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Study of the Potential Uses of Hydrochar from Grape Pomace and Walnut Shells Generated from Hydrothermal Carbonization as an Alternative for the Revalorization of Agri-Waste in Chile

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Abstract: A myriad of resources and efforts have been devoted to assessing the possibilities of using locally sourced biomass to produce energy, reduce CO_2 emissions, and, in turn, lower dependance on petroleum. Grape pomace (GP) and walnut shells (WS) are organic waste generated in Chile. Within the last decade, the potential benefits and application of biomass have received significant attention, both in terms of producing functionalized carbon materials, and the various potential applications in the field of energy storage and environmental protection. The proposed research motivation is on the development of carbonous materials through thermal decomposition processes. Few researchers have addressed the idea of developing a multipurpose carbonaceous matrix from hydrochar, and there remains a need for an efficient method to obtain hydrochar specially from grape pomace. Hence, the general objective of this research is to study the potential of grape pomace and walnut shells treated with hydrothermal carbonization (HTC) as an alternative low-cost and efficient carbonous matrix. Proximate and elemental analysis was determined to distinguish the nature of the feedstock along with the hydrochar produced. Yield and reaction severity were also studied to study the impacts of temperature and residence time for both feedstocks. Successful results from the proposed work have broad applications for increasing the sustainability biomass applications, contributing to a positive economic impact.

Keywords: grape pomace; walnut shells; hydrothermal carbonization (HTC); thermogravimetric analysis (TGA); hydrochar

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1. Introduction

The acceleration of climate change in recent decades is the result of the increase in GHGs, produced specifically by the excess use of fossil fuels [1–3]. Chile is a country highly vulnerable to the impacts generated by climate change, hence Chile's proactive stance and commitment to GHG mitigation. One of the most relevant initiatives taken at the national level is the incentive for the use of non-conventional renewable energy (NCRE), which requires that by 2025, 20% of energy generated comes from these sources [4]. It should be noted that Chile has a varied geographical distribution of these resources, which provides a natural wealth that can be used by NCRE in all its areas [5].

The motivation for this research lies in the exploration for potential uses of the residues produced from grape pomace and walnut shells, two of Chile's important NCRE resources. Through thermochemical conversion and hydrothermal carbonization (HTC), grape pomace and walnut shells become hydrochar, which has several uses, such as soil amendment, energy as pellets, or low-cost adsorbents [6–20].

Because of their improved process efficiency, flexibility, faster conversion rate, selectivity, and alternate market for byproducts, thermochemical conversion methods are commercially appealing. The use of lignocellulosic biomass poses many challenges for thermochemical conversion due its inherent high moisture content, low energy content, and inconsistencies between volume and density [21–23]. Hydrothermal conversion is a hybrid method consisting of physical and chemical pretreatment processes performed in aqueous conditions. Successful products of this method include steam explosion, autohydrolysis, liquid hot water, and subcritical water hydrolysis [21].

The repurposing and valorization of grape pomace and walnut shells is directly beneficial to the environment as it reduces feedstock waste. One of the proposed treatment of GP and WS is through what is called as circular bioeconomy (CBE) system; this approach provides promising opportunities through the optimization and repurposing of biomass waste and residual materials [24–26].

Chile's silvoagricultural industry is well-known: cattle, agriculture, and forestry account for roughly 2.9% of the country's GDP [27]. These sectors generate significant quantities of organic waste from the production and exportation of agricultural and forestry feedstocks [28], most of which is disposed of or sent to landfill [29]. The use of agricultural waste for energy is low; in 2014, eight biogas plants with a total installed capacity of 42 MWe generated 0.4% of Chile's electricity supply. Two landfills in Santiago, Chile's metropolitan region, create 83% of the country's biogas, while wastewater treatment plants produce 15%, and manure and organic waste produce 3% [30]. However, biomass electricity, which is mostly driven by forest inputs, accounts for over 2% of the country's total installed capacity, with over 500 MWe [31]. Increased use of waste-to-energy products could help to achieve climate change goals, waste reduction, increased energy security, resource efficiency, and reduced air pollution.

Chile's well-known mining makes up 13% of the nation's GDP [32]. From this industry, great economic benefit is bestowed upon mining communities, but the dangers of this industry are perhaps even greater. The industry is the culprit behind intensive consumption of oil and water, emission of particulate materials, and the generation of polluting effluents with high content of heavy metals and metalloids, all of which are harmful to the population, and require treatment or mitigation strategies [32,33]. It is estimated that globally, there are approximately 3500 active deposits of mining waste, which consist of rock and tailing dumps [32,34]. The increasing demand for essential metals, the decrease in ore grades, and the extraction of complex ore bodies have resulted in larger quantities of loss that require immediate mitigation strategies [32,35,36].

Hydrothermal carbonization (HTC), also known as wet torrefaction or wet pyrolysis, is the decomposition process of organic matter occurring in liquid water, generally in the temperature range of 180–250 °C. The water is at ambient temperature and the pressure in the system is autogenous. This process simulates the natural formation of coal on a laboratory scale [35,36]. The HTC process relies on the ability of water to break down ions from other molecules. The hydroxide anions (HO^-) and hydrogen cations (H^+) are separated from the organic molecules, forming water, while said molecules that have been dehydrated combine to form carbon that, later, will be transformed into hydrochar, similar to the way in which carbon undergoes its natural process [36].

Several studies have been conducted related to the waste generated by the wine industry [37–41], along with numerous studies describing the potential of walnut shells [42–48]. More specifically, walnut shell and grape pomace have received great attention regarding HTC processing to study a myriad of variables, such as residence time, temperature, and biomass-water ratio, obtaining results that help to determine the potential use that can be given to the waste, being reused, and preventing it from being considered solely as a waste but as a bioresource [14,16,49–59].

When organic waste is carbonized via hydrothermal carbonization (HTC), it produces interesting carbonaceous powder materials with the required properties to varying degrees, depending on the carbonization parameters and conditions. Carbon characteristics can be

precisely tuned to the required application, adjusting the temperature or reaction time of the carbonization process. As a result, biomass carbonization is a fascinating and promising process for producing environmentally friendly and bio-based materials for use in energy storage, low-cost adsorbent, and conversion technologies, as well as a powerful tool for converting organic waste streams into value-added products in the bioeconomy [60].

Consequently, this study covers a knowledge deficit by providing an up-to-date characterization of organic waste in Chile, as well as an estimate of the resource potential. Furthermore, this research examines the possibility for hydrochar production from these organic wastes in order to identify hurdles to improve bioresources usage.

2. Materials and Methods

Grape pomace was collected from Undurraga vineyard, located in Talagante, Región Metropolitana, Chile. The samples, residual pomace from the vinification process, were processed for storage. Samples were then dried at 60 °C for 48 h to remove moisture. Walnut shells were collected from San Alfonso, Cajón del Maipo, Región Metropolitana, Chile. The samples were collected from the 2018 walnut harvest process. Samples were then dried at 105 °C for 24 h to remove moisture content. Finally, all samples were carefully stored to prevent decomposition. For analytical studies, all samples were ground and then sifted to obtain samples with particle size less than 50 mesh (500 µm).

2.1. Characterization of Biomass Samples

Samples were characterized by their proximate analysis, ultimate analysis, and HHV and IR spectra. Proximate analysis was obtained using a thermogravimetric analyzer (TGA) from TA Instrument (Model TGA 5500). For each experiment, sample material was heated to 105 °C, and then to 500 °C at a heating rate of 10 °C min^{-1} under inert atmosphere, to determine the moisture and volatile matter content, respectively. After the weight equilibrium was reached, air was introduced to the reactor, and the temperature was raised to 800 °C at 10 °C min^{-1} to burn off the remaining carbon material in order to determine the amount of fixed carbon and inorganic matters. Proximate analysis was done using the same procedure as described in prior research studies [61–65]. Ultimate analysis was obtained using the Parikh, J. et al. correlation [66], along with HHV [67].

2.2. HTC Process

In this study, the hydrothermal process was carried out using three stainless steel 50 mL HTC reactors. Each HTC reactor contained a polypropylene (PPL) liner that ensured homogeneous conditions inside the reactor. PPL liners were selected based on their capability to withstand temperatures below 280 °C and pressure up to 3 MPa.

In a typical experiment, dried and ground biomass (grape pomace or walnut shells) and distilled water were poured into the liners, based on the biomass/water ratio presented in Table 1. Once the biomass/water mixture was inside the reactor, the reactor was sealed, to later be placed in a muffle furnace at the desired reaction temperature [16,68–70]. The biomass/water ratio along with the selected reaction temperatures are presented in Table 1.

Table 1. Selected HTC reaction parameters.

Feedstock	Biomass: Water Ratio	HTC Reaction Temperatures	HTC Reaction Residence Time (hrs)
Grape pomace (GP) Walnut shells (WS)	5:1	180 °C	1
		200 °C	1
		200 °C	2

Once the HTC process was completed and cooled down, the reactors were opened, and the polypropylene (PPL) liners were removed. Subsequently, the HTC products were filtered. The hydrochar obtained was then dried out and stored.

Hydrothermal severity is used to evaluate biomass degradation and conversion to understand the effect of residence time and temperature [18]. The hydrothermal process is commonly thought of as a way to prepare lignocellulosic biomass for enzymatic reactions, nutrient recovery, and/or other uses [71]. Based on the equation derived by Overend et al., hydrothermal severity (R_0) is a function of the combined influence of processing temperature and residence time [72]. Where T is temperature in Celsius, t is time in minutes, then R is a mixed severity factor, represented in Equation (2) [73].

$$R_0 = t \times \exp\left[\frac{(T - 100)}{14.75}\right] \tag{1}$$

$$R = log(R_0) - pH \tag{2}$$

3. Results and Discussion

3.1. Biomass Characterization

From a physicochemical perspective, the results obtained from this study were thoroughly analyzed. The resulting data from the analytical instruments and related correlations were substantiated through a comparison to existing literature.

As previously stated, the initial step in the research was to conduct a compositional analysis to discover the key organic and elemental components. Table 2 shows the composition of the major organics and elemental components of GP and WS, as well as the standard deviation for all the samples examined.

Table 2. Grape pomace (GP) and walnut shell (WS) physicochemical characterization.

	Grape Pomace (GP)	**Walnut Shells (WS)**
	Proximate Analysis	
Volatile Matter (VM)	64.62% ± 0.29%	71.36% ± 0.98%
Fixed Carbon (FC)	25.29% ± 0.22%	4.97% ± 0.23%
Ash content (AC)	10.09% ± 0.12%	23.67% ± 1.21%
	Elemental Analysis	
C (wt.%)	45.51% ± 0.06%	35.63% ± 0.59%
H (wt.%)	5.32% ± 0.01%	4.68% ± 0.07%
O (wt.%)	38.45% ± 0.08%	35.48% ± 0.54%
N (wt.%)	0.63% ± 0.001%	0.53% ± 0.01%
HHV (MJ/kg)	18.94% ± 0.04%	12.70% ± 0.24%

3.2. HTC Yield and Hydrochar Characterization

The proximate and elemental analysis of hydrochar is required to ensure that it is used efficiently as a fuel [73]. Figure 1 shows the proximate analysis composition of hydrochar products, varying depending on the reaction temperature and residence time for each biomass studied. The increase of residence time significantly reduces the ash content to approximately 2–3%, compared to the 10% for GP and 23% for WS. It is worth noting that, overall, hydrochar has a higher fixed carbon content, showing a minimal increase while we increase reaction temperature and residence time.

The subcritical conditions developed during the HTC process boosted high H^+ concentration, providing an excellent medium for the acid-catalyzed reaction of organic compounds without added acid [73–75]. During the HTC process, the water contained in biomass and supplied to the process was observed to be an outstanding solvent and reaction medium. However, the conditions were somewhat controlled due to the low temperatures. Figure 1 shows how the HTC process affects both feedstocks, considering their inherent differences. As stated in literature, temperatures of 200 °C showed limited degradation of cellulose, leading to a partial pyrolysis-like process [76], which can be the cause of minimal changes in volatiles and fixed carbon for both studied biomass.

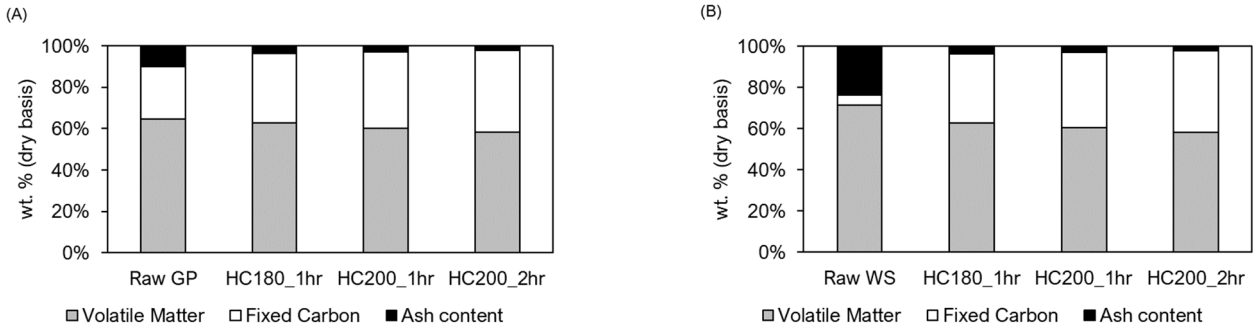

Figure 1. Hydrochar physicochemical characterization. (**A**) GP hydrochar; (**B**) WS hydrochar.

HTC modified the elemental make-up of hydrochar marginally, most notably the H/C and O/C ratios, which may have confirmed the carbonization degree of the hydrochar. Furthermore, the mass loss is highly dependent on the severity of the reaction and the biomass composition [57,73]. Table 3 displays the elemental composition of hydrochar.

Table 3. Hydrochar elemental composition and HHV. (A) Grape pomace hydrochar; (B) walnut shells hydrochar.

Biomass	Temperature (°C)	Residence Time (min)	%C	%H	%O	%N	HHV (MJ/kg)
Grape pomace	180	60	49.96	5.64	40.09	0.68	21.64
	200	60	50.82	5.65	39.86	0.68	22.36
	200	120	51.70	5.67	39.78	0.68	23.04
Walnut shells	180	60	35.47	4.65	35.18	0.53	12.7
	200	60	36.22	4.77	36.21	0.54	22.36
	200	120	35.61	4.68	35.44	0.53	23.04

Due to its strong hydrophobicity and homogenous qualities, solid residue from the HTC process is considered the primary product of the process, and can be easily separated from the suspension [73,77]. Previous research has shown that the generation of secondary hydrochar from lignocellulosic materials is highly dependent on residence time, as dissolved monomers necessitate substantial polymerization [73]. On the contrary, non-dissolved monomers may have an increased dependence on temperature. Controlling the residence time, it was thought, would affect the degree of polymerization of the soluble monomers during HTC, allowing for a pyrolysis-like process. For this study, there was a slight decrease of O/C and H/C for GP, while WS remained almost constant; these results are in line with the coalification process taking place during the HTC reaction [78,79].

The H/C and O/C ratios are critical for determining the degree of de-oxygenation and aromatic content during hydrothermal decomposition, as previously indicated.

Residence time is an important component in the production of hydrochar, and it is directly connected to the severity of the reaction. Hydrochar content was high when residence time was low, and decreased as residence time grew, according to the literature [73]. The hydrothermal severity and hydrochar output for this study are shown in Table 4.

Table 4. Hydrothermal severity and hydrochar yield.

Biomass	Temperature (°C)	Residence Time (min)	Severity Log(R_0)	Hydrochar Yield %	H/C Ratio	O/C Ratio
Grape pomace	180	60	7.35	85.23% ± 7.11%	1.354	0.602
	200	60	18.45	88.50% ± 8.09%	1.333	0.588
	200	120	11.13	67.22% ± 2.61%	1.316	0.577
Walnut shells	180	60	ND	89.32% ± 9.19%	1.573	0.744
	200	60	ND	93.10% ± 0.25%	1.582	0.750
	200	120	ND	88.89% ± 0.18%	1.577	0.747

ND: not determined.

Due to the hydrolysis and degradation of hemicellulose and cellulose in biomass, high hydrothermal severity usually results in a low hydrochar yield, as shown in Table 3, and this is consistent with the literature [73,80]. Since degradation or inhibitor development can occur when hydrochar is used for additional enzymatic hydrolysis, and the liquid product is utilized to recover nutrients such as xylose and glucose, hydrothermal severity should be regulated [73,80–82]. Typically, for the comparison of raw biomass with hydrochar, the H/C and O/C ratios are evaluated using a Van Krevelen diagram, but there was no need for this analysis, due to the lack of alterations in the data. The slight changes of H/C and O/C ratios were presented only in GP. Although lignocellulose-rich hydrochar showed a higher degree of coalification than process-derived hydrochar, the residence time and reaction temperatures may not have changed WS, and this is a strong indication that natural composition plays a key role during HTC [73]. Table 5 provides an overall schematic assessment of comparative studies done with the same feedstocks utilized under similar operative conditions.

Table 5. Overall comparative studies—proximate and elemental analysis. HC (hydrochar).

Sample Biomass		HTC		Proximate Analysis			Elemental Analysis				pH *	Ref.
		Temp. (°C)	Time (min)	VM (%)	FC (%)	AC (%)	N (%)	C (%)	H (%)	O (%)		
Grape pomace	Raw GP	-	-	67	33	5.1	1.8	54.0	5.8	38.4	-	[60]
	HC	220	120	53	47	1.5	1.7	65.4	5.4	27.5	4.1	
	HC	240	60	50	50	1.7	2	67.9	5.4	24.7	4.4	
Walnut shells	Raw WS	-	-	-	-	-	1.5	47.6	6.0	46.3	-	[81–83]

* pH Process water.

3.3. Practical Implications of This Study

Successful results from the development of future work have broad applications for increasing the sustainability biomass applications, contributing to a positive economic impact. The preliminary data obtained can be used to offer a better management of organic wastes, and evaluate the overall techno-economic and environmental benefits gained from the commercialization of the proposed technology. Novel aspect included are: understanding of locally available waste biomass studied; appropriate technology selection for the specific feedstocks; combined functionalization and surface improvement promoting in-situ hydrochar porosity; and the target of chemicals of environmental concern, making this proposal a feasible and sustainable alternative for the utilization of solid organic residue with a higher added value as biomaterials.

4. Conclusions

In this study, temperature and reaction time were studied to determine the potential of GP and WS for hydrochar formation. Detailed physicochemical analysis, including proximate and elemental analysis, were examined. The HTC process was studied using two distinctive biomass feedstocks, walnut shells (representing lignocellulosic biomass) and grape pomace (representing processed biomass), which were investigated for a single biomass to water ratio, as well as different temperatures and residence time.

Temperature and residence time controlled the severity of the reaction, as well as the hydrochar yield. However, there is still work to be done in order to increase the de-oxygenation of the biomass to create a carbon-rich hydrochar.

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