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Sustainable Extraction and Valorization of Phenolic Compounds from Sugar Maple Bark: Green Solvents, Molecular Characterization, and its Applications in Active Packaging

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Abstract

Bark, a byproduct of the forest industry, is an abundant yet underutilized source of bioactive phenolic compounds with antioxidant, antimicrobial, and UV-protective properties. In this work, sugar maple (Acer saccharum) bark was investigated as a sustainable feedstock for the recovery of phenolic-rich extracts using hot water (HW) and deep eutectic solvent (DES) extraction. Pilot-scale extractions were conducted in a 4.7 L MK reactor under HW (120–160 °C) and DES conditions (two choline chloride-based formulations at 50 °C). Extracts and treated bark were comprehensively characterized to evaluate extraction efficiency, molecular composition, and valorization potential. Total phenolic content (TPC) reached 2.76 g/L in DES extractions, exceeding HW values, although solvent residue contributed to overestimated yields. Extractive and lignin content increased after all treatments, with HW producing the most lignin-enriched liquors. GC–MS analysis identified key compounds including guaiacol, vanillin and benzoic acid, highlighting antioxidant and cosmeceutical potential. Structural analysis by MIR confirmed changes in lignocellulosic composition, while SEM–EDS revealed residual Cl and Fe after DES treatments, though all within Generally Recognized as Safe (GRAS) ranges. Combustion analysis showed that treated bark retained or exceeded the calorific value of untreated bark, suggesting post-extraction potential as a bioenergy feedstock. This integrated study demonstrates that sugar maple bark is a valuable source of phenolic-rich extracts with potential applications in active food packaging, cosmetics, and nutraceuticals, while maintaining valorization pathways for residual solids.

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Introduction

Bark typically constitutes 10–20% of the tree stem mass, depending on species, age, and growing conditions. Consequently, the global forest products industry generates millions of tons of bark annually as a byproduct of wood processing. The global forest products industry generates millions of tons of bark annually as a byproduct of wood processing, representing estimate annual bark production to be between 300 and 400 million m [1-3]. While most bark residues are currently burned for low-value energy, they are a rich and underutilized source of bioactive compounds [3,4]. In particular, hardwood barks such as sugar maple (Acer saccharum) contain significant amounts of polyphenols, flavonoids, and other extractives with antioxidant, antimicrobial, and UV-protective properties [5-7]. These compounds provide trees with natural defense against environmental stress, pathogens, and herbivory, but they also hold potential for high-value applications in food, cosmetic, pharmaceutical, and packaging sectors [8].

Among these, active food packaging has emerged as a promising application for bark-derived phenolics [5-7]. Active packaging is designed not only to serve as a barrier but also to interact with its contents or environment, thereby extending shelf life and preserving food quality. Incorporation of antioxidants, antimicrobials, or UV stabilizers into packaging materials can reduce food spoilage and waste, aligning with global sustainability goals [9]. The development of bio-based active coatings from forestry byproducts therefore offers a dual benefit: waste valorization and improved packaging performance [10].

Efficient recovery of bioactive compounds from bark requires suitable extraction methods. Hot-water (HW) extraction is a widely employed technique, primarily used in research, but also explored in some pilot-scale processes, relying on high temperature and pressure to solubilize (poly)phenolic extractives and lignin-derived phenolics [11,12]. However, HW has limitations in terms of selectivity and thermal degradation of susceptible molecules. In contrast, deep eutectic solvents (DES)—mixtures of hydrogen bond donors and acceptors that form liquids with unique solvation properties—have recently emerged as "green solvents" [13-15]. DES are inexpensive, biodegradable, and often composed of Generally Recognized as Safe (GRAS) substances, as ChCl number 67-48-1 for example, making them attractive for extracting bioactive compounds in combination with another solvents compared to traditional organic solvents or ionic liquids. Importantly, the tunable polarity of DES allows targeting specific phenolic fractions, while their low toxicity enhances compatibility with food-contact and biomedical applications.

Previous studies have reported high polyphenol content and radical scavenging activity in red maple bark extracts, underscoring the potential of maple bark as a source of antioxidants [16,17] . Yet, comprehensive investigations that combine extraction efficiency, molecular-level identification, and assessment of valorization pathways remain limited. Most prior work has focused either on optimizing total phenolic content or on characterizing a narrow set of extractives. Furthermore, little attention has been given to the downstream valorization of residual solids, which may still serve as a bioenergy feedstock or as a reinforcement material in composites after extraction.

To address these gaps, this study investigates the integrated valorization of sugar maple bark using hot-water and DES extractions at pilot scale. The objectives were to: (a) Compare extraction efficiency of HW and DES treatments in terms of yield, total phenolic content, and (poly)phenolics recovery; (b) identify and characterize key bioactive molecules using GC–MS, SEM–EDS, and MIR spectroscopy; (c) Assess sustainability and regulatory aspects of DES relative to HW and (d) Evaluate post-extraction heat values (HV) of extracted bark for energy recovery. By combining extraction optimization with molecular characterization and sustainability assessment, this work establishes a holistic framework for transforming underutilized bark residues into value added products. The findings provide new insights into the potential of maple bark phenolics as active agents in packaging and other bioproducts, while also demonstrating the complementary valorization of solid residues.

Materials and Methods

Raw Material and Chemical Characterization

Sugar maple (Acer saccharum) bark chips were obtained from a regional collaborator in New York State. Bark was classified according to SCAN-CM 40:01 and oven-dried (OD) prior to extraction. For chemical analysis, bark was ground following TAPPI/ANSI T 257 sp-21 [18,19]. The extractive content was determined according to T 204 cm-17 [20]. GENESYS 10S UV-Vis spectrophotometer (Thermo Fisher Scientific Inc) to determining the acid-insoluble lignin content according to T 222 om-21 [21]. The ash content in wood was determined via combustion at 525°C, T 211 om-22 [22].

Reagents

The extraction of sugar maple bark was performed using the following reagents: Deionized water (DI); Choline chloride (ChCl), CAS: 67481; Butyric acid (BA), CAS: 107926; Oxalic acid (OA), CAS: 144627; Gamma valerolactone (GVL), CAS: 108294 and Polyethylene glycol (PEG), CAS: 25322683. The liquid-liquid extraction and processing of extracts were carried out using the following reagents, Hexane (HEX), CAS: 110543; Ethyl Ether (EET), CAS: 60297; Chloroform (CLF), CAS: 67663; Ethyl Acetate (EA), CAS: 141786; Sodium Sulfate (SS), CAS: 67663; Pyridine (PY), CAS: 110861 and N,O-Bis(trimethylsilyl)trifluoroacetamide (BSFTA), CAS: 25561302.

Extraction Methods

Pilot-scale extractions were performed in a 4.7 L MK digester (M/K Systems Inc., Peabody, MA) in duplicate. Three treatments were applied: (1) Hot-water (HW): 160 °C, P-factor ~267; (2) DES1: Choline chloride (ChCl): Oxalic acid(OA):Polyethylene glycol (PEG) in a 4:4:9 molar ratio (20% water) at 50 °C and (3) DES2: ChCl:Butyric acid (BA): Gamma-valerolactone (GVL) in a 1:2:10 molar ratio (20% water) at 50 °C and same time of HW (90min). After extraction, the solid phase (treated bark) and liquid phase (bark extracted) were separated. Extracts were subjected to liquid-liquid extraction prior to analysis were subjected to liquid–liquid extraction prior to analysis.

Liquid–Liquid Extraction and Derivatization

Sugar maple bark extracts were fractionated using organic solvents according to Methods A and B, as illustrated in Figure 1. Method A: A volume of 50-200 ml of HW/DSE1/DSE2 extracts was transferred into individual (or three) separatory funnels, each containing one of the following solvents: Hexane (HEX), Ethyl Ether (EET) and Chloroform (CLF). Each solvent, representing different polarities, was used separately to generate three distinct organic fractions. After thorough and phase separation, the organic phase was isolated. To remove residual water, 2-3 scopes of anhydrous Sodium Sulfate (SS) were added the dried organic phase was then decanted, and the solid SS discarded. The resulting organic fractions were stored for subsequent derivatization. Method A focused on isolating HEX, EET, and CLF fractions without recombining them into a single solution. Method B: Similarly, 50-200 ml of HW extract was transferred into a separatory funnel containing Ethyl Aetate (EA). After mixing and the organic fraction separation, Method B followed the same post-fractionation procedure as Method A.

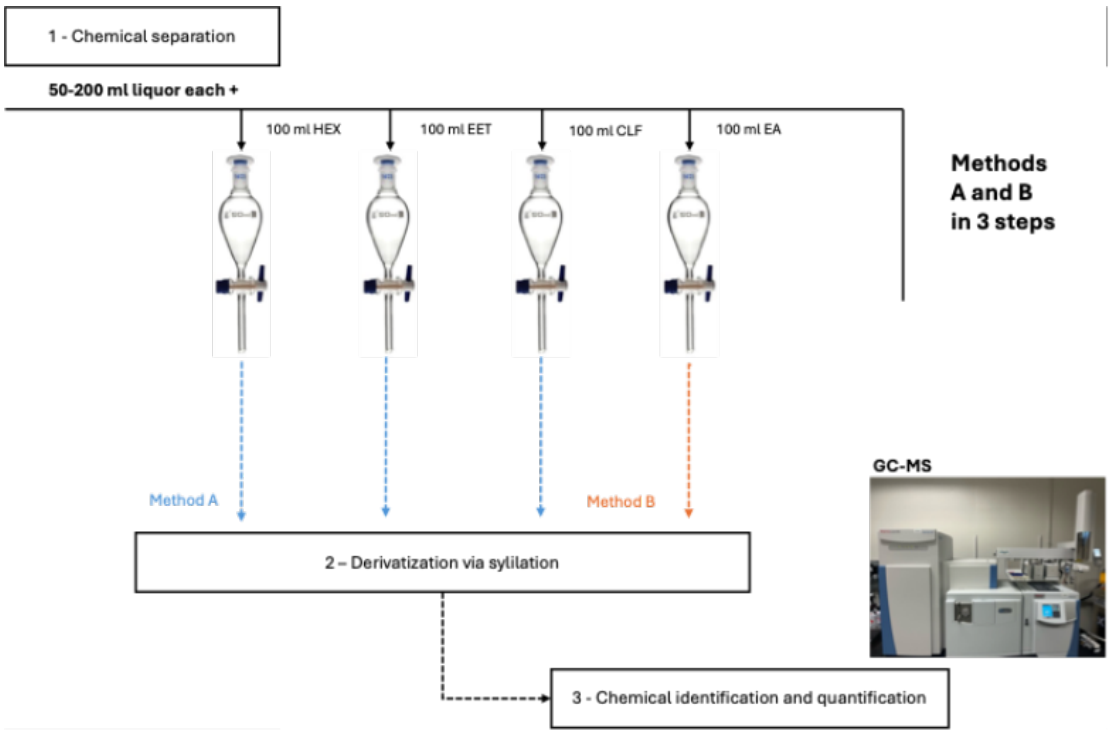


Figure 1: Method A was employed to prepare the HEX, EET, and CLF fractions from the HW, DES1 and DES2 extracts. Method B was used exclusively to obtain the EA fraction from the HW extract. All solvent fractions obtained from both methods were silylated prior to GC-MS analysis.

Analytical Methods

Total Phenolic Content (TPC)

TPC was used to determine the concentration of phenolic compounds present in the HW, DES1, and DES2 extracts. The analysis was conducted using a modified version of the method described by Kupina et al. [23]. Six test tubes were prepared, including one blank and five samples with progressively diluted concentrations. GENESYS 10S UV-Vis spectrophotometer (Thermo Fisher Scientific Inc) was calibrated, and 1 ml from each test tube was transferred into a cuvette for absorbance measurement at 765 nm. A standard calibration curve was generated, and an internal calibration equation ($R^2 = 0.9725$) was applied to calculate the phenolic concentration in the extracts. The calibration curve is presented in Formula (1) below:

$$Y\ (Abs) = 0.9657(x) + 0.0806 \quad (1)$$

where Y is the absorbance of the sample at 765 (nm); x (g/L) is the concentration of the total phenolic content in the sample solution.

Mid-Infrared Spectroscopy (MIR)

Ground bark samples obtained after scaled-up extractions were analyzed using a Perkin Elmer Frontier Fourier-Transform Infrared (FTIR) spectrometer of the MIR type. The instrument operates in the mid-IR (8300–350 cm−1) and far-IR (700–30 cm−1) ranges. The analyses were performed in MIR mode (4000 – 400 cm−1) with 15 scans per spectrum, in accordance with the equipment manual [24].

Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM–EDS)

A JEOL JSM-IT100 InTouchScope™ scanning electron microscope (SEM) equipped with a JEOL-made energy-dispersive spectroscopy (EDS) was used to acquire SEM images and determine the surface elemental composition of each solid sample, following the procedure described by Damasio (2025) [25] . The analysis was conducted to detect trace elements on the bark surface after the extraction. Table 1 summarizes the acquisition conditions for all samples.

Table 1: Energy Dispersive Spectrometry Acquisition Conditions

Sample ID	Mode	AV2(KV)	PC3 (mm)	LT4 (s)	RT5 (s)	DT[6] (%)	CR7 (CPS)
MB	SED1	5	10	117.96	120.81	3	13821
HW	SED	5	10	117.96	122.48	3	16906
DES1	SED	5	10	96.3	100.57	2	8001
DES2	SED	5	10	157.28	160.76	2	10203

[1]SED (Secondary electron detector mode); 2AV (Acceleration voltage); 3PC (Probe current); 4LT (Live time); 5RT (Real time); 6DT (Dead time) and 7CR (Count rate).

Gas Chromatography–Mass Spectrometry (GC–MS)

Samples were prepared according toa modified protocol described in [26]. A 1 µl aliquot of each sample was injected into a Thermo Orbitrap Trace 1310 gas chromatography system equipped with a TG-5SilMS column (30 m x 0.25 mm x 0.25 µm), using helium as the carrier gas. The mass spectrometer was operated in electron ionization (EI) mode with a full mass spectrum resolution of 60,000 and a scan range of 50-500 m/z. The total run time was 3-36 min, including a filament-on delay of 3 min. The oven was programmed with a maximum temperature of 350 °C, a pre-run time of 10 min, and an equilibration time of 1min. Three temperature ramps were applied: initial, ramp 1 and ramp 2, with rates of 0, 25 and 5 °C/min, reaching temperatures of 50, 280 and 325 °C, respectively. The hold times for each ramp were 4, 0 (no hold), and 13.80 min. Samples were analyzed in split mode (S/SL) at 280 °C, with a split flow of 10 mL/min, a constant carrier flow of 1 mL/min, a purge flow of 10 mL/min, and a gas saver flow of 5 mL/min with a gas saver time at 10 min. Compound identification was performed using the NIST/EPA/NIH Mass Spectral Library, including the nist_msms and nist_msms2 libraries. Additional databases included mainlib and replib (NIST EI data), nist_ri (retention index data), and Thermo Fisher's GC-Orbitrap Contaminants and Orbitrap-Metabolomics libraries. A match quality threshold of ≥89%, preferably 90–95%, was applied. To maintain optimal column performance, three solvent wash cycles were performed before injection and ten cycles after each run.

Heats of Combustion

Powdered bark samples from all treatments were ground and prepared according to ASTM E711 – 87 [27]. Small sample pellets were combusted using a PARR 6200 calorimeter coupled to a PARR 6510 water handling system, operating in a closed loop mode with controlled water parameters. The heat values, including the gross heat value (Hg) and the net heat value (Hn), were calculated according to Formula 2 below:

$$H_n = H_g - (91.23)*H \quad (2)$$

where H_n is the net heat value, H_g is the gross heat value, and H represents the percentage of hydrogen in the sample.

Statistical Analysis

In order to verify the significance considering the groups or treatments an ANOVA was conducted for each data set considerin $\alpha = 0.5$ %, followed by Tukey test in case of significance to test the significative difference between the average values assuming $\alpha = 1$ %.

Results and Discussion

Extraction Efficiency

The yields of extracted MB were notably high following DES1 and DES2 treatments, attaining 115.42 and 93.66 %, respectively, relative to the initial OD mass of MB. In comparison, the yield from the HW extraction was 85.92%. The yield of DES1 exceeded 100%, likely due to incomplete removal of residual solvent from

the extracted material. In contrast, HW extraction present a lower yield, indicating higher extracting portion of the target compounds. DES extractions particularly DES1, exhibited higher yields, reflecting its stronger dissolution capability. However, residual solvent may remain in the wood chips after extraction, contributing to the measured weight and artificially inflating the yield. This suggests that the current method may overestimate the extraction efficiency and requires further optimization for accurate yield determination. DES2 showed more reasonable yield compared to DES1, likely due to lower residual solvent in the extract. The unusually high yield observed for DES1 can be addressed by improving solvent recovery, which would reduce the influence of residual solvent.

Figure 2 shows the Total Phenolic Content-TPC (g/L) of MB extracts obtained from HW, DES1 and DES2 extractions. Among the three extracts, DES2 exhibited the highest TPC values of 2.5-3 g/L. Phenolic compounds are important and widely distributed secondary metabolites in the plant kingdom. According to, the total phenolic content of ethyl acetate and methanolic extracts from three varieties of Ceratonia siliqua L. barks ranged from 0.46 to 0.76 (g/l GAE) [28]. Lazar et al. reported that ultrasound-assisted treatment and elevated temperatures significantly enhanced the extraction of polyphenolic compounds from spruce bark, with TPC values increasing from 37.3 mg GAE g−1 at 45 °C to 43.1 mg GAE g−1 at 60 °C, the TPC values obtained in our study are within the range of values those reported for C. siliqua and spruce bark extracts, suggesting that the HW and DES-based extractions of MB achieved efficient recovery of phenolic compounds under the tested conditions [29-31].

The results reveal distinct differences between HW and DES extraction strategies. DES treatments yielded the highest total phenolic content (up to 2.76 g/L). DES solvents effectively lead to solubilization of phenolic acids and flavonoids [32]. However, DES extractions were affected by solvent retention in bark residues, leading to inflated yields and elevated ash content. In contrast, HW extraction provided lower but more reproducible yields, with liquors enriched in lignin-derived phenolics such as guaiacol and vanillin [11,12]. From a process perspective, HW represents a more consistent and scalable option, while DES offers higher selectivity that requires optimization for solvent recovery.

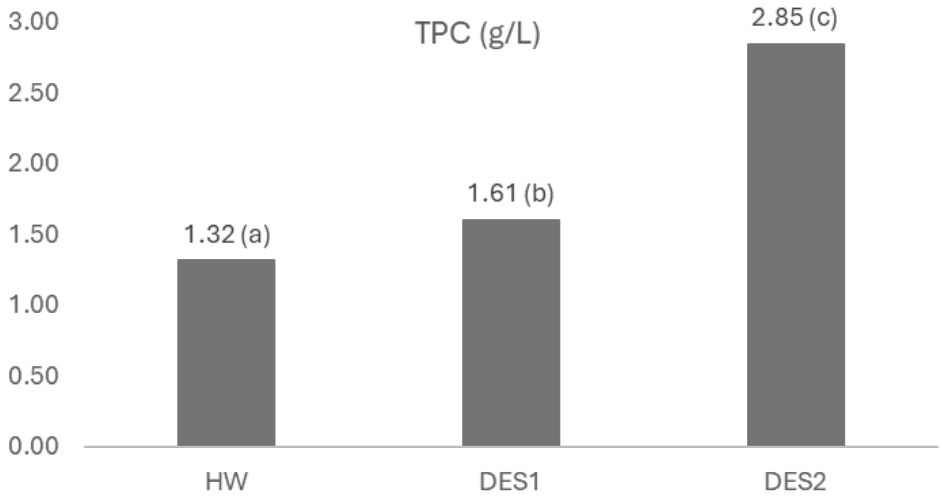


Figure 2: Total Phenolic Determination (g/l) Performance According Process Scalability. Same Letters Mean no Statistical Difference for Tukey Test at α = 1 %

Chemical Composition

A higher ash content of residual biomass after HW extraction is not expected as HW is supposed to remove some of the soluble inorganics actually when we take into consideration the yield of HW 85.92% and the ash content in MB and HW we conclude that actually some very weak "deashing" occurred - 85.92*0.0806-6.925;

(7.45-6.925)*100/7.45 = 7.04~7% of the total ash in MB was removed during HW. Ash content increased following both HW and DES extractions, with DES extraction showing a greater increase compared with HW extraction. DES removed more organic matter, thereby increasing the relative proportion of ash. This indicates that DES extraction is more effective at removing organic compounds from sugar maple bark, although residual solvent retained in the material may contribute to the elevated ash content. As shown in Figure 3, MB exhibited a total extractives content of 5.47 % and a total lignin content of 25.5 %. A previous study using the same extraction protocol and solvents reported comparable values for natural maple bark, with 5.2% total extractives and 24.1 % lignin content31. Following HW and DES extractions, the extracted MB showed significant increases in total extractives content, by 6.38 %, 12.71 % and 8.53 % for HW, DES1, and DES2, respectively, relative to the original MB total extractives (%). The lignin content also increased by more than 10 % compared to the original material. DES1 and DES2 residues remained in the bark after extraction, contributing to an increased total extractives value.

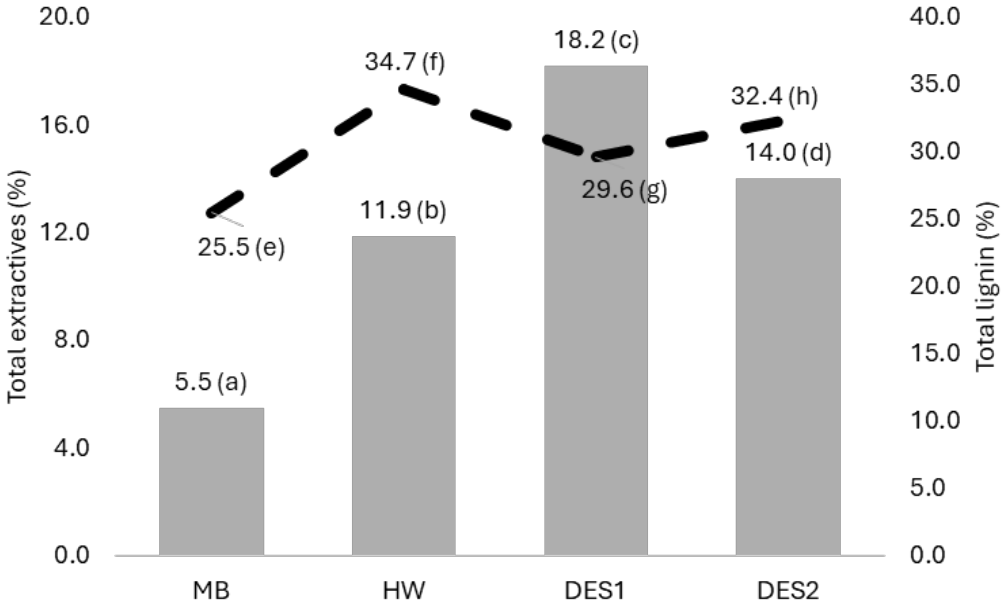


Figure 3: Extractives and Lignin Content of Bark Powders (MB untreated, HW, DES1, DES2) after Solvent–Water–Solvent Extractions. Same Letters mean no Statistical Difference for Tukey Test at α = 1 %

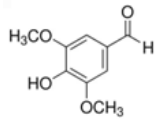
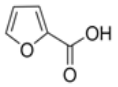
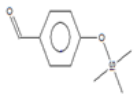
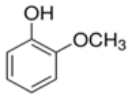
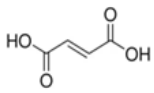
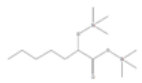
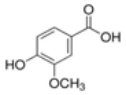
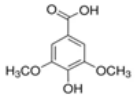
Biomolecular Characterization by GC–MS

Liquid-liquid extraction is a crucial step to separate the targeting molecules in this study. Considering the solubility parameter of each solvent used in this study, HEX (δ 14.9 MPa1/2); EET (δ 15.1 MPa1/2), CLF (δ 19 MPa1/2), EA (δ 18.6 MPa1/2) and water (δ 47.9 MPa1/2), each fraction of phenolics and additional organic acids and molecules presented a specific interaction with the chosen solvent [33]. Considering these solvent properties, Methods A and B will present different molecules classes after each liquid-liquid extraction. EA from Method B present δ similar to CFL from Method A. The closest δ, the higher the miscibility of the liquids in the separator funnel will be. CFL and EA presented the higher δ compared with HEX, and EET; closer to the water (δ 47.9 MPa1/2). All the liquors generated (HW, DES1 and DES2) present fractions of water > 20 % in their composition and this water fraction will lead to the miscibility between the two liquid phases. The liquors used in this study varied in both water content and density. Similarly, the solvents presented a range of densities that influenced the positioning of the organic fraction during extraction. Specifically, the relative densities of the solvents were: HEX: 0.70, EET: 0.71, CLF: 1.70, and EA: 0.9, with water serving as the reference (1.00) [23,34-36]. After mixing, the HEX and EET fractions were in the upper layer of the separatory funnel, and CLF settled at the bottom, reflecting their respective densities. It is known that components with higher solubility parameters are more polar and are preferentially extracted compared to those with lower solubility parameters. Consequently, a greater number of apolar and phenolic structures were identified, as summarized

in Table 2. CLF from Method A and EA from Method B exhibited higher water miscibility, in making it difficult to clearly identify the liquid-liquid separation line between the solvent and liquor due to their polarities. The extraction conditions HW at higher temperature (160 °C) and DES at a milder temperature (50 °C) may have also influenced the type of compounds identified in this study.

Table 2 lists the identified chemical compounds, along with two key parameters: molecular weight (MW) of each molecule and probability of occurrence. The molecular weight is determined by the compound's structure, while the probability of occurrence is calculated on the software analysis of data from the Orbitrap Trace 1310 Thermo Extractive Gas Chromatography system. The arithmetic average molecular weights (MW) of biomolecules were 250.24 for HW, 223.70 for DES1, and 194.95 for DES2. When compared according to extraction method and fraction, the values were: A-fraction CLF (267.64), A-fraction HEX (259.60), A-fraction EET (241.27), and B (240.96). These averages were calculated based on all detected compounds, including those with a probability of identification below 88–90%.

Table 2: Chemical Compounds Isolated and Identified after Chemical Derivatization via Gaseous Chromatography Coupled to Mass Spectroscopy (GC-MS) Accordingly their Molecular Weight (MW), Probability to Occur, Process of Extraction and Method of Preparation (A and B)

Name	ID	MW	RT per method (s)	Probability	Process	Method	Structure
Syringaldehyde - TMS	2	182	A-HEX(11.09)	>88-90	HW	A (HEX)	
2-furanoic acid - TMS	3	184	A-CFL(7.83)	>88-90	HW	A (CFL)	
4-Trimethysiloxybenzaldehyde	6	194	A-EET(9.41) and A-CFL(9.41)	>88-90	HW	A (EET, CFL)	
Guaicol - TMS	1	196	A-HEX(8.48); A-EET(8.49); A-CFL(8.48) and B(8.47)	>88-90	HW	A (HEX-,EET, CFL) and B	
Fumaric acid – 2TMS	4	260	A-EET(9.2)	>88-90	HW	A (EET)	
2-Trimethylsilyloxyheptanoic acid, trimethylsilyl ester	5	290	A-EET(9.27) and A-CFL(9.26)	>88-90	HW	A (EET, CFL)	
Vanillic acid – 2 TMS	7	312	A-EET(11.36) and A-CFL(11.37)	>88-90	HW	A (EET, CFL)	
Syringic acid - TMS	8	342	A-EET(12.02) and C-CFL(12.08)	>88-90	HW	A (EET, CFL)	

ID: Identification/tag number corresponding to GC–MS chromatograms; RT: Retention time (s), as shown in the supporting material.

The main biomolecules profiles for Method A and B contained a significant number of compounds. However, in this study, our screening focused on the most representative compounds, considering a probability of > 88-90 %. Notably, some key biomolecules with potential for pilot or future commercial applications-such as guaiacol, vanillin and benzoic acid-were detected only in the HW treatments of Method A. For both DSE1 and DSE2 in Methods A and B, the same fraction of molecules was not detected, likely due to mild extraction conditions employed. Method A which explores all three fractions, yielded diverse and commercially relevant spectrum of compounds. Guiacol-TMS was identified in all fractions of Methods A (HEX, EET and CFL), as well as in Method B. The derivatized compounds 2-Trimethylsilyloxyheptanoic acid, trimethylsilyl ester and

4-Trimethysiloxybenzaldehyde were detected in Methods A (EET and CLF fractions). Additionally, guaiacol, syringaldehyde, 2-furanoic acid, fumaric acid, vanillic acid and syringic acid was detected in their TMS (Trimethylsilyl) derivatized forms across the methods in Table 6.

GC–MS analysis confirmed the presence of guaiacol, vanillin, benzoic acid, molecules with documented antioxidant, antimicrobial, or cosmeceutical activity [28,37]. Guaiacol and vanillin are well-established lignin degradation products with strong radical scavenging potential [28,37].

Structural and Elemental Analysis

Figure 4 shows the qualitative surface evaluation using MIR mode (4000 – 400 cm−1) to characterize surface chemical groups and wood powder composition after their pilot-scale extractions. The treatments included MB (maple bark powder without extraction), HW (maple bark powder after HW extraction), DES1 (maple bark powder after DES1 extraction), and DES2 (maple bark powder after DES2 extraction).

MIR and SEM–EDS analyses provided complementary insights into extraction effects. MIR spectra confirmed partial disruption of hemicellulose and lignin structures, particularly under HW conditions. SEM–EDS revealed increased Cl and Fe in DES-treated residues, attributable to solvent formulations. While these concentrations remain within Generally Recognized as Safe (GRAS) thresholds for individual components, they underline the need for solvent recovery strategies in DES processes. Importantly, HW-treated solids showed minimal elemental contamination, strengthening their suitability for downstream uses, including food-contact applications.

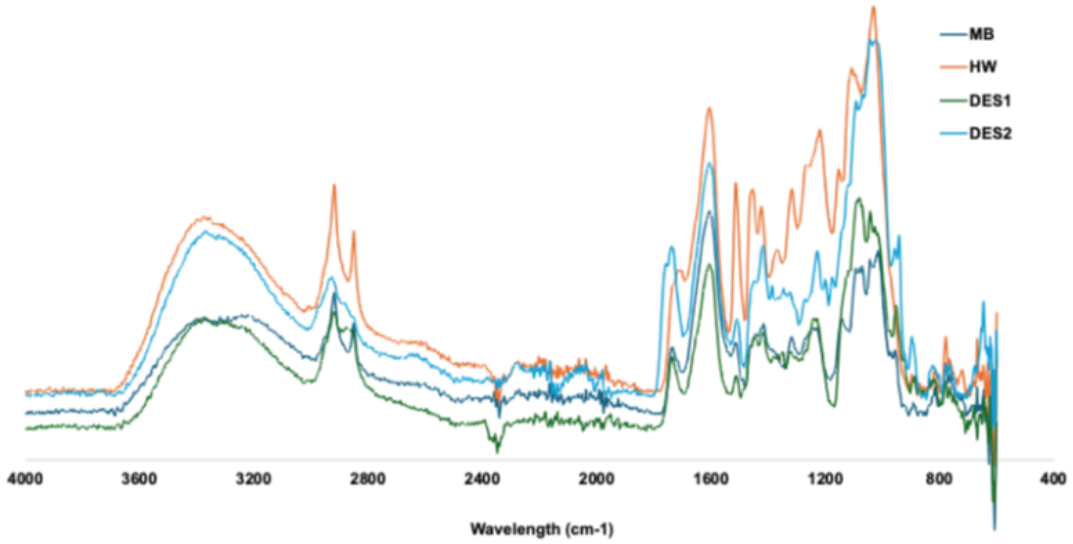


Figure 4: Qualitative Surface Evaluation throughout MIR mode (4000 – 400 cm^{-1}).

As lignocellulosic material both in higher concentrations MB, HW, DES1 and DES2 shows the OH vibrational bonds at 3.343 cm^{-1} and 2.902 cm^{-1} the vibrational linkages for aliphatic C-H [38,39]. HW and DES2 treatments, which removed certain amounts of lignin and polyphenols, showed a vibration band at 1605 cm^{-1} similar to that reported by. This band was more prominent in HW than other treatments, suggesting that lignin structures were concentrated at the bark surface. This interpretation is furhter supported by the sharper peak observed at 1025-1030 cm^{-1}, usually assigned to C-O stretching of phenolic-OH groups [38]. In contrast DES1 and DES2 did not exhibit the more prominent peaks in these vibrational bands, confirming the

extractions of possible polyphenols during treatment. The characteristic vibrational band for lignin at 1510 cm^{-1} was observed mainly in the HW treatment, in contrast to the other extractions [38]. Additionally, peaks at 1015-1025 cm^{-1} were assigned to the stretching vibrations of the C-OH side groups and the C-O-C glycosidic bonds, consistent with [38]. This qualitative evaluation highlights the most significant spectral features for HW, treatments. By comparison, the DES1 and DES2 extractions exhibit behavior similar to HW, with the exception of the superficial lignin effect.

Continuing the elemental investigation, the energy dispersive spectrometer (EDS) coupled with SEM provides broad spectrum characterization of samples without requiring prior knowledge of their composition. It also enables the identification of trace elements that could contribute to the materials' toxicity or surface reactivity.

As expected, in treatments such as DSE1 and DSE2, the mass concentration (%) of chlorine (Cl) increased due to its addition in the extraction liquor formulations, compared to the raw bark (MB). In case of HW extraction, the concentration of this element decreased, since no additional compounds were added to the liquor, which consisted mainly of water and residual materials extracted from the bark. The chlorine content increased from 0.82 % in DSE1, to 1.13 % in DSE2 compared to 0.12 % in the original MB. This increase could be significant for some applications where chlorine may pose concerns, such as in food contact, cosmetics, or biomedical materials. However, the formulation of these extraction liquors is considered safe for food contact, despite the observed increase in chlorine concentration in the solid material. Chlorine from ChCl is classified as a GRAS (Generally Recognized as Safe) substance according to 21 CFR §182.8252 and SCOGS Report No. 42., it is also important to note that, after the extraction, these chlorine residues could be present in ionic forms, potentially interacting with other components and posing safety concerns in new applications of the bark or processed bark [40].

For the HW treatment, a slight increase in carbon content was observed, likely due to the degradation of other components during extraction. The carbon percentage increased modestly from 58.03 % in MB to 59.35 % after HW treatment.

Na, Mg, Si and Ca showed a decrease from MB to DSE1, DSE2 and HW. In contrast, Si exhibited a slight increase from MB to HW, possibly due to specific deposits or accumulations in the wood material. Although a reduction in mineral content was expected the material was immersed in a liquid during treatment, Si behaved differently, likely reflecting localized retention or concentration effects. Traces of nitrogen and barium were not detected in any of the ground bark samples analyzed by SEM-EDS, likely due to their low concentrations and the technique's limited sensitivity to light elements.

Most of the trace elements detected in this study were found in the K energy level of the electron orbitals. Even though if some potentially hazardous showed slight increases, their presence in the K shell may be considered a positive aspect for material safety, as higher energy is required to alter these electrons or for them to interact with other matters.

The trace elements detected in this study primarily originate from the residual chemicals used in the extraction liquor recipes formulations. PEG (§172.210 / 172.820 / 173.310 / 173.340 / 175.105 / 175.300 / 176.180 / 178.3750), ChCl (§ 182.8252), OA (§ 177.1010 and §177.2410) and BA (§ 178.2010) are all food contact substances listed under 21 CFR, either as food additive or as GRAS (Generally Recognized as Safe) substances, in accordance with 21 CFR Parts 170-186 [40-43]. Finally, γ-Valerolactone, considered a green and non-toxic solvent for design applications, is a component of the extraction liquor but not listed by the FDA for food contact or as a food additive [44].

Table 3: Trace Elemental Composition Accordingly Chemical Elements Using Energy Dispersive Spectrometry Acquisition Conditions

TE5	Mass (%)				Atom (%)				Energy level			
	MB	HW	DSE1	DSE2	MB	HW	DSE1	DSE2	MB	HW	DSE1	DSE2
C[6]	58.03	59.35	56.73	57.8	65.59	66.87	64.66	65.66	K	K	K	K
N[7]	nd	nd	nd	nd	nd	nd	nd	nd	K	K	K	K
O[8]	39.63	38.16	40.05	39.02	33.63	32.28	34.26	33.27	K	K	K	K
Na[9]	0.07	0.1	0.05	0.1	0.04	0.06	0.03	0.06	K	K	K	K
Mg[10]	0.14	0.13	0.07	0.2	0.08	0.07	0.04	0.11	K	K	K	K
Si[11]	0.14	0.18	0.1	0.04	0.07	0.09	0.05	0.02	K	K	K	K
Cl[12]	0.12	0.07	0.82	1.13	0.05	0.03	0.32	0.43	K	K	K	K
K[13]	0.29	0.33	0.15	0.22	0.1	0.11	0.05	0.08	K	K	K	K
Ca[14]	0.65	0.85	0.96	nd	0.22	0.29	0.33	nd	K	K	K	K
Fe[15]	0.94	0.82	1.05	1.49	0.23	0.2	0.26	0.37	L	L	L	L
Ba[16]	nd	nd	nd	nd	nd	nd	nd	nd	L	L	L	L

[5]TE (Trace elements); 6C (Carbon); 7N (Nitrogen); 8O (Oxygen); 9Na (Sodium); 10Mg (Magnesium); 11Si (Silicium); 12Cl (Chlorine); 13K (Potassium); 14Ca (Calcium); 15Fe (Iron) and 16Ba (Barium).

All the images in Table 3 and Figures 5 and 6 show the presence of the trace elements as determined by SEM-EDS, using energy dispersive spectrometry acquisition mode. The samples analyzed included MB (maple bark); HW (Bark after HW extraction), DES1 (Bark after DES1 extraction) and DES2 (Bark after DES2 extraction). The images were acquired with a secondary electron detector (SED) with a probe current (PC) of 10 mm, acceleration voltage (AV) of 5 kV and scale bar of 1 mm. Compared with Figure 6, the raw MB, all images acquired with EDS, as shown in Table 3, highlight the presence of the chemical elements listed in Table 3 according to their respective energy level. All trace elements discussed C (Carbon); N (Nitrogen); O (Oxygen); Na (Sodium); Mg (Magnesium); Si (Silicium); Cl (Chlorine); K (Potassium); Ca (Calcium); Fe (Iron) and Ba (Barium) were detected in the samples. It is also important to note that, although the SEM-EDS images indicate the presence of trace elements, their concentrations are sometimes too low to be reliably quantified as is the case for nitrogen (N) and barium (Ba) in the MB, HW, DES1, and DES2 solid samples. Figure 6 shows grounded MB image with secondary electron detector (SED) using EDS mode. The elongated features visible correspond to longitudinal wood elements, while the square-like structures represent MB powder particles. The white areas, observed in the center of some powder granules likely represent a phenomenon known as charging during the image acquisition. This effect does not influence the determination of chemical trace maps. It is important to note that the variation in powder particle size can promote charging when the sample is placed in the stube, creating multiple peaks and valleys.

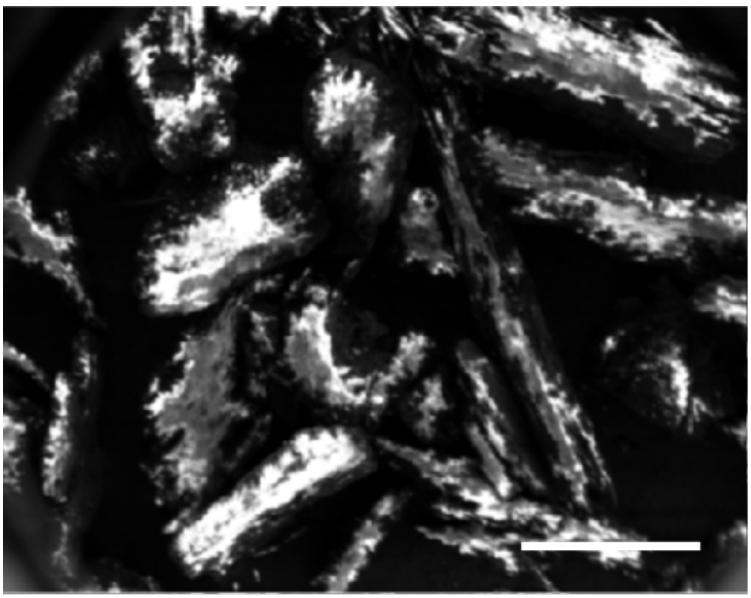


Figure 5: Maple Bark Grounded. Image Acquired with Secondary Electron Detector (SED) in an Energy Dispersive Spectrometry Mode (SEM-EDS). Probe Current (PC): 10 mm, Acceleration Voltage (AV): 5 KV and Scale bar of 1 mm.

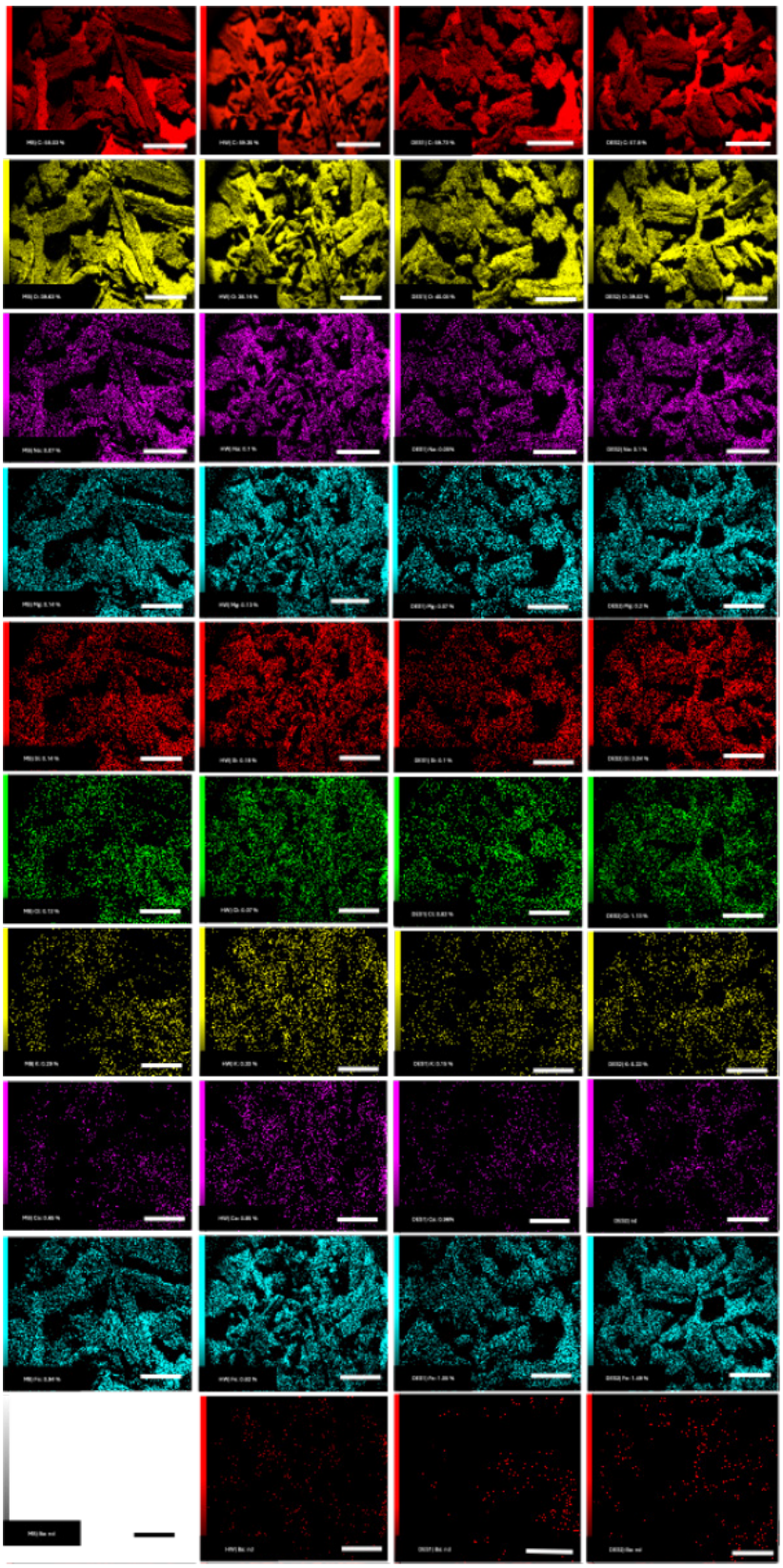


Figure 6: SEM-EDS Images of trace Elemental Composition Accordingly Chemical Elements using Energy Dispersive Spectrometry. Image Acquired with Secondary Electron Detector (SED) in an Energy Dispersive Spectrometry mode (SEM-EDS). Probe Current (PC): 10 mm, Acceleration Voltage (AV): 5 KV and scale bar of 1 mm.

Combustion Properties

Hot-water (HW) extraction is a traditional treatment that promotes lignin concentration and generates compounds with higher heat values in wood and other types of biomasses [11]. Table 4 presents the gross heat value (Hg) and net heat value (Hn) (for all bark samples after the extraction methods, as well as for the untreated bark. The HW treatment presented an Hn of 16.29 MJ/kg, which is 5.72 % higher than that of raw MB (15.36 MJ/kg). Similar results have been reported in another study under comparable extraction conditions, where HW treatment increased the heat value by 2–3% compared with MB [45]. As expected, DES1 and DES2 showed higher Hn values compared with both HW and MB, which can be attributed to the residual chemicals retained from the extraction recipes applied in this study. DES1 (16.39 MJ/kg) and DES2 (16.38 MJ/kg) exhibited net heat values (Hn) that were 6.3 % and 6.2 % higher, respectively, than that of MB (15.36 MJ/kg). Compared with HW, Hn values of DES1 and DES2 were 0.61 and 0.52 % higher, respectively. It is important to note that the differences in Hn values between HW and DES extractions are relatively small; however, when compared with the original MB, the increases observed for both treatments are significant. As discussed, the residual chemicals detected are not toxic, as they fall within the category of green solvents. This presence in the biomass was also confirmed through the total extractive analysis described above. HW once again demonstrated its technological and physio-chemical feasibility when compared with DES formulation's tests, while offering even more sustainable in the extraction recipe.

Table 4: HW and DES Bark Powder Heat Values Considering Hg (Gross Heat Value) and Hn (Net heat value). Same Letters Mean no Statistical Difference for Tukey test at $\alpha = 1$ %

ID	Hg (Gross heat value-MJ/kg)	Hn (Net heat value-MJ/kg)
MB	15.57 (a)	15.36 (a)
HW	16.50 (a)	16.29 (a)
DES1	16.60 (a)	16.39 (a)
DES2	16.59 (a)	16.38 (a)

An often-overlooked aspect of extraction processes is the fate of residual biomass. Here, calorimetric analysis showed that both HW and DES treated barks retained or exceeded the energy content of raw bark, suggesting that extracted solids could serve as a bioenergy feedstock. This co-valorization pathway enhances the overall sustainability of bark biorefineries by coupling high-value chemical recovery with energy generation from residual biomass.

Sustainability and Industrial Relevance

From a sustainability perspective, both HW and DES represent green extraction routes, each with distinct tradeoffs. HW relies exclusively on water, making it inherently safe and compatible with industrial food-contact applications. DES formulations applied in this study (choline chloride, oxalic acid, polyethylene glycol, butyric acid, and gamma-valerolactone) are either GRAS or biodegradable, however, challenges remain regarding solvent recovery and regulatory acceptance [46]. Successful integration of DES into commercial practice will depend on improving solvent recycling and ensuring validated extract purity for food and cosmetic application.

The deep eutectic solvents (DES) formulations used as liquor recipes in this study fall within the class of green solvents. Green solvents including bio-based (derived from renewable sources), water based (aqueous systems), supercritical fluids (above their critical point), and deep eutectic solvents (formed by combining two or more components)-provides sustainable alternatives to conventional organic solvents for bio-oil extraction [47]. In this study, DES 1 and DES2 are classified as green solvents, characterized by being non-toxic, non-volatile, recyclable, and biodegradable. Their use enhances the efficiency and sustainability of the extraction process, improving the overall environmental profile of the methodology. improving the overall environmental

profile of the methodology. Table 5 below summarizes the key properties of DES1 and DES2 components and based on various databases and references. Two main aspects are considered for each component: (1) regulatory and safe aspects; (2) green solvent criteria.

Table 5: Sustainability Parameters for DES Liquor Compounds Considering Key Properties: (1) Regulatory and Safe Aspects and (2) Green Solvent Requisites

	Database/Property/Index	ChCl (SMILES: C[N+](C)(C)CCO.[Cl-])	PEG (SMILES: C(CO)O)	OA (SMILES: C(=O)(C(=O)O)O)	BA (SMILES:CCCC(=O)O)	GVL (SMILES: CC1CCC(=O)O1)	Ref.	Times substance appear in databases
Regulatory requisite	Cumulative Estimated Daily Intake (CEDI)	--	27	1	6	--	45	
	Final Rules: Food Additives and Color Additives	--	5	--	--	--	45	
	Food Additive and Color Additive Petitions Under Review or Held in Abeyance	--	--	--	--	--	45	
	Food Contact Substance (FCS) Notifications that are No Longer Effective	--	--	--	--	--	45	
	GRAS Notices	--	1	--	2	--	45	
	Human Food Made with Cultured Animal Cells Inventory	--	--	--	--	--	45	
	Inventory of Effective Food Contact Substance (FCS) Notifications	--	20	1	5	--	45	
	Inventory of Environmental Impact Decisions for Food Contact Substance Notifications	--	20	1	7	--	45	
	Inventory of Food Contact Substances Listed in 21 CFR	--	59	4	4	--	45	
	New Plant Variety Consultations	--	--	--	--	--	45	
	New Protein Consultations	--	--	--	--	--	45	
	Post-market Determinations that the Use of a Substance is not GRAS	--	--	--	--	--	45	
	Premarket Meetings Regarding Food from Genome Edited Plants	--	--	--	--	--	45	
	Regulatory Status of Color Additives	--	--	--	--	--	45	
	SCOGS (Select Committee on GRAS Substances)		--	--	--	--	45	
	Submissions on Post-Consumer Recycled (PCR) Plastics for Food-Contact Articles	--	--	--	--	--	45	
	Substances Added to Food (formerly EAFUS)	2	8	--	113	--	45	

	Physical/chemical properties						
Green requisite	Source/Composition	Deep eutectic	Syntetic polymer	Syntetic organic salt	Syntetic Organic acid	Biobased	20, 47
	Biobased chain/or production option	YES	YES	YES	YES	YES	20,47,48
	Toxicity - Acute LD50 (Drug bank percentile)	11.09%	1.55%	15.32%	3.53%	1.09%	20, 47
	Volatility - Flash point (°C)	NODATA	182-287 °C	NODATA	72 °C	81 °C	20, 47
	Aqueous Solubility (Drug bank percentile)	98.99%	99.81%	93.68%	94.42%	97.71%	20, 47
	Biodegradability	YES	YES	YES	YES	YES	49, 50, 51, 52
							Level/presence or quantity

* Ref. = reference; ChCl: Choline chloride; OA: Oxalic acid; PEG: polyethylene glycol; BA: Butyric acid; GVL: gamma-valerolactone.

Considering the aspects for green solvents outlined above, regulatory and safety considerations have become a key topic across many fields as solvent applications transition from research to commercial products. Because these products are increasingly part of daily use, including handling and dietary application it is essential to ensure their safety. Regulatory requirements are established and enforced by the relevant agencies in each country or region. In the United States of America, the Food and Drug Administration (FDA) maintains a range of databases covering all the stages of substances approval, including composition, intended use, and origin ChCl, OA, BA and PEG are listed in several of these databases and are therefore considered safe by the FDA. GVL, as a relatively new substance, is not currently regulated by FDA. However, available literature indicates low or negligible certain applications, as further discussed in the following sections of this study. Finally, the second and equally important criterion for green solvents is their set of physical and chemical properties. As summarized in Table 3 including source and composition, biobased origin, toxicity, volatility, solubility and biodegradability-confirming all components of DES1 and DES2 (ChCl, OA, BA, PEG and GVL) meet these requirements, confirming their classification as green solvents [48-53].

Novelty and Outlook

This study is among the first to integrate extraction efficiency, molecular characterization, elemental analysis, and energy valorization of sugar maple bark. By demonstrating both the diversity of extractable bioactive compounds and the retention of calorific value in residual solids, the results establish bark as a dual-purpose feedstock for bioproducts and energy. Future work should focus on optimizing DES formulations to balance extraction efficiency with recovery feasibility, and on testing bark-derived extracts as functional additives in active packaging coatings.

Conclusions

Sugar maple bark represents an abundant yet underutilized forestry residue with significant potential for sustainable valorization. In this study, hot-water (HW) and deep eutectic solvent (DES) extractions were compared at pilot scale to evaluate efficiency, molecular composition, and downstream applications. DES extractions achieved the highest total phenolic content (up to 2.76 g/L), while HW produced more consistent

lignin-rich liquors with lower solvent-related variability. GC–MS analysis identified key bioactive molecules, including guaiacol, vanillin, benzoic acid, aloin, and α-muricholic acid, underscoring the antioxidant and cosmeceutical relevance of maple bark extracts. Structural and elemental analyses confirmed partial disruption of lignocellulosic components and the presence of residual elements after DES treatments, highlighting the importance of solvent recovery strategies. Importantly, bark residues retained or improved their calorific value after extraction, supporting their use as a complementary bioenergy feedstock. This dual pathway—high-value chemical recovery coupled with energy valorization of solids—enhances the overall sustainability of bark biorefining. Overall, HW extraction offers a safe and scalable route for food-contact and packaging applications, while DES provides higher phenolic yields but requires optimization for regulatory and industrial adoption. These findings establish a foundation for the development of bark-derived extracts in active packaging, cosmetics, and nutraceuticals, contributing to circular bioeconomy strategies.

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