

## Article

# Quality of Hydrochar from Wine Sludge under Variable Conditions of Hydrothermal Carbonization: The Case of Lesvos Island

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**Abstract:** Lesvos island has several food and beverage production industries and the valorization of their waste has been an unexplored task. The focus of this study is the valorization of wine sludge which is a very interesting waste stream due to the high phenolic content. This study identified all the operating wineries on the island and sampled local wine sludge. Hydrothermal carbonization (HTC) was utilized for the valorization of wine sludge and the production of hydrochar and liquid HTC liquor. The experiments had a residence time of 24 h and were performed at 200 °C. Except the uniqueness of wine sludge as a utilized material, this study performed HTC under different pressure regimes that were developed by different filling percentages of the reactor, i.e., 24–48%. The different pressure regimes influenced the measured parameters of both the liquid and the solid products of HTC. The Chemical Oxygen Demand (COD) ranged between 230 and 280 g/L with the maximum reduction was observed at a filling percentage of 32%. At the same time, lower filling percentages favored the total phenolic content (max value: 21 g/L) and higher filling percentages favored the Higher Heating Value (HHV) of the hydrochar (max value: 20.36 MJ/Kg) and the produced mass yield of hydrochar (max value: 234.3 mg). For all cases, low pH values were measured on the liquid fraction and this can be attributed to the presence of organic acids. Future work will focus on the characterization of the specific phenolic content of the liquid fraction.

**Keywords:** hydrochar; biowaste; thermochemical treatment; winery waste



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## 1. Introduction

Wine production is one of the most commercially prosperous biotechnological processes [1]. The large wine industries cover the greatest demand, although there are several small and medium-sized enterprises that also produce a significant part of the total wine production. In 2020, the global area under vines corresponding to the total area planted with vines for all purposes (wine and juices, table grapes, and raisins), including young vines that have not yet been produced, is estimated at 7.3 mha. World wine production, excluding juices and musts, in 2020 is estimated at 260 mhl, marking a slight increase of almost 3 mhl (+1%), compared to 2019. Overall, after two consecutive volatile years 2017 and 2018, 2020 is in line with the world level of wine production of 2019 which can be defined as slightly below average. Italy (49.1 mhl), France (46.6 mhl), and Spain (40.7 mhl), which together account for 53% of world wine production in 2020, saw a sharp increase in their wine production compared to 2019. Volume production in these three countries increased by 1.5 mhl (+3%), 4.4 mhl (+1%), and 7.0 mhl (+21%), respectively, compared to 2019. On the other hand, except for Germany which also had slightly increased wine

production in 2020 (8.4 mhl, +2%/2019), all other major wine producing countries in the EU recorded a decrease compared to 2019. In 2020, the production levels were: Portugal (6.4 mhl, −2%/2019), Romania (3.6 mhl, −7/2019), Austria (2.4 mhl, −3%/2019), Hungary (2.4 mhl, −12%/2019), and in Greece (2.3 mhl, −6%/2019). Global wine consumption in 2020 is estimated at 234 mhl, a decrease of 3% compared to 2019 [2].

Wine production is a natural process that requires minimal human intervention, but that each winemaker guides through different techniques. There are five basic stages: harvesting, crushing and pressing, fermentation, clarification, maturation and bottling. A very important part in the first stages of processing the grapes is the squeezing of the horns after the removal of the grapes. Good handling is required to obtain the so-called must, e.g., the liquid resulting from the squeezing and compression of grapes, consisting of organic and inorganic substances in terms of its composition. The first part of the produced must is moved to fermentation tanks. The resulting marcs still have a significant percentage of must, for the extraction of which the press is used [3]. Alcoholic fermentation is a critical part of the wine quality process and requires proper management to produce high quality wine. Fermentation takes place in tanks with the help of enzymes from sugar fungi, where the must is converted into wine. More specifically, in these tanks, the sugars of the must are converted into alcohol, with the temperature of the grape juice increasing due to the release of energy from the doughs. The appropriate temperature for the fermentation of the must is 25–30 °C. In many cases, the wine production units do not have the ability to ferment all the available must and for this reason they store the excess. To do this, the sulfation step of the must is applied to protect it from bacterial infections. The unleavened must is concentrated so that it can be stored more easily for future use. The wine sludge that results from the alcoholic fermentation consisting of grape and grapefruit residues needs to be removed by transfusion of the wine to avoid contamination. The production of organic waste is an inevitable result of the winemaking process. In addition, waste streams include marigolds, marigolds—along with the previously mentioned—wine sludge, and dehydrated sludge and are responsible for the production of strong odors [4]. As for the inorganic waste produced, these include heavy and bulky packaging materials, used containers, as well as pallets that are broken or not used [4]. Among the various waste flows from the wine making processes, wine sludge is the focus of this present study.

Studies have shown that techniques such as pyrolysis are an alternative that can be used to treat solid biomass waste from waste from wineries, mills, and citrus fruits. The study of Torres et al. [5] on quince biological waste showed that after pyrolysis of samples, bioproducts and biofuels such as biogas or bio-oil were produced with fossil fuel equivalent volume (FFEV) in a range of prices between 550 and 700 L of fossil fuel per cubic meter of biomass. Sette et al. [6] applied the processes of pyrolysis and gasification of apple and grape residues and came to the conclusion that due to the low content of sulfur and nitrogen that they have can be used for energy fuel and production of activated carbons as well as soil conditioner due to the stability of biochar that they produce, but due to the high moisture content of most food waste streams. Hydrothermal carbonation (HTC) is an interesting thermochemical alternative. It is defined as a thermochemical process that uses high pressures and intermediate temperatures to convert biomass into primarily hydrochar, i.e., a material with properties similar to low to medium grade carbon. Its mechanisms are related to a number of hydrolysis, concentration, decarboxylation, and dehydration reactions [7]. It is an exothermic process and results in three products: gases, aqueous chemicals, and a solid fuel (hydrocarbons) [8]. The three main parameters that can be changed in an HTC process are temperature, residence time, and biomass to water ratio. It has been found that each of these variables can affect the intermediate reaction and output products differently in terms of yields and composition. An increase in temperature enhances the dehydration reactions, removing oxygen from the original biomass structure, resulting in a decrease in the oxygen-to-carbon (O/C) ratio. Another key parameter that can significantly affect the composition of the final hydrocarbon is the origin of the biomass [9]. HTC has a wide range of different possible raw materials

that can be pretreated for biocarbon production. In addition, these raw materials have no limit on their moisture content; thus expanding the possibilities of materials that can be subjected to hydrothermal treatment. This is a significant advantage of this method over other conventional conversion of “waste” into energy methods, such as cracking, due to the fact that it requires less energy dissipation for drying the material [10]. The HTC process can be used to enhance the recovery of nutrients such as nitrogen and phosphorus in particular, and can be used as a soil conditioner to promote plant growth and mitigate soil desertification [9].

Hydrothermal carbonization can be applied for the treatment of biogenic municipal solid waste, industrial wastewater and food industry wastes, such as olive mills wastewater, wine sludge, and cheese whey wastewater. Zhang et al. [11] applied hydrothermal carbonization (HTC) for the conversion of fruit wastes into value-added products. The authors implemented a thorough analysis of the hydrochars and concluded that the treatment increases the fixed carbon content and the heating value of the hydrochars. Fernandez et al. [12] studied apple and grape waste (apple pomace, grape marc, grape stalk) and concluded that all three by-products have properties that make them suitable for biofuels. Treating the waste of these products with thermochemical processes can cause extraction of phenolic compounds, which are usable by the food industry. By means of hydrothermal extraction, phenols can be retrieved and with the combination of pyrolysis and gasification the treatment can minimize waste; this can be a solution for the production of environmentally friendly bioenergy. The dairy industry is one of the main sources of agricultural–industrial wastewater in Lesvos island [13] and the same applies to other food industries such as olive mills and producers of alcoholic beverages (ouzo and wine). Cheese whey wastewater has a high pollutant load with values that can exceed Carbon Oxygen Demand (COD) values of 77,000 mg/L [14] and low pH (4–5), due to the lactose content, which is broken down into lactic acid and other organic acids. It is a difficult waste to manage due to the difficulty of storing it for a long time, because the degradation takes place in a short period of time [10]. Studies have shown that the treatment of milk effluents with hydrothermal carbonation gave high yields of solid hydrocarbons (HC) up to 84%. Total acid-phenol concentrations increased during the process, but not to a large extent and their concentrations ranged around 2500 ppm [15].

Olive mill wastewater (OMMW) is a byproduct from the production of olive oil. It represents up to 50% of the total input volume, while olive oil is only 20% and the remaining 30% is a solid residue [15–17]. Mill effluents are a hazardous pollutant for surface and groundwater resources due to their high content of toxic phenolics and organic pigments and high concentration of organic matter [18,19]; consequently, it takes a long time to decompose when discarded in nature. The Biochemical Oxygen Demand (BOD) of these effluents can reach values up to 70,000 mg/L and the COD of about 200,000 ppm [18]. In the case of olive mill wastewater, hydrothermal carbonation can be applied to produce a solid product or hydrocarbon, at a relatively low temperature, between 180 and 250 °C. The hydrocarbon produced is a carbon-like bituminous material that is stable, non-toxic [20], and can be used as an energy source, for soil improvement, and as a filter in water treatment processes [21]. The results also showed that from the hydrothermal process at a temperature of 250 °C, the carbonization of the samples increased and the energy density reached up to 142% and 36 MJ/Kg [16]. According to these studies, the hydrocarbons of olive mill waste could be used as energy dense and mechanically stable biofuels.

Hydrothermal carbonation (HTC) is a thermal conversion process that can be a viable means of managing solid waste streams while minimizing greenhouse gas emissions and the production of residual material is inherently valuable. It has been reported that it converts biomass (and other organics) into a carbon-rich and energy-dense carbon that can be used for energy applications. HTC products are considered as carbon-rich materials for instant combustion or as a precursor to the creation of valuable green products [10]. This study takes into consideration that the food industry is a basic sector of the local economy in Lesvos island and identified the lack of studies on the topic of hydrothermal

carbonization of wine sludge. The research gap is expanded even more if the lack of studies about wineries in Lesvos is considered. Therefore, the first main scope of this study is to present a case study of Lesvos island and identify the existing operating wineries on the island, utilize actual wine sludge from local wineries for the production of hydrochar, and determine its quality by means of hydrothermal carbonization. The main novelty of this study is the application of different HTC operating pressures and the analysis of the pressure effect on different significant parameters of the products. On the one hand, this is a unique application that can provide insights into the underlying mechanisms. On the other hand, the valorization of wine sludge by conversion into hydrochar can be an interesting alternative pathway for the production of biofuels and biomaterials in the framework of Circular Economy.

## 2. Materials and Methods

### 2.1. Area of the Case Study

Lesvos is the third largest island in the Aegean, belongs to the group of islands of the North Aegean, and has a long history in the production of beverages. For several years now, the cultivation of the vine has developed significantly; first in the area of Eresos-Antissa and then in the areas of Kalloni and Plomari. Lesvos now has a remarkable wine production and the PGI (PGI) wine, Protection of Geographical Indication Lesvos, which was introduced at the end of 2010, gives identity to this production and makes it an excellent and equal product. In the last two decades, Lesvos has entered the wine market with six companies (Megalochori Oinoforos, Methymnaios, Akritos Oinos, Anemotias Wine, Mavromatis, and Anemotia Viticulture Association), as well as with a large number of amateur winegrowers. The types of wines produced on the island are white wine (dry, semi-dry, semi-sweet, sweet), rosé wine (dry, semi-dry, semi-sweet, sweet), and red wine (dry, semi-dry, semi-sweet, sweet). The catastrophic phylloxera that struck the island at the end of the 19th century resulted in the significant reduction in viticulture in Lesvos. Today, the most important vineyards are located in Karyonas-Skopelos Geras, in the mountainous area of Megalochori-Plomari, in the plain of Kalloni, and in the entire western volcanic part of the island. In recent years, some efforts have been directed towards high quality wines with a special character. The cultivated varieties are presented in the following section with the most important being Fokiano which, according to the data of the Directorate of Rural Development of Lesvos, is cultivated in an area of 455 acres. An extended survey of the operating local wineries in Lesvos island was implemented and the outcomes of the study are presented in Figure 1.

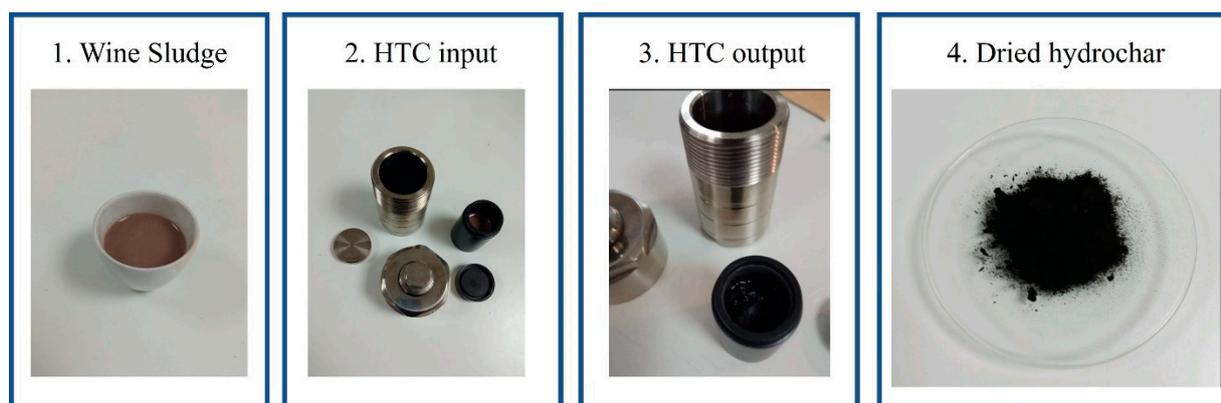
The samples that we collected for the experimental research came from the local winery “Volcano Anemotia”, which is located in the village Anemotia of the Municipality of West Lesvos. The winery was founded in the fall of 2017. It produces white, red, and rosé wines and in smaller quantities of tsipouro. The vineyards that the winery supplies its raw materials to are located at an altitude of 350 m, are arid, and with special characteristics that are betrayed by the microclimate of the caldera of Anemotia Volcano. The varieties that thrive in the area and are used for winemaking are Kalloniatiko, Mandilaria, Moschato Mavro, Fokiano, Athiri, and Assyrtiko. For the year 2021, the winery received 20,746 kg of grapes with the mass balance being reduced to 70–75%, giving a production of about 16,000 bottles of wine, with a reduction in production by 40% from the previous year due to prolonged high temperatures and reduced rainfall.



**Figure 1.** Operating wineries in Lesvos island.

## 2.2. Methods of Analysis

The main scope of this study was to sample wine sludge and valorize it under different pressure regimes of hydrothermal carbonization. The experimental analysis was conducted in the Energy Management Laboratory of the University of the Aegean, in order to further investigate the reactions of sludge samples with the process of hydrothermal carbonization. The samples were collected from local wineries on the island of Lesvos and the process of hydrothermal carbonization was utilized for the treatment and valorization of wine sludge into hydrochar. The hydrothermal reactor used for the experiments was a 25 mL reactor with a PTFE main body reactor covered with a metal casing, which allows it to generate autogenous pressures. Four experiments were performed with 6, 8, 10, and 12 mL of wine sludge that filled the hydrothermal reactor in percentages of 24%, 32%, 40%, and 48%, respectively. The reactor was then placed for each experiment in a Memmert furnace for 24 h and at a temperature of 200 °C. It is important to note that the operating pressure in each case is equal to the evolving pressure inside the reactor. The estimation of the difference between the initial and the final mass flows contained in the HTC autoclave reactor was assessed by the implementation of the mass balances for the gaseous, solid, and liquid streams, i.e., the hydrochar, the product gases, and the slurry. The mass of the gases was assessed by weighing the filled uncapped reactor before and after the HTC process. The produced hydrochar was determined by filtering the mixture through a simple coffee filter and then drying at 70–80 °C. The weight difference in the filter before and after filtration is the weight of the solid fuel fraction. For the assessment of the liquid fraction, the weight difference was measured by taking into consideration the mass of gases and the mass of the hydrochar. The raw material and the final dried hydrochar product are presented in Figure 2.



**Figure 2.** Input raw wine sludge and produced hydrochar.

The mass flows were collected during steady-state operation and the overall mass balances are shown in Equations (1)–(4).

$$Q_{in} = \dot{m} \text{ sludge} + \dot{m} \text{ OMWW} \quad (1)$$

$$Q_{out} = \dot{m} \text{ gases} + \dot{m} \text{ slurry} + \dot{m} \text{ hydrochar} \quad (2)$$

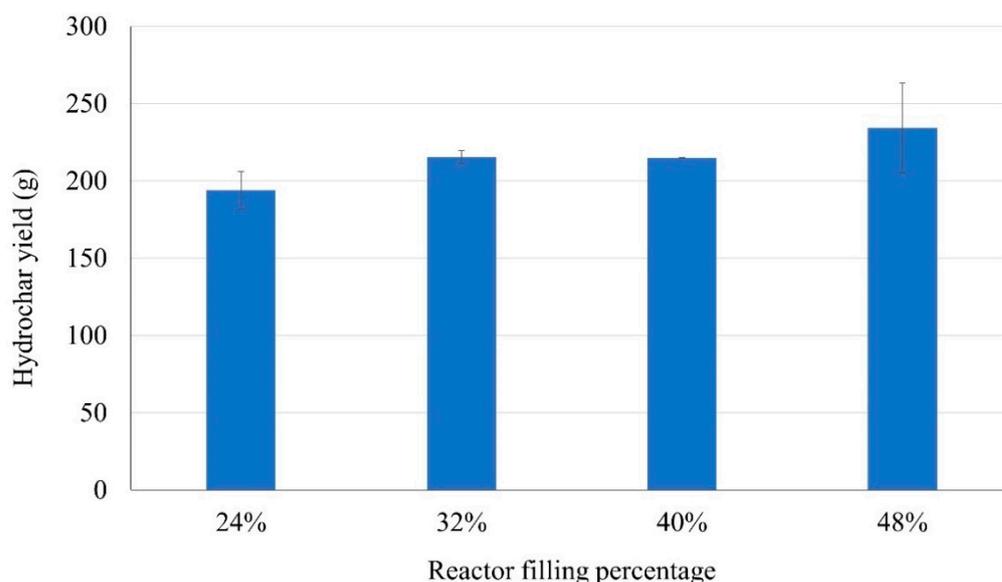
$$Q_{in} = Q_{out} \quad (3)$$

$$\dot{m} \text{ reactor\_in} = \dot{m} \text{ reactor\_out} + \dot{m} \text{ gases} \quad (4)$$

Several analyses were performed on the HTC products for the determination of the concentrations of total phenols, total suspended solids (TSS), volatile solids (VS), chemical oxygen demand (COD), pH, conductivity, the fraction of the produced hydrochar, and the assessment of the heating value. For the assessment of the total solids (TS) (moisture content), the samples were placed in porcelain containers and dried in a Memmert furnace at 105 °C for 24 h. For the measurement of volatile solids (VS), the dried samples were placed in a Nabertherm furnace, at 550 °C as described by Vakalis et al. [21]. The pH of the generated waste varies greatly, from 3 to 11, due to acidic grapes and alkaline cleaners [22]. The pH and the electrical conductivity measurements were made by two calibrated instruments: a pH CONSORT C932 m and LF95 conductivity meter. The Folin method was applied for the assessment of the total phenolic content (TPC) of wine sludge and of the hydrothermal carbonization liquid products. The method is described by Sklavos et al. [23]. Similarly, the potassium dichromate method was used for the assessment of the Chemical Oxygen Demand (COD) [24]. For the higher heating value assessment (HHV) of the hydrochars, measurements were performed on a Parr 6400 Calorimeter. Three replicates were analyzed for each sample. In the first sample, 0.2025 and 0.1854 g char of wine sludge were used, respectively, in the second 0.2184 and 0.2124 g, in the third 0.2147 and 0.2150 g, and in the fourth 0.2548 and 0.2139 g char. Each of the samples were burned with oxygen on the calorimeter using a wick. The Parr 6400 Calorimeter was calibrated with benzoic acid tablets which is the certified standard. All the results of the analysis were statistically analyzed.

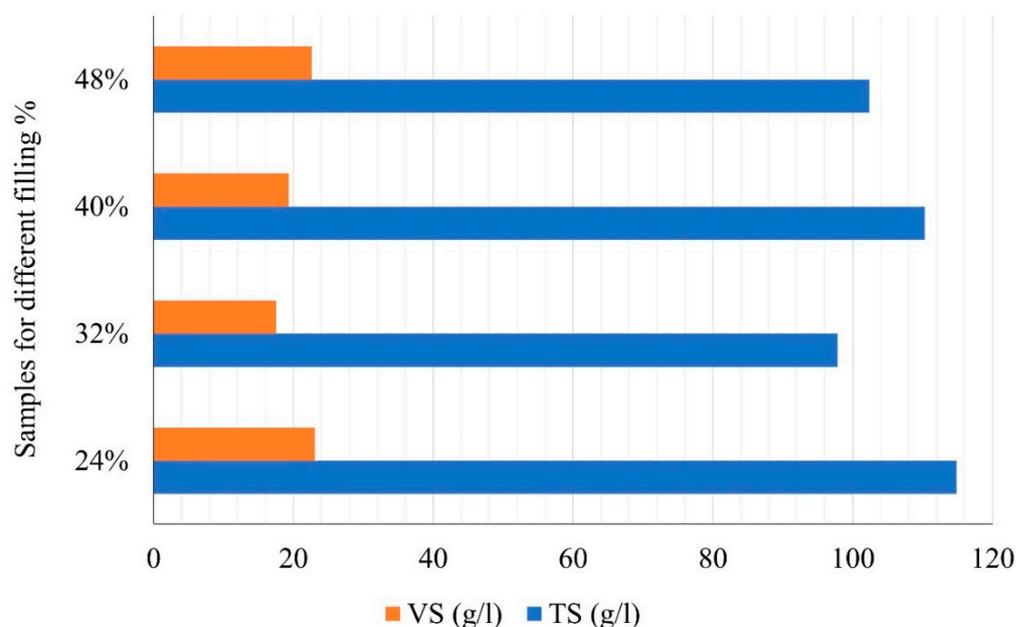
### 3. Results

Figure 3 presents the percentage of the hydrochar yield (solid product) from hydrothermal carbonization of wine sludge. As shown in the figure, increasing filling percentages of the reactor resulted in increasing hydrochar yields, although the correlation seems not to be linear or consistent. For these specific experiments, increased pressure has a positive effect on the production of hydrochar, but more experiments need to be performed in the future in order to assess the limits of this effect. An aspect to be examined is the effect of the evolved pressure on the volatility of the volatile matter. According to the work by Xu et al. [24], there is correlation between fixed carbon content and hydrochar production.



**Figure 3.** Hydrochar yield production for different filling percentages of the HTC reactor.

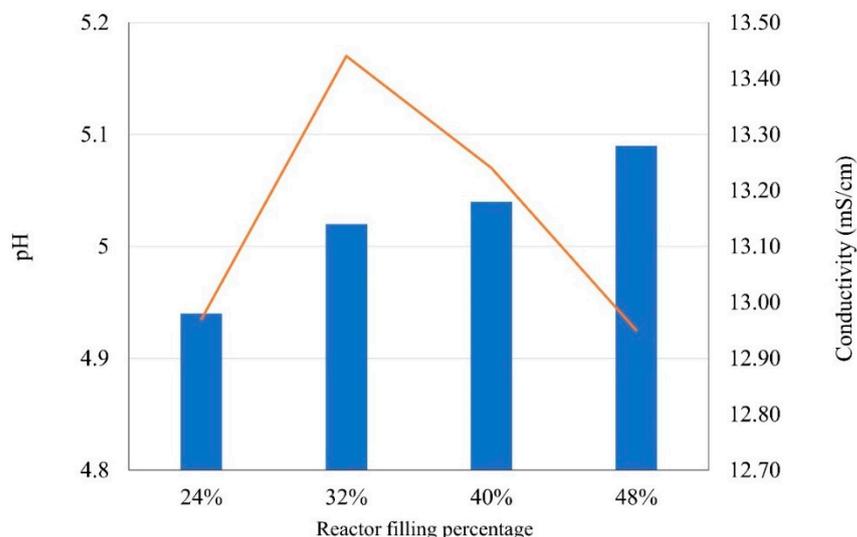
Figure 4 presents the volatile solids (VS) for different filling percentages of the HTC reactor. Lower filling percentages seem to favor the production of total solids (TS). There is a fluctuation of the effect of increasing pressure regimes on the production of total solids and the percentage of volatile solids. It should be stated that the initial moisture level was measured at 88.96% which results in a total solids content of 11.04%. An interesting parameter as presented by Zhang et al. [11] and Vakalis et al. [21] is the effect of HTC on the volatile solids content. It should be stated that the uniqueness of this present study is that different pressure regimes were utilized, and this had a profound effect on the content of volatile solids in a manner that has not been depicted in previous studies. This will be part of upcoming work in order to assess in detail the mechanisms that may cause such effects.



**Figure 4.** Total solids and volatile solids for different filling percentages of the HTC reactor.

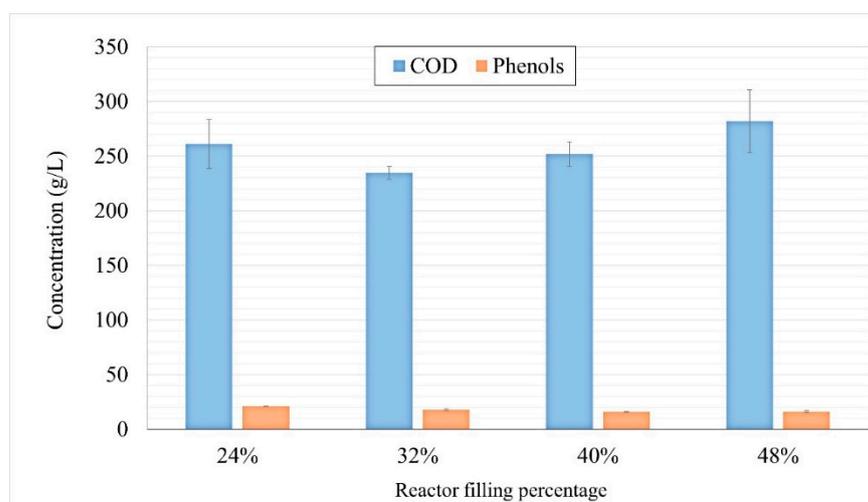
Figure 5 presents the pH and the electrical conductivity of the liquid fractions of the products from hydrothermal carbonization. The figure shows a clear tendency in respect to the pH values of the liquid products with increasing pressure. The electrical

conductivity result of the liquid samples is interesting. The HTC treatment for 32% filling of the HTC reactor had significantly higher electrical conductivity than the other samples. By combining this result with the result from Figure 3, we can assume that some elements or molecules pass to the liquid phase in the filling percentage of the reactor (pressure regime) and this affects the electrical conductivity. In addition, hydrothermal carbonization is linked to the presence of acetic acid and propanoic acid in the liquid products [23] and this can explain the low pH values of the liquid products of wine sludge HTC.



**Figure 5.** pH and conductivity for different filling percentages of the HTC reactor.

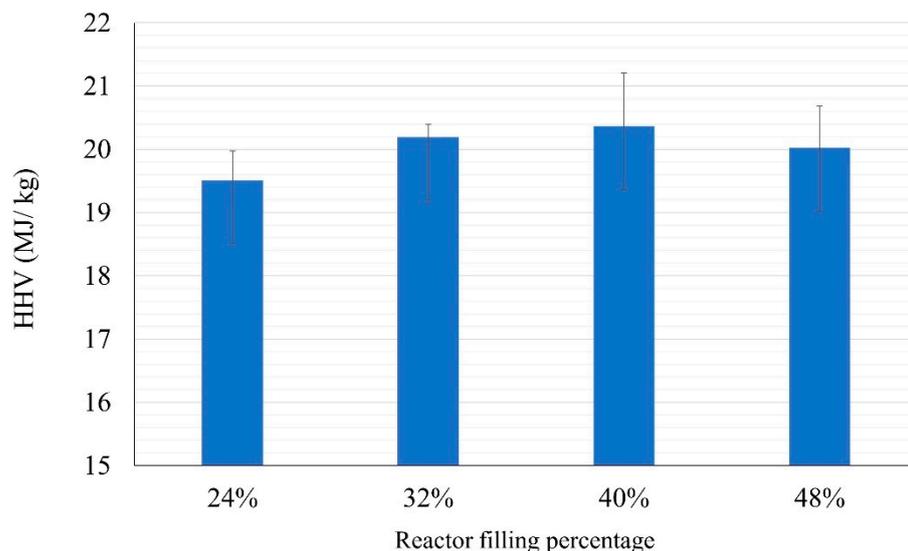
Figure 6 presents the chemical oxygen demand and the total phenolic content of the liquid fractions of the products from hydrothermal carbonization. We observe an initial drop in the COD value and then a subsequent increase. Interestingly, there was different observation in respect to the content of the total phenol. Total phenols decrease with increasing evolved pressure, but this flips at the highest filling percentage of the reactor, where the total phenolic content increases again. It should be further investigated whether a further increase in the evolved pressure will result in higher phenolic contents.



**Figure 6.** COD and TPC for different filling percentages of the HTC reactor.

Figure 7 presents the higher heating values of the solid carbonaceous products from hydrothermal carbonization, i.e., the hydrochars. The figure presents two clear tendencies. On the one hand, the samples that are treated with up to 40% of the reactor's filling per-

centage have increasing higher heating values. On the other hand, higher filling percentage results in decreasing higher heating values. The heating values are comparable to the values presented by other similar studies [25], which is a good indicator that there is potential for energetic valorization of hydrochars from wine sludge. The range of the heating value results can be explained by the selected temperature of HTC treatment, which has been shown to have an optimal effect on the heating value of hydrochar, e.g., the work presented by Shrestha et al. [26].



**Figure 7.** HHV of samples for different filling percentages of the HTC reactor.

#### 4. Discussion

The Food and Agriculture Organization estimates that 1.6 gigatonnes of agricultural products—27% of annual world production—are wasted each year. Reducing dependence on fossil fuels and reducing the amount of solid biowaste are two of the most fundamental challenges facing modern society. Global bioeconomy plans prioritize the proper management of organic resources to ensure their viability, as well as biomass sustainability [27]. It is estimated that a winemaking process produces from 1.3 to 1.5 kg of residues per liter of wine produced. The organic content of the generated waste is easily soluble and this does not allow for easy disposal by physical or chemical means [28]. Most studies have shown that about 70% of the water used will end up as liquid waste. Although winery waste is not a new situation, its special composition makes it difficult to manage and treat. The most common wastes are low pH wastes, wastes with high sulfide content, and sodium with high organic content [4,18]. Other parameters such as butyl and ethanyl ethyl esters, propanol, propionic acid, and others are found in lower concentrations. An important feature is the content of phenolic components where in white wine they amount to 280 mg/L and in red 1400 mg/L. Polyphenols are mainly in the flesh of the grapes and wine has a higher content of phenols. The deposition of wastes that are high in phenolic substances can cause complications in the microbial load of the soil and lead to alteration of its characteristics and the plants in it.

The processing of grapes for wine production annually produces large volumes of waste, which in many cases is larger than the volumes of wine produced [29]. The waste resulting from the wine production process is separated into liquids and solids. Liquid waste can be generated from various parts of the winery solid waste, usually resulting from the degranulation of grapes [26]. The waste resulting from the various stages of the wine industry has a high concentration of organic substances. Most of the waste is generated by the cleaning processes of the wineries but also by the cooling process applied in one of the wine production stages [3,29]. The amount of waste produced and the pollution load can vary greatly in relation to when the wine is produced and of course depending on the

type of wine produced, such as white, red, and others. Due to the seasonal production of the wine industries, waste occurs at specific times. Production units must identify the generated waste and adapt their procedures for their management [24]. Evidence from studies shows that up to 70% of the total amount of water from wineries ends up as waste [4]. The amounts of liquid waste that result are significant and refer to different processes. Wine, grape juice, suspended solids, and the detergents used are found there as waste. Liquid waste usually results from treatment processes. The composition of the waste generated may vary between wineries. It is important to determine the composition in order to choose the correct method for their management but also to determine the effects on the environment during their disposal. The waste produced is also seasonal, with the largest quantities being produced during the harvest [3].

## 5. Conclusions

Overall, five operating wineries were identified in Lesvos island and this study focused on the hydrothermal carbonization of wine sludge from the winery “Volcano Anemotia”, which is located in the village Anemotia of the Municipality of West Lesvos. For the year 2021, the winery received 20,746 kg of grapes and produced 16,000 bottles of wine. Hydrothermal carbonization of wine sludge was performed in a hydrothermal reactor that was filled up to 24%, 32%, 40%, and 48%, respectively, in order to have different evolved pressures. The uniqueness of this study is the utilization of different pressures on HTC treatment. Intermediate pressure regimes reduced the COD of the liquid phase from 26.1 g/L down to 23.48 g/L but higher pressures resulted in higher COD values of 28.18 g/L. The total phenolic content decreased with increasing pressure from 21 g/L down to 16.2 g/L. A positive effect was observed in the Higher Heating Value (HHV) and the mass yields of hydrochar with increased pressures. Specifically, the HHV of the hydrochar products increased from 19.5 MJ/kg for 24% filling of the reactor up to 21.36 MJ/kg for 40% filling of the reactor. Finally, increased reactor pressures resulted in increased produced hydrochar yields. A solid outcome of this work is that increased operating HTC pressure results in the production of high quality, i.e., high HHV, hydrochar. This can be a potential utilization pathway of wine sludge which would otherwise be disposed of. The study showed that the operating pressure had a profound effect on the different measured parameters which indicates the propagation of different underlying mechanisms that need to be studied in upcoming future work of the authors.

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## Abbreviations

COD:	Chemical Oxygen Demand
mha:	Millions of hectares
mhl:	Millions of hectoliters
%:	Percent
°C:	Degrees Celsius
HTC:	Hydrothermal Carbonization
O/C:	Oxygen-to-Carbon
mg/L:	Milligram per liter
HC:	Hydrocarbons
Ppm:	Parts per million
OMMW:	Olive Mill Wastewater
BOD:	Biochemical Oxygen Demand
MJ/Kg:	Megajoule per kilogram
PGI:	Protected Geographical Indication
Acre:	Area of one chain
kg:	Kilogram
g:	Gram
TSS:	Total Suspended Solids
VS:	Volatile Solids
TPC:	Total Phenolic Content
ml:	Milliliter
PTFE:	Polytetrafluoroethylene
HHV:	Higher Heating Value
TS:	Total Solids
mg:	Milligram
g/L:	Grams per liter

## References

- Moreno-Arribas, M.V.; Polo, M.C. Winemaking Biochemistry and Microbiology: Current Knowledge and Future Trends. *Crit. Rev. Food Sci. Nutr.* **2005**, *45*, 265–286. [CrossRef] [PubMed]
- OIV. International Organisation of Vine and Wine. State of the World Vitivinicultural Sector in 2020. 2021. Available online: <https://www.oiv.int/public/medias/7909/oiv-state-of-the-world-vitivinicultural-sector-in-2020.pdf> (accessed on 12 April 2022).
- Mosse, K.P.M.; Patti, A.F.; Christen, E.W.; Caagnaro, T.R. Review: Winery wastewater quality and treatment options in Australia. *Aust. J. Grape Wine Res.* **2011**, *17*, 111–122. [CrossRef]
- Christ, K.L.; Burritt, R.L. Critical environmental concerns in wine production: An integrative review. *J. Clean. Prod.* **2013**, *53*, 232–242. [CrossRef]
- Lu, X.; Jordan, B.; Berge, N.D. Thermal conversion of municipal solid waste via hydrothermal carbonization: Comparison of carbonization products to products from current waste management techniques. *Waste Manag.* **2012**, *32*, 1353–1365. [CrossRef] [PubMed]
- Torres-Sciancalepore, R.; Fernandez, A.; Asensio, D.; Riveros, M.; Fabani, M.P.; Fougá, G.; Rodríguez, R.; Mazza, G. Kinetic and thermodynamic comparative study of quince bio-waste slow pyrolysis before and after sustainable recovery of pectin compounds. *Energy Convers. Manag.* **2022**, *252*, 115076. [CrossRef]
- Sette, P.; Fernandez, A.; Soria, J.; Rodríguez, R.; Salvatori, D.; Mazza, G. Integral Valorization of Fruit Waste from Wine and Cider Industries. *J. Clean. Prod.* **2020**, *242*, 118486. [CrossRef]
- Yan, W.; Acharjee, T.C.; Coronella, J.C.; Vasquez, V.R. Thermal pretreatment of lignocellulosic biomass. *Environ. Prog. Sustain. Energy* **2009**, *28*, 435–440. [CrossRef]
- Maniscalco, M.P.; Volpe, M.; Messineo, A. Hydrothermal Carbonization as a Valuable Tool for Energy and Environmental Applications: A Review. *Energies* **2020**, *13*, 4098. [CrossRef]
- Chatzimaliakas, P.F.; Iliopoulou, A.; Vakalis, S. The Effect of Acidic Pretreatment on the Hydrothermal Carbonization of Cheese Whey Wastewater (CWW)—The Case study of Lesbos Island. In Proceedings of the 29th European Biomass Conference & Exhibition, Virtual Event, 26–29 April 2021.
- Zhang, B.; Heidari, M.; Regmi, B.; Salaudeen, S.; Arku, P.; Thimmannagari, M.; Dutta, A. Hydrothermal Carbonization of Fruit Wastes: A Promising Technique for Generating Hydrochar. *Energies* **2018**, *11*, 2022. [CrossRef]
- Fernandez, A.; Sette, P.; Echegaray, M.; Soria, J.; Salvatori, D.; Mazza, G.; Rodríguez, R. Clean recovery of phenolic compounds, pyro-gasification thermokinetics and bioenergy potential of spent agro-industrial bio-wastes. *Biomass Convers. Biorefinery* **2022**, 1–18. [CrossRef]

13. Zkeri, E.; Iliopoulou, A.; Katsara, A.; Korda, A.; Aloupi, M.; Gatidou, G.; Fountoulakis, M.S.; Stasinakis, A.S. Comparing the use of a two-stage MBBR system with a methanogenic MBBR coupled with a microalgae reactor for medium-strength dairy wastewater treatment. *Bioresour. Technol.* **2021**, *323*, 124629. [[CrossRef](#)] [[PubMed](#)]
14. Altiparmaki, G.; Kourletakis, P.; Moustakas, K.; Vakalis, S. Assessing the effect of hydrothermal treatment (HT) severity on the fate of nitrates and phosphates in dairy wastewater. *Fuel* **2022**, *312*, 122866. [[CrossRef](#)]
15. Atallah, E.; Kwapinski, W.; Ahmad, M.N.; Leahy, J.J.; Zeaiter, J. Effect of water-sludge ratio and reaction time on the hydrothermal carbonization of olive oil mill wastewater treatment: Hydrochar characterization. *J. Water Process Eng.* **2019**, *31*, 100813. [[CrossRef](#)]
16. Hashwa, F.; Mhanna, E. Aerobic and Anaerobic Biotreatment of Olive Oil Mill Wastewater in Lebanon. In *Efficient Management of Wastewater*; Baz, I., Al Otterpohl, R., Wendland, C., Eds.; Springer: Berlin/Heidelberg, Germany, 2008; pp. 187–203.
17. García, C.A.; Hodaifa, G. Real olive oil mill wastewater treatment by photo-Fenton system using artificial ultraviolet light lamps. *J. Clean. Prod.* **2017**, *162*, 743–753. [[CrossRef](#)]
18. Volpe, M.; Wüst, D.; Merzari, F.; Lucian, M.; Andreottola, G.; Kruse, A.; Fiori, L. One stage olive mill waste streams valorisation via hydrothermal carbonization. *Waste Manag.* **2018**, *80*, 224–234. [[CrossRef](#)] [[PubMed](#)]
19. Funke, A.; Ziegler, F. Hydrothermal carbonization of biomass: A summary and discussion of chemical mechanisms for process engineering. *Biofuels Bioprod. Biorefining* **2010**, *4*, 160–177. [[CrossRef](#)]
20. Libra, J.A.; Ro, K.S.; Kammann, C.; Funke, A.; Berge, N.D.; Neubauer, Y.; Titirici, M.-M.; Fuhner, C.; Bens, O.; Kern, J.; et al. Hydrothermal carbonization of biomass residuals: A comparative review of the chemistry, processes and applications of wet and dry pyrolysis. *Biofuels* **2011**, *2*, 71–106. [[CrossRef](#)]
21. Vakalis, S.; Georgiou, A.; Moustakas, K.; Fountoulakis, M. Assessing the effect of hydrothermal treatment on the volatile solids content and the biomethane potential of common reed (*Phragmites australis*). *Bioresour. Technol. Rep.* **2022**, *17*, 100923. [[CrossRef](#)]
22. Buelow, M.C.; Steenwerth, K.; Silva, L.C.R.; Parikh, S.J. Characterization of Winery Wastewater for Reuse in California. *Am. J. Enol. Vitic.* **2015**, *66*, 302–310. [[CrossRef](#)]
23. Sklavos, S.; Gatidou, G.; Stasinakis, A.S.; Haralambopoulos, D. Use of solar distillation for olive mill wastewater drying and recovery of polyphenolic compounds. *J. Environ. Manag.* **2015**, *162*, 46–52. [[CrossRef](#)]
24. Xu, X.; Tu, R.; Sun, Y.; Wu, Y.; Jiang, E.; Gong, Y.; Li, Y. The correlation of physicochemical properties and combustion performance of hydrochar with fixed carbon index. *Bioresour. Technol.* **2019**, *294*, 122053. [[CrossRef](#)] [[PubMed](#)]
25. Pawlak-Kruczek, H.; Niedzwiecki, L.; Sieradzka, M.; Mlonka-Mędrała, A.; Baranowski, M.; Serafin-Tkaczuk, M.; Magdziarz, A. Hydrothermal carbonization of agricultural and municipal solid waste digestates—Structure and energetic properties of the solid products. *Fuel* **2020**, *275*, 117837. [[CrossRef](#)]
26. Shrestha, A.; Acharya, B.; Farooque, A.A. Study of hydrochar and process water from hydrothermal carbonization of sea lettuce. *Renew. Energy* **2021**, *63*, 589–598. [[CrossRef](#)]
27. Jain, A.; Sarsayia, S.; Awasthi, M.K.; Singh, R.; Rajput, R.; Mishra, U.C.; Chen, J.; Shi, J. Bioenergy and bio-products from bio-waste and its associated modern circular economy: Current research trends, challenges, and future outlooks. *Fuel* **2022**, *307*, 121859. [[CrossRef](#)]
28. Ioannou, L.A.; Puma, G.L.; Fatta-Kassinos, D. Treatment of winery wastewater by physicochemical, biological and advanced processes: A review. *J. Hazard. Mater.* **2015**, *286*, 343–368. [[CrossRef](#)] [[PubMed](#)]
29. Puškaš, V.S.; Miljic, U.D.; Djuran, J.J.; Vucurovic, V.M. The aptitude of commercial yeast strains for lowering the ethanol content of wine. *Food Sci. Nutr.* **2020**, *8*, 1489–1498. [[CrossRef](#)]