and monosaccharides due to easier hydrolysis in an acidic medium. The remaining xylose can be extracted from the GVL solution after lignin precipitation and purified through a multistep process, which includes liquid extraction with diethyl ether and ceolite filtration. Additionally, xylose dissolved in the GVL solvent has the potential to be used for synthesizing GVL again (T. Wang et al., 2020). The purified xylose can be applied in various new applications. Currently, we are exploring the production of bio-based resins from the purified xylose, aiming to create resins that do not rely on the toxic bisphenol A as a monomer (Gürbüz et al., 2013).

**Table 1**

Lignin yield and purity from different subsequent extraction steps of coffee silverskin with optimum extraction conditions: 9/1 GVL/water, 5 w% solid, 0.075 M sulfuric acid, 140 °C, 120 min, ultrasonic pretreatment before acid addition.

Steps	Lignin yield [%]	Purity [%]
1 Extraction	61 ± 2	99 ± 1
2 Extraction	21 ± 2	96 ± 2
3 Extraction	5 ± 1	94 ± 1
Overall	87 ± 5	96 ± 1



### 3.2.2. TGA analysis of lignin isolated from coffee silverskin

An exemplary sample of extracted lignin from coffee silverskin was analyzed via thermogravimetric analysis to determine composition, purity and thermal stability. Results are shown in Fig. 3.

The structure of lignin is primarily composed of  $\beta$ -O-4 bonds, next to smaller amounts of  $\beta$ - $\beta$  and  $\beta$ -5 bonds, as shown in subsection 3.2.3. Those bonds usually degrade across a broad temperature range of 100–800 °C. In the initial stage of lignin degradation, any absorbed water from extraction or air exposure is evaporated, resulting in a water content of approximately 13 %.

This is followed by a smaller signal corresponding to the decomposition of residual carbohydrates in the lignin sample, accounting for around 9 % of the total mass. The most significant signal represents the degradation of lignin itself, primarily involving the cleavage of  $\beta$ -O-4,  $\beta$ - $\beta$ , and  $\beta$ -5 bonds between aromatic subunits, occurring up to about 350 °C. This degradation process accounts for roughly 62 % of the total mass of the sample (Giudicianni et al., 2013). The remaining char, a formation of highly condensed aromatic units, represents 16 % of the original mass and indicates the thermal stability of the lignin. Comparing with results from spruce sawdust (30 % of char), coffee silverskin lignin has a lower thermal stability. The thermal stability depends on the lignin source and its aromatic and binding compositions (Tolesa et al., 2018).

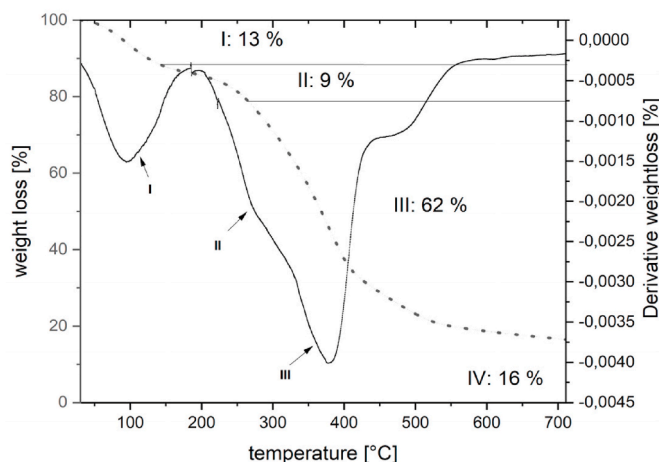
### 3.2.3. NMR analysis of lignin isolated from coffee silverskin

Lignin samples from coffee silverskin were analyzed with 2D-HSQC-NMR to determine aromatic composition and binding compositions. This analysis follows the methods described by Zijlstra et al. (2019) and the HSQC signal assignment represents 16 % of the original mass and indicates the thermal stability of the lignin (Cheng et al., 2023b; Gioia et al., 2020; Momayez et al., 2022; Shaukat et al., 2023; S. N. Sun et al., 2019; S.-L. Sun et al., 2014; Tolesa et al., 2018). The analysis revealed that the binding composition is predominantly made up of three main types of bonds:  $\beta$ -O-4,  $\beta$ - $\beta$ , and  $\beta$ -5. The aromatic subunits consist of guaiacyl, syringyl, and hydroxyphenyl groups, corresponding to the lignin-building alcohols coniferyl, sinapyl, and *p*-coumaryl alcohols (S. N. Sun et al., 2019). The HSQC-NMR results showed a composition of 27.6 % syringyl, 58.7 % guaiacyl, and 13.8 % hydroxyphenyl. In terms of binding, the lignin structure was found to contain 87.0 %  $\beta$ -O-4 (31 per 100 aromatic units), 7.3 %  $\beta$ -5 (3 per 100 aromatic units), and 5.7 %  $\beta$ - $\beta$  (2 per 100 aromatic subunits); details can be found in SI, Chapter 4.

These results are relevant, when breaking up the lignin structure into single monomers and using those for different applications. Due to its different aromatic subunits all absorbing light at around 200–300 nm, lignin or its monoaromatic subunits can be used as UV-protection ingredients in environmentally friendly food packaging applications (Anushikha and Gaikwad, 2023). The latter can be created via further lignin decomposition methods such as hydrogenolysis into monolignols (Nikafshar et al., 2021). UV-protective films can also be made using GVL as a solvent, which lignin has shown good solubility in. The lignin molecules would also show antioxidant and antimicrobial properties in such packaging films (Anushikha and Gaikwad, 2023). Lignin can also be a resource to obtain aroma substances, such as vanillin, 4-propylguaiacol and 4-propylsyringol (Fache et al., 2016; Ren et al., 2022). While vanillin can directly be produced by hydrothermal treatment of lignin (Fache et al., 2016; Isola et al., 2018), the other two aroma molecules can be synthesized in a further step of chemical modification (Ren et al., 2022). Another promising aroma product could be syringaldehyde, also made from lignin by special catalytic oxidation. Syringaldehyde might play a significant role in the treatment of diabetes in the future, as it can reduce blood sugar (Li et al., 2020; Rodrigues Pinto et al., 2012). There are many more applications, such as synthesizing epoxy resins based on dimeric lignin subunits (Nikafshar et al., 2021).

### 3.2.4. Dissolution experiments for biomass leftovers

After three extraction steps, the remaining biomass was predominantly free of lignin. Light microscopy observations indicated that with each additional extraction step, the fiber structure in the biomass became less pronounced, and the brown-colored lignin, which



**Fig. 3.** TGA and DTG of lignin from coffee silverskin extracted under optimum extraction conditions: 9/1 GVL/water, 5 w% solid, 0.075 M sulfuric acid, 140 °C, 120 min, ultrasonic pretreatment before acid addition. TGA (dotted curve) and DTG (compact curve) show the composition of extracted lignin. The decomposition of lignin is sectioned into four different stages (I, II, III, IV). I shows the evaporation of moisture; II shows the decomposition of residual carbohydrates; III shows the actual lignin-degradation; IV shows the residual condensed aromatic char, which determines the thermal stability.

acted as a sort of “fiber glue”, diminished. For further details, see SI, Chapter 5. Also, from subsection 3.2.1, it was confirmed that at least 87 % of lignin have been removed by extraction. Further UV/Vis spectroscopy experiments confirmed that the remaining lignin content in the cellulose residue, after three extraction steps, was approximately 9.9 % of the original lignin content. This corresponds to an overall lignin content of 2.1% in the residual biomass, down from the original 21 %. The cellulose yield was 30.8 % of the coffee silverskin. Without using GVL, the pulp would have been even more impure, as GVL efficiently dissolves lignin. Alternative solvents would require harsher conditions for lignin extraction, potentially leading to more degradation of the cellulose fibers. For cellulose dissolution and subsequent fiber spinning, it is crucial to reduce the lignin content. For instance, achieving a cellulose dissolution of 10 wt percent typically requires a lignin content of less than 9.5 % (Protz et al., 2021). Historically, cellulose dissolution has been achieved using various solvents, with the lyocell process being one of the most prominent. The lyocell process (De Assis et al., 2018) utilizes NMMO (N-methylmorpholine N-oxide) with a small amount of water to solubilize cellulose at temperatures between 90 and 120 °C, followed by spinning into regenerated fibers. However, at higher temperatures, NMMO can start to degrade. Recent research by Freyburger (2018) demonstrated that GVL (gamma-valerolactone) can be used as a co-solvent with NMMO monohydrate. This combination effectively dissolves microcrystalline cellulose up to 10 wt percent and significantly reduces dissolution times. However, dissolving pure biomass has been a reoccurring problem. For this reason, nearly lignin-free cellulose powder was prepared from coffee silverskin and used in dissolution experiments. Using NMMO monohydrate/GVL (60/40 w%/w%), mostly delignified cellulose isolated from water-extracted coffee silverskin was dissolved at 80 °C under stirring for up to 6 w%. Cellulose dissolution using current industrial processes is not optimal. The NMMO process can be enhanced by incorporating co-solvents like GVL and small, strong hydrogen bond acceptor additives such as lithium salts with various anions. Adding LiCl or LiLF<sub>1</sub> at 2 % (w/w) to the solution mixture can slightly increase solubility by about 1–2 %. Both LiCl and LiLF<sub>1</sub> contain strong hydrogen bond acceptor cations, which enhance cellulose solubility. Future investigations could explore the effects of different anions or other additives on cellulose dissolution. The final product was a dark brown cellulose solution with high viscosity.

Using the resulting cellulose dope, the dry-jet wet spinning method from the lyocell process can be employed to produce regenerated cellulose fibers (Azimi et al., 2022). Incorporating GVL as a co-solvent significantly enhances the lyocell process in several key areas. Our research indicates that NMMO monohydrate/GVL mixtures allow for cellulose dissolution at lower temperatures due to the reduced melting point of the binary mixture. Additionally, GVL facilitates crystallization at lower temperatures, which further lowers the processing temperature for fiber spinning. The dissolution time is also notably reduced with GVL as a co-solvent. Furthermore, GVL reduces the high viscosity of cellulose solutions, making the cellulose dope easier to handle. GVL is also environmentally friendly, complementing the improved performance of the lyocell process. It can be easily regenerated from the solvent mixture through simple vacuum distillation. The antisolvent used for spinning, such as water, can be effectively removed from the solvent system due to the significant boiling point difference between the components. The NMMO monohydrate/GVL mixture can then be efficiently reused as a cellulose solvent. Any potential degradation products of NMMO monohydrate during the process can be removed via mixed-bed ion exchange chromatography after recovering the water and GVL (Hytönen et al., 2023). Cellulose in solution might also be applicable for monomeric sugar production via enzymatic hydrolysis (Amândio et al., 2023) or as food additive for animals.

### 3.2.5. Molar mass determination of extracted lignin

The weight average and number average molar weight distribution, as well as the polydispersity index of representative lignin samples were determined using gel permeation chromatography (Lange et al., 2016). A column composed of porous polystyrene served as the stationary phase for lignin polymers travelling in the mobile phase. Larger polymers tend to be retained longer in the column's pores, resulting in longer retention times, while smaller polymers elute more quickly. The lignin sample molar mass distributions were determined from a lignin sample after the first extraction step and the second extraction step, results are presented in Fig. 4. The number-average molar mass decreased from 1212 g/mol to 633 g/mol, and the weight-average molar mass decreased from

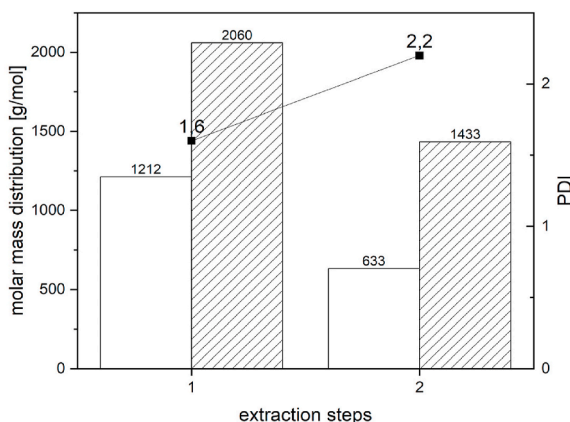


Fig. 4. GPC results for lignin from coffee silverskin extracted under optimum extraction conditions: 9/1 GVL/water, 5 w% solid, 0.075 M sulfuric acid, 140 °C, 120 min, ultrasonic pretreatment before acid addition. Results are shown for different amounts of subsequent extraction steps. The blank column depicts the number average molecular weight (Mn), the striped column depicts the mass average molecular weight (Mw), which both refer to the left y-axis. The polydispersity index (PDI) is depicted by ■ and refers to the right y-axis.

2060 g/mol to 1433 g/mol with additional extraction steps. The PDI increased with more extraction steps, indicating that while the average size of extracted lignin structures decreases, the distribution of sizes becomes broader. This broader distribution may not be ideal for applications requiring high-purity lignin oligomers. A possible explanation for the observed results could be the further degradation of lignin-hemicellulose complexes within the lignocellulose structure. Under acidic conditions in the solvent, lignin and hemicellulose degrade, dissolving in GVL and undergoing condensation reactions that produce higher molecular mass lignin oligomers. Approximately 40% of the original lignin content remains in the biomass after a single extraction. With repeated extractions under the same conditions, the local concentration of acid increases, leading to more extensive cleavage reactions and consequently lower molecular mass of the lignin. Additionally, ultrasonic pretreatment slightly reduces the molecular mass of the extracted lignin by about 5 % compared to non-ultrasonicated samples. Ultrasonic pretreatment facilitates a more consistent cleavage reaction, resulting in a slightly lower molecular mass distribution. Oligomers in this molar mass range are not favorable for synthesizing resins, which typically requires molar masses around 300 g/mol (Periyasamy et al., 2016). However, if lignin oligomers can be further reduced in size through methods such as hydrogenolysis (Li et al., 2019; Luterbacher et al., 2015; Nikafshar et al., 2021), photocatalysis (M. Zhang et al., 2023) or protecting the diol-functions with acetal protection groups followed up by hydrogenolysis of the residual ether bonds (Nikafshar et al., 2021), new opportunities for applications may become available.

### 3.3. Diagram for zero solid wastes valorization of coffee silverskin

The purpose of this work was to propose a complete valorization process of the coffee silverskin with no waste left. A representation of the different extraction steps is given in Fig. 5.

A first part of this valorization process is carried out with water as solvent, with the cycles process designed by Chemat et al. (2024). In this process, a first water extraction is performed on coffee silverskin. Then, the material is strained, the leached amount of water is added and the whole solution is used as a solvent for the next extraction. This procedure is repeated 10 to 11 times. The product obtained is an aqueous extract with a pH of 5.5, an antioxidative power of 0.552 g TE/L, 11.429 g/L of sugars and a total polyphenol content of 0.870 g gallic acid equivalent/L constituted of 0.832 g/L caffeine, 0.022 g/L chlorogenic acid, 0.0017 g/L caffeic acid and 0.0017 g/L ferulic acid.

The second phase of this valorization process began with the solids remaining from the first phase. This solid phase was largely, if not completely, depleted of caffeine and other liquid-extractable components, leaving it primarily as dietary fiber. The main components of the solid phase - cellulose, hemicellulose, and lignin - were fully separated and dissolved using the green solvent GVL and the co-solvent for cellulose dissolution NMMO monohydrate. In the initial step, lignin was extracted via heating to 140 °C for 2 h in 9/1 GVL/water and 0.075 M sulfuric acid at achieving an extraction yield of approximately  $87 \pm 5$  % and a purity of  $96 \pm 1$  % from decaffeinated coffee silverskin. The lignin samples, precipitated from the solution by adding water, were then analyzed for their molecular structure. Hemicellulose, which was co-extracted from coffee silverskin during the lignin extraction process, was dissolved in a 10/1 water/GVL mixture. The residual cellulose, free from lignin-hemicellulose matrix was dissolved, up to 8 w%, in a solvent system of NMMO monohydrate and GVL (6/4) with the addition of small percentages (2 %) of LiCl or LiLF1. Both carbohydrate solutions are available for further research on their individual applications.

At the end of the process, no original material was wasted, and the solvents were recycled. All products could be extracted and conserved in either dissolved form, which was only the case for the aqueous extract, or in both dissolved and solid form, which was the case for lignin, hemicellulose and cellulose. To preserve all products, drying or lyophilization methods could be employed. The next goal in this zero-waste valorization process for coffee silverskin is to find a suitable use for each of the products.

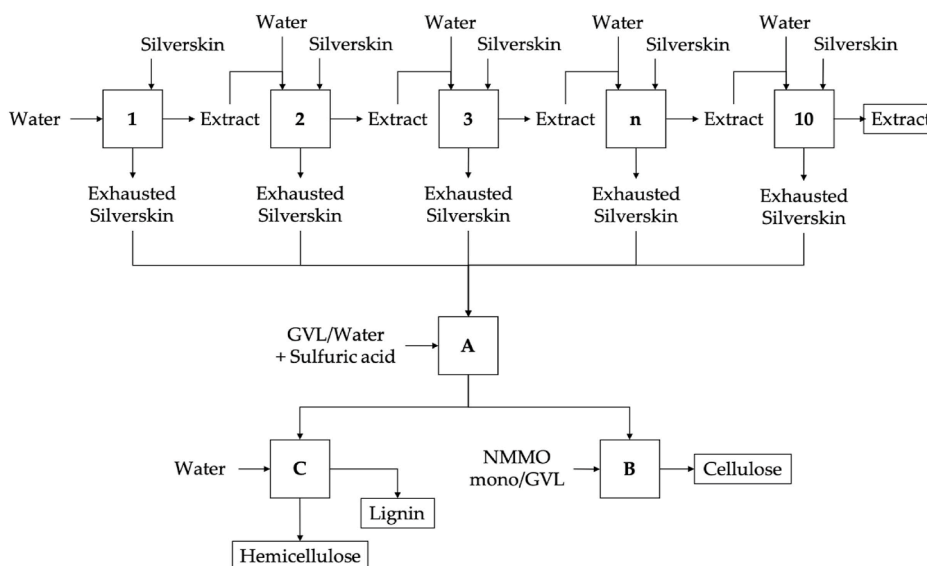


Fig. 5. Schematization of the process of cascade extractions, a zero remaining waste approach.

#### 4. Conclusion

Starting from a solid coffee silverskin, it has been shown that this waste can be completely solubilized and separated into solutions of valuable compounds using cascade extractions.

A water-rich fraction can be enriched in caffeine, sugars, electrolytes and polyphenols by cycle extraction increasing the antioxidant power of the fraction. Since the ratios of caffeine extracted to extracted compounds were constant during the 10 first cycles of water extraction, the caffeine concentrate can be diluted respecting the different ratios of these compounds. This aspect could facilitate the formulation of a beverage or flavouring product with consistent and predictable properties.

From the remaining solid fraction, lignin can be separated from the cellulose with a high yield and purity using gamma-valerolactone, a green solvent considered as an aroma (FEMA: 3103). The extracted lignin oligomers can be used in different applications. Due to its absorptivity at 250–300 nm in the UV–visible spectrum, lignin-based UV-protection films can be considered in the future. Due to lignin's antimicrobial properties, this could also be utilized in biodegradable films for food packaging. With the many hydroxy groups bonded to the benzyl rings, lignin shows great antioxidant properties. This can be useful in films, as polymer additives or as thermo-oxidative stabilizers. The role of lignin as flavor or fragrance ingredients also proves to be a promising application, as monolignols like 4-propyl-syringol or 4-propyl-guaiacol are already regarded as such, possessing a FEMA number. While the extracted lignin is still present as oligomers, there are methods to break down the polymeric structure and receive monoaromatic lignin products. The remaining solid residue after lignin extraction mostly essentially contained cellulose, which could be completely solubilized with NMMO and GVL. This viscous cellulose solution could be a starting material for fiber spinning processes, or it could be broken down to carbohydrate monomers for further use. The hemicellulose, after removal of the solvent mixture, can be used in medical purposes such as drug delivery systems or for cancer therapy. A widely studied option is also its bioconversion to ethanol and subsequent use as biofuel. An application in biodegradable films for food wrapping or coating is also viable.

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#### CRediT authorship contribution statement

**Aziadé Chemat:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Moritz Schweiger:** Writing – original draft, Investigation, Formal analysis, Data curation. **Didier Touraud:** Writing – review & editing, Validation, Supervision, Conceptualization. **Rainer Müller:** Formal analysis, Data curation. **Léo Lajoie:** Formal analysis, Data curation. **Jean Baptiste Mazzitelli:** Formal analysis, Data curation. **Christian Cravotto:** Formal analysis, Data curation. **Werner Kunz:** Writing – review & editing, Validation, Supervision, Project administration. **Anne-Sylvie Fabiano-Tixier:** Writing – review & editing, Validation, Project administration.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scp.2024.101779>.

#### References

- Adams, M.L., O'Sullivan, B., Downard, A.J., Powell, K.J., 2002. Stability constants for aluminum (III) complexes with the 1,2-dihydroxyaryl ligands caffeic acid, chlorogenic acid, DHB, and DASA in aqueous solution. *J. Chem. Eng. Data* 47 (2), 289–296. <https://doi.org/10.1021/je010279e>.
- Alghooneh, A., Mohammad Amini, A., Behrouzian, F., Razavi, S.M.A., 2017. Characterisation of cellulose from coffee silverskin. *Int. J. Food Prop.* 20 (11), 2830–2843. <https://doi.org/10.1080/10942912.2016.1253097>.
- Amândio, M.S.T., Rocha, J.M.S., Xavier, A.M.R.B., 2023. Enzymatic hydrolysis strategies for cellulosic sugars production to obtain bioethanol from *Eucalyptus globulus* bark. *Fermentation* 9 (3), 241. <https://doi.org/10.3390/fermentation9030241>.
- Anushikha, Gaikwad, K.K., 2023. Lignin as a UV blocking, antioxidant, and antimicrobial agent for food packaging applications. *Biomass Conversion and Biorefinery*. <https://doi.org/10.1007/s13399-022-03707-3>.
- Arnaud, M.J., 2005. Caffeine. In: *Encyclopedia of Human Nutrition*. Elsevier, pp. 247–253. <https://doi.org/10.1016/B0-12-226694-3/00032-6>.
- Azimi, B., Maleki, H., Gigante, V., Bagherzadeh, R., Mezzetta, A., Milazzo, M., Guazzelli, L., Cinelli, P., Lazzeri, A., Danti, S., 2022. Cellulose-based fiber spinning processes using ionic liquids. *Cellulose* 29 (6), 3079–3129. <https://doi.org/10.1007/s10570-022-04473-1>.
- Bobková, A., Poláková, K., Demianová, A., Belej, L., Bobko, M., Jurčaga, L., Gálik, B., Novotná, I., Iriondo-DeHond, A., Castillo, M.D.D., 2022. Comparative analysis of selected chemical parameters of coffee arabica, from cascara to silverskin. *Foods* 11 (8), 1082. <https://doi.org/10.3390/foods11081082>.
- Chemat, A., Touraud, D., Müller, R., Kunz, W., Fabiano-Tixier, A.-S., 2024. Valorization of coffee silverskin using extraction cycles and water as a solvent: design of process. *Molecules* 29 (6), 1318. <https://doi.org/10.3390/molecules29061318>.
- Cheng, F., Liu, S., Karlen, S.D., Kim, H., Lu, F., Ralph, J., Vázquez Ramos, L.M., Huber, G.W., Dumesic, J.A., 2023a. Poplar lignin structural changes during extraction in  $\gamma$ -valerolactone (GVL). *Green Chem.* 25 (1), 336–347. <https://doi.org/10.1039/D2GC03446H>.
- Cheng, F., Liu, S., Karlen, S.D., Kim, H., Lu, F., Ralph, J., Vázquez Ramos, L.M., Huber, G.W., Dumesic, J.A., 2023b. Poplar lignin structural changes during extraction in  $\gamma$ -valerolactone (GVL). *Green Chem.* 25 (1), 336–347. <https://doi.org/10.1039/D2GC03446H>.

- De Assis, T., Reisinger, L.W., Pal, L., Pawlak, J., Jameel, H., Gonzalez, R.W., 2018. Understanding the effect of machine technology and cellulosic fibers on tissue properties – a review. *Bioresources* 13 (2), 4593–4629. <https://doi.org/10.15376/biores.13.2.DeAssis>.
- DuBois, Michel, Gilles, K.A., Hamilton, J.K., Rebers, P.A., Smith, Fred, 1956. Colorimetric method for determination of sugars and related substances. *Anal. Chem.* 28 (3), 350–356. <https://doi.org/10.1021/ac60111a017>.
- Fache, M., Boutevin, B., Caillol, S., 2016. Vanillin production from lignin and its use as a renewable chemical. *ACS Sustain. Chem. Eng.* 4 (1), 35–46. <https://doi.org/10.1021/acssuschemeng.5b01344>.
- FAO and the sustainable development goals, 2022. FAO. <https://doi.org/10.4060/cc2063en>.
- Farhat, W., Venditti, R.A., Hubbe, M., Taha, M., Bequart, F., Ayoub, A., 2017. A review of water-resistant hemicellulose-based materials: processing and applications. *ChemSusChem* 10 (2), 305–323. <https://doi.org/10.1002/cssc.201601047>.
- Introduction to the pH of coffee: is coffee an acid or a base? 2022. Food Crumble. <https://foodcrumbles.com/introduction-to-the-ph-of-coffee-is-coffee-an-acid-or-a-base/>.
- Freyburger, A., 2018. Novel bio-based materials from cellulose and chitin. Universität Regensburg.
- Genaro-Mattos, T.C., Maurício, Â.Q., Rettori, D., Alonso, A., Hermes-Lima, M., 2015. Antioxidant activity of caffeic acid against iron-induced free radical generation—a chemical approach. *PLoS One* 10 (6), e0129963. <https://doi.org/10.1371/journal.pone.0129963>.
- Gioia, C., Colonna, M., Tagami, A., Medina, L., Sevastyanova, O., Berglund, L.A., Lawoko, M., 2020. Lignin-based epoxy resins: unravelling the relationship between structure and material properties. *Biomacromolecules* 21 (5), 1920–1928. <https://doi.org/10.1021/acs.biomac.0c00057>.
- Giudicianni, P., Cardone, G., Ragucci, R., 2013. Cellulose, hemicellulose and lignin slow steam pyrolysis: thermal decomposition of biomass components mixtures. *J. Anal. Appl. Pyrol.* 100, 213–222. <https://doi.org/10.1016/j.jaap.2012.12.026>.
- Grundl, G., Müller, M., Touraud, D., Kunz, W., 2017. Salting-out and salting-in effects of organic compounds and applications of the salting-out effect of Pentasodium phytate in different extraction processes. *J. Mol. Liq.* 236, 368–375. <https://doi.org/10.1016/j.molliq.2017.03.091>.
- Gürbüz, E.I., Gallo, J.M.R., Alonso, D.M., Wettstein, S.G., Lim, W.Y., Dumesic, J.A., 2013. Conversion of hemicellulose into furfural using solid acid catalysts in  $\gamma$ -valerolactone. *Angew. Chem.* 125 (4), 1308–1312. <https://doi.org/10.1002/ange.201207334>.
- Horváth, I.T., Mehdí, H., Fábos, V., Boda, L., Mika, L.T., 2008.  $\gamma$ -Valerolactone—a sustainable liquid for energy and carbon-based chemicals. *Green Chem.* 10 (2), 238–242. <https://doi.org/10.1039/B712863K>.
- Huang, C., Cheng, J., Zhan, Y., Liu, X., Wang, J., Wang, Y., Yoo, C.G., Fang, G., Meng, X., Ragauskas, A.J., Song, X., 2022. Utilization of guaiacol-based deep eutectic solvent for achieving a sustainable biorefinery. *Bioresour. Technol.* 362, 127771. <https://doi.org/10.1016/j.biortech.2022.127771>.
- Hunter, C.A., Sanders, J.K.M., 1990. The nature of  $\pi$ - $\pi$  interactions. *J. Am. Chem. Soc.* 112 (14), 5525–5534. <https://doi.org/10.1021/ja00170a016>.
- Hytönen, E., Sorsamäki, L., Kolehmainen, E., Sturm, M., Weymarn, N.V., 2023. Lyocell fibre production using NMMO – a simulation-based techno-economic analysis. *Bioresources* 18 (3), 6384–6411. <https://doi.org/10.15376/biores.18.3.6384-6411>.
- Iriondo-DeHond, A., Rios, M.B., Herrera, T., Rodríguez-Bertos, A., Nuñez, F., San Andres, M.L., Sanchez-Fortun, S., Del Castillo, M.D., 2019. Coffee silverskin extract: nutritional value, safety and effect on key biological functions. *Nutrients* 11 (11), 2693. <https://doi.org/10.3390/nu11112693>.
- Isola, C., Sieverding, H.L., Numan-Al-Mobin, A.M., Rajappagowda, R., Boakye, E.A., Raynie, D.E., Smirnova, A.L., Stone, J.J., 2018. Vanillin derived from lignin liquefaction: a sustainability evaluation. *Int. J. Life Cycle Assess.* 23 (9), 1761–1772. <https://doi.org/10.1007/s11367-017-1401-0>.
- Lachenmeier, D.W., Walch, S.G., 2023. The novel food regulation: a major obstacle to sustainability in the coffee industry. *ICC 2023* 8. <https://doi.org/10.3390/ICC2023-14840>.
- Lange, H., Rulli, F., Crestini, C., 2016. Gel permeation chromatography in determining molecular weights of lignins: critical aspects revisited for improved utility in the development of novel materials. *ACS Sustain. Chem. Eng.* 4 (10), 5167–5180. <https://doi.org/10.1021/acssuschemeng.6b00929>.
- Li, Y., Demir, B., Vázquez Ramos, L.M., Chen, M., Dumesic, J.A., Ralph, J., 2019. Kinetic and mechanistic insights into hydrogenolysis of lignin to monomers in a continuous flow reactor. *Green Chem.* 21 (13), 3561–3572. <https://doi.org/10.1039/C9GC00986H>.
- Li, Y., Zhu, J., Zhang, Z., Qu, Y.-S., 2020. Preparation of syringaldehyde from lignin by catalytic oxidation of perovskite-type oxides. *ACS Omega* 5 (5), 2107–2113. <https://doi.org/10.1021/acsomega.9b02379>.
- Lu, F., Wang, C., Chen, M., Yue, F., Ralph, J., 2021. A facile spectroscopic method for measuring lignin content in lignocellulosic biomass. *Green Chem.* 23 (14), 5106–5112. <https://doi.org/10.1039/D1GC01507A>.
- Luterbacher, J.S., Azarpira, A., Motagamwala, A.H., Lu, F., Ralph, J., Dumesic, J.A., 2015. Lignin monomer production integrated into the  $\gamma$ -valerolactone sugar platform. *Energy Environ. Sci.* 8 (9), 2657–2663. <https://doi.org/10.1039/C5EE01322D>.
- Momayez, F., Hedenström, M., Stagge, S., Jönsson, L.J., Martín, C., 2022. Valorization of hydrolysis lignin from a spruce-based biorefinery by applying  $\gamma$ -valerolactone treatment. *Bioresour. Technol.* 359, 127466. <https://doi.org/10.1016/j.biortech.2022.127466>.
- Narita, Y., Inouye, K., 2014. Review on utilization and composition of coffee silverskin. *Food Res. Int.* 61, 16–22. <https://doi.org/10.1016/j.foodres.2014.01.023>.
- Nemzer, B., Edwards, J., Kalita, D., 2022. Matrix-specific effects on caffeine and chlorogenic acid complexation in a novel extract of whole coffee arabica coffee cherry by NMR spectroscopy. *Molecules* 27 (22), 7803. <https://doi.org/10.3390/molecules27227803>.
- Nikafshar, S., Wang, J., Dunne, K., Sangthongantoi, P., Nejad, M., 2021. Choosing the right lignin to fully replace bisphenol A in epoxy resin formulation. *ChemSusChem* 14 (4), 1184–1195. <https://doi.org/10.1002/cssc.202002729>.
- Nolasco, A., Squillante, J., Velotto, S., D'Auria, G., Ferranti, P., Mamone, G., Errico, M.E., Avolio, R., Castaldo, R., Cirillo, T., Esposito, F., 2022. Valorization of coffee industry wastes: comprehensive physicochemical characterization of coffee silverskin and multipurpose recycling applications. *J. Clean. Prod.* 370, 133520. <https://doi.org/10.1016/j.jclepro.2022.133520>.
- Periyasamy, T., Asrafali, S.P., Muthusamy, S., Kim, S.-C., 2016. Replacing bisphenol-A with bisguaiacol-F to synthesize polybenzoxazines for a pollution-free environment. *New J. Chem.* 40 (11), 9313–9319. <https://doi.org/10.1039/C6NJ02242A>.
- Protz, R., Lehmann, A., Ganster, J., Fink, H.-P., 2021. Solubility and spinnability of cellulose-lignin blends in aqueous NMMO. *Carbohydr. Polym.* 251, 117027. <https://doi.org/10.1016/j.carbpol.2020.117027>.
- Qaseem, M.F., Shaheen, H., Wu, A.-M., 2021. Cell wall hemicellulose for sustainable industrial utilization. *Renew. Sustain. Energy Rev.* 144, 110996. <https://doi.org/10.1016/j.rser.2021.110996>.
- Ren, T., Zhang, Z., You, S., Qi, W., Su, R., He, Z., 2022. Isolation and purification of 4-propylguaiacol and 4-propylsyringol by extraction and crystallization from the products of reductive catalytic fractionation processes. *Green Chem.* 24 (19), 7355–7361. <https://doi.org/10.1039/D2GC01863B>.
- Riedel, A., Hochkogler, C.M., Lang, R., Bytof, G., Lantz, I., Hofmann, T., Somoza, V., 2014. N-Methylpyridinium, a degradation product of trigonelline upon coffee roasting, stimulates respiratory activity and promotes glucose utilization in HepG2 cells. *Food Funct.* 5 (3), 454. <https://doi.org/10.1039/c3fo60320b>.
- Rodrigues Pinto, P.C., Borges Da Silva, E.A., Rodrigues, A.E., 2012. Lignin as source of fine chemicals: vanillin and syringaldehyde. In: Baskar, C., Baskar, S., Dhillon, R.S. (Eds.), *Biomass Conversion*. Springer Berlin Heidelberg, pp. 381–420. [https://doi.org/10.1007/978-3-642-28418-2\\_12](https://doi.org/10.1007/978-3-642-28418-2_12).
- Rosenau, T., French, A.D., 2021. N-Methylmorpholine-N-oxide (NMMO): hazards in practice and pitfalls in theory. *Cellulose* 28 (10), 5985–5990. <https://doi.org/10.1007/s10570-021-03860-4>.
- Saini, S., Sharma, T., Patel, A., Kaur, R., Tripathi, S.K., Katore, O.P., Singh, B., 2020. Qbd-steered development and validation of an RP-HPLC method for quantification of ferulic acid: rational application of chemometric tools. *J. Chromatogr. B* 1155, 122300. <https://doi.org/10.1016/j.jchromb.2020.122300>.
- Santal, A.R., Pal, N., 2013. Biodegradation of melanoidin from distillery effluent: role of microbes and their potential enzymes. In: Chamy, R. (Ed.), *Biodegradation of Hazardous and Special Products*. InTech. <https://doi.org/10.5772/56252>.
- Shaukat, A., Farrukh, M.A., Chong, K.-K., Nawaz, R., Qamar, M.T., Iqbal, S., Awwad, N.S., Ibrahim, H.A., 2023. The impact of different green synthetic routes on the photocatalytic potential of FeSnO<sub>2</sub> for the removal of methylene blue and crystal violet dyes under natural sunlight exposure. *Catalysts* 13 (7), 1135. <https://doi.org/10.3390/catal13071135>.
- Shen, Y., Xiao, Y., Edkins, R.M., Youngs, T.G.A., Hughes, T.-L., Tellam, J., Edkins, K., 2023. Elucidating the hydro-tropism behaviour of aqueous caffeine and sodium benzoate solution through NMR and neutron total scattering analysis. *Int. J. Pharm.* 647, 123520. <https://doi.org/10.1016/j.ijpharm.2023.123520>.
- Sun, S.-L., Wen, J.-L., Ma, M.-G., Sun, R.-C., 2014. Structural elucidation of sorghum lignins from an integrated biorefinery process based on hydrothermal and alkaline treatments. *J. Agric. Food Chem.* 62 (32), 8120–8128. <https://doi.org/10.1021/jf501669r>.

- Sun, S.N., Chen, X., Tao, Y.H., Cao, X.F., Li, M.F., Wen, J.L., Nie, S.X., Sun, R.C., 2019. Pretreatment of Eucalyptus urophylla in  $\gamma$ -valerolactone/dilute acid system for removal of non-cellulosic components and acceleration of enzymatic hydrolysis. *Ind. Crop. Prod.* 132, 21–28. <https://doi.org/10.1016/j.indcrop.2019.02.004>.
- Taguchi, H., Sakaguchi, M., Shimabayashi, Y., 1985. Trigonelline content in coffee beans and the thermal conversion of trigonelline into nicotinic acid during the roasting of coffee beans. *Agric. Biol. Chem.* 49 (12), 3467–3471. <https://doi.org/10.1080/00021369.1985.10867295>.
- Tang, X., Zeng, X., Li, Z., Hu, L., Sun, Y., Liu, S., Lei, T., Lin, L., 2014. Production of  $\gamma$ -valerolactone from lignocellulosic biomass for sustainable fuels and chemicals supply. *Renew. Sustain. Energy Rev.* 40, 608–620. <https://doi.org/10.1016/j.rser.2014.07.209>.
- Tolesa, L.D., Gupta, B.S., Lee, M.-J., 2018. Treatment of coffee husk with ammonium-based ionic liquids: lignin extraction, degradation, and characterization. *ACS Omega* 3 (9), 10866–10876. <https://doi.org/10.1021/acsomega.8b01447>.
- Vinogradov, M.I., Golova, L.K., Makarov, I.S., Bondarenko, G.N., Levin, I.S., Arkharova, N.A., Kulichikhin, V.G., 2023. Transformation of specific dispersion interactions between cellulose and polyacrylonitrile in solutions into covalent interactions in fibers. *Materials* 16 (17), 5843. <https://doi.org/10.3390/ma16175843>.
- Wang, H.-Y., Qian, H., Yao, W.-R., 2011. Melanoidins produced by the Maillard reaction: structure and biological activity. *Food Chem.* 128 (3), 573–584. <https://doi.org/10.1016/j.foodchem.2011.03.075>.
- Wang, T., He, J., Zhang, Y., 2020. Production of  $\gamma$ -valerolactone from one-pot transformation of biomass-derived carbohydrates over chitosan-supported ruthenium catalyst combined with zeolite ZSM-5. *Eur. J. Org. Chem.* 2020 (11), 1611–1619. <https://doi.org/10.1002/ejoc.201901704>.
- Zhang, S., Chen, C., Duan, C., Hu, H., Li, H., Li, J., Liu, Y., Ma, X., Stavik, J., Ni, Y., 2018. Regenerated cellulose by the Lyocell process, a brief review of the process and properties. *Bioresources* 13 (2), 4577–4592. <https://doi.org/10.15376/biores.13.2.Zhang>.
- Zhang, M., Li, Z., Feng, Y., Xin, X., Yang, G.-Y., Lv, H., 2023. Highly selective hydrogenolysis of lignin  $\beta$ -O-4 models by a coupled polyoxometalate/CdS photocatalytic system. *Green Chem.* 25 (23), 10091–10100. <https://doi.org/10.1039/D3GC03468B>.
- Zijlstra, D.S., De Santi, A., Oldenburger, B., De Vries, J., Barta, K., Deuss, P.J., 2019. Extraction of lignin with high  $\beta$ -O-4 content by mild ethanol extraction and its effect on the depolymerization yield. *JoVE* 143, 58575. <https://doi.org/10.3791/58575>.