

Article

Valorization of Bay Tree Pruning by Autohydrolysis: Chemical Characterization and Energy Potential

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Abstract

Bay laurel (*Laurus nobilis* L.) leaves and branches represent promising lignocellulosic residues for biorefinery and bioenergy applications. The present study evaluated the effect of autohydrolysis at different temperatures and residence times on the chemical composition, structural properties, and higher heating value (HHV) of both biomass fractions. The initial characterization revealed that leaves were richer in extractives and lignin, whereas branches contained higher amounts of α -cellulose and hemicelluloses. Autohydrolysis promoted the selective solubilization of biomass components, reaching maximum values of approximately 38% for leaves and 30% for branches. Increasing treatment severity enhanced hemicellulose removal and resulted in a relative enrichment of lignin and cellulose in the solid residues, while FTIR analysis showed that the main lignocellulosic structure was largely preserved. The solid residue after polyalcohol liquefaction presented a higher heating value, improving the heating value of the resulting solids, achieving maximum HHVs of 30.08 MJ kg⁻¹ for leaves and 29.46 MJ kg⁻¹ for branches at 180 °C for 30 min. Overall, the results indicate that autohydrolysis is a suitable strategy for the selective extraction of hemicellulose-rich fractions and the production of lignin-enriched solid residues. This process contributes to the sustainable valorization of bay laurel biomass within an integrated biorefinery framework.

Keywords: autohydrolysis; bay laurel; biomass fractionation; higher heating value; liquefaction; lignocellulosic biomass



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1. Introduction

The increasing generation of agricultural and forestry residues has stimulated significant interest in the development of sustainable strategies for biomass valorization [1]. In the context of the circular bioeconomy, lignocellulosic residues are increasingly recognized as valuable renewable resources that can be converted into bio-based products, chemicals, and energy [2,3]. Among these residues, pruning biomass from perennial crops and aromatic plants represents an underutilized feedstock with considerable potential for integrated biorefinery applications.

Bay tree (*Laurus nobilis* L.) is a perennial aromatic species widely cultivated throughout the Mediterranean region for its culinary, pharmaceutical, and cosmetic applications [4]. While the leaves constitute the primary commercial product due to their high content of essential oils and bioactive compounds, such as eucalyptol, α -terpineol acetate and methyl eugenol [5,6], the extraction of these valuable components generates substantial amounts of residual biomass. In addition, periodic pruning is required to maintain plant health, productivity, and harvesting efficiency, producing considerable quantities of branches, twigs and spent leaves. These lignocellulosic residues are often discarded, burned, or otherwise inadequately managed, despite retaining significant amounts of structural carbohydrates and lignin.

In our previous study [1], we established the baseline chemical composition of bay laurel pruning residues. That work focused on the compositional characterization of leaves and branches, demonstrating that branches contained higher amounts of structural carbohydrates, with 31.96 wt.% α -cellulose and 30.65 wt.% hemicelluloses, compared with 23.82 wt.% and 23.60 wt.% in leaves, whereas leaves exhibited higher contents of Klason lignin (25.47 vs. 20.47 wt.%), extractives (23.74 vs. 14.39 wt.%), and ash (3.37 vs. 2.53 wt.%) [1]. Other studies on bay laurel wood and bark indicate that these fractions contain substantial amounts of structural polymers, making them promising feedstocks for lignocellulosic biorefinery applications. Bay laurel wood has been reported to contain 44.0–53.6 wt.% cellulose, 19.7–27.7 wt.% hemicelluloses, and 21.2–23.2 wt.% lignin, while bark contains approximately 31.5 wt.% cellulose and 29.7 wt.% lignin [7,8]. The relatively high hemicellulose content is particularly relevant for autohydrolysis, as this hydrothermal pretreatment selectively solubilizes hemicellulosic polymers into oligosaccharides and sugars while largely preserving the cellulose-rich solid fraction [9].

Autohydrolysis has emerged as an environmentally friendly pretreatment technology for lignocellulosic biomass fractionation. This process employs water under elevated temperatures and pressures to selectively solubilize hemicellulosic components without requiring the addition of chemical reagents. As a result, autohydrolysis facilitates the separation of biomass fractions while minimizing environmental impacts and reducing downstream processing requirements. During treatment, hemicelluloses undergo controlled hydrolytic solubilization and depolymerization, producing a liquid fraction rich in xylooligosaccharides (XOSs) and monomeric sugars [10]. This process is catalyzed by hydronium ions generated through water autoionization and by organic acids, particularly acetic acid, released in situ from acetyl groups present in the hemicellulosic fraction as temperature increases [10,11]. Depending on the operating conditions, the process can be optimized to recover hemicellulose either as oligosaccharides or as monomeric sugars, including xylose, mannose, and galactose, with maximum recoveries in the liquid phase reaching approximately 60% [12].

In contrast to hemicellulose, cellulose is less affected by hydrothermal pretreatment. Li et al. [13] reported that less than 22 wt% of cellulose is degraded in wood and herbaceous biomass under typical autohydrolysis conditions, highlighting the selective nature of the process. Consequently, the resulting insoluble solid fraction consists predominantly of cellulose and partially modified lignin [11,14], yielding a cellulose- and lignin-rich substrate that is more susceptible to subsequent enzymatic hydrolysis [9].

Furthermore, the generated liquid and solid fractions can serve as precursors for a wide range of applications, including the production of biofuels, platform chemicals, biomaterials, and energy carriers.

In addition to enabling biomass fractionation, autohydrolysis may influence the fuel characteristics of the remaining solid fraction by altering its chemical composition and increasing its relative lignin content. These modifications can affect key energy-related

properties such as higher heating value, fuel ratio, and combustion behavior, thereby enhancing its potential as a solid biofuel as seen before for olive tree pruning [15]. Evaluating the energy performance of both untreated and autohydrolyzed biomass is therefore essential for determining the feasibility of integrated valorization strategies.

The present study investigates the valorization of bay tree pruning residues through autohydrolysis, focusing on the chemical characterization of the raw biomass and the assessment of its energy potential. The effects of autohydrolysis on biomass composition and heating value are examined to provide insights into the suitability of this residue for biorefinery and bioenergy applications. By contributing new knowledge on the utilization of *Laurus nobilis* pruning biomass, this work supports the development of sustainable resource management practices and promotes the efficient exploitation of agricultural and forestry residues within a circular economy framework.

2. Materials and Methods

2.1. Material

Bay tree pruning residues were obtained from an agricultural holding in Viseu, located in central Portugal, after the seasonal harvesting period. The collected biomass included leaves and thin woody fractions, with branch diameters below 2 cm. After collection, the material was manually cleaned and separated to remove unsuitable fractions before size reduction.

The prepared biomass was milled using a Retsch SMI mill. (Retsch GmbH, Haan, Germany) The ground material was subsequently classified according to particle size using a Retsch AS200 sieve shaker (Retsch GmbH, Haan, Germany), operated for 20 min at 50 rpm. This procedure enabled the separation of four granulometric fractions: particles retained above 40 mesh, particles between 40 and 60 mesh, particles between 60 and 80 mesh, and particles passing through 80 mesh. The 40–60 mesh fraction, corresponding to particle sizes of 0.420–0.250 mm, was selected for the experimental work. Before chemical characterization, this fraction was dried at 105 °C for at least 24 h.

2.2. Autohydrolysis

Autohydrolysis assays were carried out in a 600 mL cylindrical glass reactor, model Parr LKT PED (Parr Instrument Company, Moline, IL, USA), equipped with double-wall insulation. In each experiment, 20 g of the selected 40–60 mesh biomass fraction was introduced into the reactor together with 200 mL of distilled water. The solid–liquid suspension was maintained under continuous agitation at 70 rpm to promote uniform contact between the biomass and the aqueous medium.

The influence of operating conditions on biomass solubilization was assessed by testing three temperatures, 140, 160 and 180 °C, combined with two reaction times, 15 and 30 min. These experimental conditions were defined to allow comparison with the liquefaction methodology previously reported [16]. Each condition was performed in duplicate. The heating period required for the reactor to reach the target internal temperature was approximately 10 min.

After each run, the treated suspension was filtered through a Buchner funnel fitted with filter paper, separating the liquid phase from the remaining solid fraction. The recovered solid residue was dried at 103 ± 2 °C until constant mass and subsequently weighed. The extent of solubilization was calculated from the mass loss of the solid fraction, according to Equation (1).

$$\text{Solubilization (\%)} = \frac{\text{Initial dry mass (g)} - \text{Solid dry residue (g)}}{\text{Initial dry mass (g)}} \times 100 \quad (1)$$

2.3. Chemical Composition of Solid Residues After Autohydrolysis

The chemical composition of the solid residues recovered after autohydrolysis was determined using established analytical methods. Lignin was quantified in extractive-free bay tree biomass by a modified Klason procedure involving two consecutive acid hydrolysis stages. Initially, the samples were treated with 72% H₂SO₄ at 30 °C for 1 h. This step was followed by hydrolysis with 3% H₂SO₄ in an autoclave at 1.2 bar for 1 h [17]. Acid-soluble lignin was determined by measuring the UV absorbance of the acid hydrolysate at 205 nm using a UV-Vis spectrophotometer, and calculated using an absorptivity coefficient of 110 L g⁻¹ cm⁻¹. Total lignin was obtained as the sum of acid-insoluble (Klason) lignin and acid-soluble lignin. Holocellulose was determined by the acid-chlorite method, which removes most of the lignin present in the lignocellulosic matrix. The α -cellulose content was measured in extractive-free material according to TAPPI 429 cm-23 [18]. Hemicellulose was calculated indirectly as the difference between holocellulose and α -cellulose contents.

2.4. Infrared Spectroscopy Analysis

The structural features of the untreated dried biomass and of the solid residues obtained after autohydrolysis were examined by Fourier-transform infrared spectroscopy with attenuated total reflectance, FTIR-ATR. Spectra were recorded using a Perkin Elmer UATR Spectrum Two spectrometer (Perkin Elmer, Bridgeport, CT, USA).

Before spectroscopic analysis, all samples were dried at 103 $\pm$ 2 °C for one week to minimize the influence of moisture on the spectra. Measurements were performed over the 4000–400 cm⁻¹ range, using a spectral resolution of 4.0 cm⁻¹ and 72 scans per spectrum. A background spectrum was collected before sample analysis using the clean ATR crystal. Each solid sample was then positioned on the crystal and pressed to ensure adequate and reproducible contact with the crystal surface. Three spectra were acquired for each sample and averaged. These measurements correspond to repeated spectral acquisitions of the same sample rather than independent autohydrolysis experiments.

The spectra were compared without mathematical post-treatment or band normalization. This procedure was adopted because ATR-FTIR allows reliable qualitative and semi-quantitative comparison when identical acquisition conditions and similar sample-crystal contact are maintained.

2.5. Liquefaction

Liquefaction experiments were performed using dried bay tree leaf and branch powder. The biomass was reacted in a glycerol–ethylene glycol solvent mixture, with sulfuric acid used as catalyst. The reaction was conducted under controlled temperature (180 °C) and stirring conditions. After completion, the reaction medium was cooled, dissolved in methanol and filtered, following the methodology previously described [16].

2.6. Heating Value

The higher heating value was determined using dried and homogenized biomass samples. The material was first dried at 105 °C and then ground to obtain a uniform powder. For calorimetric analysis, the powder was compressed at 4 tons for 10 s, producing pellets with approximately 1 cm diameter.

Each sample was analyzed in triplicate using a Parr 6400 calorimeter. The heat released during combustion was determined indirectly from the temperature increase in the water surrounding the combustion chamber. The higher heating value was then calculated based on the measured temperature variation and the heat capacity of water.

3. Results and Discussion

The chemical composition of bay branches (BBs) and bay leaves (BLs) was determined before [1]. Bay leaves contained higher amounts of ash (3.37 wt.%), dichloromethane extractives (3.05 wt.%), ethanol extractives (10.80 wt.%), and Klason lignin (25.47 wt.%) than bay branches, which contained 2.53 wt.% ash, 0.51 wt.% dichloromethane extractives, 4.91 wt.% ethanol extractives, and 20.47 wt.% lignin. In contrast, bay branches exhibited higher contents of α -cellulose (31.96 wt.%) and hemicelluloses (30.65 wt.%) compared with bay leaves (23.82 wt.% and 23.60 wt.%, respectively), while hot-water extractives were similar for both materials (8.97–9.89 wt.%). These results indicate that bay branches are richer in structural carbohydrates, whereas bay leaves contain higher levels of extractives, lignin, and mineral matter, which may influence their behavior during thermal treatment and subsequent valorization processes.

The solubilization yields obtained after autohydrolysis (Figure 1) increased with both temperature and residence time for bay branches and bay leaves, indicating a progressive dissolution of biomass components into the liquid phase as expected. This behavior is consistent with the initial chemical composition of the materials, where both fractions contained considerable amounts of hemicelluloses and extractives, which are known to be readily solubilized under hydrothermal conditions [12].

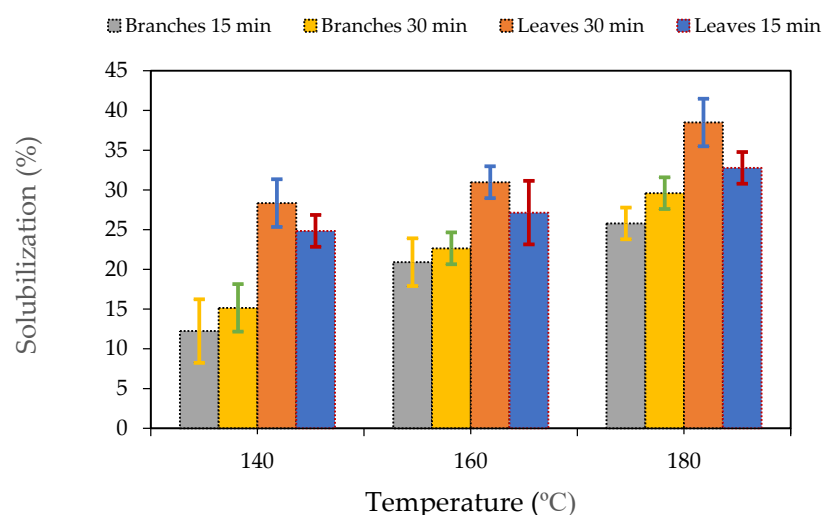


Figure 1. Solubilization percentage obtained during the autohydrolysis of bay leaves (BLs) and bay branches (BBs) as a function of treatment temperature and reaction time. Solubilization was calculated based on the mass loss relative to the initial dry biomass. Error bars represent the standard deviation of duplicate measurements.

Bay leaves exhibited consistently higher solubilization values than bay branches at all treatment conditions. At 140 °C, solubilization reached approximately 25–28% for leaves compared with 12–15% for branches, while at 180 °C it increased to about 33–38% and 26–30%, respectively. The greater susceptibility of leaves to autohydrolysis can be attributed to their higher content of extractives. Similar results were obtained before for Olive leaves with comparable solubilizations ranging between 30 and 40% [15]. The slightly higher solubilization percentage for olive leaves can be explained by the higher amount of extractives, around 42%, compared with bay laurel leaves with 24%. The abundant extractives present in leaves, particularly ethanol and dichloromethane-soluble compounds, are more easily removed during hydrothermal treatment, contributing to the higher overall mass loss. Similarly, in the autohydrolysis of hybrid poplar chips, as severity increased, the mass fraction of dissolved wood constituents was raised, with the dissolved mass fraction increasing by approximately 35% when the temperature went from 160 °C to 200 °C [19].

For both feedstocks, increasing the temperature from 140 to 180 °C resulted in a marked increase in solubilization, confirming that temperature is the main factor controlling biomass deconstruction. Higher temperatures promote the hydrolysis of acetyl groups and glycosidic bonds within hemicelluloses, leading to the formation of soluble oligosaccharides, monosaccharides, and degradation products [10,11]. However, because the liquid phase was not characterized, the composition of the solubilized fraction cannot be confirmed. This compositional analysis after hydrolysis, showed substantial reductions in hemicellulose content and a corresponding enrichment of lignin in the solid fraction (Figures 2 and 3).

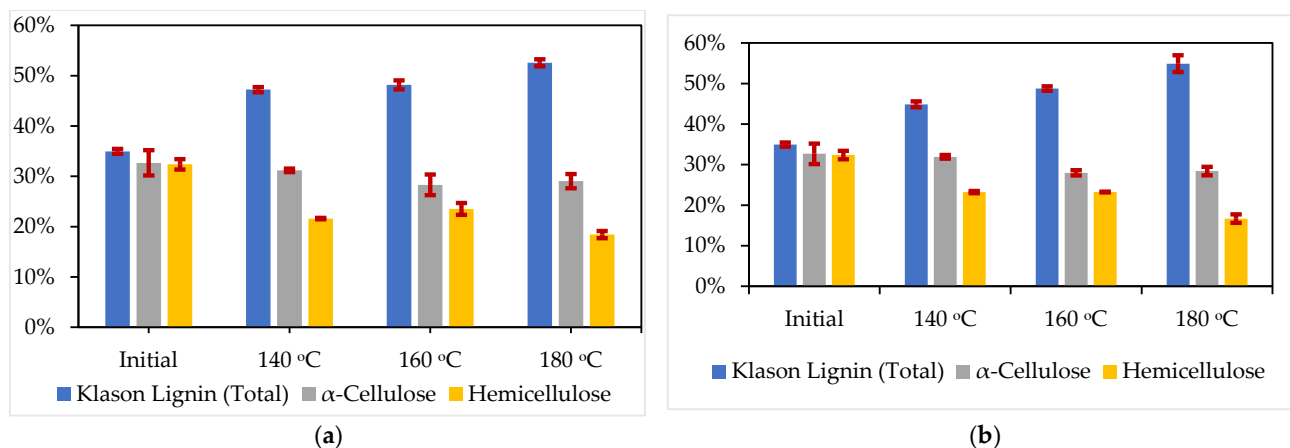


Figure 2. Chemical composition of bay leaves (BLs) after autohydrolysis for (a) 15 min; (b) 30 min. Results are expressed as the relative percentage of the quantified structural components. Error bars represent the standard deviation of triplicate measurements.

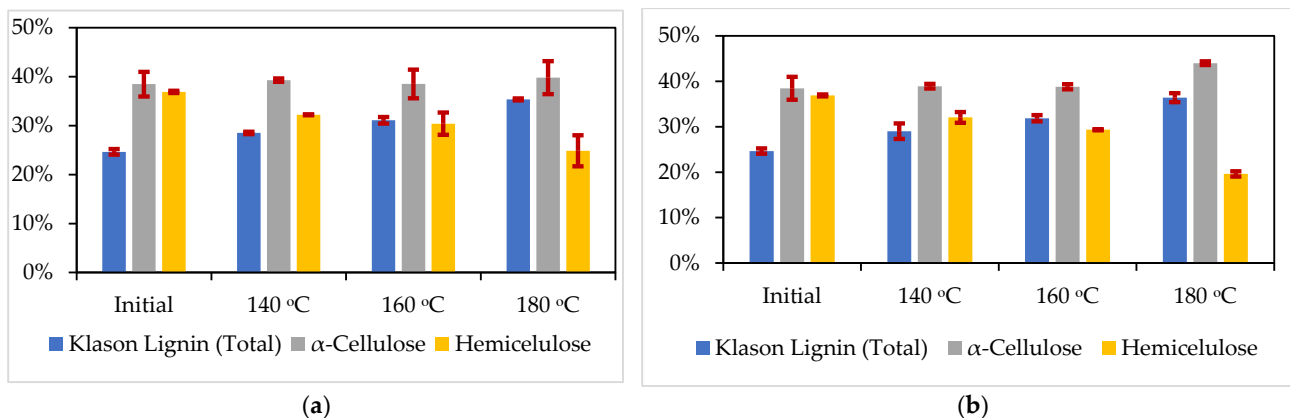


Figure 3. Chemical composition of bay branches (BBs) after autohydrolysis for (a) 15 min; (b) 30 min. Results are expressed as the relative percentage of the quantified structural components. Error bars represent the standard deviation of triplicate measurements.

Residence time also influenced solubilization, although its effect differed between the two materials. For bay branches, extending the treatment from 15 to 30 min increased solubilization at all temperatures, suggesting that prolonged exposure enhanced hemicellulose hydrolysis and dissolution. In contrast, bay leaves showed only a limited improvement with longer treatment times, particularly at 160 and 180 °C, indicating that most readily hydrolysable components had already been removed during the first 15 min.

These results agree with previous studies on lignocellulosic materials subjected to autohydrolysis, where the extent of biomass solubilization strongly depends on process severity. For instance, sweet cherry seeds reached a solubilization of 26.7% when treated

at 170 °C for 180 min [20]. Similarly, Romaní et al. [21] observed that the autohydrolysis of *Eucalyptus globulus* resulted in solid residue recoveries ranging from 18.2 to 27.6% as the severity factor increased from 3.35 to 3.94, reflecting the progressive degradation and solubilization of biomass components under harsher conditions.

Overall, the solubilization results, together with the compositional analysis of the solid residues, suggest preferential removal of the more accessible biomass fractions, particularly extractives and hemicelluloses. The higher solubilization observed for bay leaves reflects their greater extractive content, whereas the lower values for bay branches are consistent with their higher proportion of structural carbohydrates and more resistant woody matrix.

Figures 2 and 3 present the changes in the chemical composition of bay leaves and bay branches following autohydrolysis at 140, 160, and 180 °C for 15 and 30 min. The proportions of Klason lignin, α -cellulose, and hemicellulose were affected by increasing treatment temperature in both biomass fractions, although some differences between leaves and branches were observed. For both bay leaves and bay branches, Klason lignin content increased progressively with treatment temperature. In bay leaves, lignin increased from approximately 35% in the untreated material to about 53% at 180 °C (15 min) and 55% at 180 °C (30 min), while in bay branches it increased from approximately 25% to 35% and 36% at 180 °C, 15 and 30 min respectively.

The increase in lignin content is consistent with the preferential removal of polysaccharides from the solid fraction, particularly hemicellulose, during autohydrolysis as stated before [13]. Since lignin exhibits greater thermal stability than carbohydrate polymers under these conditions, its relative proportion in the residual solid fraction increases as treatment severity rises. The slightly higher lignin content observed in bay branches at 180 °C may be attributed to the inherently more lignified structure of woody tissues compared with leaves. Similar trends have been reported for a wide range of lignocellulosic biomasses subjected to autohydrolysis, where increasing treatment severity leads to an apparent enrichment of lignin in the solid residue. In *Pinus radiata*, treatments conducted at 150–190 °C for 30–90 min resulted in a progressive increase in lignin content as both temperature and reaction time increased [22]. Likewise, autohydrolysis of Scots pine (*Pinus sylvestris*) sapwood at temperatures ranging from 130 to 170 °C showed a comparable increase in the relative lignin proportion within the residual solids [23]. Consistent observations have also been reported for other agricultural and forest residues, including sweet cherry seeds [20], hazelnut shells [24], and pine nut shells [25]. This apparent increase in lignin content is mainly attributed to the preferential solubilization and removal of hemicellulosic components and other extractives, which enriches the lignin fraction in the remaining solid material, rather than indicating the formation of additional lignin.

A substantial decrease in hemicellulose content was observed in both biomass fractions. Hemicellulose in bay leaves decreased from approximately 32% to 18% (180 °C 15 min) and 17% (180 °C 30 min), whereas in bay branches it declined from approximately 37% to 25% and 20% for 15 and 30 min respectively as the temperature increased from ambient conditions to 180 °C. This pronounced reduction is consistent with that hemicellulose is the most thermally labile component of lignocellulosic biomass. Its amorphous structure and lower degree of polymerization make it particularly susceptible to hydrothermal degradation, hydrolysis, and dissolution. The results indicate that increasing autohydrolysis severity, through the combined effect of higher temperatures and longer reaction times, promoted the progressive degradation and solubilization of hemicellulosic components, which was reflected by a reduction in both the solid yield and residual hemicelluloses content. This behavior has been widely observed in lignocellulosic biomasses subjected to hydrothermal treatments. For example, in poplar wood chips, the xylan content decreased from 17.31% in untreated samples to 11.30% under the most severe processing conditions,

demonstrating the preferential hydrolysis and removal of hemicellulose fractions [26]. Likewise, Lobato-Rodríguez et al. [27] reported that the autohydrolysis of *Acacia dealbata* resulted in a substantial increase in hemicellulose solubilization, quantified as the release of xylan, arabinan, and acetyl substituents. A comparable trend was observed for *Robinia pseudoacacia* wood, where hemicellulose removal intensified with increasing temperature and residence time [28]. Specifically, treatment at 200 °C led to an increase in hemicellulose solubilization from 12% to 85% of the initial hemicellulose content when the reaction time was extended from 0 to 30 min. Similar trends are observed in wheat straw, where the hemicellulose content in the solid residue decreases from 27.06% to 0.74% as the treatment temperature increases [29]. These findings collectively confirm that autohydrolysis severity is a key factor controlling changes in the hemicellulose content of the solid fraction. Although the cleavage of glycosidic bonds and formation of soluble carbohydrates are expected during autohydrolysis, these products were not quantified in the present work. Cellulose is generally considered the most thermally stable structural polysaccharide during autohydrolysis, and numerous studies have reported its preferential retention in the solid fraction after treatment. For instance, Romání et al. [21] observed that the cellulose content of *Eucalyptus globulus* increased from 54.3% to 61.4% with increasing treatment severity, indicating an almost quantitative preservation of cellulose as the progressive removal of hemicelluloses enriched the solid residue. Similarly, Yang et al. [26] reported that the glucan content of poplar wood chips remained nearly unchanged or exhibited a slight increase during autohydrolysis. Lobato-Rodríguez et al. [27] also described a limited cellulose loss during the autohydrolysis of *Acacia dealbata*, with only a 1.87% reduction at the highest severity level.

Cellulose in bay laurel residues showed greater resistance to hydrothermal degradation compared with hemicellulose as expected. For bay laurel leaves, the α -cellulose content decreased from 33% in the untreated material to around 28% after autohydrolysis at 160 °C for both 15 and 30 min. Bay laurel branches exhibited an higher stability, with α -cellulose remaining close to 40% throughout the treatments and even increasing to 44% after treatment at 180 °C for 30 min, which can be attributed to the preferential solubilization of hemicelluloses and the consequent enrichment of cellulose in the residual solid. The extent of this enrichment is highly temperature-dependent. For example, in the autohydrolysis of castor plant pruning residues, the glucan content in the solid fraction rises from 37.08 g/100 gDWM at 160 °C to 50.28 g/100 gDWM at 200 °C [30]. This temperature dependence has been attributed to the autoionization of water, which generates hydronium ions whose concentration increases with temperature, thereby accelerating hydrolytic depolymerization [31].

Although there is a preservation of cellulose, during autohydrolysis, it undergoes partial depolymerization caused by chain scission, which occurs primarily within the reactive amorphous regions of the fiber [32,33]. As the severity of the autohydrolysis treatment increases, the hydrolysis reactions are accelerated because reaction rates increase with temperature according to the Arrhenius relationship. In addition, the increase in the ionic product of water at elevated temperatures, together with the release of acetic acid from acetylated hemicelluloses, enhances the acidic medium, promoting the cleavage of glycosidic bonds. Consequently, cellulose may undergo partial depolymerization at sufficiently severe conditions, although the extent depends on the treatment severity and biomass characteristics. The degree of polymerization of cellulose has been reported to reduce between 25 and 65% [29]. This degradation process follows a pattern where the amorphous cellulose fraction is hydrolyzed at lower temperatures, while the crystalline regions are more resistant, showing substantial cleavage only at temperatures at or above 180 °C [29]. The removal of amorphous components, principally hemicelluloses and amor-

phous cellulose, results in a measurable increase in cellulose crystallinity, typically reported in the range of 6–9% [29]. Consequently, the degree of polymerization tends to decrease until it reaches a stable value known as the leveling-off degree of polymerization [33]. The chemical degradation involves pathways such as dehydration, decarboxylation, and demethanation, active between 100 °C and 300 °C [34]. The degradation of cellulose also depends on the degree of crystallinity since kinetic analyses indicate that microcrystalline cellulose, exhibits different resistance to hydrolysis compared to alpha-cellulose [35].

Overall, the results demonstrate that thermal treatment modifies the composition of both bay laurel leaves and branches, resulting in a solid residue enriched in cellulose and lignin and depleted in hemicellulose. These compositional changes are consistent with preferential removal of hemicellulosic components during autohydrolysis, although the composition of the solubilized liquid fraction was not determined in this study. The compositional changes become more pronounced as temperature increases, with 180 °C producing the highest lignin enrichment and greatest hemicellulose removal. These findings indicate that temperature is a critical parameter for modifying the chemical composition of bay biomass and may be exploited to tailor feedstocks for biofuel production, biorefinery applications, lignin valorization, and the manufacture of lignocellulosic materials.

The FTIR spectra of bay laurel leaves and branches subjected to autohydrolysis for 30 min at different temperatures (Figure 4) indicate that the main structural features of the lignocellulosic matrix were largely preserved after treatment. However, variations in the relative intensity of some absorption bands suggest chemical modifications induced by increasing autohydrolysis severity.

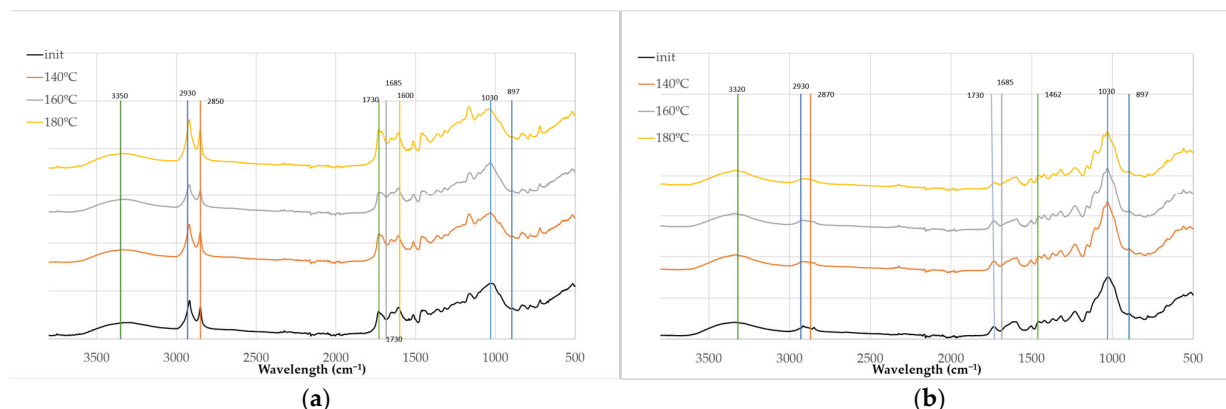


Figure 4. FTIR spectra obtained after 30 min autohydrolysis at different temperatures: (a) initial bay leaf material and solid residues; (b) initial bay branches material and solid residues.

In the high-wavenumber region (3700–3000 cm^{-1}), both materials exhibit a broad absorption band centered at approximately 3350–3320 cm^{-1} , attributed to O–H stretching vibrations of hydroxyl groups present in cellulose, hemicellulose, and phenolic compounds. No substantial changes were observed in this region following autohydrolysis.

For bay laurel leaves (Figure 4a), some variations were detected in the absorption bands around 2930 and 2850 cm^{-1} , corresponding to the asymmetric and symmetric stretching vibrations of aliphatic C–H bonds in $-\text{CH}_2$ and $-\text{CH}_3$ groups, as well as in the bands at approximately 1730 cm^{-1} , C=O stretching vibrations of unconjugated carbonyl groups and 1160 cm^{-1} , asymmetric C–O–C stretching vibrations of glycosidic linkages in polysaccharides. However, these changes did not show a clear trend with increasing treatment temperature, suggesting that autohydrolysis did not induce consistent modifications in these functional groups.

In the FTIR spectra of bay laurel branches (Figure 4b), the main variation observed was a slight increase in the absorption band around 1030 cm^{-1} at higher treatment temperatures. This band is associated with C–O stretching vibrations of cellulose and hemicellulosic polysaccharides and may indicate changes in the relative contribution or accessibility of these polysaccharide structures following autohydrolysis.

Overall, the FTIR results indicate that autohydrolysis did not affect the solid material of both leaves and branches.

The higher heating values (HHVs) obtained for the solid residue of bay laurel leaves and branches after liquefaction and autohydrolysis reveal noteworthy differences between both thermochemical treatments and between the two biomass fractions (Table 1). Overall, liquefaction led to a substantial increase in the energy density of the resulting solid residue compared with autohydrolysis, with the highest HHVs achieved under the most severe liquefaction conditions ($180\text{ }^{\circ}\text{C}$ for 30 min).

Table 1. HHV of the solid residues after liquefaction and autohydrolysis of bay branches and bay leaves.

Bay Tree	Temp. ($^{\circ}\text{C}$)	Time (Min)	Liquefaction		Autohydrolysis	
			HHV (MJ/kg)	Std Dev	HHV (MJ/kg)	Std. Dev.
Branches	$180\text{ }^{\circ}\text{C}$	15'	24.64797	0.90899	19.39205	0.31285
Branches	$180\text{ }^{\circ}\text{C}$	30'	29.45590	1.20228	19.34650	0.12180
Leaves	$180\text{ }^{\circ}\text{C}$	15'	25.35830	0.36500	22.04950	0.20060
Leaves	$180\text{ }^{\circ}\text{C}$	30'	30.08274	0.52765	22.83605	0.04475

For both bay laurel leaves and branches, increasing the liquefaction residence time from 15 to 30 min resulted in a marked improvement in HHV in the solid residue. In branches, the HHV increased from 24.65 MJ kg^{-1} after 15 min to 29.46 MJ kg^{-1} after 30 min, corresponding to an increase of approximately 19.5%. A similar trend was observed for leaves, where the HHV increased from 25.36 MJ kg^{-1} to 30.08 MJ kg^{-1} when the treatment time was extended from 15 to 30 min. These values are considerably higher than those typically observed for untreated lignocellulosic materials, indicating that liquefaction promotes the formation of an energy-rich solid fraction. This increase in HHV can be attributed to dehydration, decarboxylation, and depolymerization–repolymerization reactions that reduce the oxygen content of the biomass and promote the formation of more carbon-rich structures, thereby increasing its calorific value.

The highest HHVs were recorded for the liquefied solids obtained after 30 min at $180\text{ }^{\circ}\text{C}$, reaching 30.08 MJ kg^{-1} for leaves and 29.46 MJ kg^{-1} for branches. The slightly higher HHV of the leaf-derived product may be associated with the naturally higher content of extractives, lipids, and aromatic compounds, including essential oils and other secondary metabolites, which contribute positively to the fuel energy content.

In contrast, autohydrolysis caused only minor variations in HHV with increasing residence time. For bay branches, the HHV remained almost unchanged, with values of 19.39 MJ kg^{-1} and 19.35 MJ kg^{-1} after 15 and 30 min, respectively, indicating that the removal of hemicelluloses and other soluble components did not meaningfully alter the energy density of the remaining solid. A slight increase was observed for bay leaves, where the HHV increased from 22.05 MJ kg^{-1} at 15 min to 22.84 MJ kg^{-1} at 30 min, suggesting a moderate enrichment of energy-rich components such as lignin and extractives following the solubilization of more oxygenated carbohydrate fractions.

The increase in HHV after autohydrolysis is generally associated with the selective removal of hemicellulose, which occurs through hydrolysis catalyzed by hydronium ions generated from water autoionization and from acetic acid released during hemicellulose

deacetylation. As a result, hemicellulosic oligosaccharides and monosaccharides are transferred to the liquid phase, whereas cellulose and most lignin remain in the solid fraction, leading to a relative enrichment of lignin, and consequently, a higher energy density [10,11]. Since lignin possesses the highest calorific value among the major lignocellulosic constituents, followed by cellulose and hemicellulose, an increase in its relative concentration generally results in higher HHVs [36]. Pontes et al. [37] further demonstrated a linear relationship between HHV and lignin content, reporting that hardwoods and softwoods, which are typically richer in lignin, exhibit higher HHVs than non-woody biomass. The present observations are consistent with previous studies reporting energy densification of lignocellulosic solids after hydrothermal and acid-based pretreatments. Pontes et al. [37] reported that autohydrolysis of forest and marginal-land biomass mixtures increased the HHV from approximately 17.2 MJ kg^{-1} in the untreated materials to maximum values of $20.4\text{--}20.5 \text{ MJ kg}^{-1}$ after pretreatment. Similar behavior was observed for softwood chips, where the HHV increased from 17.9 to 20.5 MJ kg^{-1} following autohydrolysis [37]. Likewise, Cuevas-Aranda et al. [38] reported an increase in the HHV of water-insoluble solids derived from acid-pretreated almond pruning from 20.77 MJ kg^{-1} at low pretreatment severity to 21.99 MJ kg^{-1} at the highest severity level. Cuvilas and Yang [39] also demonstrated that hydrothermal treatment of spruce at 180°C increased the HHV and improved ash quality, although excessive pretreatment severity led to reductions in mass and energy yields. Palma et al. [40] established a strong positive correlation between gross calorific value and the extent of hemicellulose removal during acid hydrolysis, attributing this effect to the concentration of the more energy-rich cellulose and lignin fractions in the residual solid.

Overall, these results demonstrate that liquefaction increased more the heating value of the solid residue than autohydrolysis of Bay laurel biomass, especially at longer residence times. Nevertheless, while autohydrolysis mainly promotes the selective removal of hemicellulosic components with limited changes in calorific value, its use as a pretreatment shows high potential in a biorefinery approach.

4. Conclusions

The present study demonstrated that bay laurel leaves and branches exhibit distinct responses to thermochemical processing due to their different initial chemical compositions. Bay leaves, characterized by higher contents of extractives and lignin, were more susceptible to autohydrolysis and exhibited greater solubilization yields than branches, which contained higher proportions of structural carbohydrates and a more resistant lignocellulosic matrix.

Autohydrolysis effectively promoted the fractionation of both biomass fractions, with temperature having a more pronounced effect than residence time. Increasing treatment severity enhanced the removal of hemicellulosic components and soluble compounds, leading to a progressive enrichment of lignin and, in the case of branches, an apparent increase in cellulose content due to the preferential dissolution of less stable biomass constituents. FTIR analysis confirmed that, despite these compositional changes, the fundamental structure of the lignocellulosic matrix was largely preserved after treatment.

The energy properties of the solid residues strongly depended on the thermochemical route applied. While autohydrolysis caused only minor improvements in HHV due to its selective extraction of hemicellulose and other soluble fractions, liquefaction produced carbon-rich solids with substantially improved energy densities. As the initial HHV of the raw biomass was not determined, no direct comparison between the untreated and liquefied materials could be made. Nevertheless, the highest HHVs measured for the liquefied products were 30.08 MJ kg^{-1} for leaves and 29.46 MJ kg^{-1} for branches,

both obtained at 180 °C for 30 min. Overall, the results indicate that autohydrolysis is a suitable pretreatment for bay laurel pruning residues, promoting the preferential solubilization of hemicellulosic components and yielding lignin-enriched solid residues. These findings support the potential application of autohydrolysis as a pretreatment step within an integrated biorefinery approach.

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