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Hydrothermal Carbonization of Dry Anaerobic Digestion Residues Derived from Food and Agro Wastes in Lesvos Island

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Abstract: Biowaste management is at the center of attention in recent years due to the increased focus on Circular Economy practices. Lesvos has numerous food processing facilities and olive mills, and therefore Olive Mill Wastewater (OMWW) is a wastewater stream that requires attention. In this study, a holistic experimental set-up that combines aerobic and anaerobic treatment strategies was developed taking into consideration the hydrothermal carbonization of AD digestate along with locally available OMWW. The study focuses on the hydrothermal carbonization (HTC) of anaerobic residues from biogas production, and food waste was co-utilized with spent coffee grounds (SCG). The reduced volatile solids of SCG have some effects on the final products. AD produced methane yields of 54.7% for the food waste and 52.4%. for the feedstock with added SCG. At the same time, the feedstock that contained SCG produced more hydrochar that reached up to 50% of the yield. Hydrothermal carbonization in a water medium produced liquids with basic pH values around 8 and conductivities of 4–5 mS/cm, while the samples that were treated in OMWW medium had pH values close to 5.5 and conductivities of around 12 mS/cm. The produced hydrochars have significant calorific values that exceeded 20 MJ/kg for almost all the samples. Overall, HTC with OMWW as a medium was able significantly reduce the COD of OMWW while resulting in hydrochars with increased heating values.

Keywords: food waste; hydrothermal carbonization; hydrochar; biowaste; anaerobic digestion

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1. Introduction

Since 2015, the Circular Economy concept has dynamically entered the conversation and has been introduced in legislative form by the European Commission [1]. Among other sectors of economic activities, the Circular Economy action plan aims to restructure the waste management industry by simultaneously aiming to prevent waste generation in the first place and to prolong the utilization of each material in the value chains before final disposal. At the same time, biomass resources include several different subcategories of organic material, from the typical woody biomass to food waste and liquid biowaste. In most cases, the locally developed valorization scenarios are entangled with the locally available biomass. An interesting parameter is that biowaste resources can be converted—except for electricity and heat—into biofuels and valuable bioproducts [2]. The crucial importance of integrating food waste (and generally biowaste) management solutions into a "Circular Economy Concept" has been denoted by Loizidou et al. (2019) due to the significant and readily available quantities. The authors presented several case studies where other biofuels and especially bioethanol have been developed by treating and valorizing food waste [3]. Another interesting point that has been presented in the recent literature is that in the framework of Circular Economy, the valorization of food waste can also target the recovery of nutrients [4]. In addition, the added benefit of using biomaterials downstream in the value chain is an aspect of carbon neutrality that may assist the effort for an overall reduction of the carbon footprint [5]. A critical parameter to be considered is that biomass cannot be considered carbon neutral per se, since advanced cultivation and transportation activities can be very impactful. However, the utilization of food waste, as an end-use material with no further value, can be considered to have a positive effect on the overall carbon balance, particularly when considering landfill as the alternative scenario [6].

Biowaste valorization strategies may vary significantly due to local biowaste characteristics and availability. The issue gets exacerbated in the case of islands with, arguably, finite quantities of biowaste feedstock. In most cases, the necessary volume that could justify big investments—and take advantage of the economy of scale—is not there. Thus, the case of Lesvos is particularly interesting due to the significant sizes of the olive mills and the dairy industries (comparative to the size of the island). The year-round population has been measured to be slightly higher than 100.000 inhabitants, a number that includes both local citizens and tourists. Two different sources have assessed the tree plantation areas of the island to be between 37–47 thousand hectares, with olive trees occupying almost the totality of these areas [7]. Thus, agro-waste (primarily pruning) can be a significant source of biomass on the island. At the national level, a recent study showcased a calculative method for assessing the pruning available potential from agricultural biomass and it could be interesting to investigate the applicability of the approach in Lesvos, where several tree plantation areas are not easily accessible [8]. Overall, at the level of the European Union, agricultural practices emit approximately 10% of the overall GHG emissions [9]. With respect to the municipal waste, the metropolitan area of Mytilene (capital of Lesvos) has been measured to produce a little bit less than 20,000 tons of solid waste per year [10], and the whole island is projected to annually produce approximately 40,000 tons of MSW by 2030 according to the Regional Authority of North Aegean [7]. Biowastes account for approximately 50% of the total MSW. The same source estimated the annual dehydrated sludge production (20–25% solids) at around 1800 tons. At the same time, Lesvos island has been reported to have eighteen dairy processing facilities and more than 50 olive mills, both of which have wastewater effluents at the level of hundreds of tons per day. A recent study assessed that the main available biowaste for the island of Lesvos (except the clear-cut case of olive tree pruning) would be olive oil pomace (at around 19 thousand cubic meters), whey from dairy processing facilities and garden waste, which are assessed to be around 9000 tons/year [11].

Organic fraction of municipal solid waste in European Union is estimated to consist of 40% and the majority of this percent accounts for food waste (FW) [12]. Conventional disposing practice is landfilling, which poses environmental risks and social and economic issues, i.e., greenhouse gas emissions (CH_4, COx, NOx, etc.), odors, and underground water pollution-contamination. It is reported that in 2000, EU landfills were emitting over 75% of the total CH_4 gas emissions from diverse waste and wastewater treatment plants. Mak et al. (2020) have estimated that the rejected or disposed food from the global food chain corresponds to USD 900 billion [13]. Moreover, avoiding food waste production and implementation of new sustainable methods are in the direction of the United Nations Sustainable Development Goals by 2030. Nevertheless, food waste management has difficulties due to its specific physical and chemical characteristics such as high content of organic matter, loose structure, high quantities of salt and oil, high density and low C/N ratio [14]. Another environmental issue particularly in Mediterranean countries is olive mill waste (OMW). The latter are categorized as olive mill solid waste (OMSW) and olive mill wastewater (OMWW). The properties that characterize OMW are low pH, high moisture, high chemical oxygen demand (COD), antioxidant substances such as polyphenols, lipids and organic acids. All these characteristics highlight that olive mill waste is difficult to manage in a sustainable and cost-effective matter [15].

Spent coffee grounds (SCG) are the waste produced at the consumption stage of the coffee chain during the preparation of the coffee brew. In 2020–2021, coffee consumption all over the world was 10 million tons [16]. This large quantity of waste cannot disposed directly due to its toxicity, which can cause significant environmental problems. Atabani et al. (2019) state that SCG consisted of more than 1000 organic compounds and, moreover, in their research report that after the brewing of the coffee more than 700 volatile compounds remain in SCG [17]. These remaining components can be valorized and produce a never ending list of value-added products such as compost, biochar, bioethanol, biobutanol, bio-oil, biohydrogen, biogas, biodiesel, bio-dye, construction materials aggregates, cosmetics, food compounds, pharmaceutical ingredients, chemical ingredients, adsorbents and others [18,19]. The present research focused on the effect of SCG on the anaerobic digestion of food waste and the produced biogas.

The main valorization strategy for food waste has primarily been a biological process, i.e., anaerobic digestion (AD), which is an economically viable pathway toward bioenergy production [20]. Negri et al. (2020) presented an interesting argument that AD of food waste could be a more environmentally sustainable alternative to energy crops and mentioned the potential performance improvements that can be achieved by means of pretreatment [21]. Angelidaki et al. (2018) studied biogas production from sludge and suggested the option of enzymatic treatment for the case of sludge as well. In addition, the authors went slightly further downstream and discussed the potential of biogas upgrading into fuels of higher purity and quality such as biomethane [22]. A recent interesting development has been the co-treatment in the AD of food waste and sludge with the nuance of microwave pretreatment [23]. Similarly, co-AD with food waste and wastewater from horticultural activities was presented by Zhang et al. (2020) [24]. Apart from blending different types of biowaste, biochar has been utilized for enhancing biogas production [25]. This approach appears to be promising for using novel carbonaceous products in co-digestion processes. Investigating the pathway of biochar production, it is straightforward that it can be produced from pyrolysis of carbon-rich feedstock of relatively low-moisture [26]. Thus, material with high water content, such as the available biowaste in Lesvos, cannot be treated conventionally with thermal technologies, except if excessive amounts of energy are utilized for drying the material. Hydrothermal Carbonization (HTC) is a process that utilizes high pressures and intermediate temperatures for converting (primarily) wet biomass into hydrochar and other by-products such as phenols and syngas [27]. The process works well with food waste and can also be used for the co-treatment of food waste with other fuels [28,29]. An interesting recent development has been the ability to co-treat mixtures of municipal solid biowaste and agricultural waste by means of hydrothermal carbonization [30].

This study takes into consideration the recently published academic literature and has identified an abundance of high-level studies on specific technical applications, but very few (practically nonexistent) studies that approach the issue of biowaste holistically by taking into account different applied waste management chains for co-treated biowaste. The design of a complete guide for biowaste management and utilization requires the inclusion of practical methods for treating organic food waste which, at the moment, are aerobic (composting) and anaerobic biodegradation (AD). In addition, most studies focus only on one parameter (usually biogas or hydrochar production) and have not investigated complex liquid mediums for HTC. On the contrary, this present study utilizes OMWW not only as a feedstock, but also as a hydrothermal medium for co-treating food waste. The raw material that is investigated is an organic fraction of MSW, which occupies a large fraction of the annual biowaste production on the island.

2. Materials and Methods

Food waste was selected from the rejections of a catering business and consisted of fresh unconsumed boiled potatoes (74%), beans (22%) and meat (4%). The rationale behind the selection of the catering was the supply of huge quantities of uncontaminated and separated types of food waste. Moreover, residues from the olive oil production were used such as olive tree branches, biphasic olive mill kernel (BOMK) and olive mill wastewater (OMWW). All materials were preserved in a refrigeration room at −4 °C. The physicochemical characteristics of the materials are presented in Table 1.

Table 1. Physicochemical characteristics of the initial materials.

	Beans	Potatoes	Chicken	Olive Branches	Biphasic Olive Mill Kernel	OMWW	SCG
pH	6.53 ± 0.03	4.85 ± 0.02	6.86 ± 0.03	5.66 ± 0.02	4.98 ± 0.01	4.6 ± 0.01	6.3 ± 0.01
Moist. (%)	83.78 ± 1.20	82.75 ± 1.75	57.44 ± 2.63	9.99 ± 2.1	51.42 ± 0.81	93.3 ± 1.15	66.52 ± 2.30
TS (%)	16.22 ± 1.43	17.25 ± 1.34	42.56 ± 2.76	90.01 ± 1.94	48.58 ± 1.87	6.7 ± 1.06	33.4 ± 2.3
VS (%)	11.35 ± 1.90	13.80 ± 1.76	27.66 ± 1.69	72 ± 2.01	24.29 ± 1.08	6.5 ± 1.72	14.7 ± 2.5
TOC (%)	48.4 ± 1.53	50.45 ± 1.78	53 ± 1. 89	28.95 ± 0.88	53.1 ± 0.76	3.3 ± 0.06	42.5 ± 0.19
TN (%)	5.07 ± 0.71	1.42 ± 0.34	8.02 ± 0.67	1.03 ± 0.05	0.83 ± 0.13	nd	2.6 ± 0.11
C/N ratio	19.09	35.63	6.61	28.35	64.2	nd	16.4

nd: not determined.

2.1. Waste Valorization Technologies

The overall waste management scheme is presented in Figure 1 where all the materials, processes and end products are described. The idea as presented in this study is to use, treat and eventually valorize several—if possible, all types of biomasses available on the island—in order to optimally design a holistic action plan with increased performance. Therefore, we are analyzing two main pathways—aerobic and anaerobic—that can result in different end products or by-products, respectively.

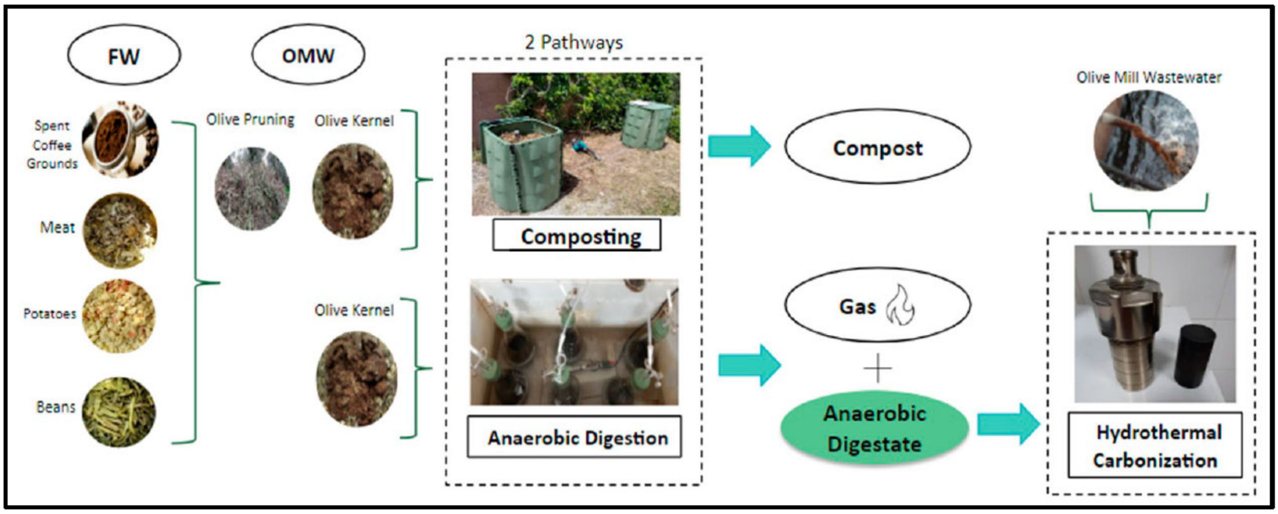

Figure 1. Overall scheme of applied biowaste valorization strategies.

2.1.1. Composting

Composting has been applied—as the aerobic pathway—but is not at the focus of this present study and thus, the experimental process is briefly presented here. With the method of aerobic biodegradation (i.e., composting), the recovery of nutrients is achieved through the mineralization of organic substances in biowaste. The maturation of the final product was completed in 120 days in a closed composter (home composting bin) with an active ventilation system that supplied the compost at regular intervals. Both temperature and oxygen content were monitored daily, while pH and humidity were monitored on a weekly basis. The composting process was applied in two modified composting bins with different compositions in the treated materials—the one with food waste and the second food waste mixed with olive mill pomace—(14% of the total mass). In both cases, food waste was mixed with pruning to provide optimal ventilation conditions, and also enhance the structure of the final compost. In Table 2 is illustrated the composition of composters K1 and K2.

Table 2. Initial material composition of composters K1 and K2.

	K1		K2	
	kg	**% *w/w* (avg.)**	**kg**	**% *w/w* (avg.)**
Meat	16.7 ± 0.82	7.8	14.1 ± 0.23	6.56
Beans	25.5 ± 0.76	11.8	21.6 ± 0.63	10
Potatoes	154 ± 1.53	71.3	131 ± 1.04	60.7
Biphasic Olive Mill Kernel	0	0	29.3 ± 2.13	13.6
Brunches	21.5 ± 1.18	10	21.5 ± 1.13	10
Total Food (avg.)	196.2	90.9	196	90.86
Total Material (avg.)	217.7	100.9	217.5	100.86

2.1.2. Anaerobic Digestion

Anaerobic digestion (pathway) is proposed as a diverse option that both produces biogas (end product) as well as digestate (byproduct) in the overall scheme. An experimental setup was organized in the facilities of the Waste Management Laboratory of the Department of Environment (University of the Aegean), where a set of six 2L bottles was placed in a heating bath of 40 °C for supporting dry anaerobic digestion. The water content was removed by compression and the bottles were filled with nitrogen to create an inert environment. The composition of the three different samples is presented in Table 3. As seen in Table, the tested samples were (a) sludge (to subtract the endogenous methane of the sludge), (b) sludge + food waste (FW100), and (c) sludge + food waste + spent coffee grounds (FW80). As food waste was used, we used the same percentage composition as in composting (Figure 1). Spent coffee grounds were collected from the cafeteria running in the university campus. Gas sampling bags were air-tightly connected to the bottles and the gas was analyzed directly from the sampling bags by means of a GEOTECH BIOGAS 5000 portable biogas analyzer. Cumulative methane production was measured, and the specific methane production (SMP) was calculated as the produced methane per unit of VS added (L CH_4/g V S_{in}).

Table 3. The composition of the samples treated with AD.

Sample ID	Sludge	Food Waste	SCG
0	350 g	0%	0%
FW80	350 g	80%	20%
FW100	350 g	100%	0%

Hydrothermal Carbonization. The digestate from the above samples was subsequently treated in a hydrothermal autoclave. The external reactor is designed from SS304L stainless steel and is air tightly closed with a screw-seal. The inner reactor vessel is 25 mL, is constructed from PPL and has maximum safe operating temperature of 280 °C and maximum operating pressure of 3 MPa. The inert PPL chamber can withstand acidic corrosion and is leakproof. In the present study, the digestate residues from the tested samples (Table 1) were treated along with liquid mediums, which were either water or olive mill wastewater (OMWW). The composition of the feedstock introduced in the HTC reactor vessel was:

- ➢ 1 g of digestate (all the available samples);
- ➢ 8 mL H_2O or 8 mL olive mill wastewater.

The experimental tests were performed in the oven at 200 °C and elevated pressure that reached 2.2 MPa. The standard temperature of the method ranges between 170–200 °C. The duration of each experiment was set to 1 or 3 days. The profile of all the different combinations of samples that were used in the hydrothermal reactor is presented in Table 4. As follows, the definition of samples is explained in Table 2 with an expanded description.

The first part of the sample name is the sample ID from anaerobic digestion, i.e., 0, 101 and 801. The second part corresponds to the liquid medium, with N representing water and K representing olive mill wastewater. Finally, the last number of the ID corresponds to the days of the hydrothermal carbonization experiment, with 1 corresponding to one day and 3 corresponding to three days.

Table 4. The feedstock mixtures in the hydrothermal reactor.

Sample ID	Mixture
0K1	Sludge/OMWW (1 day of HTC)
0K3	Sludge/OMWW (3 days of HTC)
0N1	Sludge/Water (1 day of HTC)
0N3	Sludge/Water (3 day of HTC)
101N1	Sludge + FW/Water (1 day of HTC)
101N3	Sludge + FW/Water (3 day of HTC)
101K1	Sludge + FW/OMWW (1 day of HTC)
101K3	Sludge + FW/OMWW (3 day of HTC)
801N1	Sludge + FW (80%) + SPG (20%)/Water (1 day of HTC)
801N3	Sludge + FW (80%) + SPG (20%)/Water (3 day of HTC)
801K1	Sludge + FW (80%) + SPG (20%)/OMWW (1 day of HTC)
801K3	Sludge + FW (80%) + SPG (20%)/OMWW (3 day of HTC)

As the main target object of this research, solid residue is one of the final fractions in hydrothermal carbonization. This solid product, named "hydrochar", lacking moisture in carbon form, could have a high heating potential as an alternative fuel resource. Hydrochar, a carbon-rich product obtained from the hydrothermal carbonization of biomass, exhibits a significant heating value due to its high carbon content and low moisture content [31]. Research conducted by Xu et al. (2020) demonstrated that the heating value of hydrochar can range from 20 to 32 MJ/kg, depending on the feedstock and process conditions, making it a promising energy source for heat generation and fuel production [32]. A study by Titirici et al. (2015) investigated the influence of hydrochar production parameters on its heating value and found that higher temperatures and longer reaction times during hydrothermal carbonization led to an increase in the heating value, highlighting the potential for tailored hydrochar production with desired energy properties [33]. To investigate the ratio of dry carbon in HTC treatment, it needs a mass balance between input and output substances. The mass balance of the hydrothermal treatment is determined by the variance in weight between the initial quantity and the final quantity held in the HTC autoclave reactor. As a result, the three fractions of the treatment were isolated.

In order to estimate the mass balance, it is mandatory to calculate all samples and the testing chamber weight before. After processing in the heated oven, the sealed container is weighed and opened. The gaseous fraction that has been produced after the reaction is released immediately out of the closed system. The gas fraction is measured as the weight difference before and after the treatment due to the release of gases from the container. There are also gas losses, which can be approximated through the deduction balance of the final chamber weight. As for the remaining fractions into the inner PPL chamber—solid and liquid—they are included in the final sample mass. The solid mass was determined by filtering the mixture using filter paper (20 μm) and then drying at 105 °C. The weight difference of the filter before and after filtration is the weight of the solid fuel fraction. The liquid fraction of the mixture is estimated indirectly after the measurement of solid and gas fractions. The pH acidity was measured at the non-filtered supernatant fluid with a pH meter. The electrical conductivity of E. C was tested with a CONSORT C932 electrochemical analyzer in an undiluted supernatant liquid sample.

To estimate the calorific value of the produced hydrochar, the solid fraction of the samples was measured in a Bomb Calorimeter (Parr Instrument Company, 6400 Calorimeter, United States). The conversion of the hydrochar samples into pellets in a small-scale pelletizer was proved to be the most consistent approach for the faster and more efficient measurement of the fuel in the calorimeter. For a successful test to take a heating value measurement, at least 0.1 g of material was placed in a specialized container inside the calorimeter. Then, the sample was heated up (pre period) and combusted in a pure oxygen environment (post-period) for the calculation of the heating value in MJ/kg of fuel.

The by-product of hydrothermal treatment with the highest potential to pollute is liquid residue and is assessed by several parameters such as the COD value. The determination of the chemical oxygen demand, i.e., COD, in the liquid fraction of the hydrothermal treatment products, was performed with a closed reflux colorimetric method that used a High Range reagent due to the high aggravating power of the liquids. Specifically, 1.2 mL of High Range solution and 2.8 mL of H_2SO_4 were added to the vials. Then, 2 mL of a diluted 1% *v*/*v* sample was added to each vial and placed in the COD reactor for 2 h for heating. The measurement was then performed on a spectrophotometer with the user program 978 COD-GG-HR 1000 rpm. The process chain is presented in Figure 2.

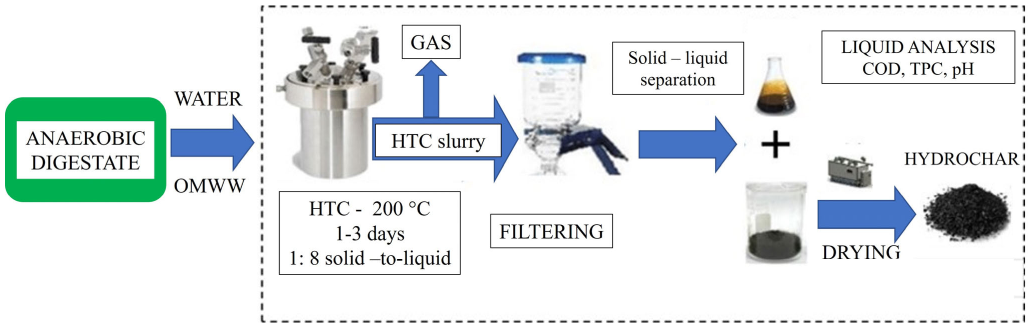

Figure 2. Hydrothermal carbonization process of AD residues and analysis.

3. Results

3.1. Composting

To simulate the utilization of biowaste in the first pathway through the aerobic treatment, a mixture of materials was composed of typical food residues. In the first place, K1 had an initial weight of 217.1 g with a volume of 0.3 m^3. On the contrary K2 had also an initial weight of 217.03 g with a volume of 0.3 m^3, but including a part of olive kernel as a testing application to valorize agro-waste for composting (FW + Olive kernel).

3.2. Anaerobic Digestion

The average biogas composition for the two samples is presented in Figure 3. The sole food waste samples averaged slightly higher methane yields of 54.7% in comparison to the food waste plus spent coffee ground samples that averaged 52.4%. The higher methane yield of the feedstock that consists only of food waste can be attributed to the fact that spent coffee grounds have lower volatile solids in comparison to food waste or lignocellulosic biomass since the coffee grounds are roasted and volatiles have already been removed before their use for coffee production [2]. The other major gas is carbon dioxide, with the food waste sample having 44.9% and the other sample 47.4%. The balance gas in both cases is oxygen with values below 0.5%. The heating value of biogas is dependent on the methane composition, which was measured to be from low to mid −50%. As reported by Kapoor et al. (2020) [34], similar anaerobic digestion experiments of food waste have methane compositions between 40–60% and our results are well within this range [23]. The specific methane production (SMP) in FW100 was 0.402 $LCH_4/g\ VS_{in}$ and in FW80 was 0.406 $LCH_4/g\ VS_{in}$. Similar nearby values are reported in the research of Kapoor et al. (2020) for mixture of SCG and FW. A methane yield less than 0.4 $LCH_4/g\ VS_{in}$ is considered as an indication of inhibited methanation [34]. Volatile solid removal efficiency was also nearby with values of 38.2% and 37.33 for FW100 and FW80, respectively. More detailed discussions should be available in future publications relevant to specific experiments.

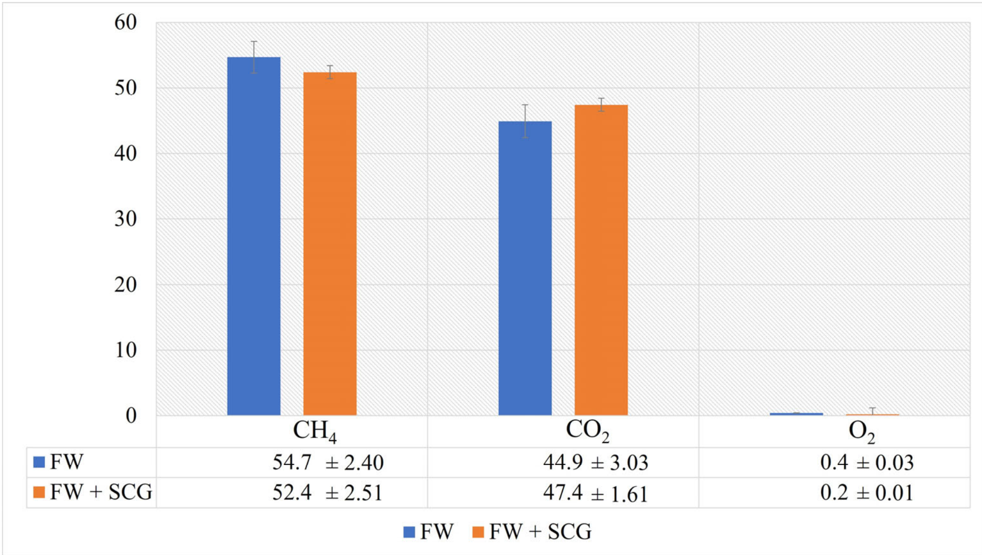

Figure 3. Biogas composition analysis.

3.3. Hydrothermal Carbonisation

There were two different experiment recipes applied with one replicate for 1 day and another for 3 days of residence in the oven. In practice, the process entailed co-treating a wet solid residue with some Olive Mill Wastewater and another recipe with water. In Figure 4, the proportions of gaseous, liquid, and solid products obtained from hydrothermal carbonization are displayed. The data reveal that when only sludge was used as the feedstock, the resulting products were mostly gaseous, accounting for more than half of the total mass in most cases. Additionally, the data show that introducing spent coffee grounds to the feedstock led to a greater amount of solid product, specifically the hydrochar. This is an extremely interesting, but not surprising, result. As shown by Vakalis et al. (2019), spent coffee grounds have fewer volatile solids than a conventional biomass (or food waste) since the coffee beans are roasted and a higher percentage of fixed carbon in the feedstock is linked to a lower proportion of volatile solids [2].

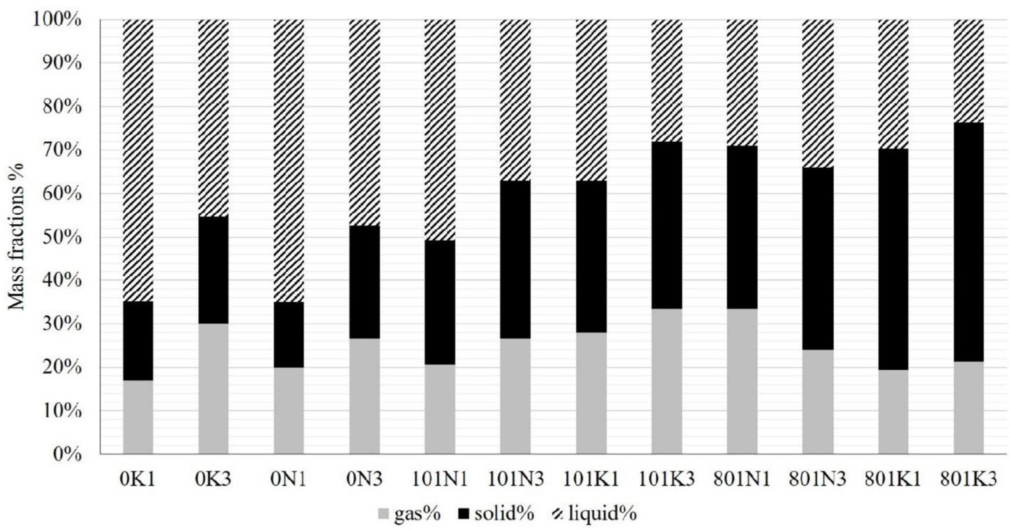

Figure 4. Mass fractions of HTC products.

The pH and electrical conductivity of the liquid products from hydrothermal carbonization are presented in Figure 5. The data exhibit a noticeable pattern with regard to the pH behavior of the liquid products. The samples that were treated in water medium were basic with a pH value consistently close to 8. The samples that were treated in OMWW medium were acidic with pH values close to 5.5. This significant finding can open a new cycle of future experiments, including HPLC analysis, to identify the full profile of the substances of each liquid sample and affect pH. Figure 6 presents the electrical conductivity of the liquid samples, there are two distinct groups. The samples that were treated in water have conductivities of 4–5 mS/cm, contrary to the samples that were treated in OMWW that have conductivities of around 12 mS/cm.

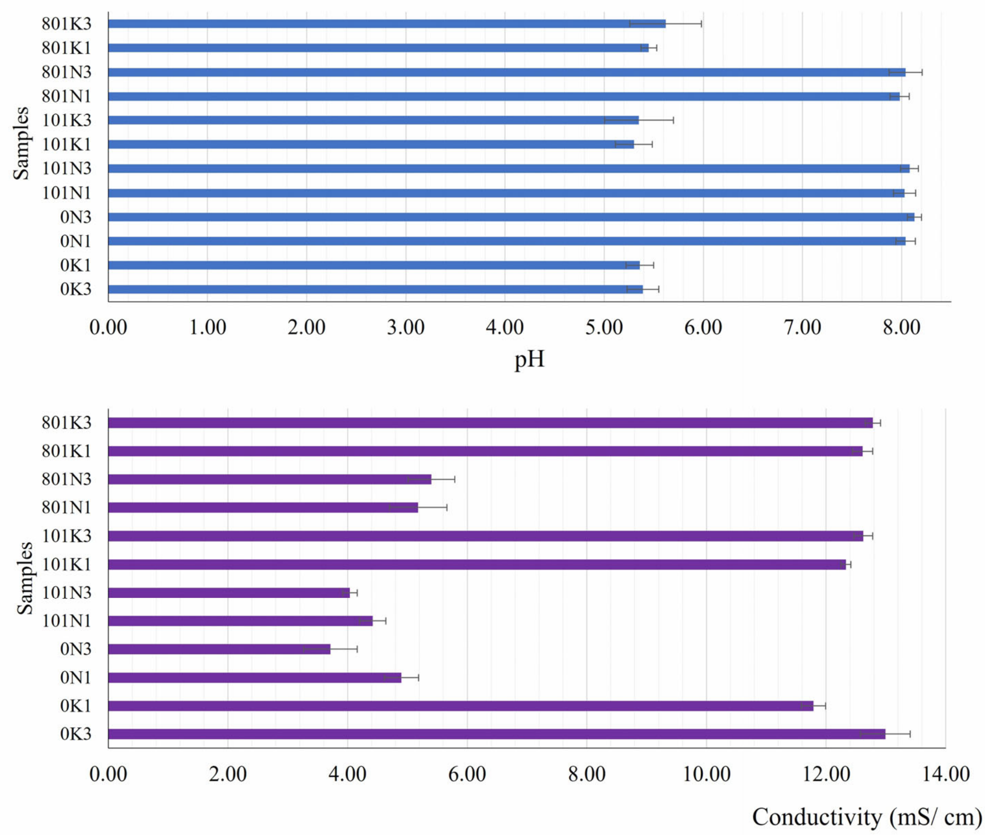

Figure 5. Characteristics of the liquid fractions from HTC: pH and conductivity.

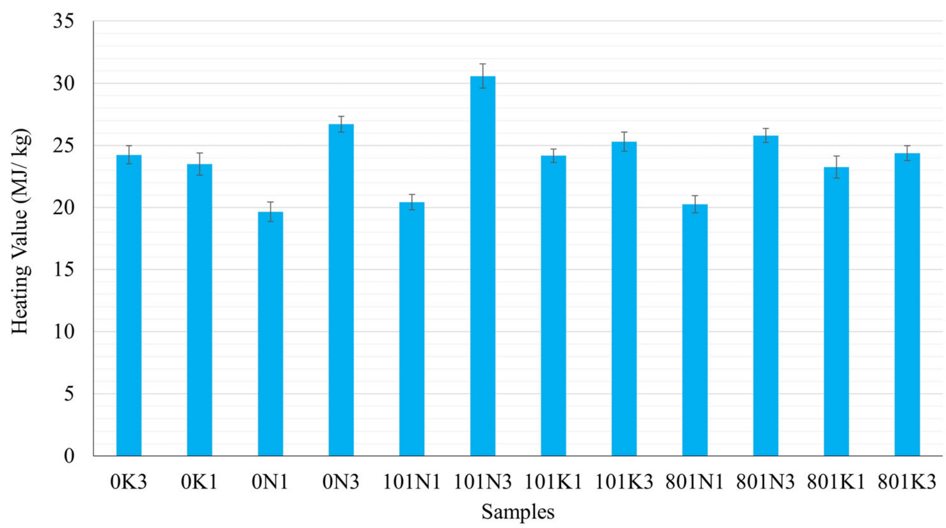

Figure 6. Higher heating values of hydrochar products from HTC.

The calorific values of the solid carbonaceous products derived from hydrothermal carbonization, specifically the hydrochars, are illustrated in Figure 6. The data highlight two distinct trends. Firstly, the energy densities of the samples subjected to a three-day treatment are consistently greater than those of samples that underwent treatment for only one day. At a second level, the samples that were reformed in water have consistently higher energy densities than the same samples that were treated in OMWW. Despite this, in nearly all cases, the heating values are substantial and surpass those found in other similar studies [34]. This indicates that there is potential for using hydrochars derived from food waste as an energy source. The outcomes of the heating value measurements, which exceeded expectations, can be accounted for by the chosen temperature of hydrothermal carbonization (HTC) treatment. It has been demonstrated that this temperature has an optimal impact on the heating value of hydrochar, as illustrated in the work done by Shrestha et al. (2021) [35].

Figure 7 presents the chemical oxygen demand of the liquid fractions of the products from hydrothermal carbonization. Once again, it has to be noted that the utilization of OMWW as a hydrothermal medium directly affects the characteristics of liquid products. The samples that were treated with OMWW have a chemical oxygen demand between 350–450 mg/L, contrary to the samples that were treated with water that have a chemical oxygen demand between 10–90 mg/L. In addition, the water samples seem to have increased COD with increased duration of treatment, but there is no clear tendency for the OMWW samples. The difference in the COD levels was expected since the COD of OMWW is in the several thousands. However, what is very interesting is that HTC significantly reduces the COD in OMWW samples since the release of carbon-oxides reduces the COD. This is a very interesting result that indicates a pathway for combined energetic valorization and simultaneous reduction of the environmental impact.

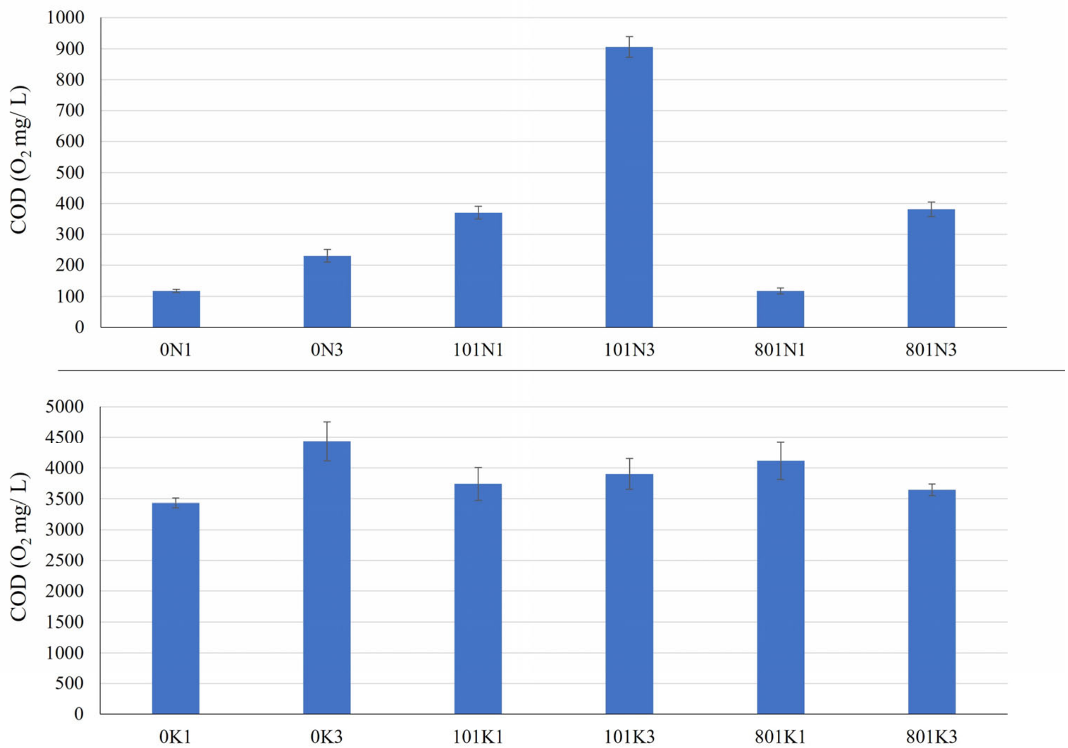

Figure 7. COD of the liquid fractions from HTC (**upper** subplot: samples treated in water, **lower** subplot: samples treated in OMWW).

4. Discussion

A few final considerations on this study can be the following. The acidic profile of HTC with OMWW may have assisted the production of hydrochar. Zhang et al. (2021) denoted that acidic environments in HTC may accelerate the hydrolysis process and thus enhance the reforming [36]. Another hypothesis could be that OMWW is more volatile than water and for the same temperatures it may have developed higher pressure profiles that can assist the production of hydrochar. Overall, the physicochemical properties of hydrothermal carbonization (HTC) liquor, the liquid byproduct of the HTC process, have been extensively studied. Research by Zhang et al. (2017) revealed that HTC liquor is typically characterized by high organic carbon content, complex molecular composition, acidic pH, and high levels of dissolved carbon and nutrients [37]. A study conducted by Chen et al. (2018) investigated the effects of reaction temperature and residence time on the physicochemical properties of HTC liquor [38]. They found that higher reaction temperatures and longer residence times resulted in increased carbon content, higher pH, and improved stability of the liquor, indicating a potential for tailored production of HTC liquor with desired characteristics. Wu et al. (2020) investigated the compositional changes and evolution of functional groups in HTC liquor during the hydrothermal carbonization process. Their findings highlighted the transformation of lignocellulosic compounds into more stable aromatic and aliphatic structures, leading to improved thermal properties and potential applications as a feedstock for bioenergy and value-added chemicals [39].

A future next step is the utilization of hydrochar back inside the anaerobic bottles for assisting the AD process in a way similar to the assistance of AD by co-AD with conventional biochar. This is a step towards circular co-treatment and will elevate this work to the next level. As mentioned before, HPLC analysis will be performed in the immediate future for the identification of the full profile of the substances of each liquid sample. Finally, upcoming work will present the results from the composting experiments. Food waste along with spent coffee grounds were treated in parallel in aerobic, i.e., composting, and anaerobic, i.e., AD, treatments. This study investigates the holistic management of biowaste and focuses on the co-treatment of AD residues by means of hydrothermal treatment. The additional feedstock that was utilized was local agro-waste and liquid biowaste of Lesvos. A unique application that is presented is the utilization of OMWW not only as HTC feedstock, but also as a hydrothermal medium for the treatment of food waste (plus some samples that contained additionally spent coffee grounds), and the results are compared with similar samples treated with HTC and water as the main hydrothermal medium.

The utilization of OMWW as a hydrothermal medium consistently returns higher hydrochar yields in comparison to water HTC. In addition, the samples that contained spent coffee grounds had increased hydrochar yields that exceeded 50%, due to the higher fixed carbon of the feedstock. On the one hand, liquid samples from OMWW HTC had lower pH, higher COD and higher conductivity than the water HTC samples. On the other hand, the water HTC samples had higher heating values that exceeded 25 MJ/kg in several cases, and the energy density was increased for samples that were treated for longer periods of time. Finally, HTC treatment led to a significant reduction of the COD in the liquid products, although OMWW has very high COD and OMWW HTC samples had significantly higher COD than water HTC samples.

5. Conclusions

The focus of the study revolves around the hydrothermal carbonization (HTC) process applied to anaerobic residues obtained from biogas production. In this study, food waste was combined with spent coffee grounds (SCG) for co-utilization. The presence of SCG had an impact on the final products due to the reduced volatile solids it contained. Methane yields from anaerobic digestion (AD) were recorded at 54.7% for food waste alone and 52.4% when SCG was added to the feedstock. Notably, the feedstock with SCG produced a higher quantity of hydrochar, reaching up to 50% in terms of yield. During hydrothermal carbonization in a water medium, the resulting liquids exhibited alkaline pH values around

8 and conductivities of 4–5 mS/cm. Conversely, samples treated in an olive mill wastewater (OMWW) medium displayed pH values close to 5.5 and conductivities around 12 mS/cm. The hydrochars produced possessed notable calorific values, surpassing 20 MJ/kg for almost all samples. Overall, using OMWW as a medium in HTC proved effective in significantly reducing the chemical oxygen demand (COD) of OMWW, while yielding hydrochars with enhanced heating values. Additionally, samples treated in water consistently exhibited higher energy densities compared to those treated in OMWW. Despite this, the heating values of the hydrochars remained substantial and surpassed those reported in similar studies. These findings indicate the potential of utilizing hydrochars derived from food waste as a viable energy source. The unexpectedly high heating values can be attributed to the chosen temperature for the hydrothermal carbonization (HTC) treatment.

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