

Article

Lignocellulosic Residues from Fruit Trees: Availability, Characterization, and Energetic Potential Valorization

Gianluca Cavalaglio ¹, Giacomo Fabbri ^{2,*}, Filippo Cardelli ², Leonardo Lorenzi ², Mariarosaria Angrisano ¹ and Andrea Nicolini ²

¹ Department of Engineering, Pegaso Telematic University, 80143 Naples, Italy

² CIRIAF-CRB (Biomass Research Centre), Department of Engineering, Università degli Studi di Perugia, via G. Duranti, 67, 06125 Perugia, Italy

* Correspondence: giacomo.fabbri@unipg.it

Abstract: Reducing the carbon footprint of energy production is one of the most pressing challenges facing humanity today. Lignocellulosic biomass residues from fruit production industries show promise as a viable energy source. This paper presents a study of the Italian context concerning the utilization of orchard lignocellulosic residues for energy production as electricity or bioethanol. The potential of various orchard residues was assessed through chemical and physical analyses, and an equivalent electrical energy of about 6441.62 GWh or an amount of 0.48 Mt/y of bioethanol was obtained based on the average annual dry residue mass availability of about 3.04 Mt/y. These data represent 9.30% of the national electrical energy production from renewable sources, as well as 6.21% of the Italian demand for gasoline in 2022. Electricity generation from these residues has shown its potential as a reliable and sustainable baseload power source, as well as a source of renewable transportation fuel. The studied process could be a valuable reference to expand these concepts on a global scale to achieve a greener and more sustainable energy future.

Keywords: biofuels; bioenergy; agricultural orchards residues; bio-based economy; fruit production estimates; allocated lands



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1. Introduction

Recurring energy crises highlight the importance of diversifying energy sources. Achieving energy parity is difficult for countries that strongly rely on fossil fuels [1]. Biomass has long been recognized as a renewable energy source that can help bridge this gap while minimizing greenhouse gas emissions due to its distinct advantages, including carbon neutrality, carbon sequestration, energy storage capabilities, higher energy density, residue utilization, and the potential for baseload power generation providing a constant and consistent energy supply [2]. There is a growing interest in using agricultural residues among the various types of biomass due to their abundance and no competition with food industries [3,4]. Orchard residues offer an untapped opportunity for sustainable energy generation and the Italian context is a good case scenario due to its abundant fruit industry. This study aims to quantify the amount of energy that can be achieved from the exploitation of these residues, thereby shedding light on the potential of the fruit industry residues as a key energy resource. To perform this evaluation, data on the production scale and yield of the Italian fruit industry were collected from reliable sources, including governmental reports and industry databases, estimating the yearly available amount of lignocellulosic residues. Furthermore, detailed information on the chemical composition and physical properties of orchard residues was analyzed to assess their suitability for energy conversion processes. The energy retrieval potential is estimated by considering two valorization pathways, cogeneration and biofuel production through the availability assessment of lignocellulosic biomass orchard-derived residues and their energy retrieval potential in

the Italian fruit industry scenario. This study aims to contribute valuable insights into sustainable energy generation.

1.1. Background Context

Italy has historically been one of the main fruit-producing countries in Europe and the Mediterranean area, owing to its orographic and climatic conditions, accounting for 20.5% and 34.3% of European total fresh fruits and nuts production, respectively [5]. As a consequence, the country also generates a large amount of lignocellulosic residues from fruit production activities, which are usually burned or buried and rarely used as animal feed [6,7]. Burning prunings, although sometimes tolerated, is an illegal waste disposal method that can negatively impact the air quality [8] and pose a fire risk, particularly in dry periods [9]. This practice can also lead to decreased soil fertility and necessitates the addition of appropriate nitrogen fertilizers [10]. Shredding residues in the field may also have potential negative effects, such as increasing the occurrence of fungal diseases [11]. Harvesting, storing, and further using prunings to produce energy in the form of heat and electricity is a feasible and promising option that is still largely unexploited in several countries, including Italy, and has potential as a renewable energy source when applying circular economy principles [12]. Lignocellulosic residues from the fruit industry, properly stored and treated as wood chips, pellets, or briquettes, can be used as fuel in boilers for heating and/or water vapor production, which can be used in a thermodynamic turbine-alternator circuit to generate electricity [13]. Lignocellulosic residues can also be used to produce liquid biofuels, such as biodiesel, bioalcohols (e.g., bioethanol, biomethanol, biobutanol), biogas, and syngas [12,14]. However, the suitability of residues for these purposes depends on their constituent structures, particularly regarding their cellulose, hemicellulose, and lignin contents [15]. Due to its Mediterranean climate, the Italian fruit industry primarily produces olives, grapes, and citrus fruits, which also account for substantial volumes in relation to European and global productions [7]. In minor quantities, the industry also produces apples, peaches, cherries, plums, apricots, and other fruits in smaller quantities. Italy is among the top European producers of dried fruits, including hazelnuts, almonds, walnuts, as well as pistachios and pecans [7,16]. In the ISTAT Annual Report 2021 [17], the annual production of fruits in Italy is reported. The dataset covers the five-year period from 2016 to 2020. From the subsequent analysis of these data, the produced mass (shown in kilotonnes (kT)) of the most important productions, such as olives, grapes, and citrus fruit, were excluded because alone they account for $79,884 \pm 4581$ kT, $25,577 \pm 3090$ kT, and $27,034 \pm 1704$ kT, respectively, produced on average between 2016–2020. The secondarily important fruits, such as apricot, cherry, peach, nectarines, plum, apple, pear, actinidia, almond, hazelnut, and carob jointly produce 5319 ± 597 kT of fruit mass on average per year in the same period. Figure 1 shows data reported in the ISTAT Annual Report 2021 [17], illustrating the annual production of the secondarily produced fruits in Italy.

In the ISTAT Annual Report 2021 are also available data regarding the amount of allocated land per fruit species in hectares for the same investigated period. Figure 2 displays the data indicating the hectares of land allocated to produce each of the main fruit species produced in Italy. The data are presented on average. As well as in the case of the harvested produced mass of fruit, also in this case, the data regarding olive, grapes, and citrus fruit production were excluded from the analysis because they account for $681,000 \pm 12,000$ ha, $1,144,000 \pm 3000$ ha, and $138,000 \pm 9000$ ha, respectively, on average on the 2016–2020 five-year period.

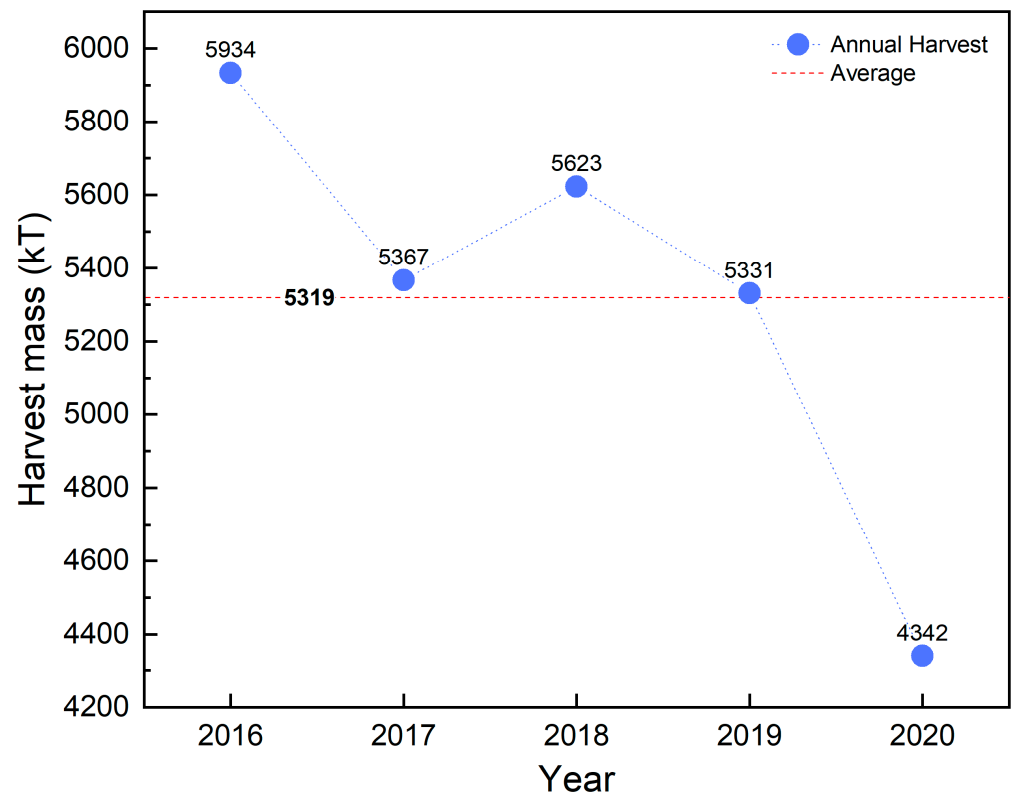


Figure 1. Annual production of the secondarily produced fruits in Italy. Data are obtained from the ISTAT Annual Report 2021 [17].

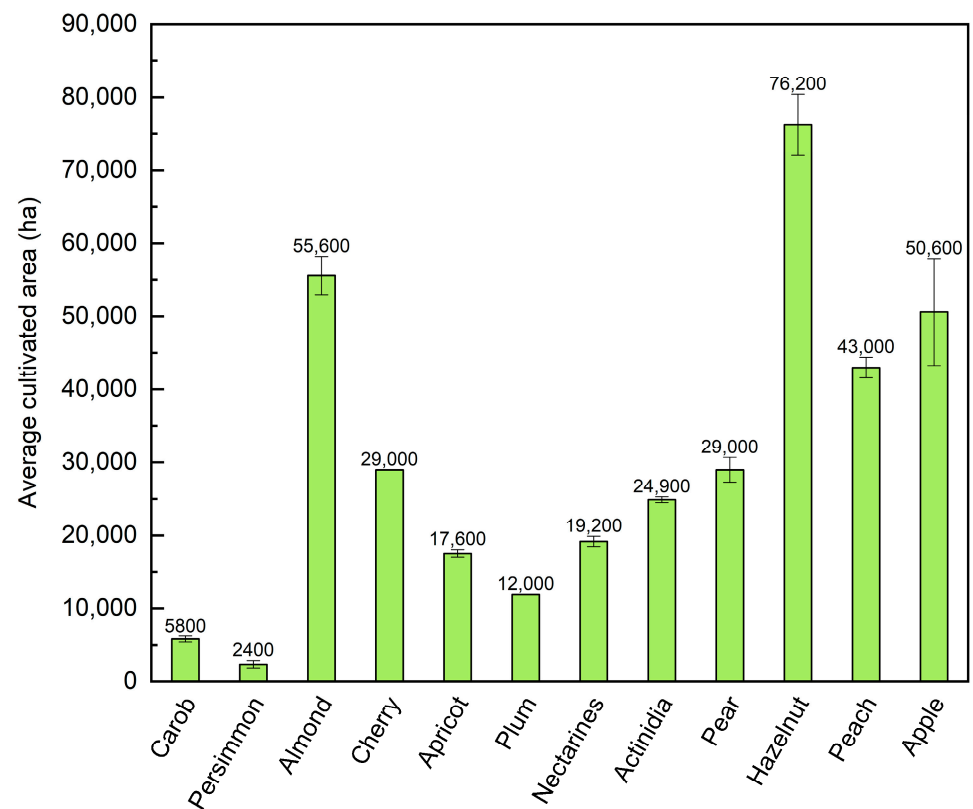


Figure 2. The cultivated area for fruit production in Italy is broken down by the main species on average. Data are obtained from the ISTAT Annual Report 2021 [17] and are referred to as the period 2016–2020.

Figure 2 was further analyzed to determine the distribution in the percentage of areas on a total average area allocated for the fruit production of $365,400 \pm 9972$ ha. The results are presented in Figure 3. These data illustrate the percentage distribution of the average land area that is allocated to the cultivation of each one of the fruit species in Italy between 2016 and 2020. The joint amount of hazelnut-, almond-, and apple-allocated areas represents half of the total allocated area, with an average value of $49.92 \pm 0.03\%$.

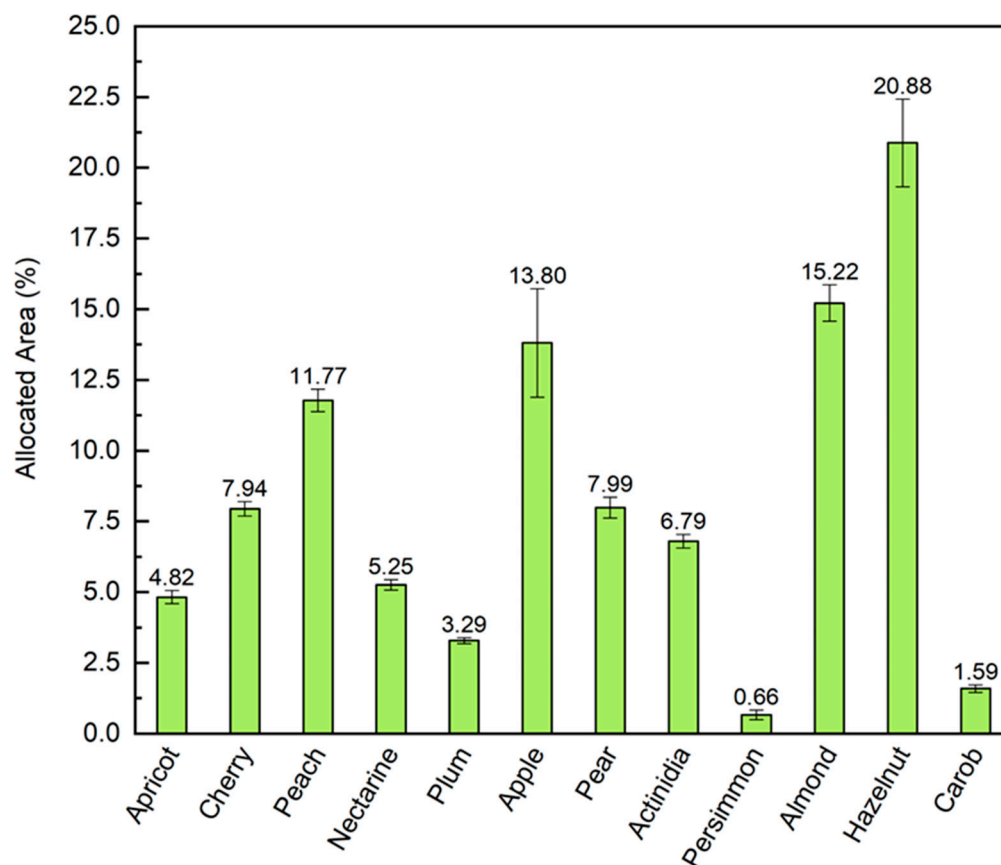


Figure 3. The percentage distribution of areas allocated to fruit cultivation per species in Italy. Data are obtained from the ISTAT Annual Report 2021 [17] and are referred to as the period 2016–2020.

All data reported by ISTAT [17] were compared with other data from other sources regarding the area cultivated in Italy. The joint report by the National Agency for the Protection of the Environment (ANPA) and the National Observatory on Waste (ONR) entitled “Waste in the agro-food sector—Sector study” [18] was used to collect data. According to this report, in Italy, 15,000 ha of land is allocated to apricots, 95,000 ha to peach, 12,000 ha to plums, 65,000 ha to apples, 45,000 ha to pears, and 70,000 ha to hazelnut orchards. The Biomass Research Centre (CRB) provided additional data on the allocated area in its “NPBAEU-CRB” [19], indicating that 93,000 ha, 62,000 ha, 43,000 ha, 87,000 ha, and 69,000 ha (according to ITABIA estimates) are allocated, respectively, to produce peach, apple, pear, almond, and hazelnut. In the end, Di Blasi [20] collected more data, indicating that 82,000 ha, 39,900 ha, 78,700 ha, 118,200 ha, and 69,300 ha of land are allocated to apple, pear, peach, almond, and hazelnut production, respectively. These data were collected and reported in Figure 4 for comparison purposes. The process of collecting and estimating data is different from report to report; for this reason, there is a fluctuation in the values. For a further comparison, in Figure 4, the average data value was plotted. As in the previous dataset, the area allocated to olives, grapes, and citrus fruit production was not taken into consideration.

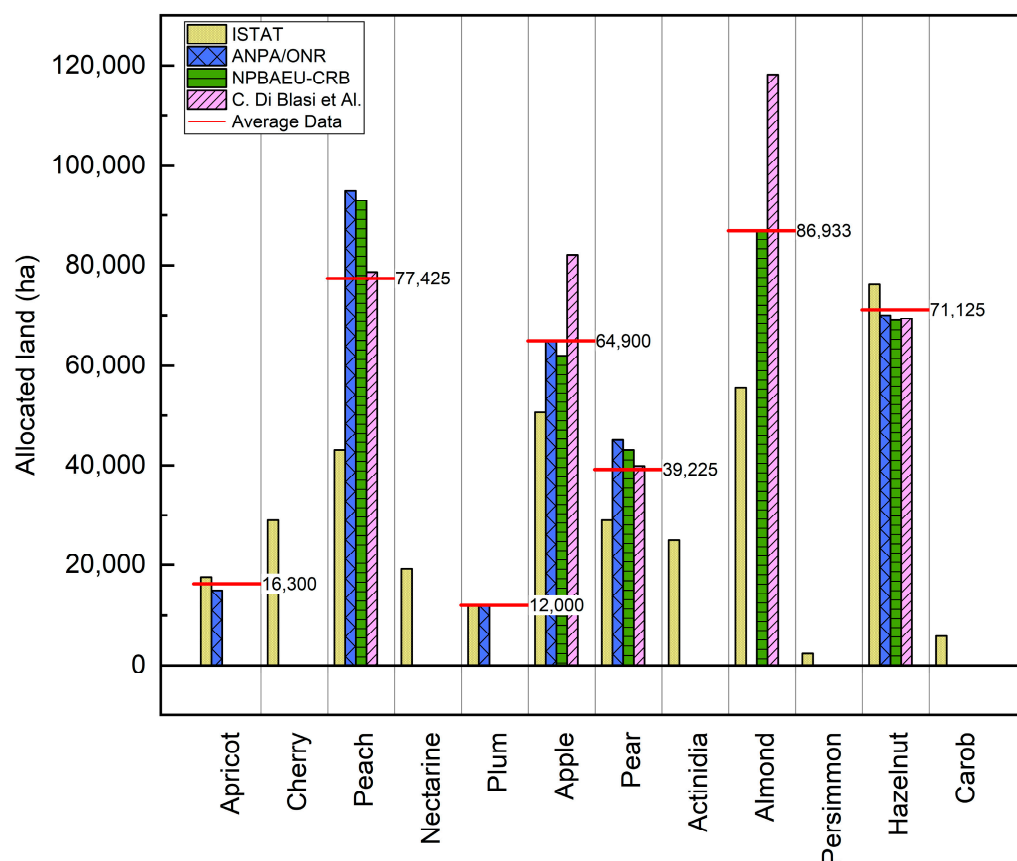


Figure 4. Data comparison between different studies about the allocated area for fruit production in Italy. The average data are reported as a red stick at the corresponding value. C. Di Biasi et al. [20].

1.2. The Lignocellulosic Residues from Fruit Industries

To properly maintain a productive orchard, it is necessary to perform a periodical pruning campaign. Pruning residues can be distinguished into different types based on their pruning methods and based on chemical characteristics, which vary depending on the fruit tree species selected. Generally, residues have a moisture content between 35% and 45% at the time of harvest, gravimetrically measured in an oven at 50 °C until reaching a constant weight [12]. An accurate estimation of residual biomass quantities is crucial for the effective planning of biomass energy strategies [21]. Table 1 shows the estimates of annual lignocellulosic residues' mass production derived from the prunings of various fruit tree species in Italy. The data were obtained from different sources and pertain to different time periods. However, the estimates are largely similar and can be considered reliable references. An average data of dry residues produced yearly for each species is reported without considering data for fresh prunings.

Table 1. Estimates of annual lignocellulosic pruning production from fruit trees in Italy. Different datasets are reported in this table. Specification of the data and the source are included in the legend table.

Prunings	A (Mt/y)	B (Mt/y)	C (Mt/y)	D (Mt/y)	E (Mt/y)	F (Mt/y)	G (Mt/y)	H (Mt/y)	Average (Mt/y)
Grape	2.90	1.50	1.28	1.11	1.19	1.47	1.58	0.88	1.29 ± 0.23
Olive	2.40	1.20	1.14	1.07	1.15	1.34	1.43	0.80	1.16 ± 0.19
Apple	0.20	0.10	0.09	0.13	0.12	0.29	0.28	0.09	0.16 ± 0.08
Pear	0.10	0.05	0.05	0.05	0.03	0.18	0.17	0.05	0.08 ± 0.05
Peach	0.20	0.10	0.16	0.19	0.14	0.46	0.42	0.15	0.23 ± 0.13

Table 1. Cont.

Prunings	A (Mt/y)	B (Mt/y)	C (Mt/y)	D (Mt/y)	E (Mt/y)	F (Mt/y)	G (Mt/y)	H (Mt/y)	Average (Mt/y)
Lemon	0.30	0.20	0.19	0.67 *	0.67*	0.77 *	0.80 *	0.48	0.29 ± 0.13 (0.73 ± 0.06) *
Almond	0.20	0.10	0.15	0.12	0.12	0.22	0.12	0.09	0.13 ± 0.04
Hazelnut	0.20	0.10	0.07	0.14	0.09	0.22	0.17	0.08	0.12 ± 0.05
Total	-	-	-	-	-	-	-	-	3.46 ± 0.37

Table Legend

Column name	Content and references
A	Fresh prunings estimated mass by Di Blasi [20]
B	Dry prunings estimated mass by Di Blasi [20]
C	Dry prunings estimated mass by ITABIA [19]
D	Dry prunings estimated mass by CRPA [19]
E	Dry prunings estimated mass by ANPA ONR [18]
F	Dry pruning mass, including the contribution of the residual biomass at the end of the production cycle. Estimate by CRPA [19]
G	Dry pruning mass, including the contribution of the residual biomass at the end of the production cycle. Estimate by ANPA ONR [18]
H	Dry residues estimated mass by ITABIA [22]

* Residues from citrus fruit trees and not only from lemons.

Columns A and B present data on the total quantity of residues produced in the wet state immediately after cutting and in the dry state, respectively [20]. The total quantity of green residues (column A) was estimated by multiplying the specific production of residues (expressed in t/ha) [20] by the invested area. The data in column B were derived by considering the moisture percentage of the green residue. The data in columns C, D, and F were obtained from the ITABIA reports. Column C reports the data that considers the dry residue that is estimated to be effectively available for energy production over a three-year period (2000–2002). The actual availability of dry residue from fruit tree pruning might be 45–50% of the maximum potential availability due to logistical–economic considerations, allocation of different production areas, size of companies, and their organization [19]. Column D presents data processed by the Agency for Protection of the Environment and Technical Services (APAT), which merged in 2008 into the ISPRA Higher Institute for Environmental Protection and Research. The data shows the availability of dry residue referring to the year 2002. Finally, the data of column F were processed considering the lignocellulosic biomasses also coming from the final tree cut. The data in columns E and G were processed by the National Agency for the Protection of the Environment (ANPA) and the National Observatory on Waste (ONR). In column E, only pruning waste was considered, while in column G, contributions of wood at the end of the production cycle were considered [18]. The two separated datasets were obtained based on the calculation of regional masses of residues from the statistical data relating to agricultural production, integrated with the bibliographic data on the relationship between the number of residues per unit of product (by-product/product ratio). To obtain the dataset of column G, an elaboration was carried out taking into account for each fruit species: the area in production, the quantity of collected product, the main waste (prunings)/product ratio, the average moisture at collection, the fraction of waste currently recycled, and the secondary waste (wood) available at the end of the production cycle. Of this fraction was monitored the average life cycle of the tree plant between planting and cutting, the average moisture of the wood at pruning-time, and the fraction of the secondary waste currently recycled. In the end, column H shows the dry residue estimates available in 2008 by the Italian Biomass Association ITABIA [22]. To obtain the dataset, the authors collected data from the main studies carried out in the years prior to 2008, both on a local, regional, and national scale, considering all lignocellulosic matrix wastes from the cultivation of herbaceous

and arboreal plants in the national territory, including residues used for animal bedding and fertilization. Since residue yields vary depending on factors such as tree species, cultivation techniques, production technologies, geographic location, production land, seasons, harvesting methods, and pruning methods, obtaining reliable and accurate data requires extensive field surveys and rigorous survey classification. As a result, estimating lignocellulosic biomass residues is a complex and costly activity [23]. According to all the databases, the total amount of dry residue that can be collected in Italian orchards can be estimated as 3.46 ± 0.37 Mt/y.

2. Materials and Methods

Samples of lignocellulosic residues were collected at Unipg's experimental orchards, located in Fosso di Provancio, Perugia. The pruning process and the residue collection were performed between November 2022 and March 2023. The sampled fruit tree species were the Abate pear variety, Florina variety of apple, President variety of plum, Redhaven variety of peach, T. Giffoni variety hazelnut, and lotus. Olive tree samples were obtained from a local production site near Perugia, consisting of the Frantoio, Moraiolo, and Leccino varieties, which are commonly found in central Italy. Samples were taken from trees of varying ages, from 8 to 25 years old, and located in random positions in the different orchards. Branches of different types were sampled, e.g., various thicknesses, fruit-bearing branches, and vertical shoots. After the pruning, leaves were totally removed from each of the sampled branches. This sampling procedure was performed to obtain a tree representative biomass average composition. The collected samples were air-dried for three weeks and then reduced in size using an industrial chipper to obtain pieces of around 25–40 mm. The woodchips were then further processed using a rotary blade mill (RETSCH, Haan, Germany) and an ultra-mill (RETSCH, Haan, Germany) to obtain particles with a diameter of 0.5–1 mm, which was required to perform all the characterization processes. The higher heating value (HHV) was determined using a LECO AC-350 calorimeter (St. Joseph, MI, USA). To conduct the analysis, each milled sample was transformed into a pellet using a Parr 2811 Pellet Press manual pelletizer (Parr Instrument Company, Moline, IL, USA). The pellets were formed with only the pressure of the piston and residual humidity, without adding any additives. The mass and moisture were determined for each pellet analyzed. A TGA-701 LECO Thermogravimetric Analyzer (St. Joseph, MI, USA) was employed to determine the moisture, dry matter, volatile matter, and ash contents as well as to determine the combustion profile of each sample with a 10 °C/min ramp from 30 to 950 °C in oxidant (100% oxygen, 1 L/min) and inert atmospheres (100% nitrogen, 1 L/min). Prior to each combustion profile analysis, a 30 min flux with the oxidant or inert gas was, respectively, performed before the analysis to ensure the desired atmosphere at the start. The content of carbon, hydrogen, and nitrogen was determined by a Truspec CHN LECO Elementary Analyzer (St. Joseph, MI, USA) in compliance with the ASTM D-5373 standard procedure [24]. The hydrogen content was used to determine the lower heating value (LHV) on a dry basis using Equation (1) in accordance with standard procedure [25] ISO 18125:2017 as follows:

$$\text{LHV}(\text{MJ}/\text{kg}) = [(\text{HHV}(\text{MJ}/\text{kg}) * 1000) - (206 * \%H)]/1000 \quad (1)$$

where %H is the content of hydrogen.

To assess the potential of these biomasses as sources of glucose to produce liquid biofuel, a lignocellulosic characterization was carried out using an internal procedure derived from NREL 42618 [26] to determine the contents of cellulose, hemicellulose, and lignin. The characterization process involved a two-step acid hydrolysis of the sample. In the first step, a solution of 3 mL of 72% H_2SO_4 (*w/w*) was added to a 300 ± 10 mg sample of biomass with a moisture content lower than 10% and incubated at 32 °C for 60 min. In the second step, the solution was diluted to 4% H_2SO_4 (*w/w*) through the addition of water and incubated at 121 °C in an autoclave for 60 min. At the end of the process, the acid-insoluble lignin (lignin) was gravimetrically determined, while the liquid fraction was analyzed with a Dionex Ultimate 3000 HPLC (Thermo Fisher Scientific, Sunnyvale, CA, USA) equipped

with an ERC RefractoMax 520 refractive index detector (Thermo Fisher Scientific, Waltham, MA, USA) and a Bio-Rad Aminex HPX-87H column (Bio-Rad Laboratories, Hercules, CA, USA) to determine the sugar monomers (determined via Equations (2) and (3)), deriving from the cellulosic and hemicellulosic fraction of the biomass, glucose, xylose, mannose and galactose, respectively. Due to column limits, xylose, mannose, and galactose (XMG) chromatographically coelute as a single peak. Eluent was a 0.05 M H₂SO₄ solution, and the flux was set to 0.6 mL/min. To determine the content of heavy metals in ashes, an Optima 8000 ICP-OES (Perkin Elmer, Waltham, MA, USA) with 20 L/min argon, 8 L/min nitrogen, and 10 L/min high purity oil-free air was used. For each experimental procedure and each sample, analyses were performed in triple to ensure replicability and to obtain a standard deviation in measurements.

$$\text{Cellulose content (\%)} = \text{HPLC-Glu}_{\text{concentration}} \text{ (mg/mL)} * \text{dilution factor} * 0.9 \quad (2)$$

$$\text{Hemicellulose content (\%)} = \text{HPLC-XMG}_{\text{concentration}} \text{ (mg/mL)} * \text{dilution factor} * 0.88 \quad (3)$$

where

- 0.9 and 0.88, respectively, are the anhydro corrections that are needed to calculate the concentration of the polymeric sugars from the concentration of the corresponding monomeric sugars.
- HPLC-Glu_{concentration} is the concentration of glucose determined via HPLC.
- HPLC-XMG_{concentration} is the concentration of XMG determined via HPLC.

3. Results

Table 2 displays all the data obtained for the eight fruit tree samples about the physical and chemical characterizations. The results from the proximate analysis (volatile matter, ash, fixed carbon, and moisture), ultimate analysis (carbon, nitrogen, and hydrogen content), and calorific values (higher heating value and lower heating value) are reported along with their standard deviation. All the data are reported on a dry basis.

Table 2. Average results of the calorific values, proximate and ultimate analyses.

Species	Proximate Analysis (wt.% d.b.)				Ultimate Analysis (wt.% d.b.)				
	Moisture (%)	Volatile Matter (%)	Fixed Carbon (%)	Ash (%)	Nitrogen Content (%)	Carbon Content (%)	Hydrogen Content (%)	HHV (MJ/kg)	LHV (MJ/kg)
Pear	11.63 ± 0.01	76.26 ± 0.04	20.24 ± 0.02	3.50 ± 0.02	0.4 ± 0.2	42.9 ± 0.8	6.10 ± 0.14	18.03 ± 0.05	16.8 ± 0.7
Persimmon	9.87 ± 0.03	74.8 ± 0.3	20.8 ± 0.2	4.4 ± 0.1	0.39 ± 0.03	42.9 ± 0.6	6.10 ± 0.05	18.63 ± 0.09	17.4 ± 0.7
Plum	15.40 ± 0.01	77.3 ± 0.2	19.9 ± 0.2	2.82 ± 0.03	0.03 ± 0.01	41.1 ± 0.7	6.3 ± 0.2	17.32 ± 0.09	16.1 ± 0.5
Peach	9.30 ± 0.03	76.9 ± 0.1	18.33 ± 0.08	4.71 ± 0.07	0.23 ± 0.04	42.6 ± 0.6	6.05 ± 0.09	17.55 ± 0.01	16.3 ± 0.6
Hazelnut	10.39 ± 0.05	77.4 ± 0.1	20.03 ± 0.07	2.59 ± 0.07	0.16 ± 0.03	43.8 ± 0.8	6.1 ± 0.1	17.56 ± 0.01	16.3 ± 0.6
Olive	10.75 ± 0.07	77.9 ± 0.4	19.1 ± 0.4	2.99 ± 0.05	0.19 ± 0.02	42.5 ± 1.1	6.3 ± 0.4	17.1 ± 0.4	15.9 ± 0.2
Grape	17.83 ± 0.07	76.9 ± 0.1	19.5 ± 0.1	3.65 ± 0.01	0.05 ± 0.01	40.67 ± 0.05	5.34 ± 0.07	18.23 ± 0.02	17.1 ± 0.5
Apple	10.23 ± 0.09	77.50 ± 0.08	18.97 ± 0.07	3.53 ± 0.02	0.22 ± 0.01	43.9 ± 0.3	5.85 ± 0.02	17.5 ± 0.2	16.3 ± 0.4

The measured values for the calorific values can be compared and validated by consulting data available in the literature. The study by Stolarsky [27], which reports values for fruit tree lignocellulosic biomass samples collected in the Poznan region of Poland, are listed as the following values: peach tree HHV 20.10 MJ/kg, LHV 18.80 MJ/kg; pear tree UHV 19.20 MJ/kg, LHV 17.80 MJ/kg; apple tree HHV 19.20 MJ/kg, LHV 17.90 MJ/kg; hazelnut tree HHV 19.60 MJ/kg, LHV 18.20 MJ/kg; plum tree HHV 19.60 MJ/kg, LHV 18.20 MJ/kg. Zivkovic [23] reports the following HHV values: plum tree 18.65 MJ/kg, apple tree 17.8 MJ/kg, pear tree 18.0 MJ/kg, peach tree 19.4 MJ/kg, grape tree 18.3 MJ/kg collected in Serbia. Monarca [28] reports a HHV of 17.67 MJ/kg and a LHV of 16.45 MJ/kg for hazelnut samples collected from the Cimini and Sabatini mountains in Viterbo (Italy). Bilandzija [29] surveyed hazelnut production in Croatia and obtained a LHV of 17.47 MJ/kg

on a dry basis. Di Giacinto [30] sampled hazelnut prunings with values of 19.70 MJ/kg and 18.39 MJ/kg being reported for the HHV and LHV, respectively. Zambon [31] reported a HHV of 19.02 MJ/kg and a LHV of 16.71 MJ/kg for hazelnut prunings. Finally, in the case of olive tree pruning, Zambon [32] reported a HHV of 19.47 MJ/kg and a LHV of 16.17 MJ/kg, while Di Giacinto [30] reported a HHV of 19.93 MJ/kg and a LHV of 17.85 MJ/kg. Borja Velázquez [31] indicated a HHV of 15.23 MJ/kg. To compare the data obtained in this study with other literature, Figure 5 summarizes the situation for hazelnuts with LHVs and HHVs from different sources.

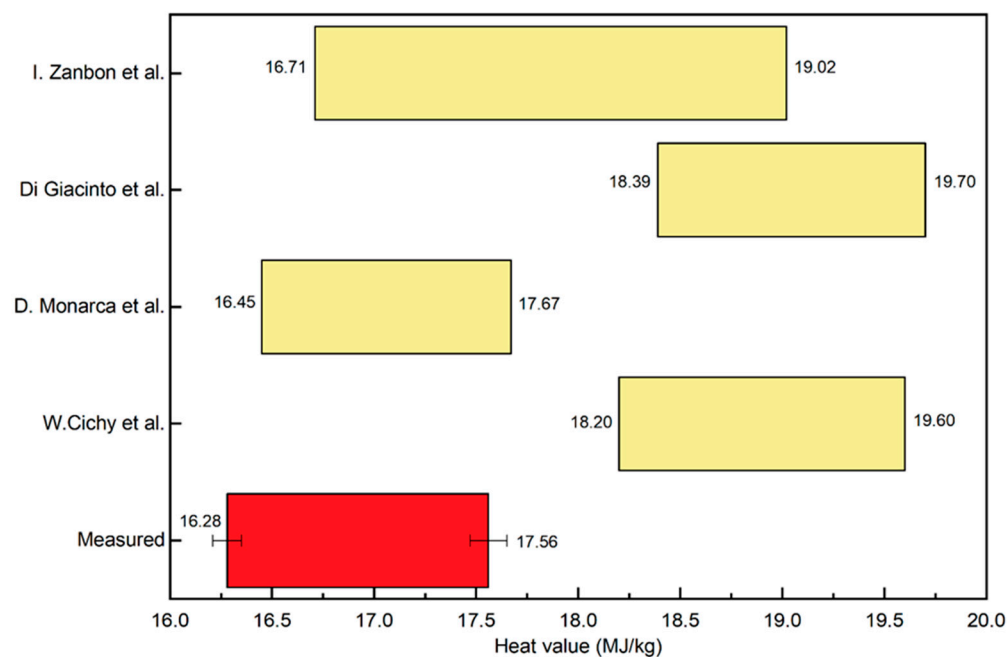


Figure 5. Comparison between this study's measurements of the HHV and LHV of hazelnut prunings with measurements of other studies. At the near ends of each floating bar, the value for LHV (on the left) and HHV (on the right) is shown [28,30,31,33].

The ultimate analysis, obtained through CHN analysis, can be compared and validated by consulting data available in the literature. Table 2 shows the average content values of the nitrogen (N%), hydrogen (H%), and carbon (C%) measured for each biomass, along with their respective standard deviations. Several comparisons with bibliographical data are possible. Stolarsky [27] reports the following percentage values: peach tree C% 51.1, H% 6.3, N% 0.9; pear tree C% 49.0, H% 6.3, N% 0.8; apple tree C% 48.6, H% 6.2, N% 0.5; hazelnut tree C% 49.8, H% 6.4, N% 0.8; plum tree C% 49.5, H% 6.3, N% 0.6.

About the hazelnut tree: Monarca [28] reports C% 47.78, H% 5.61, and N% 0.35, respectively; Bilandzija [29] reports C% 46.46, H% 6.57, and N% 0.78; Di Giacinto [30] reports C% 48.7, H% 6.17, and N% 1.09. Finally, another dataset by Borja Velázquez [34] reports the following values: C% 37.97, H% 6.91, and N% 0.55 for the olive tree.

Finally, the proximate analysis data obtained through TGA can be compared to data found in the literature to assess the likelihood of our orchard residues to others. Particularly, Stolarsky [27] reports the following ash content values: peach tree 2.0%, pear tree 3.8%, apple tree 1.9%, hazelnut 2.5%, and plum tree 1.5%. Di Giacinto [30] reported an ash value of 6.57% for hazelnut trees and 5.01% for olive trees. Furthermore, with LECO TGA-701, a combustion behavior test was performed in oxidant (oxy-DTG) and inert (inert-DTG) atmospheres, respectively. The data are displayed in Figure 6 as differential thermogravimetric (DTG) curves (% wt./min) in both atmospheres, showing the mass changes in varying temperatures with a peak near 100 °C.

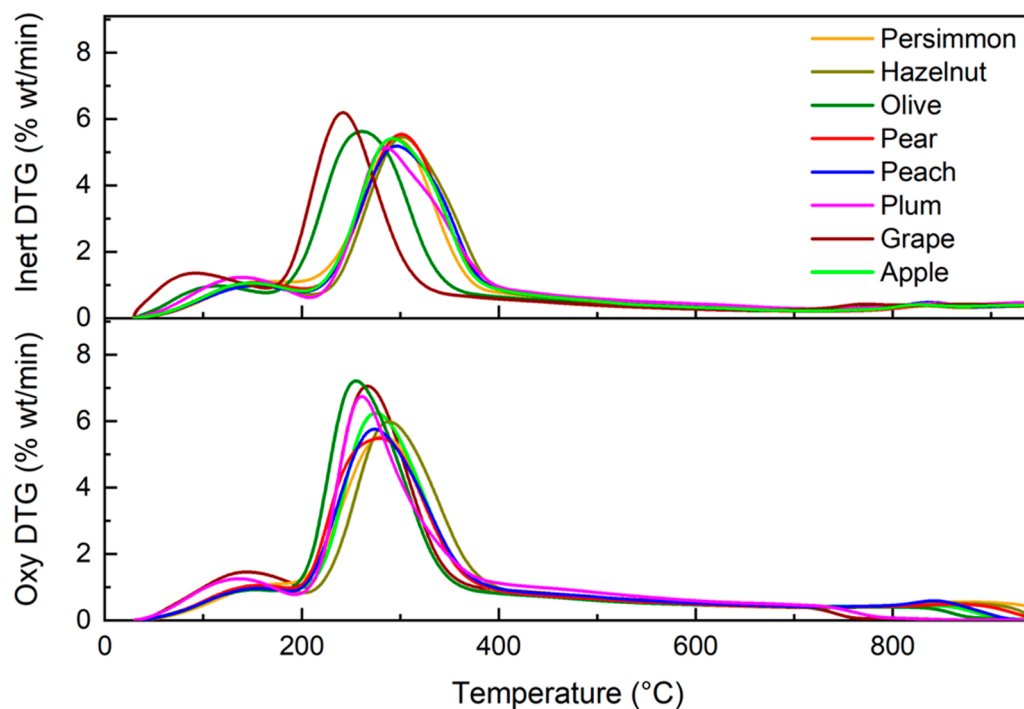


Figure 6. DTG combustion behavior of the lignocellulosic orchard residues samples in inert and oxidant atmospheres, respectively.

This behavior of the samples is attributed to moisture evaporation. The DTG curves also show a similar result for each sample with another peak of weight loss between 200–400 °C, but in Oxy-DTG, the presence of oxygen produces a moderate anticipation of the weight loss in terms of temperature, resulting in almost any case in a DTG peak temperature lower in Oxy-DTG. These peaks are due to the volatiles' release and decomposition of the different woods. In Table 3, when comparing the data, it can be seen how the presence of oxygen enhances the decomposition at a certain temperature, where the oxygen will cause ignition of the volatiles; in fact, the DTG max is higher in Oxy-DTG, and at the same time, when the temperature is high enough, oxygen promotes the heterogeneous oxidation of the remaining char, obtaining a lower solid residue, mainly constituted only by ash. The behavior of the DTG curves of these samples was found in accordance with previous studies [35,36]

Table 3. DTG analyses of inert and oxidant atmospheres.

Samples	Inert Atmosphere			Oxydant Atmosphere		
	DTG Peak Temperature (°C)	DTG Max (%/Min)	Solid Residue Char + Ash (%)	DTG Peak Temperature (°C)	DTG Max (%/Min)	Solid Residue Ash (%)
Pear	290.1	5.82	6.06	297.2	5.54	2.42
Persimmon	283.0	5.54	8.44	290.7	5.82	2.77
Plum	276.5	5.83	1.78	254.2	8.11	1.88
Peach	286.5	5.57	5.75	264.9	6.22	2.96
Hazelnut	297.2	5.99	6.18	274.4	6.28	2.11
Olive	264.5	5.85	3.17	242.1	7.86	1.93
Grape	243.0	7.00	2.36	278.7	7.26	2.23
Apple	279.6	5.76	4.74	258.3	6.40	2.30

In Figure 6, it can be seen that at temperatures between 50–150 °C, a small weight change occurs.

To complete the ash analysis, a measurement of heavy metals has been assessed, showing low values for each of the considered elements, particularly for cadmium. The ashes analysis is reported in Table 4.

Table 4. Ashes' heavy metal content. The cadmium instrumental detection limit was set to 0.01 ppm.

Elements	Species Content (mg/kg)							
	Apple	Grape	Olive	Hazelnut	Peach	Plum	Persimmon	Pear
Cadmium (Cd)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Chromium (Cr)	0.5 ± 0.1	1.7 ± 0.3	0.6 ± 0.2	1.1 ± 0.1	0.7 ± 0.1	1.8 ± 0.2	0.4 ± 0.1	0.9 ± 0.1
Copper (Cu)	5.0 ± 0.5	197.2 ± 0.6	21.2 ± 0.1	79.9 ± 0.8	5.7 ± 0.2	20.0 ± 0.4	3.0 ± 0.2	4.0 ± 0.9
Nickel (Ni)	1.1 ± 0.2	36.4 ± 0.6	2.6 ± 0.1	21.2 ± 0.2	0.9 ± 0.1	1.0 ± 0.3	0.9 ± 0.2	3.9 ± 0.4
Lead (Pb)	1.4 ± 0.2	0.7 ± 0.1	1.8 ± 0.2	1.2 ± 0.3	0.8 ± 0.3	1.2 ± 0.4	0.6 ± 0.1	0.9 ± 0.2
Zinc (Zn)	46.0 ± 0.4	0.7 ± 0.2	13.1 ± 0.3	25.4 ± 0.6	32.4 ± 0.4	51.0 ± 0.7	18.1 ± 0.6	30.3 ± 0.5

Finally, a lignocellulosic characterization process was performed to determine the contents of cellulose, hemicellulose, and lignin. Data are shown in Table 5.

Table 5. Lignocellulosic characterization of the 8 residual lignocellulosic biomasses collected from Unipg experimental orchards.

Species	Hemicellulose (%)	Cellulose (%)	Lignin (%)
Pear	16.45 ± 0.12	34.60 ± 0.22	19.90 ± 1.21
Persimmon	14.98 ± 0.14	35.55 ± 0.52	28.24 ± 0.79
Plum	16.25 ± 0.15	36.73 ± 0.48	24.26 ± 1.25
Peach	12.70 ± 0.07	38.38 ± 0.63	23.31 ± 2.21
Hazelnut	16.78 ± 0.09	39.88 ± 0.17	22.98 ± 1.12
Olive	15.52 ± 0.16	40.00 ± 0.59	23.12 ± 0.98
Grape	12.93 ± 0.24	40.33 ± 0.25	22.93 ± 1.14
Apple	13.70 ± 0.14	40.90 ± 0.47	25.31 ± 1.06

Comparing the obtained data with the literature, Senol [37] reports the following percentage values for hazelnut trees: hemicellulose 33.20%, cellulose 47.78%, and lignin 18.07%. Mamani [38] reports the following percentage values for olive tree residues: hemicellulose 17.26%, cellulose 31.88%, lignin 9.26%, and ash 3.29%. It is important to note that the lignocellulosic residues used in different studies may come from different geographical areas and that the characterization procedures may differ from the NREL method used in this study. An analysis of the lignocellulosic characterization results reveals that a percentage of lignin greater than 20% was found for all biomasses (22.93–28.24%), except in the case of olive trees (19.90%). According to Yuan [39], a lignin percentage higher than 20% strongly inhibits the yields of the enzymatic hydrolysis process required to transform the obtained cellulose. Therefore, pretreatment to reduce the lignin content of these biomasses should be considered before using them as feedstock in a biorefinery. Steam explosion or organosolv processes are options that can be used for obtaining a high-in-cellulose and low-in-lignin raw material that can undergo enzymatic hydrolysis followed by a fermentation process [40].

Estimation of the Potential Energy Production from Orchard Lignocellulosic Residues

To obtain an estimate of the potential annual energy production that orchard lignocellulosic biomass could produce, data from the average residue production must be taken into consideration for each species and then processed using the chemical and physical information obtained as a result, as performed during this experimental campaign. The estimate for the equivalent electrical energy was derived by assuming an average national thermoelectric system efficiency of around 46% [41]. To estimate the maximum potential bioethanol amount after a delignification pretreatment, an enzymatic hydrolysis efficiency

of 70% and a conversion factor from glucose to ethanol of 51% has been considered [26]. Data about the potential energy and bioethanol production are shown in Table 6.

Table 6. Energy production is potentially available from lignocellulosic biomass sources on a yearly basis from some fruit tree species in Italy.

Species	Dry Residue Mass (Mt/y)	LHV (Mj/kg)	Cellulose Content (%)	Equivalent Electrical Energy (GWh)	Bioethanol (Mt/y)
Grape	1.29 ± 0.23	17.13 ± 0.54	40.33 ± 0.25	2823.60 ± 503.4	0.20 ± 0.03
Olive	1.16 ± 0.19	15.88 ± 0.20	40.00 ± 0.59	2353.77 ± 385.5	0.18 ± 0.03
Apple	0.16 ± 0.08	16.26 ± 0.37	40.90 ± 0.47	332.43 ± 166.2	0.030 ± 0.015
Pear	0.08 ± 0.05	16.77 ± 0.69	34.60 ± 0.22	171.43 ± 107.1	0.010 ± 0.006
Peach	0.23 ± 0.13	17.38 ± 0.72	38.38 ± 0.63	510.78 ± 288.7	0.030 ± 0.017
Hazelnut	0.12 ± 0.05	16.28 ± 0.63	39.88 ± 0.17	249.63 ± 104.0	0.020 ± 0.008
Total	3.04 ± 0.34			6441.62 ± 731.7	0.48 ± 0.05

In 2020, Italy's gross electricity production was 280.5 TWh, of which 24.7% was generated from renewable sources, including wind, geothermal, photovoltaic, hydropower, and bioenergy [32]. The data analysis reveals that the equivalent electrical energy that could potentially be produced only from the lignocellulosic orchard cultivation residues derived from six species amounts to approximately 2.30% of the country's gross national electricity production and has the potential to contribute up to 9.30% of the national electrical energy production from renewable sources. Italian demand for gasoline in 2022 was 7.88 Mt [42], and European gasoline demand in 2019 was 98 Mt [43]. The contribution from Italian lignocellulosic residues of these six species could, respectively, be 6.21% and 0.49% of the total demand, with a range of selling prices being between 4.7–0.17 USD/L [43]. It has been estimated that worldwide, from only 123 crop species taken into consideration, 474.4 Mt/y of residue can be collected and consequently used to answer the energy demands [44], potentially providing hundreds of the amount of energy produced in the Italian orchard case scenario.

4. Conclusions

This study investigated the potential of utilizing orchard lignocellulosic residues for energy production in the Italian context, focusing on electricity generation and bioethanol production. These possibilities offer sustainable alternatives to fossil fuels, reducing greenhouse gas emissions. Worldwide, similar strategies can be applied, leveraging the abundant agricultural residues also found in fruit industries. Technological advancements, policy support, circular economy principles, and global collaboration are essential for the widespread adoption and transition to renewable energy sources. This study emphasizes the significance of orchard residues in achieving a greener and more sustainable energy future through the production of electricity and bioethanol.

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