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Recovery and valorization for energy purposes of residual biomasses coming from agro-industrial chains

(S.S.D. AGR/09)

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Corso di Dottorato di Ricerca in
Engineering for Energy and Environment
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Recupero e valorizzazione ai fini energetici di biomasse residuali provenienti da filiere agroindustriali

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TITOLO TESI DI DOTTORATO DI RICERCA
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Abstract

Every year, a large amount of agricultural, agro-industrial, urban and forestry residues are treated as waste, but they could be recovered and used to produce energy. Among the main types of agro-industrial waste, coffee residues account for a significant amount worldwide. Because of their composition, they can be used in biodiesel production, as a source of sugar, or as a sorbent for metal removal. Orchards also generate a lot of pruning waste each year. Currently, prunings of hazelnut and olive trees in the best of cases, are chopped and left on the ground however; they are often burned in the field and this involves the generation of CO_2 emissions and wasting a resource that could have been exploited differently.

The purpose of this thesis was to assess the employability of coffee grounds by looking at their energetical features and also to improve the characteristics of pruning residues of hazelnut and olive groves. The research activity has moved through chemical and physical characterizations, pelletizing tests to obtain a commercially viable product, combustion tests to analyse atmospheric emissions, evaluation of the life cycle of supply chains for the recovery and pelletizing of coffee grounds by considering different alternative waste-to-energy scenarios, comparison and modelling with traditional biomass for the development of a predictive model of the higher heating value and evaluation of the impact of mechanical pre-treatment on the quality of pruning residues of hazelnut and olive trees on anaerobic biodegradability.

The results show that spent coffee grounds are excellent as biomass, with excellent values in terms of heating power and low ash content, the production of 98% coffee pellets suggests that they are highly suitable for use in thermal conversion systems. The major environmental impact is given by the pelletizing process with the exception of ozone formation and terrestrial ecotoxicity, which are mainly influenced by the transport process in the stage of coffee grounds collection. The environmental benefits of spent coffee ground pelletizing are the mitigation of climate change, and reduction of freshwater eutrophication. Among the waste-to-energy scenarios, biodiesel is the worst; on the other hand, pellet production and bio-oil demonstrate the most favourable environmental profiles. Through composition and energy analysis of coffee grounds, it was possible to fix linear models that can link elemental composition to biomass energy yield. Spent coffee grounds showed a higher HHV than any other woody and herbaceous plant, manifesting great potential from the perspective of energy.

In the mechanical process, the coarser products that were obtained from the pruning residues, were characterised by a high reduction in ash and nitrogen content. The best products from the processing were subjected to anaerobic digestion. The finest product from hazelnut processing achieved a 70.1% higher methane yield than the untreated substrate, while their analogues from the olive pruning processing, achieved a methane yield of approximately +93.5% compared to the untreated feedstock.

In conclusion, the results indicate that is an excellent candidate for use in energy conversion systems; furthermore, the mechanical process that was studied, could be successfully used to improve the quality of olive and hazelnut prunings and establish new markets.

Key words: Residual Biomass, Spent Coffee Ground, Pruning, LCA, Modelling.

Riassunto

Ogni anno, una grande quantità di residui agricoli, agro-industriali, urbani e forestali sono trattati come rifiuti, ma possono essere recuperati e utilizzati per produrre energia. Tra i principali tipi di rifiuti agro-industriali, i residui di caffè rappresentano una quantità significativa in tutto il mondo. Grazie alla loro composizione, possono essere utilizzati nella produzione di biodiesel, come fonte di zucchero o come sorbente per la rimozione dei metalli pesanti. Anche nei frutteti si generano molti residui di potatura ogni anno. Attualmente potature di nocciolo ed olivo nel migliore dei casi vengono trinciate e lasciate a terra, ma spesso vengono bruciate in campo comportando emissioni di CO_2 e sprecando una risorsa che potrebbe essere valorizzata diversamente. Lo scopo di questo lavoro di tesi è stato valutare la possibilità di valorizzare dal punto di vista energetico i fondi di caffè e migliorare le caratteristiche di residui di potatura di noccioleti ed oliveti. L’attività di ricerca si è mossa attraverso caratterizzazioni chimico-fisiche, prove di pellettizzazione per ottenere un prodotto commercialmente valido, prove di combustione per analizzare le emissioni in atmosfera, valutazione del ciclo di vita di filiere per il recupero e pellettizzazione di fondi caffè secondo differenti scenari alternativi di termovalorizzazione, confronto e modellizzazione con biomasse tradizionali per la valutazione di un modello previsionale del potere calorifico superiore e valutazione di un pretrattamento meccanico sulla qualità di residui di potatura di nocciolo ed olivo sulla biodegradabilità anaerobica. I risultati mostrano che i fondi di caffè sono eccellenti come biomassa, con ottimi valori in termini di potere calorifico e basso contenuto di ceneri, la produzione di pellet di caffè al 98% suggerisce che sono altamente adatti per l'uso in sistemi di conversione termica. L’impatto ambientale maggiore è dato dal processo di pellettizzazione ad eccezione della formazione di ozono e l'ecotossicità terrestre, che è influenzata principalmente dal processo di trasporto nella fase di raccolta dei fondi di caffè. I vantaggi ambientali della pellettizzazione i fondi di caffè sono la mitigazione del cambiamento climatico, e alla riduzione dell'eutrofizzazione dell'acqua dolce. Tra le tipologie di conversione della biomassa, la produzione di biodiesel è risultata la peggiore, mentre la produzione di pellet e il bio-olio dimostrano i profili ambientali più favorevoli. Attraverso l'analisi della composizione ed energetica dei fondi di caffè, è stato possibile fissare modelli lineari in grado di collegare la composizione elementare alla resa energetica della biomassa. I fondi di caffè hanno mostrato un HHV superiore a qualsiasi altra pianta legnosa ed erbacea, manifestando un grande potenziale dal punto di vista energetico. Nel processo meccanico, i prodotti più grossolani ottenuti dai residui di potatura, si distinguono per l'elevata riduzione del contenuto di ceneri e di azoto. I prodotti migliori della lavorazione sono stati sottoposti a digestione anaerobica. Il prodotto più fine dalla lavorazione delle nocciole ha raggiunto una resa in metano maggiore del 70,1% rispetto al substrato non trattato, mentre l'analogo della lavorazione delle potature dell’olivo ha raggiunto una resa in metano di circa +93,5% rispetto alla materia prima non trattata. In conclusione, i risultati indicano che i fondi di caffè sono un eccellente candidato per l'uso in sistemi di conversione energetica; inoltre, il processo meccanico studiato potrebbe essere utilizzato con successo per migliorare la qualità delle potature di olivo e nocciolo e stabilire nuovi mercati.

Contents

List of acronyms

ANOVA: Analysis of Variance

IPCC: Intergovernmental Panel on Climate Change

LCA: Life Cycle Assessment

MAE: Mean Absolute Error

MBE: Mean Bias Error

OLS: Ordinary Least Squares

PCA: Principal Component Analysis

QR: Quantile Regression

RES: Renewable energy resources

RMSE: Mean Square Route Error

S: Sawdust

SCG: Spent Coffee Grounds

Preface

This thesis presents the activities that were carried out and the results that were obtained during the three-year period (November 2018 - October 2021) of the PhD in "Engineering for energy and environment", Curriculum: "Biosystems and environment", titled "Recovery and valorisation for energy purposes of residual biomass from agro-industrial supply chains", performed at the Department of Agricultural and Forestry Sciences (DAFNE) of the University of Tuscia. The research line is focused on the evaluation of the recovery and valorisation of the agroforestry and agro-industrial wastes for energy purposes.

Climate change and the lack of energy sources have prompted the still ongoing search for alternatives to fossil fuels. In this context, biomass seems to be one of the most interesting renewable sources, being also the fourth energy source in the world after oil, coal and natural gas (Bocci *et al.*, 2014; Pala *et al.*, 2017; Thapa *et al.*, 2017).

Biomasses lend themselves to be used in both biochemical and thermochemical conversion processes and in this perspective residual biomasses represent an interesting source (Colantoni *et al.*, 2019; Villarini *et al.*, 2019).

The increasing production of waste has led for some time now, to see in agroforestry and agro-industrial residues, opportunities for energy conversion. These residues are also interesting for other types of uses such as the synthesis of materials and the extraction of molecules for industrial, pharmaceutical, food, etc. purposes. (Scarlat *et al.*, 2015).

According to the three principles of circular economy: designing without waste and pollution, preserving products and materials that are in use and regenerating systems and products, recovering waste and scraps from these sectors is essential. It therefore seeks to promote reuse and increase alternative uses, including the one for energy.

Thus, the intention is to use scarce biomass such as agroforestry and agro-industrial residues, sustainably. The challenges when interfacing with these resources are logistics, collection costs and the seasonality with which they are available.

1. Introduction

The global energy market is ever-evolving and going through a crucial phase of change. This explains why more and more private companies and energy producers are devoting themselves to the development of new plants for the implementation and identification of alternative sources. The environment issue is at the core of international policy and this gives it priority over other issues. Global pollution, especially that of the atmosphere, is largely due to greenhouse gases and carbon dioxide produced by the increasingly significant use of fossil fuels, the so-called non-renewable exhaustible sources. The concern that fossil fuel deposits have long been exploited, has only recently led the so-called renewable sources, which use natural resources, to be looked at as potential alternative means for the production of energy.

It should be noted that the technologies used to exploit the renewable sources are constantly evolving and that the use of these energy sources is a valid contribution for the production of cleaner energy, even if we are still far from a definitive solution to the problem of meeting the world's energy needs. The main challenges to be faced are the threat of climate change with its possible deleterious and destructive effects, the progressive reduction in the security of energy supplies, rising energy prices, and the growing energy demand of developing countries. It is not an exaggeration to say that sustainable economic development will only be possible if reliable and affordable energy supplies can be ensured by identifying low-carbon, efficient and environmentally friendly energy sources.

The international energy system is moving towards the path of unsustainable development, and policy interventions are needed to encourage the development of a wide range of innovative energy technologies.

1.1. The energy situation

The current development model involves the massive use of fossil energy resources (oil, coal, gas) for energy production, which is unsustainable from an environmental, economic, and social point of view. The main challenges it faces, are the threat of climate change with possible deleterious and destructive effects, the progressive reduction in the security of the energy supply, the growth and volatility of energy prices and the increasing energy demand of developing countries. It is no exaggeration to say that sustainable economic development will only be possible if reliable and affordable energy supplies can be secured by making a rapid shift towards efficient and environmentally friendly low-carbon energy supplies (ENEA, 2013).

An analysis of historical data and trend scenarios developed by the International Energy Agency (IEA) and the Energy Information Administration shows that the international energy system is moving towards a path of unsustainable development and that policy interventions are needed to encourage the development of a wide range of innovative energy technologies. The International Energy Agency (IEA) highlights the need for an energy revolution based on low-carbon technologies on a global scale. This conversion process, which will initially have high investment costs, will be more than offset by the benefits in terms of reducing climate impacts, improving energy security and supporting economic development (ENEA, 2013).

1.2. Analysis of energy production and consumption at a European level

Between 2017 and 2018, in the European Union (EU) there was a decline in primary energy production. This decrease approximates 1%, standing at 635 million tonnes of oil equivalent (Mtoe) in 2018. This decrease is in line with the trend that had already been observed from 2008 to 2018, with some exceptions in 2010 and 2012-2013, when increases were recorded. In ten years, primary energy production in the EU has decreased by 9.2% (Figure 1). This trend can be associated, at least in part, with the depletion of raw material sources or the reduced economic use of available ones (Eurostat, 2020).

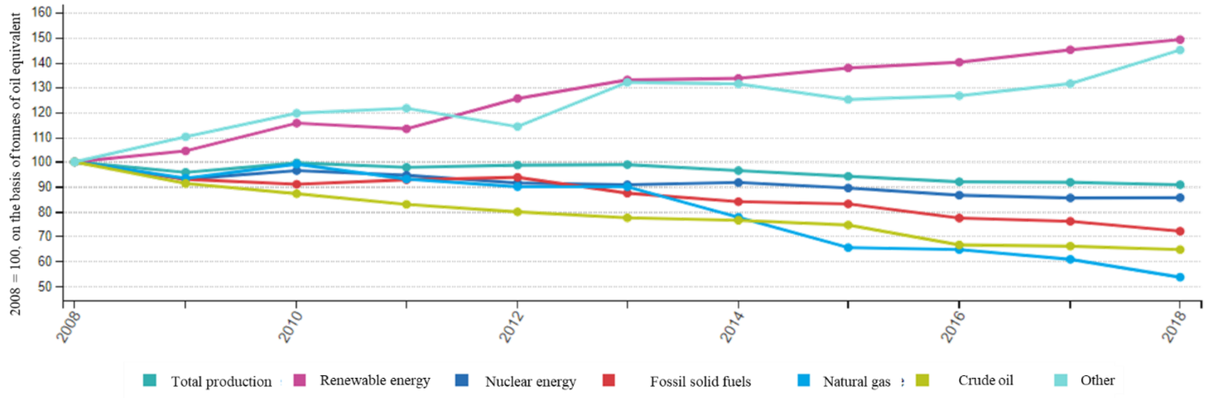

Figure 1 - Primary energy production by fuel type, EU-27, 2008-2018 (Source: Eurostat 2020).

The countries producing the most energy in 2018 were France (21.7%), Germany (17.8%) Poland (9.7%) and Italy (5.9%). In the decade 2008-2018, some countries increased their production compared to the total for the EU: France (+2.3%), Italy (+1.2%), Spain (+1.1%), Sweden (+1.1%), while others reduced their production: the Netherlands (-3.9%), Germany (-1.7%) and Denmark (-1.6%).

In the same period, in absolute terms, Italy, Spain, Sweden, Ireland and Finland recorded an increase in primary energy production, respectively 4.5, 4.4, 4.0, 3.4 and 3.2 Mtoe. Overall, the increase was observed in 14 of the 27 Member States. While the Netherlands, Germany and Denmark recorded decreases, respectively -31.2, -23.4 and -12.7 Mtoe (Eurostat, 2020).

In 2018, more than a third of the primary energy production came from renewable sources, or 34.2% of the total EU production. Of this, as much as 59.9% came from bioenergy and waste. In any case, the EU uses various energy sources.

Renewables are followed by nuclear energy (30.8%), which accounts for 78% of the total energy produced in France, 63.1% in Belgium and 62.7% in Slovakia. For the other European countries, in ten countries it did not reach half of the national production whilst in fourteen it was not present.

Solid fossil fuels accounted for 18.3 %, natural gas for 9.3 % and crude oil for 3.4 % (Figure 2) (Eurostat, 2020).

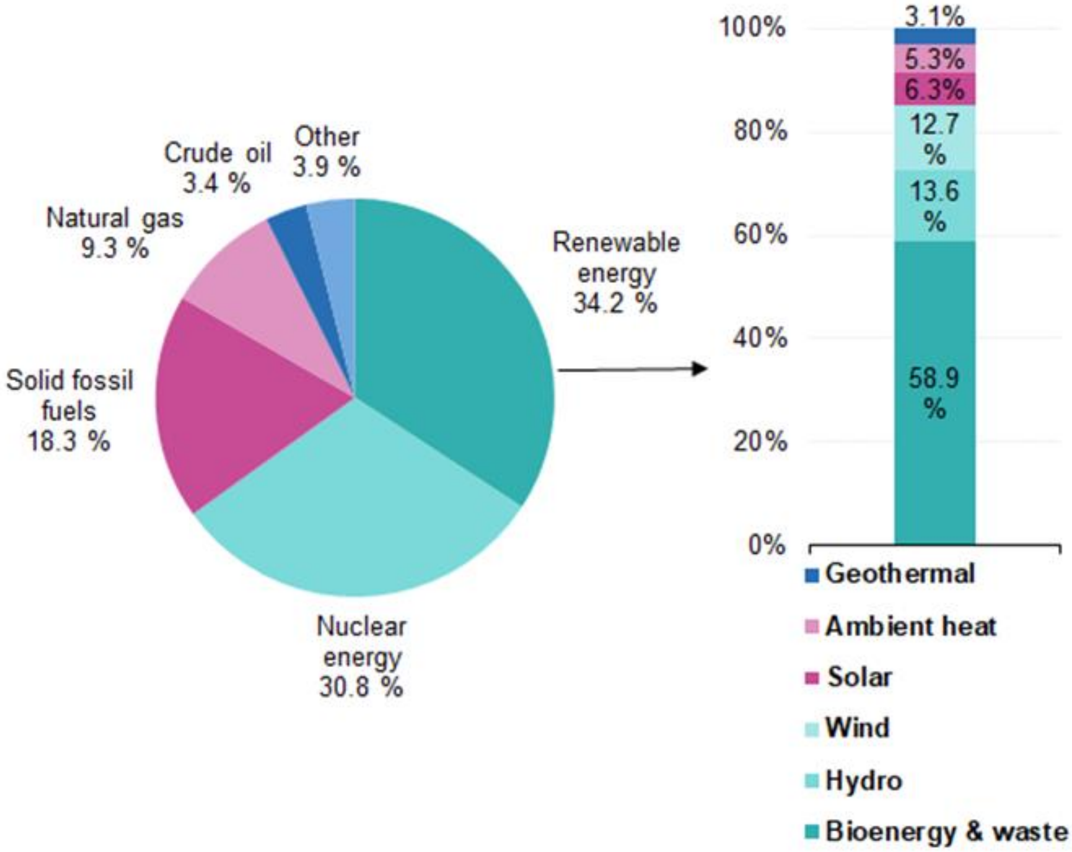

Figure 2 - Primary energy production, EU-27, 2018. Percentage of the total, based on tonnes of oil equivalent (Source: Eurostat, 2020).

Primary energy production has seen a significant increase mostly as a result of the use of renewable sources, and the increase has been steady. Production from renewable sources grew by 49.2%, while natural gas, crude oil, solid fossil fuels and nuclear energy decreased by -46.4%, -35.3%, -27.9% and 14.4% respectively (Figure 3).
These reductions have led to an increase in the imports of energy raw materials, but also of secondary energy sources (diesel fuel and diesel oil); the imports exceeded the exports by 886 Mtoe in 2018. The largest net energy importers in absolute terms were Germany, Italy, France, and Spain. Russia is the largest supplier of the main energy raw materials for the EU: hard coal (42.4 %), crude oil (between 32.1 % and 35.6 %) and natural gas (40.4 %). However, between 2008 and 2015, imports of hard coal from Colombia almost doubled, going from 11.7 % to 21.1 %. Situation very different from the previous decade (Barberis, 2013).

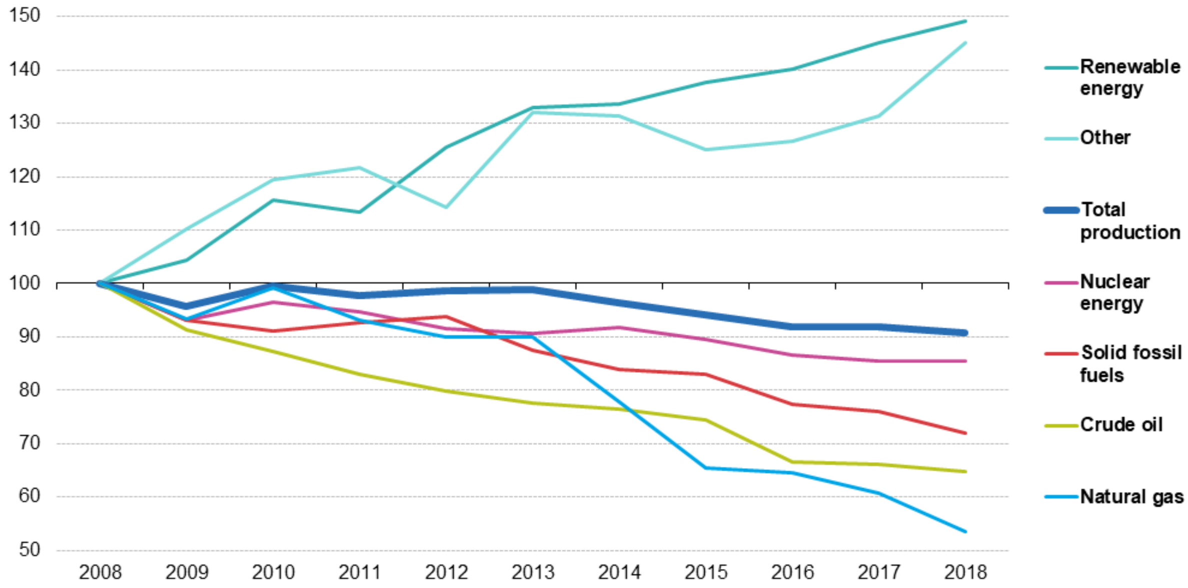

Figure 3 - Production of primary energy by fuel type, EU 27, 2008-2018. 2008=100, based on tonnes of oil e equivalent (Source: Eurostat 2020).

1.3. Legislative framework

The interest for renewable energies is steadily increasing, and this is mainly related to supply issues. The main example of this is the Kyoto Protocol of 1997, which was followed by the 2009/28/EC Directive of the European Community, whose commitments include reducing greenhouse gases and increasing the share of energy from renewable sources to 20% of the gross total energy consumption and up to 10% in transport (Mancini *et al.*, 2011). Following this, each country has adopted its own National Action Plan (NAP) on renewable energy. The Plan includes the development of the electricity sector, the strengthening of heating and cooling systems and a greater focus on biomass, biofuels including biomethane. In short, the Plan focuses on biomass, which, together with solar energy, is the renewable energy source with the greatest development potential (Mancini *et al.*, 2011). In the implementation of the 2009/28/EC Directive, Legislative Decree 28 of the 3rd March 2011 was issued, which defines the tools, mechanisms, incentives, and the institutional, financial and legal framework necessary to achieve the targets for the overall renewable sources' share of energy in the gross total energy consumption (17% in Italy) and the share of energy from renewable sources for transport. The main innovations introduced by the decree can be traced back to the following topics:

- authorization procedures for installations;
- requirements and specifications for plants;
- provisions for promoting the use of biomethane;
- development of district heating and cooling infrastructure;
- incentives for energy efficiency and thermal renewables;
- incentives for electricity production;
- fourth photovoltaic energy account;
- biofuels and their sustainability.

The Ministerial Decree of the 6^{th}July 2012 is the regulation that is referred to for the electricity production from biomass. This decree regulates the incentive rates applied for the production of energy from renewable sources other than photovoltaics. The Decree still determines electricity as the main element to consider for determining the incentives for production employing bioenergy, but it provides a bonus rate for high-efficiency cogeneration plants powered by biomass.

The principal reference for environmental legislation in our country and, therefore, also for the environmental effects related to the construction of new energy plants, is the so-called Environmental Consolidation Act, i.e., Legislative Decree 152/2006 (as amended). This regulation is divided into 6 parts: I. General framework; II. Strategic Environmental Assessment (SEA), Environmental Impact Assessment (EIA), and Integrated Environmental Authorisation (IEA); III. Standards for soil protection and combating desertification; standards for the protection of water from pollution; standards for the management of water resources; IV. Waste management and reclamation of polluted sites; V. Rules on air protection and reduction of emissions into the atmosphere; VI. Rules on compensation for environmental damage.

Currently, the European energy policy aims at finding a compromise between the increasing energy demand and the need to reduce the environmental impact. Therefore, the EU has set as "climate and energy targets" (20-20-20 Plan), 2030 and 2050. The 20-20-20 Plan includes: reducing greenhouse gas emissions by at least 20% compared to the 1990 levels, obtaining 20% of the energy from renewable sources and improving the energy efficiency by 20%. For 2030, the targets are more restrictive and include: reducing greenhouse gas emissions by 40%, obtaining 27% of the energy from RES and increasing energy efficiency by 27-30%. The EU has published the Energy Roadmap Communication, which provides guidelines for reducing greenhouse gas emissions by 80-95% of the 1990 levels by 2050.

1.4.Biomass

Biomass is defined as "the biodegradable fraction of products, waste and residues of biological origin from agriculture (including vegetal and animal substances), forestry and related industries, including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste" (European Parliament, 2009).

Fossil fuels such as oil, coal and natural gas still account for 80% of the overall consumption, but are expected to run out in 40-50 years (Saidur *et al.*, 2011). Given that, and the environmental damage that has been caused by climate change and given also the water, air and soil pollution; the aim is to reduce carbon emissions by using renewable sources such as wind and solar power, biomass, etc. (Koh and Hoi, 2003; Sasaki *et al.*, 2009).

Temperature is expected to rise between 1.4 and 5.8 °C until 2100, as reported by the Intergovernmental Panel on Climate Change (IPCC) (Mahmoud, Shuhaimi and Abdel Samed, 2009). In this perspective, biomass represents an important alternative and currently, contributes to 10-15% of the world's energy demand which corresponds to about 45 EJ. In industrialised countries, this share is equal to 9-14% and in developing countries it is significantly increased (Khan *et al.*, 2009). In rural areas, it is often the only accessible source of energy (Demirbas, 2004). Biomass is composed of carbohydrates and is a very versatile energy source that can be used to produce biogas, liquid fuels and electricity and does not present the same storage problems as solar or wind power (*Renewable Energy Focus - Solar, wind, wave and hydro power news, jobs, events and more*, no date; Roni *et al.*, 2017). Biomass is a renewable source of energy because it is always possible to grow trees and dedicated crops, just as there will always be waste (Australian Institute of Energy, 2004; Need, 2018). Primary energy comes from the sun and it is used by plants during the photosynthesis process, to convert carbon dioxide into sugars. Biomass is the world's fourth largest energy source with a 14% consumption, which is higher than the 12% of coal and similar to the 15% of gas (Bowyer, 2006; Need, 2018).

Biomass can be considered to be a renewable resource as it can result from: forest use, dedicated tree plantations, dedicated agricultural crops, wood processing waste or crop by-products, offcuts, or livestock manure. In the latter case, not only is it a renewable resource, but it also contributes to the re-use of waste that would be otherwise destined for landfill or sometimes even to be burnt in the field without any emission control.

Thus, the main types of biomass can be considered to be:

- Forest residues, firewood, virgin lignocellulosic products;
- Agro-industrial, agricultural, artisanal, industrial, and civil residues (e.g., straw, marc, dried fruit shells, olive pomace, rice husks, etc.);
- Dedicated energy crops (Short Rotation Forestry).

The main difference between using processing residues or using virgin material from energy crops, is their cost. Residues, being mainly waste products from industry and agriculture, carry with them a disposal cost, which can be enhanced if they are employed in an energy process such as pyrolysis or gasification. Pertaining to the material that is harvested from energy crops or that comes from forest maintenance, there is always a primary energy consumption associated with its cultivation, harvesting, transport, processing, storage, and therefore, additional costs that need to be considered. In the case of energy crops, these costs are easy to compute however, there are many variables for the exploitation of Agro-forestry residues, and they can be easily increased by the high spatial distribution of the resource and the low volume density (Trinkaus, 1998).

The physical and chemical characteristics and also, the state of a fuel are crucial for the application of a specific biomass. These characteristics determine its properties, quality, but possible problems too (Saidur *et al.*, 2011).

The main constituents of a biomass are lignin, cellulose and hemicellulose, to which are added small amounts of lipids, proteins, simple sugars and starches (Zhang, Xu and Champagne, 2010). The first three components account for about half of the plant material that is produced, the most abundant being cellulose, followed by hemicellulose and finally lignin. While cellulose and hemicellulose are macromolecules that are built from different sugars, lignin is an aromatic polymer that is synthesised from phenylpropanoid precursors.

The ultimate analysis is used both to assess the percentage of N, S and Cl, in order to study the environmental impact of the biomass and to calculate the percentage of C, H, O so as to estimate the heating value.

The proximate analysis, that is important for the combustion process, is used to evaluate the percentage of volatile matter, fixed carbon, and ash content. For example, ash content can cause ignition and combustion problems. Problems with fouling and slagging are caused by a low ash melting point. High fixed carbon and volatile matter increase the heating value.

The ash composition of the biomass is highly dependent on the species and the part of the plant that is used. Available nutrients, soil quality, fertilisers and weather conditions have a significant impact on the content of potassium, sodium, chlorine, and phosphorus. In general, biomass fuels can be divided into three groups based on their ash composition:

- Biomass with ash that is rich in Ca, K and lean in Si. Woody biomass ash is typically rich in calcium (Ca) and potassium (K).
- Biomass with ash that is rich in Si and lean in Ca, K. Most of the fuels in this group belong to the herbaceous or agricultural biofuels. Some fuels, such as cereal straw also have relatively high potassium (K) and chlorine (Cl) content. Rice husk and bagasse have a very high SiO_2 content in the ash.
- Biomass with ash that is rich in Ca, K and P. Sunflower stalk and rapeseed cake

ash, generated during food production, are examples of the third type of Agro-biomass ash, having K2O, CaO and P2O5 as their main ash components.

Saidur *et al.*, (2011) combined the correlations into three groups, in accordance with the approaches used in the literature: upper heating value estimation based on proximate, ultimate, and structural analysis.

The lignin content of the lignocellulosic fuel, in most cases strongly correlates with its heating value. The high heating values of lignin are reportedly higher than those of cellulose and hemicellulos; with the latter having a lower heating value due to its higher degree of oxidation.

The biomass's heating value can be described by the higher heating value (HHV), which is basically the energy content on a dry basis. The lower heating value (LHV) can be computed by subtracting the energy that is required to evaporate the moisture content of the fuel, from the higher heating value (HHV). C and H tend to increase the heating value of the biomass while oxygen tends to decrease it (Khan *et al.*, 2009).

Biomass is composed of wet and dry fractions. According to the ratio between these two fractions, it is possible to choose the energy conversion process however, the chemical-physical characteristics and in particular the ratio between carbon and nitrogen (C/N) also need to be taken into consideration. For thermochemical conversions, the biomass should have a C/N ratio>30, a water content <30% and a lower heating value LHV>10MJ kg^{-1}. For biochemical conversions, it should have a C/N ratio<30 and a water content>30%. Suitable for biochemical processes are aquatic crops, some crop by-products such as leaves and stems of beet, potato, vegetables, etc., livestock manure and some processing wastes such as water from oil mills, as well as heterogeneous organic biomass that is stored in controlled landfills.

The Environmental Consolidation Act D.lgs. 152/06 with an amendment in 2012 has also enabled the employment for energy purposes of clippings and prunings derived from the maintenance of public and private green areas, that were previously identified as waste. This represents an additional opportunity for the valorisation of by-products. All of the organic matter that can be used as fuel, can be considered as biomass for energy purposes (Faaij, 2006). Examples of biomass can be: the by-products of herbaceous and arboreal productions and of the first agro-industrial processing; the by-products of forestry operations, such as those resulting from forest management and timber production, and of the first processing of wood or other; crops specifically intended for the production of biofuels; zootechnical waste for the production of biogas; the organic part of urban waste; unusable residues originating from productions intended for human or animal consumption.

Biomass residues are organic substances of animal or vegetal origin that derive from waste and residues of different agricultural, forestry or agro-industrial productions (Di Renzo *et al.*, 2011).

Among the various herbaceous biomass residues, there are the straw of cereals such as wheat, oats, barley, rye, rice, as well as the stalks and cobs of corn and also sunflower stalks; among the arboreal biomass residues, there are olive, vine, apple, pear, peach, nectarine, plum, apricot, citrus, hazelnut, almond and Actinidia prunings. Generally, when we mention Actinidia prunings, we refer to the tree's branches however, when talking about the agro-industrial sector, the dried shells of its fruits are to be included as well. From the processing of agricultural products, it is possible to obtain additional by-products with interesting applications such as:

- Residues from the production of oil: virgin and exhausted pomace
- Residues from the production of spirits: fresh and exhausted pomace
- Residues from the production of rice: chaff, husks, etc.
- Residues from the canning industry: fresh fruit stones, seeds, and tomato peels

tomato skins.

Figure 4 shows the distribution in Italy of the pruning residues of olive trees, according to the estimated regional availability (ENAMA, 2011).

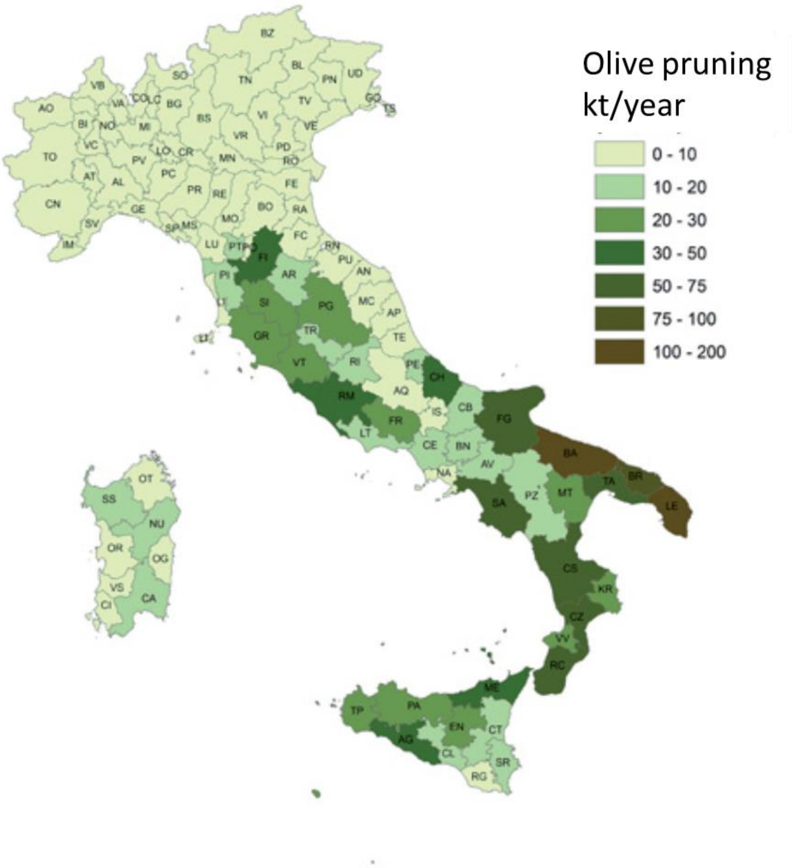

Figure 4 - Distribution of the pruning residues of olive trees (Source: ENAMA, 2011).

Olive tree pruning residues are an appealing energy source in Mediterranean countries however, it is still largely unexploited due to the lack of cost-effective harvesting technologies (Spinelli and Picchi, 2010). According to the FAO, there are about 8.6 million ha that have been planted with olive trees hence, requiring frequent pruning, and these generate at least 1 dry tonne (ODT) of biomass per ha (*FAOSTAT*, no date; ANPA, 2001). In Italy, pruning of olive groves, vineyards and other orchards generates 2.85 million tonnes of residues (Di Blasi, Tanzi and Lanzetta, 1997). However, such residues are an issue because of their burden and disposal logistics(Spinelli and Picchi, 2010). Currently, pruning waste is piled up and burned in the field or mulched, but this costs between 100 and 200 €ha^{-1} (Bordoni, Romagnoli and Pedretti, 2009).

The same practice is adopted for hazelnut pruning residues (Colantoni *et al.*, 2016).

Biomass production from the management of hazelnut crops, is equivalent to about 1.4 t/ha (Colantoni *et al.*, 2015).

It has been observed that the amount of pruning residue being produced, is strongly influenced by the type of mechanical or manual pruning. Mechanical pruning has a lower biomass yield than manual pruning (Monarca *et al.*, 2013). Biomass resulting from the pruning of hazelnut trees, can be seen too as a suitable solution for energy production through thermochemical processes, i.e., combustion, gasification, and pyrolysis. The large quantities that are produced, can meet the growing energy demand and can be used effectively for domestic heating or district heating (Monarca *et al.*, 2011).

The agricultural sector can produce large quantities of biomass that could be employed in the production of energy, making use of certain crop residues that would otherwise be difficult to process and manage. The biomass originated by the agricultural sector can be extremely diverse from a chemical and physical point of view. Such biomass consists only of the proportion of crop residues that are qualitatively suitable and technically collectable. The strengths of this resource mainly lie in its chemical and physical characteristics, in its consistency in terms of quantity, in its distribution, which is almost ubiquitous, and finally, and this is important yet a bit obvious, its production does not affect the areas of the food industry that were involved. On the other hand, there are also some weaknesses: mainly the costs, that in some cases are high, for the recovery, packaging, and transport of herbaceous and tree crop residues. Their characteristics greatly influence the choice of the type of transformation process that needs to be employed, the technological specifications of the plant and the problems that can arise at various stages of the chain. Among the short supply chains that can contribute to the activation of agricultural multifunctionality, linked to the protection and redevelopment of the territory is the energy valorisation of vine pruning residues; this makes it possible to transform what is currently a problem into an income opportunity for farms, through the activation of local short supply chains and it can thus have positive repercussions both for the management of the farms themselves and for the rural territory (ENAMA, 2011).

1.5. Spent Coffee Grounds

Coffee is one of the most popular beverages in the world and is the second most traded product in the world, produced in about 80 countries (Murthy and Madhava Naidu, 2012b)

It is also a major source of waste, or by-products. The waste generated by coffee production is classified into pulp, skin, silver membrane, which are by-products obtained during the processing of the fruit, and lastly, there are the coffee grounds that are obtained after the consumption of the drink. It is estimated that one tonne of green coffee produces 650 kg of spent grounds (Janissen and Huynh, 2018b). With a global production of 11-13 million tonnes of coffee, it is estimated that 6,000,000 tonnes of spent coffee grounds alone are being produced worldwide every year (Mussatto, Ercília M. S. Machado, *et al.*, 2011; Janissen and Huynh, 2018b). According to the International Coffee Organisation from 2010 to 2017 coffee production grew from 140 to 152 million bags (60 kg bags). The forecast for 2018/2019 is 174.5 million bags which is a record figure (USDA, 2018). Which on the one hand could be a problem but on the other hand it could be seen as an opportunity, since there is the big challenge of repurposing all of the by-products derived from coffee growing, processing and consumption.

Many authors call coffee grounds a problem, as far as disposal is concerned, due to the high oxygen demand during decomposition and the potential release of residual caffeine, tannin and polyphenol contaminants into the environment (Vardon *et al.*, 2013). The energetic valorisation of this residue seems to be a promising alternative to produce biodiesel, syngas, bio-oil and biochar, thus generating stabilised solids for carbon storage and soil conditioners (Vardon *et al.*, 2013).

Since 2010, there has also been a significant increase in the scientific interest for coffee grounds recovery, from 0/1 article per year to 77 articles in 2018, according to a Scopus keyword search: Spent coffee ground. Compared to a total of 291 articles between 1984 and 2018, as many as 284 were published from 2010 to 2018. Looking at the trend in scientific research from a spatial perspective, it emerges that the countries in which there were published the most papers, are among the largest producers or consumers of coffee (e.g., Portugal, South Korea, Italy, Brazil). The increase in the production and the growing number of publications indicate a growing interest in both the industry and science.

Coffee by-products have various uses depending on different factors, such as plant variety, soil and climate characteristics of the growing site, processing techniques and also from the parts of the fruit, all of which affect the chemical and physical characteristics of the by-product.

Spent coffee grounds contain a high carbohydrate content (82g/100g of dry material) (Mussatto, Ercília M. S. Machado, *et al.*, 2011) with the main constituents being hemicellulose (36.7g/100g) and mannose (21.2g/100g). The high carbohydrate content and high calorific value (20 MJ kg^{-1}), suggest an added value in biofuel production processes (Silva *et al.*, 1998). However, the emission of NOx and CO_2 appears to be high in the combustion of coffee grounds (S. B. Kang *et al.*, 2017); this affects global climates thus, recommending the use with other thermochemical processes.

Some authors provide data on the chemical characteristics of coffee grounds (Tab.1)

Table 1: Some examples from the literature, of the chemical characteristics of spent coffee grounds (%wt).

(Janissen and Huynh, 2018a)		(S. B. Kang *et al.*, 2017)		(Vardon *et al.*, 2013)	
Carbohydrates	82	Water content	11.69		
Cellulose	8.6	Ash	2.06		
Hemicellulose	36.7	Volatile matter	70.03		
Lipids	6	Fixed Carbon	16.22		
Total fibers	60.5	C	53.05	C	56.1
Proteins	13.6	H	7.19	H	7.2
Nitrogen	2.3	O	36.2	O	34.0
Caffeine	0.4	N	1.45	N	2.4
Tannins	0.02	S	0.05	S	0.14
Chlorogenic acid	11.45			P	0.18
Moisture	11.69				
Ash	1.6				

The lower heating value is between 18.8 - 20.9 MJ kg^{-1} for the dried material (S. B. Kang *et al.*, 2017), up to 23 MJ kg^{-1} (Vardon *et al.*, 2013). These values design the product as an excellent material for thermochemical processes, since oak wood, for example, has a calorific value of around 19 MJ kg^{-1} (S. B. Kang *et al.*, 2017).

Spent coffee grounds lend themselves to multiple uses, because they contain a high number of organic compounds, are easily transformed through thermochemical processes and are easy to find given the huge amount produced and their low cost (Peshev *et al.*, 2018).

At present, the uses of coffee waste are manifold, only for the fraction of spent grounds are noted uses for the production of antioxidants, biodiesel, cellulase, chlorogenic acid, coffee oil, compost, dietary fibre, ethanol, culture substrate for fungi and vermicompost (Murthy and Manonmani, 2008; N Kondamudi, Mohapatra and Misra, 2008; Adi and Noor, 2009; Burton, Fan and Austic, 2010; Hachicha *et al.*, 2012b; Murthy and Madhava Naidu, 2012a; Woldesenbet *et al.*, 2013; Ballesteros, Teixeira and Mussatto, 2014; Buntić *et al.*, 2016).

1.6. Thermochemical and biochemical conversion

The combustion process.

The combustion process consists of the complete oxidation of the substance in the presence of oxygen. During this reaction, the chemical energy contained in the fuel is released in the form of heat. Depending on the nature of the fuel, the type of plant and the combustion conditions, emissions generated can be characterised by different values of organic and inorganic micropollutants, NO_X, SO_X, CO, and PM. The optimal conditions for complete combustion are generally: the air (oxidising agent) that must be supplied in excess, the residence time of the fuel gas in the reaction area, the temperature, and the characteristics of the biomass. Combustion comprises the following steps:

- Heating of the biomass to a temperature below 100°C;
- Drying of the biomass between 100°C and 150°C;
- Pyrolysis, with decomposition of wood components between 150°C and 230°C;
- Biomass gasification between 230°C and 500°C, solid carbon gasification from

500°C to 700°C and oxidation of combustible gases from 700°C to about 1,400°C.

Depending on the chemical composition of the organic matrix, the temperature reached and the amount of oxygen available, different types of residual products such as ash, coal (biochar), tar, oils and emissions can be produced.

Thermal boilers lit with lignocellulosic biomass such as wood chips, chopped pellets of crop residues (vine, olive, straw, etc.) produce heat that can warm air, water, or both through special heat exchangers. The characteristics of the fuel that most influence the efficiency of the process, are its water content, calorific value, particle size, ash, ash fusibility, chlorine, and sulphur content. The combined production of electricity and heat (cogeneration) from solid biofuels takes place through two different cogeneration systems where essentially the biomass is:

- directly combusted in a boiler, producing heat, and transferring it to an energy product that feeds the thermodynamic cycle of the electricity production system;
- chemically broken down into volatile molecules in special thermochemical reactors (pyrogasifiers) with the production of low-calorific gases (syngas) which can be directly combusted in alternative internal combustion engines or gas turbines after filtering out unburned particles (tars, dust, etc.).

In both systems the electricity is produced by alternators coupled to reciprocating engines or gas turbines or micro-turbines as in commercial cogeneration systems fuelled by gas, biogas, vegetable oils etc (Carnevale, 2020).

<u>The pyrolysis process</u>

Pyrolysis is the first step in any gasification process and consists of the thermochemical decomposition of the biomass obtained at temperatures between 400 and 800 °C, in the absence or with a very small amount of oxidising agent. This phenomenon causes a devolatilization of the biomass with the production of a complex mixture of gases (CO, CO_2, H_2, CH_4, H_2O), condensable vapours and charcoal.

The size of the biomass particles, their heating rate, and the temperature at which they are heated, determine the speed of the pyrolysis process and consequently the composition of the final products. We can have reactions of fast pyrolysis and slow pyrolysis, the slow pyrolysis that is characterized by a modest heating speed, is prevalent in updraft gasifiers but also in downdraft gasifiers where in the presence of a material with a coarse size it maximizes the char production, even if tar is always present in the form of vapours.

With sufficiently high heating rates of the material, we can have fast pyrolysis, producing a high quantity of hydrocarbons at high temperatures, above 700°C, or liquids in the case of lower temperatures, below 600°C, and a small fraction of char. Considering a woody biomass, consisting of: lignin (20-25%), cellulose (40-50%) and hemicellulose (25-40%), during pyrolysis first the hemicellulose decomposes between 200-300°C, then the cellulose breaks down between 250-300°C and finally the lignin between 300-500°C. Therefore, as the composition, density and thermal permeability of the biomass change, the course of the pyrolysis reaction and the interaction between the chemical and physical processes involved also vary greatly.

In addition to the composition and size of the particles, another important factor influencing the process of pyrolysis is the heating rate. Fast heating, in the order of 100°C/min, reduces the residence time at low temperatures, limiting the secondary decomposition of the volatile parts, thus decreasing the production of gas and char, in favour of a large quantity of products in the liquid phase or in the form of vapours such as heavy hydrocarbons (tar). With lower heating rates, secondary reactions improve, with greater gas and char production (Basu, 2013). The pyrolysis products have a composition that can vary greatly, but it is not necessary to determine this precisely and exhaustively as it is the subsequent gasification reaction that will lead to the formation of syngas and their influence on the final product is marginal. Products in the form of condensable liquids (tar) or vapours, on the other hand, can create problems in the next step and compromise the final synthesis gas (Kirubakaran *et al.*, 2009). The pyrolysis tests examined in this paper were carried out using an up-draft reactor, designed for experimental purposes through the collaboration between CREA-IT and the University of Tuscia (Fig. 5) (Carnevale, 2020).

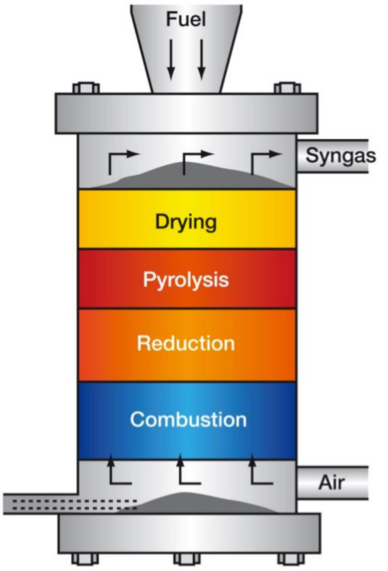

Figure 5 - Schematic representation of the prototype pyrolizer used for biochar production

The cylindrical reactor is made up of stainless steel and has an internal grid that holds the biomass and allows for the passage and diffusion of air through the biomass. The biomass is loaded from the top while air is blown through a nozzle at the bottom of the reactor. A duct at the top releases the fumes produced during the process. The conversion of biomass into biochar takes place as the pyrolysis front progresses from the top of the reactor downwards. A collector is provided under the grate for the recovery of the solid residue.

The gasification process

Gasification is a thermal degradation process that takes place at high temperatures (above 700-800 °C), in the presence of an oxidising agent, typically air, oxygen or steam. The resulting gaseous mixture is what is known as a synthesis gas (syngas) consisting mainly of carbon monoxide (CO), carbon dioxide (CO_2), hydrogen (H_2), methane (CH_4), other hydrocarbons such as ethylene (C_2H_4) and ethane (CH_3), water (H_2O), nitrogen (N) and other substances such as ash, coal particles, tar, and oil. The gas produced is suitable for use as a common gaseous fuel, thus easy to supply and transport, or for use in other industrial processes (Higman, 2008).

The gasification process takes place in a reactor and can be divided into two main stages:

- A first stage at a temperature below 600°C in which the volatile components of the fuel are released. What remains from the pyrolysis process is mainly char and ash. Char is a complex agglomerate consisting of carbon, ash, sulphur compounds and volatile hydrocarbons.

- The second stage is the gasification of the pyrolysis products until the gases and vapours in them are decomposed and the solid char contained in them is converted. This last phase is the most important reaction of the gasification and process and, being the slowest phase, it conditions all of the kinetics of the process.

The gasifier prototype that was considered in this paper is a downdraft reactor with fixed bed in stainless steel, with manual loading of the biomass; this too was manufactured for experimental purposes in collaboration with the University of Tuscia.

The external surface, between the throat area and the grate, is covered in a layer of rock wool for thermal insulation. Inside the reactor, in the throat area, there are five nozzles for air distribution, while in the lower part there is a grid equipped with an electric motor to shake the collected coal, in order to improve its conversion into syngas. The syngas is sucked in by a fan, while the solid residue is collected in the tank below the grate. The air flow is introduced into the reactor, in the throat area, as a result of the air vacuum produced in the reactor by the downstream fan. The fan is equipped with an inverter to set the air flow rate.

Prior to gasification, the biomass is shredded and air-dried to reduce its size and moisture content. The gasification procedure follows four steps:

1. Manual loading of the biomass into the reactor;

2. Adjustment of the air flow;

3. Ignition of the biomass (flame ignition) to start the process;

4. Monitoring of the process parameters and sampling of the syngas.

During the process it is possible to monitor the following parameters: air flow rate and temperature, through a thermocouple inserted in a stainless steel thermowell placed in the syngas outlet and also the time needed for the complete gasification of the biomass. The syngas can be collected, at approximately 30°C, using Tedlar bags at a sampling point located on the pipe between the fan and the torch. Subsequently, the syngas samples can be characterised using the Micro GC Inficon 3000 gas analyser to obtain their composition.

Biochemical conversion

Anaerobic digestion is a set of biological processes through which, complex organic substances (lipids, proteins, carbohydrates) contained in substrates are "digested" in the absence of oxygen, leading to the production of a combustible gas (biogas), a liquid and sludge with potential fertilising properties.

Anaerobic digestion is a natural chemical-biological process that leads to the degradation of organic matter molecules in special reactors called digesters to obtain different products that can be used for energy and/or agricultural purposes. The reaction is catalysed by bacteria that live in anaerobiosis, i.e., they do not need oxygen for their metabolism. The transformation process takes place in several stages, whereby organic matter is transformed into acetic acid (CH_3COOH), carbon dioxide (CO_2) and hydrogen (H) by anaerobic microorganisms, through the three stages of hydrolysis, acidogenesis and acetogenesis. This is followed by methanogenesis to form methane which, together with CO_2, is the main component of biogas.

The processing times are relatively long compared to other procedures, but the advantage is that complex organic matter is converted to methane and carbon dioxide, leading to the final production of a fuel gas with medium heating value. The reaction environment, usually referred to as the digester, must maintain the following parameters to allow for the growth of all the micro-organisms involved: pH between 7÷7.5 and a temperature of around 35°C if mesophilic bacteria are used, or around 55°C if thermophilic bacteria are used. A very important factor regulating the efficiency of the process is temperature, which varies according to the quantity and type of material used and the site where the plant is installed. In fact, for some substrates mesophilic bacteria, which "work" well at temperatures between +20 and +45°C, will be more suitable, while for other substrates thermophilic bacteria will be indicated, which prefer temperatures between +45 and +120°C; rarely are psychrophilic organisms used, which live at temperatures between 0 and +20°C. The temperature parameter also has a direct effect on the retention time: the higher the operating temperature, the shorter the time that is required for biogas production. Biogas can be used to produce a biofuel that is very useful for replacing traditional fuels through refining methods: the so-called "biomethane". Biomethane can: either be combusted in the form of biogas to produce electricity and heat (used on site or possibly fed into the grid), or added to the gas distribution network for use in households, or it can also be used for automotive purposes. By means of a carbon dioxide removal process called upgrading, the biogas can be transformed into a gas that is similar to natural gas, depending on the specific upgrading technology adopted. The technologies employed for the chemical-physical process of transforming biogas into biomethane, capable of producing a quality gas to be used as a transport fuel or to be injected into the natural gas network, are already commercially available and have proven to be technically and economically feasible however, studies to optimise and develop further innovative processes are constantly evolving. Depending on the raw composition of the biogas, upgrading includes separation of carbon dioxide, drying of the gas, removal of trace substances such as oxygen, nitrogen, hydrogen sulphide, ammonia, or siloxanes, as well as compression for subsequent reuse of the gas. The treatments included in the transformation are:

- Purification: dehumidification or drying and desulphurisation;
- Removal of gaseous ammonia, nitrogen, siloxanes, dust;
- Refining (upgrading);
- Final conditioning: odorization and/or compression;
- Mixing and feeding.

Purification or dehumidification and desulphurisation consist of the removal of water vapour, which can create condensation in the gas lines and cause corrosion, and the removal of hydrogen sulphide (H_2S). This can be achieved through the application of various technologies, based on different physical and chemical principles.
The methods that are currently in use are: oscillating pressure adsorption or PSA, pressure water washing or PWS, washing with organic solvents, membranes or with monoethanolamine, MEA. The main upgrading processes (Petersson and Wellinger, 2009).
During pressurised water scrubbing, the biogas is compressed and conveyed into a filling tank with water flowing in the opposite direction. CO_2 and H_2S are more soluble than methane in water, so the biogas will be methane-rich and water-saturated. In order to reduce the water vapour, the biogas is subsequently dried and dehumidified, while the CO_2 is conveyed to a tank where there is reduced pressure; sometimes the process is intensified by stripping with air or operating under vacuum.
During the chemical absorption phase with amine solutions, the dehumidified and desulphurised biogas rises through a tower where an aqueous amine solution flows from top to bottom and is sprayed uniformly over both the column section and the bed of some filling bodies. The filling bodies have a contact surface that favours the interchange between the gaseous state and the liquid state, in which the carbon dioxide is absorbed by the amine solution. In contrast to CO_2, methane molecules do not dissolve in the washing liquid due to their apolarity and leave the tower as a gas without any significant reduction. The absorption of acid gases is carried out with alkaline solvents such as ethanolamines, monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), and methyl diethanolamine (MDEA) or potassium carbonate solutions. It is also possible to separate carbon dioxide from the biogas by adsorption on activated carbon beds or molecular sieves.
During the Pressure Swing Adsorption (PSA) phase, dry enrichment occurs with methane and CO_2 adsorption, as the pressure on the activated carbon molecular filter increases. PSA plants usually consist of four adsorption units. High pressure biogas is

flushed through a first unit and CO_2 is adsorbed until the molecular carbon is saturated. To complete the regeneration, a vacuum is applied to create a negative pressure.

As far as separation processes with membranes are concerned, there are gas-phase or gas-liquid systems and, if the liquid is an amine and, the system has a higher selectivity. The system works based on the different sizes of the molecules and therefore their different permeability through the membrane. Other factors to consider are the different pressures created between the two sides of the membranes and the temperature of the gas. Hence, CO_2 and H_2O pass freely through the membrane while methane is separated. High concentrations of methane can be achieved with several membranes in series.

Cryogenic treatments are based on the compression and subsequent cooling of the biogas through heat exchangers followed by an expansion phase. After the removal of the CO_2, the gas is cooled further to condense the methane as well. Methane has a boiling point of -160 °C at atmospheric pressure, whereas the boiling point of CO_2 is -78 °C. Therefore, CO_2 can be separated from the biogas in the form of a liquid by cooling the biogas at high pressure. It is difficult to make a comparison between different biogas upgrading technologies, because many essential parameters strongly depend on the local context. Moreover, the capabilities of a certain technology often do not represent the most economical choice. In this respect, it is useful to perform a detailed analysis of the specific expected costs and to consider all of the possible upgrading technologies (Bekkering, Broekhuis, and van Gemert 2010; Hullu *et al*. 2008; Persson 2003). With regards to the economic evaluations, it can be observed that specific costs decrease as the size of the plant increases. Specific costs also decrease between plants operating predominantly with dedicated energy crops and plants operating predominantly with livestock manure, due to the decrease in the cost of the substrate being used.

In addition to biogas, the anaerobic digestion process also produces digestate, a mixture of solid and liquid fractions, defined as a co-product. When it is produced from the exclusive digestion of uncontaminated biomass, it can be reused as a soil conditioner, as an alternative to chemical fertilisers, in accordance with Directive 91/676/EEC, better known as the Nitrates Directive, implemented in Italy by the Legislative Decree No 152 of the 11th May 1999, which aims at protecting surface freshwater and groundwater from nitrate pollution coming from agricultural sources.

The main critical elements that need consideration, in order to favour the rapid development of a biogas-biomethane chain, concern the application of the Decree of the 5th December 2013 whose main focus is on the modalities of incentives for biomethane fed into the natural gas network, the need to favour the use of local biomasses with the maximum result in terms of increasing the carbon content in the soil and, in general, reducing greenhouse gas emissions, moreover, the awareness that the development of plants is an element of integration and not competition with already existing traditional agricultural supply chains (Vismara *et al.*, 2011).

1.7.Aim of the study

The aim of this thesis was to study the possibility of producing energy through the exploitation of alternative sources.

The repurposing of agricultural and agro-industrial waste has long been at the centre of attention, both to avoid waste production and because that kind of waste often has interesting energy characteristics.

Coffee is a beverage being consumed all over the world that leads to the production of huge quantities of waste. The aim of this study was to investigate the possibility of using coffee wastes as a source of energy, through an extensive characterisation; as well as evaluating the possibility of producing quality pellets from coffee wastes and using them in combustion processes, in addition to evaluating emissions into the atmosphere. Furthermore, different supply chain scenarios for the production and energy valorisation process of pellets from spent coffee grounds in the Lazio region were hypothesised, with the aim of verifying their environmental impact through the LCA method.

The research then focused on the comparison between coffee residues and other traditional biomasses, to verify the possibility of modelling the heating value by creating a homogeneous data set starting from the composition of the different types of biomasses.

In addition, agricultural waste from the pruning of hazelnuts and olive trees was explored as it is currently burned in fields, against current regulations and it represents an interesting resource. The aim of the investigation was to verify the impact of mechanical pre-treatment, using an industrial-scale device, on the quality of the resource and the production of methane, through a detailed analysis of the chemical and physical composition of the treated biomass.

Environmental sustainability in the use of residual biomasses is not only accounted for by the chemical and physical characteristics of the resource, but it also takes into account other phases of the possible supply chains, from treatment to transport to the release of further substances and molecules into the environment due to various processes**.** In this analysis, the aim was to address the aforementioned issue using different analytical approaches and, in some cases, with different applications.

2. General methods

2.1. Chemical-physical characterisation

The chemical characterisation of coffee grounds and hazelnut and olive tree pruning residues was carried out at the Agro-Energy Laboratory of the Department of Agricultural and Forestry Sciences of the University of Tuscia and partly at the Laboratory of Experimental Activities - Renewable Energies from Biomass (LAS-ER-B) of CREA-IT in Monterotondo.

For moisture content analysis, reference was made to the standard UNI EN ISO 18134-1:2015 (replaces UNI EN 14774:2010) Solid biofuels - Determination of moisture content - Oven drying method - Part 1: Total moisture - reference method (*UNI EN ISO 18134-1:2015*, 2015). The biomass sample was dried in an oven at 105±2°C for 24 hours (Fig. 6). The moisture content was calculated from the weight loss of the sample before and after drying. Specifically, the moisture content on a wet basis was calculated according to the following relationship:

Figure 6 - Stove Memmert UFP800

The moisture content, Mar of the test portion, as received, expressed as a percentage by mass, shall be calculated in accordance with Formula (1):

$$Mar = \frac{(m2 - m3) - (m4 - m5)}{(m2 - m1)} X100 \qquad (1)$$

Where:

m1 is the mass of the empty tray used for the test portion;

m2 is the mass of tray and test portion before drying (weight in room temp);

m3 is the mass of tray and test portion after drying (weight when still hot);

m4 is the mass of the reference tray before drying (weight in room temp);

m5 is the mass of the reference tray after drying (weight when still hot).

For the analysis of the ash content, reference was made to the standard UNI EN ISO 18122:2016 (replaces UNI EN 14775:2010): Solid biofuels - Determination of ash content (*UNI EN ISO 18122:2016*, 2016). The biomass sample (1 g) was placed inside porcelain crucibles and placed in the furnace where it was heated first up to 250°C with a ramp of 6.5°C/min and then up to 550°C with a ramp of 10°C/min (Fig. 7).

Figure 7 - Muffle furnace Lenton EF/11 8B

The ash content was calculated according to the following relationship however, as the dry sample was obtained from moisture, the Mad term is equal to 0 and thus the formula is simplified.

The ash content on dry basis Ad, of the sample expressed as a percentage by mass on a dry basis shall be calculated using Formula 2:

$$Ad = \frac{(\mathrm{m3-m1})}{(\mathrm{m2-m1})} \; x \; 100 \; x \; \frac{100}{100-Mad} \qquad (2)$$

Where:

m1 is the mass of empty dish;

m2 is the mass of the dish plus the test portion;

m3 is the mass of the dish plus ash;

Mad is the % moisture content of the test portion used for determination.

For the analysis of the heating value, reference was made to the standard UNI EN ISO 18125:2018 (replaces UNI EN 14918:2010): Solid biofuels - Determination of heating value (*UNI EN ISO 18125:2018*, 2018). The biomass sample was pressed so as to obtain a pellet tablet, which was then placed in a crucible inside the calorimetric bomb.

The sample was placed in contact with a cotton thread, which was in turn connected to two electrodes (Fig. 8).

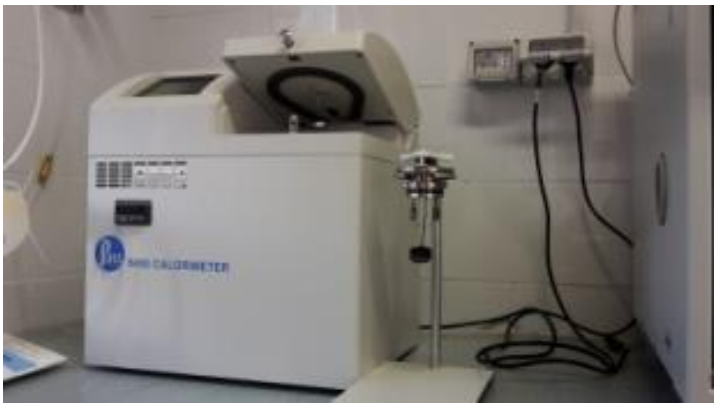

Figure 8 - Anton Calorimeter Parr 6400

When the bomb was closed, the envelope containing the sample was saturated with oxygen and following the passage of current through the electrodes, combustion of the wire and consequently of the sample, was obtained.

The combustion of the sample resulted in the release of heat and thus in an increase in temperature following which, the gross heating value (GCP) was determined. From this, it was possible to derive the value of the lower heating value (LHV) given by the hydrogen content.

For the analysis of carbon, hydrogen and nitrogen (C, H, N), reference was made to the standard UNI EN ISO 16948:2015 (replaces UNI EN 15104:2011): Solid biofuels - Determination of the total carbon, hydrogen and nitrogen content (*UNI EN ISO 16948:2015*, 2015). The sample of about 0.1 mg was enclosed in a tin capsule and then, using a pneumatic carousel, it was inserted into the furnace of the instrument where following combustion, it released gaseous compounds (Fig. 9).

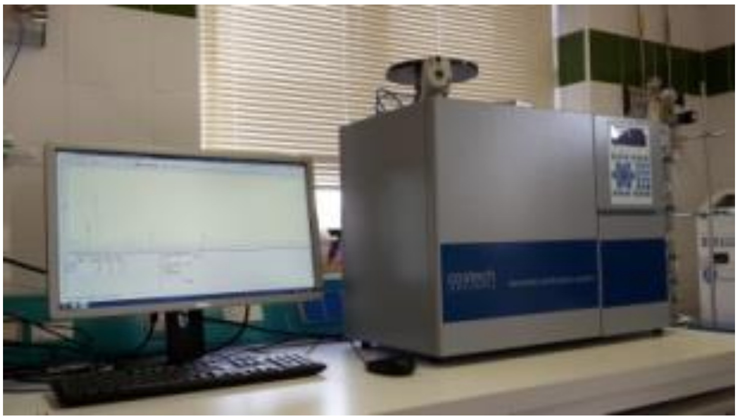

Figure 9 - Costech ECS 4010 elemental analyser

These compounds passed through the chromatographic column at different times and as a result, a chromatogram with spaced peaks was obtained, with each peak being associated with a particular element (C, H and N) and with an area proportional to the concentration of that element.
The instrument also allows the determination of sulphur (S) for which however, there is another reference standard. That being said, sulphur content of biomasses is generally negligible.
For the analysis of organic micropollutants, the reference standards are UNI EN ISO 16968:2015: Solid biofuels - Determination of trace elements (i.e. As, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, V, Zn) and UNI EN ISO 16967:2015: Solid biofuels - Determination of trace elements (i.e. Al, Ca, Fe, Mg, P, K, Si, Na, Ti) (UNI EN ISO 16967:2015, 2015).

For the analysis of inorganic micropollutants, the above standards were not used because they require mixtures that were incompatible with the instrument used and below is the (experimental) procedure that was adopted.

For the sample preparation, an aliquot of each sample (approximately 500 mg) was transferred into Teflon containers and subjected to acid attack using a microwave digester (Start D, Milestone, Italy). The attack mixture that was used, consisted of 4 ml HNO_3 and 2 ml H_2O_2. All of the solutions that were obtained, were brought to a final volume of 100 ml with the addition of ultrapure water and were analysed.

The Agilent 7700 Series ICP-MS spectrometer was used for the determination of the elements (Fig. 10).

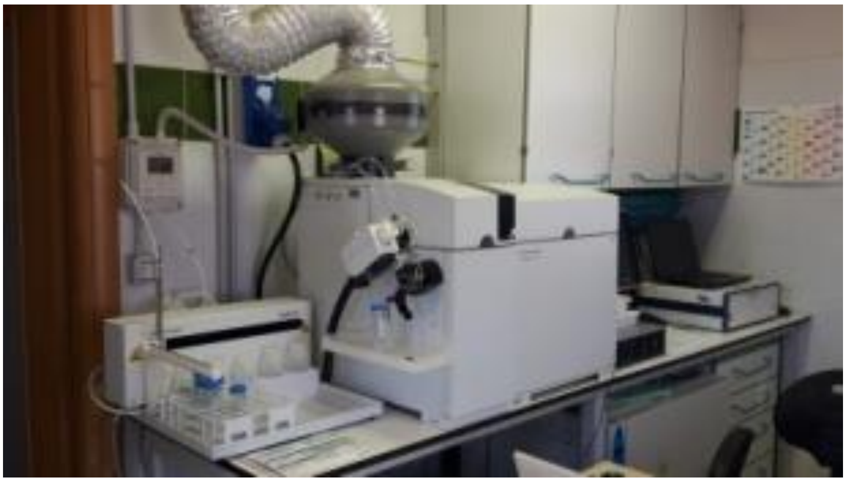

Figure 10 - Agilent 7700 Series ICP-MS spectrometer

The instrument was calibrated using multi-element standards (Standard mix, 10 ppm metal concentration), prepared in 1% HNO_3 acidified aqueous solution. The calibration line was constructed using 5 standards in increasing concentration from 5 to 100 ppb. Y was used as the internal standard, through the automatic input system with which the instrument is equipped.

2.2. Pellet production

Following the chemical-physical characterisation of the coffee grounds, pelletising tests were carried out using a Master 380 C Bianco-Line pelletizer, in order to verify the best system for thickening the grounds and obtaining the fuel.

The tests were carried out as follows:

1. 100% coffee grounds;
2. 85% coffee grounds and 15% sawdust;
3. 75% coffee grounds and 25% sawdust;
4. 33% coffee grounds and 66% sawdust.

Subsequently, the pellets that were obtained, were characterised from a chemical-physical point of view as described above for the coffee grounds (elemental analysis, ash, higher and lower heating value).

A further test was carried out using another type of binder in the production phase: corn starch. This option was contemplated given the unsatisfactory mechanical and durability characteristics of the previous tests. Maize starch was used by mixing it with coffee grounds at 2%, since the ENplus pellet certification regulation allows the use of a binder up to 2% of dry weight for all of the 3 categories: A1, A2 and B. The pellets that were obtained, were analysed from the point of view of their higher heating value.

2.3. Emissions

For combustion in the boiler, about 80 kg of coffee skins with 2% corn starch were produced.

For the evaluation of the emissions, a GSA/80 biomass boiler (D'Alessandro Termomeccanica GSA 80KW series) was used which was fed with coffee pellets at a rate of 20 kg h^{-1} (Fig. 11) by means of motorised blades conveying the fuel towards the drop hole in the upper auger.

Figure 11 - on the left, the boiler used for the tests; on the right, the pellets inside the tank.

Emissions were characterised at the LAS-ER-B laboratory using a Dadolab HP1 probe connected to a Horiba PG250 multi-parameter detector for monitoring CO, CO_2, NO, NO_x, SO_x and O_2. The same probe was also interfaced with the Ratfish RS 53-T FID detector for Total Organic Carbon (TOC) analysis. The Dadolab HP5 probe interfaced with a Dadolab Source Tester ST5 pump and the Dadolab SC5 Smart Chiller refrigerated whirlpool system allowed for the total dust to be sampled (Fig. 12). Particulate matter was sampled on a glass filter with 30-minute isokinetic sampling being performed in triplicate. CO, CO_2, NO_x, SO_2, O_2, were acquired with a multi-parameter sampler. Metals were sampled with a quartz filter and bubblers with 1 part in 10 of nitric acid and hydrogen peroxide, for 30 minutes repeated for 3 times.

Figure 12 - Instrumentation used for emission sampling during coffee pellet combustion. a) Dadolab HP1 probe, b) Horiba PG250, c) FID Ratfish RS 53-T, d) Dadolab HP5 probe, e) Dadolab Source Tester ST5, f) Dadolab SC5 Smart Chillerha.

2.4.Harvesting and processing

Hazelnut and olive pruning's were harvested in the winter 2020 in the province of Viterbo, central Italy, using a COMBI TR160 harvester. The raw materials were then packed and stored in a covered and ventilated area to be dried naturally until the early summer 2020. The dried raw materials were comminuted with a knife mill to a length of approximately 30 mm. An industrial-scale device, designed for the grinding and fractionation of raw materials with a high dry matter content (>70%), was used to process the wood chips (Ba *et al*., 2010). The ground material was then screened through a plane screen into three fractions, namely C (Coarse), M (Medium), F (Fines). The fines were further classified according to their size, shape, and density into two fractions (called F1 and F2) through a centrifugal classifier.

The power that was absorbed by the device was measured with a wattmeter (MTME-485, ABB-SACE, Italy); power, supply voltage, current and time were recorded on a PC card at one-second intervals. The specific energy (MJ kg^{-1}) required for grinding was determined by integrating the area under the power demand curve by the total time required to grind the 30 kg sample. The tests were performed in duplicate.

The particle size distribution of the products was determined according to the ASABE standard S319.3 (Wilcox, Deyoe and Pfost, 2016). During this test, mass percentages were measured as a function of particle size by being run through sieves of specified mesh size. A sieve analyser used twelve ISO sieves (2.000, 1.400, 1.180, 1.000, 0.700, 0.600, 0.500, 0.425, 0.300, 0.212, 0.150 and 0.090 mm). Each time, the sieve was operated for 15 minutes and the mass of the samples for particle size analysis was approximately 250 g.

2.5.Anaerobic digestion

Biogas production experiments were carried out on the samples of raw materials and on the F1 and F2 fractions of their processing, to evaluate biogas and methane yields. The experiments were carried out in anaerobic batch reactors with a working volume of 2 litres and equipped with mixing and thermostating systems; the reactors were operated under mesophilic conditions (38°C). Anaerobic sludge from a mesophilic digester, containing 3.67% total solids (TS) and 2.68% volatile solids (VS), was used as inoculum to initiate the biological process. The inoculum/substrate ratio was in the range of 2.04 - 2.1 on an SV basis, resulting in a substrate loading in the range of 49-50 g_{TS}/L. The experiments lasted for 28 days, and each experiment was run in triplicate, including two controls with only inoculum sludge; the gas produced by the controls was subtracted from the actual gas that was produced through media digestion.

Biogas production was measured daily in average samples according to standard methods (American Water Works Association, 2017). The composition of the biogas, with reference to the methane (CH_4) content, was measured using a portable automatic SG06IOMX6 analyser (B.A.G.I. srl, Milan, Italy).

2.6.LCA

The Society of Environmental Toxicology and Chemistry (SETAC) defines LCA as: "a process for identifying the environmental loads associated with a product, process or activity, from extraction and transformation of raw materials, product manufacture, transport and distribution, use, reuse, storage, recycling, to disposal". Life Cycle Assessment (LCA) is a standardized approach (ISO, 14040 Environmental management - Life cycle assessment - Principles and framework) based on a general view of the entire industrial apparatus or production cycle that allows to evaluate and quantify the energy loads and potential environmental impact that may result from one or more phases of the life cycle of products and/or services. The phases of LCA are composed of:

- Definition of goal and scope;
- Inventory analysis;
- Impact Assessment (LCIA);
- Interpretation of results.

In the phase of defining the goal, scope and boundaries of the system, the objectives are set and the type of audience to which it is addressed, and the scope are defined; in addition, the functional unit and the reference flow, the boundaries of the system and the quality of data (primary, secondary and tertiary) are also established. The functional unit represents the quantity of product taken as reference for the entire study, and the system's boundaries are represented by all of those aspects that should be included in the study. The boundaries can be:

- From cradle to grave: represents all of the phases that are part of a production process, from the extraction of raw materials to the disposal of the good that is being produced;
- From cradle to gate: represents the stages owing to the use of raw materials, excluding distribution, use, disposal and end of life;
- Gate to gate: represents the processes taking place within the company;
- Zero burden: refers to waste management systems, beginning from when the waste starts being defined as such, including treatment processes and concluding

with its final disposal.

For most industrial systems, there is an identification of the major processes and related environmental interventions:

- Major production;
- Secondary or co-product production;
- Ancillary materials production;
- Energy production;
- Energy consumption;
- Transportation;
- Waste treatment.

LCI is the collection of the data related to qualitative and quantitative input and output streams. Inputs include the raw materials used and the thermal and electrical energy that power the processes; outputs, on the other hand, represent the output products during and/or at the end of the process, including emissions into the air, water, and soil.

Data can be:

- Primary: collected directly in the field and associated to the production process that is being considered;
- Secondary: contained in LCA databases;
- Tertiary: contained in manuals, scientific publications and encyclopaedias.

Subsequently, there is the phase of allocation in the system of incoming and outgoing flows that are based upon:

- Relationships of physical characteristics;
- Economic value.

The impact assessment phase aims at understanding and assessing the significance of the potential environmental impacts of a product in all of its phases. Products should be grouped into impact categories (acidification, global warming, eutrophication, stratospheric ozone depletion, land use change, etc.). Each of these categories becomes more specific by reference to a characterization factor calculated for the time period to which it relates.

Impact categories are divided into midpoints and endpoints. The formers are measured according to units of equivalent substances without these being associated with the effect on a specific target (e.g. human health, ecosystems, etc.); the latter, on the other hand, are expressed through indicators having their own units of measurement associated with a specific effect.

The analysis of the results consists in representing graphically the results of LCI and LCIA. This step defines and improves the reliability and trustworthiness of the results of this study. During this phase, a completeness check is performed, a sensitivity check that assesses the reliability of the final results, and a consistency check that determines whether the assumptions, methods, and data are consistent with the objective and scope of the study.

The study was conducted in a cradle-to-grave scope with the three possible scenarios for extracting energy from SCG also being defined: SCG biodiesel, SCG direct combustion and SCG bio-oil. The environmental footprint of each production and combustion scenario was calculated and compared to SCG pellet production. The selected functional unit was 1 MJ of energy product, to allow for the comparison of the different energy valorisation approaches. The life cycle assessment methodology has four steps: objective and purpose, inventory analysis, impact assessment and interpretation of results (Berg and Lindholm, 2005; Stichnothe and Azapagic, 2009; Ji *et al.*, 2018). LCA was used to identify the environmental impact associated with the production, processing, application, and end-of-life of pellets from spent coffee grounds. The footprints were calculated using the SimaPro software (version 8.3.0), according to the ISO 14040:2006 requirements (ISO - ISO 14040:2006 - Environmental management — Life cycle assessment — Principles and framework, 2016). The SCG was collected from twenty distribution companies in the Lazio region and transferred directly to the pellet factory. The productivity of the pellet factory was assumed to be 357 kg h^{-1} with 2000 working hours per year. The average transport distance from coffee consumers to the pellet factory was estimated to be 38.69 km. The assumption is based on the average distance of important vending machine companies located in eleven cities in the Lazio region from the province of Rome, where the pellet company operates. As mode of transportation, road transport was considered according to Ecoinvent (Wernet *et al.*, 2016).

The data associated with the operation of the pelletising plant was obtained from the literature (Fantozzi and Buratti, 2010b; Rajabi Hamedani, Colantoni, *et al.*, 2019). The power and energy required for grinding and drying were estimated based on (Yoder *et al.*, 2011; Rajabi Hamedani, Del Zotto, *et al.*, 2019).

Emissions from SCG pellet combustion were also obtained from the literature (A. Colantoni *et al.*, 2021). Colantoni *et al.* measured these pollutants (A. Colantoni *et al.*, 2021).

Additionally, SCG management includes various valorisation routes for energy purposes including transesterification, pyrolysis and incineration of SCG (McNutt and He, 2019).

The LCA model was developed using the SimaPro software (version 9.0.49). In this study, the ReCiPe 2016 v1.03 method (Huijbregts *et al.*, 2016) at both midpoint (H) and endpoint (E) levels converts the data inventory into conversational indicators. At the midpoint level, the environmental results are normalised and characterised to understand the meaning of the indicators and present them in relatively abstract units such as CO_2 equivalent. On the other hand, at the endpoint level the results are interpreted as damage to human health and ecosystem quality and resources. This method follows the objective of obtaining a comprehensive environmental perspective on the production and consumption of SCG pellets. The ReCiPe method has been used in other studies on SCG application (Schmidt Rivera *et al.*, 2020) and pellet production (Buratti *et al.*, 2015; Laschi, Marchi and González-García, 2016; Rajabi Hamedani, Colantoni, *et al.*, 2019). Out of a total of eighteen impact categories being assessed, the following eight categories with significant effects were evaluated: Global warming, terrestrial ecotoxicity, freshwater ecotoxicity, marine ecotoxicity, human carcinogenic toxicity, human non-carcinogenic toxicity, fossil resource scarcity, water consumption.

2.7. Data analysis and modelling

Biomass characterisation (Spent Coffee Grounds and hazelnut and olive pruning residues) and pellet tests were analysed using a one-factor analysis of variance (ANOVA) and Pearson's correlation test. Significance between means was determined using the Tukey post hoc test for multiple comparisons of means tests at the 95% confidence level ($P = 0.05$). Before proceeding, normality and homogeneity of variance were checked using the Shapiro-Wilk test and Levene's test, respectively ($P = 0.05$ for both). All statistical analyses were performed using the JMP PRO 15 (Trial version ©SAS Institute Inc.). Pearson's correlation and ANOVA with Tukey test were applied to determine the relationship between elemental analysis, ash, and upper and lower heating value, first to characterize SCG and also for the pellet test.

Conversely, the ANOVA test was applied to moisture, elemental analysis, heating value and methane yield to observe differences between the particle size treatments of hazelnut and olive residues.

Data from different works and projects was collected for biomass comparison and modelling analysis. With regards to modelling, the statistical analysis was carried out entirely in R ver. 3.6.1. The differences between the species were tested by means of a One-Way ANOVA at the 0.05 level of significance, making it possible to assess the importance of the biomass factor on the energy and compositional parameters. The identification of these differences was subsequently obtained with the Tukey-HSD post hoc test. Shapiro-Wilk and F tests were performed to assess both normality and homoscedasticity of the biomass characterisation variables. Since many variables did not show a Gaussian trend, Friedman's test and Conover's test were performed to understand the difference between the biomasses. Multivariate analysis of the data was carried out using principal component analysis (PCA) to assess the relationships between biomass properties. Cluster analysis was performed using the Ward technique, the aim of which was to obtain a hierarchical classification by minimising the variance of the variables within each group. At each stage, the groups producing the smallest increase in the total variance within the groups were merged (Ward, 1963).

Since the characterisation variables are neither normal nor homoscedastic, quantile regression (QR) has been used to construct linear models that could predict HHV from C, H and N. This method is most accurate when the basic requirements for the application of ordinary least squares (OLS) are not met, particularly in the presence of outliers. Quantile regression is able to provide a much broader analysis of the relationships between variables than the OLS model.

Over the years, QR has been used as an extension of the linear regression model and this allows to do what linear regression does for the mean, on quantiles. By exploiting the estimated parameters, it is possible to consider the quantile value of the response variable as a function of a set of regressors. This makes it possible to appreciate the behaviour of the response variable not only in the mean but also in its entire distribution. By varying the quantile of the regression between zero and one (τ) it is possible to obtain the entire conditional distribution. To assess the quality of the prediction, the mean square route error (RMSE), the mean absolute error (MAE) and the mean bias error (MBE) were calculated. The MBE gives information on the mean forecast error which represents the systematic error of a forecasting model and the MAE gives the mean magnitude of the forecast errors whilst, with the RMSE more weight is given to larger errors (Kato, 2016).

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3. Results organization

The results of this thesis work consist of four articles that relate to my PhD research activity.

Research activities included:

- An extensive characterization of coffee wastes for energy purposes through physical and chemical analyses highlighting the most significant quality indices, the interactions between them and the quantification of their importance. Pelletization trials carried out during the PhD research work, with the aim of obtaining pellets with the highest possible percentage of coffee grounds. This objective is due to the quality of coffee as a fuel, to the large quantity of product available and to the type of product that is not influenced by seasonality. Combustion tests for the characterization of atmospheric emissions.
- The evaluation of the eco-sustainability of the use of spent coffee grounds as a fuel for energy conversion and waste management. The aim of this evaluation is to conduct a life cycle assessment of spent coffee grounds in the form of pellets to evaluate the environmental impacts of the valorisation process, through a life cycle model for the production and application of spent coffee grounds pellets in the Lazio region.
- Comparison of data from conventional lignocellulosic biomass and coffee grounds, modeling the data to verify a prediction. According to the principle of circular economy, coffee companies, in their waste, already have a valuable resource that can be used in a heat generator for the roasting process.
- The effects of a mechanical process on solid fuel quality and anaerobic biodegradability of hazelnut and olive prunings. Every year huge quantities of prunings are wasted, it is a long time that we try to exploit the prunings of olive and hazelnut, these tests have involved mechanical pretreatment and anaerobic digestion tests to observe the effects of these treatments.

3.1.Paper details

Here are the details of the papers, specifying for each paper the status and position in terms of bibliometric indices.

- Andrea Colantoni, Enrico Paris, **Leonardo Bianchini**, Serena Ferri, Vera Marcantonio, Monica Carnevale, Adriano Palma, Vincenzo Civitarese & Francesco Gallucci (2021). Spent coffee ground characterization, pelletization test and emissions assessment in the combustion process. Scientific Report, 1-14.

  Journal bibliometric classification: Scientific Report: IF 5.13; category JIF quartile Q1.

  Leonardo Bianchini role and contribution in this paper: data curation, formal analysis, validation, writing, review and editing.
- Sara Rajabi Hamedani, **Leonardo Bianchini**, Monica Carnavale, Enrico Paris, Mauro Villarini, Andrea Colantoni, Francesco Gallucci (2021). Environmental life cycle assessment of spent coffee ground pellet. Science of the total environment (submitted).

  Journal bibliometric classification: Science of the total environment. IF 7.963; category JIF quartile Q1.

  Leonardo Bianchini role and contribution in this paper: Conceptualization, investigation, data curation, validation, writing, review, visualization.
- Adriano Palma, Andrea Colantoni, Beatrice Vincenti, **Leonardo Bianchini**, Monica Carnevale, Enrico Paris, Francesco Gallucci (2021). Comparison between coffee and common lignocellulosic biomass for energetic potential prediction. Environmental Engineering and Management Journal, 10, 20.

  Journal bibliometric classification: Environmental Engineering and Management Journal: IF 0.916; category JIF quartile Q3.

  Leonardo Bianchini role and contribution in this paper: data curation, formal analysis, validation.
- **Leonardo Bianchini**, Paolo Costa, Pier Paolo Dell'Omo, Andrea Colantoni, Massimo Cecchini and Danilo Monarca (2021). An industrial scale, mechanical

process for improving pellet quality and biogas production from hazelnut and olive pruning. Energies 14, 1–13.

Journal bibliometric classification: Energies: IF 3.004; category JIF quartile Q2.

Leonardo Bianchini role and contribution in this paper: data curation, writing, review and editing, visualization.

3.2. Article 1

Spent coffee ground characterization, pelletization test and emissions assessment in the combustion process (Scientific Reports)

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Spent coffee ground characterization, pelletization test and emissions assessment in the combustion process

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Industrial development and increased energy requirements have led to high consumption of fossil fuels. Thus, environmental pollution has become a profound problem. Every year, a large amount of agro-industrial, municipal and forest residues are treated as waste, but they can be recovered and used to produce thermal and electrical energy through biological or thermochemical conversion processes. Among the main types of agro-industrial waste, soluble coffee residues represent a significant quantity all over the world. Silver skin and spent coffee grounds (SCG) are the main residues of the coffee industry. The many organic compounds contained in coffee residues suggest that their recovery and use could be very beneficial. Indeed, thanks to their composition, they can be used in the production of biodiesel, as a source of sugar, as a precursor for the creation of active carbon or as a sorbent for the removal of metals. After a careful evaluation of the possible uses of coffee grounds, the aim of this research was to show a broad characterization of coffee waste for energy purposes through physical and chemical analyses that highlight the most significant quality indexes, the interactions between them and the quantification of their importance. Results identify important tools for the qualification and quantification of the effects of coffee waste properties on energy production processes. They show that (SCG) are an excellent raw material as biomass, with excellent values in terms of calorific value and low ash content, allowing the production of 98% coffee pellets that are highly suitable for use in thermal conversion systems. Combustion tests were also carried out in an 80kW$_{th}$ boiler and the resulting emissions without any type of abatement filter were characterized.

Day by day the massive usage of fossil fuels, due to the increasing energy demand, has led to a serious issue of environmental pollution. Every year, a large amount of agro-industrial, municipal, and forestry residues are treated as waste, while recent research indicates they can be recovered to produce thermal and electrical energy using biological or thermo-chemical conversion processes[1]. Identifying alternative energy sources is becoming increasingly important worldwide and their use has become essential in fulfilling the growing demand for energy, while at the same time trying to reduce possible environmental repercussions[2]. The European Union supports policies and strategies to develop greater awareness of sustainable attitudes and the use of renewable energy is one of the key targets[3,4]. Worldwide biomass ranks fourth as an energy resource, providing approximately 14% of the world's energy needs. Electricity production using renewable energy increased from 18.91% in 2008 to 25.60% in 2018, while CO_2 emissions associated with worldwide electricity production increased from 28,605 MCO_2 in 2008 to 32,915 MCO_2 in 2018[5]. Among the main kinds of agro-industrial wastes, the residue of soluble coffee represents a significant amount worldwide. In fact, coffee is the second most traded commodity in the world after oil, and one of the most widely consumed beverages in the world[6]. Sustainable treatment and management solutions are needed to reduce the environmental impact of agro-food waste. These waste products produce odor and harborage for insects, which can increase environmental pollution if these by-products are not processed further[7]. Furthermore, the residues obtained from its production are proportionally increasing with growth in coffee consumption. Coffee silver skin and spent coffee grounds (SCG) are the most common coffee industry residues but also mucilage and parchment[8–10]. SCG residue obtained by combining raw coffee powder with hot

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water or steam for instant coffee preparation has fine particle size and high humidity (≈80 wt%), organic load and acidity. Moreover, this residue is produced in large amounts, with a worldwide annual generation of 6 million tons[11]. On average, one ton of green coffee generates about 650 kg of SCG and about 2 kg of wet SCG are generated for every single kg of soluble coffee produced[12]. As such, waste residue represents 50% of the input mass of coffee feedstock[13]. The many organic compounds contained in coffee residues suggest that their recovery and use could be very beneficial. Several researchers have studied coffee waste as a bio-resource for various valuable compounds. In the context of a circular economy, it is essential to re-use the many resources present in this residue, for example through fractionation, as demonstrated by Kovalcika et al. (2018)[14]; Caetano et al.[15] evaluated the possibility of producing biodiesel from coffee waste; Mussatto et al.[8] investigated coffee waste as a source of sugar; Kante et al.[16] and Pappa et al.[17] analyzed coffee waste as a precursor for creation of activated carbon and Oliveira et al.[18] explored the possibility of using coffee waste as a sorbent for metal removal. The scope of the present work is to show an extensive characterization of coffee wastes for energy purposes through physical and chemical analyses that highlight the most significant quality indices, the interactions among them and the quantification of their importance. In addition, this research assesses SCG pelletizing at different blends of sawdust and gas and particulate emissions of the produced pellets. Note that the SCG have been collected and delivered by a coffee company without taking into account of the storage method which can have an effect on the energy yield of the biomass[19]. The residual biomass from the coffee that has been used in this work has been taken from the GEDAP company (located in Viterbo, in the center of Italy) and analyzed in the LASER-B laboratories of CREA—IT (located in Monterotondo, Rome).

Materials and methods

Biomass characterization.

The SCG were provided by a local Viterbo company. The blend they use consists of 30% Arabica and the green beans are roasted between 200–230 degrees centigrade for about ten minutes. The characterization of SCG was investigated through chemical and physical analysis. The moisture content was determined in accordance with ISO 18134-1 (2015)[20]. The biomass sample was dried in a Memmert UFP800 oven at 105 ± 2 °C for 24 h. The moisture content was calculated by measuring the weight of the sample before and after drying. For biomass ashes analysis, the sample (1 g) was placed inside porcelain crucibles and then placed in the oven where it was first heated up to 250° C for 2 h with a ramp of 6.5 °C / min and then up to 550 °C for 1 h with a ramp of 10 °C / min, in accordance with ISO 18122. The higher heating value (HHV) was assessed using an Anton Paar 6400 isoperibol calorimeter. It was possible to obtain, by means of the value of the hydrogen content, lower heating value (LHV). The LHV was calculated using the relationship between HHV and LHV given by formula (1):

$$LHV = HHV - (206 * H/1000) \tag{1}$$

where H equals the hydrogen percentages of the received tested fuels. The analysis of the higher heating value was made in accordance with ISO 18125.

The elemental composition in terms of carbon (C),hydrogen (H), nitrogen (N) and sulphur (S) was measured by means of the Costech ECS 4010 CHNS-O elemental analyzer and in accordance with EN 15104 (2011)[21]. Tin capsules, containing about 1 mg of the sample were prepared and inserted within the combustion furnace of the analyzer through a pneumatic carousel[22].

The metal content was determinate by means of the ICP-MS 7700 Agilent in accordance with ISO 17294-2 (2016)[23]. To prepare the samples, an aliquot of each sample (about 500 mg) was transferred to special Teflon containers and subjected to acid attack using a microwave digester (Start D, Milestone, Italy). The etching mixture used was composed of 6 ml of HNO_3 and 3 ml of H_2O_2. The determination of the metal content was carried out by ICP-MS (Inductively Coupled Plasma–Mass Spectrometer). All the solutions obtained were brought to a final volume of 100 ml with the addition of ultrapure water and subjected to analysis. The calibration of the instrument was carried out using multi-element standards (Standard mix, concentration 10 ppm in metal), prepared in aqueous solution acidified with 1% of HNO_3. The calibration line was built using 5 standards in increasing concentration from 5 to 100 ppb. The Y was used as the internal standard through the automatic input system provided by the instrument[22].

Pellet.

Following the chemical-physical characterization of the coffee grounds, pelletizing tests were carried out using a Master 380 C Bianco-Line pellet machine and making various mixtures with sawdust, to check the best blend to use as the biomass (Fig. 1).The granular nature of the SGC requires an optimization of the mixture to be introduced into the pellet machine. The final product must have satisfactory structural properties without compromising the energy qualities of the starting matrix. The tests carried out were divided as follows:

1. 100% SCG;
2. 85% SCG and 15% sawdust;
3. 75% SCG and 25% sawdust;
4. 33% SCG and 66% sawdust.

The treatment without sawdust was obtained by mixing the SCG with 2% starch which was used as a binder. This percentage is within allowed limits of voluntary certification of the "ENplus" pellets.

Subsequently, the resulting pellets were analyzed for chemical-physical characteristics, as previously described for the SCG (elemental analysis, ash, higher and lower heating value).

Figure 1. Spent coffee ground (SCG) before (left) and after (right) the pelletizing process.

Sampling and combustion values		
Velocity	1.33	[$^{m}/_{sec}$]
Stack temperature	161.91	[°C]
Stack pressure	101.34	[kPa]
Velocity at nozzle	1.311	[$^{m}/_{sec}$]
Probe temperature	114.4	[°C]
Filter temperature	155.6	[°C]
Outlet temperature	133.5	[°C]
Aux temperature	31.3	[°C]
Ambient pressure	101.35	[kPa]
Flow rate	0.0652	[$^{m^3}/_{sec}$]
Biomass burning rate	21.22	[kg/h]

Table 1. Average combustion parameters.

Emission. The study of the emissions produced by the combustion of the pellets made from SCG was conducted using a GSA / 80 boiler (D'Alessandro Termomeccanica GSA 80kWth Series). The boiler was equipped with a cast iron burner with a mechanical auger hearth and a cylindrical-shaped fuel loading hopper with a mechanical stirrer. The auger for the transport of fuel allows for adjustable speed which enables optimization of the biomass feeding. The auger also has an adjustable primary and secondary combustion air system. The stack is equipped with several flanges that allow the insertion of monitoring instruments and emission sampling devices. Table 1 shows the combustion parameters.

The online TOC analysis was conducted with a Ratfisch RS-53 T flame ionization detector (FID), compliant with the EN 12619 (2013)[24] regulations, while the online analysis of NOx, CO, CO_2, SO_2 and O_2 was carried out with a multiparametric detector Horiba PG-250, also in accordance with the main sampling methods and regulations. The instruments were calibrated before sampling with standard gas mixtures with defined concentration.Sampling of particulates, metals and VOCs were carried out in three different phases via the Dadolab HP5 heating probe interface with the stack. This probe is coupled to a pump Dadolab ST5 that allows sampling under isokinetic conditions (Fig. 2). The particulate matter was collected on a quartz fiber filter (ø 47 mm) suitably pretreated and preweighed as indicated by the European method EN 13284-1 (2017)[25] and EPA 201A (2018)[26]. This filter was placed inside the heated chamber of the probe at 125 ± 5 °C and each sampling lasted 30 min.The metals following the ISO 14385 (2014)[27] were sampled isokinetically with the same system, placing downstream of the quartz filter 3 bubblers maintained in a bath thermostated at 5 °C. The extremely volatile metals that manage to pass the quartz filter are thus trapped and condensed by the absorbent solutions contained in the bubblers. Each bubbler contained a solution of equal parts of HNO_3 and H_20_2 diluted in 9 parts of milliQ water. The third bubbler is defined as "control" and indicates that sampling is valid and meaningful only if the metals inside do not exceed 5% of those present in the 2 previous bubblers. The volatile organic compounds were sampled following the EN 13649 (2015)[28] method by using self-made ACF (Activated Carbon Fibers) adsorbent traps suitable for subsequent thermal desorption. Each tube was interfaced with the probe via a swagelock fitting perpendicular to the emissive flow and a backup tube was placed at the end of it.Two volumes (40 ml and 160 ml) were sampled in

Figure 2. Combustion chamber (left) and probe system for sampling on the stack (right).

Operative parameters	
Carrier gas	He
Column	DB 502.2
Flow	1.2 ml/min
Mode (GC)	Constant Flow
Oven ramp	35 °C (5 min.) + 5 °C/min to 230 (5 min.)
Ion source	EI
Inlet	200 °C
MS source	230 °C
MSD transfer line	240 °C
Mode (MS)	Full scan 35–450 m/z

Table 2. VOC's analysis operative parameters.

triplicate with the aid of a suction pump located downstream of the system. The backup tube was used to verify that the volume breakthrough was not exceeded during sampling.

As part of the solution developed, the pretreated filters and the adsorbent tubes were kept aside and considered as analytical blanks. The PM (Total Suspended Particulate Matter TSP) was subsequently calculated by the quartz filter by gravimetry in relation to the volume of gas that passed through it. Metals were measured by ICP-MS by analyzing the quartz filter and the bubbled solutions. VOCs were measured with a thermal desorber (TD 100xr, Markes) coupled to a gascromatograph–mass spectrometer system (GC/MS–QQQ Agilent 7000).

The VOC's analysis was performed with a 100-xr TD (Markes international) coupled to an Agilent 7000 GC/MS system. The tubes were thermo-desorbed with a flow of 50 ml / min up to a temperature of 350 °C for 10 min in splitless mode. They were collected on a focusing trap at the temperature of − 22 °C and then were redesorbed from the focusing trap for 1 min with a 1:10 split. The GC–MS analysis was carried out in splitless mode with following parameters specified in Table 2. The quantitative analysis was carried out by making calibration lines using a mixture of standards suitably produced by ULTRA Scientific Italia s.r.l. The qualitative analysis we resorted to the use of the Masshunter software interfaced with the NIST 08 library and the recognition was realized taking into consideration only the data with a match factor over 80%.

Process modelling. The software Aspen Plus was chosen to model the experimental process. The following assumptions were made for the simulation:

- the process is steady state and isothermal[29];
- drying and pyrolysis take place instantaneously and volatile products mainly consist of H_2, CO, CO_2, CH_4 and H_2O[25][30];
- char is 100% carbon[31];
- all gases behave ideally.

The process flow sheet is shown in Fig. 3.

The stream BIOMASS was specified as a non-conventional stream, as defined by its proximate and ultimate analysis. The BIOMASS stream goes to the RYELD reactor used to simulate the decomposition of the

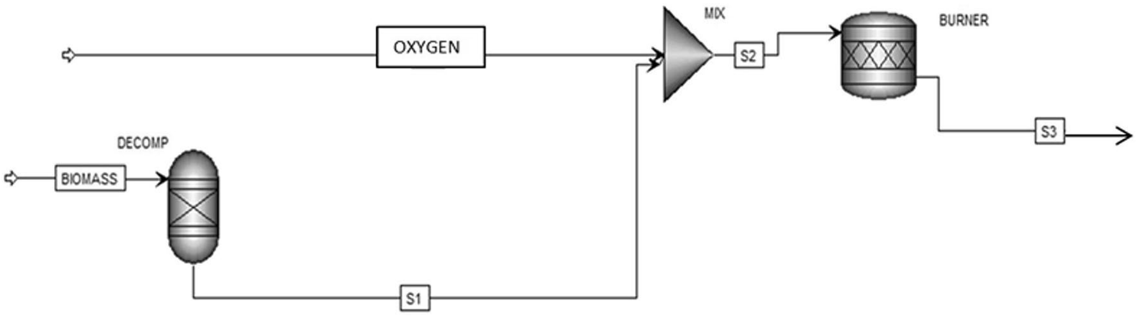

Figure 3. Flowchart of the plant evaluated in this study.

Reaction number	Reaction equation
1	$C + 2H_2 \rightarrow CH_4$
2	$C + O_2 \rightarrow CO_2$
3	$C + 0.5O_2 \rightarrow CO$
4	$H_2 + 0.5O_2 \rightarrow H_2O$
5	$N_2 + 3H_2 \rightarrow 2NH_3$

Table 3. Chemical reaction considered in the combustor[63].

ASPEN Plus name	Block ID	Description
RYIELD	DECOMP	Yield reactor—converts the non-conventional stream "BIOMASS" into its conventional components
MIXER	MIX	Mixer—mixes oxidising fluid with S1 stream that represents combustible fluid
RSTOIC	BURNER	Rstoic reactor—simulates the combustion process

Table 4. Description of ASPEN Plus flowsheet unit operation presented in Fig. 3.

unconventional feed into its conventional components (carbon, hydrogen, oxygen, sulphur, nitrogen, and ash by the specification of the yield according to biomass ultimate analysis reported in Table 5). Off products from DECOMP moves into the mixer MIX in order to add the oxidising fluid, compose of pure air, to the combustible and then the resulting mixed S2 goes into the BURNER, to simulate the combustion process. The fumes out of the combustor are represented by stream S3.

Equations (1)–(4) listed in Table 3 are the chemical reactions evaluated in this work for the combustion process.

The following Table 4 shows the ASPEN units of the flowchart presented in Fig. 3.

Statistical analysis. The characterization of biomass and pellet tests was performed using three samples as independent replicates. Data were analyzed using a one-factor analysis of variance (ANOVA) and a Pearson correlation test. Significance between means was determined using the Tukey post hoc multiple comparisons of means test at the 95% family-wise confidence level ($P = 0.05$). Before proceeding, normality and homogeneity of variance were checked via the Shapiro–Wilk test and Levene's test, respectively ($P = 0.05$ for both of them). All statistical analyses were performed using JMP PRO 15 (Trial Version ©SAS Institute Inc.). The Pearson correlation and ANOVA with Tukey tests were applied to determine the relationship between elemental analysis, ash, and higher and lower heating value, first to characterize the SCG and second for pellet testing.

Results

Biomass characterization. The characterization allowed us to identify the features of biomass which are similar to the values reported in the literature (on average: C:68.52, H:11.04, N:1.40)[32]. SGS have a higher hydrogen content than other waste biomass such as olive, vine or hazelnut pruning (3.8%, 3.50%, 3.76% respectively); however, the amount of nitrogen is similar[33]. The moisture content plays an important role for the optimization of efficiency of thermal conversion processes. The samples as received had high moisture content of about 42% due to using water to prepare the drink. As a result, for all subsequent tests, SGS were dried, as described in materials and methods. As far as ash is concerned, SCG have shown excellent characteristics, with values not exceeding 1.3%, well below the range of 2–4% of common solid biomass. The lower heating value gave excellent results with values of about 20 MJ/kg and above on dry basis for the same biomass from timber, moreover the values showed stability in all samples tested (Table 5).

Samples	UM	SCG
Moisture	%	42.31 ± 6.85
Ash	%	0.90 ± 0.12
HHV	MJ/Kg	22.24 ± 0.05
LHV	MJ/Kg	19.97 ± 0.05
C	%	68.52 ± 10.20
H	%	11.04 ± 3.05
N	%	1.40 ± 1.20
S	%	< LoQ
Mg	mg/Kg	1981.71 ± 18.2
K	mg/Kg	1684.12 ± 7.14
Ca	mg/Kg	250.09 ± 4.3
Na	mg/Kg	37.15 ± 1.2
Al	mg/Kg	21.44 ± 3.6
B	mg/Kg	10.6 ± 4.5
Mn	mg/Kg	10.52 ± 2.6
Sr	mg/Kg	10.51 ± 2.01
Ga	mg/Kg	0.27 ± 0.3
Be	mg/Kg	< LoQ
Cr	mg/Kg	< LoQ
Co	mg/Kg	< LoQ
Ge	mg/Kg	< LoQ
As	mg/Kg	< LoQ
Ag	mg/Kg	< LoQ
Cd	mg/Kg	< LoQ
Fe	mg/Kg	9.87 ± 1.5
Cu	mg/Kg	9.82 ± 3.5
Zn	mg/Kg	3.57 ± 1.04
Ba	mg/Kg	3.17 ± 0.9
Ni	mg/Kg	1.23 ± 0.5
Li	mg/Kg	0.53 ± 0.5
In	mg/Kg	< LoQ
Sn	mg/Kg	< LoQ
Sb	mg/Kg	< LoQ
Cs	mg/Kg	< LoQ
Tl	mg/Kg	< LoQ
Pb	mg/Kg	< LoQ

Table 5. Results of the SCG characterization and metals detected in SCG. Data are presented as mean ± standard deviation.

The values of the elemental analysis were consistent with other biomass.

The analysis in ICP-MS allowed a characterization of the SGC matrix as regards to the metals present (Table 5). Large concentrations of macro elements are present, such as Mg, K, Ca and Na. In fact, besides being among the main characteristic metals of biomass, they are also the main mineral salts present in water and consequently their accumulation in the SGC is a consequence of making coffee. This is particularly important as it suggests that SGC coming from different areas with waters that have different chemical profiles will have different metal contents, as well as for all drinking water processes for instance ion exchangers for water softening. Otherwise, other metals have been detected in traces under the limit of quantification.

According to the Pearson correlation test results, it was determined that there was a significant negative correlation between HHV, LHV and C with ash ($P \leq 0.05$) and significant positive correlations between C and H with HHV and LHV ($P \leq 0.05$) (Fig. 4). The correlation matrix provides interesting data indicating that heating values decrease with the increase of the ashes. This is because a higher percentage of ashes implies a greater quantity of unburnt products and consequently a lower calorific yield. Even nitrogen is involved in this effect as it is the only element whose increase in percentage corresponds to a decrease in heating value. This is partly due to the fact that a higher percentage of N corresponds to lower percentages of C, H and O (elements whose presence positively affects the increase in HHV and LHV); more significantly, the structure of nitrogen-rich biomasses contains more N atoms usually bonded with elements such as Si, Ca, K, Mn and others that are typically present in ashes. During combustion, nitrogen is emitted and all the elements bonded to it are found in ashes, increasing the percentage of the latter.

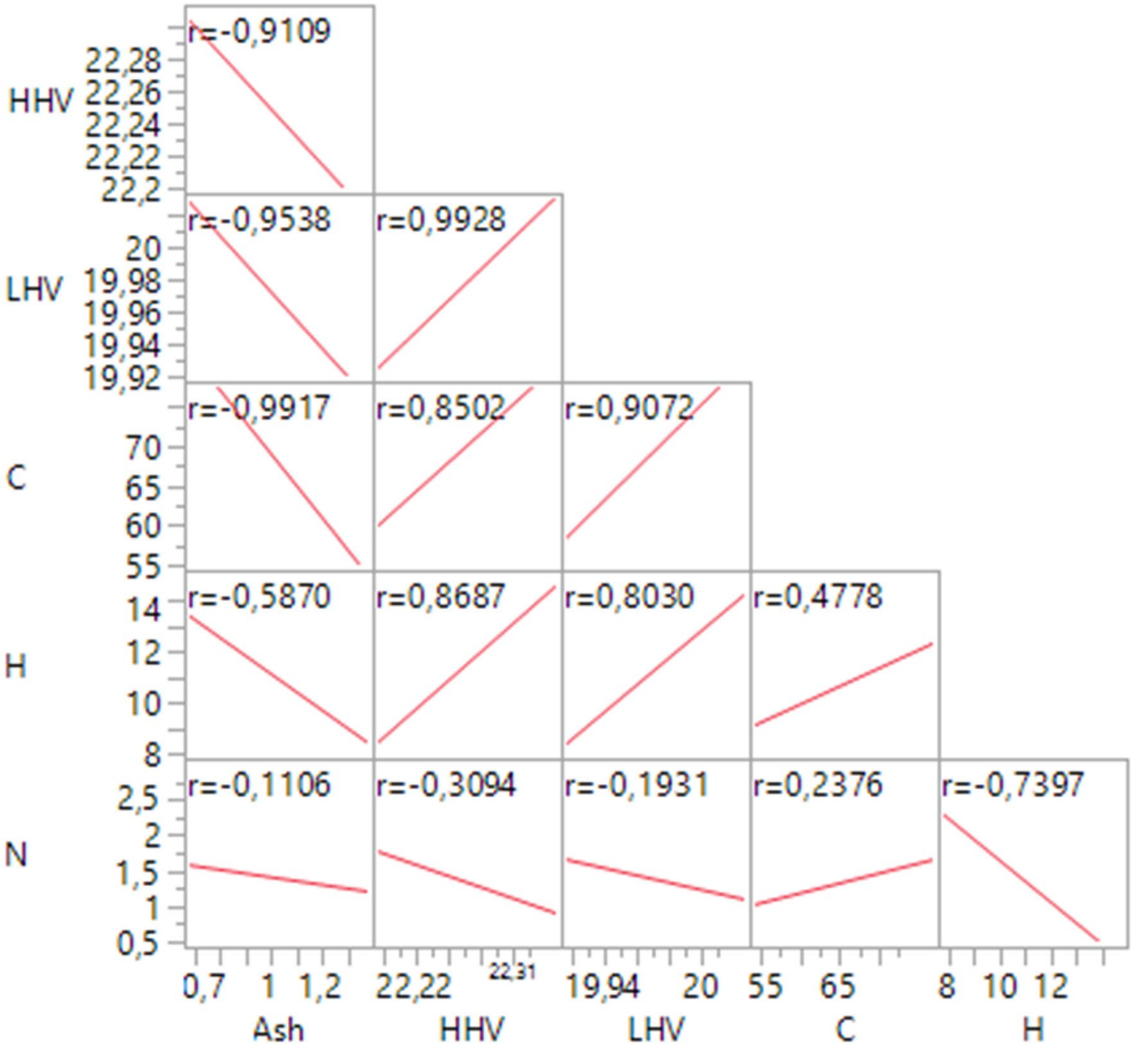

Figure 4. Matrix of Pearson correlation test of SCG characterization with 95% confidence interval.

% sawdust	Ash (%)	C (%)	H (%)	N (%)
0	$2.19^{a} \pm 0.27$	$51.32^{a} \pm 0.41$	$3.09^{a} \pm 0.19$	$2.97^{a} \pm 0.01$
15	$1.91^{ab} \pm 0.22$	$49.76^{a} \pm 0.10$	$2.97^{a} \pm 0.19$	$2.47^{b} \pm 0.15$
25	$1.75^{ab} \pm 0.19$	$50.40^{a} \pm 0.16$	$2.74^{a} \pm 0.18$	$2.27^{b} \pm 0.01$
66	$1.19^{b} \pm 0.21$	$51.48^{a} \pm 0.29$	$2.62^{a} \pm 0.06$	$1.75^{c} \pm 0.12$

Table 6. Elemental analysis and ashes of the 4 tests carried out. Data are presented as mean ± standard error. The letter in each row indicates a significant difference between the sawdust content at $P \leq 0.05$.

Pellet. For the evaluation of the physico-chemical characteristics and heating values, four tests were performed mixing the coffee grounds with different percentages of sawdust (0%, 15%, 25%, 66%), to verify the presence of differences in the resulting pellets. The tests carried out with pellets made from SCG mixed with sawdust were analyzed in terms of heating value and elementary characterization. There were no sigificant differences in the carbon values of the treatments containing 0%, 15%, 25% and 66% of sawdust in the analysis of the variance ANOVA ($P = 0.6602$), although the treatments at the extremes (0% and 66%) resulted in greater percentage of carbon. The same was true for the hydrogen values including a higher presence of hydrogen in the treatment without sawdust. Significant differences were found in nitrogen and ash (Table 6) between the treatments with 66% sawdust and with no sawdust, while amounts of nitrogen and ash were similar for the treatments with 15% and 25% sawdust. As such, slightly higher values in ash and nitrogen were observed for the treatment using no sawdust.

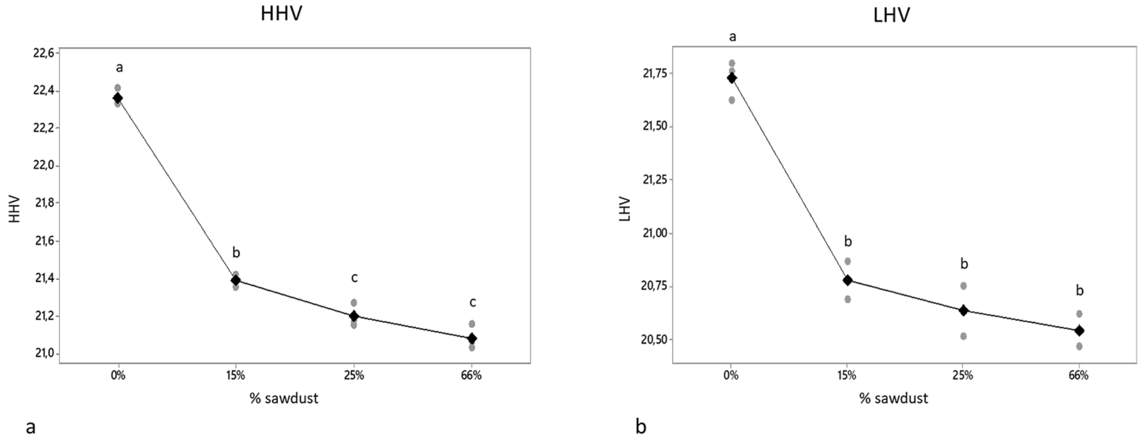

Figure 5. Higher and lower heating value of the pellet. The four types of pellets produced with the percentage of are indicated on the x axis sawdust. The letters indicate a significant difference between the sawdust content at P ≤ 0.05.

Time h	CO_2(%)	CO	NOx	SO_2	TOC
1	9.22	3077.53	959.9	4.0	144.2
2	8.40	2129.25	1121.8	11.4	142.8
3	7.71	2153.74	1078.3	1.7	140.1

Table 7. Emission levels at different hours expressed in mg/Nm^3.

The pellets have an excellent level of heating value compare to other types of waste and to other biomasses, a fact that emerges from the comparison made by Zuorro and Lavecchia (2012) between SCG and other agricultural and forestry biomass or waste of which they report HHV, such as forest residues with 21.70 MJ/kg and a percentage variation of 3.04% with the HHV value of SCG obtained in this work, rice husks (15.29 MJ/kg, 46.24%), oak wood (18.70 MJ/kg, 19.57%), olive kernel (20.40 MJ/kg, 9.61%) and others[34]. The literature reports high levels of residual oil, which may be partially responsible for the high heating value[35].The analysis showed decreasing values of HHV and LHV with increases in the percentage of sawdust. The best results were produced by the treatment without sawdust and the treatment consisting of 15% sawdust (Fig. 5), HHV values of 22.36 MJ/kg and 21.39 MJ/kg respectively. On the other hand, by increasing the percentage of sawdust in the pellets, a decrease in the amount of ash, a reduction in the amount of nitrogen and an increase in calorific value was observed. Hydrogen also showed a reduction; however, it was not statistically significant.

With regard to carbon, no differences were observed between the various pellets.

Emission. After conducting the tests of the pellets obtained by mixing SGC and sawdust, it was clear that the addition of the latter, despite having an extraordinary amending effect, drastically lowered the extraordinary calorific value of the coffee (Fig. 5). Therefore, the water content of the starting matrix was optimized in order to eliminate sawdust and use water as a soil conditioner during the pelletizing phase. The optimization process led to the creation of pellets made of 90% dry SGC and 10% water, by weight (mean ± standard deviation 9.93 ± 0.51). The pellet produced was used in a boiler and the emissions produced by the combustion process were monitored.

Macropollutants. For atmospheric emissions, CO, NOx, O_2, SO_2, CO_2 and carbon and TOC were evaluated. The hourly averages of emissions during the combustion process of 100% SCG are shown in Table 7. In addition, total particulate (TSP) was sampled and a value of 245.53 mg / Nm3 was found.

The obtained emission values are high for carbon monoxide, nitrogen oxides and powders. It is very important to specify that the simulated process is direct combustion without any abatement filter. It is likely that these values would be lower in common domestic boilers with abatement filters.

The Italian Legislative Decree 183/17 (which transposes Directive (UE) 2015/2193) establishes the limits for the emissions of boilers that use biomass by comparing pollutants to an oxygen content of 6% according to the formula (2):

$$C = [((21 - O\_2r))/((21 - O\_2m))] \times Cm \quad (2)$$

where O_2r is the percentage of reference oxygen content; O_2m is the percentage of oxygen measured and Cm is the concentation of analyte measured. According to current legislation, there are no limits for CO2, CO and TOC for boilers with low thermal power (the lower limit is 0.15 MW). The only limit values indicated refer to NOx,

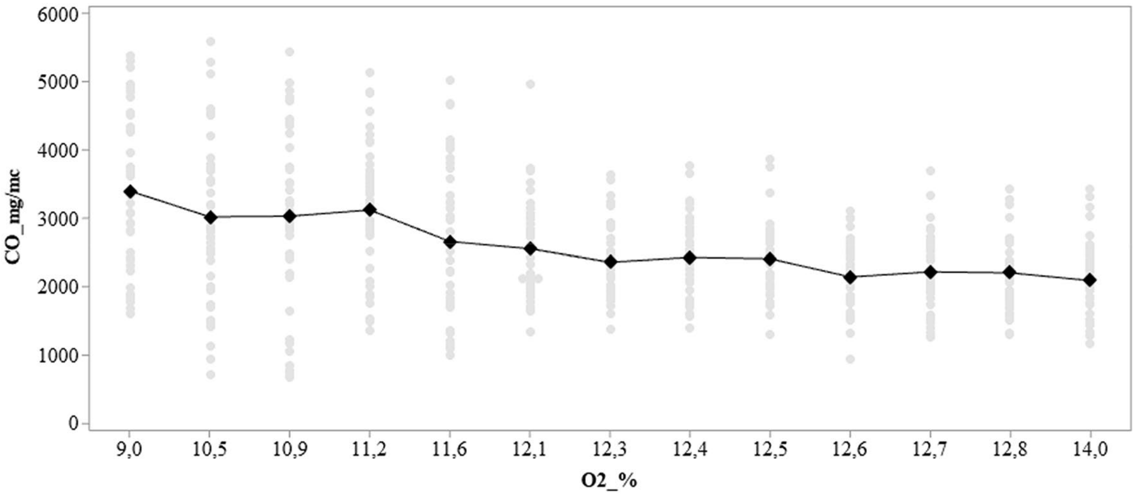

Figure 6. The decreasing CO trend is evident as the O_2 content increases.The average CO trend tends to decline as the oxygen content increases.The oxygen levels represented on the X-axis reproduce the most frequent oxygen values found.

Compounds	Concentration (mg/Nm^3)	Emission factor (mg/kg fuel)	IARC Classification
2-Butene. 2-methyl-	4.99	55.17	–
Acetonitrile	1.51	16.69	–
Hexane	4.73	52.30	–
Benzene	3.74	41.35	1
Toluene	0.52	5.75	3
Ethylbenzene	0.26	2.87	2B
m.p-Xylene	0.31	3.43	3
o-Xylene	0.23	2.54	3
Benzene. 1.2.4-trimethyl-	3.16	34.94	–

Table 8. Main VOCs identified in the emissions. Bold the BTEXs and their classification for IARC.

SO2 and PM: 600 Mg/Nm^3 NOx, 2000 Mg/Nm^3 SO2, 200 Mg/Nm^3 PM. However, if we take into consideration the values for low power boilers (0.15—5 MW), the CO limit is 525 mg / Nm3. NO_x and CO are above these limits (in particular CO is more than about 10 times the limit). CO was certainly the most important pollutant generated by the combustion process. The high concentration of these values is probably due to the bad combustion conditions in terms of poor oxygen content during the combustion, with which it was operated. In fact, by graphing (Fig. 6) the trend of the CO as a function of the oxygen content, it can be observed that this significantly decreases with the increase of the comburent. In fact, a greater quantity of oxygen would allow compliance with stoichiometric ratios and a decrease in the formation of CO in favor of CO_2, a zero-impact pollutant in the combustion of biomass, largely compensated by the sequestration of CO_2 carried out by the growing biomass. Looking at the graph, it can be argued that by operating with greater quantities of oxidisers, it is already possible to significantly reduce pollutants, not to mention that the data shown was obtained without the use of abatement systems. As such, it is clearly possible to further decrease emissions.

VOCs. Forty-one main VOCs were identified by analyzing the tubes for thermal desorption. Usually the analysis of BTEX (Benzene, Toluene, Ethylbenzene, Xylenes) produces a highly indicative picture of VOC emissions (Table 8). These compounds are the most frequently monitored as they are the main volatile aromatic hydrocarbons which develop following all combustion processes. Of these, Benzene is certainly the most dangerous for humans and is designated a type 1 carcinogen by the IARC. We have chosen to quantify these compounds together with the other more prevelent compounds. The qualitative result of the profile of the generated VOCs is summarized in Appendix I.

The emission limit of benzene, in the Italian legislation relating to the emission limits for substances deemed carcinogenic and / or toxic for reproduction and / or mutagenic (in according to Italian Law n. 152/06 which transposes Directive (UE) 2015/2193), is equal to 5 mg/Nm^3. In this case results are therefore well below the imposed limit.

Metal	mg/Nm^3	mg/kg fuel
B	18.20	201.22
Na	0.78	8.62
Mg	0.31	3.43
Al	0.78	8.62
K	0.55	6.08
Ca	0.75	8.3
Ti	0.35	3.87
Cr	0.02	0.22
Mn	0.01	0.11
Fe	0.23	2.54
Co	<LOQ	<LOQ
Ni	0.02	0.22
Cu	0.01	0.11
Zn	0.10	1.1
Ga	<LOQ	<LOQ
Se	0.45	4.98
Sr	<LOQ	<LOQ
Cd	<LOQ	<LOQ
Ba	<LOQ	<LOQ
Sc	0.22	2.43

Table 9. Concentration of metals in emissions and factor emission.

Na	Mg	Al	K	Ca	Cr	Mn	Fe
331.1892	4838.1773	184.2970	12,540.1292	4506.9221	11.3248	181.1106	645.6462
Ni	Cu	Zn	Ga	Sr	Ag	Cd	Ba
4.4608	42.9340	10.0459	1.3651	34.9875	0.0003	0.0080	26.2636
Tl	Pb	Bi					
0.0001	0.1105	0.0030					

Table 10. Bottom ashes express in mg/kg.

Metals. Since the starting biomass is naturally low in metals except for those in the water used in the preparation process, the inorganic pollutants observed in the emissions have decidedly low concentrations (Table 9). It is important to note that heavy metals concentrations are very low and are even lower than LoQ.

Flyning ashes were decidedly poor in terms of metals, providing further proof that the matrix itself is quite free of metal contaminants. The problem of volatile and solid heavy metal compounds in emissions was analyzed to evaluate their behaviors. Results indicated that certain metals are less volatile and, for agricultural biomass, are concentrated in the ash.

In Table 10 is show the metal contenent in residual bottom ashes. The results underline that large parte of metals are concentred in this fraction.

Combustion products obtained by Aspen Plus simulation. A model simulation using Aspen Plus software has been carried out in order to highlight the feasibility of the process. The level of CO2 in the emissions has been found to be around 10 mg/Nm^3 while the level of NOx and SO2 are around 1000 mg/Nm^3 and 10 mg/Nm^3 respectively.

Considering a steady state simulation, with a biomass feed rate of 21.22 kg/h and an oxygen rate of 155 kg/h, the composition of the stream S3 is reported in Table 11. The process parameters of the burner are 700 °C and 1 bar.

In Table 11, the simulation results for the combustor outlet stream are compared with the results reported in Ref.[36], achieved with air-combustion in a bubbling fluidised bed combustor. In Ref.[36] the biomass considered is wood, since wood has similar properties to SCG, except for lower values of LHV, HHV, C%, N% and H% as showed in Ref[37], this comparison makes sense and can be considered valid. and given the comparable features of SCG, the comparison can be considered valid. As shown in Table 11, the model results in more conservative values, perhaps due to the air staging method used in the experiment of ref.[36], which is a well-known and effective method to control NOx emissions from solid fuel combustion boilers. Then, comparing the results of Table 11 with the results of Table 6, the values are consistent, showing the usefulness of the developed model.

	Model results	Literature data[38]
CO (mg/Nm^3)	2679.23	3088.86
CO_2 (mg/Nm^3)	13.67	19.4
SO_2 (mg/Nm^3)	7.6	Not evaluated
NO_x(mg/Nm^3)	789.88	801.1

Table 11. Composition of the products of combustion.

Discussion

Results identify important tools for the qualification and quantification of the effects of coffee waste properties on energy production processes.

The aim of the present study was to assess SCG pelletization with different blends of sawdust and gas, including the particulate emissions of the produced pellets (100% SCG).

Physico-chemical compositions of SCG, as well as the properties of the different pellets with different percentages of sawdust (0%, 15%, 25%, 66%), are presented in Tables 5 and 6 respectively. According to Table 6, the weight fractions of the different elements for SCG are similar to those present in the literature[38–40].The main differences concern the ashes and nitrogen with average values of 0.90% and 1.40% respectively for SCG used in this study and 1.94% and 2.91% respectively from the study of Limousy et al. 2013[40]. The nitrogen content also varies widely in other studies; for example, Ktori[41] and Liu[42] found higher nitrogen values, respectively 3.51 and 2.48 (wt%), compared to 1.4 wt% in this study. This may be due to the influence of different geographical provenances and different coffee production systems. In fact, many studies have shown differences in the elementary composition of coffee based on geographical origin, as well as the type and quantity of metals present. Valentin and Watling (2013)[43] have shown that, through elementary analysis, it is possible to distinguish the origins of coffee starting from the continent to the province, and in some cases, even to the plantation of origin, as verified by Habte et al. 2016[44] in Ethiopia. Furthermore, their results show that these classifications are not affected by the roasting process, degree of ripeness or harvest date[43]. The results from this study showed that SCG have excellent values in terms of heating value and low ash content, and this is also seen in other studies[40]. This is due to the increased concentration of sawdust which, regardless of species, has a lower calorific value than coffee grounds. Overall SCG presents as a typical biomass[45] and has similar characteristics to both other coffee residues and other agro-industrial residues such as solid olive mill waste or grape vine[33,46,47]. In contrast, another coffee residue, mucilage, is different in its characteristics: (w/w) 85–91% water and between 6.2% and 7.4% sugars, with a high presence of nitrogen, It is used as fertilizer, feed or compost or for energy purposes in anaerobic digestion processes or for the production of ethanol, hydrogen and lactic acid[9,48].

The presence of inorganic micropollutants that would proscribe the use of SCG as fuel was not found. However, the storage of biomass is an extremely important aspect, even more so if the purpose is energy use. **D**ifferent conditions and storage times on a matrix with a high level of humidity may or may not favour the proliferation of micro-organisms that may affect the physico-chemical characteristics and the energy yield[49]. Considering the high moisture content of SCG found, it is very important to act quickly for drying and storage and from what emerged during the trials, open air drying is not effective as a system due to the high hygroscopicity of the material, except at favourable latitudes and in the right season such as in the Mediterranean basin in the summer season, where temperatures and air humidity favour a stabilization of the biomass[19]. Whether or not to use inadequately stored biomass depends on the storage time, the climatic conditions, the composition and shape of the biomass, as well as the geometry and structure of the storage pile[49].

Some properties obtained were compared with the limits of voluntary certification of the "ENplus" pellet. This certification system refers to the most important international regulations for pellet characteristics and makes them more stringent. Table 12 shows the limits of metals with the values obtained in this study. Some of these are well below the limits, while others—the ashes and nitrogen—are slightly higher.

The pelletizing process is not easy to carry out, but the optimization of the process has made it possible to obtain pellets with a percentage of 90% of SCG with 2% starch, used as a binder. Furthermore, a significant reduction in the heating value was observed as the percentage of sawdust increases, as shown in Fig. 5, going from HHV of 22.42 MJ/kg to 21.03 respectively for 0% and 66% of sawdust.

The values of higher heating value were compared with those of other biomasses and it emerged that with HHV of 22.24 MJ/kg, the SCG were found to have the highest value among those investigated[365241].

Many studies have investigated the pellet of coffee grounds and some have found slightly lower heating values (18.8 MJ/kg[50], 19.6 MJ/kg[51]) than that reported in this study while other report much higher heating values (23.4 MJ/kg[7], 25.7 MJ/kg[52]). Other studies have verified the pelletizing process through mixtures with other types of waste[53] or materials[54,55], or with different percentages of moisture. Still others have modified other parameters such as die height, Lisowski et al. (2019)[56] and have verified how the moisture of the matrix can be determined in the pelletizing process. In any case, it follows that coffee grounds have a great potential in energy conversion processes. In terms of chemical characteristics, the percentage of sawdust does not significantly affect the amount of C and H but affects nitrogen and ash which both decrease with increasing sawdust.

Some emission values (PM, CO and NOx) were higher than regulatory limits, however it should be considered that the sampling was carried out in direct combustion without having any type of abatement system (multicyclone or bag filter).The presence of CO, however, rather than fuel, is attributable to the combustion conditions.

Property	Unit of measure	Limit	SCG
Moisture	%	≤ 10	9.93
Ash	%	≤ 2.0	2.19
LHV	MJ/kg	≥ 16.56	21.39
N	%	≤ 1.0	2.97
S	%	≤ 0.05	< LoQ
As	mg/kg	≤ 1	< LoQ
Cd	mg/kg	≤ 0.5	< LoQ
Cr	mg/kg	≤ 10	< LoQ
Cu	mg/kg	≤ 10	9.82
Pb	mg/kg	≤ 10	< LoQ
Ni	mg/kg	≤ 10	1.23
Zn	mg/kg	≤ 100	3.57
Hg	mg/kg	≤ 0.1	< LoQ

Table 12. Property of SCG pellet and limits of ENplus.

It has been assumed (as shown in Fig. 6) that an increase in the oxidizer can improve the combustion conditions and lower the onset of CO.

Considering the relationship between metals content and emissions, the amount of alkali metals by pellets of various raw materials may be predicted based on fuel alkali metal content, K, and K + Na + Cl; both factors correlated with emissions. These findings highlight the importance of alkali metals with regard to PM1 emissions. Furthermore, CO decreased but there were higher NOX, SO2, and HCl emissions. In addition, fuel N content was found to correlate well with the NO_X emissions[45].

By comparing the results of pellets from lignocellulosic and herbaceous biomass, the inorganic aerosol fractions are characterized by macro-pollutants as K, and high S concentrations in the emissions from combustion. Moreover, the contents of the easily volatile metals Zn, Pb, and Cd in emissions increased for wood fuels (standard softwood pellets, poplar). However, they can contain considerable amounts of transition metals, namely zinc[57–59]. In cases of just about complete combustion, zinc is the reason behind most of the cytotoxic studies[60–62]. Unlike agroforestry biomass, which results in emissions and ash with a higher content of metals, the use of SCG is advantageous due to its low metal concentration in both emissions and ash. This allows better management of the residual ash from the combustion of SCG which can be used as is, unlike the ash derived from biomass, which requires further treatment before disposal.

Conclusions

For this study, SCGs of a local Viterbo (Italy) company was used. The physical–chemical characteristics of the SCGs confirmed the very high quality of the raw material as a biomass, much higher than that for wood biomass, showing excellent levels of calorific value (HHV 22.36 MJ/kg) and negligible values of polluting metals. The dusty nature of SCG causes some difficulties in the pelletizing phase. This obstacle can be easily overcome by mixing the SCG matrix with sawdust; however, results indicate that this practice significantly reduces the energy qualities of the SCG. The best alternative was therefore to use a mixture of wet and dry coffee in order to establish the optimum moisture content for pelletization.

High values were evident for some of the atmospheric emissions, but it is important to point out that the process used was direct combustion without any abatement filter. It is likely that these values would be lower when using common domestic boilers with abatement filters.

SPG have excellent values in terms of calorific value and low ash content. The optimization of the process allowed the production of pellets containing 90% SCG. The results indicate that SCG an excellent candidate for use in energy conversion systems.

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3.3 Article 2

Environmental life cycle assessment of spent coffee ground pellet (Science of the total environment)

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Environmental life cycle assessment of spent coffee ground pellet

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Abstract:

Waste to energy proposes renewable energy from recovering energy in solid or liquid wastes via various treatment methods. Coffee, the most globally prevalent beverage, leaves abundant waste after brewing which entails environmental and economic consequences. This study investigates the environmental performance of the spent coffee ground application in pellet production as a valuable bio-product by life cycle assessment. System boundaries comprise four stages: (1) spent coffee ground collection; (2) pellet production; (3) thermal energy generation; and (4) waste disposal. The functional unit is 1 MJ of thermal energy, and the LCA model is interpreted by ReCipe 2016 in both midpoint and endpoint levels considering ten impact categories. Alternative waste to energy approaches into transesterification, pyrolysis, and direct combustion of spent coffee ground are also assessed.

The impact results show that the pelletizing process significantly contributes to all impact categories except ozone formation and terrestrial ecotoxicity, which is influenced primarily by the transportation process in the spent coffee ground collection stage. The spent coffee ground pellet can lead to climate change mitigation, and reduction in freshwater eutrophication, and use of resources due to credits from ash disposed to landfill.

Biodiesel is the worst potential option among alternative scenarios, while pellet production and bio-oil demonstrate the most favourable environmental profiles for all impact categories. Damage assessment indicates that pellet production and all alternative scenarios mainly influence human health.

Keywords: SCG; LCA; food waste; bioenergy; waste management

1. Introduction

The global interest in waste management and valorization has led to the energy policy coming across the challenge of sustainable production―increasing resource efficiency while reducing environmental impact (Janosik, 2005; WRAP, 2015; Lindauere *et al.*, 2020; Lühmann, 2020; World Economic Forum, 2020). This approach to sustainability represents a bio-economy strategy that aims to convert materials such as food waste, agricultural residues and livestock wastes to resources and valuable products (Lühmann, 2020). Many attempts are made to valorize solid and liquid residues―biogas production from olive and hazelnut pruning waste considering mechanical pretreatment enhancement (Bianchini *et al.*, 2021); electricity and heat generation from anaerobic co-digestion of waste (Hamedani *et al.*, 2020); application in biorefinery systems (Roig, Cayuela and Sánchez-Monedero, 2006; Hachicha *et al.*, 2012a; Donner, Gohier and Vries, 2020; Vu *et al.*, 2020; Palma *et al.*, 2021).
Coffee, the second-largest worldwide beverage after tea (Scully, Jaiswal and Abu-Ghannam, 2016), is a product of the food industry, which derives a continuous increasing amount of waste, 1.88 kg of spent coffee ground (SCGs) per kg of coffee beans (Cameron and O'Malley, 2016). Coffee companies produce more than 2 billion tons of spent coffee grounds (SCG) per year (Jiménez-Zamora, Pastoriza and Rufián-Henares, 2015). Recent data in 2018 show that 9.58 million t of coffee was produced in the global economy (International Coffee Organization (ICO), 2018). In trading point of view, coffee is second only to petroleum (Hernández, 2014; Oliveira and Franca, 2015; Gurram *et al.*, 2016). In large quantities, the concentration of coffee waste can damage the environment due to a high oxygen demand during decomposition and contains many harmful components (residual caffeine, tannin, and polyphenol contaminants). Therefore, it cannot be used as compost on a large scale but disposed to landfills which impose high economic and environmental costs (McNutt and He, 2019). For these reasons, the management of coffee waste is requisite as a product that lends itself well to valorization in the bio-economy context (Karmee, 2018).

The composition of SCG motivates its utilization to produce a wide range of products. For instance, it is an appropriate candidate in the food and health sector due to its high antioxidant and phenolic compound content (Anna *et al.*, 2017; Severini, Derossi and Fiore, 2017). Furthermore, Santos et al. perceived SCG potential as fertilizer under specific conditions (Santos *et al.*, 2016). Within these applications, bioenergy from SCG has gained much attention in recent years. Coffee waste is fascinating because of two main advantages that differentiate it from other agro-industrial biomasses: the absence of seasonality and its widespread distribution. Coffee grounds are available all year round, given the consumption of the drink, and they are also well distributed throughout the territory, which makes them accessible. Not to mention the quantities available, as mentioned above. These aspects, included in a supply chain perspective, attract the interest of companies and researchers. The use of SCG in energy conversion systems as thermochemical and biochemical processes represents a valid solution to counter the problems related to the disposal of this waste. Therefore, the production of bioethanol from hydrolysis of SCG hemicellulose sugars (Chiyanzy *et al.*, 2014; Woo *et al.*, 2016); bio-oil (Li, Strezov and Kan, 2014), syngas (Cho *et al.*, 2016) and biogas (Kim *et al.*, 2016) from SCG cellulose; and biodiesel from SCG oil extraction (Najdanovic-visak *et al.*, 2017; Tuntiwiwattanapun, Usapein and Tongcumpou, 2017) are taken into account. Besides, the densification process, which converts biomass into pellet as solid biofuel with higher energy density, is a promising approach for energy valorization of SCG. Despite the recent researches exploring pellet potential from SCGs (Allesina *et al.*, 2017; Lisowski *et al.*, 2019; Sohn *et al.*, 2019; Colantoni *et al.*, 2020; Nosek, Tun and Juchelkova, 2020; A Colantoni *et al.*, 2021), no study is dedicated to the prospective environmental efficiency of SCG pellet. Therefore, this study focuses on the circular economy model concerning the environmental impact and waste conservation. Therefore, the goal is to evaluate the eco-sustainability of using SCG as fuel through developing a life cycle model following the life cycle assessment methodology for SCG pellet production and application in the Lazio region.

2. Materials and methods

The life cycle assessment methodology (LCA) includes four steps: goal and scope, inventory analysis, impact assessment, and interpretation of results (International Organization for Standardization.ISO 14040, 2006). This study aims to assess the total environmental impacts associated with the production, combustion and waste disposal phase of pellets from SCG. Therefore, the study was conducted in a cradle to the grave scope considering collecting waste, pelletizing in a pellet plant, thermal-energy conversion process in the boiler and ash disposal to the landfill (Figure 1).

In order to carry out a robust analysis, the three viable scenarios to extract energy from SCG are also defined— SCG biodiesel, SCG direct combustion and SCG bio-oil. The environmental footprint of each scenario related to production and its combustion is calculated and compared with SCG pellet environmental burdens. The functional unit selected is 1 MJ of thermal energy produced to enable different energy oriented-valorization approaches to compare.

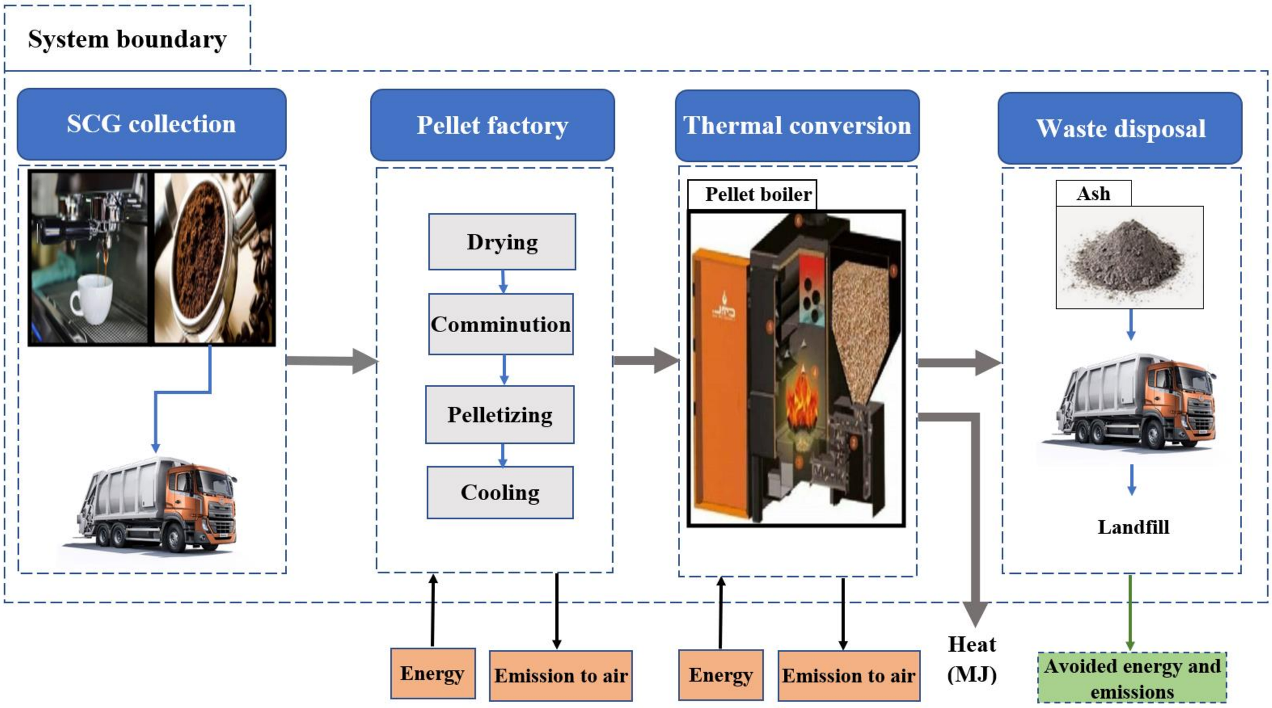

Fig. 1. The diagram of the system boundary of the life cycle of SCG pellet production

The bioenergy production chains under alternative scenarios are depicted in Fig. 2.

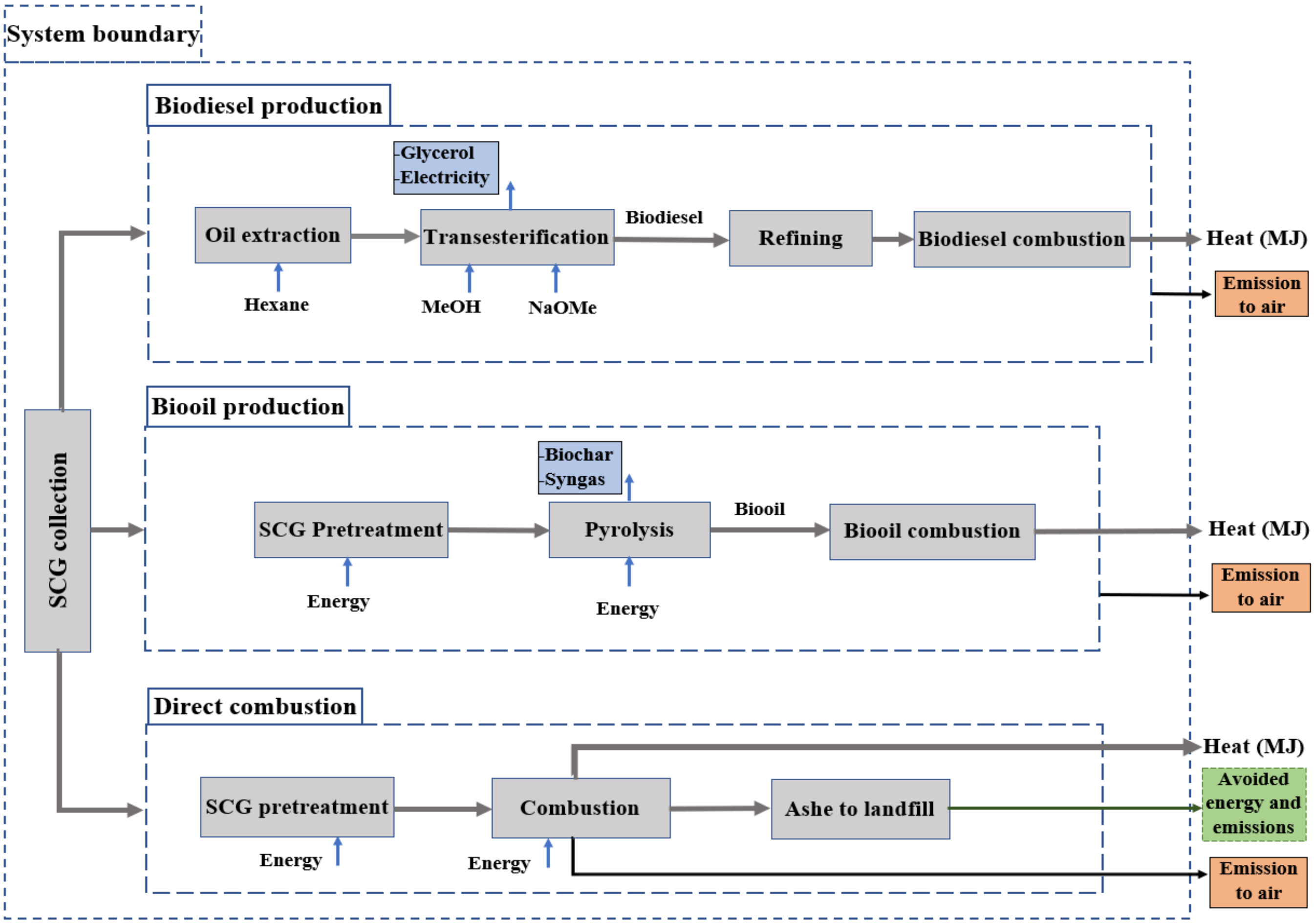

Fig. 2. The diagram of the system boundary of alternative scenarios

2.1 Life Cycle Inventory (LCI)

2.1.1 Pellet production

The SCG collection stage includes transport operations. The SCG was collected by twenty vending companies in the Lazio region and directly transferred to the pellet factory. The average transport distance from coffee consumers to the pellet plant was estimated to be 38.69 km. The assumption rests on the average distance from prominent vending machine companies located in eleven cities in the Lazio region to Rome province, where the pellet company operates. Road freight by waste collection truck is taken into account according to Ecoinvent database V3 (The ecoinvent database version 3, 2017).
The production stage includes pellet production from SCG with the following characteristics:

The SCG moisture content of 42% (A Colantoni *et al.*, 2021), in compliance with (ISO 18134-1, 2015); 1.3% ash concentrate on a dry basis as a result of heating one gram sample to 250 ˚C for two h with a ramp of 6.5 ˚C per minute and reheating it to 550 ˚C for one h with a ramp of 10 ˚C per minute, following (ISO 18122, 2015) and the higher heating value (HHV) of 22.24 kg/MJ on the dry basis estimated using an Anton Paar 6400 isoperibol calorimeter following (ISO 18125, 2017). The pellet produced without any additive has a higher heating value of 22.36 MJ/kg with 2.19% ash and 10% moisture content.

The productivity of the pellet plant was assumed as 357 kg h^{-1} with 2000 h working hours per year.

Data associated with the operation of pelletizing plant is elaborated from the literature (Fantozzi and Buratti, 2010a; Rajabi Hamedani, Colantoni, *et al.*, 2019), while the power and energy required for grinding and drying were estimated based on (Yoder *et al.*, 2011; Rajabi Hamedani, Del Zotto, *et al.*, 2019).

The last stage consists of thermal energy conversion via SCG pellet burning in a small boiler with a nominal power of 80 kW_{th} and 90% efficiency. Electricity requirements of a pellet boiler for the operation of air fan, pellet igniter, mechanical stoker, pump, hopper conveyor and grate motor (Pełka, Luboń and Malik, 2018) are considered. The remained ashes were disposed to landfill by a waste collection truck and considering an average transport distance of 20 km.

The emissions arising from the SCG pellet combustion were obtained from the literature (A Colantoni *et al.*, 2021). (A Colantoni *et al.*, 2021) measured these pollutants via the online TOC (total organic compound) analysis with a Ratfisch RS-53 T flame ionization detector (FID), by the regulations (EN12619, 2013), while a multiparametric detector Horiba PG-250 was applied for the online analysis of NOx, CO, CO_2, SO_2 and O_2. The instruments were calibrated based on a standard gas and determined concentrations mixtures.

The quartz filter in the combustion chamber and subsequent absorbent solutions could trap the highly volatile metals. PM (Total Suspended Particulate Matter TSP) was counted by gravimetry concerning the volume of gas that passed through the quartz filter. Metal concentration was measured by ICP-MS and by analyzing the quartz filter and the absorbent solutions. In addition, a thermal desorber (TD 100xr, Markes) coupled to a gas chromatograph-mass spectrometer system (GC/MS–QQQ Agilent 7000) was employed to determine VOCs (volatile organic compounds).

Table 1 presents input-output inventory and emissions from pellet combustion per 1 MJ pellet. Energy and material related to the pellet plant construction are excluded from the model.

Table 1. Inventory table for pellet production from SCG per functional unit (1 MJ_{th}).

Items	Unit	Quantity (Unit MJ^{-1})
A. Output	MJ	1
B. Input from technosphere		
1. SCG (42% wt)	kg	0.0864
2. Transport SCG to pellet plant	tkm	0.0033
3. Heat	MJ	
Drying		0.0911
4. Electricity	kWh	
Grinding		0.0024
Pelletizing		0.0001
Cooling		4.49E-5
Pellet boiler		0.00112
5. Diesel	kg	4.94E-4
6. Transport of Ash to landfill	tkm	1.3E-5
C. Output to environment		
Emission to air	kg	
1. Pellet production		
CO_2		2.07E-5
N_2O		1.24E-8
CH_4		6.23E-8
2. Pellet combustion		
CO, biogenic		1.48E-3
NO_x		4.38E-4
SO_2		4.21E-6
2-Butene-2-methyl		2.77E-6
Acetonitrile		7.38E-7
Hexane		2.62E-6
Benzene		2.07E-6
Toluene		2.88E-7
Ethylbenzene		1.44E-7
m.p-Xylene		1.72E-7
o-Xylene		1.27E-7
Benzene.1.2.4-trimethyl		1.75E-6
D. Output to technosphere		
Waste		
Ash to landfill	kg	9.84E-4

Alternative scenarios

SCG management also covers various valorization routes for energy purposes, including transesterification, pyrolysis and direct combustion of SCG (McNutt and He, 2019). Therefore, in this section life cycle of each process is evaluated considering 1 MJ of energy products as the functional unit. The transport distance from SCG collecting points to the valorizing plants is assumed to be 38.69 km since authors presume all plants are situated in the same area. The construction of corresponding plants is not included in data inventories.

2.2.2 Biodiesel production

Waste recovery into biodiesel production is considered an effective resolution from an economic and environmental perspective to produce second-generation biofuels. Meanwhile, SCG as a waste source rich in oil has recently attracted immense attention to generating biodiesel (Kamil *et al.*, 2019).
The biodiesel production process from SCG commences with oil extraction from SCG and consequently transeterifies the extracted oil into Fatty Acid Methyl Esters (FAME), identified prevalently as biodiesel. Mass and energy flow for SCG biodiesel production and emissions from its combustion have been elaborated from (Kookos, 2018) and (Efthymiopoulos *et al.*, 2019). Regarding the average SCG biodiesel HHV (40.96 MJ/kg) (Haile, Asfaw and Asfaw, 2013; Vardon *et al.*, 2013; Haile, 2014; Efthymiopoulos *et al.*, 2019), inventory data related to biodiesel production and consumption into the combustion engine are reported in Table 2.

Table 2. Inventory table for biodiesel production from SCG per functional unit (1 MJ_{th}).

Items	Unit	Quantity (Unit MJ^{-1})	Energy allocation (%)
A.Output			
1.Biodiesel	MJ	1	48.58
Co-products			
2.Gelycerol	kg	0.0025	2.49
3.Electricity	kWh	0.2563	48.93
B.Input from technospere			
1.SCG (42% wt)	kg	0.3565	
2.Transport SCG to transesterification plant	tkm	0.0138	
3.Heat	MJ	0.3743	
4.Hexane	kg	0.0002	
5.Methanol (MeOH)	kg	0.0022	
6.Sodium methoxide (NaOMe)	kg	0.0006	
7.Hydrochloric acid (HCI)	kg	0.0003	
8.Steam	kg	0.0432	
9.Cooling water	kg	2.277	
C.Output to the environment			
Emission to air	kg		
1.Biodiesel combustion			
NOx		3.204E-8	
CO, biogenic		1.507E-8	

2.2.3 Bio-oil production

Pyrolysis is a promising method to produce bio-oil from SCG (Vardon *et al.*, 2013; Matrapazi and Zabaniotou, 2020). It is a thermochemical conversion technique to thermally decompose biomass to biochar, bio-oil and syngas (Jahirul *et al.*, 2012; Kanaujia *et al.*, 2014). The proportion of pyrolytic yields are controlled by the pyrolysis temperature and heating rates (Alsbou and Faculty, 2014). Bio-oil is inferred as a substitute for crude oil due to its potential for energy production via direct combustion and even engine applications in quality upgrading (Xiu and Shahbazi, 2012). Inventory data for SCG bio-oil is based on (Li, Strezov and Kan, 2014), which evaluated energy recovery from SCG via a pyrolysis process with an 83.4% efficiency. The products at 500 ˚C and heating rate of 10 ˚C/min are 65.2%, 22.6%, and 12.2% of $W_{pyrolytic\ product}$ with corresponding high calorific values 17.23, 31.1, and 14.84 MJ/kg for bio-oil, biochar and syngas (Li, Strezov and Kan, 2014). Bio-oil is the main product obtained alongside biochar and syngas considered co-products; an energy allocation is applied for inventory analysis (Table 3). Pyrolysis heat demand for decomposition reaction and moisture evaporation is considered 0.7 $MJ/kg_{feedstock}$ (Li, Strezov and Kan, 2014). The particle and gas emissions from burning bio-oil in boiler are estimated based on gas emission measurements via a Fourier transform infrared (Kajolinna *et al.*, 2019).

Table 3. Inventory table for bio-oil production from SCG per functional unit (1 MJ_{th}).

Items	Unit	Quantity (Unit MJ^{-1})	Energy allocation (%)
A.Output			
1.Bio-oil	MJ	1	55.97
Co-products			
2.Biochar	MJ	0.625	35.01
3.Biogas	MJ	0.161	9.02
B.Input from technospere			
1.SCG (42% wt)	kg	0.154	
2.Transport SCG to pyrolysis plant	tkm	5.9E-3	
Pretreatment			
3.Heat	MJ		
Drying		0.075	
4.Electricity	kWh		
Grinding		4.4E-3	
Pyrolysis			
5.Heat	MJ	0.062	
C.Output to the environment			
Emission to air	kg		
1.Bio-oil combustion			
NOx		0.015	
CO		3.86E-4	
SO_2		9.67E-4	
PM		5.9E-3	

2.2.4 Direct combustion

Spent coffee grounds can be used as solid biofuels and combusted in boilers. The estimation of input-output data for SCG combustion (Table 4) is based on the study (B. S. Kang *et al.*, 2017).

Kang et al. (B. S. Kang *et al.*, 2017) investigated combustion emissions (CO and NOx) of SCG with a lower heating value of 20 MJ/kg on a dry basis and 2.06 w% ash content. SCG is dried up to 10 w% water content and then burned in a small boiler (6.5 kW_{th} based on $LHV_{biomass}$) with 64% efficiency. The electricity demand of the boiler is taken into account (Pełka, Luboń and Malik, 2018). The remained ash is transferred by the waste collection truck to the landfill 20 km from the combustion plant.
According to spent coffee ground hydrogen content (7.19%) (B. S. Kang *et al.*, 2017), Table 4 outlines the inventory data per 1 MJ of heat produced in higher heating value.

Table 4. Inventory table for SCG direct combustion per functional unit (1 MJ_{th} heat energy).

Items	Unit	Quantity (Unit MJ^{-1})
A.Output		
1.Heat	MJ	1
B.Input from technospere		
1.SCG (42% wt)	kg	0.112
2.Transport SCG to boiler	tkm	4.33E-3
Pretreatment		
3.Heat	MJ	
Drying		0.084
Combustion		
4.Electricity	kWh	2.2E-3
5.Ash transport to landfill	tkm	2.84E-5
C.Output to the environment		
Emission to air	kg	
NOx		8.8E-4
CO		5.3E-4
D.Output to technosphere		
Waste		
Ash to landfill		1.4E-3

2.3. Impact Assessment

LCA model is developed in SimaPro software (version 9.0.0.49). In this study, ReCiPe 2016 v1.03 method (Huijbregts *et al.*, 2017) in both midpoint (H) and endpoint (E) level convert data inventory to conversational indicators. At the midpoint level, environmental results are normalized and characterized to comprehend the significance of indicators and present them into relatively abstract units such as CO_2 equivalent. In contrast, results are interpreted as damages on human health and ecosystem quality and resources at the endpoint level. This method follows the goal to obtain a comprehensive environmental perspective on the life cycle of SCG pellets. The ReCiPe method has been used in other studies on SCG application (Schmidt Rivera *et al.*, 2020) and pellet production (Buratti *et al.*, 2014; Laschi, Marchi and Gonz, 2016; Rajabi Hamedani, Colantoni, *et al.*, 2019). Among a total of eighteen impact categories assessed, the following ten categories with significant effects have been assessed: Global warming, Ozone formation-human health, Ozone formation-terrestrial ecosystems, Freshwater eutrophication, Terrestrial ecotoxicity, Freshwater ecotoxicity, Marine ecotoxicity, Human carcinogenic toxicity, Human non-carcinogenic toxicity, Fossil resource scarcity, Water consumption.

3. Results and Discussion

3.1 Pellet production

In order to simplify LCIA interpretation and be more applicable for decision-making, the results are described concerning their magnificence based on the normalization factor at a global scale as recommended by (Pizzol *et al.*, 2016). Table 5 and Fig. 3 outline the results of the LCA model of SCG pellet according to selected impact categories.

Table 5. Characterization results of pellet production process-cradel to grave (ReCipe, FU: 1 MJ_{th})

Impact category	Unit	Value	SCG collection (%)	Pelletizing plant (%)	Thermal conversion (%)	Waste disposal (%)
GWP	kg CO_2 eq	1.22E-2	35.30	63.78	4.04	-3.14
OF	kg No_x eq	8.11E-5	75.70	17.65	6.35	0.28
FEu	kg P eq	6.87E-7	17.44	75.64	24.66	-17.80
TEc	kg 1,4-DCB	7.53E-3	67.76	25.27	6.74	0.21
FEc	kg 1,4-DCB	6.63E-05	24.54	57.34	18.01	0.09
MEc	kg 1,4-DCB	1.06E-04	25.54	59.38	14.98	0.08
HT	kg 1,4-DCB	1.73E-3	38.23	47.18	14.44	0.13
FRS	kg oil eq	4.97E-3	28.66	68.59	2.89	-0.16

Global warming (GWP), Ozone formation (OF), Freshwater eutrophication (FEu), Terrestrial ecotoxicity (TEc), Freshwater ecotoxicity (FEc), Marine ecotoxicity (MEc), Human toxicity (HT), Fossil resource scarcity (FRS)

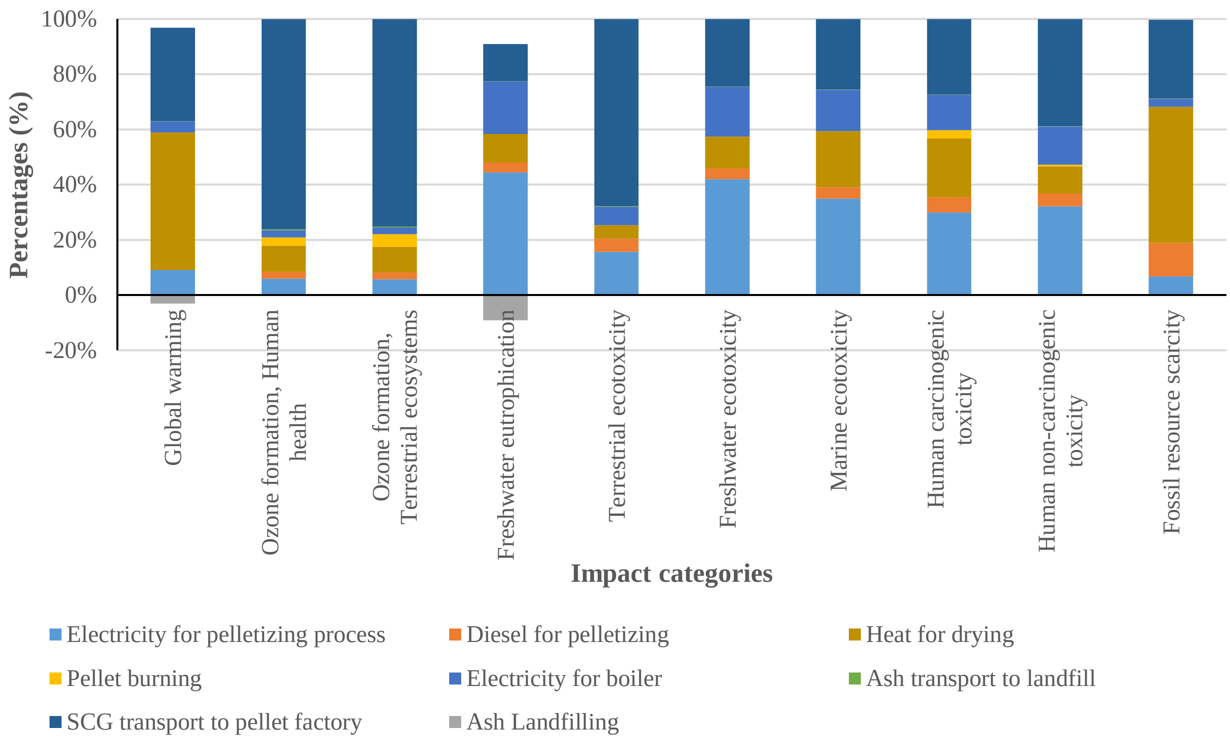

Fig. 3. Environmental profile and impact categories of SCG pellet production per 1 MJ_{th}

3.1.1 Ecotoxicity

Aquatic and terrestrial ecotoxicity indicate the effect of hazardous chemical stressors on freshwater. The transportation process, including diesel fuel consumption and air emissions from fuel combustion for collecting and delivering SCG to the pellet plant, has an immense impact on the terrestrial ecosystem. Electricity used for grinding SCG, instead, is the main responsible for aquatic ecotoxicity.

3.1.2 Human toxicity

This category measured in kg 1,4-dichlorobenzene equivalent addresses the fate and exposure risks of toxic chemicals in contact with air and drinking water on human health. This category declares cancer and non-cancer related human disease risk. Electricity and heat used as well as transport processes for SCG collecting entail the most significant human toxicity in pellet production.

3.1.3 Fossil resource scarcity

This category is stated as the ratio between the higher heating value of a fossil resource and the energy content of crude oil (Hischier and Weidema, 2010; Huijbregts *et al.*, 2017) and measured in kg oil-eq. Heat consumed for SCG drying in the pelletizing phase followed by the SCG transport process represents the major contribution to the total impact, while ash disposal slightly diminishes this impact.

3.1.4 Global warming

This category measured in kg CO_2 equivalent consists of the greenhouse gases carbon dioxide (CO_2), methane (CH_4) and dinitrogen monoxide (N_2O), together with families of gases including hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs). Emissions arising from heat consumption for SCG drying and electricity mainly used in pelletization phase of SCG alongside transport process are primarily in charge of global warming impact. Landfilling ash supports environmental benefits and decreases global warming impact for the whole process by 3%.

3.1.5 Ozone formation

This indicator in kg NO_x eq describes the effects of change in ambient ozone concentration on human health into breathing difficulties (Zelm *et al.*, 2016) and on terrestrial ecosystem into PDF of forest and grassland species (T M W J Van Goethem *et al.*, 2013; Thomas M W J Van Goethem *et al.*, 2013). The emission of a precursor (nitrogen oxides or non-methane volatile organic compounds (NMVOC)) changes the ambient concentration of ozone. The emission concentration sensitivities matrices for emitted precursors from the global source-receptor model TM5-FASST predicts the impact. Transportation of SCG to the pellet plant has a significant contribution to the total impact.

3.1.6 Freshwater eutrophication

This indicator measures the fate of phosphorus kg P to freshwater equivalents. The universal fate factors for phosphorus emissions to freshwater are taken from (Helmes *et al.*, 2012) in ReCipe method. The primary stressors are SCG collecting and electricity consumption in the pellet plant and afterwards in the boiler. On the contrary, the biodegradable nature of ash disposed involves benefits in alleviating aquatic eutrophication by 17% during the life cycle of the SCG pellet.

All LCA studies performed on pellet production and thermal energy extraction consider forest and agricultural residues as the primary material. Although impact assessment results of these studies are distinctive due to the impact of methodological aspects such as different kinds of biomass, system boundary, impact assessment method and functional unit, comparison with results obtained from the present SCG pellet study can be helpful.

Two LCA studies on wood-based combustion systems (Quinteiro *et al.*, 2019) and pellet production in different levels, centralized, decentralized and household (Quinteiro *et al.*, 2020), including four stages: forest management, maritime pine pellet production, distribution and thermal energy production phases, revealed that the pellet production stage is significantly relevant for the impact categories of global warming, freshwater eutrophication and fossil resource scarcity where the main contributor for these impacts are heat generation for wood drying and electricity consumption during the process of pellet production. Comparing GWP of the wood pellet (7.79E-3 kg CO_2 eq), SCG pellet presents an adverse result (1.22E-2 kg CO_2 eq) justified by higher SCG moisture content and heat requirement for the drying process. In agro-pellet production from orchard woody biomass (Rajabi Hamedani, Colantoni, *et al.*, 2019) which includes biomass production, woodchip production and pellet manufacturing, pelletizing stage following the biomass production phase is responsible for all relevant impacts. SCG pellet supports more favourable impact results in freshwater eutrophication, aquatic ecotoxicity and human ecotoxicity than pellet produced from woody biomass.

Life cycle assessment of pellet production from roundwood and sawmill residues excluding energy generation phase showed energy use in pellet mill has a significant contribution to ecotoxicity and human toxicity impacts (Morrison and Golden, 2016). Jiang et al. (Jiang *et al.*, 2020) reported that all emissions from straw pellet production are associated with electricity consumption in the pelletizing phase. In forest wood pellet-small scale local CHP plant, fuel and energy consumed for transport, drying, comminution and hauling cause the most significant portion of GWP impact (Havukainen *et al.*, 2017). The impact assessment results of pellet production from roundwood logs and sawdust represented as a single score showed that the pelletization process due to electricity consumed is a primary stressor on total impacts (Pergola *et al.*, 2018).

3.2 Alternative scenarios

In order to simplify comparing different valorization ways for SCG waste, a single score indicator is applied. This indicator expresses environmental burdens into a score so that a higher value merely correlates to contributing more (Cioccolanti, Rajabi Hamedani and Villarini, 2019; Rajabi Hamedani, Kuppens, *et al.*, 2019). According to Fig. 4., which represents single scores and process contributions, damages caused by pellet production and all alternative scenarios for SCG waste management related to human health. Whereas these bioenergy systems slightly affect the use of resources. In addition, one can conclude that 1 MJ_{th} production from SCG bio-oil followed by SCG pellet is preferred over 1 MJ_{th} production from other alternatives considered in this study. Comparisons among scenarios signify that SCG biodiesel entails higher overall impacts per 1 MJ_{th}. It is justified by higher energy and material consumed in the transesterification process of SCG oil per 1 MJ_{th}.

The critical key message from Fig. 4. is that in all scenarios, SCG collection connected with transport process alongside heat requirements for drying process cause considerable damage to human health and consequently overall environmental load. Open-air dry is recommended to tackle this problem.

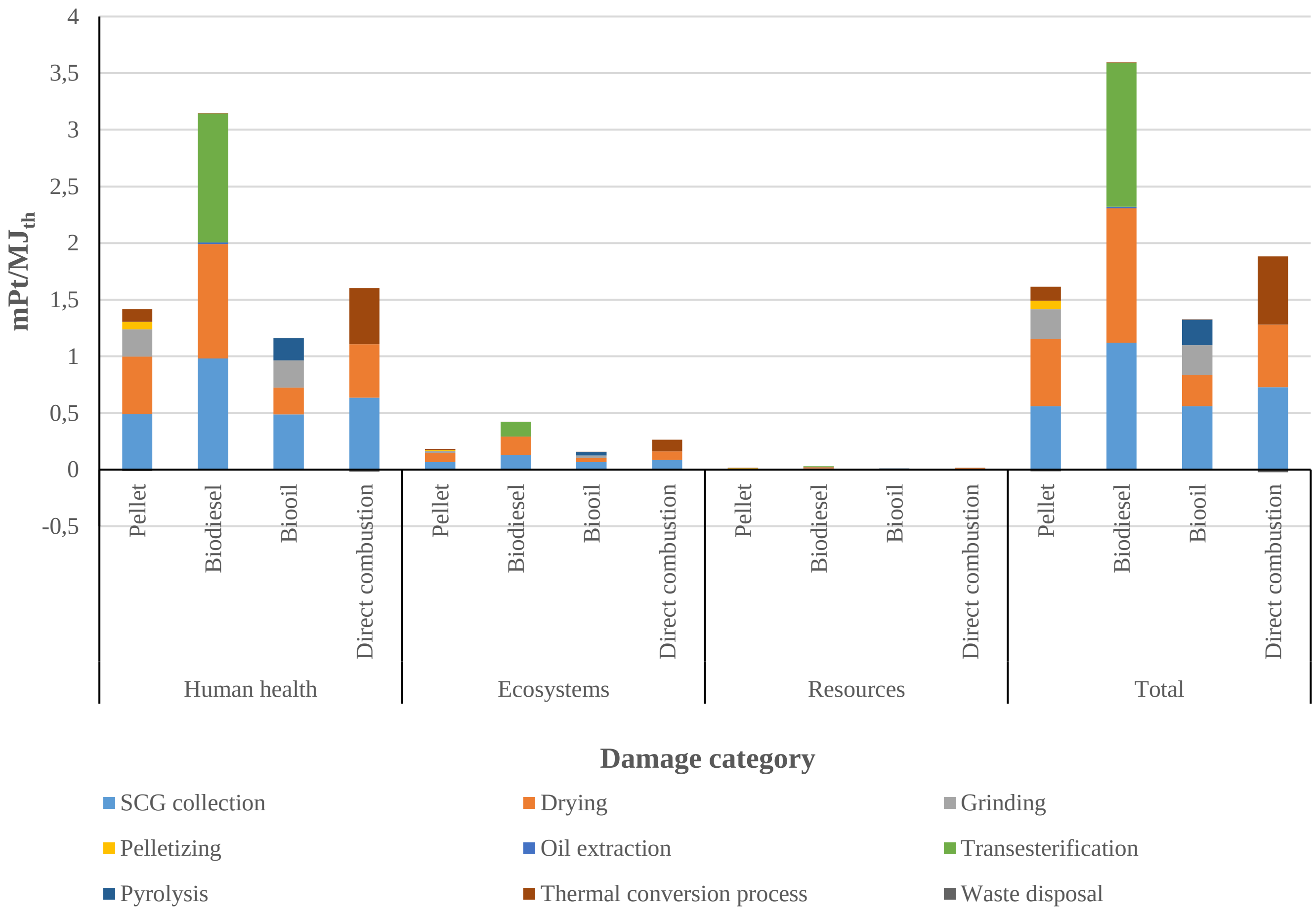

Fig. 4. Damage assessment results for 1 MJ_{th} produced from the SCG pellet and alternative scenarios

4. Conclusions

This study has assessed the environmental profile and impact of pellet production from the spent coffee ground by using life cycle assessment in a cradle to grave scope. As regards results, the LCA study revealed that all environmental burdens are imposed mainly by pelletizing process due to heat demand for SCG drying. Hence, approaches such as open-air dry are encouraged, leading to a decrease in the environmental impacts of pellets from SCG. In terms of damage assessment, SCG pellet affects significantly human health, comparing other damage categories. On the contrary, thermal conversion and waste disposal phases have a minor effect on the environment. The SCG pellet production can benefit from ash disposal credits and contribute to climate change mitigation, fossil resource uses and freshwater eutrophication reduction from 0.16% to 17.8%.

Alternative scenario analysis also indicated that SCG collection and drying stages contributed to all impact categories. According to overall impacts, the most environmentally sustainable option is bio-oil production from SCG waste followed by pellet produced from this residue.

Biodiesel production is the least preferred option considering the highest impact on all damage categories.
These specific findings as a pattern can assist decision-makers to comprehend relevant environmental burdens to pellet production and selecting the efficient options for valorizing SCG waste from an environmental perspective.

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3.4 Article 3

Comparison between coffee and common lignocellulosic biomass for energetic potential prediction (Environmental Engineering and Management Journal)

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COMPARISON BETWEEN COFFEE AND COMMON LIGNOCELLULOSIC BIOMASS FOR ENERGETIC POTENTIAL PREDICTION

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Abstract

Energy production from renewable and waste materials is an attractive alternative to conventional production chains that involve agricultural products. Residual biomass from cultivars and coffee production chain, despite their widespread availability, aren't enough considered in energy models and economic development. In addition to lignocellulosic biomass, coffee can be considered as a new material usable in such processes. ICO (International Coffee Organization) data showed that the Spent Coffee Grounds (SCG) production worldwide is about 6 million of tons per year. In the work presented, calorific value, ash content, and elemental analysis of lignocellulosic biomass and SCG pellets, were firstly examined. The aim was to compare SCG with conventional lignocellulosic biomass already used in thermal production. Compositional and energetic analysis permit to fix linear models for biomass energetic yield prediction. Models that relate the higher heating value (HHV) to the compositional analysis mostly date to the late 19th century. Estimation of HHV from the elemental composition of fuel is one of the basic steps in performance modelling and calculation for thermal systems. The possibility to perform statistical analysis on data collected in the same laboratory gave the opportunity to reliably compare conventional and unconventional biomass. The linear regression model fitted on the whole dataset had an R Squared of 0.85 showing a good HHV prediction from elemental analysis. Coffee appeared as a feedstock with peculiar characteristics that differentiate it from the others, while herbaceous and arboreal biomass mostly differentiated for ash and moisture content.
SCG showed an HHV higher than any other woody and herbaceous plant, manifesting a great potential from an energetic point of view. According to the concept of circular economy, coffee companies, in their waste, have already a valid resource usable in a heat generator for the roasting process.

Key words: biomass, modelling, spent coffee grounds (SCG), ultimate analysis

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1. Introduction

Large amounts of agricultural and forestry residues, usually treated as waste, can be considered as a significant resource for energy production through biological or thermo-chemical processes (Bianchini et al., 2021; Carnevale et al., 2020; Paris et al., 2019a; Schmitt et al., 2019; Sun et al., 2018). To date, processes and models for the exploitation of ligno-cellosic biomass are mainly based on forest resources (Tomassetti et al., 2019; Torre et al., 2019). Despite the considerable volumes produced, residual biomasses from agricultural crops are rarely considered in energy models and economic development. Alternative energy sources are increasing their importance both to meet the energy

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growing demand and to reduce the environmental impact. Given the high volumes produced every year, soluble coffee residues represent an important unexplored resource in the agro-industrial sector. Coffee has one of the most developed markets in the world and together with tea, it is among the most consumed beverages (Park et al., 2019). Its annual worldwide generation reach the 6 million tons (Mussatto et al., 2011). The organic molecules present in coffee suggest that the recovery of such resource can be economically advantageous, leading to the synthesis of valuable compounds. (Kibret et al., 2021; Kondamudi et al., 2008; Kua et al., 2016; Liu et al., 2017; Murthy and Madhava Naidu, 2012; Mussatto et al., 2018). Studies regarding the potential thermal exploitation of spent coffee grounds (SCG) are increasing and the reason of such interest in coffee waste is explained by its big market volume. ICO (international Coffee Organization) data showed that the apparent consumption of coffee in Italy between 2004 and 2016 oscillates from 5.46 to 6 million of 60 kg green bean bags (Sette, 2017).

The large amount of waste production in the coffee market unavoidably leads to questioning on the possible utilization of such waste inside a circular economy model. Combustion is one of the thermal production processes more rooted and used in common living, especially through the domestic fireplace and stoves. The feasibility of SCG thermal valorization has to be discussed both from the logistic and energetic point of view (Volpi et al., 2019). The possibility to use a new material like coffee in established thermal conversion methods was already investigated in previous works (Colantoni et al., 2021; 2020). Biomass fuels are considered a renewable resource both for their continuous production and because they do not affect the overall balance of CO_2 in the atmosphere.

Knowing the physicochemical properties of biomass is essential for its use in power plants. These raw materials are experimentally characterized by analyzing the elemental composition, energy efficiency, and fusibility of the ashes (Pari et al., 2018). Such analyzes are regulated by standards to ensure the quality and comparability of the measurement results. The calorific value of biomass is a fundamental parameter for the exploitation of this type of fuel in power plants. The higher calorific value (HHV) consists of the amount of heat produced by the complete combustion of a unit quantity (by mass or volume) of fuel under certain conditions, when the reaction pressure is kept constant. The lower calorific value (LHV) is obtained when the energy used for the evaporation of the water formed during combustion is subtracted from the total energy produced. Numerous models have been published to relate the energy produced by the fuel to the elemental composition of the fuel itself. (Friedl et al., 2005). For these reasons, the calorific value of such wastes is regarded as the most significant parameter that defines the fuel quality. The estimation of the calorific value based on the chemical composition of biomass has also been in great demand when reliable analysis results are present.

Macromolecular ingredients such as hemicellulose, cellulose, and lignin account for most of the organic part of the biomass while some others include starch, proteins, triglycerides, lipids, etc. Accordingly, some kinds of biomass, particularly woody ones, are generally defined as lignocellulosic. On the other hand, although these macromolecular components are consisted mostly of carbon, hydrogen, and oxygen, their molecular configurations and structures are highly different (Ozyuguran et al., 2018).

Many correlations for the estimation of HHV from elemental composition are available in literature, the most important have been presented in Channiwala and Parikh (2002), and most of these relations have been derived for coals. Furthermore, the majority of these correlations, when referred to lignocellulosic biomass, use mixed datasets with data provided from different studies, obtained with different instruments and sometimes with different methods. To carry out the analyzes in the same laboratory permits to minimize the data variability coming methods, instruments and operators. For these reasons, the present work is marked with the intention to create a homogeneous dataset to set up the HHV modeling from compositional analysis of different kinds of biomass.

2. Materials and methods

2.1. Biomass description

The biomass coming from different projects and relative works, were collected for more than a year, starting from October 2019. The modeling analysis has been carried out on 41 samples composed of different mixtures of lignocellulosic biomass. The complete biomass description is provided in Table 1.

2.2. Ultimate and proximate analysis

Ultimate and proximate analysis was carried out adopting always the same procedure following European standards for biomass characterization. The biomass humidity was measured through the Memmert UFP800 drying oven at a temperature of 105 ± 2°C for 24 hours, according to ISO 18134-2 (2017). For characterization, the dried sample was grinded first with the Retsch SM 100 cutting mill for a preliminary size reduction and thereafter through the Retsch ZM 200 rotor mill.

Ash content was measured by a Lenton EF11/8B muffle furnace according to ISO 18122 (2015). The higher heating value (HHV) was determined by the Paar 6400 isoperibol calorimeter following the ISO 18125 (2017), while the lower heating value (LHV) was calculated from the higher heating value, according to ISO 18125 (2017).

Table 1. Biomass used for experimental and modeling analysis

Biomass	***Group***	***Appearance***	***References***	***Notes***
Grapevine	Fruit Cultivar Tree	Chipwood	Proto et al. (2021)	*Vitis spp*. Harvested in Calabria, Southern Italy
Olive	Fruit Cultivar Tree	Chipwood	Proto et al. (2021)	*Olea spp*. Harvested in Calabria Southern Italy
Citrus	Fruit Cultivar Tree	Chipwood	Proto et al. (2021)	*Citrus spp*. Harvested in Calabria Southern Italy
Cultivars mix	Fruit Cultivar Tree	Pellet	Vincenti et al. (2020)	Mixed pellet of *Citrus*, *Olea*, and Kiwi (*Actinidia spp*) harvested in Calabria, southern Italy
Wheat straw	Straw Herbal	Chipwood	Paris et al. (2019b)	*Triticum aestuvum L*. produced by the CREA of Monterotondo
Rice straw	Straw Herbal	Chipwood	Paris et al. (2019b)	*Oryza sativa L*. imported from different areas of Pakistan (Punjab, Azad Jammu and Kashmir (AJK), and Sindh)
Hemp	Hemp Herbal	Chipwood	Not published	*Cannabis spp*. Produced by the CREA of Monterotondo
Forest mix	Forest Tree	Pellet	Vincenti et al. (2020)	Mixed pellet of fir (*Abies spp*), beech (*Fagus sylvatica*) and chestnut (*Castanea sativa*)
Coffee	SCG	Pellet	Colantoni et al. (2020; 2021)	*Coffea spp*. Mixed pellet obtained with different sawdust percentages (0, 15, 25, 33, 66)

The elemental composition, carbon content (C), hydrogen content (H), and nitrogen content (N) was measured with the elemental analyzer Costech ECS 4010 CHNS-O according to ISO 16948 (2015).

2.3. Statistical analysis

The statistical analysis was entirely conducted in R ver. 3.6.1. Different statistical tests and analysis resulted useful for the data comprehension. Since the biomass' description was one of the goals of this study, differences between species were tested through a One-Way ANOVA at the 0.05 significance level, permitting to evaluate the importance of the biomass factor on energetic and compositional parameters. The individuation of such differences is subsequently obtained with the post hoc Tukey-HSD test, able to compare groups means and to define weather the variables assumed significant differences according to the plant species. Shapiro-Wilk and F tests were performed to evaluate both normality and homoscedasticity of biomass characterization variables. Since many variables didn't show a Gaussian trend, the Friedman test and the Conover test were performed to understand the difference between biomass. The multivariate data analysis was conducted by Principal Component Analysis (PCA) to evaluate the relationships between biomass properties. The cluster analysis was performed by the Ward technique, whose aim is to achieve a hierarchical classification by minimizing the variance of the variables within each group. At each stage, the groups that produce the smallest increase in the total variance within the groups are merged (Ward, 1963).

Since the characterization variables are neither normal nor homoscedastic, the quantile regression (QR) has been used to build linear models able to predict HHV from C, H, and N. This method results more accurate when the basic requirements for applying ordinary least squares (OLS) are not met, particularly in the presence of outlier values. Quantile regression is able to provide a much broader analysis of the relationships between variables than the OLS model. Over the years, QR has been used as an extension of the linear regression model and it allows to do the analogue of what linear regression does for the mean, on quantiles. By exploiting the estimated parameters, it is possible to consider the quantile value of the response variable, depending on a set of regressors. This allows to appreciate the behavior of the response variable not only in average but also in its entire distribution. By varying the quantile of the regression between zero and one (τ) it is possible to obtain the entire conditional distribution. To evaluate the forecast quality, the root means square error (RMSE), mean absolute error (MAE) and mean bias error (MBE), were calculated. The MBE gives information regarding the average forecast error representing the systematic error of a forecast model, MAE gives the forecast errors average magnitude, while with RMSE more weight is attributed to the largest errors (Kato, 2016).

3. Results and discussion

3.1. Proximate and Ultimate Analysis

From the proximate and ultimate analysis (Fig. 1), SCG resulted a biomass with peculiar characteristics, both from a compositional and an energetic point of view. The samples listed in Table 1 were grouped in three branches depending on the physical structure of the biomass: Coffee, Herbal and Tree (Fig. 1). Through the Friedman test applied to compositional variables, real differences are pointed out. It's clear that SCG has more C and N percentages

(Fig. 1a-b) than herbaceous and arboreal biomass at the expense of H, which shows a very low content for SCG (Fig. 1c). Many other studies, concerning both biomass and hydrocarbons (Demirbas et al., 2018; Ozyuguran et al., 2018), relate the compositional analysis to the HHV. For biomass, in general, it is overt that C is strictly positively related to HHV. In this case, coffee is a very surprising material, inasmuch its HHV is significantly higher than any other biomass taken into account (Fig. 1d). Proximate analysis concerning humidity and ash reveals coffee as a biomass with a higher content in water and normal content of ash.

Regarding the elevated humidity tenor (Fig. 1e), it is due to the nature of SCG which derives from a process where coffee is crossed by water. In this case, processes related to transportation, stock and drying are fundamental (Schmidt Rivera et al., 2020). The other two kinds of biomass, arboreal and herbal, usually behave in a similar way except for C, HHV, and ash. Herbaceous biomass has the worst energetic characteristics with lower HHV and C content, and higher ash production during combustion (Fig. 1f). Such data indicate low potential in thermochemical conversion processes.

3.2. PCA analysis

Some of the trends described above can be more formally elucidated through the application of multivariate statistical techniques. Other studies already tried to classify different lignocellulosic biomass through a multivariate approach (Jenkins et al., 1998). Fig. 2 gives PCA results using the ultimate and proximate analysis for the 41 observations in the dataset. Differences between the four main classes have been highlighted in the figures: straw, coffee, wood pellet, and wood chip. Fig. 2 is a plot of the first principal component PC1 respect to the the second principal component PC2.

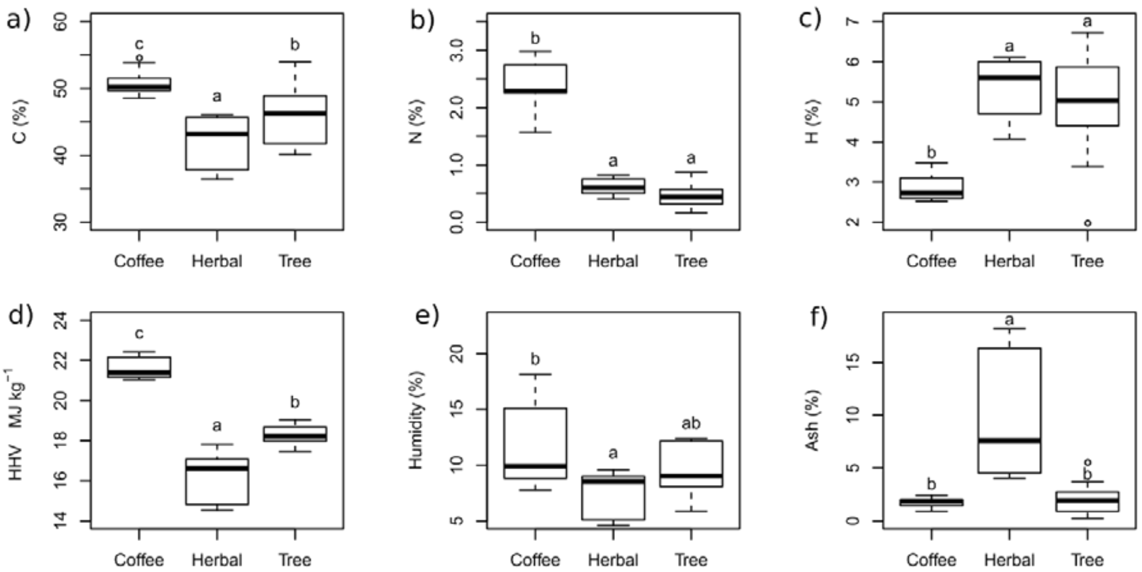

Fig. 1. Boxplots of ultimate and proximate analysis parameters for Coffee, Herbal and Tree biomass. Carbon content (a), Nitrogen content (b), Hydrogen content (c), Higher Heating Value (d), Humidity (e) and Ash content (f). The boxes represent the minimum (Q1 - 1.5*Interquantile Range), 25th percentile (Q1), 50th percentile (Q2), 75th percentile (Q3) and maximum (Q3 + 1.5 Interquantile Range). Groups with different letter are significantly different by using post hoc Tukey-HSD test ($p<0.05$)

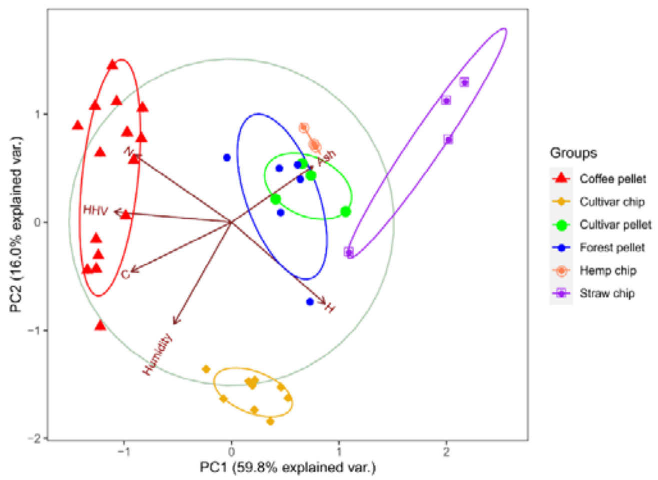

Fig. 2. Principal Component Analysis biplot obtained with the parameters obtained from ultimate analysis and proximate analysis

These two components explain the 75.8% of the total variance in the data. PC1 has a strong negative correlation with HHV, C, and N, while a positive correlation is shown for ash and H. For PC2, the most influent parameter is humidity with whom is negatively correlated. From this grouping it is possible to appreciate how biomass vary depending on many factors. It is evident that woody biomass can vary their moisture content if they undergo a pelletizing process or not. Coffee is clearly an uncommon biomass with HHV and N higher than any other sample considered, as already seen in previous works (Colantoni et al., 2021). Furthermore, the coffee group shows an inner variability explained especially by humidity, this is probably due to the different kinds of blend produced with many sawdust percentages which bring to the moisture content decrease. Close to the woody pellets are placed the hemp samples that, despite the different nature respect arboreal biomass, have comparable composition and energetic yield. Hemp is therefore confirmed as feedstock of interest for many purposes such as textiles, pharmaceutic and energetic (Qamar et al., 2021; Rheay et al., 2021; Vandepitte et al., 2020). Like all herbaceous and straw species, hemp presents higher ash production in combustion, but if compared to the other straw samples, the amount is irrelevant.

Through the hierarchical cluster analysis (Fig. 3) using the Ward's minimum variance method are finally individuated four groups on which have been based the subsequent modeling evaluations. Principally, the arboreal biomass is divided in chipped and pelletized, while the SCG and straw biomass form other two distinct groups. Comparing such results with the trends shown through the ultimate analysis, three different linear models are proposed to better understand the link between composition and heating value in many kinds of biomass.

3.3. Correlations and modeling

From the compositional analysis it has been possible to fix a model for the HHV estimation for the biomass considered. Usually for statistical analysis, ordinary least squares (OLS) are mostly used and the fit quality evaluation is made by the coefficient of determination (COD) R^2. However the RQ models are more robust since they permit a more complete analysis of the conditional distribution of a variable depending on many predictors (Ranganai, 2016).

Despite the R^2 isn't properly used for quantile regression models, which are based on median or other quantiles, its calculation strengthens anyway the models built on the ultimate analysis and resumed in Table 2.When the complete dataset is considered, a strong correlation (R^2=0.85) is indicated for the Eq. (1). This model shows the smallest MBE, indicating a reduced systematic error to under and over forecast, but high MAE and hence higher forecast errors magnitude (Table 2).

Focusing deeply on the different groups identified through the PCA analysis, different models can be proposed for the estimation of HHV from the ultimate analysis. Since SCG has shown a relation between ultimate analysis and HHV closer to the herbaceous plant, the dataset has been divided into two groups: herbaceous and arboreal. Two different regression models are applied to these sub-datasets and the equations are resumed in Table 2.

Fig. 3. Ward hierarchical cluster analysis of the biomass

Table 2. Models and relative accuracy parameters

Group	*Model*	R^2	*RMSE*	*MAE*	*MBE*	*Eq*
Complete	*HHV = 0.14C + 1.22N - 0.16H + 11.81*	0.85	0.1	0.58	0.01	*(1)*
Herbaceous	*HHV = 0.38C + 1.65N + 0.37H - 2.64*	0.96	0.06	0.38	0.02	*(2)*
Arboreal	*HHV = 0.08C - 0.49N - 0.03H + 14.93*	0.51	0.2	0.23	0.07	*(3)*

The higher variability in compositional analysis shown by arboreal species (Fig. 1) is reflected in the model quality too; for this group the smallest coefficient of regression R^2 has been calculated. Furthermore, such variability is detected by the RMSE too, which indicates the presence of large errors in the forecast (Table 2). The quantile regression fitted for herbaceous resulted the most accurate, with the smallest errors (RMSE = 0.06). When the calculated and predicted HHV values are compared, it can be seen that the plotted values are close to the curves of HHV estimated-HHV real, indicating good correlation accuracy (Fig. 4). In particular (Fig. 4), four quantile regression lines, in addition to the medians in bold, have been estimated for four values of τ (0.1, 0.25, 0.75, 0.9) for each model proposed. The same graph shows in blue the quantile regression lines for the herbaceous group, in black the arboreal ones, and in red the complete dataset regression lines. The lines estimated through quantile regression include almost all points on the graph.

Eq. (2) seems to be more accurate compared to Eq. (1) and (3) considering the presence of more outliers produced by the latter. In the upper-right corner of the graph are distinguishable coffee HHV values confirming the high energetic power of this matrix; in the middle part of the graph are present mostly arboreal species with some introgression of other herbaceous species, principally hemp; in the low-left corner the three straw biomasses bring out their lower predisposition to energy exploitation.

Many empirical correlations have been studied to predict the HHV from elemental composition, mostly for coals and other hydrocarbon fuels (e.g., biomass, char, oil) as well. Since it is well established that carbon and hydrogen contribute significantly to the biomass energy potential (Sheng and Azevedo, 2005), these two constituents are taken into account deeply. When hydrocarbons are evaluated it's known that a higher H content brings to higher HHV; saturated hydrocarbons are the simplest of the hydrocarbon species, they are composed entirely of single bonds, saturated with hydrogen and show higher HHV respect the unsaturated species with stronger bonds (Demirbas et al., 2018). For lignocellulosic biomass, the same reasoning can't be valid. In literature is confirmed that a positive correlation exists between C and HHV, while for hydrogen and HHV a clear trend isn't always observed (Jenkins M. et al., 1998).

In Sheng and Azevedo (2005), for example, the positive correlation observed between H and HHV is limited to a slight trend visible from data plotting without any statistical confirmation. In the present study, a positive correlation between C and HHV is observed (Fig. 5c) (Spearman: ρ = 0.74), but when H is considered (Figs. 5 d-f) , contrary to what is expressed in other works in literature (Mateus et al., 2021) a negative correlation (Spearman: ρ = - 0.64) can be observed (Fig. 5f). This behavior is strongly driven by SCG, which presents low H content and high HHV, differentiating itself from the other biomass considered in the models found in literature. Moreover, if we consider all biomass except SCG, the trend between H and HHV is negative tending to 0 (Spearman: ρ = -0.07), showing an absence of correlation between these two variables (p-value = 0.72). H content and HHV of arboreal species isn't correlated (Spearman: ρ = 0.05) (Fig. 5d), while only herbaceous species, including SCG, showed a negative correlation between the two parameters (Spearman: ρ = -0.54) (Fig. 5e).

When C-HHV correlation is examined, it can be noted that SCG better follows the trend shown by the herbaceous plants and the correlation between C and HHV for only SCG and herbaceous species increases till 0.92 (Fig. 5b). If only arboreal species are considered, the correlation decreases due to the higher variability of the compositional parameters. It is also noticeable that the quantile model fitted for only the arboreal species (Fig. 5a) underestimates the higher values of HHV and overestimates the lower ones.

This is probably due to the diversity of the biomass considered; for these biomass different storage methods have been used, furthermore the structural composition of tree biomass is usually considered more heterogenous with samples varying in bark and wood percentage and therefore in lignin and cellulose content (Barmina et al., 2013).

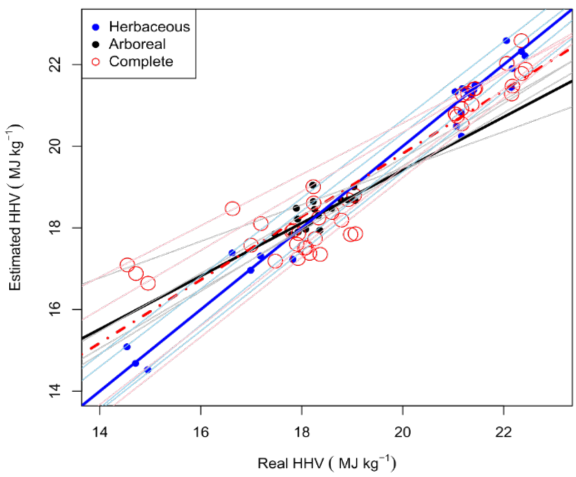

Fig. 4. Comparison between real and estimated HHV values for the three models

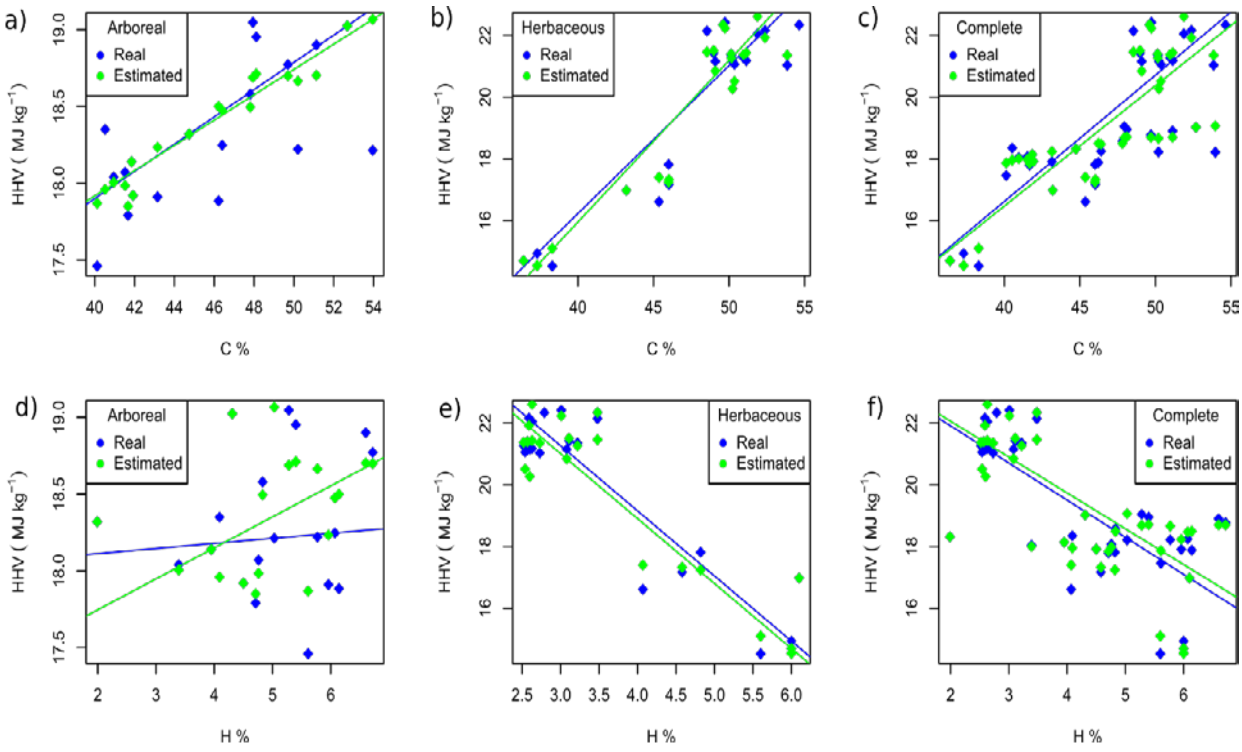

Fig. 5. Correlations between C and HHV for arboreal species (a), herbaceous (b), and for the whole dataset (c). Correlations between H and HHV for arboreal species (d), herbaceous (e), and for the whole dataset (f)

From the observations mentioned above, it follows that the relation between elemental composition and energetic yield isn't so homogeneous when the datasets comprehend many kinds of species with different physiology and physical structure. Studies that deepen and do not neglect such differences, are useful for a better comprehension of the processes involved in biomass energetic valorization, permitting better and wider modeling.

4. Conclusions

Through the PCA and cluster analysis, it has been possible to group the biomass and understand the energetic behavior depending on the ultimate and proximate analysis. In the two main groups highlighted (herbaceous and arboreal), linear quantile models have been applied for the prediction of HHV from compositional analysis (C, H, N). Such models show a good accuracy and confirm themself as a useful tool able to give information on biomass energy potential.

Arboreal species were marked by a higher variability in composition and the model fitted to them resulted less accurate, while Eq. (2) gave the best fit for herbaceous. Despite the typical differences between the studied biomass, Eq. (1) was able to give a good estimate of HHV.

In these models and calculations, SCG always shows the best energetic yield and the predicted values of each model concerning SCG are able to give extremely accurate values for this uncommon biomass. Straw biomass is the worst feedstock from the energetic point of view while arboreal and hemp place themselves between SCG and straw, but especially arboreal ones have already good and easy ongoing practices (harvesting, storage and drying) for their exploiting, thus resulting biomass easier to use in thermochemical processes.

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3.5 Article 4

An industrial scale, mechanical process for improving pellet quality and biogas production from hazelnut and olive pruning (Energies)

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An Industrial Scale, Mechanical Process for Improving Pellet Quality and Biogas Production from Hazelnut and Olive Pruning

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Abstract: The effects of a mechanical process on the solid fuel quality and anaerobic biodegradability of hazelnut and olive pruning were determined. The feedstock was treated using a two-stage dry milling process, followed by fractionation into four different products. The coarser products from the processing of both the raw materials, named C and M, were notable for the high reduction in both the ash and nitrogen content. Therefore, for hazelnut, they met the requirement of the EN ISO 17225-2 standard for both the industrial and residential pellets, whereas C and M from olive processing met the requirements only for the industrial pellet. The raw materials and the finest products from processing, named F1 and F2, were anaerobically digested in batch reactors under mesophilic conditions. The F2 product from hazelnut processing reached a methane yield of 118.1 $Nm^3\ t_{VS}{}^{-1}$, corresponding to a +70.1% gain over the untreated substrate, whereas F2 from olive pruning processing reached 176.5 $Nm^3\ t_{VS}{}^{-1}$, corresponding to a methane yield gain of about +93.5% over the untreated raw material. These results suggest that the investigated process could be successfully used to improve the quality of pruning and establish new markets for them.

Keywords: pruning; anaerobic digestion; biogas; pellet; hazelnut; olive

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1. Introduction

One of the reasons for the increased interest in renewable energy production is the concern about the use of fossil fuels and the environmental damage they cause.

On 10 January 2007, the European Commission drew up a long-term vision for the EU (European Union) to generate energy from renewable sources [1]. This led to the proposal to establish a target by the year 2020 that 20% of the overall energy consumption in the EU shall be from renewable sources. In addition, it proposed establishing, also by 2020, that a binding 10% of the overall energy consumption in the transport sector shall be from renewable sources.

In 2012, the total EU27 biomass supply for electricity, heating and cooling amounted to 103.3 Mtoe, accounting for about two-thirds of all renewable energy consumption in the EU, and it is projected to increase to 132 Mtoe by 2020. Therefore, wood for energy and materials will become scarcer, and new resources will be necessary to meet the increasing demand through domestic supply [1].

In Italy alone, the annual amount of residue derived from the pruning of olive and hazelnut groves, vineyards and other orchards has been estimated to 3.7 million tons of dry matter. Among them, 1.7 million tons are reasonably available for energetic exploitation [2].

Currently, mulching or briquetting pruning residues is the norm, with an estimated respective cost of 100 and 200 € ha^{-1} [3], so they are not considered an additional income opportunity. However, the development of harvesting equipment improves technical and economic sustainability [4,5]. Therefore, biomass from pruning may represent a real economic opportunity and fuel source in Italy [6,7] and beyond [8].

Compared to wood, prunings have a higher ash content and a higher concentration of metals, which influence emissions and cause problems during combustion [9]. Dust emissions consist of both carbonaceous particles and alkali metals, sulphur and chlorine [10–12]. Inorganic species in biomass fuels, such as silica, alkali oxides and salts, can increase ash deposition on the heat transfer surfaces of boilers [11,12]. High concentrations of sulphur (S), chlorine (Cl) and nitrogen (N) increase the emissions of sulphur dioxide (SO_2), hydrogen chloride (HCl) and nitrogen oxides (NO_x), respectively [12–14]. In addition, incomplete combustion of organic material in the presence of chlorine causes the formation of dioxins [11,13].

The emission of particulate matter generated by the combustion of pruning can be controlled if medium to large boilers are used, which are usually equipped with flue gas control systems. Nevertheless, these medium-large scale plants require a large procurement basin; thus, transport distances are excessive for pruning residues. The economic sustainability rapidly decreases for transport distances greater than 10 km, mostly be-cause of the low bulk density of the resulting biomass and the relatively low hourly productivity of the harvesting machines [13,14].

As an alternative, pruning biomass can be processed into pellets. Commercial pellets made from fruit tree pruning have been studied [13,15]. They had very good characteristics but also had the disadvantages of higher ash content and NO_x and SO_2 emissions. The high ash content lowers the calorific value and negatively affects the milling and pelletizing equipment [15].

Biochemical conversion of pruning into biogas is also of interest, because of its high thermodynamic efficiency [16,17].

In October 2014, the Ministry of Economic Development introduced the obligation to prioritize placing the so-called “advanced biofuels”, i.e., biofuels, on the Italian fuel market, including biomethane, which are produced exclusively from specific feedstocks, such as straw, dedicated lignocellulosic crops and residual woody biomass. The mandatory share of advanced biofuels for the year, 2018, is set at 1.7% of energy demand in the transport sector, rising to 2% in 2022 [18].

In Italy, the GSE (Gestore dei Servizi Energetici, Energy Services Manager) has the task of preparing a report on the monitoring of the degree of achievement of the national and regional targets in terms of the share of gross final energy consumption from renewable sources, at an overall level and with reference to the electricity, heat and transport sectors. In Italy in 2018, energy production from solid biomass amounted to 564 ktoe and 718 ktoe for the biogas for the electricity sector. While consumption for the thermal sector 6458 ktoe for solid biomass and 54 ktoe for biogas and bio-methane. This showed an increasing trend over an analysed period from 2012 to 2018. [19].

The use of biomethane would contribute to the reduction of greenhouse gas emissions to a much greater extent (>80%) than the minimum required by the European Directive [18] and can be easily distributed through the existing pipeline network.

Woody biomass is not widely used for methane production because of its low biodegradability, given the high content of structural carbohydrates and lignin. Therefore, to improve biodegradability, a pre-treatment step is necessary to weaken the lignocellulosic structure and increase the surface area for enzymatic attack. There are many studies on the use of olive mill solid waste and hazelnut shells [20,21]. Many studies are also underway to improve the digestion process of these products. Among them, pre-treatment with organic solvents gave highly effective results [22,23]; however, in the opinion of the authors, it would take enormous sizes—over 200,000 t/year of biomass—to ensure the viability of the installation. Hydrothermal and dilute acid pre-treatment of olive and vineyards pruning gave poor results, also using commercial enzyme addition in the digestion sludge; steam explosion proved to be the more effective pre-treatment, especially for olive pruning;

however, the authors did not compare the results with those obtained for the untreated material [24].

Milling steps following one another have also been considered as a pre-treatment procedure in the lignocellulose bio-refinery; however, currently, they are not considered cost-effective because of the high energy demand [25]. Nevertheless, there is increasing research interest in mechanical pre-treatment processes due to the advantages of speed and absence of effluent.

Dry milling, and subsequent fractionation by sieving and/or and density separation, is a well-known technique in the food industry, used to obtain several specific ingredients, especially proteins, from a single feedstock, such as cereals and legumes [26,27].

Dry milling and fractionation of corn have also been proposed to recover germ and fibre as valuable coproducts prior to fermentation for ethanol production [28].

Disc milling and subsequent sieving were used to separate wheat straw into two fractions, which were then pre-treated with dilute acid. The classification was particularly effective with respect to the separation of the non-lignocellulosic components, i.e., protein and extractives [29].

To the best of our knowledge, dry fractionation of wood, and particularly of pruning, in order to improve both their quality as solid fuel and their anaerobic degradability has never been investigated in the literature before.

The aim of this study was to assess the performance of an industrial-scale device used to mill and classify pruning into four different products, in order to obtain better-quality solid fuels and fractions with improved anaerobic degradability. Through a detailed analysis of the chemical and elemental composition and a set of anaerobic digestion and calorimetric experiments, both the methane yield and the heat from combustion of the materials were determined. The quality of the solid fuels was also assessed, particularly concerning their ash and nitrogen content. Lastly, an evaluation of the energy balance of the process was carried out.

2. Materials and Methods

2.1. Harvesting and Processing

Hazelnut and olive prunings were harvested in winter 2020 in the Viterbo province, Central Italy, by a COMBI TR160 pruning harvester. The baled raw materials were then stored in a covered and ventilated area to be naturally dried until early summer 2020. The dried raw materials were chopped by a knife mill to an average length of about 30 mm; a portion of these chips was used as a reference.

An industrial-scale device designed for milling and fractionating feedstock with a high dry matter content (>70%) was used to process the chips. Included was a two-stage mill: the first acts by impact, maximizing the number of impacts to achieve a significant breakage, and the second exerts strong shear actions (Figure 1) [30]. The milled material is then sieved through a plan sifter into three fractions, namely C (Coarse), M (Medium) and F (Fine). The fine fractions are further classified according to their dimensions, shape and density, into two fractions (named F1 and F2) through a centrifugal classifier (Table 1).

Thirty kilograms of chips of both materials were then processed in the previously described device, obtaining in each case four different products. A screw conveyer fed the mill at a constant mass flow rate, which was 990 kg h^{-1} and 1100 kg h^{-1} for hazelnut and olive pruning, respectively. A wattmeter (MTME-485, ABB-SACE, Italy) was used to observe the power absorbed by the device; power, supply voltage, current and time were recorded at one-second intervals. By integrating the area under the power demand curve by the total time required to grind the 30 kg sample, the specific energy (MJ kg^{-1}) required for milling was obtained.

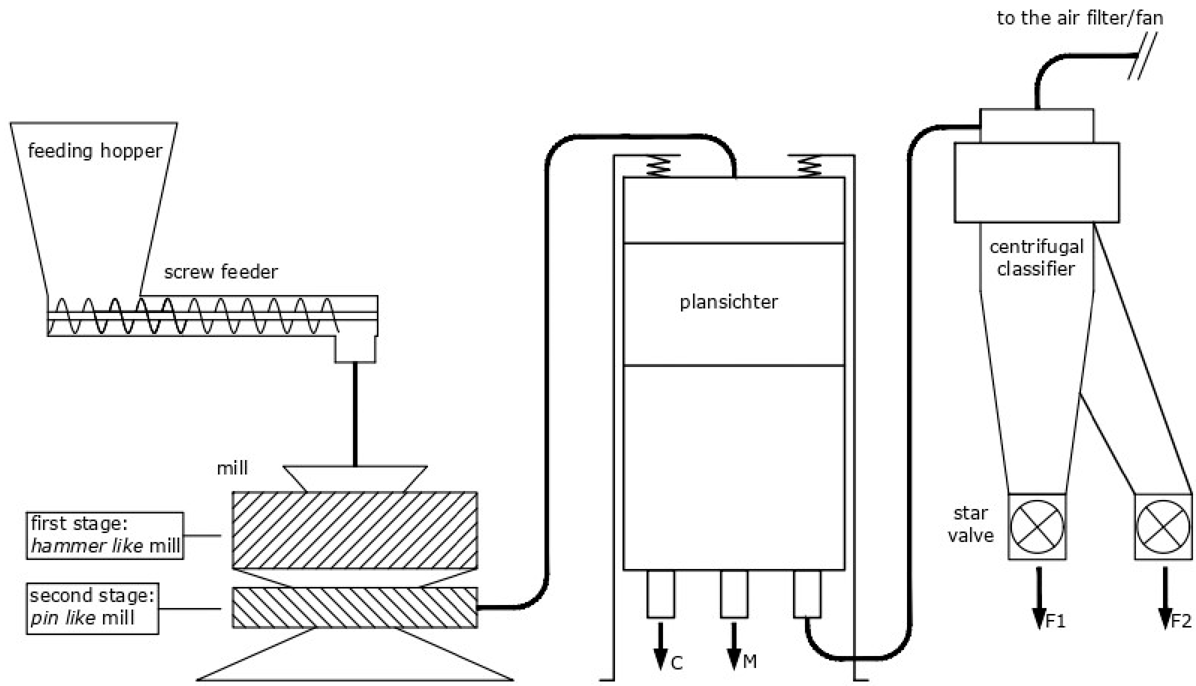

Figure 1. Industrial-scale device from which the different fractions were obtained: C, M, F1, F2.

Table 1. Different fractions obtained.

ID	Species	Product
HP	hazelnut	Chopped Pruning
HC	hazelnut	Coarse
HM	hazelnut	Medium
HF1	hazelnut	Fines type 1
HF2	hazelnut	Fines type 2
OP	olive	Chopped Pruning
OC	olive	Coarse
OM	olive	Medium
OF1	olive	Fines type 1
OF2	olive	Fines type 2

2.2. Chemical and Elemental Composition Analysis

Both raw and processed materials were analysed for total and volatile solids (TS and VS, respectively) according to APHA standard methods [31]. The final elemental composition (C, N, H) was determined according to ISO 16948:2015; oxygen (O) was determined by difference with C, N and H [32]. The tests were performed in triplicate.

2.3. Particle Size Analysis

The particle size of the materials was measured according to the ASABE standard S319.3 [33]. In this test, mass percentages were determined as a function of particle size by passing through sieves of the specified mesh size. A sieve analyser used twelve ISO sieves (2.000, 1.400, 1.180, 1.000, 0.700, 0.600, 0.500, 0.425, 0.300, 0.212, 0.150 and 0.090 mm). We ran the sieve for 15 min each time, and the mass of the samples for particle size analysis was about 250 g.

2.4. Heating Value

The higher heating value according to ISO 18125:2017 (HHV, MJ $kg_{dm}{}^{-1}$) was evaluated, and the lower heating value (LHV) was calculated according to the following equation n [34,35]:

$$LHV = (HHV - 2.45 \times 0.09 \cdot H) \times (1 - U) - 2.45 \cdot U \ [MJ\ kg^{-1}] \quad (1)$$

where 2.45 MJ kg^{-1} is the heat of evaporation of water at 20 °C, H and U the hydrogen and the moisture content (%). These tests were performed in triplicate.

2.5. Anaerobic Digestion

To observe the methane and biogas yields, tests were carried out on samples of raw materials and the F1 and F2 fractions of their processing. The experiments were carried out in batch anaerobic reactors with a working volume of 2 litres and equipped with mixing and thermostating systems; the tests were performed under mesophilic conditions (38 °C). Anaerobic sludge from a mesophilic digester containing 3.67% total solids (TS) and 2.68% volatile solids (VS) was used as inoculum. The inoculum/substrate ratio was in the range of 2.04–2.1 on an SV basis, resulting in a substrate loading in the range of 49–50 g_{TS}/L. The experiments were carried out in triplicate and lasted 28 days, with two controls using only inoculum sludge; the gas produced by the controls was subtracted from the actual gas produced through media digestion.

Biogas production was measured daily in average samples according to standard methods [31]. The composition of the biogas, with reference to the methane (CH_4) content, was measured using a portable automatic analyzer SG06IOMX6 (B.A.G.I. srl, Milan, Italy).

3. Results and Discussion

Processing of hazelnut pruning gave four products, named HC, HM, HF1 and HF2, whose masses amounted to 8.8 kg, 7.0 kg, 8.4 kg and 5.1 kg respectively, equivalent to 29.5%, 23.3%, 27.9% and 17.1% of the raw material.

Processing of olive pruning gave four products, named OC, OM, OF1 and OF2, whose masses amounted to 8.6 kg, 5.2 kg, 9.5 kg and 5.7 kg, respectively, equivalent to 28.6%, 17.5%, 31.7% and 19.0% of the raw material.

The processing loss was 2.3% and 3.2%, for hazelnut and olive respectively, mainly due to moisture reduction after milling.

3.1. Specific Energy Requirement

The mean power absorbed by the device was 72.0 kW for hazelnuts, with a specific energy demand of 72.4 kWh t^{-1} (260.6 ± 7.3 kJ kg^{-1}), and 70.1 kW for olives, with a specific energy demand of 63.0 kWh t^{-1} (226.8 ± 6.9 kJ kg^{-1}), including the requirement for the feed conveyor and pneumatic transport of the material.

Additional energy was needed for the preliminary chipping of the raw materials. In this case, the knife mill was manually fed, and therefore, the experimental determination of the specific energy consumption would have been unreliable. Therefore, reference is made to data widely available in the literature, which indicate a consumption of about 15 kWh t^{-1} of processed material [36–38].

3.2. Characterization of the Biomasses

The investigated process significantly modified the nitrogen and ash content of the products with respect to the raw material. In particular, the fractions HC and HM from hazelnut processing showed an ash content of 1.3% and 1.7% respectively, far below that of hazelnut pruning, 3.7% (Table 2).

Table 2. Moisture and ash of raw and processed pruning. For each sequence, means followed by the same letter in the same column are not statistically different with a p-value < 0.05 (Tukey test).

	Moisture [%]	Ash [$\%_{DM}$]
HP	10.1 ± 0.6 a	3.6 ± 0.3 a
HC	7.9 ± 0.5 b	1.3 ± 0.2 b
HM	8.9 ± 0.2 c	1.7 ± 0.2 b
HF1	9.4 ± 0.4 c	4.0 ± 0.3 c
HF2	9.9 ± 0.4 c	9.1 ± 0.2 d
OP	9.2 ± 0.5 a	4.1 ± 0.2 a
OC	7.9 ± 0.4 b	2.1 ± 0.2 b
OM	7.8 ± 0.2 b	2.6 ± 0.2 b
OF1	7.1 ± 0.4 bc	5.3 ± 0.2 c
OF2	6.8 ± 0.4 c	6.1 ± 0.2 d

The ash content of raw olive was 4.1%, whereas it decreased to 2.1% and 2.6% for products OC and OM, respectively. The highest ash concentrations were found in the F1 and F2 products from both materials—3.96% and 9.08% in HF1 and HF2, respectively, the last being about 2.5 times the value observed in the raw material, and 5.28% and 6.15% in OF1 and OF2 respectively, the last being about 1.5 times the value observed in OP.

The C and M fractions from both materials were also notable for the high reduction in the nitrogen content. The product HC from hazelnut processing showed a nitrogen content of 0.02%, which was only 1/36 of that of the raw material (0.64%); the product HM showed a nitrogen content of 0.2%, a third smaller than it was in hazelnut pruning. Particularly concerning olive products, the nitrogen content of OC and OM was 0.07% and 0.1% respectively, versus 0.39% for the raw material.

The nitrogen content significantly increased in both F2 fractions compared to the raw materials, +73.4% for hazelnut (HF2) and +105.1% for olive (OF2). For olive pruning, the nitrogen in OF1 was 0.41%, slightly higher than 0.38% observed for the raw material, whereas in HF1, it was slightly lower than that observed in the raw material (0.54% vs. 0.64%) (Table 3).

Table 3. Elemental analysis of raw and processed pruning. For each sequence, means followed by the same letter in the same column are not statistically different, with a p-value < 0.05 (Tukey test).

	C [$\%_{DM}$]	N [$\%_{DM}$]	H [$\%_{DM}$]	O [$\%_{DM}$]	C/N
HP	42.8 ± 0.51 a	0.64 ± 0.004 a	5.61 ± 0.18 a	50.95	66.9 ± 1.2 a
HC	41.3 ± 0.20 b	0.02 ± 0.001 b	5.63 ± 0.07 a	53.05	2367.1 ± 147 b
HM	43.0 ± 0.10 a	0.19 ± 0.004 c	5.72 ± 0.11 a	51.09	220.6 ± 5.0 c
HF1	42.5 ± 0.32 a	0.54 ± 0.003 d	5.61 ± 0.13 a	51.35	78.2 ± 1.0 d
HF2	39.3 ± 0.21 d	1.11 ± 0.003 e	5.28 ± 0.09 d	54.31	35.4 ± 0.3 e
OP	42.9 ± 0.45 ad	0.39 ± 0.007 a	6.54 ± 0.21 b	50.17	110.7 ± 3.0 a
OC	41.5 ± 0.31 b	0.07 ± 0.002 b	6.52 ± 0.09 b	51.91	592.2 ± 21.1 b
OM	41.8 ± 0.59 bc	0.10 ± 0.002 c	6.53 ± 0.12 b	51.57	415.5 ± 14.2 c
OF1	42.2 ± 0.44 bc	0.42 ± 0.004 d	6.55 ± 0.08 b	50.83	101.5 ± 1.9 d
OF2	42.6 ± 0.5 dc	0.79 ± 0.005 e	6.59 ± 0.15 b	50.02	53.6 ± 1.0 e

As regards the carbon content, no relevant differences were observed between the raw materials and their respective products, apart from HF2, whose carbon content was 8.2% lower than that measured for HP. As a result, the F2 products from both raw materials showed a C/N ratio far below those of the untreated pruning, which were excessively high for anaerobic digestion, namely 66.9 and 110.7 for hazelnut and olive, respectively. HF2 from hazelnut reached a value of 35.4, very close to the optimal range for anaerobic digestion (i.e., 20–30:1), whereas the C/N ratio was 53.6 for OF2, 52.1% below that of olive pruning. A C/N ratio smaller than that of the raw material was also observed for OF1 (101.5 vs. 110.7), whereas it was higher for HF1, namely 78.2 versus 66.9 for hazelnut pruning.

3.3. Biogas Yield and Quality

The untreated pruning showed a methane yield of 69.4 $Nm^3\ t_{VS}^{-1}$ (±5.1 $Nm^3\ t_{VS}^{-1}$) for hazelnut (HP) and 91.2 $Nm^3\ t_{VS}^{-1}$ (±5.7 $Nm^3\ t_{VS}^{-1}$) with LHV 16.00 MJ/kg, and for olive (OP) with LHV 15.93 MJ/kg (Tables 4 and 5). The HF2 product from hazelnut processing reached a yield of 118.1 $Nm^3\ t_{VS}^{-1}$ (±5.5 $Nm^3\ t_{VS}^{-1}$), corresponding to a +70.1% gain over the untreated substrate, whereas OF2 from olive reached a yield of 176.5 $Nm^3\ t_{VS}^{-1}$ (±4.2 $Nm^3\ t_{VS}^{-1}$), corresponding to a +93.5% gain over the untreated feedstock (Table 5).

Table 4. Median particle size, higher and lower heating values. Means followed by the same letter in the same column are not statistically different, with a p-value < 0.05 (Tukey test).

	d_{50} [μm]	HHV [MJ/kg_{DM}]	LHV [MJ/kg]
HP		19.3 ± 2.0 bc	16.0 ± 2.1 b
HC	1600	19.0 ± 0.3 b	16.3 ± 0.7 b
HM	700	20.1 ± 0.3 c	16.9 ± 0.6 b
HF1	310	19.8 ± 0.3 c	16.6 ± 0.6 b
HF2	180	18.2 ± 0.4 b	15.3 ± 0.7 b
OP		19.2 ± 1.0 d	15.9 ± 1.3 c
OC	1800	19.2 ± 0.3 d	16.2 ± 0.6 c
OM	750	19.2 ± 0.1 d	16.2 ± 0.6 c
OF1	300	19.2 ± 0.2 d	16.3 ± 0.5 c
OF2	160	20.0 ± 0.1 d	17.1 ± 0.5 c

Table 5. Methane yield and biogas composition for raw and processed pruning. Values followed by the same letter in the same column are not statistically different, with a p-value < 0.05 (Tukey test).

	BMP-CH_4 [Nm^3/t]	BMP-CH_4 [Nm^3/t_{SV}]	%CH_4 [Nm^3/t_{SV}]
HP	59.8 ± 4.5 a	69.4 ± 5.1 a	49.8 ± 0.4 a
HF1	67.3 ± 3.6 a	78.7 ± 4.0 a	50.0 ± 0.1 a
HF2	96.8 ± 3.8 b	118.1 ± 4.2 b	49.8 ± 0.1 a
OP	79.4 ± 5.4 a	91.2 ± 5.7 a	49.3 ± 0.4 a
OF1	101.3 ± 4.7 b	115.6 ± 4.9 b	49.7 ± 0.1 a
OF2	153.8 ± 4.4 c	176.5 ± 4.2 c	50.4 ± 0.2 b

OF1 showed a biomethane yield gain, namely +26.7%, compared with the raw material. No statistically significant yield gain was observed for HF1. Except for OF2, no statistically significant differences were observed in the chemical composition of the biogas, whose methane content in the biogas was 50.4% and 49.3% in the feedstock.

As expected, methane production was faster in the processed material than in the untreated feedstock. HF2 reached 50% of the cumulative production during the third day from the start of the test (Figure 2). HF1 reached the same amount during the 4th day, while HP took about 5 days. OF2 and OF1 reached 50% of the cumulative production during the 8th day of digestion, while OP took approximately 11 days (Figure 3).

The methane production rate for the F2 fractions was high, reaching the maximum of about 17.5 $Nm^3\ t_{VS}^{-1}\ day^{-1}$ between the 2nd and 3rd day of digestion for HF2, whereas the maximum for OF2 was about 15 $Nm^3\ t_{VS}^{-1}\ day^{-1}$ during the 3rd day of digestion. Regarding feedstock, maximum production rates were only 11.1 $Nm^3\ t_{VS}^{-1}\ day^{-1}$ and 6.4 $Nm^3\ t_{VS}^{-1}\ day^{-1}$ for hazelnut and olive, respectively.

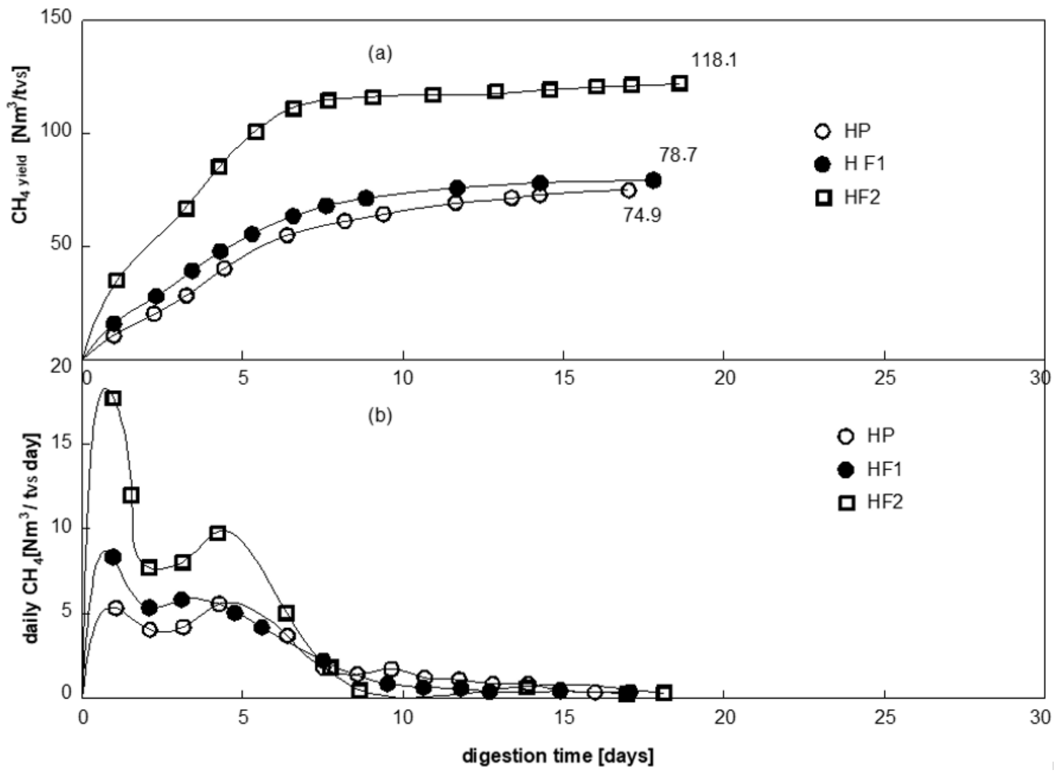

Figure 2. Cumulative methane yield of hazelnut pruning and fraction HF1 and HF2 from processing (**a**) and daily methane yield (**b**).

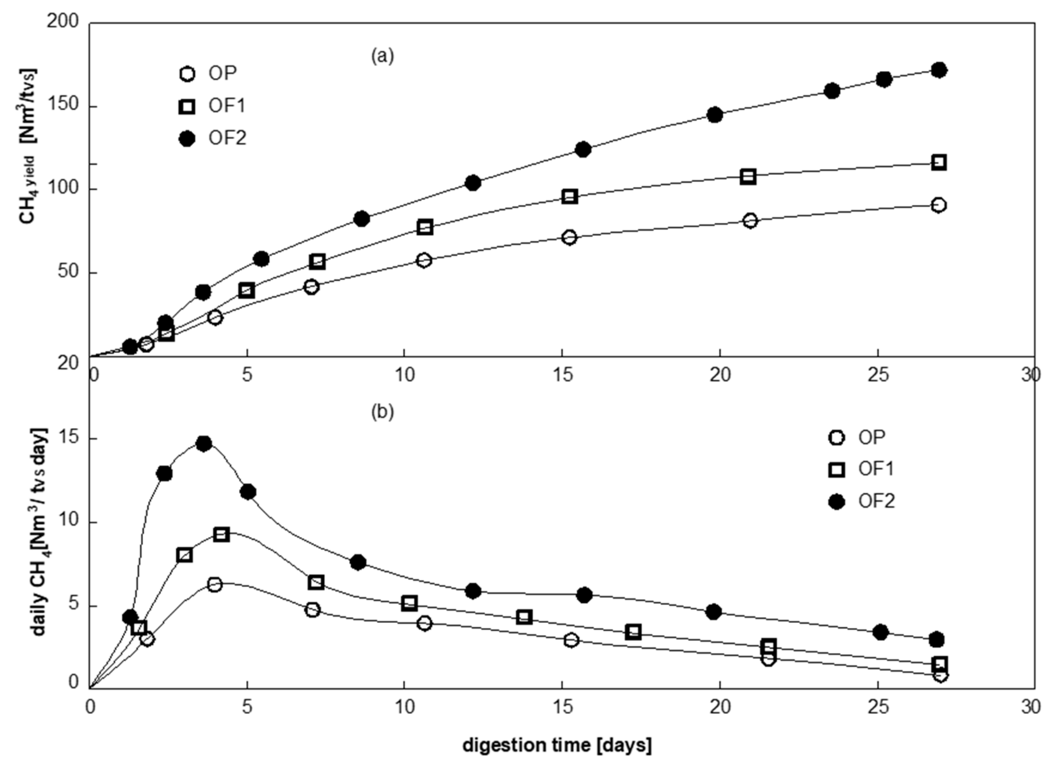

Figure 3. Cumulative methane yield of olive pruning and fraction OF1 and OF2 from processing (**a**) and daily methane yield (**b**).

3.4. Higher and Lower Heating Values

There were no statistically significant differences between the higher and lower heating values of the feedstock and those of their respective products (Table 4).

4. Discussion

The investigated process enhanced the pruning quality as solid fuel, allowing their convenient use in pellet supply chains, and it was also effective in producing biomass with highly improved anaerobic digestibility.

The products C and M from both the feedstock showed an improved quality as solid fuel, since they had a highly reduced ash content compared with the raw material. Ash adversely affects the calorific value, the dust emissions and the combustion plant performance because of the formation of unburnt material, accompanied by corrosion, erosion and fouling; they showed a highly reduced nitrogen content compared with the raw pruning, and nitrogen is an undesired element since in the combustion process it generates nitrogen oxides, responsible for irritant effects on humans and the formation of photochemical smog [39]. In small-scale combustion systems in which the flue gas temperature are above 1300 °C nitrogen oxides are assumed to be formed mainly from fuel nitrogen during biomass combustion [40].

Both HP and OP did not meet the specification for industrial pellets given in the EN ISO 17225-2 standard [41], because their ash content was too high for OP and their nitrogen and ash contents were too high for HP. The LHVs of both the feedstock were slightly below the lower limit (16 MJ kg^{-1}) given in the standard; however, this was due to the high amount of moisture in the raw materials, namely10.1% and 9.25% for HP and OP, respectively. Likewise, both HP and OP did not meet the specification for residential pellets given in the EN ISO 17225-2 [41], because their ash content exceeded the limit of 2% stated for the lower class B (Table 6), as was also observed by Stelte et al. (2011) [42]. However, the operating parameters should be considered in a possible combustion process, as highlighted by Venturini et al. (2018). In order to limit pollutant emissions from pellet boilers, it is important to consider the quality of the pellets, but attention should also be paid to the combustion conditions of the stove, as the formation of pollutants such as carbon compounds or polycyclic aromatic hydrocarbons seem to be influenced by the heat output of the boiler [43].

Table 6. Compliance of raw pruning and respective products C and M with the European standard EN ISO 17225-2 for industrial and residential use. I1, I2, I3, A1, A2, B represent the quality categories of pellets, I for industrial and A/B for residential.

		Moisture %	LHV MJ/kg	Ash $\%_{TS}$	N $\%_{TS}$
ISO 17225-2 industrial pellets	I1	≤10	≥16.5	≤1	≤0.3
	I2	≤10	≥16.5	≤1.5	≤0.3
	I3	≤10	≥16.5	≤3	≤0.6
ISO 17225-2 non industrial pellets	A1	≤10	≥16.5	≤0.7	≤0.3
	A2	≤10	≥16.5	≤1.2	≤0.5
	B	≤10	≥16.5	≤2	≤1
Hazelnut	HP	10.1	16.0	3.6	0.6
	HC	7.4	16.3	1.3	0.0
	HM	8.9	16.9	1.7	0.2
Olive	OP	9.2	15.9	4.1	0.4
	OC	7.9	16.2	2.1	0.1
	OM	7.8	16.2	2.6	0.1

On the other hand, the nitrogen content met the requirement of class B for HP and class A2 for OP. In order to meet the minimum lower heating value required by the standard, a moisture content between 6% and 7% is needed for hazelnut pruning and no more than 6% for olive pruning.

With regard to products, HM from hazelnut processing met the requirements of class B for residential pellets and class I3 for industrial pellets. In both cases, the limiting factor was the ash content at 1.73%, which too high to achieve class A2 for residential use (upper limit 1.2%) and class I2 for industrial use (upper limit 1.5%) [41]. With the exception of the lower heating value, slightly lower than 16.5 MJ kg^{-1}, HC met the requirements of class B for residential pellets and class I2 for industrial use. The limiting factor was the ash content. For both HC and HM, the nitrogen content was far below the upper limit permitted for the top classes A1 and I1, whereas the raw material did not comply with the EU standard.

With the exception of the lower heating values, products OC and OM from olive processing met the requirements for the industrial class I3. However, they did not meet the requirements for residential pellet, the limiting factor being the ash content at 2.09% and 2.56%, respectively, too high for the 2% upper limit required for the lower class B. In this case as well, the nitrogen content was far below the upper limit permitted for the top classes.

The fine fractions F1 and F2 from both feedstock were suitable for the biochemical conversion by anaerobic digestion. The high concentration of nitrogenous matter made their C/N ratios smaller than those of the respective raw materials and far better for anaerobic digestion. As is well known, a 20–30:1 ratio of C to N is needed for optimal anaerobic digestion, since microorganisms utilize carbon 25–30 times faster than nitrogen [44]. In particular, HF2 reached a ratio of 35.4, very close to the optimal range, with a reduction of about 49% compared with HP. The methane yield reached 118.1 Nm^3 ${t_{VS}}^{-1}$, corresponding to a +70.1% gain over the untreated substrate, whereas for OF2, the C/N ratio was 53.6, with a reduction of about 59.6%, and the methane production was very high, reaching 176.5 Nm^3 ${t_{VS}}^{-1}$, corresponding to a yield gain of about +93.5% over the untreated raw material. Serrano et al. (2019) report methane production rates of 163 $\pm$ 28 mL CH4/(g_{VS}·d) for Olive Mill Solid Waste, which confirms the excellent potential of these raw materials [20]. Weide et al. (2019) also showed that the addition of agricultural wastes such as grass silage, maize silage, chicken manure, triticale straw, maize straw, horse manure, and hay can increase biomethane yields, also by regulating the intervention of enzymes in the process [45].

Biomethane yield of OF1 increased compared with the raw material (+26.7%), corresponding to a slight reduction of the C/N ratio, which was 101.5 vs. 110.7 of the feedstock. For HF1, the methane production was 78.7 Nm^3 ${t_{VS}}^{-1}$ and there was no statistically significant difference compared to the raw material 69.4 Nm^3 ${t_{VS}}^{-1}$; however, the production was significantly faster. The C/N ratio of HF1 was slightly higher than that of the raw material (78.2 vs. 66.9).

The process revealed a low energy consumption, which was 85.1 kWh t^{-1} to 87.4 kWh t^{-1} for olive and hazelnut pruning, respectively. In order to assess its energy efficiency, we compared the energy consumption with the energy output from the products F1 and F2 after anaerobic digestion and electric energy production through a standard CHP engine. Under the assumption of a conversion rate of 4 kWh $(m^3CH_4)^{-1}$, the energy output from the methane was 168.6 kWh per processed ton of hazelnut pruning and 245.3 kWh t^{-1} for olive, which made the energy balance largely positive. Under the further assumptions that the sell price for F1 and F2 was 0.45 EUR/m^3CH_4—the standard value for corn silage—their overall market value was EUR 19 per ton of processed hazelnut pruning and 27.6 EUR/t for olive pruning. Therefore, they exceeded the energy cost of the process, which was 15.7 EUR/t and 15.3 EUR/t for hazelnut and olive pruning respectively, assuming 0.18 EUR kWh^{-1} the cost for electric energy. It is interesting to note that more and more studies are finding the potential of pruning waste, as observed by Maccarini et al. (2020), who, with pruning waste from the urban environment, estimated the potential production of 1.406 MWe, with 6.77 tons day^{-1} of residues in eight hours per day, generated using standard CHP engines [46].

These results suggest that the investigated process could be successfully used to improve the quality of pruning and establish new markets for them.

5. Conclusions

Orchard prunings are well known for their poor quality as a fuel, especially in small-scale boilers, mainly due to the high ash and nitrogen content. A mechanical, commercial-scale process was investigated for treating hazelnut and olive pruning through multiple milling stages and subsequent classification into four different products. The coarser products (C and M) showed reduced ash and nitrogen content. Thus, hazelnut met the ISO 17225-2 parameters for both industrial and residential pellets, and olive met the parameters for industrial pellets only.

The fine fractions F1 and F2 from both feedstock were suitable for the biochemical conversion by anaerobic digestion, due to the high concentration of nitrogenous matter, which made their C/N ratios smaller than those of the respective raw materials. In particular, the methane yield of the finest products from processing was 118.1 $Nm^3\ t_{VS}^{-1}$ for hazelnut, corresponding to a +70.1% gain over the untreated substrate, and 176.5 $Nm^3\ t_{VS}^{-1}$ for olive, corresponding to a yield gain of about +93.5% over the untreated raw material.

The energy efficiency of the process was assessed, and it was largely positive considering only the electric energy output from the methane. Likewise, the overall market value of the product for anaerobic digestion exceeded the energy cost needed to process the raw materials.

These results suggest that the investigated process could be successfully used to improve the quality of pruning and establish new markets for them. Moreover, products suitable for anaerobic digestion and the production of advanced biomethane can be generated.

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1. Conclusion

This dissertation focuses on the study and valorisation of agroforestry and agro-industrial waste for energy purposes, paying special attention to exhausted coffee grounds and hazelnut and olive tree pruning residues. In particular, for the evaluation, a very detailed characterization of the raw material was carried out, as well as modelling analyses for some types of biomasses; whereas for the valorisation, pelletizing and then combustion tests were performed in order to assess the use of the new product that was produced from the waste and its atmospheric emissions. Pre-treatment tests on hazelnut and olive tree pruning residues were made to verify the improvement of their characteristics as biomass, and an LCA analysis was completed so as to determine the actual environmental convenience of possible alternatives for the coffee grounds recovery chain.

The aim was specifically to:

- Carry out an extensive chemical-physical characterization of coffee grounds and evaluate the interaction of the various indices and their relevance, evaluate pelletization with sawdust being added to different mixtures so as to obtain pellets with the highest percentage of coffee grounds and evaluate the atmospheric emissions of the final product.
- Evaluate the life cycle of a coffee grounds valorisation chain according to various scenarios, also observing the environmental impacts.
- Create a homogeneous dataset of the composition of different types of biomasses to set up the modelling of the higher heating value.
- Evaluate an industrial-scale device to mechanically pre-treat pruning residues to obtain fractions with improved anaerobic degradability, assessing the detailed characterization.

Coffee grounds have proven to be of excellent quality from a chemical and physical point of view, often superior to woody biomass. In particular, with a high calorific value and very low amounts of polluting metals compared to other residual biomasses. The pelletising process brought about some difficulties due to the size of the coffee powder and the hygroscopic nature of the material, which can lose and recover moisture very quickly. The addition of sawdust provided for better mechanical characteristics of the pellets, but it reduced their energetical qualities. The use of 2 % corn starch, which is allowed for pelletising, gave pellets the necessary mechanical characteristics without losing energy characteristics. While atmospheric emissions showed some high parameters of CO and NO_x, the combustion process however, was carried out without applying any pollutant abatement system.

The cradle-to-grave life cycle study of leather made from coffee grounds, revealed that environmental burdens mostly result from the pelletising process and are due to the heat demand for SCG drying thus, natural drying would be desirable. Pellets also have a significant effect on human health, while thermal conversion and the different stages of waste disposal have a minor effect on the environment. SCG pellet production can benefit from ash disposal credits and contributes to climate change mitigation, fossil resource use and reduction of freshwater eutrophication. The analysis of alternative approaches also indicated that the collection and drying phases of the SCG contributed to all of the impact categories. According to the overall impacts, the most environmentally sustainable option is the production of bio-oil from SCG waste followed by pellets produced from this residue. Biodiesel production is the least preferred option considering its highest impact on all damage categories.

PCA and Cluster Analysis applied on the ultimate and proximal analysis allowed for biomasses to be clustered and linear quantile models were applied and from the composition analysis to predict the higher heating value. These models are a useful tool for the energy potential of biomass and have shown excellent levels of accuracy. The model that was adopted for herbaceous species proved to be very accurate however, it was less so for tree species, due to their variability. These models always showed coffee grounds to be superior to other biomasses, with straw being the worst, and hemp and tree species being in the middle.

Orchard prunings are difficult to use due to their high moisture content and sometimes high ash and nitrogen content. The mechanical process by successive grinding studied on hazelnut and olive pruning residues allowed for the products to be classified into four classes with different properties. The larger size classes had a reduced ash and nitrogen content. Hazel met the ISO 17225-2 parameters for both industrial and residential pellets, and olive met the parameters only for industrial pellets. The finer fractions were more suitable for anaerobic digestion, which is characterised by a low C/N due to the high nitrogen content. The methane yield of the improved processing products was 70% higher than that of the untreated products for stone and 93.5% higher for olive. The energy efficiency assessment of the methane that has been produced, and the overall market value of the anaerobic digestion product, were largely positive.

In conclusion, the results show that SCG is an excellent candidate for use in energy conversion systems. The evaluations that were carried out, can help to understand the environmental impacts of pellet production in order to choose the best alternatives to valorise coffee grounds. Coffee grounds models are able to give extremely accurate values. In addition, the mechanical process could be used to improve the quality of pruning residues and open up new markets

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