



Review

# Thermochemical Technologies for the Optimization of Olive Wood Biomass Energy Exploitation: A Review

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**Abstract:** The use of biomass can be a strategic way to realize a carbon-neutral energy plan, ensuring a fuel feedstock. Residual biomass arising from pruning is demonstrated to be an important energy resource in terms of quantity and quality. In the Salento peninsula, Apulia Region, in the south of Italy, a dramatic outbreak of Xylella fastidiosa has decimated olive trees since 2013, gaining a considerable amount of wood biomass. This paper, starting from the need to find a way to optimize the use of this available stock, reviews the main technologies on the utilization of olive wood for energy purposes. In particular, processes and products are here described, and an energy analysis compares lower heating value (LHV), higher heating value (HHV), mass yield, process operating conditions, and energy generated and spent by the process in order to find the most effective technology in order to optimize the energy use of olive biomass. The conclusions show the advantages and disadvantages of each technology. Pyrolysis performs well, showing the best results for both char HHV and syngas yield under different operating conditions. Gasification seems to be the most appropriate among conversion technologies to optimize olive tree pruning for energy purposes, as it can be used to produce both electrical and thermal energy. In terms of economic valorization, char is the most promising material representing a value-added product, the quality and versatility of which ranges from fuel to soil improvers and additives for the construction of supercapacitors. Conversely, its disadvantages are mainly represented by high ash content, which can slightly decrease the boiler efficiency. Finally, the amount of alkali metals can produce several problems, such as fouling, slagging, corrosion, etc., posing a challenge for combustion control and pollutant minimization.

Keywords: olive tree pruning; combustion; gasification; pyrolysis; hydrothermal carbonization



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## 1. Introduction

The circular economy represents a novel paradigm to conciliate both economic growth and sustainable development goals [1] for the conversion of communities to a less carbon-intensive energy system [2]. It recommends reducing waste by recycling and reusing products for closing materials and energy loops. The use of wastes like vegetal residual biomass, from a circular economy perspective [3], not only avoids their disposal costs [4–6] but creates an optimized way to realize a carbon-neutral energy system [2]. Several studies have demonstrated that vegetal residual biomass is an important energy resource in terms of quantity and quality [7–11], representing a large feedstock for clean energy production [12], with a significant role in reducing the environmental impacts arising from the use of fossil fuel sources [13]. In this context, the concept of energy communities, which are based on self-production and self-consumption [14], has emerged [15], and biomass, being locally and ubiquitously available, is very suitable. The agricultural sector produces large quantities of processing residues, and olive growing [16–18] represents one of the principal areas for the economy of the Mediterranean basin [19], with plantations that cover significant lands in the basin. Usually, the unproductive branches of olive trees are cut every two years, leading

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to a large amount of olive tree pruning (OTP) as waste has to be removed from the fields to avoid the circulation of vegetal pests [20]. Kougioumtzis et al. [21] reported an intensive olive harvesting campaign in Agios Konstantinos, Greece, performed for two consecutive years, which gave a total amount of 252 dry Mg of pruning waste. There is a growing need to discover better ways to efficiently use OTP [22]. In fact, bio-residues can be used for direct energy production or biofuel generation via thermochemical conversion [23]. In particular, wood is recognized to be a strategic resource for supporting global energy demand [24–26], contributing to reaching the fundamental target of greenhouse gas emission reduction [27]. In addition, lignocellulosic biomass, which is considered a high-quality carbon-neutral energy source, often provides an additional source of income to agricultural food production [28,29], capturing large amounts of CO<sub>2</sub> during its growth [30,31]. Nevertheless, due to the intrinsic characteristics of the biomass, such as low density, low heating value, high moisture content, high volatile components, etc., this natural material is not yet considered an ideal fuel [32–37]. OTP represents an abundant source of biomass to be used for energy purposes, as well as a raw material for added-value products, but it is still rather unexploited, considering the absence of a cost-effective harvesting technology for this economic market [21]. Nowadays OTP is, in most cases, stacked and burned in rural fields [38], which is the most spread disposal method, with both economic costs and environmental risks and discarding an energy and bioproduct source [39]. This is not an optimal use of the raw biomass, as conversion into carbon materials not only leads to its improved calorific value as a fuel for energy purposes, but through valorization technologies, OTP can represent a potential large feedstock for bio-fertilizers, as well as bio-based materials [40]. OTP valorization is founded on the concept of the circular economy, first extracting valuable biological components and then using the residual biomass to produce added-value outputs associated with the practices of recycling and recovering [41]. The conversion technologies referred to as OTP are mainly based on thermochemical (for producing electricity and heat) or biochemical (e.g., anaerobic digestion) processes or the integration of different biorefinery technologies [42,43]. OTP processed via dry, as torrefaction and pyrolysis, and wet, as hydrothermal carbonization, treatments created solid, liquid, and gaseous products [44]. The torrefaction and pyrolysis of biomass, through the direct thermal decomposition of the organic matter under inert atmosphere, gives back an extensive range of fuels, chemicals, solvents, and other products and byproducts [45,46]. Trigeneration represents a way to obtain cooling and heating capacity, in addition to electric power [20]: small-scale installations (up to 7.5 kW) fueled by OTP and working through the organic Rankine cycle showed a high rate of feasibility and reliability [47]. Amirante et al. [48] demonstrated that such a plant leads to a payback period of 6 years, a 21% internal rate of return and a reduction in CO<sub>2</sub> emissions. In 2021, the International Energy Agency (IEA) created a roadmap for global energy decarbonization by 2050, and among the key pillars, biorefineries play a very important role, since generation from bioenergy sources must be increased from 40 EJ in 2020 to 100 EJ in 2050. From this perspective, 45% of the stock used for bioenergy production should arise from organic wastes and 20% from woody residues [49,50]. Salento peninsula, sited in the Apulia Region in the south of Italy, has been affected by a dramatic outbreak of Xylella fastidiosa that has decimated olive trees (it is estimated over 20 million) since 2013 [51]. This epidemic led to an environmental problem that represents the starting point of this review: a considerable amount of residual biomass from trunks to branches and leaves that could be used for energy purposes in spite of their disposal. This paper aims to review and compare processes for the energy-based use of olive wood biomass from the perspective of energy self-production and self-consumption for local communities.

#### 2. Process Analysis

## 2.1. Combustion

Picchi et al. [22] examined the physical and chemical features of OTP for direct combustion, concluding that OTP seems the most suitable (compared to other pruning materials) for direct combustion as it contains lower concentrations of critical compounds, such as N, S, and Cl. Chip and pellet production represents a low-cost way to internalize a potential

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cost of waste disposal, turning it into an energy resource. This process can be implemented near the area of pruning collection because of the ubiquity of the biomass, avoiding road transportation and packaging for external sales, with a benefit for local farmers. In order to obtain a high-quality pellet from OTP, high temperatures, low moisture content (less than 15% [52]), and reduced particle dimension represent crucial factors, while the compression force is not so significant. In the case of olive trees affected by Xylella fastidiosa, moisture content is minimal because of the action of the bacterium that dries the lymphatic vessels, leading to the death of the plant. The pelleting process slightly improves the calorific value of olive wood [53]. Kougioumtzis et al. [54] compared combustion in an industrial boiler of OTP to sunflower husk (SH) pellets: lower emissions of CO and NOx were found for OTP pellets, while dust emissions were high for both fuels, suggesting that particulate matter abatement equipment should be installed in the combustion facilities. OTP seems suitable for direct combustion with respect to other common European orchards crops, like vine, apple, pear, and hazelnut, probably because the olive crops are cultivated in a less intensive way and, thus, receive fewer chemical inputs [22], fulfilling set specifications for direct combustion. If, on one hand, OTP satisfies the industrial pellets specification given in the European Standard EN ISO 17225-2:2021, then, on the other hand, this standard does not make it suitable for residential uses given the high ash and nitrogen contents [55,56]. Nevertheless, a study by Soltero et al. [19] carried out a methodology that calculated the potential value of the trunks of olive trees, without bark, to be used as biomass in the form of domestic pellets in a case study carried out in Andalusia (Spain). The obtained pellets complied with the features defined in the Standard ISO 17225-2:2014, classified as type A1/A2, on the basis of olive variety. Furthermore, this study estimated, in 97 years, the ideal bioenergy life cycle by analyzing the amount of sustainably available residues at the end of the olive grove life and optimizing the benefits through an analysis of the costs and profits of the whole process. There are some open issues related to direct combustion: firstly, it represents an inefficient process of energy conversion, producing large biogenic CO<sub>2</sub> emissions—1.7 kg of biogenic CO<sub>2</sub> would be released into the atmosphere per kg of burnt pruning waste, starting from OTP with an average carbon content of 45.3% [53,57,58]. Furthermore, recent studies confirm the permanence of chemicals (e.g., from pesticides) on pruning residues that may not be totally removed through natural weathering, thus increasing the potentially toxic impact of energy production from OTP [53].

#### 2.2. Gasification

Gasification is a technology that realizes a partial oxidation of hydrocarbons based on a controlled amount of steam or oxygen at high temperatures (>700 °C) [59-62]. It does not lead to combustion, and the products are syngas (H2 and CO mostly) and byproducts in the form of condensable organic compounds [53]. Gasification applied to biomass has attracted considerable interest because of the use of a new substrate for this technology [63]. Focusing on the gasification of OTP, Vera et al. [64] modelled a downdraft gasifier and a gas engine grid connected on a small-scale plant, able to produce 110 kW of thermal power and 70 kW of electric power when fueled with 105 kg/h of biomass operating in steady-state conditions. The LHV of the syngas was 3.7 MJ/kg because of the high OTP ash content (8.7%), and it was a relatively low value due to the high air-to-OTP ratio (2.7) that amplified N2 formation. A better performance in terms of syngas LHV was found in a pilot plant located in Andalusia (Spain) through the cogeneration of thermal and electric power through a downdraft gasifier, gas cooling-cleaning stage, and spark ignition engine with a modified carburetor that showed an LHV of 4.8 MJ/kg [65]. An example of local energy self-supply has been carried out in the province of Foggia (Apulia region, Southern Italy) with OTP from a 10 ha olive grove by Zabaniotou et al. [63]. The plant was a gasification-based circular system on a bubbling fluidized bed gasifier, which worked at about 800 °C. The obtained syngas was used for electricity in a microturbine with a Brayton Cycle, producing 34.4 MWh. Biomass storage and tar contamination in syngas represent the current challenges for biomass gasification [66]. A laboratory fixed-bed gasification of

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olive kernels and olive tree cuttings was tested by Skoulou et al. [67]: gas produced via OTP at 950 °C and with an air equivalence ratio of 0.42 showed a higher LHV of 9.41 MJ/Nm³, while olive kernels showed an LHV of 8.60 MJ/Nm³. Olive kernels could be considered a feedstock for carbonaceous material production since they formed more char with a higher content of fixed carbon (16.4 w/w%) than OTP. Nilsson et al. [68] experimented with the gasification of char from OTP in a fluidized bed with temperatures between 760 and 900 °C, adopting gas mixtures containing H<sub>2</sub>O, CO<sub>2</sub>, H<sub>2</sub>, CO, and N<sub>2</sub> in various proportions. The results demonstrated that the inhibition effects produced by CO and H<sub>2</sub> were significant. The reaction rate using H<sub>2</sub>O was 3–4 times higher than that with CO<sub>2</sub>.

## 2.3. Pyrolysis

Pyrolysis works in an inert atmosphere under the absence of oxygen, capturing the off-gases arising from the thermal decomposition of biomass. The matter is divided into smaller sizes under specified operating conditions [69]. Pyrolysis is a very complex process that involves a huge number of chemical reactions within seconds or minutes [70,71]. Products are mainly bio-oils made of hydrocarbon molecules arising from condensed hot vapors, biochar rich in carbon, and bio-syngas [53]. Biochar is mostly used as a soil amendment for agricultural and environmental purposes, while charcoal is used for heat or as a reducing agent in metallurgical applications, as well as an adsorbent material. Zambon et al. [52] obtained biochar via the pyrolysis of OTP pellets with an LHV and HHV of 30.5 and 31.7 MJ/kg, respectively, with a mean conversion rate of 0.21. In a study by Calahorro et al. [72], olive wood sawdust, branch barks, leaves, and twigs (small branches of 1 cm) were subjected to pyrolysis under operating conditions of 400, 500, and 600 °C; a 10 °C/min heating rate; a 20 min residence time; and a 200 cm<sup>3</sup>/min N<sub>2</sub> stream. The high ash and volatile content, together with the low process yield, made the resulting charcoal a low-quality product. The same authors tested charcoal obtained via the pyrolysis of wood (sawdust or cubes), twigs, and branch bark, excluding leaves that were more appropriate to be used for feed cattle: the results showed that charcoal can be recognized as suitable for the manufacture of briquettes. A pyrolysis-based circular system from OTP arising from a 10 ha olive grove produced 8.5 t of bio-oil (LHV of 31 MJ/kg), 9.9 t of syngas, and 7.4 t of biochar (LHV 29 MJ/kg) [63]. A microwave-assisted process of OTP pyrolysis was analyzed by Bartoli et al. [73]: among products, biochar had calorific power up to 25 MJ/kg, while bio-oils showed interesting biochemical compounds, like acetic acid, furans, and aromatics. This last finding represented, for the authors, a potential for reducing the disposal environmental risks of these chemicals and fuels. Furthermore, bio-oils are of great interest since they could substitute diesel in internal combustion engines [63]. The pyrolysis of OTP is largely influenced by lignin content that is difficult to be decomposed, given its slight mass loss over a wide temperature range [74]. Torrefaction is a pretreatment suitable for combustion or pyrolysis applied to enhance biomass properties, limiting its biological degradation and stabilizing it. Chars from pyrolysis registered the higher HHV, with a carbon percentage between 76 and 85 wt%, but also higher ash quantity (ranging from 6 to 9 wt%). Torrefaction had the higher mass yields showing the lowest energy consumption (between 5.8 and 20.8 MJ/kg char) and the highest energy contents with 11 MJ/kg char. Martin-Lara et al. [75] studied the effects of torrefaction (300 °C, 60 min) on the properties of OTP. The results showed an increased ratio of fixed carbon to volatiles, and the elemental analysis showed that the composition of OTP changed from lignocellulosic biomass to coal (i.e., from O/C and H/C ratios of 1.02 and 0.17, respectively, for raw biomass to 0.90 and 0.15 for a torrefied sample at 300 °C). The gaseous phase arising from pyrolysis shows a gas composed of H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub> and some other hydrocarbons, including butane, pentene, hexane, heptane, or toluene [76], that could be used for energy purposes, assuming a theoretical large-scale plant [77].

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## 2.4. HydroThermal Carbonization

HydroThermal Carbonization (HTC), also known as wet pyrolysis, is a form of thermochemical conversion through pressurized water under sub-critical conditions (usually between 180 and 280 °C) and autogenous saturated vapor conditions (10–80 bars), originating from residual biomass into highly dense carbonaceous materials [78] with a high heating value (HHV) and a high carbon content [79–82]. This process generally includes hydrolysis, dehydration, and decarboxylation. At high temperatures and pressures, water experiences a dramatic change in properties and acts more as an organic solvent with an increased ion product that promotes reactions, usually catalyzed by acids or bases, favoring biomass decomposition through hydrolysis, dehydration, and decarboxylation reactions [83,84], followed by condensation, as well as aromatization reactions [66]. Volpe et al. [85] carried out a study to compare HTC and torrefaction in a 50 mL batch reactor and low-temperature pyrolysis (LTP) in a fixed bed reactor with OTP, with the aim of producing performing solid biofuels. The results demonstrated that the hydrothermally obtained biochar (hydrochar hereinafter) had a higher energy densification, whereas the torrefied biochar had a higher mass yield. González-Arias et al. [86] tested three reaction temperatures (220, 250, and 280 °C) and reaction times (3, 6, and 9 h), analyzing the obtained hydrochars to study their behavior as fuel; with reference to O/C and H/C ratios and HHV, the products arising from more severe conditions are comparable to lignite coal, with values of HHV up to 29.6 MJ/kg. The higher stability of the solid is demonstrated by the rise in the activation energy ( $\approx$ 60 kJ/mol) and the ignition temperatures being close to 400  $^{\circ}$ C. Nowadays, this process is a promising technology, being useful in a large range of applications ranging from energy applications to soil improvement and nutrient recovery fields [78]. Environmental uses are mainly used for air or water remediation [87]. González-Arias et al. [88] proposed the application of a waste called off-specification compost (OSC) via Co-HTC (HTC of coal and biomass) with OTP, evaluating the energy recovery. The results showed that the blend of 75% of biomass and 25% of OSC presented good chemical specifications for use as a solid fuel, showing an HHV of 26.2 MJ/kg, which was the best energy yield and energy densification ratio. Saba et al. [89] expanded research into the synergistic effects of coal and miscanthus during HTC monitoring mass yields and energy content through an ultimate and proximate study. Hydrochar generated at 260 °C had LHV (27.3  $\pm$  0.6 MJ/kg) with low sulfur and low ash concentration and was homogeneous according to SEM imaging because miscanthus-derived hydrochar was formed on the coal surface. Furthermore, Co-HTC hydrochars were pelletized in a single-press pellet press: the energy densities of these products were improved to 32.4 GJ/m<sup>3</sup>, with HTC coal having an energy density of 28 GJ/m<sup>3</sup>. Despite these promising applications, this process can find its best application for biomasses with high initial moisture content, since HTC works well under wet conditions [72].

#### 3. Products

#### 3.1. Solid Materials

High porosity, high carbon content, high surface area, low thermal conductivity, renewability, high stability, and bulk density make char a sustainable coal-like solid: it has less calorific value than standard coal, but produces less ashes during the combustion process [90]. Several studies investigated the effects of residence time and reaction temperature on hydrochar mass yields and features [83,91–93], asserting that the principal contribution to biomass degradation and, thus, the increase in the calorific value, is represented by the reaction temperature rather than the residence time [94]. Lucian et al. [91] noted an improvement in the heating value of olive trimming from 22.6 to 27.8 MJ/kg when the temperature of HTC was raised from 180 to 250 °C. The high reaction temperature and energy consumption represent an issue with the advance of HTC technology. Conventional batch reactors couple pressure and temperature at saturated states. Yu et al. [27] have developed Decoupled Temperature and Pressure Hydrothermal (DTPH) reactions through a method that decreased the temperature of the HTC reaction of lignocellulosic biomass (poplar

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leaves and rice straw). The results allowed us to realize HTC at a temperature of 200 °C in spite of the lower bound of 230 °C adopted in the conventional process. The scientific community is concentrating on developing supercapacitors with activated carbon derived from olive pruning that can provide an improvement in energy storage in terms of the specific area and surface composition [72]. The results of OTP application as a supercapacitor electrode [95,96] represent a promising method of developing competitive energy storage devices based on agro-industrial wastes. Activated carbon, obtained through KOH [95], reached a BET surface of 4083 m<sup>2</sup>/g and, when applied as a supercapacitor electrode, generated a high specific capacitance of 264.4 F/g at a current density of 0.5 A/g, with high values of energy density (17.8 Wh/kg) and power density (65 W/kg). An excellent performance supercapacitor was demonstrated by electrode materials derived from OTP with chemically activated carbon working as electrode material and PVA-KOH hydrogel working as an electrolyte: they present a capacitance of 1.15 F at 5 mA, a voltage of 1.2 V, and equivalent series resistance of 1.42  $\Omega$  [96]. OTP-activated carbon was also applied as a detoxifying agent, allowing the elimination of inhibitory compounds prior to fermentation of the hydrolyzed liquid for ethanol production [86]. The removal quantities of inhibitor compounds were 89.2%, 91.8%, and 32.6% for polyphenols, furfural and hydroxymethylfurfural, respectively. Biochar pellets arising from wood pellets have been found to produce an HHV equal to 31.5 MJ/kg [97]. Biochar production via biomass pyrolysis is a practical and attractive process for storing carbon and lowering greenhouse gas (GHG) emissions, and its stability (carbon recalcitrance) represents a significant characteristic that determines the carbon sequestration capacity [69]. Char is expected to have an even larger market in the next few years: the breakeven selling price of Co-HTC hydrochar was found USD 117 per ton for a 110 Mwe, and sensitivity studies indicated that it can reach USD 106 per ton for a higher capacity plant [89]. The lignocellulosic composition of OTP presents high thermal stability, resulting in higher mass yield (approx. 50%) and fixed carbon (9%) with respect to protein-based and fruit wastes [78].

## Biochar and Hydrochar

Biomass can be thermochemically converted into stable carbon-rich byproducts [98] with valuable applications [99,100], such as biochar through slow-pyrolysis, gasification, and hydrochar through HTC [98]. The char produced via these two operating processes results in a product with different physical and chemical properties that affect the effects in carbon sequestration, bioenergy production, soil amelioration, and wastewater pollution remediation [98]. The biochar arising from gasification shows a high amount of alkali and alkaline earth metals (Ca, K, Si, Mg, etc.) and polyaromatic hydrocarbons (PAHs), which are recognized to be highly toxic compounds due to their high-temperature reactions [101]. The high alkali and alkaline earth metallic composition of biomass shows hazardous behavior, such as klinker formation, slagging, fouling, corrosion, etc., during biomass combustion [102], and, thus, their presence represents a crucial challenge for applications in the energy sector. Hydrochar has a reduced alkali and alkaline earth and heavy metal concentration, together with an improved HHV with respect to the biochar produced at the same operating process temperature and is, thus, considered superior to biochar for some aspects.

#### 3.2. Liquid Materials

OTP lignin extracted using deep eutectic solvents (DES) is a promising environmental-friendly method [103]; the product of reaction shows a high antioxidant activity. As a sugar-rich matter with low lignin content and high cellulose content, olive pruning debris represent an excellent substrate for bioethanol production. With respect to the first and third generation of bioethanol production from lignocellulosic biomass, it has the advantage of reducing the cost of raw materials and proposing suitable solutions for environmental problems when agro-industrial wastes are processed [104]. Actually, the process includes four stages: pretreatment, hydrolysis, fermentation, and ethanol concentration [53,105].

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The pretreatment of lignocellulosic biomass is a crucial step in both technical and economic terms [39], being necessary because of its intrinsic recalcitrant nature to degradation, in turn necessary for the production of valuable chemicals [106]. The beginning of the pretreatment stage is the breakdown of hemicellulose to sugars, followed by the opening of the structure of the cellulose. Lignin can be extracted from cellulose through an alkaline solution with oxidizing agents, such as  $H_2O_2$  [107]. This process reduces the volume of the hydrolysis reactor and increases sugar content, reducing energy demand during cellulose hydrolysis. Major pretreatments include ultrasound, ozonation, steam explosion, extrusion, diluted-acid hydrolysis [108-113], alkaline peroxide pretreatment, autohydrolysis or liquid hot water pretreatment [53,114], electron beam, gamma ray, microwave, high hydrostatic pressure, high-pressure homogenization, and pulsed-electric field [106]. Two of the most widely adopted pretreatment methods are steam explosion and liquid hot water: results published by Romero-Garcia et al. [39] show that they performed similarly, even though the second one yielded the highest overall sugar recovery, i.e., 92%, at a lower operation temperature (180 °C) versus 80.4% for steam explosion at 220 °C. Ethanol production resulted in a solution of about 4.4% (v/v) with a yield that was slightly better for steam explosion-pretreated samples, i.e., 72%, compared to 63% in liquid hot water samples, albeit at different temperatures (220 °C against 200 °C). Mineral acid hydrolysis can penetrate lignin without pretreatment and more quickly than enzymatic hydrolysis; on the other hand, it occurs under mild conditions of temperature (between 40 and 50 °C) and pH (around 5.0) [53]. Fermentation follows hydrolysis. Scheffersomyces stipites and Escherichia coli are the yeasts mainly used to ferment pre-hydrolysates derived from olive pruning [115,116]. The ethanol yield from the fermentation of hemicellulosic sugars solubilized in the pretreatment stage, plus the simultaneous saccharification and fermentation of pretreated cellulose, is around 0.16 kg/kg of olive pruning waste [115–117]. Ethanol concentration obtained by Candida sake BCs88 was found to be 3.3 g/L [95]. The use of enzymes and two fermentation stages makes the production of ethanol from OTP practically negligible due to economic non-feasibility [53]. Martínez-Patiño et al. [115] used a pretreatment as follows: 0.9% H<sub>2</sub>SO<sub>4</sub>, 164 °C, 10 min, and 15% solid concentration, followed by 15 FPU Cellic-Ctec3 enzymatic hydrolysis and the fermentation of slurry with Escherichia coli. Fernandes-Klajn et al. [118] pretreated OTP with 1.4% NaOH (110 °C, 30 min) and 0.9% H<sub>2</sub>SO<sub>4</sub> (164 °C, 10 min) in slurry, detoxification with NH<sub>4</sub>OH 5 N, 5% solid concentration adopting pre-saccharification and co-fermentation configuration with 15 FPU Cellic CTec-2, supplemented by  $\beta$ -glucanase, and Escherichia coli. OTP is also a source of mannitol (around 1–5.2%) [118–120]. A study by Servian-Rivas et al. [49] focused on the environmental assessment and economic performance of two biorefinery schemes, using 100 t/day of olive tree pruning waste as feedstock, based on a multiproduct biorefinery producing ethanol, xylitol, and antioxidants on one hand, as well as standalone production of antioxidants on the other hand. The results showed that antioxidants produced from OTP are promising in terms of both environmental performance and process economics with respect to the multiproduct scheme.

# 3.3. Gaseous Materials

A low C/N ratios and high concentrations of nitrogenous matter make olive pruning suitable for anaerobic digestion. Nevertheless, only the finest particles of pruning debris are considerable for methane production. They are produced through a fractionation process, followed by batch anaerobic digestion at 38 °C. The process is recognized to be highly energy efficient, with the highest methane yield achieved equal to 176.5 Nm³ per t of volatile solids [55]. Biomass typically contains 6% hydrogen by weight and lends itself to both thermal and biological conversion processes to this energy vector: direct gasification and pyrolysis represent the thermal way to produce hydrogen, while fermentation and bio-photolysis are the biological paths. Other routes [121] are new technologies such as microwave gasification, solar gasification, integrated pyrolysis-gasification, plasma gasification, and catalytic gasification. Wood gasification on a fixed bed without a catalyst

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showed a hydrogen yield of 7.7% at 550 °C [12]. A hydrogen-rich syngas produced from the lignocellulosic biomass via catalytic gasification was investigated by Ghodke et al. [121]. They carried out an investigation into the performance of several lignocellulosic biomass gasification systems with and without catalysts. An aspect to be considered for the gasification process is tar production. Tars are high-molecular-weight hydrocarbons, constituting undesirable by-products of gasification. Methods to minimize their formation are catalysis, pretreatment technologies, and the optimal design of both gasifier and operating conditions [12]. Several catalysts (as oxides of calcium) increased syngas quality and quantity, reducing tar and carbon deposition; alkali and alkaline earth metal catalysts significantly reduced tar production, as well as resistance to the carbon deposition, while Ni and alkaline metals were used as standalone catalysts in dry and steam gasification and gave a good performance in the hydrogen concentration in syngas [121]. A gasification method using a metal oxide sorbent, such as calcium oxide, water gas shift (WGS), integrated with steam-hydrocarbon reaction, and CO<sub>2</sub> absorption in a single reactor received considerable attention: the presence of a metal oxide sorbent can involve an in situ CO<sub>2</sub> capture, and, if properly designed, the exothermic CO<sub>2</sub> absorption can be coupled with the endothermic biomass gasification reaction [12]. This principle is at the basis of HyPr-RING (hydrogen production via reaction-integrated novel gasification), a technology that adopts chemical looping with the calcium cycle, in which CaO (or Ca(OH)<sub>2</sub>) captures CO<sub>2</sub> during coal gasification to form CaCO<sub>3</sub> and release heat for gasification to produce near pure hydrogen in one gasifier [122]. Crossflow tube reactors represent a special design for producing hydrogen via ethanol steam reforming. Nevertheless, these reactors would yield a high concentration of carbon monoxide, detrimental to applications of the gas arising from steam reforming, especially hydrogen purification. This technical issue can be overcome with a water gas shift reaction unit installed in the steam reformer. The results show that in the system combined with ethanol steam reforming and water gas shift reaction, the steam/ethanol ratio of 3 is ideal for hydrogen production and CO reduction with low reaction temperatures favorable for hydrogen production [80]. A study analyzed the best pretreatment conditions required for OTP to produce bio-hydrogen [123]. The results demonstrated that the best hydrogen yields were 0.83 and 0.91 mol H<sub>2</sub>/mol, reducing sugar for oxalic acid pretreatment and sulfuric acid pretreatment, respectively, showing the potential of OTP to be used in bioenergy production.

#### 4. Discussion

#### 4.1. Process Analysis Summary

Table 1 summarizes the operating characteristics of the four thermochemical processes. Combustion is the method with the highest operating temperature values, while gasification works for a very short time with respect to the other processes. Pyrolysis and HTC produce valuable products as solid, liquid, and gaseous matter. Regarding gas, gasification shows the best yield.

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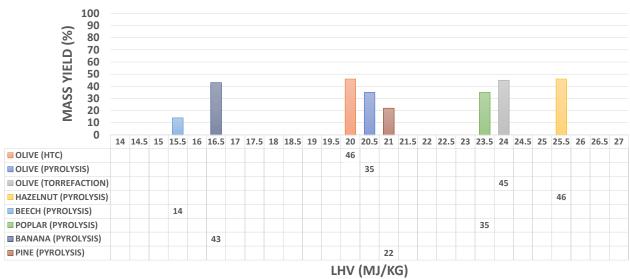
Thermochemical Process	Operating Temperature (°C)	Pressure	Time (Range)	Oxidizing Agent	Byproducts	Ref.
Combustion	750–1500 °C	0-0.6 MPa	/	oxygen	ashes	[21,54]
Gasification	600−1200 °C	/	10–20 s	oxygen	char: <10% and condensable organic compounds	[21,59–62,105]
Pyrolysis	400–600 °C	0–13 MPa	0.3–1 h	absent		[21,44,52]
HTC	220–350 °C	0–13 MPa	1–9 h	vapor steam		[21,44]

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# 4.2. Energy Analysis

In this section, several parameters have been investigated, such as mass yield and LHV among several lignocellulosic crops, HHV contained in char arising from different process treatments (pyrolysis, torrefaction, and HTC), and syngas yield for the same processes. With reference to Figure 1, olive, hazelnut, beech, poplar, banana, and pine char production from the pyrolysis process have been compared, as have HTC and torrefaction of olive pruning. Olive torrefaction shows the best compromise between LHV and mass yield, followed by poplar with an important decrease (10%) for mass yield. Hazelnut has the best performance for both measures. The worst performance is for beech with the lower mass yield and LHV. Banana has a very good mass yield but a relatively low LHV. Finally, pine shows a low mass yield with an LHV that is in the middle of the reported values.

# CHAR PRODUCTION: EFFECTIVE ENERGY FOR LIGNOCELLULOSIC CROPS



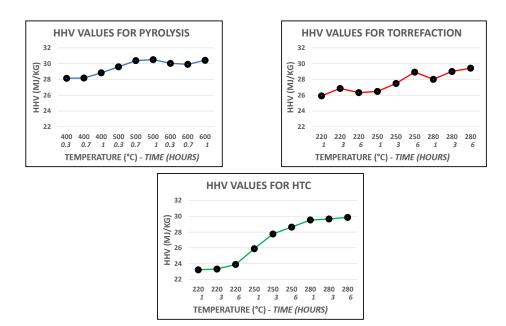
**Figure 1.** Effective energy for several lignocellulosic crops for char production. Data sources: olive HTC, olive pyrolysis and olive torrefaction [44], hazelnut pyrolysis [52], beech pyrolysis [124], poplar pyrolysis [125], banana pyrolysis [126], and pine pyrolysis [127,128].

Figure 2 shows the HHV values as a function of operating conditions, temperature, and time for each OTP process (pyrolysis, torrefaction, and HTC). Data are extracted from Table 1 of [44]. In Figures 2 and 3, the first values on the X-axis represent the temperature (400, 500, and 600 °C for pyrolysis and 220, 250, and 280 °C for torrefaction and HTC), whereas the second values are referred to the time as a fraction of an hour (0.3, 0.7, 1, 3, 6). Figure 2 shows that HHV values for pyrolysis are not severely affected by the operating conditions, since the trend is always higher than 28 MJ/kg, with a slight improvement after 500 °C for 0.7 h. Torrefaction has an increase starting from 250 °C for 6 h. HTC shows an increasing trend linked to the increasing temperature with an evident change in the slope of the curve starting from 220 to 250 °C.

Figure 3 represents the syngas yield produced from OTP under different operating conditions. Pyrolysis shows the best performance, with a constant trend always over 44.6%, with a slight decrease from 400 to 500  $^{\circ}$ C. Torrefaction increases syngas production from 250  $^{\circ}$ C (+8.4%), while HTC is not a good process for syngas generation because values are around 10%.

Figure 4 illustrates the energy yield (EY) referring to OTP feedstock under different operating conditions of HTC [86]. EY represents an important parameter used to assess the effect on solid fuel production, giving information about the energy recovery and the efficiency of the treatment. The graph follows an overall decreasing trend from the least severe treatment (220  $^{\circ}$ C, 3 h) of EY from 47.7 to 31.9% at 280  $^{\circ}$ C for 6 h, with peaks in correspondence with the longer time (9 h) for each one of the three tested temperatures.

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**Figure 2.** Comparison of HHV values for pyrolysis, torrefaction, and HTC under different operating conditions. Data source: [44].

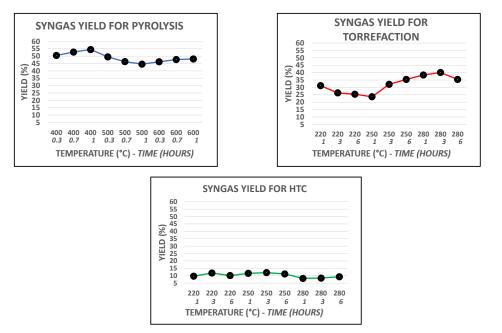


Figure 3. Syngas yield from OTP after pyrolysis, torrefaction, and HTC processes. Data source: [44].

In order to make a comparison between the main technologies used for the energy conversion of olive wood biomass, an energy analysis was carried out. In particular, LHV is calculated, starting from the chemical composition of the sources reported in Table 2, through the following formulas [129]:

$$LHV = HHV [1 - (w/100) - 2.447(w/100) - 2.447(h/100)9.01[1 - (w/100)]]$$
 (1)

Whereas

$$HHV = 0.3491XC + 1.1783XH + 0.1005XS - 0.0151XN - 0.1034XO - 0.0211Xash$$
 (2)

where HHV is the higher heating value, w is the moisture content (%); h is the hydrogen content (%); and XC, XH, XS, XN, XO, and Xash are the mass fraction on dry basis, re-

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spectively, of carbon, hydrogen, sulfur, nitrogen, oxygen, and ashes. For syngas LHV, the formula is [130]

$$LHV = (12.622CO + 10.788H_2 + 35.814CH_4)/100$$
 (3)

where CO,  $H_2$ , and  $CH_4$  are expressed as % of volume. With reference to Table 2, the yield is referred to as kg of solid product or  $Nm^3$  of syngas obtained through the processes. The LHV is for 1 kg or  $Nm^3$  of each product considered in the table, while the effective energy is the result of the mathematical product between yield and LHV. Energy for the process is referred to as the energy necessary to process 1 kg of olive wood. Energy balance is the result of the difference between effective energy and energy for the process. All values are calculated with respect to the functional unit of 1 kg of olive wood.

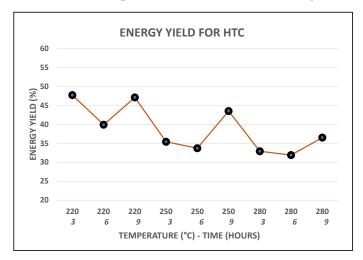


Figure 4. Energy Yield (EY) from OTP after HTC process. Data source: [86].

**Table 2.** Energy analysis of the main technologies used for the optimization of olive wood biomass for energy purposes.

	Chips	Pellet	Hydrochar	Char from Pyrolysis	Char from Torrefaction	Syngas	Refs.
YIELD (kg <sub>product</sub> or Nm <sup>3</sup> , syngas/kg <sub>olive wood</sub> )	1	0.8	0.46	0.35	0.45	2.5	[44,62,131]
LHV (MJ/kg <sub>product</sub> )	14.2	17.8	21.0	21.3	23.8	4.1	[44,54,124,132]
EFFECTIVE ENERGY (MJ/kg <sub>olive wood</sub> )	14.2	14.3	9.7	7.4	10.7	10.3	
ENERGY FOR THE PROCESS (MJ/kg <sub>olive wood</sub> )	0.04	1.4	3.9	1.4	3.3	0.04	[44,52,133,134]
ENERGY BALANCE (MJ/kg <sub>olive wood</sub> )	14.1	12.9	5.8	6.0	7.4	10.3	

# 5. Conclusions and Future Perspectives

All thermochemical treatments of OTP change the initial structure of the biomass, allowing products to be evaluated as energy fuel. Torrefaction represents a good compromise between mass yield and LHV, as reported in Figure 1, but it is only a profitable process for energy purposes if the solid phase is considered as a valuable output. Among the three processes considered for OTP in Figures 2 and 3, namely pyrolysis, torrefaction, and HTC, the first one shows the best performance for both char HHV and syngas yield

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under different operating conditions, even though it is a process that concentrates inorganic matter in the char, resulting in higher ash concentration with respect to HTC and torrefaction. Regarding the energy analysis results, the optimal energy balance is obtained through chips and pellets and, thus, the use of combustion as a process of wood conversion. Nevertheless, OTP pellets also have high ash content due to the leaf and soil contamination arising from the harvesting stage, leading to a slight decrease in the boiler efficiency. The choice of chips would reduce the supply chain by one step compared to pellets, avoiding the industrial processing necessary to compress wood chips, but on the other hand, the storage of chips can lead to biological deterioration phenomena, which risk reducing part of the biomass in terms of effective weight, making it unusable. The energy balance is also influenced by the pretreatment necessary to dry the biomass. HydroThermal Carbonization does not require drying of the biomass like combustion, gasification, or pyrolysis. Thus, an important aspect to be taken into account is the water content: the higher the water content of the wood, the lower its LHV. As for hydrochar and biochar, their characterization is fundamental for industry and the environment: a biochar with low carbon content and high ash content is not suitable for use in energy products. On the other hand, a biochar that shows a high adsorption capacity and high surface area is highly suitable for agriculture and wastewater treatment. The amount of alkali and alkaline earth metals is related to the ash percentage in the raw feedstock; thus, the challenge is to reduce their presence in ash composition, making char highly advantageous when used for energy production. In a circular economy perspective, the efficient use of wastewater arising from the HTC process represents a challenge for the application of this technology on an industrial scale. Recirculating water from the HTC process could solve this problem, reducing wastewater treatment cost and recovering heat. Actually, excluding combustion, gasification seems to be the most appropriate technology to optimize olive wood for the advantage of enabling the cogeneration of electricity and heat. In addition, natural gas or oil-fired boilers do not continuously operate and lead to significant combustion problems stemming from the high production of NOx and CO; with a gasifier, the production of pollutants is greatly reduced because of the lower percentage of nitrogen. While gasification represents the energy optimization of olive wood biomass among conversion technologies, the enhancement occurs in biochar because it represents a value-added product, the quality and versatility of which can find a wide market of applications, ranging from soil conditioners to additives for supercapacitor construction. In particular, biochar is an attractive material because it has low thermal conductivity, high surface area, high porosity, high stability, and high carbon content. Bioethanol is a potentially strategic fuel, but the use of two enzymes and two fermentation steps does not make bioethanol production from olive wood economically feasible. Technologies for producing hydrogen-rich syngas show signs of promise, but they still need to be improved in terms of selectivity, efficiency, and cost-effectiveness.

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